LABORATORY INVESTIGATIONS OF ATMOSPHERIC NANOPARTICLE FORMATION AND GROWTH

by

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ABSTRACT

Atmospheric nanoparticles are suspended particulate matter with diameters of 100 nm and smaller, and present a deleterious impact on human health and global climate. Particles within this size range can effectively alter the Earth's radiative energy balance either directly by scattering or absorbing incident sunlight, or indirectly by modifying the formation and properties of cloud droplets. Nanoparticles represent the greatest fraction of ambient particulate matter by number, and the majority of these particles are formed directly within the atmosphere through a process by which gas molecules partition together to form molecular clusters on the order of 1 nm, which subsequently grow to larger sizes. The rapid growth of these particles up to a diameter of approximately 50 nm is crucial to their atmospheric survival and their climatic relevance, however the factors affecting this growth process remain poorly understood, leading to one of the greatest uncertainties in current climate models. Ultimately, a better understanding of the chemical processes underlying nanoparticle formation and growth is needed in order to refine future predictions in climate change due to atmospheric particles.

This thesis aims to evaluate the potential for atmospheric nanoparticle formation and growth to occur by secondary chemical mechanisms that are currently under-represented or completely unaccounted for in today's atmospheric climate models. First, the formation of particulate organic nitrogen-containing compounds occurring in aqueous nanodroplets was investigated using a combination of particle size characterization and mass spectrometry techniques. It is shown that aqueous

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reactions involving ammonium sulfate and atmospherically relevant dicarbonyls occur in nano-scale droplets, and can be a significant source of atmospheric organic particulate matter. Combined molecular and elemental composition measurements using mass spectrometry were utilized to determine the organic nitrogen-to-carbon ratio (N/C) of the droplets, and revealed a dependence on relative humidity, as well as organic precursor identity. Furthermore, this chemistry can help explain high amounts of particulate nitrogen measured in ambient nanoparticles during summertime new particle formation events that occurred in Lewes, Delaware, a location where gasphase concentrations of water-soluble organics are significant.

Next, the implementation of a custom-built aerosol flow tube reactor is described in order to investigate the effect of the ubiquitous anthropogenic pollutant sulfur dioxide on nanoparticle formation and growth during the ozonolysis of various biogenic alkenes. Experiments were conducted in the presence of dry, monodisperse ammonium sulfate seed particles and an OH scavenger at a low relative humidity of 15%. Without sulfur dioxide, new particle formation was not observed, and seed particle growth was consistent with condensation of low-volatility oxidation products produced from each organic precursor. With sulfur dioxide, new particle formation was observed from every precursor studied, consistent with sulfuric acid formation by reaction of sulfur dioxide with carbonyl oxides (i.e. Criegee Intermediates) produced during alkene ozonolysis. The presence of SO₂ was also found to alter the chemical composition of the particulate organic material via the formation of organosulfate compounds in the condensed phase.

This investigation was then further expanded upon by conducting the same experiment for two of the organic precursors (α -pinene and β -pinene) under more

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atmospherically relevant conditions of higher relative humidity and aerosol liquid water content. In the absence of SO₂, it was found that higher relative humidity led to a minor increase in seed particle growth from both precursors, whereas the effect of higher aerosol liquid water content on particle growth was precursor-dependent. In the presence of SO₂, higher relative humidity led to a dramatic increase in the number of nucleated particles from both precursors when dry seed particles were used, however a decrease in nucleation was observed in the presence of deliquesced seeds. Additionally, organosulfates were detected in deliquesced particles from both α -pinene and β -pinene ozonolysis when SO₂ was present, although their formation does not appear to depend on aerosol liquid water, and growth rates remained comparable to trials using effloresced seed particles. Finally, under all conditions studied, addition of SO₂ was found to have no significant effect on particle growth by ozonolysis of αpinene, but was found to dramatically increase particle growth by β -pinene. These results suggest that a previously unidentified pathway to particle growth activated by SO₂ may alter aerosol climate effects in regions with significant anthropogenicbiogenic interactions.

Chapter 1

INTRODUCTION

1.1 Classification of Atmospheric Aerosols

Aerosols, defined as solid or liquid particles suspended within a gas, are ubiquitous in the Earth's atmosphere. Because many airborne particles are nonspherical in their physical shape, they are commonly classified according to their aerodynamic size, which can be thought of as the diameter of an ideal spherical particle containing the same settling velocity as an irregular particle¹. Atmospheric particles span a broad range of aerodynamic sizes, and are typically categorized as being ultrafine (<100 nm), fine (~100-2500 nm), or coarse (>2500 nm) in diameter.

The coarse mode encompasses particles that mainly enter the atmosphere via primary emissions, the sources of which can include wind erosion, pollen and spores, and sea salt sprays². Due to their large size and mass, which scales as the cube of a particle's diameter, coarse particles exit the atmosphere by gravitational settling, typically within a few hours of production².

The fine mode consists of particles primarily formed from combustion processes, and includes anthropogenic sources such as emissions from cooking, vehicles, power plants, and other sources of fossil fuel burning, as well as biogenic, for instance biomass burning³. In addition, fine mode particles can also be formed by coagulation and/or condensational growth of smaller particles. Because of their smaller size, fine particles have average atmospheric lifetimes of a few days to weeks, and are more susceptible to long-range transport⁴. Ultrafine particles, also referred to as nanoparticles, comprise the nuclei (<10 nm) and Aitken (10-100 nm) modes⁵. A large fraction of these particles are formed through secondary chemical processes directly in the atmosphere. This occurs through homogeneous nucleation, i.e. condensation of low-volatility vapor molecules produced primarily by photochemically triggered gas-phase reactions⁶, and will be described in more detail in section 1.2. Although ultrafine particles contribute very little to the total ambient particle mass loading, they account for the largest number of atmospheric particles globally². Because of their high number concentrations, nanoparticles are very susceptible to collisions with each other and with larger particles, and so generally exist in the atmosphere for a few minutes to days⁴.

Along with greenhouse gases, atmospheric particles are prominent air pollutants with adverse effects on both human health and the environment. From a health perspective, the risk posed by airborne particles increases as the size of the particle becomes smaller. Upon inhalation, coarse particles deposit in the upper airways of the respiratory tract, and can be cleared by swallowing or coughing, whereas fine particles can penetrate deeper into the conducting airways of the lungs². The greatest health risk arises from ultrafine particles due to their small size and high chemical reactivity owing to their large surface area. Because of this, ultrafine particles are capable of entering the pulmonary region of the lungs and be absorbed into the blood stream, where they can be transported throughout the body into the central nervous system, the brain, and vital organs such as the heart and liver⁷. Prolonged inhalation of ultrafine particles have been linked to a large number of health issues, including impaired lung function, aggravated asthma and allergies leading to

difficulty breathing, respiratory infections such as measles and tuberculosis, and even cardiovascular failure^{8,9}.

In addition to their impacts on human health, atmospheric particles also have a great effect on the Earth's climate. Their impacts on climate can be divided into direct and indirect effects on Earth's energy balance. The direct effect refers to the ability of particles to scatter or absorb incident solar radiation. When sunlight is scattered by a particle, a part of the energy is redirected back to space, resulting in a net cooling effect on the Earth. When a particle absorbs sunlight, the result is a warming effect similar to greenhouse gases. Because the majority of airborne particles contributing to the direct effect are non-absorbing, the overall contribution to the Earth's energy balance due to aerosol particles is planetary cooling.

The other way that atmospheric particles can impact climate is through the indirect effect. This refers to the ability of hygroscopic particles to act as effective sinks for condensation of water vapor, which can lead to the formation of cloud droplets. For this reason, these particles are commonly referred to as cloud condensation nuclei (CCN). Generally, a particle must grow to a diameter of at least ~50 nm before being able to act as a CCN. Essentially all particles above 100 nm are considered to be CCN, whereas particles in the range of 50-100 nm can act as CCN depending on their size and composition, which determines their hygroscopicity. The formation of CCN can ultimately impact the numbers, sizes, and lifetimes of cloud droplets in the atmosphere. This in turn leads to an enhancement in the scattering of solar radiation, contributing to a net cooling effect of the Earth.

The magnitude that aerosol particles have on altering the Earth's energy balance is quantified by their degree of radiative forcing. By definition, this describes the difference between energy from the sun that is absorbed by the Earth and that which is radiated back to space¹⁰. Radiative forcing is typically expressed in units of watts per square meter (W m⁻²). Combined together, the direct and indirect aerosol effects have been estimated by the Intergovernmental Panel on Climate Change (IPCC) to contribute to a radiative forcing of -1.2 W m⁻², however the uncertainty in this estimate is quite large, ranging from -2.7 to -0.4 W m^{-2 11}. In particular, the indirect effect of aerosols currently represents one of the largest ambiguities in global climate models¹¹. In order to minimize this uncertainty in aerosol climate effects, it is critical to understand the chemical mechanisms by which particles form and grow in the atmosphere.

1.2 New Particle Formation and Growth

A larger fraction of particles in the global atmosphere arise from secondary formation rather than primary emissions^{12,13}. The process by which these particles form is known as new particle formation (NPF), and involves the clustering of gas molecules followed by their subsequent growth into the CCN size range¹⁴. NPF events are a frequent occurrence that have been observed to take place in almost every environment throughout the world, including boreal forests, coastal regions, and heavily polluted megacities^{6,15,16}.

In the ambient atmosphere, the primary driver of NPF is sulfuric acid because of its low vapor pressure at typical ambient temperatures and its large mixing enthalpy with water molecules, which are ubiquitous in the atmosphere^{17–19}. Sulfuric acid is mainly generated by photooxidation of sulfur dioxide (SO₂) by the hydroxyl radical (OH) during the daytime²⁰. One necessary condition for the onset of a NPF event is a gas-phase sulfuric acid concentration in excess of 10⁵ molecules cm^{-3 21,22}. In addition

to sulfuric acid, other stabilizing species including ammonia, amines, iodine oxides, and organic acids can act as nucleating precursors²⁰.



Figure 1-1. Overview of the new particle formation (NPF) process. Adapted from Reference 23.

The initial formation of the molecular cluster is driven by random collisions of the nucleating vapor molecules. If the collision rate is faster than the rate at which the molecules dissociate back to the gas phase, the cluster can reach a thermodynamically stable size where further growth becomes spontaneous. This is known as the critical nucleus, and occurs when the cluster reaches a size of approximately 1.5 nm²⁴. The nucleation rate, or rate at which formation of the critical nucleus occurs, is therefore dependent on the gas-phase concentrations, as well as the chemical makeup, of nucleating vapor molecules²⁵.

Once the critical nucleus is formed, it can either continue to grow through further condensation or partitioning of vapor molecules, or it can become scavenged by coagulation with a preexisting larger particle. Preexisting particles are also a condensation sink for nucleating vapor molecules, and can reduce their concentrations, thereby inhibiting the rate at which nucleation occurs. It has generally been thought that high number concentrations of preexisting particles will decrease the survival probability of newly formed particles. This is because the atmospheric lifetime of a nucleated cluster, as well as the nucleating vapors, is inversely proportional to the condensation sink^{26,27}. For this reason, NPF is not expected to occur in environments with significantly high loadings of preexisting particles. However, NPF has been observed to occur frequently in highly polluted megacities such as Beijing and Shanghai^{28,29}. This suggests that there exist one or more chemical mechanism(s) to nanoparticle nucleation and growth that occur in highly polluted environments which have not been previously recognized. This topic will be discussed more extensively in Chapter 4.

If the critical nucleus is not scavenged by a preexisting particle, it can continue to grow to larger sizes and survive as a new particle. The growth of the critical nucleus up to the size range of 50-100 nm is particularly important to the climatic impact of an aerosol particle, as this is the size where particles become effective scatterers of sunlight and CCN³⁰. As detailed in Figure 1-1, the major contributors to the growth of aerosols from the critical nucleus up to this size range are organic compounds. Due to the chemical complexity underlying particle growth by organics and the vast number and diversity of organic species that can contribute, a detailed scientific understanding of the growth process of atmospheric nanoparticles is lacking. The scope of this thesis

thereby aims at better understanding the contributions of organic compounds to atmospheric nanoparticle growth.

1.3 Nanoparticle Growth by Secondary Organic Aerosol

The dominant pathways by which nanoparticles grow in the atmosphere are condensation of low-volatility vapors and reversible partitioning of semivolatile vapors²⁰. The vast majority of these species are organic compounds arising from the oxidation of higher-volatility organic gases released from either biogenic or anthropogenic sources. The primary atmospheric oxidant during the daytime is OH since it is photolytically produced, whereas ozone (O₃) and other oxidants such as the nitrate radical (NO₃) dominate at nighttime^{31,32}. Oxidation of volatile organic compounds (VOCs) leads to the formation of more functionalized, lower volatility oxidation products that can undergo condensation or particles²³. Particles formed or grown by oxidized organic vapors are commonly referred to as secondary organic aerosol (SOA), and constitute a major fraction of submicron atmospheric aerosol around the world^{33,34}.

Oxidation of an individual VOC can initiate a complex series of chemical reactions that lead to multiple generations of oxidation products, each having differing volatilities. Organic oxidation products are commonly grouped according to their volatilities, since it is the main factor that determines how significantly they contribute to SOA mass³⁵. Oxidized organics with moderate vapor pressures that partition between the gas and particle phases are often referred to as semivolatile (SVOC) or intermediate-volatility (IVOC) organic compounds, whereas highly oxidized organics

with low vapor pressures that irreversibly condense to the particle phase are known as low-volatility (LVOC) or extremely low-volatility (ELVOC) organic compounds^{35,36}. These latter products represent the major contributors to SOA formation, and will hereafter be referred to as highly oxidized multifunctional molecules (HOMs).

In addition to condensation and partitioning, organic compounds can also contribute to SOA through heterogeneous chemistry involving reactions between particle-phase organics, or gas-phase compounds and particles³⁷. For instance, reactions between two or more particle-phase organic compounds can lead to the formation of accretion products such as organic dimers, trimers, or even higher order oligomers with lower volatilities than the precursor monomers^{38,39}. Also, reactions between organic and inorganic species such as sulfate can lead to the production of particle-phase products like organosulfates, a subject that will be discussed in more detail in Chapter 4⁴⁰. The role of heterogeneous chemistry in SOA formation is currently not well understood, and is an area of intensive research³⁷.

One type of heterogeneous pathway to SOA formation that has recently received significant attention is that which occurs in atmospheric waters, referred to as "aqueous secondary organic aerosol" (aqSOA)⁴¹. Through this pathway, soluble organic compounds can be oxidized within cloud or fog droplets to form nonvolatile products that remain in the condensed phase upon water evaporation⁴². Additionally, chemical reactions occurring within the aqueous phase of deliquesced hygroscopic particles, referred to as aerosol liquid water, can effectively form aqSOA⁴³. It is important to note that the efficiency of aqSOA formation is dependent on the concentrations of the reacting species within the aqueous phase. Therefore, evaporation of water can significantly enhance this process by forming a more highly

concentrated solute environment, effectively increasing reaction rates⁴⁴. For this reason, the formation of high molecular weight compounds is greater in the aqueous phase of deliquesced aerosol particles rather than cloud or fog droplets, since aerosol liquid water promotes higher solute concentrations⁴⁵.



Figure 1-2. Generalized scheme of particle growth by secondary organic aerosol formation.

Whereas SOA formation through gas-phase oxidation/condensation requires species with considerably low vapor pressures, aqSOA formation is driven by the solubility of the organic precursors, as well as the availability of aerosol liquid water⁴¹.

This allows for small organic molecules to contribute to organic aerosol mass that would otherwise remain too volatile to partition to the particle phase upon gas-phase oxidation. The solubility of an organic gas is typically represented by the Henry's law constant, K_H, which is defined as the concentration of a species dissolved in a liquid phase over its gas-phase partial pressure above the liquid under equilibrium conditions⁴⁶. Henry's law is generally valid only for highly dilute solutions, and so in more concentrated solutions such as aerosol liquid water, factors such as the chemical composition and ionic strength of dissolved electrolytes can cause deviations in the Henry's law constant^{44,47}. These deviations are designated as "salting-in" and "saltingout" effects, and will be explained in more detail in Chapter 3⁴⁴.

1.4 Scope of This Thesis

The uncertainty associated with aerosol climate effects currently represents the largest barrier in achieving reliable model predictions of future climate change⁴⁸. The underlying cause for this problem is that a thorough understanding of the formation and growth pathways of atmospheric aerosols is still lacking. For instance, current state-of-the-art climate models treat SOA sources in a very simplified manner, which often results in an extreme under-prediction of measured SOA mass concentrations, in some cases up to a few orders of magnitude^{49–51}. Complex factors affecting organic aerosol formation such as aqueous-phase reactions, anthropogenic-biogenic interactions and heterogeneous chemistry have yet to be fully incorporated into current models^{23,41,52}. Predictions of sulfuric acid and ambient sulfate particle concentrations have been much lower than those measured for both coastal and boreal forest environments, signifying that additional oxidants likely exist that are presently unaccounted for in models^{53,54}.

To this end, the scope of this thesis is to investigate chemical pathways to atmospheric aerosol formation and growth that are currently under-represented or entirely absent from climate models, with the goal of contributing to the improvement of our current-day understanding of aerosol climate effects. Chapter 2 details the analytical methodology and techniques used to conduct laboratory investigations of nanoparticle formation and growth. Chapter 3 discusses the formation of particle-phase organic nitrogen compounds in aqueous nanodroplets, and its atmospheric implications. Chapter 4 discusses the effect of sulfur dioxide on particle formation and growth during biogenic alkene ozonolysis. Chapter 5 expands on this study and discusses the effect of relative humidity and particle phase state on nucleation and growth from biogenic alkene ozonolysis in the absence and presence of sulfur dioxide. Finally, chapter 6 summarizes the principal conclusions of this research, and proposes objectives for future investigations that would further elucidate the roles of SO₂ and water on atmospheric nanoparticle formation and growth.

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Chapter 2

ANALYTICAL METHODOLOGY

2.1 Scanning Mobility Particle Sizer

In order to understand the critical factors affecting the formation and growth of nanoparticles, it is crucial to measure the dynamics of their size and number concentration with sufficient time resolution. For the experiments described herein, this has been achieved using a scanning mobility particle sizer (SMPS). The SMPS is a spectrometer which utilizes the electrical mobility property of charged particles smaller than 0.1 μ m in aerodynamic diameter to characterize the size distribution of a polydisperse aerosol.



Figure 2-1. Diagram of the Scanning Mobility Particle Sizer (SMPS) Spectrometer.

The SMPS consists of three parts: the electrostatic classifier, the differential mobility analyzer (DMA), and the condensation particle counter (CPC). The primary role of the electrostatic classifier is to apply an electric charge to the incoming particles, and carry them into and through the DMA via a precisely controlled sheath flow of air. Upon introduction into the inlet, particles first travel through an aerosol neutralizer containing radioactive polonium metal (210 Po) which creates a bipolar ionic atmosphere. Within the neutralizer, the particles undergo collisions with the bipolar ions, leading to a stationary state charge distribution surrounding zero, with a fraction of the particles receiving a charge of ±1, and a smaller fraction receiving a charge of ±2. The fraction of particles at a given size that receive a single charge is determined by the Wiedensohler approximation, which describes the equilibrium charge probability as a function of diameter for particles smaller than 1 micrometer¹. For the range of particle sizes studied herein, approximately 1-20% of particles are expected to have a single charge.

After exiting the neutralizer, the charged particles are directed through an impactor which assists in removing unwanted larger particles from the aerosol flow. The impactor consists of a stainless steel orifice with 0.071 cm i.d. followed by a baffle plate. Particles within the size range of interest traverse through the air streamlines around the plate, whereas large particles impact the plate and are removed. The remaining particles are then directed into the top of the DMA for size classification.

The purpose of the DMA is to separate particles based on their electrical mobility, which is defined as the ratio of the velocity a charged particle reaches in an

electric field relative to the strength of the electric field². This property is dependent on both the size and charge state of a particle.



Figure 2-2. Cross-section of the differential mobility analyzer (DMA).
As illustrated in Figure 2-2, the polydisperse aerosol entering the DMA is carried downward at a constant rate via a precisely controlled sheath air flow. The aerosol travels through the DMA column which consists of a grounded outer tube and a center rod with a high voltage applied to it. The resulting electric field manipulates the radial trajectory of the charged particles as they travel down the column, such that small particles with a higher electrical mobility are drawn towards the center rod faster than larger particles with a lower electrical mobility. In addition, charged particles with the same polarity as the center rod will be deflected and impact the outer tube, and neutral particles will pass through the column unaffected. The bottom of the center rod contains a slit through which only particles containing a specific electrical mobility will pass through and exit the DMA as a monodisperse aerosol flow. In this way, the voltage applied to the center rod determines the particle size allowed to exit the DMA outlet.

To measure the number concentration of particles exiting the DMA, the aerosol flow is then directed into the inlet of a condensation particle counter (CPC). The CPC functions by first growing the particles by sending them through a cooled region that is super-saturated with water vapor, followed by a heated region that causes water to rapidly condense onto the particles. This effectively transforms the particles into liquid droplets on the order of a few micrometers in diameter. The droplets are then sent into an optics unit that counts the number concentration using laser light scattering with a response time of ~0.4 seconds.

With the SMPS, the voltage applied to the center rod of the DMA is scanned over time, allowing the CPC to count the size-classified particles and generate a size distribution. Optionally, the DMA voltage can be held static to keep the particle size

constant, and the particles directed into an aerosol reactor rather than a CPC. In this way, experiments can be conducted using size-selected monodisperse seed particles, such as in the experiments described in Chapters 4 and 5.

2.2 Nano Aerosol Mass Spectrometer

The nano aerosol mass spectrometer (NAMS) is a home-built single particle laser mass spectrometer capable of measuring the elemental composition of nanoparticles. Figure 2-3 gives an illustration of NAMS as it was configured for this work. Particles were first drawn into the inlet through a 0.18 mm i.d. flow-limiting orifice at a flow rate of approximately 0.25 liters per minute. The particles are then directed downward and travel through a differentially-pumped aerodynamic lens consisting of a series of three cylindrical focusing elements containing orifices with inner diameters of 4 mm, 3.75 mm, and 3.5 mm going from top to bottom. The purpose of the aerodynamic lens is to converge the particles into a tight beam, which is subsequently directed into the ionization source region of the instrument. The lens assembly employed for this work allows effective focusing of particles down to an aerodynamic diameter of ~40 nm, below which particle transmission is drastically reduced³.

The particle beam then enters through a hole in the top of a ring electrode which is pulsed at a rate of 5 Hz with a voltage of +1000V. A Nd:YAG laser (Quantel CFR-400) with 532 nm wavelength and ~200 mJ pulse energy is fired at the same 5 Hz rate as the ring electrode. The laser beam is directed orthogonally to the particle beam, entering through a hole in the side of the ring electrode. The beam is focused through a lens with 71 mm focal length into a spot size of ~0.1 mm in the center of the

ring electrode. Because particle trapping was not employed, ionization occurred only when a particle was present within the focal point of the laser beam.



Figure 2-3. Diagram of the Nano Aerosol Mass Spectrometer as configured for this work.

When a particle was ablated by the laser pulse, a plasma was formed which disintegrated the particle into positive, multiply charged atomic ions. Given the energy of the laser pulse, ions up to a charge state of +5 were typically observed. The ions were then ejected into a time-of-flight mass analyzer via two extraction plates at each end of the ring electrode, with the plate further from the analyzer set to a voltage of -1.8 kV, and the plate closer to the analyzer set to a voltage of +1.5 kV. Upon entering the mass analyzer, the ions were repelled at a downward angle by a deflector plate set to -1.05 kV. Their horizontal trajectory was then reversed by a reflector set to +1.13

kV, which directed the ions to impact a microchannel plate detector used to measure the ion signal. A digitizer was then used to collect the mass spectra with a sampling interval of 2 ns.

Quantitative elemental composition analysis with NAMS was achieved in several steps involving data collection and averaging, spectral calibration, peak area integration, and isobaric peak apportionment. For a given aerosol sample, a minimum of 100 individual particle spectra was typically collected. A bootstrapping method was applied to each raw dataset such that 20 individual particles were randomly sampled with replacement and averaged together, and this process repeated 100 times to create a 100-sample "averaged" dataset from which the mean elemental mole fractions and their standard deviations were determined. This method has been described previously by Klems et al., and has been shown to be sufficient for assessing the precision of the elemental analysis by NAMS⁴. Averaging the data in this manner is necessary for overcoming variations that occur between each spectrum collected due to uncontrollable fluctuations in the energetics of the laser plume, which in turn affects the charge state distribution of the generated ions⁴.

Calibration was then performed in order to determine the nominal flight times of each ion. This was achieved by analyzing laboratory-generated nanoparticle standards of sucrose ($C_{12}H_{22}O_{11}$) and HEPES (4-(2-hydroxyethyl)-1peperazineethanesulfonic acid, $C_8H_{18}N_2O_4S$) as calibrants. Peak areas were then integrated using the calibrated flight times. These calibrants were also used to deconvolute the isobaric peaks that occur at m/z 4 (overlap of C^{3+} and O^{4+}), 8 (overlap of O^{2+} and S^{4+}), and 16 (overlap of O^+ and S^{2+}) according to the method of Zordan et al⁵. Finally, the relative mole fractions of each element were determined by summing



Figure 2-4. An example NAMS mass spectrum of 80 nm ammonium sulfate nanoparticles, showing detection of nitrogen, oxygen, and sulfur ions up to the +5 charge state. The spectrum shown is an average of 34 single particles analyzed.

the integrated peak areas at all observed charge states of a particular element, and dividing by the total area of all peaks in the mass spectrum. Performing the data analysis in this manner typically allows determination of the elemental composition with an accuracy of $\pm 10\%$ of the true value based on analyses of known particle standards⁵.

2.3 High-Resolution Electrospray Ionization Mass Spectrometry

The organic component of atmospheric aerosols typically consists of hundreds to thousands of unique molecular species with molecular weights of approximately 100-500 Da⁶. In addition, many species can have the same nominal mass, with multiple compounds often within a window of 0.1 Dalton. In order to investigate the molecular composition of the organic fraction of aerosols studied in this work, direct infusion electrospray ionization mass spectrometry was performed using a high-resolution Thermo Q Exactive Orbitrap mass spectrometer.

The combination of high mass accuracy and high mass resolving power of this instrument allowed for the assignment of unambiguous elemental formulas to the majority of ion peaks observed throughout each mass spectrum. Scans were typically performed in the mass range of m/z 50-750, with a mass resolving power of m/ $\Delta m = 100,000$ at m/z 100. Removal of background ions was performed by omitting peaks with a signal-to-noise ratio less than 5 and a relative intensity less than 0.5%. For the remaining peaks, elemental formulas were assigned within a 5 ppm mass accuracy window using Thermo Xcalibur software (version 3.0) with assignment parameters of C₁₋₃₀, H₂₋₆₀, O₀₋₁₅, N₀₋₁₀, S₀₋₂, and, for positive mode analysis, Na₀₋₁.

2.4 Aerosol Flow Tube Reactor

The experiments discussed in Chapters 4 and 5 were conducted using a homebuilt aerosol flow tube reactor. The flow tube was constructed using a fused quartz tube (1.52 m length, 0.2 m i.d., 6 mm wall thickness) fitted with custom machined stainless steel funnels on each end that reduce the inner diameter down to 0.051 m. The total volume of the tube and entrance and exit funnels is 52.4 L, giving a surfaceto-volume ratio (SA/V) of 0.24 cm⁻¹.

The entrance funnel is coupled with an 8-inch straight tri-clamp tube fitting that allows carrier/reactant gases and optionally seed particles to enter the tube via an

axial inlet port and continuously flow through the entire length of the reactor during the course of an experiment. The inlet fitting also contains a 70 cm long x 5.3 mm i.d. "injector" tube mounted axially in the center of the flow tube, which is used for introduction of organic vapors. The injector allows the organic gases to be introduced past the entrance funnel where the inner tube diameter is the largest, which allows for a constant exposure to the oxidant.

The exit funnel is coupled with an 18 cm long concentric reducer that converges the flow exiting the tube down to an inner diameter of 1.3 cm. The end of the reducer is fitted with numerous sampling ports so that the aerosol can be analyzed upon exiting the tube, with the excess flow directed through a waste line. A detailed description of the setup and configuration of the flow tube specific to the experiments conducted in this dissertation will be given in section 4.5.



Figure 2-5. Diagram of the aerosol flow tube reactor (not drawn to scale).

2.5 Nano Aerosol Sampler

Chapter 5 discusses experiments in which atomized seed particles were deliquesced prior to introduction into the flow tube. This was achieved by passing the aerosol through a humidifier device herein referred to as the "nano aerosol sampler" (NAS). The key benefit of the NAS is that the aerosol is exposed to supersaturated conditions which ensure water uptake by the particles, which is difficult to achieve by simply mixing the aerosol flow with humidified air. The NAS consists of a 3/8" i.d. x 11.8" long wet-walled condensation growth tube that is divided into three individually temperature-controlled regions. The first section is a "conditioner" region that is cooled to 5°C which creates flow conditions of low temperature and high relative humidity. The second region is the "initiator" which is heated to 45°C to increase the water vapor concentration of the aerosol flow. In this region, water from the heated walls diffuses into the flow faster than the flow warms, due to the higher mass diffusivity of water vapor vs. the thermal diffusivity of air. This results in the flow becoming supersaturated, allowing for particle activation. The final region is the "moderator" which gives the time to allow the particles to grow into droplets on the order of 1.5-3 µm aerodynamic diameter while lowering the relative humidity back down to a manageable level. For this work, the NAS was operated with an aerosol flow rate of approximately 1.6 liters per minute, resulting in a laminar flow (Re=242) that minimized particle loss. A schematic of the NAS is shown in Figure 2-6.



Figure 2-6. Schematic of the nano aerosol sampler (NAS). A magnified view of the condensation growth tube is shown to the right of the figure.

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Chapter 3

FORMATION OF ORGANIC NITROGEN IN AQUEOUS SECONDARY ORGANIC AEROSOL

The following chapter discusses the formation mechanisms and atmospheric implications of organic nitrogen-containing compounds within aqueous nanodroplets. This work has been previously published under the following reference:

Stangl, C. M.; Johnston, M. V., Aqueous Reaction of Dicarbonyls with Ammonia as a Potential Source of Organic Nitrogen in Airborne Nanoparticles. *J. Phys. Chem. A* **2017**, *121*(19), 3720-3727.

3.1 Formation of Aqueous Secondary Organic Aerosol

Uptake of low-volatility organic vapors by atmospheric particulate matter is known to contribute substantially to the global aerosol mass budget, and can impact climate by dominating nanoparticle growth and leading to the formation of cloud condensation nuclei. A ubiquitous source of such low-volatility organics comes from photochemical oxidation of volatile organic compounds (VOCs) in the gas phase leading to the formation of secondary organic aerosol (SOA)¹. An alternative pathway to SOA formation, and one that recently has been receiving significant attention, occurs via aqueous-phase chemical reactions of organic compounds partitioned into aerosol liquid water to form aqueous SOA (aqSOA)².

Numerous laboratory and computational studies have shown that chemical reactions following uptake of water-soluble organic gases into the aqueous phase, i.e. in cloud/fog droplets or deliquesced particles, can lead to the formation of low-

volatility organic compounds that will remain in the condensed phase following water evaporation^{2–6}. A large number of such gaseous precursors shown to undergo aqueous reaction and form aqSOA are photooxidation products of isoprene, including glyoxal^{7,8}, methylglyoxal⁹, glycolaldehyde¹⁰, and isoprene epoxydiols (IEPOX)¹¹, due to their high atmospheric gas-phase concentrations and effective Henry's Law constants^{12,13}. Glyoxal, for instance, is a well-established aqSOA precursor, and is known to form a variety of lower volatility products through numerous reaction pathways once in the condensed phase. These include, but are not limited to, hydrate formation and self-oligomerization¹⁴, hydroxyl radical oxidation to form oxalic acid¹⁵, and irreversible formation of organic nitrogen-containing species (e.g. imidazoles) by reaction with amines or ammonium salts^{16–18}. The generation of nitrogen-containing organics is of particular interest because this reaction is not photochemically induced and so can occur in the dark, has the potential to form light-absorbing "brown carbon" products that can directly impact radiative forcing¹⁹, and, as is a focus of this work, can potentially explain significant levels of particulate nitrogen observed in ambient measurements of nanoparticle chemical composition.



Figure 3-1. Generalized mechanism of organic nitrogen formation from the aqueous reaction of glyoxal and ammonia, showing some of known products.

Because aqSOA formation is dependent on the availability of an aqueous phase^{20,21}, as well as the potential of the gaseous precursor to partition to the aqueous phase (i.e. the Henry's law constant), which itself is affected by the preexisting aqueous phase composition², the extent to which aqSOA contributes to particulate matter is likely to vary by location²². Consequently, it is suggested that aqSOA formation is most significant in the eastern United States during the summertime, when water-soluble VOC emissions and aerosol water concentrations are highest²³. It is thought that aqSOA formation can help explain the discrepancy between regional SOA concentrations measured in ambient studies with those predicted by aerosol models relying mainly on partitioning theory, which are typically much lower²⁴.

3.2 Excess Nitrogen Measured in Ambient Nanoparticles

Recently, nanoparticle chemical composition was measured during new particle formation (NPF) events occurring in both urban^{25,26} and rural locations²⁷ in the United States. NPF involves the formation and stabilization of molecular clusters that grow quickly, often to climatically relevant sizes 28 . In these studies, quantitative elemental composition measurements revealed a substantial amount of nitrogen often present in the growing nanoparticles, independent of the measurement location. Periods when the nitrogen mole fraction (N) exceeded twice the sulfur mole fraction (S) were often observed, indicative of particle-phase nitrogen unassociated with sulfate neutralization, herein referred to as "excess N" (N-2S). During a field study, conducted 23 July to 31 August 2012 in Lewes, Delaware²⁷, concurrent molecular composition measurements aided in characterization of the excess N, and revealed that the most plausible source was organic nitrogen-containing compounds such as imines and imidazoles, which could form via aqueous reaction. In addition, increases in excess N always correlated with a simultaneous decrease in relative humidity, which again suggested that organic nitrogen-containing species, such as those formed through aqueous reaction of glyoxal or methylglyoxal with ammonium sulfate, could be a source of excess N, as such reactions are greatly enhanced by water evaporation⁵.



Figure 3-2. Trend in excess N and relative humidity for three NPF event days measured during the 2012 field campaign in Lewes, DE.

Herein, results are reported from a series of laboratory experiments designed to gauge the potential for water-soluble organic compounds (WSOC) relevant to the eastern U.S. to form organic nitrogen through aqueous reaction with ammonium sulfate in nanodroplets. The results suggest that such reactions are plausible sources of the excess N observed during ambient measurements of NPF in Lewes, Delaware.

3.3 Generation and Collection of Dried Nanodroplets

Aqueous solutions containing either glyoxal (GLY, 40% in H₂O, Acros Organics), methylglyoxal (MGLY, ~40% in H₂O, Sigma-Aldrich), or glycolaldehyde (GCA, solid dimer, Sigma-Aldrich) and ammonium sulfate (AS, 99.9999%, Acros Organics) were prepared to be 5 mM organic/5 mM (NH₄)₂SO₄ using ultrapure water (18.2 M Ω ·cm). All solutions had a pH in the range of 4-5, measured with a pH probe (accuTupH, Fisher Scientific), as expected for an aqueous ammonium sulfate solution. No attempt was made to investigate lower pH values since ambient nanoparticle composition measurements relevant to this study suggest a 2:1 mole ratio of ammonia to sulfuric acid. Assuming a Henry's law constant for glyoxal of 2.4x10⁷ M/atm, reported by Ip et al. (2009) for an aqueous solution containing a sulfate:glyoxal molar ratio of 1:1²⁹, this would give an approximate gas phase mixing ratio of 0.2 ppb for glyoxal above solution in these experiments, which is within the range of ambient glyoxal concentrations of 0.01-5 ppb^{7,13,21,30,31}.

Polydisperse aerosol was generated from each solution via nebulization (ATM 226, Topas GmbH, Dresden, Germany) to produce internally-mixed nanodroplets with an expected theoretical size range of 0.1-0.5 μm. The droplets were subsequently passed through one or more home-built diffusion dryer tubes containing silica gel beads surrounding the aerosol flow path to lower the relative humidity and promote the reaction. Residence time of particles in each dryer tube was 1-2 seconds, resulting in a short reaction time for each aerosol system studied. In most experiments, two dryers were used to maintain a relative humidity of about 60% as measured with a hygrometer (Fisher Scientific). Depending on the number of dryers used (0 to 3) and the system studied, the relative humidity at the exit of the assembly could be maintained in four separate regimes: 90-95%, 70-75%, 55-60%, and 25-40%. During any individual experiment, the relative humidity varied less than +/- 2%. The size distribution of aerosol exiting the dryer tube assembly was measured with a scanning mobility particle sizer (model 3081 DMA, model 3788 N-WCPC, TSI, Inc.), and found to have a mode diameter of 50-60 nm for all systems studied.



Figure 3-3. Experimental setup for the dried nanodroplet studies.

3.4 Collection and Extraction of Dried Nanodroplets

Upon exiting the dryer tube(s), particles were collected onto a quartz microfiber filter (Whatman GF/D, GE Life Sciences) continuously for 1 hour, allowing ~500 μ g of mass to be collected, determined by weighing the filter before and after collection (Accu-124D, Fisher Scientific). Extraction of the captured material was performed immediately following collection by sonicating each filter in 2 mL of 1:1 acetonitrile/water (Optima grade, Fisher Scientific) for a final concentration of ~0.2 mg/mL. All samples were stored at -20°C immediately following extraction and analyzed within 24 hours of particle collection. In addition, 200 μ L bulk aliquots of each solution were dried under vacuum overnight, and the brown residue redissolved in 1:1 ACN/H₂O to ~0.2 mg/mL.

3.5 Offline Molecular Analysis by High-resolution Electrospray Ionization Mass Spectrometry

Molecular composition analysis of the particle extracts was performed by positive-ion mode direct infusion high-resolution electrospray ionization mass spectrometry (ESI-MS) as described in Chapter 2. Background subtraction was carried out using a filter blank (sonication of a clean filter in 1:1 ACN/H₂O). Following elemental formula assignment, N/C ratios and mass-weighted intensity fractions (MIF) were calculated. MIF accounts for the fact that peaks with larger masses and intensities likely represent a larger fraction of the overall sample mass, and is determined by:

$$MIF_i = \frac{(\frac{m}{z})_i I_i}{\sum_i (\frac{m}{z})_i I_i},$$

where $(m/z)_i$ and I_i represent the mass-to-charge ratio and intensity of peak *i*, respectively³². Mass-intensity weighted N/C ratios for each sample were then determined by:

$$\overline{N/C}_{weighted} = \sum_i N/C_i \times MIF_i$$

It should be noted that the weighted N/C ratio using MIF gives an accurate representation of the true N/C ratio of the sample only under the assumption that all species in each positive ion spectrum have the same response factors³².

3.6 Online Elemental Composition Analysis by NAMS

Elemental composition of the dried particles produced from each nanodroplet system was measured by NAMS. The working principle of NAMS has been described in Chapter 2. At least 150 particle spectra were obtained for each experiment. For this study, mole fractions of C, O, N, and S were determined for each system investigated (although H was observed, it is not quantitative by NAMS analysis and so was omitted from the elemental mole fraction apportionment). Excess N, if present, was calculated as N-2S, and the N/C ratio of the organic fraction of the particles was calculated as Excess N / C.

3.7 Results of High-resolution ESI-MS Analysis

Figure 3-4 shows an ESI mass spectrum of the GLY/AS droplets collected onto a filter following drying to ~60% RH. Nitrogen-containing species (red peaks) were found to comprise the majority of products.



Figure 3-4. High-resolution ESI mass spectrum of dried nanodroplets containing glyoxal and ammonium sulfate.

Molecular formulas assigned to reaction products via accurate mass measurements matched those previously reported by Kampf et al. for bulk aqueous solutions of glyoxal/ $(NH_4)_2SO_4^{34}$. The proposed structures and exact masses for these major peaks are given in Figure 3-5.



Figure 3-5. Proposed structures and measured m/z values for the major reaction products identified in the glyoxal/ammonium sulfate dried nanodroplets.

Table 1 shows the mass-intensity weighted N/C ratios determined for each bulk solution and dried nanodroplet system by ESI-MS. In the case of the GLY/AS system, no statistically significant difference is observed between N/C_{weighted} of the dried bulk solutions and dried nanodroplets, and in fact the two spectra appear nearly identical, suggesting that organo-nitrogen formation by aqueous reaction occurs to a similar extent in both cases. Given the short time period between nanodroplet drying and collection (<3s), this suggests that the formation of N-containing organics occurs very rapidly via reaction between GLY and ammonia when water is actively removed from the droplet, and that aqueous reaction in ultrafine aerosol is likely to proceed via the same manner as extensive drying over long time periods in bulk solution. In the case of the MGLY/AS system, mass spectra of the dried bulk solution and dried nanodroplets were again both comprised largely of N-containing imidazole compounds, however a slightly lower mean N/C_{weighted} was found for the aerosol.

Reaction system	Avg. N/Cweighted
Bulk	
5 mM glyoxal/5mM (NH ₄) ₂ SO ₄	0.60
5 mM methylglyoxal/5mM (NH ₄) ₂ SO ₄	0.29
5 mM glycolaldehyde/5mM (NH ₄) ₂ SO ₄	0.27
Aerosol	
5 mM glyoxal/5mM (NH ₄) ₂ SO ₄	$0.59_{\pm 0.05}$
5 mM methylglyoxal/5mM (NH ₄) ₂ SO ₄	$0.24_{\pm 0.06}$
5 mM glycolaldehyde/5mM (NH ₄) ₂ SO ₄	Not Detected

Table 3-1. Mass-intensity weighted N/C ratios of aqSOA products produced by drying nanodroplets and bulk solutions of each system investigated, as determined by positive mode ESI-MS.



Figure 3-6. ESI mass spectrum and neutral formulas corresponding to the most intense N-containing products identified in the methylglyoxal/ammonium sulfate dried nanodroplets.

Interestingly, no imidazole formation was observed in the GCA/AS dried nanodroplets by ESI-MS, and only a small abundance of N-containing products identified as imines were observed in the dried bulk solution. Further, all three systems studied left a brown solid residue upon drying of the bulk solutions (Figure 3-7), however only the filters used for collection of the dried GLY- and MGLY-containing nanodroplets showed browning (Figure 3-8), suggesting a lack of formation of lightabsorbing organo-nitrogen products in the dried GCA/AS nanodroplets.



Figure 3-7. Photographs of the dried bulk solutions containing the three carbonyls studied mixed with ammonium sulfate.



Figure 3-8. Photographs of filters used to collect the dried nanodroplet samples.

The lack of imidazole formation in this system may be explained by the inability of glycolaldehyde to form a diimine, which has been proposed to be an essential intermediate species in the reaction⁴. Aqueous imidazole formation is thought to occur via a two-step mechanism that begins with attack of both neighboring aldehyde groups of an α -dicarbonyl (e.g. glyoxal, methylglyoxal) by a nitrogen species such as ammonia or a primary imine, forming a diimine. The diimine can then attack the carbonyl group of e.g. glyoxal monomer, generating an acyclic enol intermediate, which will ultimately undergo rearrangement and ring closure to form the imidazole⁴.

To confirm that the observed organo-nitrogen species were in fact formed by the droplet drying process, a control sample for each system was collected in which the nanodroplets were collected directly onto a filter without drying. For all three systems, nitrogen-containing organics were completely absent in the spectra, suggesting that the reactants remained too dilute in the droplets to effectively form organic nitrogen on the timescale of the experiment. These results also suggest that reaction does not occur on the filter. To investigate the possibility of organo-nitrogen formation occurring within the ionization source region of the mass spectrometer, diluted aliquots of each bulk solution were taken and analyzed without prior atomization or drying. Again, a complete absence of N-containing organics was observed, suggesting that exposure to instrumental conditions does not influence the observed spectra, and that all N-containing peaks are due to the droplet drying process.

3.8 Results of NAMS Analysis

On-line elemental composition analysis of the dried nanodroplets was performed by directing the aerosol flow path exiting the diffusion dryer to the inlet of NAMS. Figure 3-9 shows the averaged mass spectrum of the ~200 individual particle

spectra collected for the glyoxal/ammonium sulfate dried nanodroplets after drying to a relative humidity of ~60%. Mean elemental mole fractions and their standard deviations for this and other experiments are given in Table 2.



Figure 3-9. NAMS averaged mass spectrum of ~200 individual particle spectra collected from the glyoxal/ammonium sulfate nanodroplets after drying to 60% relative humidity.

To determine the organic N/C ratio for each system, the excess N mole fraction was first calculated for each averaged spectrum, as described in the experimental section, then divided by the C mole fraction to determine the N/C ratio apportioned to the organic matter in the particles (N/C_{org}). This assumed that all carbon and all excess

N measured by NAMS-II was d	ue to the aqueous	formation of org	ganic compounds
during droplet drying.			

Reaction system	RH	С	0	Ν	S	Excess	N/Corganic
						Ν	_
5 mM glyoxal/	$91_{\pm 1.5}\%$	0.27	0.54	0.16	0.03	0.09	$0.33_{\pm 0.04}$
5mM (NH ₄) ₂ SO ₄							
	$72_{\pm 1.5}\%$	0.17	0.62	0.16	0.05	0.06	$0.35{\scriptstyle \pm 0.07}$
	$60_{\pm 1.5}\%$	0.16	0.63	0.16	0.05	0.06	$0.38_{\pm0.06}$
	$38_{\pm1.5}\%$	0.11	0.68	0.16	0.05	0.06	$0.55_{\pm0.08}$
5 mM methylglyoxal/	$95_{\pm 1.5}\%$	0.21	0.49	0.23	0.07	0.09	$0.41_{\pm 0.07}$
5mM (NH ₄) ₂ SO ₄							
	$70_{\pm 1.5}\%$	0.15	0.50	0.25	0.11	0.04	$0.27_{\pm 0.09}$
	$55_{\pm 1.5}\%$	0.11	0.51	0.26	0.12	0.02	$0.18_{\pm 0.13}$
	$28_{\pm1.5}\%$	0.03	0.56	0.27	0.14	0	0

Table 3-2. Mean elemental mole fractions, excess N mole fraction, and organic N/C ratio measured by NAMS for each of the dried nanodroplet systems studied at various relative humidities.

No excess N was observed in nanodroplets produced by atomizing a 5 mM solution of pure ammonium sulfate. In contrast, excess N was often observed in nanodroplets produced by atomizing solutions that also contained aldehydes. The likely origin of the excess N detected in these latter droplets was partitioning of additional gas-phase NH_{3(g)} into the droplets as a result of the chemical reaction. Gas-phase ammonia was expected to be present in these experiments owing to the partitioning of NH_{3(aq)} (in equilibrium with NH₄⁺_(aq) at the pH of ammonium sulfate solution)³⁵ to NH_{3(g)} inside the atomizer where droplets were formed³⁶, as well as possible trace levels of ammonia present in the carrier air supply or the water used to

make the solution, which were not quantified here. Because a large reservoir volume of solution containing ammonium sulfate was always present inside the atomizer, the small absolute amount of NH_3 lost from this solution by partitioning to the gas phase did not significantly alter its composition or the composition of atomized droplets produced from it. Subsequently, when $NH_{3(aq)}$ irreversibly reacted with aldehyde in the nanodroplet to form organic nitrogen compounds, more $NH_{3(g)}$ was driven into the droplet to maintain sulfate neutralization, resulting in a measured N/S ratio greater than 2.

NAMS analysis of the dried GLY/AS and MGLY/AS (Figure 3-10) nanodroplets revealed evidence of organic nitrogen formation in both systems, with a larger N/C_{org} for the GLY-containing droplets (Table 2) as with the off-line molecular composition measurements.



Figure 3-10. Average NAMS spectrum of nanodroplets produced from an atomized solution containing 5 mM methylglyoxal and 5 mM ammonium sulfate after drying to ~55% RH.

NAMS analysis of the GCA/AS dried droplets showed complete absence of a carbon signal (Figure 3-11), suggesting that glycolaldehyde completely evaporated from the drying droplets before any particle-phase organics could be formed, also in agreement with the off-line measurements. Glycolaldehyde has previously been suggested to undergo complete evaporation from dried microdroplets containing ammonium sulfate, rather than react to form additional aerosol³⁷.



Figure 3-11. Average NAMS spectrum of nanodroplets produced from an atomized solution containing 5 mM glycolaldehyde and 5 mM ammonium sulfate after drying to ~60% RH.

For the GLY/AS and MGLY/AS systems, mean organic O/C ratios (O/C_{org}) were also determined by apportioning all non-sulfate oxygen (i.e. O-4S) to the organic fraction of the particles. This resulted in an O/C_{org} of 2.7 for the GLY/AS droplets dried to 60% RH, which is significantly higher than what could be explained by previously characterized aqueous reaction products of glyoxal and ammonium sulfate (O/C \approx 0.2-0.8) or glyoxal oligomerization (O/C \approx 1.0-1.5)^{34,38}. A plausible explanation is the presence of residual particle-phase water, which may not completely

evaporate during the drying process before the droplet is analyzed. Galloway et al. reported residual particle volumes >100% for dried microdroplets containing a 1:1 molar ratio of glyoxal and ammonium sulfate, and suggested this to be due to retained water, which is kinetically limited in its evaporation from the drying droplets³⁷. Hawkins et al. noted increased viscosity of dried droplets containing glyoxal and amines, thought to be caused by oligomeric reaction products³⁹. In addition, Smith et al. studied the hygroscopic phase transitions of particles containing ammonium sulfate and isoprene photo-oxidation products, and found that the efflorescence relative humidity decreased with increasing organic volume fraction (ϵ), with efflorescence being eliminated when $\epsilon \ge 0.6^{40}$. NAMS analysis of dried (RH \approx 60%) pure glyoxal droplets in the absence of ammonium sulfate (Figure 3-12), however, yielded an O/C ratio consistent with previously identified glyoxal oligomerization products, suggesting that aqueous reactions caused by the presence of ammonium sulfate inhibit the loss of water in the dried particles³⁸.



Figure 3-12. Average NAMS spectrum of nanodroplets produced from an atomized solution containing 5 mM glyoxal in the absence of ammonium sulfate after drying to ~60% RH.

Interestingly, O/C_{org} of the dried MGLY/AS droplets was 0.3, which is consistent with aldol condensation products of methylglyoxal, proposed to account for the vast majority of aerosol-phase material produced by methylglyoxal and enhanced by particle phase ammonia in evaporated droplets⁴¹. This observation suggests that glyoxal increases droplet viscosity to a greater extent than methylglyoxal via reaction with ammonium sulfate.

3.9 Relative Humidity Dependence on Excess N

To investigate the dependence of organic nitrogen formation on relative humidity, additional experiments were performed in which the number of diffusion dryer tubes that the GLY/AS and MGLY/AS droplets passed through prior to analysis was varied from 0-3. Figure 3-13 shows the change in N/C_{org} as a function of the relative humidity to which the droplets are dried before entering NAMS.



Figure 3-13. RH dependence of the organic N/C ratio measured by NAMS for the glyoxal/ammonium sulfate and methylglyoxal/ammonium sulfate dried droplets. The y-error bars represent the uncertainty of the hygrometer probe (±1.5%)

A clear trend is observed in which N/Corg of the GLY/AS droplets increases as the extent of drying increases, i.e. RH decreases. This can be explained by an increase in solute concentrations as more solvent is evaporated from the droplets, which promotes formation of organo-nitrogen compounds by increasing molecular interactions between GLY and ammonia as the solutes become supersaturated⁵. In addition, evaporative loss of glyoxal to the gas phase is slow due to its high effective Henry's law constant, which has been shown to increase exponentially with ammonium sulfate concentration and sulfate ionic strength, i.e. "salting-in"^{8,29,42,43}. For MGLY/AS droplets, the opposite trend was observed where N/Corg decreased as the extent of droplet drying increased and RH decreased. This observation suggests that, unlike glyoxal, methylglyoxal evaporates from the drying droplets faster than it reacts to produce organo-nitrogen species, with less remaining in the condensed phase as the relative humidity is lowered. In addition, a continuous decrease in both the C mole fraction and the excess N mole fraction was found as drying increased, again suggesting that less organic remained in the droplets to promote NH_3 uptake and form particle-phase organic nitrogen. In a trial carried out where the droplets were dried to ~27% RH, the C mole fraction was nearly zero, and excess N was completely absent in these measurements. Methylglyoxal has a lower effective Henry's law constant than glyoxal in pure water, and has been shown to decrease substantially with increasing sulfate ionic strength, i.e. "salting-out"⁴⁴. In agreement with the results of Galloway et al., the authors suggest that methylglyoxal heavily evaporates out early in the drying process as the droplets are still dilute, leaving little to react with ammonium sulfate³⁷.

Additionally, the effect of RH on the C/S ratios of the GLY/AS and MGLY/AS dried nanodroplets was investigated using NAMS. C/S gives an idea of the

amount of semivolatile organic remaining in the particle phase available for reaction relative to nonvolatile sulfate. As shown in Figure 3-14, C/S was found to decrease with decreasing RH for both the GLY/AS and MGLY/AS nanodroplets. This was expected, as decreasing the RH decreases the volume of aerosol liquid water, and hence the amount of dissolved organic, while the moles of sulfate remains constant.



Figure 3-14. RH dependence of the C/S ratio measured by NAMS for the glyoxal/ammonium sulfate and methylglyoxal/ammonium sulfate dried droplets.

It should be reinforced that although the mole ratio of organics to AS decreases in the experiments during drying, the molal concentrations of both organics and AS in the droplets increase. In addition, C/S is much larger in both systems at the highest RH studied, since in those trials the aerosol did not pass through a diffusion dryer that aids in removing volatile species, hence equilibrium gas phase mixing ratios of organics were likely much higher than in trials utilizing one or more dryer tubes. C/S was consistently lower for the MGLY/AS system, likely due to enhanced loss of methylglyoxal to the gas phase with increased drying (salting-out). Although glyoxal also evaporates with increased drying, the increase in particle viscosity at lower RH, as well as the salting-in effect, offset the loss of glyoxal to the gas phase, and contribute to a consistently larger C/S ratio observed in these measurements. Based on the results of Waxman et al. (2015), for a bulk aqueous solution of ammonium sulfate and GLY, an increase in $[SO_4^{2-}]$ by a factor of 2 would lead to an estimated increase in the effective Henry's law constant of glyoxal by a factor of $\sim 2.7^{44}$. However, my observations suggest that such aqueous carbonyl chemistry occurring in the aerosol phase is complicated by a number of additional factors including dynamic changes in liquid water content, reactant concentrations, Henry's law constants, particle viscosity, and irreversible product formation, and so the exact effects of such chemistry on ambient organic aerosol formation and growth warrants further research.

3.10 Implications for Ambient New Particle Formation

The ambient nanoparticle composition measurements behind the motivation of this work took place from 23 July to 31 August 2012 in Lewes, Delaware, a coastal location in the eastern U.S²⁷. Considering three representative NPF events during which excess N was observed (12, 13, and 21 August), the excess N mole fractions

ranged from ~0.05-0.06 at their maxima, leading to N/C_{org} = 0.1-0.2. A recurring observation during these events was that the increase in excess N mole fraction occurred just following a sharp decrease in relative humidity (Figure 3-2). On 12 August, for instance, RH dropped from about 95% at 6:00 EST to 60% by 12:00 EST, while over the same time period the sulfur (sulfate) fraction increased by a factor of 5 and excess N increased by a factor of 3, leading to N/C_{org} \approx 0.2 and C/S \approx 8. This observation suggests that if imines and imidazoles are the cause of excess N, a decrease in liquid water content of the particles coupled with an increase of sulfate mass fraction was enhancing their formation, in agreement with my laboratory results.

Other studies have also shown that the formation rate of nitrogen-containing species in aqueous GLY/AS and MGLY/AS aerosols is greatly increased as the solute environment is concentrated when water is actively removed from the particles^{5,6}. In my experiments where the nanodroplets were dried to a comparable relative humidity of 55-60%, both glyoxal and methylglyoxal produced large enough N/C_{org} ratios (~0.4 and ~0.2, respectively) to be considered plausible contributors to the formation of organic nitrogen observed in Lewes.

Based on these results, if methylglyoxal is considered to be the major contributor to the N/C_{org} in Lewes, almost all of the carbonaceous matter in those particles would have had to arise from methylglyoxal chemistry, which seems unlikely. In addition, the C/S ratio measured in my experiments for MGLY/AS at a comparable RH was far lower than the C/S ratio observed in Lewes. Alternatively, if glyoxal is considered to be the major contributor, approximately half of the carbonaceous matter in Lewes could be explained by glyoxal chemistry, with the remainder likely due to condensation of other oxygenated organics from e.g.
monoterpenes. In this case, approximately half of the observed C/S ratio of ~8 during NPF could be explained by glyoxal chemistry, which is comparable to the C/S measured in my laboratory experiments for GLY/AS at a comparable RH.

Recently, Boone et al. reported an average N/C ratio of 0.24 for compounds containing carbon, hydrogen, oxygen and nitrogen (CHON) identified in positive mode ESI-MS spectra of cloudwater samples collected over Alabama in the summer of 2013, and stated that a large fraction of the observed compounds corresponded to isoprene oxidation products⁴⁵. Altieri et al. analyzed cloudwater samples collected in New Jersey by ultrahigh-resolution mass spectrometry, and reported an average N/C ratio of 0.16 for the >200 CHON compounds that were identified, suggesting that many of those compounds were likely formed by secondary atmospheric processes involving reduced nitrogen species⁴⁶. It should be noted that these N/C ratios are in good agreement with those observed for the growing nanoparticles measured in the ambient studies in Lewes.

Nguyen et al. investigated the formation of nitrogen-containing organic compounds by photooxidation of isoprene in a Teflon chamber under both low and high-NO_x conditions, and found the average N/C ratio of the SOA produced in the high-NO_x system to only be 0.019^{47} , which is insufficient to explain excess N in Lewes. In addition, the organic nitrogen was found to be in the form of organic nitrates, which was ruled out as a possible source of the excess N in Lewes due to the low abundance of particle-phase nitrates²⁷. Liu et al. studied the reactive uptake of gas-phase ammonia by SOA derived from α -pinene ozonolysis and OH oxidation of m-xylene, and found the mean N/C ratios of the reacted aerosols to be 0.016 ± 0.004 and 0.065 ± 0.011 , respectively⁴⁸. These values are also too small for these sources to

be significant contributors to excess N in Lewes, and provide further support for the hypothesis that aqueous reaction of water-soluble dicarbonyls such as glyoxal by reaction with reduced nitrogen compounds is the more likely source in ambient aerosol.

3.11 Conclusions

In the laboratory studies reported here, glyoxal contributed to the largest mole fraction of organic nitrogen formed by aqueous reaction with ammonium sulfate in drying nanodroplets, suggesting that if such a process was responsible for the excess N observed in Lewes, glyoxal was likely a large contributor. It is possible that methylglyoxal could explain a portion of the organic nitrogen observed in Lewes as well, although its contribution is likely smaller, as N/Corg was observed to decrease along with relative humidity in the laboratory experiments, opposite of the trend observed in the ambient measurements. Glycolaldehyde likely did not contribute to organic nitrogen formation in Lewes, as it was found to completely evaporate in the dried droplet studies before reacting with ammonium sulfate, in agreement with other previously published studies³⁷. It should be noted that nanoparticle size, as well as the rate of droplet/particle drying, differed between the laboratory and ambient studies, and so only a qualitative comparison between the two can be made at this time. Overall, these results suggest that aqueous dicarbonyl chemistry may in fact play a significant role in altering the chemical composition of growing ambient nanoparticles in locations such as the eastern U.S., and for the specific case of Lewes, Delaware in summertime this chemistry could explain half of the organic matter in growing nanoparticles during NPF. Future work should be directed towards investigating the

contributions of such reactions on the growth rate and composition in particle formation experiments.

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Chapter 4

EFFECT OF SULFUR DIOXIDE ON PARTICLE FORMATION AND GROWTH FROM OZONOLYSIS OF MONOTERPENES AND ISOPRENE

4.1 **Biogenic Emissions and Formation of SOA**

Direct emissions of biogenic volatile organic compounds (BVOCs) from vegetation and biomass burning represent the largest sources of nonfossil carbon in ambient organic aerosol^{1–3}. Atmospheric oxidation of these species results in complex chemical transformations that lead to secondary organic aerosol (SOA) formation. BVOC dominate over anthropogenic VOCs as the major contributors to atmospheric SOA formation⁴. The most important BVOCs emitted into the atmosphere on a global scale are isoprene and terpenes^{1,4}.

4.1.1 SOA Formation from Isoprene

On a mass loading basis, isoprene is the most abundant BVOC emitted by terrestrial vegetation, with a global emission flux estimated to be around 503 TgC yr⁻¹ ⁵. The primary removal pathway of isoprene in the atmosphere is by reaction with the OH radical, which leads to the formation of an organic peroxy radical (ISOPO₂)⁶.

In pristine, low-NO_x environments, the primary fates of ISOPO₂ are reaction with a hydroperoxyl radical (HO₂) to form an isoprene hydroxyl hydroperoxide (ISOPOOH), reaction with another organic peroxy radical to form functionalized carbonyls and hydroxylated products, or isomerization reactions^{7–9}. In general, the first-generation products of isoprene are too volatile to partition to the condensed phase, however second- and higher-order generation products formed via subsequent oxidation steps are more likely to contribute to SOA formation¹⁰. For example, addition of OH and successive isomerization of ISOPOOH can produce isoprene epoxydiols (IEPOX) with molar yields of \geq 75%⁷. IEPOX is highly soluble, and in the presence of aqueous acidic seed particles can undergo partitioning and subsequent multiphase chemistry to form lower-volatility species including oligomers and organosulfates that can lead to SOA formation^{11–14}.

In addition to OH oxidation, isoprene can also undergo oxidation by ozone or the nitrate radical, although these reactions occur to a lesser extent in the atmosphere.⁶ Nonetheless, ozonolysis of isoprene has been shown to be an important pathway to SOA formation, as this reaction can lead to the production of both gas- and particlephase highly oxidized molecules (HOMs)^{15–17}. This reaction is also of particular interest due to the formation of a stabilized Criegee intermediate (sCI) following decomposition of the isoprene primary ozonide, which has been reported to be produced in molar yields of ~26%¹⁸. The sCI can then undergo subsequent reactions to form OH radicals with reported yields of 25-27%¹⁹, as well as further oxidation to form high molecular weight products¹⁷.

Reactions of the sCIs with other isoprene ozonolysis products such as carboxylic acids have been linked to the formation of oligomeric hydroperoxides^{15,16}. It is also proposed that oxidized products of isoprene ozonolysis can significantly contribute to SOA formation through multiphase reactions occurring in the condensed phase, which are catalyzed in the presence of acidic seed aerosol¹⁷. Isoprene-derived sCIs can also undergo bimolecular reactions in the gas phase, for instance with SO₂ to form SO₃, which will be discussed in more detail later.

4.1.2 SOA Formation from Monoterpenes

Monoterpenes are biogenic volatile organic compounds (BVOCs) with the general molecular formula $C_{10}H_{16}$. They are naturally emitted by a wide variety of vegetation, but their most significant sources are from boreal and tropical forests^{20–23}. Although the total global emission rate of monoterpenes (~95 TgC yr⁻¹) is less than that of isoprene, monoterpenes contribute substantially greater to the atmospheric SOA budget²⁴. Unlike isoprene, the dominant fate of monoterpenes is thought to be reaction with ozone, which can occur at nighttime as well as daytime^{25,26}. For instance, ozonolysis has been reported to contribute about 80% of the SOA produced from α -pinene degradation in the troposphere.²⁷ This reaction primarily forms semivolatile carbonyls, aldehydes, alcohols and carboxylic acids that play key roles in SOA formation, but further transformations of these products through gas- and condensed-phase reactions (e.g. accretion chemistry, acid/base chemistry) and multiphase chemistry are possible, resulting in multifunctional products with extremely low volatilities (i.e. HOM formation) that can comprise a major fraction of atmospheric SOA^{6,26,28–30}.

The most abundant monoterpene emitted globally is α -pinene, with an estimated budget of 32 Tg yr⁻¹, accounting for roughly 34% of total monoterpene emissions²⁴. The next most abundant monoterpenes are β -pinene and limonene, contributing approximately 17% and 9%, respectively, to the total monoterpene emission flux²⁴. Similar to the ozonolysis of isoprene, ozonolysis of monoterpenes produces both OH radicals as well as Criegee intermediates that can themselves act as atmospheric oxidants. As will be discussed later, the yields of these products from

monoterpene ozonolysis is dependent on the molecular structure, in particular the location of the double bond(s), of the monoterpene, and hence affects the HOM yield³¹.

	α-pinene	β-pinene	limonene	isoprene
Structure				-
MW	136.238 g mol ⁻¹	136.238 g mol ⁻¹	136.238 g mol ⁻¹	68.119 g mol ⁻¹
Formula	$C_{10}H_{16}$	$C_{10}H_{16}$	$C_{10}H_{16}$	C5H8
Ozonolysis Rate Constant, k (cm ³ molec ⁻¹ s ⁻¹) ^a	8.4x10 ⁻¹⁷	2.2x10 ⁻¹⁷	2.1x10 ⁻¹⁸	1.3x10 ⁻¹⁸
Ozonolysis OH Yield (%) ^b	85	35	86	27
Ozonolysis sCI Yield (%)	15°	60 ^d	27°	58°
Ozonolysis HOM Yield (%) ^e	3.4	0.12	5.3	0.01

Table 4-1. Structures, ozonolysis rate constants, and selected product yields for the four biogenic SOA precursors studied in this work. Values were obtained from the following references: ^aReference 32; ^bReference 19; ^cReference 33; ^dReference 23; ^eReference 34.

4.2 Mechanism of Alkene Ozonolysis

The general mechanism of the reaction of ozone with alkenes begins with cycloaddition of the ozone molecule to the double bond of the alkene to form a 1,2,3-trioxolane intermediate, commonly referred to as the primary ozonide (POZ)²⁹. This reaction is highly exothermic, and so the POZ will retain this excess energy and

become vibrationally excited, followed by rapid unimolecular decomposition or isomerization, depending on the structure of the parent alkene³⁵. For asymmetrically substituted alkenes such as monoterpenes, this results in the formation of a carbonyl molecule and a chemically activated carbonyl oxide biradical, commonly called the Criegee intermediate (CI). It is important to note that, for alkenes containing endocyclic double bonds (e.g. α -pinene), the carbonyl and CI moieties remain on different branches of the same molecule, allowing for further interaction of the two²³. For larger endocyclic alkenes (e.g. sesquiterpenes), this interaction can potentially form a secondary ozonide, however this is expected to be negligible for monoterpenes due to the high steric strain placed on the ring³⁶. It has also been proposed that the formation of a secondary ozonide is more relevant to ozonolysis of alkenes in the condensed phase, since solvent cage effects constrain the proximity between the carbonyl and CI moieties^{29,37}.

One very important aspect dictating the atmospheric reactivity of a CI is its molecular conformation. For monoalkyl-substituted CIs, the presence of the alkyl substituent on the same side of the molecule as the terminal oxygen atom results in a *syn*-CI, whereas the alkyl group being placed on the opposite side as the terminal oxygen results in an *anti*-CI. This not only impacts the rate at which a CI can undergo bimolecular reactions following stabilization (described in more detail later), but also the yield of OH radicals formed upon decomposition of the CI³⁸. The structures and conformers of the CIs possible from the alkene ozonolysis reactions studied in this work are shown in Figure 4-1.



Figure 4-1. Structures of the different conformers of Criegee intermediates possible from each of the alkenes studied in this work.

Following initial formation, CIs can either undergo unimolecular reactions, or become collisionally stabilized, allowing for bimolecular reactions to occur. For unsubstituted CIs (i.e. •CH₂OO•, formed during ozonolysis of β-pinene, limonene, and isoprene), unimolecular decomposition occurs first by ring closure to form an excited dioxirane, followed quickly by isomerization to an activated formic acid molecule²⁹. Subsequent fragmentation of this molecule can then yield stable products including formaldehyde, H₂O, CO, CO₂, and •OH²⁹. Additionally, •CH₂OO• can undergo collision with another gas molecule (e.g. O₂, N₂), which results in the formation of a thermally stabilized Criegee intermediate (sCI).

In addition to the above pathways, disubstituted CIs and CIs containing an alkyl substituent in the *syn* position can also follow a "hydroperoxide" channel³⁹. Through this channel, the CI can isomerize to give an excited vinylhydroperoxide, which subsequently decomposes to yield a vinyloxyl radical and \cdot OH³⁹. For monosubstituted CIs containing the alkyl substituent in the *anti* position, an "ester" channel is possible, in which isomerization leads to a dioxirane that subsequently forms an ester and decomposition products such as CO, CO₂, H₂O, methane and \cdot OH^{40,41}.

Figure 4-2 summarizes the general mechanism of the ozonolysis reaction of α pinene, showing the major stable first-generation products. Although not explicitly shown, the reaction occurs similarly for β -pinene, limonene, and isoprene, however the specific reaction products vary due to the structural differences of each alkene.



Figure 4-2. General reaction scheme of α-pinene ozonolysis, showing various Criegee intermediates (red boxes) and major first-generation products (black boxes). Based on the mechanism of Camredon et al. (Reference 42).

4.3 Stabilized Criegee Intermediate Chemistry

As mentioned above, collisional stabilization of an excited CI can occur, producing an sCI with a sufficiently long atmospheric lifetime to undergo reactions with other atmospheric trace compounds⁴³. Bimolecular reactions of sCIs with H₂O, SO₂, NO₂, and organic species including acetaldehyde, acetic acid, methanol, formic acid and dimethyl sulfide have been reported^{18,23,29,33,35,44,45}. It has been proposed that the dominant sink of the simplest sCI (•CH₂OO•) in the atmosphere is reaction with water, which is expected to occur primarily with the dimer form ((H₂O)₂)^{46–51}. This is due to the large first-order rate constant of •CH₂OO• water, which is estimated to be $8.7x10^{-16}$ and $1.4x10^{-12}$ cm³ molec⁻¹ sec⁻¹ (at 298K) for water monomer and dimer, respectively²³. Unimolecular decomposition of •CH₂OO• is expected to be <10 s⁻¹, and is therefore thought to be a negligible sink for this sCI in the atmosphere^{47,52}.

Reaction rates of water with larger sCIs, such as those produced from monoterpenes, have been shown to be largely dependent on the sCI structure^{53–55}. Similar to •CH₂OO•, mono-substituted sCIs with an *anti* conformation undergo rapid reaction with water due to their high potential energy, and this is thought to be their dominant sink in the atmosphere. sCIs with a *syn* conformation, on the other hand, react with water orders of magnitude more slowly, and are more likely to undergo unimolecular isomerization or decomposition via the aforementioned hydroperoxide channel, as well as bimolecular reactions with species other than water, such as SO₂ and organic acids^{23,55}.

4.4 Influence of Anthropogenic Emissions on Organic Aerosol

Changes in atmospheric aerosol concentrations and size distributions over the past century have been heavily influenced by anthropogenic activity. Recently, the influence of anthropogenic emissions on the formation of biogenic SOA (BSOA) has garnered significant attention^{56–60}. A number of recent field studies in forests have shown alterations in BSOA formation with increased anthropogenic emissions, underlining the important effects of the interactions between biogenic VOC (BVOC) emissions and pollutant plumes on the regional climate^{57,58,61–63}. In particular, SO₂ has been thought to play a significant role in altering BSOA formation by interacting with reactive species formed during BVOC oxidation, namely the stabilized Criegee Intermediates (sCIs) produced during ozonolysis of alkenes^{33,46,64,65}. sCIs have been shown to oxidize SO₂, leading to sulfuric acid production via SO₃ formation^{65,66}.

Field studies in both coastal⁶⁷ and boreal forest⁶⁴ environments have revealed a non-OH source of atmospheric sulfuric acid leading to increased sulfate aerosol production, thought to arise from sCI-induced oxidation of SO₂. Ye et al. (2018) studied BSOA formation from α -pinene and limonene ozonolysis in the presence of SO₂, and found that limonene SOA was enhanced, whereas SOA by α -pinene was not affected⁵⁶. They suggested that organosulfate formation from reaction of SO₂ with the sCI or organic peroxides is responsible for altering the SOA yields. Liu et al. (2017) showed that the SOA yield from cyclohexene photooxidation is suppressed by SO₂ under atmospherically relevant concentrations⁶⁸. They attributed this decrease to the reaction of SO₂ with OH, which competes with cyclohexene oxidation and outweighs any acid-catalyzed SOA enhancement effect that would occur from sulfuric acid formation. While these studies show that SOA formation can be affected uniquely for

different precursors, the chemical processes behind these interactions and their influence on aerosol climate effects are not yet fully understood.

In this chapter, the effect of SO₂ on the growth of monodisperse ammonium sulfate seed particles during ozonolysis of α -pinene, β -pinene, limonene and isoprene in a flow tube in the presence of an OH scavenger under dry conditions is examined. The primary goal was to investigate the impact of SO₂ on the growth of Aitken mode particles in order to better understand how SO₂ may alter CCN concentrations over forested regions. The secondary goal was to investigate the extent of new particle formation caused by reaction of SO₂ with sCIs produced from different biogenic alkenes. The results provide insight into important atmospheric processes that may significantly impact aerosol climate effects in regions where interactions of biogenic and anthropogenic emissions occur.

4.5 Experimental Procedure

Nanoparticle formation and growth during BVOC ozonolysis in the absence and presence of SO₂ was studied using a quartz flow tube with a mean residence time of 232±15 seconds under the conditions studied. The setup is illustrated in Figure 4-3. Experiments were conducted in three consecutive steps. In the first step, a mixture of zero air, ozone, and 50 nm monodisperse ammonium sulfate seed particles were introduced into the inlet of the flow tube and their concentrations allowed to stabilize. The seed particles were produced via atomization of an aqueous 5 mM (NH₄)₂SO₄ solution, effloresced using a Nafion drier (Model MD-700, Perma Pure, Lakewood, NJ), and size-selected with a differential mobility analyzer (3081 DMA, TSI Inc., Shoreview, MN) prior to introduction into the flow tube. In the second step, liquid α pinene (98%, Sigma-Aldrich, St. Louis, MO), β -pinene (98%, Sigma-Aldrich, St. Louis, MO), d-limonene (MP Biomedicals, Santa Ana, CA), or isoprene (99%, Alfa Aesar, Haverhill, MA) was evaporated into a gently heated air flow via a syringe pump, and a precisely controlled portion of the flow was sent through an injector tube slightly downstream of the ozone and seed particles to ensure proper mixing within the flow tube. In all experiments, H₂ (99.999%, Keen Gas, Wilmington, DE), used as an OH scavenger, was also introduced along with the BVOC vapor. In the third step, a low flow of SO₂ from a stock calibration cylinder (5.0 ppmv balanced in N₂, Gasco, Oldsmar, FL) was added at the flow tube inlet. Particle size and concentration at the flow tube outlet were continuously measured with a scanning mobility particle sizer (Model 3938 SMPS, TSI Inc., Shoreview, MN), as well as ozone concentration with an O₃ analyzer (Model 49i, Thermo Fisher Scientific, Waltham, MA). In addition, relative humidity and temperature were constantly monitored, which remained at $15\pm3\%$ and 24 ± 1 °C, respectively, over the course of all experiments.



Figure 4-3. Schematic of the flow tube reactor, flow setup and experimental conditions as configured for this study.

4.6 Particle Composition Measurements

Offline molecular composition measurements of the particles grown by α pinene and limonene ozonolysis, both with and without SO₂ present, were conducted using high-resolution electrospray ionization mass spectrometry (ESI-MS). For each condition, 10 µg of particles were collected onto a 25 mm quartz microfiber filter (GF/D, Whatman, Maidstone, UK), subsequently extracted using 2 mL of acetonitrile (Optima grade, Fisher Scientific, Hampton, NH) and concentrated under vacuum to a final volume of 40 µL, resulting in a concentration of ~0.1 µg/µL. For analysis, 5 µL injections of the concentrated extracts were analyzed by direct infusion electrospray ionization on a high resolution Thermo Q-Exactive Orbitrap mass spectrometer operated in negative ion mode. Molecular characterization of particles grown by β pinene and isoprene ozonolysis could not be achieved due to insufficient organic mass formed in those experiments, as will be discussed later.

In addition, online elemental composition measurements were conducted using a modified version of the Nano Aerosol Mass Spectrometer (NAMS) described elsewhere^{69,70}. Briefly, particles exiting the flow tube are drawn through an aerodynamic lens system into the instrument and ionized by creating a laser-induced plasma, which quantitatively converts nanoparticles into positive atomic ions that are subsequently extracted and separated by time-of-flight. The version of the NAMS used in these experiments has significantly reduced transmission efficiency of particles \leq 40 nm into the source region of the mass spectrometer⁶⁹. For this reason, the NAMS results are interpreted as elemental composition measurements of the seed particles, even if nucleation of small nanoparticles also occurred during the experiment.

BVOC	α-pinene	limonene	β-pinene	isoprene
initial [BVOC] (ppbv)	4.1	1.8	23	29
[O ₃] (ppbv)	138±2	138±2	138±2	138±2
[H ₂] (v/v %)	0.1	0.1	0.1	0.1
[SO ₂] (<i>ppbv</i>)	8	8	8	8
$\frac{k_{\rm BVOC+O3}}{(cm^3 \ molec^{-1} \ s^{-1})}$	8.7x10 ⁻¹⁷	2.0x10 ⁻¹⁶	1.5x10 ⁻¹⁷	1.2×10^{-17}
t (s)	232±15	232±15	232±15	232±15
reacted [BVOC] (molec. cm ⁻³)	6.9x10 ⁹	6.6x10 ⁹	7.0x10 ⁹	6.6x10 ⁹

Table 4-2. Gas-phase mixing ratios and ozonolysis rate constants used to determine reacted [BVOC] in flow tube experiments.

4.7 Effect of SO₂ Addition During Biogenic Alkene Ozonolysis

Figure 4-4 shows the time-resolved particle size and number concentrations measured during each experiment in which SO_2 was added during BVOC ozonolysis in the presence of dry monodisperse ammonium sulfate seed particles and H₂. The ozone mixing ratio was monitored through a sampling port at the flow tube outlet, and remained at 138±2 ppbv over the course of each experiment. Mixing ratios of BVOC at the point of introduction into the flow tube are given in Table 4-2.



Figure 4-4. Time-resolved particle number (N_{total}) and median seed diameter (d_{seeds}) measured at the exit of the flow tube following addition of BVOC (first vertical line, green) and SO₂ (second vertical line, red). The ozone and SO₂ mixing ratios at the inlet were 138±3 ppbv and ~8 ppbv, respectively, for all trials. Dots represent raw data points, whereas solid traces are 8-point moving averages of the data. Colored horizontal brackets indicate periods where the data was averaged to obtain the steady-state size distributions shown in Figure 4-5.

Depending on which BVOC was being used, the injection rate of the syringe pump was adjusted such that approximately the same number of molecules of each BVOC reacted with ozone over the course of the residence time in the flow tube. The necessary BVOC mixing ratios were determined based on the ozonolysis rate constants of the four BVOCs studied (Table 4-2). Steady-state mixing ratios of H₂ and SO₂ (when present) were calculated based on the gas flow rates and the dilution factor inside the flow tube, and were approximately 0.1% and 8 ppbv, respectively, for every experiment. Upon introduction of SO₂, a distribution of newly formed particles smaller than the seed particles was observed for all BVOCs studied. For this reason, the diameter change of the seed particles is reported as d_{seeds} (Figure 4-4), which is defined as the median diameter of particles spanning 45-100 nm electrical mobility diameter. This range represents only the distribution of ammonium sulfate seed particles, and distinguishes their growth from that of the newly formed particles.

This is illustrated more clearly in Figure 4-5, which shows the average size distributions during the steady-state periods indicated by the horizontal brackets above the plots in Figure 4-4. The concentrations of total particle number (N_{total}) are also shown in Figure 4-4, and these values span the entire measured size range of 3-100 nm electrical mobility diameter, therefore representing both newly formed particles and seed particles.



Figure 4-5. Particle size distributions averaged over steady-state periods indicated by the horizontal brackets in Figure 2. Black dots represent the distributions of seed particles + ozone + H₂ only; Green lines represent the distributions following the addition of BVOC; Red lines represent the distributions following the addition of SO₂. Reported values are the average and standard deviation of the change in median seed particle diameter following addition of BVOC (green) and SO₂ (red) relative to the initial seed diameter. Data to the right of the break at 45 nm is shown on rescaled axes for ease of visibility.

4.7.1 α-Pinene and Limonene Ozonolysis

Each experiment began with the addition of ozone, H₂, and seed particles, which were allowed to stabilize prior to introduction of the BVOC. Upon addition of α -pinene, d_{seeds} grew quickly from 50.5 nm to 51.9 nm, however N_{total} remained constant (Figure 4-4a). This growth is therefore attributed to condensation of low volatility, highly oxidized molecules (HOMs) produced during the ozonolysis reaction. Indeed, the high-resolution ESI mass spectrum of these particles (Figure 4-6) consisted primarily of known monomers of SOA produced from α -pinene ozonolysis, e.g. pinic acid (C₉H₁₄O₄; RI=100%), norpinic acid (C₈H₁₂O₄; RI=49%), OH-pinonic acid (C₁₀H₁₆O₄; RI=16%), and terebic acid (C₇H₁₀O₄; RI=13%)^{71,72}. In addition, an intensity-weighted O/C ratio of 0.47 was determined for the mass spectrum based on the method of Heaton et al. (2009)⁷³, which is in agreement with previous measurements of SOA produced from α -pinene ozonolysis⁷⁴. Furthermore, very little dimer formation was observed, supporting that the observed seed particle growth was due to HOM condensation, and particle-phase accretion chemistry likely did not contribute.

Upon addition of SO₂, a burst of new particle formation occurred, resulting in an increase in N_{total} by about a factor of 5. This nucleation can be explained by the formation of sulfuric acid arising from the reaction of SO₂ with the sCI formed during α -pinene ozonolysis, which has been widely discussed as an important pathway to atmospheric H₂SO₄ formation^{33,46,75}. To help support this interpretation, a control experiment was performed in which SO₂ was added to the flow tube in the absence of monoterpene, and no new particle formation or enhancement in the growth of the seed particles was observed. The control experiment confirmed that the sCI (or other non-OH oxidation products of α -pinene ozonolysis) was necessary for oxidation of SO₂.



Figure 4-6. Comparison of high-resolution ESI mass spectra of α-pinene SOA collected without (top) and with (bottom, inverted) SO₂ present in the flow tube. Peaks colored in red correspond to proposed organosulfates based on accurate mass formula assignments. Labels give m/z (-) and the corresponding formula for some of the major peaks. All red peaks that are labeled were confirmed as sulfate-containing products by MS/MS analysis.

Despite substantial increases in the total particle number concentrations owing to SO₂-induced nucleation, no significant change was observed in the growth of the seed particles for either alkene, with d_{seeds} remaining practically constant in both experiments. One might expect d_{seeds} to decrease following SO₂ addition for two reasons: First, the presence of SO₂ may decrease HOM production due to competition of SO₂ and organic molecules for reaction with the sCI. In the aforementioned study by Liu et al. (2017), the presence of SO₂ led to a decrease in SOA formation from cyclohexene photooxidation in their chamber experiments, which they attributed to competition of OH reaction between SO₂ and cyclohexene⁶⁸. Second, the formation of new particles increases the total particle surface area on which HOMs can condense (i.e. condensation sink), therefore HOM condensation onto the newly formed particles would result in fewer HOMs condensing onto the seed particles, reducing their growth. The total particle condensation sink at steady-state was calculated for each experiment before and after SO₂ addition based on the method of Dal Maso et al. $(2002)^{76}$, and the values are summarized in Table 4-3.

BVOC	CS, before SO ₂ (s^{-1})	CS, after SO ₂ (s^{-1})	Increase (%)
α-pinene	0.010	0.020	100
limonene	0.010	0.025	150
β-pinene	0.006	0.072	1100
isoprene	0.009	0.025	178

Table 4-3. Values of Condensation Sink (CS) calculated before and after SO₂ addition for each BVOC studied

Following SO₂ addition, the seed particles only contributed 50% and 40% to the total particle condensation sink in the α -pinene and limonene experiments, respectively. As no decrease in *d_{seeds}* was observed, a possible explanation is that

condensation of gas-phase H_2SO_4 (formed via SO_2 oxidation) onto the seed particles was compensating for the decrease in SOA mass from HOM condensation.

ESI-MS analysis of the particles collected in the presence of SO₂ revealed a number of newly formed organosulfur species in both the α -pinene and limonene experiments (Figures 4-6 and 4-7), which were further confirmed as organosulfates by MS/MS analysis (e.g. Figure 4-8). Therefore, it is likely that condensation of sulfuric acid and subsequent reaction with organics occurred on the seed particles. Organosulfate formation from both α -pinene and limonene ozonolysis has been previously reported to be greatly enhanced in the presence of acidic seed particles⁷⁷. A recent study by Ye et al. (2018)⁵⁶ also reported formation of organosulfates when α pinene and limonene ozonolysis was performed in the presence of SO₂, many of which match those identified in Figures 4-6 and 4-7.



Figure 4-7. Comparison of high-resolution ESI mass spectra of limonene SOA collected without (top) and with (bottom, inverted) SO₂ present in the flow tube. Peaks colored in red correspond to proposed organosulfates based on accurate mass formula assignments. Labels give m/z (-) and the corresponding formula for some of the major peaks. All red peaks that are labeled were confirmed as organosulfates by MS/MS analysis.



Figure 4-8. MS/MS spectrum of the m/z 279.05 ion observed in the particles grown by α -pinene ozonolysis in the presence of SO₂. Structures of the organosulfate product and corresponding monomer precursor are proposed.

NAMS analysis of the seed particles grown by α -pinene and limonene ozonolysis also revealed a change in the elemental composition caused by SO₂ addition (Figures 4-9 and 4-10). In the absence of SO₂, a significant carbon signal was observed in both experiments, again supporting that the observed growth was due to HOM condensation. Following addition of SO₂, an increase in the sulfur-to-carbon mole ratio (S/C) was observed in both experiments, increasing from 0.5 to 0.7 in the α pinene trial and 0.2 to 0.5 in the limonene trial. This again suggests that the overall particle composition was becoming more sulfur rich in the presence of SO₂, in agreement with the observed organosulfate formation by ESI-MS.



Figure 4-9. Overlaid NAMS mass spectra for particles grown by α -pinene ozonolysis in the absence (blue) and presence (red) of SO₂. The S/C ratio increased from 0.5 to 0.7 upon addition of SO₂. Each spectrum is an average of ~50 single particles analyzed.



Figure 4-10. Overlaid NAMS mass spectra for particles grown by limonene ozonolysis in the absence (blue) and presence (red) of SO₂. The S/C ratio increased from 0.2 to 0.5 upon addition of SO₂. Each spectrum is an average of ~50 single particles analyzed.

4.7.2 β-Pinene and Isoprene Ozonolysis

Upon addition of β -pinene, a small increase in the seed particle diameter of ~0.6 nm was observed (Figures 4-4c and 4-5c), consistent with its lower reported HOM yield relative to α -pinene or limonene^{28,34}. Upon addition of SO₂, however, *d_{seeds}* was found to increase substantially by an additional ~1.5 nm. In fact, the diameter growth of the seed particles in the presence of β -pinene and SO₂ was essentially the same as the diameter growth in the presence of α -pinene and SO₂. Particle nucleation was also observed with β -pinene in the presence of SO₂, and the number concentration was about a factor of 5 higher than that achieved with α -pinene for approximately the same number of molecules oxidized. This suggests that the yield of H₂SO₄ produced

by oxidation of SO₂ during β -pinene ozonolysis is much greater than from α -pinene ozonolysis, which is in line with a reported higher sCI yield from β -pinene than α -pinene^{23,43}. Due to this substantial new particle formation, the seed particles only contributed less than 10% to the total condensation sink after SO₂ addition. Interestingly, however, seed particle growth was still significantly enhanced, suggesting that an additional growth mechanism other than HOM condensation was likely taking place.

Similarly, the presence of SO₂ was found to enhance seed particle growth during isoprene ozonolysis. As an acyclic alkene, isoprene has been shown to give a substantially smaller HOM yield from its reaction with ozone relative to the three monoterpenes studied, however it still produces a significant sCI yield^{33,34}. In the absence of SO₂, addition of isoprene led to a minimal increase in d_{seeds} of ~0.2 nm (Figures 4-4d and 4-5d). Upon introduction of SO₂, however, d_{seeds} increased an additional 0.7 nm, and new particle formation was also observed, suggesting that oxidation of SO₂ during isoprene ozonolysis was responsible.

NAMS spectra of the seed particles grown by β -pinene and isoprene ozonolysis in the absence of SO₂ both showed only a trace carbon signal (Figures 4-11 and 4-12), consistent with the small amount of growth observed in the particle size measurements. Due to the low signal intensity, an accurate S/C ratio could not be quantified for these spectra. Interestingly, however, the same particles collected in the presence of SO₂ showed no further increase in carbon, revealing that the additional growth could not be attributed to organic matter. These measurements suggest that the enhanced seed particle growth observed in the β -pinene and isoprene experiments was

likely due entirely to inorganic sulfate formation. In principle, this sulfate could arise from condensation of gas-phase H₂SO₄ and/or multiphase chemistry of SO₂.



Figure 4-11. Overlaid NAMS mass spectra for particles grown by β-pinene ozonolysis in the absence (blue) and presence (red) of SO₂. Due to the trace carbon signal observed, an S/C ratio could not be reliably quantified. Each spectrum is an average of ~50 single particles analyzed.



Figure 4-12. Overlaid NAMS mass spectra for particles grown by isoprene ozonolysis in the absence (blue) and presence (red) of SO₂. Due to the trace carbon signal observed, an S/C ratio could not be reliably quantified. Each spectrum is an average of ~50 single particles analyzed.

4.8 Ozone Dependence Experiments

To further investigate the dependence of the observed nucleation and seed particle growth on the abundance of sCIs, additional experiments were carried out in which seed particles, H₂, and BVOC were introduced into the flow tube either in the absence or presence of ~8 ppbv SO₂, and the ozone concentration incrementally raised. Figure 4-13 shows the measured increase in seed particle diameter (delta median) and corresponding growth rate at each ozone mixing ratio investigated for each BVOC in the absence and presence of SO₂. For the α -pinene and limonene experiments, the increase in seed particle diameter was very similar over the entire range of ozone concentrations studied, regardless of whether SO₂ was present.


Figure 4-13. Increase in median seed diameter (left vertical axis) and corresponding growth rate (right vertical axis) as a function of ozone mixing ratio (bottom horizontal axis) and concentration of BVOC reacted (top horizontal axis) for each BVOC studied. Dotted lines represent data collected in the absence of SO₂, and solid lines represent data collected in the presence of ~8 ppbv SO₂.

In the case of β -pinene and isoprene, however, the seed particle growth rates were faster at every ozone concentration in the presence of SO₂, and this enhancement was found to be greater at higher ozone concentrations. These results are consistent with the previous experiments from Figures 4-4 and 4-5, and suggest that in the presence of SO₂, the growth rates of seed particles grown by β -pinene and isoprene ozonolysis are enhanced to a greater extent as sCI production is increased.

The ozone concentration dependence on new particle formation produced from each BVOC in the presence of SO₂ was also investigated. Figure 4-14 shows the number concentration of newly formed particles (excluding the seed particles) as a function of the ozone mixing ratio for each alkene. For every BVOC studied, the amount of nucleation observed increased linearly with ozone over the range of concentrations investigated. Of the three monoterpenes, β -pinene produced by far the largest yield of new particles, followed by limonene and α -pinene. This difference is likely due to the different yields of sCIs reactive towards SO₂ from each monoterpene.



Figure 4-14. Number concentration of nucleated particles plotted versus ozone mixing ratio for each BVOC studied in the presence of ~8 ppbv SO₂.

Recently, it has been shown that different sizes and structural conformers (i.e. anti- and syn-) of sCIs, with different rates of reactivity, may be produced from ozonolysis of an individual unsaturated hydrocarbon^{33,53–55,78}. Numerous studies have suggested that the dominant fate of the smallest sCI (CH₂OO) is reaction with water ⁴⁶⁻⁴⁸, whereas larger sCIs, such as those produced by ozonolysis of monoterpenes, can be less reactive to water, in particular the syn conformers 53,54. For instance, Newland et al. $(2018)^{23}$ proposed mechanisms for the formation of four unique C₁₀ Criegee intermediates from α -pinene ozonolysis (one *anti*- and three *syn*- conformers), seven unique Criegee intermediates from limonene ozonolysis (two C₁₀ anti- conformers, two C₁₀ syn- conformers, two C₉ syn- conformers, and CH₂OO), and three unique Criegee intermediates from β -pinene ozonolysis (two *syn*- conformers and CH₂OO). The number and structural conformations of the unique CIs produced are dependent on the molecular structure, in particular the location of the double bond, of the precursor alkene, as this determines the number of ways in which the primary ozonide(s) can decompose. Many experimental studies have shown the total sCI yield to vary considerably amongst different alkenes^{18,33,43,79}. Further, the relative yields of the different possible conformers of sCIs produced from various alkenes have been estimated both experimentally and theoretically, and are themselves ultimately dependent on the precursor structures⁸⁰⁻⁸². Newland et al. (2018)²³ also proposed yields for the syn-sCIs produced from the same three monoterpenes studied in this work, and suggest that the yield increases in the order β -pinene > limonene > α pinene. The amount of nucleation observed here following SO₂ addition follows this same order, and is in good qualitative agreement with the suggested yields.

Interestingly, the amount of particle nucleation observed from isoprene at each ozone mixing ratio studied in this experiment was nearly the same as that from limonene (Figure 4-14). Isoprene has been previously reported to give a significantly higher *total* yield of sCIs from its reaction with ozone relative to α -pinene or limonene³³. These results then suggest that only a fraction of the total isoprene sCI yield reacts with SO₂, with the remainder likely scavenged by water vapor, which can occur rapidly even at a fairly low relative humidity of ~15% as used in this study²³.

4.9 Enhanced Growth From β-Pinene and Isoprene

The enhancement observed in seed particle growth from β -pinene and isoprene ozonolysis in the presence of SO₂ was a surprising result, and gives insight into possible aerosol growth mechanisms that have not been previously explored. Before SO_2 addition, seed particle growth in these experiments was qualitatively in order with what would be expected based on previously published ozonolysis HOM yields from each precursor (i.e. limonene > α -pinene > β -pinene > isoprene)³⁴. Because the seed particles were dried below efflorescence and the RH was kept low in these experiments, the seeds are expected to be solid, with possibly one or more monolayers of water molecules adsorbed onto the surface, which has been shown to occur with ultrafine ammonium sulfate particles well below the deliquescence RH^{83,84}. When enough HOMs condense onto the solid seeds, they can form a coating around the solid ammonium sulfate particle. It is possible that in experiments where more HOMs are produced (i.e. α -pinene and limonene), the SOA coating completely surrounds the seed, blocking interactions of gas-phase molecules with the ammonium sulfate core⁸⁵. ESI-MS of the particles grown by α -pinene ozonolysis in the absence of SO₂ consisted primarily of acid monomers. Organic acids such as these are generally considered to

be hydrophobic⁸⁶, and so it is unlikely that any water would be on the surface of the particles following significant HOM condensation.

In experiments with lower HOM production (i.e. β -pinene and isoprene), the resulting SOA coating may only partially surround the seed, still allowing gas molecules to contact the ammonium sulfate core. It is possible that water molecules adsorbed onto the surface of the seed particles facilitated heterogeneous chemistry leading to enhanced sulfate production. The oxidation of SO₂ at the air-water interface of aqueous surfaces has recently been proposed as a potentially important pathway to ambient sulfate formation, and has not yet been thoroughly explored on nano-sized aerosols^{87,88}. A pathway such as this could have significant implications for understanding increased sulfate aerosol production in highly polluted environments^{86,89,90}. Future work will be aimed at elucidating the enhanced particle growth from β -pinene and isoprene ozonolysis in the presence of SO₂, and the role of aerosol water on this effect.

4.10 Conclusions

This chapter discussed an investigation of the effect of SO₂ on particle formation and growth during ozonolysis of four biogenic alkenes (α -pinene, β -pinene, limonene and isoprene) under dry conditions. The results show that the growth of Aitken mode ammonium sulfate particles by alkene ozonolysis can be significantly altered in the presence of SO₂. In the absence of SO₂, new particle formation did not occur, and the increase in seed particle diameter was consistent with condensational growth by HOMs. In the presence of SO₂, the formation of new particles was observed from every alkene studied, and the amount of nucleation was consistent with the yield of stabilized Criegee intermediates expected to be produced from each alkene,

suggesting SO₂ oxidation was responsible. The effect of SO₂ on seed particle growth was found to be dependent on the specific alkene being oxidized. With α -pinene and limonene, no additional growth was observed, however the detection of organosulfates by ESI-MS confirmed that particulate sulfate was present and altering the organic composition of the particles. With β -pinene and isoprene, a significant growth enhancement was observed, which was found to be due entirely to inorganic sulfate formation. These results provide insight into a potentially important pathway to aerosol formation and growth triggered by SO₂, and suggest that this discovery may alter CCN concentrations in regions with significant anthropogenic-biogenic interactions.

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Chapter 5

EFFECT OF RELATIVE HUMIDITY AND AEROSOL LIQUID WATER ON NANOPARTICLE GROWTH FROM MONOTERPENE OZONOLYSIS IN THE PRESENCE OF SULFUR DIOXIDE

5.1 Role of Aerosol Liquid Water in SOA Formation

Water can be an abundant component of atmospheric aerosols, opening pathways for reactions to occur in the aqueous phase. The total mass of aerosol liquid water (ALW) is about a factor of 2-3 larger than the total dry particle mass on a global scale^{1,2}. Recently, ALW has been widely discussed as a critical factor that can affect SOA formation by influencing processes such as particle-phase oligomerization, organic salt formation, and air-particle heterogeneous reactions^{3–10}. ALW can also alter the phase state of particles, transforming them from solid to liquid-like droplets. This impacts both the thermodynamics of oligomerization reactions and the particle viscosity, which in turn affects the reactive uptake of gas-phase SOA precursors by modifying diffusion rates within the particles^{11,12}.

Until recently, models developed to predict SOA mass only accounted for its formation via vapor pressure-driven partitioning of low- and semi-volatility compounds formed in the gas phase^{1,13–15}. Failure to incorporate additional sources of SOA formation resulted in the frequent under-prediction of not only total ambient SOA mass, but also its overall extent of oxidation (i.e. O/C ratio)^{16–22}. Recently, SOA models such as the Community Multiscale Air Quality (CMAQ) model have been updated to include aqueous SOA formation pathways, and showed improved

agreement with ambient measurements of total organic carbon loadings in regions where aqueous SOA is expected to be significant, such as the southeastern United States^{23–28}.

Although substantial progress has been made in understanding the impact of water on atmospheric SOA formation, few studies to date have been carried out to investigate how such chemistry may be affected by the presence of anthropogenic pollutants, namely SO₂. This is especially important since aqueous SOA formation is driven by the availability of ALW, which itself is controlled not only by the relative humidity, but also by particle number concentration and hygroscopicity²⁹. As shown in Chapter 4, the presence of SO₂ during alkene ozonolysis can alter the organic component of aerosol particles to a more sulfate-rich composition, likely enhancing their hygroscopicity, as well as form new hygroscopic sulfate particles.

This chapter discusses experiments which build off of those described in Chapter 4. The goal was to investigate how particle formation and growth by monoterpene ozonolysis in the absence and presence of SO₂ is affected by 1) a higher gas-phase water concentration (i.e. higher relative humidity), and 2) a higher particlephase water concentration (i.e. higher aerosol liquid water content). The results suggest that water can play an important role in altering aerosol mass by influencing SOA and new particle formation.

5.2 Experimental Design

The experiments described herein were carried out using the same flow tube setup as the experiments detailed in Chapter 4, with three modifications. First, the injector port at the inlet was removed, allowing organic vapors and H_2 to be introduced at the same point as the seed particles, ozone, and SO₂ (when applicable),

rather than further downstream in the tube. Recent computational fluid dynamics simulations by our group have shown that this configuration improves the stability of laminar flow conditions through the tube, while having a minimal effect on the aerosol residence time³⁰, which also improves the accuracy of modeling chemical processes inside the flow tube.

Second, a diverter assembly containing a glass bubbler filled with ultrapure water was added to the make-up air flow that mixes with the seed particles, allowing the relative humidity of the aerosol entering the flow tube to be increased. For experiments where the bubbler was bypassed (herein referred to as "low RH" experiments), the steady-state relative humidity measured at the flow tube outlet was $15\pm3\%$. For experiments where the make-up air flow was directed through the bubbler (herein referred to as "high RH" experiments), the steady-state relative humidity measured at the exit of the tube was $60\pm3\%$.

Third, for experiments where the effect of ALW was investigated (herein referred to as "wet seed" experiments), the dry ammonium sulfate seed particles exiting the DMA used for size-selection were sent through the nano-aerosol sampler (NAS) prior to mixing with the make-up air flow and subsequently entering the flow tube inlet. The working principle of the NAS has been described in section 2.5. Here, the NAS was used to transform the dry monodisperse seed particles into liquid droplets by exposing them to a relative humidity above the deliquescence RH of ammonium sulfate (>79%)^{31,32}. The RH of the aerosol exiting the NAS was continuously monitored with an RH probe to ensure deliquescence of the seed particles was being reached, which always read 90±5%.



Figure 5-1. Schematic of the flow setup and experimental conditions as configured for this study. Modifications to the setup described in Chapter 4 are outlined in dotted boxes.

Using this experimental setup, the growth of ammonium sulfate seed particles by ozonolysis of two different monoterpenes (α -pinene and β -pinene) was studied in the absence and presence of SO₂ under three different conditions. These were 1) effloresced seeds at 15±3% RH, 2) effloresced seeds at 60±3% RH, and 3) deliquesced seeds at 60±3% RH. Regardless of these conditions, the experimental procedure remained the same as for the experiments detailed in section 4.5. Briefly, each experiment was carried out in three consecutive steps. First, 50 nm monodisperse ammonium sulfate seed particles, ozone, and a makeup flow of zero air were mixed together and introduced into the flow tube. Once steady-state conditions were reached, monoterpene vapor and hydrogen (acting as an OH scavenger) were introduced into the flow tube. After approximately one hour, a low flow of SO₂ was added to the mixture of seed particles, ozone, and zero air entering the tube.

Measurements of particle size distribution, ozone mixing ratio, temperature, and relative humidity were continuously taken at the exit of the flow tube for every experiment. The measured ozone mixing ratio remained at 140±3 ppbv over the course of all trials. The initial concentrations of SO₂ and H₂ were calculated based on the dilution factor inside the tube, and were ~8 ppbv and ~0.1 % v/v, respectively. The initial concentrations of α -pinene and β -pinene were 4.1 ppbv and 23 ppbv, respectively, resulting in a similar number of molecules reacted (~7x10⁹ molec. cm⁻³) for each alkene over the 232±15 second residence time of the flow tube, as described in Chapter 2.6. Each trial was performed in triplicate to assess the experimental precision.

For the deliquesced seed experiments, particles exiting the flow tube were sampled through a diffusion dryer tube which brought the RH of the aerosol down to ~15% prior to SMPS measurement. Therefore, the size distributions are representative of the dry particle diameter, and so are directly comparable to those measured in the experiments utilizing effloresced seed particles. Furthermore, drying the deliquesced seeds prior to measurement promotes evaporation of the more volatile SOA components, and so any additional growth observed in these trials is most likely due to the irreversible formation of low-volatility products formed within the aqueous phase.

It is also important to emphasize that the experiments utilizing effloresced seeds and deliquesced seeds were both carried out at the exact same relative humidity of $60\pm3\%$. This is between the deliquescence (~79% RH) and efflorescence (~28%

RH) points of 50 nm ammonium sulfate particles, and so in these experiments, the particles will remain in their initial phases throughout their entire residence time in the flow tube³¹. This was confirmed through SMPS measurements of the seed particle "wet" and "dry" diameters, as will be described in section 5.5. Furthermore, keeping the RH exactly the same allowed for both experiments to be conducted under identical states of wall conditioning, essentially normalizing the extent of wall loss of gas-phase species inside the flow tube³³.

To investigate the effect of ALW on the molecular composition of SOA, additional trials using deliquesced seeds were conducted in which the particles were collected onto quartz microfiber filters following growth by ozonolysis in both the absence and presence of SO₂. The collected particles were subsequently extracted by sonication of the filters in acetonitrile, concentrated under vacuum to a final concentration of ~0.1 mg/mL, and analyzed via negative mode high-resolution electrospray ionization mass spectrometry (ESI-MS) as described in section 4.6.

5.3 Effloresced Seeds at Low Relative Humidity

The experiments conducted at $15\pm3\%$ RH using effloresced seeds were carried out identically to those described in Chapter 4 for α -pinene and β -pinene, with the exception of having the injector tube in place on the flow tube inlet. As mentioned, removal of the injector had very little effect on the amount of seed particle growth observed following addition of monoterpene. Addition of α -pinene led to an increase in the median seed particle diameter (Δd_{seeds}) of 1.53 ± 0.03 nm, whereas addition of β pinene caused an increase in Δd_{seeds} of 0.45 ± 0.08 nm. Once again, a complete lack of new particle formation was observed in both experiments in the absence of SO₂, and

so the observed seed particle growth was attributed to condensation of highly oxidized molecules produced from the ozonolysis reaction of each precursor.

Upon addition of SO₂, new particle formation was observed with both precursors, with the number concentration of nucleated particles being roughly a factor of 14 greater for β -pinene. This is primarily due to the larger yield of sCIs reactive towards SO₂ from β -pinene than α -pinene, resulting in greater SO₂ oxidation and subsequent H₂SO₄ formation. As detailed in section 4.3, the reactivity of sCIs towards water vs. other gas-phase molecules varies depending on the structural conformation of a given sCI, with *anti* sCIs reacting very quickly with water, and *syn* sCIs reacting orders of magnitude more slowly. The slower reaction of the *syn*-sCIs with water has been attributed to steric hindrance caused by the alkyl group on the carbonyl oxide structure, whereby the alkyl group has greater overlap with the COO group, resulting in an increased electron-releasing effect and obstructing addition of the oxygen atom of water to the carbon atom of the carbonyl oxide³⁴.

The total sCI yield for β -pinene has been reported to be 0.46, only a factor of ~3 greater than α -pinene, with a reported yield of 0.15³⁵. If every sCI produced from each monoterpene resulted in oxidation of SO₂, one would expect the number concentration of newly formed particles upon SO₂ addition to be roughly 3 times greater for β -pinene. The fact that the observed nucleation was ~14 times greater for β -pinene suggests that a larger fraction of the total sCI yield produced from this precursor reacts with SO₂ than from α -pinene. This is in agreement with previous findings that the ozonolysis of β -pinene produces roughly 3 times more *syn*-sCIs than α -pinene³⁵.

Greater particle nucleation from β -pinene was also observed in the previous experiments carried out at low relative humidity reported in Chapter 4. In those trials, however, the number concentrations of nucleated particles were somewhat greater from both precursors, with β -pinene producing roughly 10 times more particles than α pinene in the presence of SO₂. Additionally, the nucleated particles in the previous trials reached slightly larger diameters, with the size distributions of the nucleation modes tailing out to roughly 20-30 nm, rather than 10-15 nm as observed in the current trials. This difference is most likely because the trials in Chapter 4 were carried out with the injector tube in place, which makes the air flow traveling through the beginning of the flow tube more susceptible to recirculation, as supported from recent computational modeling studies³⁰. As mentioned before, removal of the injector had a minimal effect on the growth of the larger seed particles, however reduced recirculation of the nucleated particles resulted in a shorter residence time, explaining both the smaller diameters and number concentrations of these particles in the current trials. Nevertheless, the relative amount of nucleation observed between the two organic precursors is in good qualitative agreement with the previous experiments, again supporting a higher *syn*-sCI yield from β -pinene than α -pinene.

5.4 Effloresced Seeds at High Relative Humidity

The same experiments were then repeated at a relative humidity of $60\pm3\%$ in the flow tube. In this case, the increase in median seed particle diameter following addition of monoterpene was slightly enhanced for both precursors, with $\Delta d_{seeds} =$ 1.9 ± 0.1 nm for α -pinene and 0.6 ± 0.1 nm for β -pinene (Figure 5-5). Thus, the observed growth here was approximately 23% greater for α -pinene and 29% greater for β -pinene. Previous studies have found similar increases in SOA mass yield from

monoterpene ozonolysis at higher relative humidity. Tillmann et al. (2010) reported greater aerosol mass concentrations from α -pinene ozonolysis in the absence of seed particles at 44% RH vs. <1% RH, which they attributed to a greater molar yield of the oxidation product pinonaldehyde³⁶. Cocker et al. (2001) also found the aerosol yield to be slightly greater from α -pinene ozonolysis carried out in the presence of dry ammonium sulfate seed particles and an OH scavenger at a relative humidity between 39-49% than at a relative humidity of <2%³⁷. This was attributed to absorption of water into the organic layer of the particles, which lowers the average molecular weight of the organic phase and thereby enhances partitioning of semivolatile oxidation products of the monoterpene³⁸.

Upon addition of SO₂, a trend similar to the low RH experiments was observed in the median seed particle diameter, where in the case of α -pinene ozonolysis, there was no statistically significant change in Δ d_{seeds}, but in the case of β -pinene ozonolysis, a strong enhancement was observed in seed particle growth, with Δ d_{seeds} doubling from 0.6±0.1 nm to 1.2±0.1 nm. Although the observed growth following addition of β -pinene in the absence of SO₂ was slightly greater than at low RH, hinting to enhanced partitioning of semivolatile SOA products, the seed diameter following addition of SO₂ was the same as at low RH. Thus, the effect of SO₂ on the seed particle growth rate appears to be insensitive to water vapor for the range of RH studied here.

Interestingly, the amount of particle nucleation observed following SO₂ addition was significantly enhanced for both α -pinene and β -pinene relative to the experiments carried out at low RH (Figures 5-2 and 5-3). As mentioned, water can efficiently scavenge sCIs with an *anti*- conformation, and so it might be expected that

particle nucleation would be decreased at higher RH due to water competing with SO₂ for reaction with these sCIs. However, it has been shown previously that the reaction between *anti*-sCIs and SO₂ becomes negligible above an RH of ~10% ^{35,39,40}. Newland et al. (2018) measured the loss of SO₂ during ozonolysis of both α -pinene and β -pinene, and found that SO₂ loss became insensitive to the water vapor concentration at RH values above ~2.5% for α -pinene, and ~10% for β -pinene³⁵, which they say supports the idea of there being two chemically distinct sCI conformers present (*anti* and *syn*). Thus, it is likely that at the "low" RH of 15%, all of the *anti* sCIs (including CH₂OO) are already scavenged quickly by water, and their reaction with SO₂ is negligible, whereas the *syn* sCIs react much slower with water, and the factor of 4 increase in [H₂O] going from 15% RH to 60% RH does not significantly affect the loss of those sCIs, so they react with SO₂ to a similar extent under both conditions. Therefore, the extent of particle nucleation did not decrease at higher RH.

Contrarily, nucleation caused by the addition of SO₂ was observed to increase quite substantially at 60% RH for both monoterpenes. This is likely due to the enhanced clustering of sulfuric acid and water molecules caused by the increased availability of gas-phase water, leading to enhanced nucleation rates. Many studies of the relative humidity dependence on sulfate particle nucleation have shown that nucleation rates are increased at higher RH for this reason⁴¹. Zollner et al. (ACP 2012) reported a strong RH dependency of the nucleation rate *J* of particles composed of sulfuric acid, water, and nitrogen base molecules, with *J* increasing roughly an order of magnitude from 14% RH to 20% RH, and an additional factor of ~5 increase at 40% RH⁴¹. Numerous other studies have reported similar increases in *J* with increasing RH at constant $[H_2SO_4]^{42-48}$.



Figure 5-2. Steady-state size distributions of the nucleated particles following addition of SO_2 during ozonolysis of α -pinene (top) and β -pinene (bottom) under the various experimental conditions investigated.



Figure 5-3. Number concentrations of the nucleated particles following SO₂ addition during ozonolysis of α -pinene (left) and β -pinene (right) under the various experimental conditions investigated. Error bars represent one standard deviation of three replicate trials.

5.5 Deliquesced Seeds at High Relative Humidity

After investigating the effect of low vs. high relative humidity on the growth of dry seed particles, a third trial was carried out in triplicate for each monoterpene under the same "high RH" of 60%, but with deliquesced seed particles to investigate the impact of aerosol liquid water on particle growth. As mentioned previously, this was achieved by passing the dry, size-selected seed particles through the NAS, exposing the seeds to a relative humidity above the deliquescence point of ammonium sulfate (~79% RH). For these experiments, it was assured that the relative humidity of the aerosol exiting the NAS was always above this point, which was continuously measured to be in the range of 85-95%.

Furthermore, deliquescence of the seed particles was confirmed by measuring the size distribution exiting the flow tube prior to the addition of monoterpene or SO_2

without drying the seeds before the SMPS inlet, with the RH of the SMPS sheath flow equilibrated to that of the aerosol flow exiting the flow tube. Because the RH inside both the flow tube and the SMPS remained above the efflorescence point of ammonium sulfate (~29%), this allowed the "wet diameter" (59.6 nm) of the seeds to be measured, which was approximately 8 nm larger than their "dry diameter" (51.4 nm) measured by sending the aerosol through a diffusion dryer tube just prior to the SMPS inlet. This diameter increase corresponds to a growth factor (GF) of 1.16 ± 0.02 , which is in good agreement with Gao et al. (2006), who determined a GF of ~1.24 for 50 nm (dry diameter) ammonium sulfate particles at a comparable RH, based on a theoretically predicted molality of about 16 mol kg^{-1 31}. A comparison of the dry vs. wet seed particle size distribution is shown in Figure 5-4.



Figure 5-4. Comparison of dry diameter (solid line) vs. wet diameter (dotted line) seed particle size distributions.

For the sake of obtaining a direct comparison of seed particle growth with dry vs. wet seeds, the particles in these experiments were dried prior to SMPS measurement such that the bar graphs in Figure 5-4 are all representative of the "dry diameter" of the seeds in every experiment. In the absence of SO₂, it was found that the higher aerosol liquid water content in the wet seeds resulted in a slight decrease in Δd_{seeds} for particles grown by α -pinene ozonolysis, which dropped from 1.9±0.1 nm with dry seeds to 1.7 ± 0.1 nm with wet seeds. This finding is consistent with a previous study by Cocker III et al. (2001), who found that the yield of organic aerosol from the ozonolysis of α -pinene was reduced in the presence of aqueous ammonium sulfate seeds relative to dry seed or unseeded conditions³⁷. They suggest that this effect might be explained by organic-salt interactions in the aqueous phase of the aerosol, which can lead to a "salting-out" effect of the condensed organic material, such as that described for methylglyoxal/ammonium sulfate aqueous aerosols in section 3.9.

Additionally, they suggest that this effect might also result from the formation of two distinct liquid phases in the particles; one containing mostly organic material, and the other containing mostly dissolved salt. This could impact the solubility and diffusion rates of the condensing material, resulting in a reduced organic aerosol yield. It has been shown that aqueous solutions containing ammonium sulfate and dissolved pinic acid, a major condensable oxidation product of α -pinene ozonolysis, does indeed lead to two separate liquid phases³⁷. In addition, a large number of both computational and experimental studies have suggested that liquid-liquid phase separation is very likely to occur in mixed organic-inorganic aerosols over a wide range of RH, and that this may reduce hygroscopic growth^{49–55}. Faust et al. (2017) have suggested that the

presence of an organic shell surrounding an aqueous inorganic core could cause gasphase organic molecules that strike the particle surface to be less likely to partition to the particle phase, which would otherwise be expected to increase due to enhanced Henry's law partitioning of HOMs into an aqueous phase³³. Other studies have suggested that liquid-liquid phase separation is less likely to occur in particles within the size range studied here, although these specific particle compositions have not yet been investigated, and this should be an area of future work^{56,57}.



Figure 5-5. Bar graph comparison of the change in median seed particle diameter following addition of monoterpene (green) and SO₂ (red) under each of the experimental conditions studied. Error bars represent the standard deviation of three replicate trials. ap = α -pinene; bp = β -pinene.

Interestingly, the opposite trend was observed in the case of β -pinene, where in the absence of SO₂, having a higher aerosol liquid water content in the wet seeds resulted in a slight increase in Δ d_{seeds} of ~0.2 nm relative to dry seeds. This may be due to the different types of gas-phase oxidation products formed from β -pinene relative to α -pinene, which can differ in hygroscopicity and solubility into the aqueous phase. Upon addition of SO₂, however, a significant increase in Δ d_{seeds} was observed, growing from 0.8±0.1 to 1.3±0.1. This enhancement in particle growth following SO₂ addition is similar to the previous trial carried out in the presence of dry seeds, suggesting that increased aerosol liquid water content does not affect this growth enhancement.

A significant decrease in the number concentration of nucleated particles following SO₂ addition was observed for both α -pinene and β -pinene ozonolysis, with the concentration being lower than that of the dry seed/low RH trials (Figures 5-2 and 5-3). This may be due to the larger total particle surface area caused by the increased diameter of the wet seeds, which corresponds to a much greater condensation sink for the gas-phase species. In fact, the deliquesced/effloresced seed particle surface area ratio was ~1.4, corresponding to a 31% increase in the total particle condensation sink, calculated using the same method as stated in section 4.7.1. Despite this, the effect of SO₂ addition on seed particle growth was very comparable to that observed in the presence of dry seeds for both monoterpene precursors, where growth from α -pinene ozonolysis was largely unaffected, whereas growth from β -pinene ozonolysis increased significantly. This latter case is of particular interest, as it shows that even under atmospherically realistic conditions of higher relative humidity and aerosol

liquid water content, the presence of SO_2 leads to an increase in nanoparticle growth greater than what is currently predicted by atmospheric aerosol models.

Total particle volume concentrations (V_{total}) before and after addition of SO₂ were also investigated for each experimental condition studied (Figure 5-6). Although the average values suggest that V_{total} increased following SO₂ addition for every experiment due to the formation of new particles, the relatively large amount of scatter in the SMPS-measured volume concentrations makes it difficult to determine the statistical significance of these changes. Thus, due to the higher accuracy and precision of particle diameter measurements by the SMPS, these measurements were preferable to determine the extent of particle growth in these experiments.



Figure 5-6. Bar graphs of total particle volume concentrations following addition of monoterpene (green) and SO₂ (red) under each of the experimental conditions studied. Error bars represent the standard deviation of three replicate trials. ap = α -pinene; bp = β -pinene.

Precursor	Wet	RH	$\Delta d_{\text{seeds}} (\text{nm})$	$\Delta d_{\text{seeds}} (\text{nm})$	$N_{nucleation}$ (cm ⁻³)
	Seeds?	(%)	0 ppbv SO ₂	~8 ppbv SO ₂	~8 ppbv SO ₂
α-pinene	No	15	1.5±0.1	1.6±0.1	14 000±2 100
α-pinene	No	60	1.9±0.1	1.8±0.2	49 000±8 400
α-pinene	Yes	60	1.7±0.1	1.8±0.2	3 100±370
β-pinene	No	15	0.5±0.1	1.5±0.3	190 000±44 000
β-pinene	No	60	0.6±0.1	1.2±0.1	270 000±43 000
β-pinene	Yes	60	0.8±0.1	1.3±0.1	160 000±2 700

Table 5-1. Summary of seed particle growth (Δ d_{seeds}) in the absence and presence of SO₂, and nucleated particle number concentration (N_{nucleation}) in the presence of SO₂ for each of the experimental conditions studied. Reported errors are one standard deviation of the three replicate trials carried out for each condition.

5.5.1 High-Resolution ESI-MS Analysis of Deliquesced Seeds

For the experiments utilizing deliquesced seed particles, additional trials were carried out in which the wet seeds grown by monoterpene ozonolysis in the absence and presence of SO₂ were collected onto quartz microfiber filters for analysis by high-resolution electrospray ionization mass spectrometry (ESI-MS). For both α -pinene and β -pinene systems, the only differences in the mass spectra of the deliquesced particles before and after addition of SO₂ were observed in the mass range of 200-300 Da. The comparative negative mode mass spectra of this region is shown in Figures 5-7 (α -pinene) and 5-8 (β -pinene). Within this range, a number of new ions which were assigned accurate mass formulas corresponding to organosulfates were detected in both precursor systems only after SO₂ was added to the flow tube.

The spectra collected for deliquesced seeds grown by α -pinene ozonolysis appear very similar to those shown in Figure 4-6 for dry seeds collected at low RH.

Many of the same organosulfate formulas reappear, for instance $[C_9H_{15}O_5S]^-$ at m/z 235, $[C_9H_{13}O_7S]^-$ at m/z 265, and $[C_{10}H_{15}O_7S]^-$ at m/z 279. Interestingly, however, the distribution of these ions appears to differ considerably from the dry seed/low RH spectrum, in that not all organosulfates observed with dry seeds are detected with wet seeds, and those that do reappear are present at different relative intensities. This may suggest that, although the formation of organosulfates occurs with both deliquesced and effloresced seed particles, the presence of aerosol liquid water may play a role in altering the formation of specific products.

ESI-MS analysis of the wet seeds grown by β -pinene ozonolysis in the presence of SO₂ also revealed strong signals corresponding to sulfate-containing species, such as the ions at m/z 233, with formula [C₉H₁₃O₅S]⁻, and m/z 281, with formula [C₁₀H₁₇O₇S]⁻ (Figure 5-8). The ion observed at m/z 249, assigned with the formula [C₁₀H₁₇O₅S]⁻, has been previously identified as an organosulfate in laboratory studies of SOA formation from β -pinene ozonolysis in the presence of acidic sulfate seeds, and is suspected to form by addition of sulfate to β -pinene oxide, a product of the ozonolysis reaction⁵⁸. The same β -pinene-derived organosulfate has also been detected in ambient SOA samples collected from a forest site in northeastern Bavaria, Germany⁵⁸.



Figure 5-7. Comparison of high-resolution ESI mass spectra of α-pinene SOA collected without (top) and with (bottom, inverted) SO₂ added to the flow tube in the presence of deliquesced seeds at 60% RH. Peaks colored in red correspond to proposed organosulfates based on accurate mass formula assignments. Labels give m/z (-) and the corresponding formula for some of the major peaks.



Figure 5-8. Comparison of high-resolution ESI mass spectra of β -pinene SOA collected without (top) and with (bottom, inverted) SO₂ added to the flow tube in the presence of deliquesced seeds at 60% RH. Peaks colored in red correspond to proposed organosulfates based on accurate mass formula assignments. Labels give m/z (-) and the corresponding formula for some of the major peaks.

An interesting observation was the detection of the ion at m/z 294, assigned the formula $[C_{10}H_{16}O_7NS]^-$, in the spectra of wet seeds grown by both α -pinene and β -pinene in the presence of SO₂. This was the only organosulfate observed in both monoterpene systems, suggesting this species is likely derived from a common oxidation product of both α -pinene and β -pinene. This ion has been previously

identified as a monoterpene-derived nitrooxy organosulfate, and has been detected in ambient samples from southern Sweden and the southeastern United States^{59–61}. This ion was also observed in the dry seeds grown by α -pinene ozonolysis in the presence of SO₂ (Figure 4-6), and so its formation is apparently not dependent on the presence of an aqueous phase. Although these experiments were considered to be conducted under low-NOx conditions, nitrogen oxides were not explicitly quantified, and it is possible that trace levels may have been present, facilitating the formation of this ion.

As previously mentioned, seed particle growth from β -pinene ozonolysis in the absence of SO₂ was found to be slightly enhanced when the seed particles were deliquesced. To investigate this further, ESI-MS analysis was also carried out for effloresced seed particles grown by β -pinene ozonolysis and compared to the deliquesced particle spectrum (Figure 5-9). Interestingly, the two spectra appear nearly identical, consisting primarily of monomer species spanning the mass range of 150-200 Da, and only one dimer product observed at m/z 293 ([C₁₇H₂₅O₄]⁻). This suggests that the enhanced growth observed in the deliquesced seed particles is not due to additional organic product formation, and might instead be caused by the presence of aerosol liquid water remaining in these particles during size characterization.

Although the particles were passed through a diffusion dryer just before entering the SMPS, it is possible that some water still remained in the particles during measurement. β -pinene SOA is well known to be highly viscous and to decrease the efflorescence point of aqueous sulfate aerosol⁶², and so its incorporation into the seed particles likely increased the viscocity of the aqueous phase, slowing the evaporation rate of water during the drying process. Additionally, if the condensed organic material formed a viscous coating around the aqueous seed particle core, this would
also lower the diffusivity of water through the organic layer, causing water to be trapped in the particles during measurement⁶².



Figure 5-9. Comparative ESI mass spectra of β -pinene SOA collected with effloresced (top) and deliquesced (bottom, inverted) ammonium sulfate seed particles in the flow tube in the absence of SO₂.

5.6 Conclusions

In this chapter, the effect of relative humidity and aerosol phase state on particle formation and growth by monoterpene ozonolysis was investigated in both the presence and absence of SO₂. It was found that higher relative humidity led to a slight increase in the growth rates of dry ammonium sulfate seed particles from both α pinene and β -pinene ozonolysis in the absence of SO₂, and a dramatic increase in the number of newly formed particles from both precursors in the presence of SO₂. The effect of increased aerosol liquid water on seed particle growth was precursordependent, with a slight decrease observed for α -pinene ozonolysis, and a slight increase observed for β -pinene ozonolysis. The amount of particle nucleation following SO₂ addition was drastically lower in the presence of deliquesced seeds relative to effloresced seeds for both monoterpene systems. Additionally, molecular composition measurements by high-resolution mass spectrometry revealed the formation of organosulfates in deliquesced particles from both α -pinene and β -pinene ozonolysis when SO₂ was present, although their formation does not appear to depend on aerosol liquid water, and growth rates remained comparable to trials using effloresced seed particles. Finally, under all conditions studied, addition of SO₂ was found to have no significant effect on particle growth by ozonolysis of α -pinene, but was found to dramatically increase particle growth by β -pinene. As this effect was observed even under more atmospherically relevant conditions than the experiments in Chapter 4, a more thorough investigation of the chemical mechanisms underlying this phenomenon, and their incorporation into aerosol climate models, should be a focus of future work.

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Chapter 6

CONCLUSIONS AND FUTURE DIRECTIONS

This dissertation details laboratory investigations of pathways to atmospheric nanoparticle formation and growth that are poorly represented or completely absent from current-day aerosol climate models. First, a combination of high-resolution electrospray ionization mass spectrometry and online single-particle mass spectrometry was utilized to investigate the formation of nitrogen-containing compounds in aqueous nanodroplets. It was found that aqueous reactions involving ammonium sulfate and small, water-soluble organic compounds can lead to the formation of imidazole and its derivatives, which can contribute to secondary organic aerosol mass. Molecular composition analysis revealed that such products are formed only from organic precursors containing a dicarbonyl functionality, and that their formation is greatly accelerated in the highly-concentrated solute environment of an aqueous nanodroplet compared to that of a dilute bulk solution. Droplet drying studies revealed both glyoxal and methylglyoxal as potential precursors to the aqueous formation of organic nitrogen; however, product yields were found to depend on both precursor identity and the extent of droplet drying. As the relative humidity to which the droplets were dried was lowered, an increase in the nitrogen-to-carbon ratio of the organic matter was observed for droplets containing glyoxal and ammonium sulfate, whereas a decrease in the nitrogen-to carbon ratio was observed for droplets containing methylglyoxal and ammonium sulfate. These observations were attributed to the salting-in effect of glyoxal and salting-out effect of methylglyoxal with

increasing sulfate ionic strength. Based on these results, glyoxal was elucidated as a potential contributor to particulate organic nitrogen previously measured in ambient nanoparticles during summertime new particle formation events in Lewes, Delaware.

Next, the development and implementation of a custom-built aerosol flow tube reactor was described to investigate the effect of sulfur dioxide on nanoparticle formation and growth during the ozonolysis of atmospherically abundant biogenic alkenes. Initial experiments were conducted in the presence of dry monodisperse ammonium sulfate seed particles and a hydroxyl radical scavenger under low relative humidity conditions. Without sulfur dioxide, new particle formation was not observed, and growth rates of the seed particles were consistent with condensation of lowvolatility oxidation products produced from the ozonolysis of each alkene. When sulfur dioxide was added, new particle formation was observed from every alkene system studied, attributed to sulfuric acid formation caused by the reaction of sulfur dioxide with carbonyl oxide intermediates produced during alkene ozonolysis. The presence of SO₂ did not significantly affect seed particle growth rates from α -pinene and limonene ozonolysis, although chemical composition measurements revealed the presence of organosulfates in the particles following SO2 exposure. Contrarily, the growth of seeds by β -pinene and isoprene ozonolysis was considerably enhanced by SO₂, and chemical composition measurements revealed that the enhanced growth was not due to additional organic material, suggesting that inorganic particle-phase sulfate was likely responsible.

This study was then further expanded upon by conducting additional trials of α -pinene and β -pinene ozonolysis under more atmospherically realistic conditions of higher relative humidity and aerosol liquid water content. In the absence of SO₂, it was

found that increasing the relative humidity to 60% led to a slight increase in the growth rates of dry seed particles from both α -pinene and β -pinene ozonolysis. In the presence of SO₂, a significant increase in the number of nucleated particles was observed, attributed to enhanced cluster formation involving gas-phase sulfuric acid and water molecules. When these experiments were repeated in the presence of deliquesced seed particles, the effect on their growth was found to be dependent on the identity of the alkene being oxidized, with a slight decrease observed for α -pinene ozonolysis, and a slight increase observed for β -pinene ozonolysis. When SO₂ was added, the number of nucleated particles was found to be much lower for both alkene systems relative to trials using effloresced seed particles. Additionally, molecular composition measurements revealed the formation of organosulfates in deliquesced particles from both α -pinene and β -pinene ozonolysis when SO₂ was present. Under all conditions studied, the presence of SO₂ was found to have no significant effect on particle growth during ozonolysis of α -pinene, but was found to dramatically increase particle growth by β -pinene ozonolysis. These results ultimately suggest that a previously unreported pathway to particle growth activated by SO_2 may alter the production of cloud condensation nuclei over regions where interactions of anthropogenic and biogenic gases are significant.

The research reported in this dissertation provides valuable insight into atmospheric processes which can significantly impact aerosol climate effects; however, a number of questions still remain that open the door for future research. In the future, a number of complementary experiments should be conducted to further elucidate the chemical mechanisms underlying the observed effects of gas- and particle-phase water on nanoparticle formation and growth rates. First, the dramatic

decrease in particle nucleation that was observed following SO_2 addition during monoterpene ozonolysis in the presence of deliquesced seed particles relative to effloresced seeds warrants further research. Kinetic modeling of the formation of gasphase sulfuric acid from the SO_2 + Criegee Intermediate reaction should be performed to help elucidate whether the observed decrease could be due solely to the larger condensation sink, or if additional heterogeneous processes could be taking place to inhibit nucleation.

Second, a quantitative investigation of the production of gas-phase sulfuric acid from the reaction of SO_2 with the Criegee Intermediates produced during ozonolysis of the alkenes studied in Chapter 4 would be beneficial. This can be performed by use of a chemical ionization mass spectrometer (CIMS) and employing a reagent ion such as NO_3^- to selectively detect sulfuric acid through the formation of ion clusters. The ratio of the signal intensities of the ion cluster to the reagent ion can then be used to quantify the sulfuric acid concentration. This method can also provide an indirect measurement of the concentrations of Criegee Intermediates reactive towards SO_2 that are produced from various alkenes.

Third, the morphology and phase-state of deliquesced and effloresced seed particles grown by alkene ozonolysis in the presence and absence of SO₂ should be investigated through the use of transmission electron microscopy (TEM) imaging. It would be useful to know if liquid-liquid phase separation occurs in the deliquesced seed particles grown by ozonolysis of α -pinene/ β -pinene in order to better understand the reduction/enhancement observed in seed particle growth relative to experiments using effloresced seeds. Imaging of seed particles grown by β -pinene ozonolysis in the absence and presence of SO₂ would also be of great benefit to help elucidate the

chemistry leading to enhanced particle growth consistently observed following addition of SO₂.

Finally, an investigation of how seed particle diameter affects the measured growth rates from β -pinene ozonolysis in the presence of SO₂ would be of great benefit. Such a study could help clarify whether the enhanced growth observed following addition of SO₂ is due to a surface- or volume-limited process. If reactions only occur on the particle surface, growth rate should be independent of the seed particle size, whereas if reactions occur within the bulk of the particle, the growth rate should increase as the seed particle diameter increases.

The work presented in this dissertation builds a strong foundation for understanding secondary chemical processes impacting atmospheric nanoparticle formation and growth. It is my hope that this research can contribute to the improvement of atmospheric models, and ultimately advance our current-day understanding of aerosol climate effects.

Appendix A

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Chapter 3

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