Towards a Molecular-level Understanding of Organic Aerosol Composition

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Towards a Molecular-level Understanding of Organic Aerosol Composition

Laxminarasimha Reddy Yatavelli

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Department of Atmospheric Sciences

Aerosol organic matter significantly contributes to the total aerosol burden in the atmosphere, but significant uncertainties related to sources and removal processes persist due, in part, to a poor understanding of the species which make up gas and aerosol-phase organic matter. Fast, in-situ, and speciated measurements are needed to elucidate chemical and physical mechanisms controlling the sources and sinks of aerosol organics. This dissertation describes the development of a novel technique to provide high time resolution, in-situ speciated measurements of gas and aerosol-phase organic matter.

The method is termed micro orifice volatilization impactor - chemical ionization mass spectrometer (MOVI-CIMS) and couples two well proven techniques, inertial impaction and chemical ionization. Gas-phase compounds are analyzed while particles are collected on a post. This collection step is followed by thermal desorption in an inert atmosphere to detect condensed-phase compounds. Differentiation between gas and condensed-phase compounds can likely occur on hourly or shorter timescales. The
unique aspects of this approach are the use of an impactor with 100 nozzles that allows particle collection at a pressure within 15% of ambient and the ability to use a wide suite of negative and positive reagent ions. A sample flow rate of 10 L min$^{-1}$ results in a cut-point diameter ($d_{50}$, diameter of 50% collection efficiency) of 0.13 $\mu$m. I demonstrate the capabilities of this technique by applying it to the determination of mono- and di-carboxylic acid vapor pressures and studies of the heterogeneous oxidation of oleic acid aerosol particles using a Quadrupole mass spectrometer (QMS).

To eliminate the inherent limitation that QMSs have, I modified the MOVI-CIMS technique by coupling it to a high-resolution time-of-flight mass spectrometer (MOVI-CI-HTOFMS). The TOF analyzer allows collection of a large range (>500 Th) of molecular ions in fraction of a second. In addition, the high mass resolving power and mass accuracy provided by the HTOF analyzer aids in accurate mass determination of the detected compounds thus making it possible to estimate their elemental composition. Preliminary calibrations show that the technique is very sensitive with detection limit in the nanogram range, especially for dicarboxylic acids.
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1. Introduction

1.1 Organic Aerosol

Organic Aerosol (OA) is ubiquitous in the Earth’s atmosphere and constitutes a major fraction of submicron atmospheric aerosols (aerodynamic diameter ≤ 2.5 µm, PM$_{2.5}$). Depending on location and season they are estimated to contribute 10 – 90% of the PM$_{2.5}$ mass (Andreae and Crutzen, 1997; Zhang, 2007). OA affects water uptake by aerosol particles with implications for visibility and cloud formation, thus making it an important part of the Earth’s climate system (Kanakidou et al., 2005; Quinn et al., 2005b; Mochida et al., 2008b; Hallquist et al., 2009). In addition, OA can increase the toxicity and thus exacerbate the impacts of PM$_{2.5}$ on human health (Jacobson et al., 2000; Mauderly and Chow, 2008). Therefore, understanding the sources of OA, its chemical transformations and effects on the physical and chemical properties of the aerosol particles is important.

OA originates from emissions of both natural (e.g. tree emissions, forest fires) and anthropogenic sources (e.g., motor vehicles, industries, agriculture). When emitted directly into the atmosphere it is referred to as primary organic matter (POA), and when formed in-situ from condensation of low volatility oxidation products of gas-phase precursors (volatile organic compounds, VOCs) it is referred to as secondary organic matter (SOA). Although, proximity to sources, meteorological conditions, and oxidant levels all affect the relative contribution of POA and SOA to PM$_{2.5}$ (Zhang, 2007), recent field studies have shown that even close to large emission sources (i.e. urban areas) SOA
is a major fraction of OA mass (de Gouw et al., 2005; Volkamer et al., 2006; Kleinman et al., 2008; Jimenez et al., 2009).

Estimates of OA that account for both anthropogenic and biogenic sources and their uncertainties range between 50 – 90 TgC yr\(^{-1}\) (Halliquist et al., 2009). On the other hand, top-down estimates can reach an order of magnitude higher than these bottom-up estimates (Goldstein and Galbally, 2007). Halliquist et al. (2009) revised the top down estimates using recent field measurements and approximated the total organic carbon flux to be much lower, 80 – 225 TgC yr\(^{-1}\). This estimate is also comparable to the 150 TgC yr\(^{-1}\) calculated by Heald et al. (2010b) using satellite measurements of aerosol optical depth and the GEOS-chem global model.

Recent studies provide a new framework for improving our understanding of POA evolution and SOA formation in the atmosphere. Robinson et al. (2007) showed that much of the POA that is emitted by vehicles is in fact semi-volatile in nature, contrary to the current belief that POA is nonvolatile. They showed that as the concentrated plume gets diluted a large fraction of POA evaporates, oxidizes in the gas-phase to low volatility compounds, which condenses back onto existing particles as SOA. Using this concept and a volatility-based lumping scheme, known as the volatility basis set, they were able to improve regional-scale simulation of OA. Jimenez et al. (2009) modified the 1-D volatility-basis set into a 2-D framework (2D-VBS) by adding the degree of oxidation of OA (Oxygen-to-Carbon ratio, O:C) as the second dimension. This parameterization has proven successful in explaining the evolution of semi-volatile components of the SOA, but discrepancies arise when attempting to predict the lowest-
volatility OA. More recently, Kroll et al. (2011) used a similar approach where they used carbon oxidation state and the number of carbons in the organic compounds to understand the composition between fragmentation (C-C bond cleavage) and functionalization (addition of polar functional groups to the carbon chain) pathways during hydrocarbon oxidation using laboratory and field data. Figure 1.1 shows a conceptual schematic of the various pathways in which a hydrocarbon can be transformed in the gas and particle-phases and/or at the gas-particle interface.

Understanding OA evolution (when exposed to oxidants) in the atmosphere is difficult not only due to changing concentrations but also due to changing composition and physical properties. This is made even more challenging by the fact that OA contains hundreds, if not thousands of compounds (Hamilton et al., 2004b; Williams et al., 2006b). Over the past decade, due to improvements in real-time analysis techniques, measurements of ensemble averaged elemental composition of OA at high time and spatial resolution has been possible.

Heald et al. (2010a) using data from laboratory oxidation studies of model organic aerosol particles and field data identified a linear trend when the average oxygen-to-carbon ratio (O:C) is plotted against the hydrogen-to-carbon ratio (H:C) in a Van Krevelen diagram. The data was observed to follow a straight line with a slope of -1 indicating that as the aging progresses either carboxylic acid (C(O)OH) functional groups or an approximately equal combination of carbonyl (C=O) and alcohol (OH) functionalities are added to the compounds resulting in this trend. Using a similar analytical technique, but adding more recent field and laboratory data, Ng et al. (2011)
showed that the initial stages in the aging process add carbonyl and alcohol groups but as
the aging progresses carboxylic acids are formed along with alcohols resulting in a linear
trend that has a shallower slope of approximately -0.5. The main reason for Heald et al.
(2010a) observing a move negative trend is probably because they did not resolve the OA
into non-oxidized and oxidized portions. Russell et al. (2011) using Fourier Transform
Infrared Spectroscopy data from various field and laboratory filter samples identified the
dominant functional groups in submicron aerosol particles. The distribution of these
groups is characteristic of the regions where the samples are collected. Two prominent
findings were the dominance of alkanes over other functional groups in most of the
samples, except for the ones that were collected in clean marine sites, and the other was
the near absence of carbonyls groups in combustion emissions. Carboxylic acids and
alcohols were the other two major functional groups observed in majority of the samples.
These findings explain the -0.5 slope observed by Ng et al. (2011) in their analysis. These
studies indicate the dynamic nature of the species that make up OA and the importance of
understanding OA aging to understand the changes in physical properties of aerosol
particles.

Along with improvements in our understanding of the OA evolution with aging,
there has also being improvements in our knowledge of new OA sources. Isoprene, a C₅
compound, was thought be have too small of a carbon chain to form any semi- or low-
volatility products, was identified as a significant global SOA source (Claeys, 2004). This
study has led to the investigation of other smaller VOCs such as Acetylene, 2-Methyl-3-
Buten-2-ol (MBO), and aromatic compounds such as Naphthalene and Alkynaphthalenes (Chan et al., 2009a; 2009b; Volkamer et al., 2009).

Despite this recent progress, SOA formation mechanisms and its dominance in atmospheric aerosols are poorly simulated by computer models (Jimenez et al., 2009). Even models that explicitly consider a large number of reactions and track every product have difficulty reproducing the observed SOA evolution and magnitude indicating that our understanding of source strength and burden of POA and SOA is still far from complete (Johnson et al., 2006).

1.2 Real-time Instrumentation for OA Analysis

OA contains hundreds, if not thousands of compounds (Hamilton et al., 2004b; Williams et al., 2006b). Therefore, over the past decade there has been intense research on improvement and development of new analytical techniques that can measure ensemble and single particle OA mass fraction and composition. These new techniques have provided new insights into OA formation, transformation and loss processes but still much has to be understood about the formation mechanisms and gas-particle partitioning. Until recently, the gas-phase oxidation of hydrocarbons was though to produce only few semi-volatile compounds which react in gas-phase or partition to particle-phase; and once partitioned, the compounds do not undergo any further reactions. Semi-volatile formation and partitioning is in fact much more complex and dynamic as shown in the schematic presented in Figure 1.2. Although, only one product is shown in the figure in reality there are numerous products that form from a single oxidation reaction and they in turn react in
gas and particle-phases. Therefore, improving our understanding of SOA formation needs instruments that quantitatively speciate both gas and particle-phase compounds simultaneously, on a fast timescale. In addition, providing real-time volatility information of these compounds will help us understand the dynamic nature of the gas-particle partitioning and SOA formation.

Chapter 2 describes the design and characterization of a new gas and aerosol separation technique using the Quadrupole-based mass spectrometer. The technique is called micro-orifice volatilization impactor (MOVI) and uses chemical ionization to convert neutral molecules to molecular ions before detection by the mass spectrometer. Application of this technique to measurement of the vapor pressure of three low-vapor pressure organic acids along with the study of heterogeneous oxidation of oleic acids aerosol-particles is also presented.

Chapter 3 details the coupling of the MOVI-CIMS technique to a high-resolution, time-of-flight mass spectrometer. Initial characterization experiments and its advantages over other presently used techniques are highlighted.

1.3 Secondary OA formation from VOC oxidation

Measurements from both laboratory chamber studies and field experiments show that there is a significant amount of oxidized organic material missing leading to a discrepancy in carbon mass balance (Goldstein and Galbally, 2007; Heald et al., 2008). Monitoring the molecular composition of gas and particle-phase organic species with high time resolution and the ability to calculate the elemental composition of these
identified products will provide the necessary information to understand the formation mechanisms and the precursor VOCs, thus aiding in reducing the discrepancy. Therefore, to understand the ability of the MOVI-CIMS technique in characterizing real world SOA, α-pinene (a major biogenic VOC) was oxidized by Ozone and OH radicals in a flow through chamber. These experiments are described in the first part of chapter 4.

Alkanes are estimated to contribute a third of volatile organic compound emissions in urban areas, yet their potential as SOA sources has not been thoroughly studied. Therefore, a series of oxidation experiments are being conducted in the Caltech environmental chamber with various straight chain and cyclic alkanes, at low and high NOx conditions and at oxidation time scales of 18 and 36 hours. Acetate (CH3C(O)O⁻) and H3O⁺ reagent ions are used to detect a whole suite of oxidation products. Second part of Chapter 4 describes preliminary analysis of these experiments.
Figure 1.1 A conceptual schematic of the fragmentation, functionalization, and oligomerization pathways during atmospheric oxidation of organic molecules. (Modified and adapted from Jimenez et al. (2009)).
Figure 1.2 Schematic of the gas-particle partitioning of VOC oxidation products showing the complexity of semi-volatile products reacting in gas and particle-phases and the gas-particle partitioning of these products (Adapted from Kroll and Seinfeld (2008)).
2. Particulate Organic Matter Detection Using a Micro-Orifice Volatilization Impactor Coupled to a Chemical Ionization Mass Spectrometer (MOVI-CIMS)*

2.1 Introduction

Particulate organic matter (POM) is an important constituent of fine aerosol (≤ 2.5 µm) typically contributing 30 – 60% of total aerosol mass, depending on the location and season, and up to 90% in forested regions (Andreae and Crutzen, 1997; Murphy et al., 2006; Zhang et al., 2007). POM can affect the water content of aerosol particles with implications for multiphase chemistry, visibility, cloud formation, and climate (Novakov and Penner, 1993; O'Dowd et al., 2004; Kanakidou et al., 2005; Quinn et al., 2005a; Mochida et al., 2008a); yet its sources and transformations are highly uncertain. For example, several recent studies have indicated that the organic mass predicted by models is currently substantially lower, sometimes by as much as a factor of 10 to 100, than that inferred from measurements (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006; de Gouw et al., 2008; Kleinman et al., 2008). Knowledge of the temporal and spatial variation in POM, its chemical composition and phase state, and its thermodynamic parameters are clearly needed to understand its climate and human health effects (Fuzzi et al., 2006).

Particulate Organic Matter (POM) measurement is traditionally done by laboratory analysis of quartz filter samples collected on timescales ranging from a few hours to few days. But, due to the integrated nature of the measurements and delayed analysis, critical information on the time evolution of POM is often lost. Nevertheless, data from offline techniques has significantly improved our understanding of aerosol particle speciation (Hamilton et al., 2004a), and guided the research community for many decades. Since offline analysis is not the focus of this paper, the reader is referred to Chow (1995), and Chow et al. (2008) for a more comprehensive review.

Over the past decade, numerous continuous and semi-continuous techniques have been developed that provide POM mass and speciation data on a faster timescale. POM in atmospheric aerosols is complex and fragile. As a result, no single instrument currently gives the information needed to completely understand the sources and gas-particle partitioning of POM in the atmosphere (Sullivan and Prather, 2005).

Two thermal-optical instruments that are widely used in field studies are Sunset Laboratory Inc. (Tigard, OR) organic/elemental carbon analyzer (Turpin et al., 1990) and Rupprecht & Patashnick Co. Inc. (east Greenbush, NY) Series 5400 carbon analyzer (Rupprecht et al., 1995). Recently, Sullivan et al. (2004) coupled the particle into liquid sampler (PILS) to a total organic carbon analyzer and measured the water soluble fraction of POM. These techniques are quantitative and have fast sampling times, but they lack organic speciation at the molecular-level, which is useful in understanding the chemical mechanisms associated with POM evolution and source identification.
Mass spectrometry (MS) has become an important tool in real-time detection and analysis of aerosol particles (Sullivan and Prather, 2005; Nash et al., 2006). Many variations of aerosol mass spectrometers (AMS) have been developed for organic and inorganic compounds, differing in sampling inlets, desorption/ionization and detection methods employed. Two main categories are instruments that analyze (a) single and (b) ensembles of aerosol particles.

Single-particle AMS allows the mixing state and composition of individual particles within a population to be assessed (Prather et al., 1994; Murphy and Thomson, 1995; Thomson et al., 2000; Lake et al., 2003; Su et al., 2004; Zelenyuk and Imre, 2005). In most cases, aerosol particles are sampled through an aerodynamic lens, desorbed and ionized using a single or combination of lasers, and the ion cloud is then analyzed by a quadrupole or time-of-flight MS. Laser-desorption/ionization is generally qualitative or semi-quantitative at best, compared to other ionization methods. The high-energy UV lasers used for simultaneous desorption and ionization tend to cause excessive fragmentation of organic compounds. In addition, the high density of ions can lead to matrix effects, limiting their use for POM quantification or speciation (Nash et al., 2006). Nevertheless, single particle AMS provide valuable information on aerosol particle mixing state and certain composition markers (Murphy et al., 2006). In addition, recent improvements such as the separation of desorption and ionization steps by vacuum ultraviolet (VUV) photoionization have reduced some of these limitations (Woods III et al., 2001).
Analyzing an ensemble, rather than individual aerosol particles has proven to be quite useful for POM quantification and/or speciation. Instruments so far developed generally use either a quadrupole MS (Tobias and Ziemann, 1999; Jayne et al., 2000; Voisin et al., 2003; Hearn and Smith, 2004a), quadrupole ion trap MS (Held et al., 2009; Thornberry et al., 2009), or a gas chromatograph (GC) coupled to an MS (Williams et al., 2006a; Goldstein et al., 2008; Kreisberg et al., 2009).

Temperature-programmed thermal desorption particle beam MS (TD-PBMS) (Tobias and Ziemann, 1999), and the Aerodyne AMS (Jayne et al., 2000) use similar sampling and ionization techniques. The sample is first thermally desorbed, then ionized using electron impact (EI) ionization, and detected with a quadrupole or a time-of-flight MS (Drewnick et al., 2005; DeCarlo et al., 2006). These techniques allow quantification of non-refractory organic carbon and its speciation into general classes such as more or less oxidized carbonaceous material. But, similar to laser ionization methods, EI uses a high energy of ionization (70 eV) which excessively fragments organic molecules making it difficult to quantify specific molecular species (Zhang et al., 2005; Zhang et al., 2007). However, with programmed desorption, TD-PBMS is able to enhance speciation especially if the aerosol components have a large volatility spectrum (Tobias and Ziemann, 1999).

As in single particle AMS instruments, recent developments in soft laser ionization methods have been used in those based on bulk analysis. Photoelectron resonance capture ionization MS (PERCI) uses a very low energy pulsed UV laser focused onto a metal surface to generate photoelectrons that ionize analyte molecules.
The low energy EI (<10 eV) coupled with thermal desorption causes minimal fragmentation making it suitable to detect various functional groups in aerosol particles (LaFranchi et al., 2004; LaFranchi and Petrucci, 2006). Photoionization AMS (PIAMS) uses IR laser desorption followed by coherent VUV radiation (10.5 eV) for analysis of ensemble aerosol particles. Although some fragmentation is reported due to laser desorption, aliphatic and aromatic compounds have been detected with low detection limits using PIAMS (Oktem et al., 2004).

GC/MS has been in use for offline analysis of aerosol samples for several decades (Chow et al., 2008). Recently, GC/MS has been successfully used for in-situ analysis of ambient POM (Williams et al., 2006a; Goldstein et al., 2008; Kreisberg et al., 2009). The aerosol sample is initially humidified, then pre-concentrated using inertial impaction before thermal desorption and subsequent analysis. Although this approach provides data at the compound level, in-situ quantification of highly oxygenated and polar functional groups can be a challenge due to the need for multiple columns or long separation times.

Thermal desorption followed by chemical ionization MS (CIMS) is another technique that has proven effective in analyzing complex organic aerosol particles (Hoffmann et al., 1998; Hearn and Smith, 2004a; 2006; Thornberry et al., 2009). Chemical ionization is a soft ionization technique and is well suited for POM in ambient aerosol particles (Nash et al., 2006). A semi-continuous technique, recently developed by Smith and co-workers (Voisin et al., 2003; Smith et al., 2004; Smith and Rathbone, 2008; Held et al., 2009), couples CIMS to an electrostatic precipitator for collection of sub-20 nm aerosol particles. They report very low detection limits for sulfate, ammonium and
carboxylic acids in Aitken mode but have not yet investigated accumulation mode particles, which are responsible for climate and health effects and where the majority of organic mass resides. Hearn and Smith (2006), using a cold trap to concentrate compounds thermally desorbed from aerosol particles, reported detection of non-volatile and semi-volatile organics with various functionalities. Recently, Thornberry et al. (2009) developed a semi-continuous technique for particulate organic compounds. They use a single nozzle, under choked flow conditions to impact particles on a post held at low pressures (8 – 20 torr). The impacted material is flash volatilized and detected with PTR-MS using quadrupole ion trap.

These existing analytical techniques certainly provide a wealth of information on bulk and single particle compositions, greatly improving our knowledge of POM. But other complementary methods are needed to fully acquire a molecular-level understanding of the evolution of POM, its abundance, and speciation in the atmosphere.

A similarity of all techniques aimed at both quantification and speciation of POM at the molecular-level is mass accumulation by pre-collection. This chapter describes the development and initial characterization of one such aerosol-collection thermal-desorption technique directly coupled to a selected negative-ion, quadrupole-based CIMS, which we designate as the Micro-Orifice Volatilization Impactor (MOVI)-CIMS. The novel features of this method which distinguish it from the previously described techniques include: a multi-orifice aerosol impactor, similar to a single stage microorifice uniform deposited impactor (MOUDI) (Marple et al., 1991), particle accumulation at 85% of ambient pressure (760 torr), the ability to perform programmed thermal
desorption or near-flash volatilization, and the use of a selected negative chemical ionization scheme that can improve selectivity and thus molecular specificity. Design details along with various evaluation tests conducted to characterize MOVI-CIMS performance are discussed below.

2.2 Method Description

The MOVI process has 3 steps: particle collection, volatilization, and chemical analysis. Particle laden sample air is drawn through a custom impactor, collecting particles while monitoring gaseous composition with the CIMS. In the second step, the sample air is replaced with dry ultra high purity (UHP) N\textsubscript{2} and simultaneously the collection plate is heated volatilizing the sampled POM. In the third step, specific volatilized species are detected and quantified using CIMS. Below we describe the components and operation involved in these three steps.

2.2.1 Micro-Orifice Impactor

The impaction unit consists of a single stage, multi-jet impactor with 100 nozzles, each having a diameter \( D_n = 0.15 \text{ mm} \) drilled into the blank face of a 1.27 cm OD aluminum rod, bored to 1.06 cm ID. The nozzles are approximately 0.76 mm in length. The collection surface, a 1.17 cm diameter disc machined from brass and soldered to a 1.27 cm OD stainless steel tube, is placed at a distance of <1 mm (~ 4\( D_n \)) from the nozzle plate. We chose brass for the collection surface because of the combination of its thermal
conductivity, coefficient of thermal expansion and relative inertness in an oxidizing atmosphere. A schematic of the MOVI is given in figure 2.1.

Both the nozzle tube and the collection surface tube are fixed relative to one another by means of an aluminum manifold block using Swagelok compression fittings having PTFE ferrules. To reduce the condensation of organic vapors on the inside walls of the manifold block, it is constantly maintained at 75 ± 5 °C. Although the PTFE ferrules do not provide perfect thermal insulation, they isolate the impaction surface from the heated manifold block. This isolation along with the cooling provided by the large gas flow has kept the collection surface at 25 °C during laboratory sampling. Active cooling of the impaction surface, while not used in this prototype, is readily possible with this design by immersion of the support post in a temperature-controlled bath or by using a thermoelectric cooler (Tobias and Ziemann, 1999; Thornberry et al., 2009).

The manifold block is 2.5 X 3 X 3.8 cm in dimension and has 3, 0.95 cm (3/8") NPT female ports. The manifold block and the ion-molecule region (of the CIMS) are separated by a 0.55 mm diameter critical orifice oriented perpendicular to the nozzle flow axis. This critical orifice drops the pressure in the ion-molecule region to 60 Torr and restricts the flow entering the CIMS to 2.0 L min⁻¹. A small diaphragm pump is connected to the third 0.95 cm Swagelok compression fitting on the manifold block and another critical orifice inline to this diaphragm pump, along with the CIMS pump, maintains a total sample flow of 10 L min⁻¹ through the nozzles.

Negative artifacts, due to loss of semivolatile species, are potentially a major limitation for impactors operating at low pressures. Therefore, the goal of this design was
to develop an impactor which not only minimizes the pressure drop across the nozzles but also has a low cut-point. For the design and flow conditions above, the pressure drop across the nozzles is only $14.8 \pm 0.2\%$ of ambient, resulting in a pressure of $647 \pm 2$ torr at the collection surface for ambient pressures of 760 torr. Using the sample flow and the pressure drop, the calculated jet velocity is $110 \, \text{m s}^{-1}$, Reynolds number (Re) = 991 and the theoretical cut-point ($d_{50}$) = 0.140 μm. The theoretical $d_{50}$ is calculated using the critical Stokes number (Stokes number corresponding to 50% collection efficiency) for round-jet impactors (Hinds, 1999). The cross-flow interferences usually common for multi-jet impactors are estimated using the expression given by Kwon et al. (2002) and are minimal for this design.

During sampling, aerosols are collected on the brass impaction surface, while a portion ($2 \, \text{L min}^{-1}$) of the total flow is drawn into the IMR region. This CIMS sample flow also likely contains particles below the $d_{50}$. The remainder of the total flow is pumped away by a diaphragm pump. In the IMR region, the gas is ionized by the reagent ions and a small part of it (~10%) is sampled into the quadrupole chamber and mass analyzed. After sampling particle-laden air for a predetermined time, a valve between the manifold and the diaphragm pump (not shown in figure 2.1) closes, dropping the flow rate through the nozzles to that sampled by the CIMS ($2 \, \text{L min}^{-1}$). This CIMS sample flow is largely dry UHP N$_2$ achieved by overflowing the nozzle tube via a flow controller. Simultaneously, the underside of the impaction surface is resistively heated using a 0.95 cm OD, 5 cm long cartridge heater (200 watts) inserted into the stainless tube and controlled by an Omega temperature controller. The temperature of the
impaction surface is monitored using a thermocouple inserted into a notch drilled into the side of the impaction body, just below the surface.

For rapid volatilization, the collection surface is heated for 90 sec, during which the surface temperature is raised to 120 ± 1 °C, and the collected POM desorbs into the carrier gas. This method of rapid heating is consistent with other studies (Williams et al., 2006a; Thornberry et al., 2009). We chose the maximum desorption temperature by repeatedly impacting (or manually depositing) a constant amount of test organic compounds and increasing the maximum desorption temperature until the relevant CIMS signal passed through a maximum. Some very low vapor pressure material likely remains on the surface of the impactor for our current desorption temperature. However, we prefer to minimize thermal decomposition and degraded CIMS operation observed with very high desorption temperature. After the volatilization cycle, the cartridge heater is turned off and the inline valve is opened again increasing the flow through the nozzles to 10 L min⁻¹. In addition, 2 small AC-powered fans are turned on to aid in the cooling process.

2.2.2 Chemical Ionization Mass Spectrometry (CIMS)

Chemical Ionization (CI) is a technique which has found application in many fields to measure inorganic and organic compounds (Jennings, 1979; Harrison, 1983; Arnold and Hauck, 1985; Budzikiewicz, 1986; Viggiano, 1993; Huey et al., 1995; Hansel et al., 1998; Huey, 2006; de Gouw and Warneke, 2007). It is sensitive, with pptv or lower detection thresholds possible, and has a fast response limited ultimately by the reaction
time in the ion-molecule region. In this present study, we use selected negative ion CIMS (here-on referred to as only CIMS), with $I^-$ and $SF_6^-$ as reagent ions to specifically detect organic acids in gas and condensed-phases. These reagent ions are in wide use for atmospheric chemistry studies (Huey et al., 1995). The reaction of an organic acid with $I^-$ proceeds through ion association and that of $SF_6^-$ is through fluoride ($F^-$) transfer and/or proton transfer

$$I^- + RC(O)OH \rightarrow IRC(O)OH^- \quad \text{(R2.1)}$$

$$SF_6^- + RC(O)OH \rightarrow FRC(O)OH^- + SF_5^- \quad \text{(R2.2)}$$

$$SF_6^- + RC(O)OH \rightarrow SF_5^-RC(O)O^- + HF \quad \text{(R2.3)}$$

Here we focused only on the ion association products (R1 and R2). These reactions allow the detection of a sample molecule with minimal (essentially undetectable) fragmentation at the parent mass plus 126.9 amu or 19 amu for $I^-$ and $SF_6^-$, respectively. Because of the decrease in binding energy of the adduct ion with halide ion radius ($r_{\text{ion}}, F^- < Cl^- < Br^- < I^-$), $I^-$ ions are much more selective than $F^-$ towards acids as opposed to alcohols or aldehydes (Caldwell et al., 1989). We successfully exploited this aspect to detect organic acids within a mixture containing several oxygenated functionalities.

Apart from negative reagent ions, gaseous organic molecules have also been detected using positive ions such as $H_3O^+$, $O_2^+$, and $NO^+$ (e.g. Hearn and Smith (2004a)), among which $H_3O^+$ is most widely used for proton-transfer reaction mass spectrometry, PTR-MS (Hansel et al., 1998; de Gouw and Warneke, 2007). Species with a proton affinity greater than $H_2O$, which includes essentially all oxygenated VOCs (OVOCs), are
thus ionized. PTR-MS is quite sensitive, but not entirely selective, making the mass spectra more challenging to interpret if a complex mixture of POM is analyzed as is generally the case for ambient aerosol (Hamilton et al., 2004a; Williams et al., 2006a). On the other hand, negative reagent ions can be very selective. Using negative ions for specific organic compounds, appreciable sensitivity and selectivity can be achieved. In an earlier study, Hearn and Smith (2004a), while testing CIMS for analysis of organic aerosol particles reported that negative reagent ions such as $O_2^-$, $F^-$, and $SF_6^-$ were less sensitive than the protonated water cluster ion, $H^+(H_2O)_2$, for detection of organic acids. But recently, acetate ($CH_3C(O)O^-$) ion has been demonstrated for organic acid detection and is reported to have high sensitivity (Veres et al., 2008). Therefore, our future work will involve testing the MOVI-CIMS sensitivity with this new ion for organic acids.

The CIMS approach used in this work, except for the inlet impactor, is similar to that described earlier (McNeill et al., 2007; Kercher et al., 2009). First, the analyte molecules are sampled through a stainless steel orifice at 2.0 L min$^{-1}$ into an ion-molecule region (IMR), maintained at a pressure of 60 Torr by means of a rotary vane pump, and react with $I^-$ or $SF_6^-$ reagent ions. $I^-$ ions are generated by flowing 2.0 L min$^{-1}$ N$_2$ over a permeation tube maintained at 45 – 50 °C containing methyl iodide (CH$_3$I, Acros Organics) and then through a $^{210}$Po α-particle radioactive source (NRD model 2021). $SF_6^-$ is produced by adding a trace flow of pure sulfur hexafluoride gas (SF$_6$, Scott Specialty Gases, 99.99%) to 2.0 L min$^{-1}$ of dry N$_2$ prior to the radioactive source. The α-particle radioactive source is biased to -20 V relative to ground. Product ions are then
focused through an orifice biased at -20 V relative to ground into a collisional
dissociation chamber (CDC) maintained at 0.75 torr.

Reagent and product ions cluster with water molecules present in the sample gas.
Very high $[H_2O]$ in the IMR can spread the product ions across several m/z associated
with different coordination numbers of $H_2O$ clustered with the parent product ion. Use of
a CDC can minimize this effect. Cluster ions are dissociated through collisions with the
bath gas enhanced by means of an electric field. The stronger the electric field, the higher
the fragmentation of cluster ions. Therefore, care has to be taken not to fragment the
parent molecule by using excessively high electric fields. In this study, the optimal
electric field was found to be 1.1 V cm$^{-1}$. Water clusters with analyte ions were not
observed and this field maximized the sensitivity for $I^-/F^-\cdot$organic acid clusters.

The quadrupole mass spectrometer (QMS) is computer controlled by custom lab-
view software, which also records and stores the data. Each mass-to-charge (m/z) ratio is
counted for 100 ms, leading to a sampling frequency of approximately 1 Hz per m/z
during a typical experiment where 10 m/z are monitored simultaneously.

2.2.3 MOVI-CIMS Coupled System

The process of sampling, volatilization, and ion detection is illustrated in figure 2.2. The
figure shows a time trace of the ion abundance of two compounds produced during the
heterogeneous OH oxidation of palmitic acid (PA, C$_{16}$H$_{32}$O$_2$) particles as described by
McNeill et al. (2008). For these experiments the volume weighted mean particle radius
was 0.15 μm with a geometric standard deviation, $\sigma_g = 1.35$. The CIMS signal at m/z 100 amu increased during impaction, suggesting that the compound with that m/z had high enough volatility to be present largely in the gas-phase. In contrast, the signal for 270 amu (PA + 14 amu) had much lower volatility, thereby remaining in the condensed-phase and detected only when the collection surface was heated. It is possible that some semivolatile species on particles smaller than the impactor cut point may partition to the gas phase within their transit through the IMR, thereby adding systematic uncertainties to our MOVI-CIMS measurements. Presently we do not have any experimental data to quantify this potential artifact, which will affect all instruments transmitting particles through a low-pressure region. Moreover, the magnitude of such an artifact will be species dependent. We roughly estimate that for a 50 nm particle containing species with vapor pressures of $10^{-3} – 10^{-6}$ Pa, less than 1% of the mass would volatilize during the 50 ms residence time in the IMR.

2.2.4 Data Analysis

The signal for each m/z ratio in the condensed-phase is converted to concentration using the procedure described below. Figure 2.3 shows a schematic of the ion signal from a typical experiment, followed by a blank desorption (sampling particle-free N$_2$) along with a trace indicating the instrument state. First, each ion signal from a volatilization cycle is normalized against the reagent ion signal collected simultaneously in order to account for changes in instrument sensitivity on short timescales (seconds to minutes). Such changes are mainly caused by fluctuations in ion transmission or abundance related to variations
in the flow, pressure, or water vapor mixing ratios (Kercher et al., 2009). Second, a 10-
point running mean filter is applied to the data and the resulting smoothed signal is
corrected for baseline noise determined when sampling N₂ with the cartridge heater off.
Third, the signal under the ion peak is integrated to get the total area (normalized counts).

As shown in the Figure 2.3, apart from the main initial peak in ion signal, the
baseline (typically detector noise) is small, but a non-negligible secondary peak is usually
observed upon volatilization. We assume this secondary peak is the contribution from
material deposited or adsorbed on the inside walls of the manifold block or on the nozzle
tube, i.e. surfaces not in direct contact with the heater cartridge. To quantify this
contribution, intermittently, particle free dry N₂ is analyzed, shown as the “blank signal”
peak in the figure. The area under the blank peak is calculated the same way as described
above with normalization and smoothing. The blank area is then subtracted from the total
integrated sample area. The resulting area is divided by a calibration factor, \( C_f \), in
normalized counts \( \mu g^{-1} \), to convert the observed signal into a deposited mass. This
procedure is repeated for all heating cycles and each ion monitored.

2.3 Method Evaluation

2.3.1 Particle Collection Efficiency

Particle collection efficiency experiments were performed using monodisperse PA and
oleic acid (OA, \( C_{18}H_{34}O_{2} \)) aerosol particles. PA (Acros organics, 90%) particles were
generated by flowing 0.3 L min\(^{-1}\) of dry N₂ over solid PA powder in a 30.5 cm long, 1.27
cm O.D. horizontal Pyrex tube. The tube was heated to 110 ± 0.5 °C and the temperature
controlled using a programmed temperature controller (Omega). This method of aerosol generation is similar to that described by Thornton et al. (2003). OA (Fisher Scientific, NF/FCC) aerosol particles were nucleated by heating a small quantity of the liquid in a round flask with a dry \( \text{N}_2 \) flow rate of 0.2 L min\(^{-1}\) through the source. Using a temperature controller the particle source was maintained at 120 ± 0.5 °C.

The aerosol sample was diluted into a 0.5 L min\(^{-1}\) dry \( \text{N}_2 \) flow and allowed to equilibrate in a small flow tube. From this flow tube, a 0.3 L min\(^{-1}\) flow was drawn into a DMA (model 3080, TSI, Inc.) for size selection and the excess flow was exhausted. After selecting aerosol particles with diameters between 0.065 - 0.4μm, the sample was diluted into a 10 L min\(^{-1}\) dry \( \text{N}_2 \) flow to increase the total flow rate to the impactor sampling conditions. As noted in the main section, during these experiments the impactor was isolated from the IMR so that the total flow (10 L min\(^{-1}\)) goes through the diaphragm pump. Upstream particle concentrations were continuously monitored using a GRIMM CPC with a flow rate of 0.3 L min\(^{-1}\) before being sampled by the MOVI. The downstream (post impaction) particle concentration was measured using a TSI CPC (model 3776), also operating at a sample flow rate of 0.3 L min\(^{-1}\). Particle count data was corrected for reduced pressure at the collection surface. For these experiments the impactor was isolated from the IMR so that the total flow (10 L min\(^{-1}\)) goes through the diaphragm pump.

Figure 2.4 shows the collection efficiency curves as a function of particle aerodynamic diameter. As predicted by impaction theory, experimental data for each particle type falls on a single curve with a \( d_{50} \) of 0.13 μm. The experimental \( d_{50} \) is in good
agreement with the theoretical estimate of 0.14 μm based on the impaction design (shown as + in the figure). The critical stokes number is 0.21 and is similar to that suggested for round jet impactors (Hinds, 1999). For OA particles, the particle collection efficiency exceeds more than 90% for particles with $d_p \sim 0.25$ μm and for PA particles with $d_p \sim 0.4$ μm. It is assumed that the collection of particles occurs primarily on the impaction surface but total collection inferred from this figure is likely enhanced by the inside walls of the manifold block.

We hypothesize that the difference between the collection efficiencies of OA and PA aerosol particles is probably due to the difference in particle phase. OA particles are liquid, therefore showing higher particle collection efficiency. On the other hand, pure PA particles may have a rough crystalline morphology resulting in higher particle bounce or shattering, causing lower collection efficiency. Data from the linearity and sensitivity experiments, explained in the next section, provides additional support for particle bounce as a reason for differences in PA and OA collection. We presently do not have a good explanation for the higher collection efficiency of PA aerosol particles at lower sizes. This effect was very reproducible and may indicate a bias in our estimated aerodynamic diameters for PA particles, which, for simplicity, we assumed to be spherical. Future efforts should focus on re-measuring the collection efficiency with various compounds (both inorganic and organic).

2.3.2 Linearity and Sensitivity
The MOVI-CIMS linearity and sensitivity were assessed for organic acids using PA, OA, and azelaic acid (AA, C\textsubscript{9}H\textsubscript{16}O\textsubscript{4}) as representative compounds. Two different methods were used for these experiments. In the first, homogeneously nucleated, polydisperse PA and OA aerosol particles with volume weighted mean radius $r_p = 0.33$ and $0.16 \, \mu m$ and $\sigma_g = 1.2$ and $1.25$, respectively were sampled. Figure 2.5 shows the particle size distributions during these experiments. Aerosol generation is similar to that described in the previous section. To vary the amount of collected mass, the particle sampling time was varied from 45 to 210 sec while the particle mass concentration was maintained at a relatively constant value. A differential mobility analyzer/condensation particle counter (DMA/CPC, Grimm technologies) was used to monitor the size and number distribution during the sampling cycle. For chemical ionization we used $I^-$ as the reagent ion in these experiments.

The second method relied on direct deposition of a solution, containing individual organic acid in acetone, on the collection surface using a microliter syringe. The concentrations were 0.4 and 0.6 mM for PA and OA solutions, respectively. AA was also tested once to estimate the sensitivity of the method for dicarboxylic acids with a 0.9 mM solution. After deposition, the manifold block was reassembled and the collection surface was pre-heated at $33 \, ^\circ C$ for 15 min. The cartridge heater was then ramped for 90 sec to vaporize the deposited sample. This procedure was repeated, varying the amount of solution deposited on the collection surface to span a range in the organic acid mass on the impactor.
The ion peak area versus sampled and deposited organic acid mass is shown in figure 2.6. Both PA and OA peak areas are linear with sample mass over the range studied. This linearity indicates minimal post depositional losses at longer sampling times. In addition to the linear relationship, we observed differences for impacted and deposited samples of PA and OA. The possible reasons for these differences are discussed below.

For PA, the area from syringe deposition is higher than that from impaction for the same amount of mass exposed to the collection surface. If we treat syringe deposition as a 100% collection efficiency case, then the PA data shows that there is approximately 35% loss of mass due to either lower collection efficiency or particle bounce. Based on the mean geometric size of the PA aerosol particles used during the impaction experiments we expect a collection efficiency of more than 95%. Therefore, we conclude that particle bounce is the main reason for the discrepancy between the deposited and impacted PA.

Particle bounce is a concern with impaction methods, especially for dry collection surfaces (Lai et al., 2008). It can be minimized by greasing the collection surface, so long as the grease does not interfere with chemical analysis, or by humidifying the sample air stream before impaction (Williams et al., 2006a). Humidification of the sample stream may further improve the collection efficiency of the MOVI-CIMS, as long as the particles are hygroscopic.

For OA, we observe good agreement between deposited and impacted mass indicating minimal bounce, as expected for liquid particles. But the integrated area is
lower than that for PA possibly due to two reasons: 1) decomposition of OA prior to or upon heating, or 2) lower transmission efficiency of larger molecules in the quadrupole region. The first possibility is reasonable in the sense that OA stored for extended periods is known to degrade through light or oxidant mediated processes. The OA used here was 5 yrs old and not purified. The second possible reason for the low sensitivity of OA may be related to the transmission efficiency for larger m/z molecules in a QMS. The mass transmission of a QMS decreases exponentially, due to fringing field effects, and reaches 20% by m/z 205 (Kim et al., 2009). Although the above mentioned study was done with a different quadrupole, we assume that this effect occurs in CIMS quadrupole. At this time we speculate that some combination of the above two reasons accounts for the different sensitivities to PA and OA.

The calibration factor, $C_f$, for condensed-phase organic acids is the slope of the least squares fit to the calibration data shown in figure 2.6. Using $I^-$ as the reagent ion, the calculated $C_f$ for impacted and syringe deposited PA is $0.9 \pm 0.03$ and $1.5 \pm 0.1$ normalized counts $\mu g^{-1}$, respectively and $0.5 \pm 0.08$ normalized counts $\mu g^{-1}$ for OA. Azelaic acid, a straight-chain dicarboxylic acid, yielded the same sensitivity as the saturated monocarboxylic acid, PA. The agreement between PA and AA sensitivities, in contrast to that observed for OA, is more consistent with our expectations about the iodide ion chemistry, i.e. similar sensitivities towards most carboxylic acids.

2.3.3 Precision and Accuracy

We estimate the precision of the method by using replicate experiments involving PA impaction. The error bars in Figure 2.6 indicate the typical 1σ deviation in signal
obtained while sampling a constant PA mass concentration. For this data, dry N₂ flow containing constant aerosol number concentration was sampled and analyzed by the MOVI-CIMS three times, with the collection time remaining constant. Volatilization followed by CIMS detection was as described before. The fluctuations in aerosol concentration were ~ 5%, resulting in a 1σ error of 0.05 normalized counts μg⁻¹ for area calculation. Using these estimates we calculate a relative precision of 15% for our measurements.

Ideally, the accuracy of our method could be tied to the accuracy of known standards of organic compounds in aerosol particles. By performing calibrations similar to that described above we can quantify possible biases and correct them, thereby improving accuracy. Here we estimate the total uncertainty in the calculated mass from the measured signal using errors in the calibration data (shown in Figure 2.6) as an estimate of the accuracy. For signals measured by the MOVI-CIMS for which there is no standard available, we would then extrapolate this uncertainty assuming that the chemical ionization signal is similar for similar acid amounts.

For estimating uncertainty, the data from PA and OA impaction experiments is plotted as signal versus mass (instead of mass versus signal) and a linear least squares line is fit to that data. The mass concentration (M) of a compound of interest in a collected sample is given by the expression

\[ M \pm \delta M = (S \pm \delta S) \cdot (m \pm \delta m) + (B \pm \delta B) \]  

(Eq. 2.1)

where S is the average signal measured (integrated ion peak area), m is the slope of the linear least squares line, and B is the intercept. \( \delta M \), \( \delta S \), \( \delta m \), and \( \delta B \) are the errors.
associated with the corresponding quantities. Rearranging Eq. (2), and solving
for \( \delta M \), neglecting cross-terms between \( \delta S \) and \( \delta m \)
yields the error propagation formula

\[
\delta M = S \delta m + m \delta S + \delta B
\]  

(Eq. 2.2)

The quantities on the right-hand side in Eq. (2.2) are estimated from the signal versus mass plot, except for \( \delta S \), which is the precision reported earlier based on replicate experiments. With an average signal of 0.48 and 0.28 normalized counts, corresponding to a mass of 0.56 and 0.58 \( \mu \text{g} \), we report an accuracy of 15 and 26\% for PA and OA, respectively.

2.3.4 Detection Limit

The detection limit for organic acids calculated using the data similar to that shown in Figure 5 and the expression

\[
\frac{S}{N} = \frac{C_f M}{\sigma_{\text{total}}}
\]  

(Eq. 2.3)

where,

\[
\sigma_{\text{total}} = \sqrt{\sigma_{\text{sample peak area}}^2 + \sigma_{\text{blank peak area}}^2 + \sigma_{\text{instantaneous signal}}^2}
\]  

(Eq. 2.4)

The numerator in Eq. (2.3) provides the total signal produced for a given organic acid mass on the impactor, \( M \), by means of a calibration factor \( C_f \). The denominator represents the total noise associated with a measurement, i.e., the uncertainty in integrated ion peak area from the deposited sample, blank, and the instantaneous signal. For PA, the variance
associated with the sample peak area, \( \sigma_{\text{sample peak area}}^2 \), contributes the most to the total uncertainty and is calculated to be 0.025 counts \( \mu g^{-1} \). The combined variance due to changes in blank peak area and the instantaneous background signal is approximately 35% of the sample peak variance.

Using the measured sensitivity \((C_f)\) with our current laboratory CIMS instrument, \(\sigma_{\text{total}}\) calculated above, and a signal-to-noise ratio \((S/N)\) of 2, detection limits of 80 ± 10 and 120 ± 20 ng are obtained with the deposited and impacted PA, respectively. For the OA sensitivity reported here, we estimate a somewhat higher detection limit than that calculated above. The values reported here are based on a typical sample rate for 10 individual m/z, each scanned for 100 ms. Beyond this number of m/z the detection limit decreases approximately by \(1/\sqrt{N}\), where \(N\) is the number of m/z monitored, for a constant dwell time (100 ms).

Our field-deployable CIMS instrument used for measurement of gas-phase nitrogen oxides and halogen species (Wolfe et al., 2007; Kercher et al., 2009) exhibits 10x larger sensitivity towards these species than the laboratory CIMS described here. Not wanting to unnecessarily contaminate the field system, we’ve refrained from using the MOVI apparatus on it. But, assuming we would achieve a factor of 10 in sensitivity on that system, we estimate the detection limits for straight-chain, saturated mono- and dicarboxylic acids to be ~8 - 12 ng on our field system. Presently, we are in the process of converting the laboratory CIMS into a more sensitive version.
2.4 Method Application

To assess the performance of the MOVI-CIMS technique we performed two sets of experiments (a) vapor pressure measurements of PA, OA and AA using temperature programmed desorption (TPD) similar to those described by Cappa et al. (2007; 2008a), and (b) heterogeneous oxidation of OA aerosol particles by ozone. These tests allow comparison of the results obtained with our technique to those obtained by independent investigations and instruments.

2.4.1 Vapor Pressure Measurement using TPD

One of the key parameters that is needed to model the partitioning of organic compounds between gas and aerosol phases is their saturation vapor pressure (Pankow, 1994a, 1994b). Vapor pressure, and therefore partitioning of a compound, is affected by many factors such as temperature, solubility in water, number of carbons, functional groups, and its mole fraction (Goldstein and Galbally, 2007). There is limited experimental data for low volatility and semi-volatile compounds that partition into the aerosol phase, and even for those that have been studied, the reported values differ by more than 2 orders of magnitude (Chattopadhyay and Ziemann, 2005; Cappa et al., 2007, 2008a). Therefore, below we describe some initial experiments performed with PA, OA and AA to test the performance of the MOVI-CIMS technique to measure vapor pressures of compounds using TPD.
PA and OA aerosol particles were generated by homogeneous nucleation as described in the above section. AA aerosol particles were also generated similar to that of PA using a dry N\textsubscript{2} flow rate of 0.5 L min\textsuperscript{-1} while maintaining the source at 96 ± 0.5 °C. The polydisperse aerosol particles are sampled at room temperature, while maintaining the manifold block at 75 °C. For this analysis, we assume that the deposited samples were cylindrical in shape with a cross-sectional diameter equal to the diameter of the nozzle, \(D_n = 0.15\) mm. The height of the deposited sample is calculated by assuming that the mass sampled is equally divided between the 100 nozzles.

After sample collection for a pre-determined amount of time, the collection surface temperature is linearly increased at 4 K/min, and the evaporating molecules detected using CIMS with \(I^-\) as the reagent ion to monitor the sample ion abundance \((E, \text{molecules s}^{-1})\) as a function of desorption temperature \((T)\). Slow heating minimizes changes in instrument sensitivity that can occur due to depletion of the reagent ion, which is sometimes observed during rapid heating. The data obtained using MOVI-CIMS is binned into 1 °C temperature bins before analysis. A sample desorption profile of the organic acids is shown in Figure 7a.

The measured evaporation rate \((E(T), \text{molecules s}^{-1})\) at every temperature was converted to vapor pressure using the Hertz-Knudsen equation (Cappa et al., 2007),

\[
J_e(T) = \frac{E(T)}{SA(T)} = \frac{\gamma_e p^0(T)}{\sqrt{2\pi mkT}}
\]  
(Eq. 2.5)

Here, \(J_e(T)\) is the evaporation flux (molecules m\textsuperscript{-2} s\textsuperscript{-1}), \(SA(T)\) is the sample surface area (m\textsuperscript{2}), \(p^0(T)\) is the vapor pressure (Pa), m is the molecular mass (kg molecule\textsuperscript{-1}), k is the
Boltzmann’s constant (J K\(^{-1}\)), and T is the temperature (K). \(\gamma_e\) is called the evaporation coefficient and is considered to be temperature independent and equal to unity. SA was varied with desorption temperature using a technique developed by Cappa et al. (2007).

The calculated values of \(p^0(T)\) are converted to \(\ln(p^0(T))\) and plotted verses 1/T over a limited temperature range. A least squares line fit to the linear portion of the data gives a slope equal to \(\Delta H_{\text{sub}}/R\) and an intercept approximately equal to \(\Delta S_{\text{sub}}/R\), where \(\Delta H_{\text{sub}}\) is the enthalpy of sublimation, \(\Delta S_{\text{sub}}\) is the entropy of sublimation, and R is the universal gas constant (J mol\(^{-1}\) K\(^{-1}\)) (Cappa et al., 2007). Figure 6b shows \(\ln(p^0(T))\) versus 1000/RT for the three organic acids. The linear region of the data for least squares regression was visually selected as done in a previous study by Ziemann and coworkers (2005).

To facilitate comparison with other studies, the values of \(\Delta H_{\text{sub}}\) and \(\Delta S_{\text{sub}}\) are converted to standard values at 298 K using an expression given by Atkins et al. (2006) and a value of -50 J mol\(^{-1}\) K\(^{-1}\) for the standard molar heat capacity of sublimation (\(\Delta C_p\)) as estimated by Burkinshaw and Mortimer (1984). These standard values are used to calculate \(p^0(298 \text{ K})\) using the equation

\[
p^0(298 \text{ K}) = 1.013 \times 10^5 \times e^{\left(\frac{-\Delta H_{\text{sub}}}{RT} + \Delta S_{\text{sub}}^0 \right) / R}
\]  
(Eq. 2.6)

The sublimation enthalpies, entropies and vapor pressures (\(p^0_{\text{sub}}(298 \text{ K})\), \(\Delta H_{\text{sub}}^0\), and \(\Delta S_{\text{sub}}^0\)) measured for PA, and AA are reported in table 2.1 for standard conditions of 1 atm and 298 K. Also reported in the table are the enthalpy and entropy of vaporization, and the liquid-phase vapor pressure for OA. The uncertainty range reported for all values is 1 standard deviation of results obtained from at least 3 or more individual experiments.
(reported in the column “N”). Recently, Cappa et al. (2008b) showed that in a multicomponent mixture individual organic compounds exhibit a liquid-like behavior and suggested that compounds in ambient POM may behave in a similar way. Therefore, we also report the liquid-phase vapor pressure and the related thermodynamic parameters ($p_{Liq}^0 (298K)$, $\Delta H_{vap}^0$, and $\Delta S_{vap}^0$) for the organic acids studied here. For this purpose, the enthalpy of vaporization, $\Delta H_{vap}^0$, is calculated using the expression $\Delta H_{vap}^0 = \Delta H_{sub}^0 - \Delta S_{fus}^0 \cdot T_m$, and the entropy of vaporization using $\Delta S_{vap}^0 = \Delta S_{sub}^0 - \Delta S_{fus}^0$, where $\Delta S_{fus}^0$ is the entropy of fusion and $T_m$ is the melting point (Cappa et al., 2008a). The values of $\Delta S_{fus}^0$ and $T_m$ for PA and AA are 160 and 86 J mol$^{-1}$ K$^{-1}$, and 335.7 and 380 K, respectively (Afeefy et al., 2008).

Figure 7a shows sample mass spectral signals as a function of desorption temperature and figure 7b shows $\ln(p^0(T))$ verses 1000/RT for the three organic acids. The vapor pressures measured in this study for all the three acids are within a factor of 2 of those measured by Cappa et al. (2007; 2008a), but about 1 to 2 orders of magnitude lower than other previous measurements (Tao and McMurry, 1989; da Silva et al., 1999; Bilde et al., 2003; Chattopadhyay and Ziemann, 2005). Whereas, $\Delta H_{sub}^0$ and $\Delta S_{sub}^0$ are within the range reported in the literature. Cappa et al. (2007) suggested that the higher vapor pressures observed in previous studies (Tao and McMurry, 1989; da Silva et al., 1999; Bilde et al., 2003; Chattopadhyay and Ziemann, 2005) were due to the presence of residual solvent molecules in the bulk, from aerosol generation schemes. The residual solvent molecules increase the measured $p_{sub}^0 (298K)$ by increasing the evaporation flux.
at lower temperatures. To avoid this, Cappa, et al. pre-heated the deposited aerosol sample for 30 min at 70 °C prior to thermal desorption. In our study we use homogeneous nucleation to deposit pure organic acid aerosol particles, and therefore remove any such potential positive biases, leading to similar results to that of Cappa et al. (2007; 2008a). Our values were determined from measurements made at 647 torr, while those of Cappa et al. were made at 0.5 – 0.7 torr. The agreement between the two techniques suggests possible diffusion related effects were negligible.

Comparing to the values reported by Cappa et al. (2007; 2008a) (shown as the second number in table 2.1), the $p^0_{\text{sub}}(298K)$ calculated for PA and AA is 48 and 36% lower. Although this difference seems large, it is much smaller than the range reported in the literature for these two acids. For OA, $p^0_{\text{Liq}}(298K)$ and its associated thermodynamic parameters are in excellent agreement to that reported by Cappa et al. (2008a), although lower than that calculated by SPARC (6.7 x 10$^{-6}$ Pa) and Yaws (6.7 x 10$^{-5}$ Pa) (Yaws, 2003; Hilal et al., 2007).

One feature that is observed in Figure 7a is the long tail at high temperatures for PA. A possible reason for this tailing may be physical or chemical interactions of long-chain organic molecules with the bare brass collection surface. Chattopadhyay and Ziemann (2005) reported that pentadecanoic acid (C$_{15}$H$_{30}$O$_2$), when deposited on gold surfaces, desorbed at a higher temperature with a long tail in the desorption profile. To overcome this artifact, they coated the aerosol collection surface with Kisscote (a hydrophobic polymer, KISS Polymers LLC, Tampa) and observed lower desorption
temperatures and no change in sample peak. Therefore, our future improvements will likely involve similarly coating the collection surface.

The above experiments and comparisons indicate that this method can be successfully used in SOA chamber and field experiments to determine the vapor pressure and other thermodynamic parameters of compounds in POM.

2.4.2 Ozonolysis of Unsaturated Organic Aerosol Particles

As a means to study the advantages and disadvantages of the MOVI-CIMS as a tool for laboratory/chamber studies of POM processing, we performed an array of experiments probing the reactive uptake of ozone (O$_3$) on liquid OA aerosol particles. This reaction has become a standard benchmark against which new methods are assessed (Zahardis and Petrucci, 2007).

Experimental Setup

Polydisperse OA aerosol particles were generated as described previously in the Aerosol Generation section. To the sample flow, 0.8 L min$^{-1}$ dry N$_2$ and 0.4 L min$^{-1}$ O$_2$ was added. Ozone was added immediately before the particle-laden flow entered a reaction chamber, increasing the total flow to 2.0 L min$^{-1}$. This resulted in a reaction time of 15 sec and O$_3$ concentration of 0 to 2.8x10$^{14}$ molecules cm$^{-3}$. The reaction chamber is a quartz photocell 25.4 cm long and 5 cm in diameter with a 1 cm inner sleeve. All experiments were performed at 1 atm and 298 K. O$_2$ was added to simulate atmosphere condition in the reactor.
O₃ was generated continuously by flowing a mixture of dry N₂ and O₂ through a cell containing a 185 nm Hg pen-ray lamp (UVP). O₃ concentration was monitored by measuring its absorbance at 254 nm before it was added to the aerosol flow. This was done by flowing the O₃/N₂/O₂ mixture into a UV absorbance cell, fitted with another Hg pen-ray lamp (Jelight) coated to primarily emit 254 nm, a 254 nm interference filter, and a photodiode (Thorlabs). O₃ concentration was controlled by changing the flows of N₂ or O₂. The mobility size and number concentration exiting the reaction chamber were monitored using a DMA/CPC unit. Intermittently, the DMA inlet was connected at the end of the aerosol source to measure the unreacted mobility size (rₒ) and number concentration. An O₃-scrubbing diffusion tube was used to remove the unreacted O₃ upstream of the MOVI. SF₆ is the reagent ion used for these experiments.

**Theoretical Analysis**

The decay of OA is given as (Worsnop et al., 2002),

\[
\frac{d[OA]}{dt} = - \frac{3n_{gas} \bar{c} r^{O_3}_{meas}}{4r_p} \quad \text{(Eq. 2.7)}
\]

where, \(n_{gas}\) is the number density of O₃ (molecules cm\(^{-3}\)), \(\bar{c}\) the mean thermal velocity of O₃ molecules (cm s\(^{-1}\)), \(r_p\) is the particle radius (cm) and \(\gamma^{O_3}_{meas}\) is the measured reaction probability of O₃ with OA particles. But \(\gamma^{O_3}_{meas}\) is a combination of various other microphysical parameters and thus has to be decoupled from individual components to obtain the true value, \(\gamma^{O_3}_{true}\). Typically \(\gamma^{O_3}\) is calculated by using five limiting cases. These
cases are: (a) uptake limited by gas-phase diffusion of the oxidant, $\Gamma_{diff}^g$, or mass accommodation, $\alpha$, (b) uptake controlled by fast reaction, (c) uptake controlled by slow reaction, (d) uptake limited by reaction at the surface, and finally (e) uptake limited by particle-phase diffusion of the oxidant, $\Gamma_{diff}^p$. Some studies have reported that OA is depleted in sub-surface layers (approximately <5% of the particle radius) suggesting a fast reaction of O$_3$ with OA, as in case 2 (Moise and Rudich, 2002; Morris et al., 2002). In contrast Hearn et al. (2005) have argued that the reaction between OA and O$_3$ is mainly surface limited.

Therefore, the solution for the case where it is assumed that the reacto-diffusive length is much smaller than the particle diameter is (Worsnop et al., 2002),

$$\sqrt{\frac{OA(t)}{OA_0}} = 1 - \frac{3RTn_{gas}^cH\sqrt{D_{OA}^p k}}{2r_p\sqrt{OA_0} t}$$

(Eq. 2.7)

and $\gamma'^3$ can be calculated using the expression,

$$\gamma'^3 = \frac{4HT\sqrt{D_{OA}^p k OA_0}}{c}$$

(Eq. 2.8)

where, $R$ is the universal gas constant (8.206x10$^{-2}$ atm K$^{-1}$ M$^{-1}$), $T$ is temperature (K), $H$ is the Henry’s law coefficient (M atm$^{-1}$ L$^{-1}$), $k$ is the second order rate constant for the reaction of OA with O$_3$, $OA_0$ is the initial particle-phase concentration of OA at time $t=0$ ($OA_0 = 3.15$ M). Eq. (2.7) indicates that a plot of $\sqrt{OA/OA_0}$ as a function of O$_3$ exposure yield straight lines with slopes inversely proportional to the particle radius. The straight line (---) (shown in Figure 8) is the fit using Eq. (2.7) with $H\sqrt{D_{OA}^p k} = 0.17$ M$^{1/2}$ atm$^{-1}$ cm
s\(^{-1}\). Substituting this value into Eq. (2.8) yields the reaction probability for O\(_3\) on OA aerosol particles, \(\gamma_{O_3} = (8.1\pm3) \times 10^{-4}\).

Figures 8 shows the loss of OA as a function of O\(_3\) exposure for aerosol particles having a volume-weighted mean mobility radius of 93 nm. The straight line is the model fit, which assumes that the reacto-diffusive length is much smaller than the particle diameter.

The value of the ozone - particle reaction probability, \(\gamma_{O_3}\), calculated from the kinetic model is \((8.1\pm3) \times 10^{-4}\). This value is similar to that obtained by other OA-O\(_3\) kinetic studies (Moise and Rudich, 2002; Thornberry and Abbatt, 2004; Hearn and Smith, 2004b; Hearn, 2005; Knopf et al., 2005; Ziemann, 2005; Sage et al., 2009). Hearn and Smith (2004b) measured \(\gamma_{O_3} = (7.5\pm1.2) \times 10^{-4}\) for particle sizes ranging from 0.8 to 1.5 \(\mu\)m with a maximum O\(_3\) exposure of \(5 \times 10^{-4}\) atm s. Both Moise and Rudich (2002), and Thornberry and Abbatt (2004) using OA coated tubes and measuring the loss of gas-phase O\(_3\) with a CIMS reported \(\gamma_{O_3} = (8.3\pm0.2) \times 10^{-4}\) and \((8.0\pm1) \times 10^{-4}\), respectively. Morris et al. (2002) using an aerosol mass spectrometer measured \(\gamma_{O_3} = (1.6\pm0.2) \times 10^{-3}\) on particles of sizes 0.2 to 0.6 \(\mu\)m. Ziemann (2005) reported observing \(\gamma_{O_3} = (6.1\pm5) \times 10^{-4}\) using 0.2 \(\mu\)m particles and the TD-PBMS. Therefore, this study which uses smaller particles than others indicates that for monitoring the same chemical process, i.e. ozonolysis, the MOVI-CIMS technique yields results that are similar to those obtained by independent groups using unrelated instruments.
The decrease in oleic acid loss rate observed at higher ozone exposures has been reported by several studies and is characteristic of this reaction. Hearn et al. (2007) suggest that oleic acid-O$_3$ reaction is mainly limited to the surface of the aerosol particle due to the orientation of the oleic acid molecule as a closely –spaced, “quasi-smectic” structure. They postulate that this structure limits O$_3$ diffusion into the oleic acid particle decreasing $\gamma^{O_3}$. More recently, Sage et al. (2009) indicate that the decrease in $\gamma^{O_3}$ is due to the decreasing oleic acid mass fraction (mass concentration of oleic acid/mass concentration of organic aerosol) which decreases the second order reaction rate between O$_3$ and oleic acid within the particle volume, and thus $\gamma^{O_3}$.

Figure 9 shows the evolution of three major OA oxidation products, 9-Oxononanoic acid, nonanoic acid, and AA as a function of O$_3$ exposure from the MOVI-CIMS experiments. Organic peroxides and nonanal are other products commonly observed from heterogeneous ozonolysis of OA (Ziemann, 2005; Zahardis and Petrucci, 2007). But due to the ion chemistry used in this study only acids are detected. AA has been reported to have a much smaller yield, 1 – 6%, than the other 3 products, consistent with the relative signals shown in Figure 9. Since we did not calibrate CIMS for any of the products during this test phase, we do not know the sensitivity for these compounds and therefore do not calculate their absolute yields from the data. But, the instrument sensitivity is likely similar for 9-Oxononanoic acid, nonanoic acid and AA so we can calculate their relative yields.

As shown in Figure 9, 9-Oxononanoic acid has a relative yield approximately 3.5 times that of nonanoic acid and 5 times that of AA, which is consistent with other
literature reports (Zahardis and Petrucci, 2007). One interesting point is that we observe nonanoic acid in the particle phase (Ziemann, 2005), which is puzzling as nonanoic acid is much more volatile than the other products. We presently do not have a good explanation for this observation but it is consistent with earlier experiments by our group using a completely different detection method (McNeill et al., 2007).

2.5 Summary

NI-CIMS is typically very selective, allowing the detection of compounds containing only specific functional groups. Although its specificity is an advantage in that it reduces the inherent complexity of compound identification, this trait can also be viewed as a limitation in that it cannot be used for identification of all the compounds present in ambient aerosol particles. The MOVI-CIMS technique has shown good reliability, especially for sampling liquid particles, and proved to be a useful tool for simultaneously characterizing gas and condensed phases of laboratory generated reaction mixtures. The impactor design allows high flow rates (10 L min$^{-1}$), making it suitable for in-situ analysis on the hourly timescale. The experimental cut-point is 0.13 μm and compares well with the theoretically predicted value of 0.14 μm. Using $I^-$ as reagent ion, the detection limit for monocarboxylic acids using our lower sensitivity laboratory-based CIMS is estimated to be 80 ± 10 ng. Future experiments will be performed with other reagent ions and a CIMS instrument that is likely 10x more sensitive.

Temperature-programmed desorption experiments using MOVI-CIMS were conducted to calculate the vapor pressure and thermodynamic parameters of PA, OA, and
AA. The $\Delta H_{\text{sub}}^0$ and $\Delta S_{\text{sub}}^0$ obtained are within the range reported by various studies for PA and AA, whereas the $\Delta H_{\text{vap}}^0$ and $\Delta S_{\text{vap}}^0$ for OA agreed very well to the most recent estimate of Cappa et al. (2008a). The calculated vapor pressures for PA and AA are generally lower than the recent estimate. Nevertheless, these experiments support the use of this technique for vapor pressure determination of complex mixtures of POM.

The kinetics of the heterogeneous oxidation of OA by O$_3$ was also investigated using the MOVI-CIMS. The reaction probability, $\gamma^{\text{OH}}$, was inferred to be $(8.1\pm3) \times 10^{-4}$, similar to that reported by various studies. While our focus so far has been to characterize the technique, and not to determine the yields of gas- and condensed-phase products or their vapor pressures, such studies will be part of future research. Moreover, our approach should allow facile quantification of many functionalized organic species, in the gas and particulate phase, during chamber or laboratory studies of POM evolution.
Table 2.1 Vapor pressures and thermodynamic parameters for palmitic, azelaic, and oleic acids at 298 K and 1 atm measured using the MOVI-CIMS. The uncertainty reported is $1\sigma$ calculated from $n$ individual experiments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$p_{\text{sub}}^0$</th>
<th>$\Delta H_{\text{sub}}^0$</th>
<th>$\Delta S_{\text{sub}}^0$</th>
<th>$p_{\text{Liq}}^0$</th>
<th>$\Delta H_{\text{vap}}^0$</th>
<th>$\Delta S_{\text{vap}}^0$</th>
<th>$\Delta T^c$</th>
<th>$n^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (Hexadecanoic) acid</td>
<td>(6.8±1.8) x 10^{-7}</td>
<td>180±10</td>
<td>389±36</td>
<td>(7.6±2) x 10^{-5}</td>
<td>126±10</td>
<td>229±34</td>
<td>3</td>
<td>52 - 62</td>
</tr>
<tr>
<td>Azelaic (Nonanedioic) acid</td>
<td>(7±2.8) x 10^{-8}</td>
<td>153±6</td>
<td>279±18</td>
<td>(1.2±0.4) x 10^{-5}</td>
<td>120±6</td>
<td>193±18</td>
<td>4</td>
<td>48 - 67</td>
</tr>
<tr>
<td>Oleic (Octadecenoic) acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(2±1) x 10^{-6}</td>
<td>135±8</td>
<td>247±24</td>
<td>5</td>
<td>38 - 54</td>
</tr>
</tbody>
</table>

$a$The second number shown for each compound is either measured by or calculated using the data given by Cappa et al. (2007; 2008a; 2008b)

$b$Number of experiments.

$c$Temperature range considered for the calculations. Note that palmitic and azelaic acids are solids at room temperature whereas oleic acid is a liquid.
Figure 2.1 Schematic of the micro-orifice volatilization impactor. Numbers 1-4 correspond to different pressure regions during operation, with region 1 approximately at ambient pressures (760 torr), region 3 at 647 torr and region 4 at 60 torr. This is a 100-nozzle jet impactor with D = 0.15 mm. TC – thermocouple.
**Figure 2.2** Products observed during the heterogeneous oxidation of Palmitic acid by OH radicals. Signal at an m/z corresponding to an organic acid with a molecular mass of 100 amu (dashed line) was only observed during impaction, suggesting it was entirely in the gas-phase. In contrast, signal at an m/z corresponding to an organic acid with a molecular mass of 270 amu (solid line) was only observed during volatilization after impaction, suggesting it was entirely in the particle phase.
Figure 2.3 An example of palmitic acid peak evolution. The baseline is the region shaded by ‣. The area under the curve shaded by □ is considered to be the actual signal from particle impaction and is integrated. Residual signal assumed to be from vapors that adsorbed on the inside walls of the impactor or on surfaces not directly in contact with the heater are shaded by ▪ and not considered for area calculation. This residual signal changes little between adjacent sampling and “blank” cycles. Dotted line represents the instrument status during an experiment.
Figure 2.4 Collection efficiency curves for oleic (∆) and palmitic (○) acid aerosol particles. The “+” indicates the estimated theoretical cut-point ($d_{50}$) for our impactor.
Figure 2.5 Typical mass-weighted size distributions of palmitic (squares) and oleic (circles) acid aerosol particles generated using homogeneous nucleation during MOVI-CIMS calibration experiments.
**Figure 2.6** Normalized peak areas as a function of organic acid mass deposited using a syringe (open symbols) and aerosol particle impaction (filled symbols) for palmitic, oleic, and azelaic acids. The lines are least-squares fits to the data.
Figure 2.7 (a) Azelaic acid (◊), Palmitic acid (○), and Oleic acid (Δ) mass spectral signals as a function of impaction surface (desorption) temperature, and (b) \( \ln(p^0) \) vs \( 1000/RT \) curves for the same acids. The solid lines indicate the region of the curve used for least squares regression.
Figure 2.8 Oleic acid decay as a function of ozone exposure for volume-weighted mean particle radius of 93 nm. Experimental data obtained using the MOVI-CIMS system are plotted as square root of the ratio OA/OA₀ (Δ) along with the model (dashed line) from Worsnop et al., (2002).
Figure 2.9 Major condensed-phase products observed during oleic acid ozonolysis using the MOVI-CIMS apparatus; 9-Oxoronanoic acid (○), nonanoic acid (□) and azelaic acid (△) plotted versus increasing ozone exposures.

3.1 Introduction

Particulate organic matter (POM) is ubiquitous in the Earth’s atmosphere containing hundreds of compounds (Goldstein and Galbally, 2007). Recent results have shown that POM forms a large fraction of the aerosol mass potentially altering regional and global radiation budgets along with adverse effects on human health and air quality (Jimenez et al., 2009). Therefore it is important to quantify its formation, transformation, and loss processes in the atmosphere.

Current estimates of POM are highly uncertain, especially because of a lack of our understanding of the formation mechanisms and composition. Recently, several new theoretical frameworks were proposed for primary and secondary OM (POA and SOA) formation and modeling (Donahue et al., 2006, 2011; Robinson et al., 2007; Jimenez et al., 2009; Pankow and Barsanti, 2009; Paulot et al., 2009; Heald et al., 2010a; Kroll et al., 2011; Ng et al., 2011), but observational constraints using real-time field measurements are needed before they can be implemented in models. For example, the volatility basis-set framework proposed by Donahue et al. (2006; 2011), iteratively models measured POM mass concentrations by moving organic mass from high-volatility bins to low-volatility bins. The critical shortcoming of this framework is that there is no chemical
information provided essentially making it impossible to estimate the formation mechanisms and mean-molecular weights of organic compounds formed. Therefore, to test such frameworks and constrain models there is a critical need for fast, real-time, gas and particle-phase molecular composition measurements (Farmer and Jimenez, 2010).

This chapter describes the coupling and characterization of the MOVI-CIMS technique described in chapter 2 to a high-resolution time-of-flight mass spectrometer (HTOFMS). The technique uses an improved design for the MOVI and couples it to a widely used HTOFMS yielding high sensitivity and selectivity, along with the ability to provide both gas and aerosol-phase POM measurements in field and chamber studies on an hourly timescale. Here the instrument configuration and performance characteristics are described in detail. Particular attention is given to issues affecting performance during the first field deployment. The instrument’s application for laboratory flow tube and environmental chamber studies are described in the next chapter.

3.2 TOFMS for POM analysis

The application of TOF analyzers for real-time study of POM composition is relatively new, but its advantages over the more traditional quadrupole mass spectrometry (QMS) based methods are many. QMS instruments are quite sufficient for some applications (especially for detecting a few known gas-phase species), but they have major limitations when chemically speciating POM. In particular, QMS suffers from a low duty cycle. Only single ions can be mass selected and detected, which greatly reduces the speed with which a matrix of compounds can be analyzed. To acquire a mass
spectrum from 50 – 500 amu in ~ 0.25 amu steps with good signal-to-noise would require ~ 3 minutes (1800 measurements with 10 ms counting period). For comparison, the timescale over which material volatilizes from the MOVI impactor surface (described in the next chapter) is typically less than 1-2 minutes, meaning that a 3-minute scan would not be able to fully speciate the pulse of volatilized material. In contrast, a TOFMS acquires a full mass spectrum limited only by the flight time of the slowest ion in the drift region, typically well less than 10 ms. Thus, a full spectrum can be acquired at >10 Hz, ideal for fast analysis of a complex matrix such as aerosol composition.

Another drawback of a QMS is its relatively low mass resolving power and low mass accuracy. Typically QMS are limited to a peak-width at half-maximum of ~ 0.5 amu leading to a mass resolving power (R) of 1000 at 500 amu. In addition, the mass accuracy of a QMS is typically > 100 ppm. This prevents elemental analysis of detected ions as multiple combinations of different elements can usually obtain molecular masses that are similar to within 0.5 amu. When speciating compounds for a matrix with unknown composition, the ability to determine the elemental composition of a measured ion is highly desirable. TOFMS instruments can achieve high mass resolving powers >4000 at 500 amu, and high mass accuracies (< 20 ppm), thereby allowing elemental analysis (DeCarlo et al. 2006).

The applicability of TOF analyzers for single particle as well as ensemble particle analysis has been demonstrated previously. Aerosol-TOFMS (ATOFMS), single particle laser ablation TOFMS (SPLAT), and particle analysis by laser mass spectroscopy (PALMS) are the three most common single particle instruments presently used in field
studies (Prather et al., 1994; Murphy and Thomson, 1995; Zelenyuk and Imre, 2005). Although they provide useful composition and mixing state information at the single particle level, these instruments use high energy lasers to desorb and ionize aerosol particles causing excessive fragmentation of organic compounds. Recent improvements in single particle instruments include the development of the photoionization aerosol mass spectrometry (PIAMS) which uses single photon ionization minimizing fragmentation of organic molecules (Oktem et al., 2004), and the use of variable energy desorption lasers in SPLAT allowing for information of aerosol processing (Vaden et al., 2010).

TOF analyzers have also been applied for ensemble particle analysis. In-situ analysis of POM using a TOFMS was first reported by Drewnick et al. (2005) who coupled an Aerodyne aerosol mass spectrometer (Aerodyne-AMS) to a TOFMS (Tofwerk AG, Switzerland) to get detailed single and ensemble particle spectra. This instrument was later developed into a high-resolution TOF-AMS which is now widely used for detection of non-refractory particle composition (DeCarlo et al., 2006). As mentioned previously, this instrument uses an EI source for ionization which completely fragments fragile organic molecules making identification and quantification of specific molecular species impossible. However, by determining the elemental composition of fragments the average oxidation state of carbon in the aerosol particles can be inferred (Aiken et al., 2008). Most recently, proton-transfer-reaction mass spectrometry (PTR-MS), a softer ionization scheme than EI, was coupled to a HTOFMS for POM analysis (Holzinger et al., 2010). Using this instrument they reported detecting un-oxidized and
oxidized organic compounds, inorganic compounds, and organonitrate and organosulfate compounds at a high altitude site.

The MOVI-CIMS technique is unique in that it provides (1) quantitative information for both gas and particle phase organic matter nearly simultaneously, (2) when combined with the fast acquisition and high-resolution capability of a HTOFMS, and the soft and selective ionization scheme, this technique can be used to probe mechanisms and product formation pathways by estimating the elemental composition of the POM compounds and finally (3) using the thermal desorption information from the MOVI volatility of the detected compounds can be estimated. These three key traits make the MOVI-CI-HTOFMS system unique and complementary to other techniques that are presently available for POM analysis.

The HTOF analyzer used here has been used previously (Ehn et al., 2010; Junninen et al., 2010) but this is the first study that couples a MOVI and chemical ionization to a HTOF analyzer.

3.2 Instrumentation

3.2.1 Modified MOVI

Design of the MOVI is described in detail in the chapter 2. Therefore, only key modifications are discussed here which were done to minimize the adsorption and thus loss of semi and low volatility compounds on to the MOVI surfaces. The first improvement was to decrease the total surface area of the manifold block compared to the previous design. The surface area is reduced by nearly 50% in the new design by
eliminating the circular region after the MOVI pinhole (see figure 2.1). In the new design the NW 40 flange is machined into the MOVI body and couples directly to the IMR region thus having a shorter residence time before ionization. Also, the new MOVI manifold design has 4, $\frac{1}{4}'' \times 1''$ slots for cartridge heaters to programmatically heat the block during the heating cycle. In addition, the manifold block is coated with an inert material (Inertium, AMCX Corp., PA).

The second improvement is the extension of the critical orifice into the ionization region compared to the previous design where the orifice was closer to the impaction surface (see figure 2.1). Having this extended orifice design has proven critical in increasing the sensitivity of the instrument likely due to better mixing between the ionizer flow and sample flow. Finally, the third improvement is the replacement of the stainless steel-brass impaction post by an all stainless steel post along with an inert coating (SilicoNert 2000, Restek Corp.) to avoid chemical interaction of organic compounds with the impaction surface. Figure 3.1 shows a schematic of the new MOVI design.

3.2.2 Chemical Ionization Scheme

Both negative and positive reagent ions are used to characterize the instrument. Acetate ion ($\text{CH}_3\text{C(O)}\text{O}^-$) measured at a mass-to-charge ration ($m/Q$) = 59 thomson (Th), which selectively ionizes acids, is used as a negative reagent ion (Veres et al., 2008; Roberts et al., 2010), whereas H$_3$O$^+$ (H$_2$O)$_n$ is used as the positive reagent ion. Ionization schemes using H$_3$O$^+$ are commonly referred to as proton transfer reaction-mass spectrometry.
(PTR-MS) which has been extensively used to detect volatile organic compounds (VOCs) in the atmosphere (de Gouw et al., 2003).

Bertram et al. (2011) use similar ionization region and ion guides and describe the \( \text{CH}_3\text{C(O)O}^- \) ion chemistry in detail. Briefly, \( \text{CH}_3\text{C(O)O}^- \) ions are generated by bubbling 10 sccm (standard cubic centimeters per minute) of ultra high purity (UHP) \( \text{N}_2 \) through acetic anhydride (Fisher Scientific, 99.9%). During initial characterization experiments it was noticed that exposing the reagent ion solution to ambient air added contamination that complicated the mass spectra. Therefore, the solution is placed in a 250ml, sealed stainless steel container. In addition, it was also noticed that any exposure of \( \text{CH}_3\text{C(O)O}^- \) to Teflon products (PFA tubing and PTFE tape) also added background peaks to the mass spectra arising from oxygenated fluorocarbons. To minimize these effects, stainless steel transfer lines and fittings are used from the \( \text{CH}_3\text{C(O)O}^- \) reservoir to the radioactive source.

The 10 sccm acetic anhydride flow is added into a 2.3 L min\(^{-1}\) \( \text{N}_2 \) flow. A stainless steel critical orifice upstream of a \(^{210}\) Po \( \alpha \)-particle radioactive source (NRD model 2021), limits the reagent mixed \( \text{N}_2 \) flow to 2.0 L min\(^{-1}\). In the IMR, 2.0 L min\(^{-1}\) sample flow mixes with reagent ions and ion-molecule reactions occur for approximately 10 ms. During most of the experiments described here the IMR is maintained at a temperature of 100 °C. In addition, the IMR is has an inert coating (SilicoNert 2000, Restek Corp.) to minimize interactions between semi and low volatility compounds with the walls.
There are multiple channels through which negative ion-molecule reactions can occur in the IMR. Two key reactions for the \( \text{CH}_3\text{C(O)O}^- \) ion are

\[
\text{CH}_3\text{C(O)O}^- + \text{RC(O)OH} \rightarrow \text{CH}_3\text{C(O)OH} \cdot \text{RC(O)O}^- \quad \text{(R4a)}
\]

\[
\text{CH}_3\text{C(O)OH} \cdot \text{RC(O)O}^- \rightarrow \text{CH}_3\text{C(O)O}^- + \text{RC(O)OH} \quad \text{(R4b)}
\]

\[
\text{CH}_3\text{C(O)O}^- + \text{RC(O)OH} \rightarrow \text{CH}_3\text{C(O)OH} + \text{RC(O)O}^- \quad \text{(R5)}
\]

Although, proton abstraction is reported to be the dominant and expected reaction (Veres et al., 2008), ion association has also been observed during preliminary testing. For the experimental conditions used here (67 torr IMR pressure) ion association (R4a) is the dominant reaction (Bertram et al., 2011) followed by the reverse of reaction R4a (R4b) in the collision dissociation chamber to yield primarily declustered carboxylate anion products in the TOFMS.

\( \text{H}_3\text{O}^+ \) is the most common positive ion presently used for real-time \textit{in-situ} detection of VOCs. This ionization method works by donating a proton to a compound that has a proton affinity greater than that of \( \text{H}_2\text{O} \), which is the case for most VOCs, the main exception being alkanes.

\[
\text{H}^+ (\text{H}_2\text{O})_n + \text{R} \rightarrow \text{RH}^+ + (\text{H}_2\text{O})_{n-1} \quad (n = 1, 2, 3...) \quad \text{(R6)}
\]

Therefore, this ionization scheme is very general, resulting in a more congested mass spectrum. Until recently, most PTR-MS instruments were quadrupole-based where only few known masses were monitored. Holzinger et al. (2010) recently coupled a HTOFMS to a \( \text{H}_3\text{O}^+ \) source to detect various functional groups in POM. Using the high resolution and high mass accuracy offered by the HTOFMS, they were able to detect numerous
oxygenated organic compounds along with various organonitrate and organosulfate compounds even though the typical sensitivity of the instrument to single ions is substantially lower (by $\sim 20x$) than the quadrupole-based versions.

$\text{H}_3\text{O}^+$ ions were generated by flowing 2.0 L min$^{-1}$ wet $\text{N}_2$ through the $^{210}\text{Po}$ radioactive source maintained at 50 V relative to the ground. Wet $\text{N}_2$ flow was generated by bubbling 2.3 L min$^{-1}$ $\text{N}_2$ through 18M$\Omega$ milliQ water reservoir maintained at room temperature. A critical orifice controlled the $^{210}\text{Po}$ flow with the excess flow being vented out. $\text{H}_3\text{O}^+$ ions are commonly generated using hollow-cathode discharge in water vapor (de Gouw et al., 2003), but for testing and characterization purposes our simpler set up was adequate. For the experimental conditions mentioned above, the most abundant ion observed was $\text{H}^+.\text{(H}_2\text{O})_2$ with the nest dominant peak being $\text{H}^+.\text{(H}_2\text{O})_3$. Similar reagent ion distributions were also observed by other researchers, although they used lower ionization region pressures (25 and 40 torr) (Hearn and Smith, 2004; Renbaum and Smith, 2011) and the use of CDC in our instrument clearly alters the detected distribution from the actual distribution present in the IMR. In the CI-HTOFMS the $\text{H}^+.\text{(H}_2\text{O})_2$ count rates observed were typically 0.9 - 1 x $10^6$ counts s$^{-1}$.

3.2.3 HTOF-MS

The resulting product ions are focused through a 500 $\mu$m orifice biased at -40 V relative to ground into a collisional dissociation chamber (CDC) maintained at 2.1 torr using a fine throttle valve and a scroll pump (BOC Edwards). The clustered product ions collide with bathe gas in the CDC region while being guided by potential difference
applied across an RF-only quadrupole ion-guide. These collisions dissociate the ion-molecule clusters formed in the IMR. As a result, the \( CH_3COOH \cdot RC(O)O^- \) cluster is dissociated leaving the deprotonated acid (\( RC(O)O^- \)). The deprotonated acid anions or the protonated cations (in the case of positive ion chemistry) are then guided into three differentially-pumped chambers through a 1mm orifice biased to 3 V relative to ground. The first stage is maintained at a pressure of \( 1.4 \times 10^{-2} \) torr and another RF-only quadrupole further focuses the ion beam. The second chamber is separated by a 3 mm orifice and is at a pressure of \( 1.2 \times 10^{-5} \) torr and contains an ion lens assembly to maintain the ion path into the TOF region. Finally, the last section contains the ion extraction assembly and the TOF drift tube maintained at \( 7 \times 10^{-7} \) torr. Figure 3.2 shows a schematic of the instrument assembly.

The HTOF analyzer used here is manufactured by Tofwerk AG (Thun, Switzerland) and is called an orthogonal acceleration (oa)-TOFMS because the ion generation and ion acceleration (in the drift region) are at an angle of 90°. This type of design is well suited for continuous ionization sources because the ion beam can be filled simultaneously while ions, that where pulsed in the previous extraction cycle, travel the drift tube to the detector, increasing the sensitivity of the instrument (Guilhaus et al., 2000). It consists of four main components: (1) the ion extraction and pulsing assembly, (2) the TOF drift tube, (3) a reflectron, and (4) the multiple channel plate (MCP) detector. The TOF can be configured to monitor either positive or negative ions, and in two different modes, V and W, each letter corresponding to a path followed by ions in the
drift region (single reflection vs. double reflection) with drift lengths of 1.3 m and 2.9 m, respectively (DeCarlo et al., 2006). In V-mode, once the ions reach the reflectron they are deflected towards the MCP detector essentially traversing the drift tube twice. In W-mode, the ions traverse the drift tube 4 times before being detected by the MCP.

Initially, the ion beam is allowed to fill 5 to 10% (Guilhaus et al., 2000) of the extraction region before pulsing an electrode plate that pushes the ions into the drift region. The repetition rate of the pulser is tunable, the choice being determined by the operating mode, V or W, and balance between ion detection duty cycle and desired mass range. Most of experiments were conducted in V-mode, for which the pulser frequency was typically 40 μs (25 kHz) resulting in an m/Q range of 5 – 523 Th.

The mass resolving power (R) of an instrument is the ratio of the nominal mass (m/z) to the full-width at half-maximum (FWHM) of the fitted Gaussian peak for that particular m/Q.

\[
R = \frac{m}{\Delta m} \tag{3.1}
\]

In a TOFMS, with increasing path length, resolution increases but lateral broadening of the ions also increases, resulting in a loss of signal. Thus, W-mode has a higher resolution but V-mode has a higher sensitivity (DeCarlo et al., 2006). Figure 3.3 shows the R of the CI-HTOFMS as a function of m/Q using the \( \text{CH}_3\text{C(O)O}^- \) ion. At m/Q ratios greater than 250 Th, R reaches a maximum value of 5000 Th Th\(^{-1}\) in V-mode and 7300 Th Th\(^{-1}\) in W-mode. For comparison, R for quadrupole, compact-TOF, V-mode TOF, and W-mode TOF-AMS instruments are also plotted (DeCarlo et al., 2006). The higher values of R for
the CI-HTOFMS are due to a less energetic ion beam compared to the electron-impact ionization in the AMS. The W-mode resolution does not show significant gains in resolving power at this point, since the voltage tuning for this mode is only preliminary and needs more work. Using a similar Tofwerk H-TOFMS but with different pressure stages and ion optics before the extraction and drift regions, Jordan et al. (2009) report a mass resolution of 6300 Th Th^{-1} in the V-mode with H_3O^+ as the reagent ion.

The mass accuracy of the instrument is calculated using the peak center for which the most probable elemental composition and thus the exact mass can be calculated. Peak centers were determined using a custom peak fitting algorithm in Matlab 2006 (Mathworks, Boston, MA) followed by elemental composition search for each peak using an online molecular formula finder tool (www.ChemCalc.org). Figure 3.4 shows the V-mode mass accuracy for various m/Q’s determined with the procedure mentioned above. The mass spectra features were obtained by oxidizing α-pinene with OH radicals in a continuous flow chamber. The oxidation results in several well-known major carboxylic acids products. Most of the data lies within 20 ppm which is the manufacturer reported accuracy for the HTOF analyzer. Future experiments to determine the accuracy in W-mode will be undertaken.

Recently, Junninen et al. (2010) and Ehn et al. (2010) used similar ion guide and HTOFMS setup to detect atmospheric ions. The key differences between the CI-HTOFMS instrument and the one used by them are; (1) the CI-HTOFMS uses a MOVI for gas and particle composition measurements compared to their instrument which just has an orifice to pull in ambient air at 0.8 L min^{-1} (2) the CI-HTOFMS instrument has a
chemical ionization region maintained at low pressure (67 torr) whereas their setup does not have any ionization regions and their inlet is at atmospheric pressure, and finally (3) the electric fields and pressures throughout the two instruments are different.

3.2.4 Data Acquisition

Tofwerk’s TofDaq software controls the TOF timing, data acquisition, and data storage. This software is written in Labview 9 (National Instruments, Austin, TX) and runs on dual-core PC (Dell Precision, R5400 Rack Workstation). An 8-bit analog-to-digital converter (ADC) card (Acqiris, AP240, PCI module, Agilent, Geneva, Switzerland) is used to record the signals generated by the MCP detector at a 1GSample s⁻¹ rate. The ADC contains two channels. The first channel is used to record most of the signals which are amplified by a factor of 11. The second channel records only the portion of the signal that is above the full scale of the first one. This extends the dynamic range of the ADC by not only recording the large reagent ion signals but also the low intensity signals (Bertram et al., 2011).

The data are saved as hierarchical data format version 5 (HDF 5) files (HDF group, Champaign, IL) in two different forms; (1) raw mass spectra having units of accumulated signal intensity and (2) integrated “peak data” for user defined regions centered on nominal masses. The raw data is later mass calibrated and used for exact mass analysis and peak area calculations, whereas peak data can be used for quick viewing for data gaps and errors. Data processing is done using Tofwerk’s custom analysis software written in IGOR (Wavemetrics Inc, Lake Oswego, OR).
Most of the peak areas presented here are from unit mass resolution (UMR) data. The high-resolution analysis part of the software has only recently been developed by Tofwerk and needs extensive testing. Our group developed a custom peak fitting routine in Matlab 2006 (Mathworks, Boston, MA) to determine the peak center, peak height, and peak area and is used for estimating the exact mass and thus elemental composition of the mass spectral features.

3.3 Instrument Characterization

3.3.1 Sensitivity

*Gas-phase sensitivity using CH$_3$C(O)O*

The sensitivity of the instrument to gas-phase acids was evaluated using formic acid and acetate anions as the reagent ion. Dilute concentration of formic acid were produced by flowing 10 sccm of N$_2$ over a calibrated permeation tube (Kin-Tek, SRT2, 21.6 ng min$^{-1}$) maintained at 50 °C and contained in an insulated aluminum block. Formic acid concentration was varied by increasing or decreasing the flow used to overflow the inlet of the MOVI. The instrument response is measured at 45 Th. The measured acid signal is normalized by multiplying by the ratio of the reagent ion signal measured without formic acid to the signal when formic acid is present. Using the normalized counts to varying concentrations, the sensitivity of CI-HTOFMS to formic acid is 3 counts s$^{-1}$ pptv$^{-1}$. This is an order of magnitude lower than that expected from formic acid calibrations on a compact TOF (c-TOF) analyzer (Bertram et al., 2011).
Therefore, series of experiments were conducted to identify the various loss processes that might be leading to lower formic acid sensitivity. Formic acid is known to be lost in tubing and on surfaces. Therefore, the MOVI manifold block was heated to 150 °C, to minimize the adsorption of formic acid on its walls, resulting in a factor of 3 increase in sensitivity to 9 counts s\(^{-1}\) pptv\(^{-1}\). Similar sensitivity was also observed when the MOVI was replaced with a straight inlet (gas-phase inlet). With the present MOVI design it is not possible to thermally isolate the manifold block and the collection post, making it difficult to keep the post at ambient temperature for aerosol collection. Future MOVI design will eliminate this issue thereby allowing a factor of 3 gain in formic acid sensitivity.

The second factor leading to the difference in sensitivity between c-TOF and the HTOF is the instruments extraction frequency. Recent experiments (by Tim Bertram and not shown here) showed that the sensitivity increases linearly with the extraction frequency of the TOF analyzer and that the difference in extraction frequencies of the c-TOF (operating at 75 kHz) and the HTOF (25kHz) can account for another factor of 3 loss in sensitivity. This will approximately increase the 9 counts s\(^{-1}\) pptv\(^{-1}\) to 27 counts s\(^{-1}\) pptv\(^{-1}\) thereby accounting for most of the discrepancy between the c-TOF and the HTOF. It has to be noted that, the reason for operating the HTOF at a lower extraction frequency is to be able to measure a larger mass range (upto 500 Da).

Finally, using a new \(^{210}\)Po ionization source (half-life of 6 months) and a new multi-channel plate detector (MCP) will further improve the sensitivity of the instrument.
The ionization source used here for these formic acid calibration experiments is about 5 months old and the MCP is more than 1.5 years.

**Particle-phase sensitivity using CH$_3$C(O)O$^-$**

The CI-HTOFMS sensitivity for condensed phase OA was measured using two different methods similar to that described in the previous chapter. In the first, submicron polydisperse aerosols were generated using a commercial constant output atomizer (TSI 3076). A dilute methanol solution containing approximately 0.12, 0.11, and 0.11 mM of Tricarballylic acid (TA, C$_6$H$_8$O$_6$), Azelaic acid (AA, C$_9$H$_{16}$O$_4$) and Palmitic acid (PA, C$_{16}$H$_{32}$O$_2$), respectively was used as the calibration mixture. The reasons for choosing these acids was to investigate the ionization efficiency and instrument response to compounds that differed in carbon chain length, number of carboxylic acid functionalities, and volatility.

Before impaction, the aerosol particles were dried in a glass flow tube (2.5 L) heated to 54 °C and having a dilution N$_2$ flow of approximately 11 L min$^{-1}$. A differential mobility analyzer along with a condensation particle counter (GRIMM Technologies, Inc.) was used to measure the size distributions at the end of the drying tube. The outlet from this tube was connected to a 3-way, ½” OD, stainless steel manual valve which allowed to aerosol flow to be directed to either the MOVI or via a bypass to a vent. To minimize loss of aerosol particles in the transfer lines, only ½” OD stainless steel and silicon conductive tubing was used for particle transfer. To change the collected mass, the sample collection time was varied from 5 to 180 s while keeping the mass concentration
constant. The volume weighted mean diameter $d_p = 0.12 \mu m$ and the geometric mean standard deviation $\sigma_g = 2.8$. Assuming an average density of $1.23 \text{ g cm}^{-3}$, the average mass concentration was calculated to be approximately $31 \mu g \text{ m}^{-3}$. The density of TA was assumed to be equal to that of citric acid ($1.665 \text{ g cm}^{-3}$).

Mass collected on the impaction surface was calculated by correcting for the impactor collection efficiency using the PA data given in Figure 2.4 rather than the oleic acid data given that the mixed aerosol particles are more likely amorphous solids rather than liquids. In addition, we assume the components in the aerosol particles have the same mole fraction as the atomizer solution. After collecting the aerosol particles, the sampled mass is desorbed into dry $N_2$ before ionization using $\text{CH}_3\text{C(O)O}^-$ ions and detection by the HTOFMS.

In the second method, a known volume of ethanol (Mallinckrodt chemicals) containing TA, AA and PA is deposited on the collection surface using a microliter syringe. The solution concentration was 61, 60, and 63 µM for TA, AA and PA, respectively. Ethanol is allowed to evaporate into a dry $N_2$ flow before desorbing the deposited acid and detecting the ion signal with the HTOFMS. For both the methods described above, the measured acid signal is normalized by multiplying the ratio of the reagent ion signal at the start of desorption cycle to the reagent ion signal during each time step. The normalized acid signal is then integrated to get the total area under the resulting thermogram desorption peak (counts).

The instrument response to each acid was determined by integrating the detected ion signal at the corresponding deprotonated m/Q to UMR. For the acids used here the
corresponding carboxylate anions appear in the mass spectrum at 175 Th, 187 Th, and 255 Th for TA, AA, and PA, respectively. For all these acids minimal signal was observed at the m/Q corresponding to a cluster with CH$_3$C(O)O$^-$ ion. One noticeable peak, which scaled with the deposited TA mass, was observed at 157 Th. High resolution analysis of this peak had an exact m/Q that corresponded to the dehydrated TA. At present, it is not known if the dehydration is happening in the solvent, during thermal vaporization, or during the ionization process. This could also be a contamination present in the sample received from the vendor but since a large fraction of total TA signal (40 – 98%) is from 157 Th suggests that it is in fact a dehydrated product of TA. Further tests are needed to more conclusively determine its source. For the purpose of the sensitivity calculation it is assumed that it is a dehydration product of TA formed in the instrument during desorption and ionization and therefore the signal at this peak is added to the signal measured at 175 Th to get the total TA signal.

The data is shown in three different figures, each corresponding to a different acid. Figures 3.5a, b and c show the normalized PA, AA, and TA signal (total counts) during impaction and syringe deposition versus deposited mass in nanograms (ng). A linear increase in ion signal is observed with increasing mass deposited for the range studied. For PA and AA the instrument response is higher for syringe deposition compared to impaction for the same amount of acid mass. This difference in signal for syringe deposition and impaction is in fact consistent with that observed earlier (shown in figure 2.6) and some of it can be accounted for by loss of mass due to particle bounce on the impaction surface, which was estimated to be 35%. The difference observed here is
60% and therefore cannot be completely explained only by a reduction in collection efficiency due to particle bounce. Uncertainty in calibration concentrations and SMPS measurement is calculated to be 5%. Therefore the possible reasons for this difference could be either due to increased bounce (compared to the figure 2.6) or lower particle collection efficiency than that estimated from the measured size distribution. Given that these tests and others required dismantling and reconstructing the MOVI, a shift in collection efficiency is likely a primary contributor to the remaining discrepancy between syringe and impaction data shown here.

The calibration for TA is shown in Figure 3.5c and shows an opposite behavior to that observed for PA and AA. Although the normalized signal has a linear trend, for the same mass deposited the signal from impaction experiments is slightly higher than that for syringe deposition. This could be a combination of some matrix effect, since the solvents for syringe deposition and impaction are different (ethanol compared to methanol), and the assumption that 157 Th is a dehydration product of TA.

The sensitivity to each acid is the slope of the linear least squares line shown in Figures 3.5 a, b, and c and listed in Table 3.1 for PA, AA, and TA from syringe deposition and impaction experiments. For PA, sensitivity was calculated to be 24000±900 counts ng⁻¹ and 8300 ± 300 counts ng⁻¹ from syringe deposition an impaction experiments, respectively. Similarly, for AA and TA the sensitivity was calculated to be 62000 ± 4000 counts ng⁻¹ and 26000 ± 900 counts ng⁻¹, and 53000 ± 4000 counts ng⁻¹ and 76000 ± 3000 counts ng⁻¹, respectively. For TA, if we only consider the signal at 175 Th, then the sensitivity during syringe deposition decreases by an order of magnitude to 500
± 150 counts ng\(^{-1}\) and during impaction experiments decreases by 60% to 32000 ± 3000 counts ng\(^{-1}\).

Interestingly a factor of 3 increase in sensitivity is observed for each additional acid group added to the carbon chain during the impaction experiments. This increase is also observed in the syringe deposition experiments for PA and AA but not for TA. Unlike iodide ion chemistry (discussed in chapter 2) which has similar sensitivity towards mono and di-acids (shown in Figure 2.6), the sensitivity obtained using CH\(_3\)C(O)O\(^-\) ion chemistry appears to increase with increasing carboxylic acid functionalities. Since gas-phase acidities for these acids are presently not available, we hypothesize that the increase in sensitivity is due to the increase in CH\(_3\)C(O)O\(^-\) ionization probability as the acid groups increase. This conclusion could be confirmed either by testing more acids or by modeling the ion-molecule reaction thermodynamics and kinetics.

*Particle-phase sensitivity using H\(_3\)O\(^+\)*

The sensitivity of the CI-HTOFMS to condensed phase compounds was also measured using H\(_3\)O\(^+\) ionization. The H\(_3\)O\(^+\) ionization scheme as implemented in the current CI-HTOFMS needs extensive is not optimal for several reasons, but most importantly the higher pressure IMR leads to decreased proton transfer efficiency due to extensive clustering of the H\(_3\)O\(^+\) reagent ion with water molecules. Nevertheless, these calibration experiments were done to get a rough estimation of the detection capability for oxygenated VOCs at the operating conditions of the IMR and CDC. Calibrations were performed using the syringe deposition method only. Similar to the experiments
described above, a series of 7 different oxygenated organic compounds, with varying carbon chain, along with 2 alkanes were tested. Table 3.2 lists the compounds, their chemical formulae, and their concentrations used in these experiments. The average H⁺.(H₂O)₂ ion count rate was approximately 9.5 x 10⁵ counts s⁻¹ and the compounds are detected as a protonated cluster at [M+H]⁺, where M is the parent molecule.

Although alkanes are added to the calibration mixture, it has been shown that H₃O⁺ is not a suitable chemical ionization reagent for alkanes (Arnold et al., 1998). Examination of the CI-HTOFMS mass spectra confirmed this expectation. In addition, it is well established that proton transfer reactions with alcohols leads to dehydration resulting in a product ion at [M+H-18]⁺ (Spanel and Smith, 1997). For the two mono-alcohols tested, 2-Decanol and 2-Dodecanol, there were no peaks observed either at the protonated m/Q or the dehydrated m/Q. This could be a result of low sensitivity for these compounds. On the other hand, 1,12-Dodecanediol and (3R,6R)-3,6-Octanediol, which have two alcohols groups, had measurable signal at the protonated m/Q of 203 Th and 147 Th. In fact, 1,12-Dodecanediol was the most sensitive of all the oxygenated VOCs tested as shown in Figure 3.6a. The dehydrated product of 1,12-Dodecanediol at 185 Th, has the same exact mass as one of the ketones tested, 2-Dodecanone, complicating the analysis. Since 2-Decanone, a C₁₀ ketone and having 2 carbons less than 2-Dodecanone, did not show any linearity with increasing mass, it is assumed that a peak that appears at 185 Th is in fact the dehydrated product of 1,12-Dodecanediol. The m/Q corresponding to 5-hydroxy-2-pentone had a large background in the instrument and therefore the
calibration for this compound did not show any linearity, similar to the mono-alcohols and ketones.

The ability to detect organic acids with $\text{H}_3\text{O}^+$ ion chemistry was also tested. The calibration mixture of PA, AA, and TA and the analysis method was similar to that used for tests involving the $\text{CH}_3\text{C(O)O}^-$ reagent ion. The main reaction pathway for carboxylic acids with the $\text{H}_3\text{O}^+$ ion is through proton transfer but a small fraction (10%, under low pressures in a PTR-MS instrument) can lead to dehydration forming an acylium ion ($\text{RCO}^+$) (Hartungen et al., 2004). For the experimental conditions under which these calibrations were conducted, there were no peaks at the dehydrated m/Q’s corresponding to the above compounds. Therefore, the acid peaks were measured at the protonated m/Qs of 257 Th, 189 Th, and 177 Th for PA, AA, and TA, respectively.

The resulting normalized thermogram peak areas for PA, AA, and TA as a function of the deposited mass are shown in Figure 3.6b. For all three acids the peak areas are linear but the normalized signal for AA is an order of magnitude higher than PA and TA for the same mass deposited. Table 3.2 lists the CI-HTOFMS sensitivity using $\text{H}_3\text{O}^+$ ion for 1,12-Dodecanediol, (3R,6R)-3,6-Octanediol, PA, AA, and TA. Sensitivities for 1,12-Dodecanediol and AA are similar and is observed to be approximately 29000 ± 600 counts ng$^{-1}$. Sensitivity for (3R,6R)-3,6-Octanediol is a factor of 2.5 lower, 12000 ± 800 counts ng$^{-1}$, whereas that for PA and TA is an order of magnitude lower than 1,12-Dodecanediol, 2000 ± 80 counts ng$^{-1}$ and 2300 ± 200 counts ng$^{-1}$ for PA and TA, respectively.
3.3.2 Precision, Accuracy, and Detection Limit

To estimate the precision of the method, replicate calibration experiments were performed for the three organic acids using the syringe deposition method. The error bars in figures 3.5a, b, and c represent the 1σ uncertainty calculated from three replicate peak areas. Assuming the uncertainty in calibration mixture preparation and syringe deposition to be less than 5%, the relative measurement precision for PA, AA, and TA is calculated to be 8, 16, and 19%, respectively.

Accuracy was calculated using the procedure explained in section 2.2.3 and using Eq (2.1) and (2.2). As above, data from syringe deposition method is used here. For an average signal of $9.65 \times 10^5$, $1.67 \times 10^6$, and $1.37 \times 10^6$ counts, corresponding to a mass of 40.5 ng, 28.4ng, and 26.9ng, we report an accuracy of 8 % 14, and 21% for PA, AA, and TA respectively.

Detection limit of the CI-HTOFMS instrument for organic acids using the $\text{CH}_3\text{C(O)O}^-$ ion is calculated using the uncertainty in the signal peak areas ($\sigma_{\text{sample peak area}}$), which is the precision mentioned above, and uncertainty in the blank heating peak areas ($\sigma_{\text{blank peak area}}$) which is calculated to be 719, 1828, and 13726 counts for PA, AA, and TA, respectively. The signal-to-noise ratio can be expressed as

$$\frac{S}{N} = \frac{C_f M}{\sqrt{(\sigma_{\text{sample peak area}} C_f M)^2 + (\sigma_{\text{blank peak area}})^2}} \quad \text{Eq (3.2)}$$

Where $C_f$ is the sensitivity calculated in the previous section and $M$ is the organic acid mass (ng). Using a signal-to-noise ratio of 3 in Eq (3.2), for the syringe deposition method, we calculate a detection limit of 90 pg, 100 pg, and 0.95 ng for PA, AA, and TA,
respectively. Assuming the same uncertainty in sample peak areas for impaction method as for syringe deposition, the detection limits are 270 pg, 240 pg, and 0.65 ng. Since the uncertainties for sample peaks areas are presently not well known for H$_3$O$^+$ reagent ion, we did not calculate the detection limits for the positive-ion mode.

3.4 Performance during First Field Deployment

The CI-HTOFMS with the MOVI inlet was deployed to a ground based field site in Pasadena, CA, about 10 km northeast of downtown Los Angeles as part of the CalNex-2010 field campaign. Research at the nexus of air quality and climate change (CalNex-2010) was a major field campaign during summer 2010 (June 15$^{\text{th}}$ – July 15$^{\text{th}}$) to understand the gas and aerosol-phase pollution in and off the coast of California. This field campaign was used as a test of the field-deployable capabilities of the instrument and its performance under continuous operation using acetate as the reagent ion to detect gas and aerosol-phase organic acids.

The sampling and thermal desorption scheme was as follows. The instrument periodically sampled ambient air with the MOVI body maintained at 50 °C to minimize adsorption of semi-volatile compounds onto the walls. Each sampling period was followed by a thermal desorption cycle that consisted of ramping the body and the post separately for a total of 3.8 min. During the first minute, the body temperature was ramped from 50 °C to 125 °C. This allowed the volatilization of the condensed material on the walls of the MOVI. In the second minute, while the body temperature increased to 150 °C, the post temperature was also rapidly increased to 150 °C. In the third minute,
while the body temperature was held constant at 150 °C, the post temperature was increased 200 °C. And finally, in the last step (0.8 min), the post temperature reached 250 °C. After the thermal desorption cycle, the MOVI was allowed to cool for 10 min while sampling dry UHP N₂. N₂ was used to avoid any contamination on the post and the MOVI walls during the cooling cycle. The cooling cycle was followed by another thermal desorption cycle, similar to the one describe above but without any ambient sample, used as a “heating blank” to determine the background peaks at different temperatures. After the heating blank the MOVI cooled for another 10 minutes, and the above described sequence of sampling-heating-cooling was restarted. The complete sequence was repeated either every 53 min or 68 min, depending on the sampling cycle duration.

Figure 3.7 displays an example of the data collected during a thermal desorption cycle. Figure 3.7a shows the total aerosol organic acid signal as a function of desorption time. Reagent ion signal, known background peaks (Teflon peaks), and inorganic acid signals were subtracted from the total signal to obtain an estimate of total organic acid signal. The organic acid signal follows the post temperature until 150 °C and then decreases even though the post temperature keeps increasing, suggesting complete volatilization from the collection surface. Figure 3.7b is an average mass spectrum from region 3 showing the complexity of OA as indicated by numerous mass peaks. An expanded view of one of the peaks is shown in Figure 3.7c, demonstrating the instrument’s ability to resolve and accurately identify specific peaks. Efforts are
underway to analyze the gas and particle-phase data and compare the observed features to changes in photochemistry and meteorology.

Although there were time periods during which the instrument operated well, numerous issues of concern arose with (1) the chemical ionization scheme and (2) the thermal desorption sequence leading to large background concentrations and (3) the heater design. Below I describe these issues in detail.

One of the major issues during CalNex was the high concentration of nitrate in ambient aerosol. During the thermal desorption cycle, the aerosol nitrate volatilizes off the collection post as HNO₃ which reacts with CH₃C(O)O' resulting in NO₃⁻ ions. Due to the high concentrations of aerosol nitrate (4 – 8 µg m⁻³ but some times as high as 12 µg m⁻³), most of the reagent ion was titrated resulting in significant loss in sensitivity and instrument detection limit for organic acids. In addition, the presence of high counts of NO₃⁻ ions (6 x 10⁵ - 1x 10⁶ counts s⁻¹) complicates the mass spectrum since NO₃⁻ ions cluster with organic acids (Viidanoj et al., 1998). Also, the partitioning of gas-phase HNO₃ on the MOVI walls was another issue that was expected prior to deployment. Because of the sticky nature of this acid, there was a significant amount of background signal at 62 Th corresponding to the NO₃⁻ ion. The MOVI was intermittently (once every day) held at 200 °C for over an hour in an effort to minimize this background signal. Although this helped, the background signal would slowly build up over the course of several sample-heating cycles.

In addition to the large background signal at 62 Th, there were other background signals that affected the instrument performance. The main reason for the build-up of
background signals was due to the fact that the body was only heated to 150 °C compared to the post, which was heated to 250 °C. The hypothesis is that some of the organic material that desorbed from the post above 150 °C would adsorb on to the walls of the MOVI body and desorb during blank heating cycles. This produced blank peaks areas that were a significant portion of the actual sample peak areas resulting in lower organic acid signal. The primary limitation for the maximum temperature that the MOVI body can be heated to is the polymer clamp that couples the MOVI to the IMR. This polymer clamp is used to electrically isolate the MOVI from the IMR.

Finally, the third major issue faced during the campaign was the heater design. The ¼” OD cartridge heaters used for post heating were failing very often leading to a significant instrument downtime. It was later discovered that the main reasons for this high failure rate was the rapid heating employed during the thermal desorption step along with the temperature measurement position which had a potential for incorrect measurement at times. Recent improvements to the design appear to have solved the issues of gas and particle partitioning to the MOVI body as well as the heater failure rate. However, acetate ion chemistry will remain of limited use in regions with high particulate nitrate.

3.5 Summary
The MOVI-CI system designed at UW was successfully coupled to a high-resolution TOFMS. The new MOVI design incorporates various improvements that minimize the condensation of semi-volatiles on the inside walls. The CI-HTOFMS has high mass
resolving powers. At m/Q’s above 250 Th, the mass resolving power obtained in V and W-modes is 4700 Th Th\(^{-1}\) and 7300 Th Th\(^{-1}\), respectively. High mass resolving power along with mass accuracies below 20 ppm and selective ionization allow for reasonably robust estimates of the exact mass of the detected compounds and thus their elemental composition.

The instrument sensitivity was tested with CH\(_3\)C(O)O\(^-\) and H\(_3\)O\(^+\) reagent ions in negative and positive-ion modes, respectively. Both, syringe deposition and impaction methods were used to measure the sensitivity of Palmitic, Azelaic and Tricarballylic acids in the negative ion mode. A linear increase in ion signal is observed with increasing deposited acid mass for the range studied. For Palmitic and Azelaic acids the instrument response is higher for syringe deposition compared to impaction for the same amount of acid mass. This difference in signal for syringe deposition and impaction is consistent with that observed earlier (shown in figure 2.6) and is likely caused by particle bounce on the impaction surface. Instrument sensitivity was also measured using various low vapor pressure oxygenated organic compounds. Out of a fairly limited suite of available test compounds, diols and Azelaic acid had high enough sensitivity to be detected for the ng deposited on the post. Detection of other standards that were available was compromised either by inherent background signals at the product ion m/Q or perhaps by lower sensitivity. Future experiments with monodisperse aerosol, such as those described in chapter 2 will need to be repeated to maintain a high degree of certainty about the overall instrument sensitivity to aerosol components.
Replicate measurements and consideration of sources of error in the calibration method led to relative precision and accuracy values for PA, AA, and TA of 8, 16, and 19%, and 8, 14, and 21%, respectively. Detection limit of the CI-HTOFMS instrument for organic acids using the CH$_3$C(O)O$^-$ ion and syringe deposition method is calculated to be 90 pg, 100 pg, and 0.95 ng for PA, AA, and TA, respectively. Assuming the same uncertainty in sample peak areas for impaction as for syringe deposition, the detection limits for PA, AA, and TA, are 270 pg, 240 pg, and 0.65 ng, respectively.

The prototype instrument was deployed to the Pasadena ground site during CalNex-2010 field campaign and helped us understand some of the important issues regarding background signals and the chemical ionization scheme employed. Acetate ion has been the reagent ion used so far but future field experiments will require either a combination (ion switching) or a different reagent ion in environments where significant nitrate (or chloride) is expected to be present.
Table 3.1 Organic acids used for CI-HTOFMS calibration and their measured sensitivities using the CH$_3$(O)O$^-$ ion and syringe deposition and impaction methods.

<table>
<thead>
<tr>
<th>Compound</th>
<th>formula</th>
<th>N$^1$</th>
<th>Sensitivty Syringe dep (counts ng$^{-1}$)</th>
<th>Sensitivity Impaction (counts ng$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (Heaxadecanoic) acid</td>
<td>C$<em>{16}$H$</em>{32}$O$_2$</td>
<td>1</td>
<td>24000 ± 900</td>
<td>8300 ± 300</td>
</tr>
<tr>
<td>Azelaic (Nonanedioic) acid</td>
<td>C$<em>9$H$</em>{16}$O$_4$</td>
<td>2</td>
<td>62000 ± 4000</td>
<td>26000 ± 900</td>
</tr>
<tr>
<td>Tricarballylic (Propane-1,2,3-tricarboxylic) acid</td>
<td>C$_6$H$_8$O$_6$</td>
<td>3</td>
<td>53000 ± 4000</td>
<td>76000 ± 3000</td>
</tr>
</tbody>
</table>

$^1$Number of carboxylic acid functional groups

$^2$Sensitivity using only signal at 175 Th
Table 3.2 Compounds used to calibrate CI-HTOFMS with H$_3$O$^+$ reagent ion and syringe deposition method

<table>
<thead>
<tr>
<th>Compound</th>
<th>formula</th>
<th>M wt. (g mol$^{-1}$)</th>
<th>Conc (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Decanol</td>
<td>CH$_3$(CH$_2$)$_7$CH(OH)CH$_3$</td>
<td>158.28</td>
<td>4.2</td>
</tr>
<tr>
<td>2-Decanone</td>
<td>CH$_3$(CH$_2$)$_7$C(O)CH$_3$</td>
<td>156.27</td>
<td>4.8</td>
</tr>
<tr>
<td>2-Dodecanol</td>
<td>CH$_3$(CH$_2$)$_9$CH(OH)CH$_3$</td>
<td>186.33</td>
<td>4.0</td>
</tr>
<tr>
<td>2-Dodecanone</td>
<td>CH$_3$(CH$_2$)$_9$C(O)CH$_3$</td>
<td>184.32</td>
<td>4.0</td>
</tr>
<tr>
<td>1,12-Dodecanediol</td>
<td>HO(CH$<em>2$)$</em>{12}$OH</td>
<td>202.33</td>
<td>3.8</td>
</tr>
<tr>
<td>(3R,6R)-3,6-Octanediol</td>
<td>C$<em>8$H$</em>{18}$O$_2$</td>
<td>146.23</td>
<td>4.5</td>
</tr>
<tr>
<td>5-hydroxy-2-pentanone</td>
<td>C$<em>4$H$</em>{10}$O$_2$</td>
<td>102.13</td>
<td>4.9</td>
</tr>
<tr>
<td>Dodecane</td>
<td>C$<em>{12}$H$</em>{26}$</td>
<td>170.33</td>
<td>4.4</td>
</tr>
<tr>
<td>Cyclododecane</td>
<td>C$<em>{12}$H$</em>{24}$</td>
<td>168.32</td>
<td>5.2</td>
</tr>
</tbody>
</table>
**Table 3.3** Sensitivity for oxygenated organic compounds from syringe deposition method using $\text{H}_3\text{O}^+$ ion

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sensitivity (counts ng$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,12-Dodecanediol</td>
<td>29000 ± 600</td>
</tr>
<tr>
<td>(3R,6R)-3,6-Octanediol</td>
<td>12000 ± 800</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>2000 ± 80</td>
</tr>
<tr>
<td>Azelaic acid</td>
<td>29000 ± 1600</td>
</tr>
<tr>
<td>Tricarballylic acid</td>
<td>2300 ± 200</td>
</tr>
</tbody>
</table>
Figure 3.1 Schematic of the modified MOVI. Different numbers correspond to different pressure regions.
Figure 3.2 Schematic of the CI-HOTFMS instrument.
Figure 3.3 Mass resolving power of the CI-HTOFMS instrument in V and W-modes.
Figure 3.4 Mass accuracy of the CI-HTOFMS in V-mode.
**Figure 3.5** Normalized peaks area for (a) Palmitic acid, (b) Azelaic acid, and (c) Tricarballylic acid obtained using CH$_3$C(O)O$^-$ ion. Open symbols are data from syringe deposition and closed symbols are data from impaction method. Lines are the linear least squares fit to the data. Note the change in y-axis for each figure.
Figure 3.6 Normalized peak areas for (a) diols and (b) carboxylic acids from syringe deposition method using H$_3$O$^+$ ion. Lines are the linear least squares fit to the data. Note the change in x and y-axes scales.
Figure 3.7 Data from CI-HTOFMS collected in Los Angeles, CA. (a) Total organic acid signal in ambient aerosol during a thermal desorption cycle, (b) Average mass spectrum from region 3 indicating various organic acids detected in aerosol-phase, and (c) close-up view of a mass peak at 255 Th (on the left) and its isotope (on the right).
4. Laboratory Studies of Secondary Organic Aerosol Formation

This chapter describes results obtained during two different studies. These tests were conducted to assess the capabilities of the technique in characterizing atmospheric aerosol composition by sampling SOA generated in controlled experiments by oxidation of (1) α-pinene in a flow-through chamber and (2) photo-oxidation of alkanes in a large environmental chamber. The three key instrument features that I wanted to test were (1) the ability to differentiate between gas and particle-phase products, (2) quantification and the ability to estimate the elemental composition, and finally (3) the ability to separate the products based on their volatility.

Below I describe the experimental conditions and results of α-pinene oxidation by ozone and OH radicals in section 4.1 and preliminary analysis of alkane photo-oxidation experiments that were recently conducted at Caltech in section 4.2.

4.1 Biogenic VOC oxidation

4.1.1 Introduction

Biogenic volatile organic compounds (BVOCs) are an important source of secondary organic aerosol mass (Kanakidou et al., 2005; Goldstein et al., 2009). BVOCs are amongst the most reactive organic compounds released into the atmosphere and enhance tropospheric O₃ production rates on regional and global scales (Chameides, 1988; Atkinson, 1998; Fuentes et al., 2000; Dreyfus, 2002). Recent observations have revealed
that the forest environment can have high oxidant levels (hydroxyl radical, [OH] ~ 1x10^7 molecules cm^{-3}) and produce highly reactive unidentified BVOCs (Kurpius and Goldstein, 2003; Di Carlo et al., 2004; Holzinger et al., 2005; Choi et al., 2010). The impact of such rapid photochemistry in a forest canopy on the atmospheric composition and SOA formation is a subject of intense research (Karl et al., 2009; Paulot et al., 2009; Choi et al., 2010). Advancing our understanding of the relationship between aerosol particles and climate requires high-quality, measurement-based constraints on SOA formation and gas-phase BVOC oxidation products.

A myriad of BVOCs are emitted by land vegetation and ocean bioata during photosynthesis or as a result of stress or damage (Fuentes et al., 2000). The most prevalent and reactive species include isoprene, monoterpenes such as α- and β- pinene, and sesquiterpenes. Natural biogenic emissions are thought to produce more atmospheric reactive carbon mass than biomass burning or anthropogenic activities (Halliquist et al., 2009), and studies have shown that forests can be an important source of climatically active aerosols through the growth of newly formed particles from BVOC oxidation (Tunved, 2006). The challenge to understanding the contribution of BVOC to aerosol mass is evident when considering that the oxidation of monoterpenes or sesquiterpenes, both expected to be significant contributors to SOA, yield multiple highly functionalized products from each oxidation of a precursor (Hallquist et al., 1999). In addition, isoprene, which was previously not considered as an SOA precursor has been identified to produce an array of products that can partition into particle phase (Claeys et al., 2004; Carlton et al., 2006; Henze and Seinfeld, 2006; Paulot et al., 2009).
In order to understand the formation and partitioning of hundreds of BVOC oxidation products in the real atmosphere, it is imperative that we start with a simple system where known precursors are oxidized under controlled conditions. Therefore, \( \alpha \)-pinene \((\text{C}_10\text{H}_{16})\) is used as a model system to understand the oxidation products and their formation pathways when exposed to Ozone \((\text{O}_3)\) and OH radicals. The main reasons for choosing \( \alpha \)-pinene are that it is considered to be a major biogenic SOA precursor, it is highly reactive towards \( \text{O}_3 \) and OH radicals, and previous studies have elucidated several reaction products from its ozonolysis and OH oxidation (Winterhalter, 2003; Camredon et al., 2010).

The experiments described here were conducted in two different flow-through chambers (1) an entrained aerosol flow reactor and (2) the potential aerosol mass (PAM) chamber. \( \text{CH}_3\text{C(O)}\text{O}^- \) was used as the reagent ion during these experiments to detect gas and particle-phase acids.

4.1.2 Experimental Section

*Entrained Aerosol Flow Reactor*

The entrained aerosol flow reactor used here is similar to that used previously in this lab and described in detail by Bertram et al. (2009). Briefly, the flow reactor is a 90 cm long, 15 cm ID stainless steel tube with 5 cm deep aluminum caps on both ends. The caps have ports with Swagelok fittings to introduce effluent flows tangential to flow direction. The interior walls of the flow reactor and the caps are coated with halocarbon wax (Series...
1500 inert wax, Halocarbon Products Corp., River Edge, NJ) to minimize particle wall losses and wall interactions. Outside of the flow reactor is wrapped in 1” polyethylene foam to minimize effects due to fluctuations in room temperature. For a flow of 2 L min$^{-1}$, the residence time in the flow reactor is calculated to be 8 min.

Hydrocarbon (α-pinene, 98% Arcos organics) flow is generated by bubbling 5 sccm of UHP N$_2$ through α-pinene filled glass flask maintained at – 40 to -45 °C using a cold finger (Thermo Scientific Instruments). The temperature was decreased to minimize the vapor pressure of α-pinene and thus produce small concentration mixture. Ozone was produced using photolysis of dry O$_2$ in the presence of N$_2$ in a cell containing 185 nm Hg pen-ray lamp (UVP). Ozone was monitored using a Dasibi Environmental Corp. commercial ozone monitor and was measured to be 900 ± 70 ppb. For OH oxidation experiments, OH radicals were produced in the flow reactor by photolysis of O$_3$ at 254 nm in the presence of water vapor. Dry N$_2$ was added at the outlet of the flow reactor to match the reaction mixture flow to the sample flow rates of the MOVI (10 L min$^{-1}$). Relative humidity (RH) in the flow tube was measured before the dilution flow and aerosol particle concentrations were measured after the dilution flow. A stainless steel 3-way, ½” stainless steel valve was used to control the flow from the flow reactor to the MOVI while LabView 9.0 (NI instruments) was used to automate the sample and desorption cycles. All the tubing from the flow reactor to the MOVI was either ½” OD copper or stainless steel to minimize particle losses during transfer. No seed particles were used during these experiments.
Three different experiments were conducted using the flow reactor (1) Ozonolysis under dry conditions (2) OH radical oxidation at an RH of 7 % and (3) OH radical oxidation at an RH of 46%. The goal was to see the differences in product distribution using different oxidants and different RH conditions.

**Potential Aerosol Mass Chamber**

The PAM chamber is a recently developed concept for estimating the maximum aerosol mass that a precursor gas or mixture of gases can produce when exposed to an oxidant for a fixed processing time (Kang et al., 2007). PAM chamber is similar to the flow reactor described above. The chamber is a cylinder made of stainless steel with a volume of 16 L and maintained at atmospheric pressure. Two, 254 nm lamps are placed in a quartz tube, on either ends of the inside walls to produce OH radicals in the presence of O₃ and water vapor.

A series of experiments were conducted using the PAM chamber by changing a) the HTOF analyzer scanning mode between low (V) and high (W) resolution, b) the OH concentration in the PAM chamber while keeping the initial α-pinene concentration constant, c) the initial α-pinene concentration while keeping the OH concentration constant, and d) the mass range from 490 to 778 Th (for only for one particular set of PAM chamber conditions). Apart from these, initial baseline experiments were also performed where either only O₃ was present in the PAM chamber. Coincident
measurements were also taken with an Aerodyne HTOF-AMS, a scanning mobility particle sizer (TSI Inc) and an O₃ detector.

Described here are results from only one experiment during which α-pinene concentration was 196 ppb, OH was $5.4 \times 10^8$ molec cm$^{-3}$, and the reaction time inside the PAM chamber was 287 s resulting in an atmospheric equivalent OH processing time of 1.8 days (assuming the 24hr average OH concentration in the atmosphere of $1 \times 10^6$ molec cm$^{-3}$). The resulting particle mass concentration eluting from the PAM chamber after dilution into the MOVI sample flow was 22 μg m$^{-3}$ (using a density of 1 g cm$^{-3}$). The sample collection time was 30 min yielding approximately 1.7μg of particulate mass collected on the impaction surface. The MOVI thermal desorption rate during this experiment was approximately 8.3 °C s$^{-1}$ and the data acquisition rate was 10 Hz.

4.1.3 Results and Discussion

Below I describe the results from three different oxidation experiments (1) ozonolysis (2) low OH and (3) high OH. The analysis performed here is preliminary with several assumptions that warrant further testing; chief among them is the applicability of the instrument sensitivity for gas and particle-phase acids. In the previous chapter it was shown that the sensitivity of the instrument to carboxylic acids is dependent on the number of acids groups on the carbon chain. Therefore, the using the sensitivity of a single acid or an average of two or more acids, leads to large errors in calculated mass
fractions. Nonetheless, this exercise was useful in understanding the issues involved in quantification of the measured signals.

The total SOA mass collected, assuming a density of 1.4 g cm$^{-3}$ and spherical particles, during the $\alpha$-pinene oxidation by O$_3$ and OH radical experiments is given in Table 4.1. Also listed in the table are the total particle-phase organic acid mass concentrations calculated from the CI-HTOFMS data using sensitivity equal to of Azelaic acid Palmitic acid. For these calculations, impaction collection efficiency equal to that of solid aerosol-particles is used. The signals were normalized to changes in mass concentrations between the three experiments. In addition, blank peak areas have been subtracted to remove the background signals. Also shown in the table is the fraction of total SOA mass that can be accounted for my carboxylic acids.

The SOA mass produced was generally lower during OH oxidation experiments compared to the ozonolysis experiment by 20 - 30%. On the other hand, the total organic acid signal calculated from the CI-HTOFMS signals was higher during OH oxidation. From the organic acid mass calculated using the two different sensitivity numbers and the total SOA mass produced, it can be concluded that the sensitivity that should be used to convert the signals to mass concentrations is in between the Azelaic and Palmitic acid sensitivities. In addition, the organic acid mass calculated is also within the range estimate by other studies for organic acid fraction. Yu et al. (1999) estimated that the major ozonolysis products, such as pinic and norpinic acid, pinonic and norponinic acid, and hydroxypinonic acid, account for 73% of the total aerosol mass formed. In our ozonolysis experiment, the particle phase organic acid mass is estimated to be 7.5 and
24% using Azelaic and Palmitic acid sensitivities, respectively. This difference could be because of the difference in the experimental conditions and the oxidant and hydrocarbon concentrations between our study and theirs. For the high RH experiments, the organic acid mass fraction is much higher indicating a higher degree of oxidation.

As mentioned previously, one of the potential advantages of MOVI over other techniques is that the technique can obtain both gas and particulate-phase data simultaneously on short timescale. Figure 4.1 shows mass spectra obtained from ozonolysis of α-pinene during the particle sampling and gas-phase detection portion (a) and the particle-phase detection portion (b). Formic acid sensitivity is applied to convert the gas-phase signals to mass concentration and an average of the sensitivities of Palmitic and Azelaic acids is used for the particle-phase signals. In Figure 4.1a, the biggest peak observed is that of formic acid at 45 Th. This is the smallest gas-phase organic acid formed due to C-C bond breakage. Other major products are also observed in gas-phase but are much lower compared to formic acid suggesting there is little gas-phase abundance of carboxylic acids in the high mass range (> 200 Th), or if they exist, they have rapidly partitioned to the walls and impactor surface at ambient temperature. Partitioning to the walls seems unreasonable given the prompt evolution of the signals for these ions with impactor surface heating, whereas the walls of the impactor body heat much more slowly.

In contrast, Figure 4.1b shows the mass spectrum during desorption (particle-phase). Below m/Q 200 we see similar peaks as observed during sampling but with much higher intensity when desorbing. This suggests that most of these compounds are semi-
volatile that partitioned into particle phase. In contrast, most of the peaks above m/Q 200 are mainly observed during desorption suggesting that these are low volatility products that had more fully partitioned into particle-phase. Some of the notable peaks that correspond to products reported by other studies include Norpinonic acid at 169 Th, Norpinic acid at 171 Th, Pinonic acid at 183 Th, and hydroxy-pinonic acid at 199 Th.

Figures 4.2 a, b and 4.3 a, b correspond to OH oxidation experiments at an RH of 7 (low) and 46 % (high). The general mass spectral features are similar to that observed in Figures 4.1 a and b but with much higher gas-phase formic acid concentration. In fact, formic acid signal increases with increasing OH concentration suggesting the importance of bond scission pathway compared to isomerization. Also noticeable is the decrease in 169 Th (Norpinonic acid) and increase in 183 Th (Pinonic acid) between the ozonolysis and OH oxidation reactions. To highlight the difference in the products formed between the three experiments, a section of the mass spectrum is shown in Figure 4.4. The signals are normalized relative to 183 Th. Although, similar products are formed during ozonolysis and OH oxidation, we can clearly see the increase in the signal intensity for some of the peaks whereas others decrease with increasing OH. Significant yields of OH are produced during terpene ozonolysis (Atkinson and Arey, 1998), and since we did not use any OH scavenger during these experiments there is a possibility that some of the α-pinene is reacting with the OH radicals formed during the ozonolysis reactions. This probably explains some of the similarity in the peaks in Figure 4.4.

The ability to estimate the volatility of either a single or a group of compounds, in near real-time, is one of the major advantages that the MOVI-CI-HTOFMS provides.
Figure 4.5 shows an example of this uniqueness. The figure shows mass spectral signals as a function of the desorption temperature (mass thermogram) for major α-pinene ozonolysis products that have various functionalities. For example, cis-Pinonic acid (C_{10}H_{16}O_{3}) is a monocarboxylic acid, and thus has a high vapor pressure and desorbs earlier compared to cis-Pinic acid (C_{9}H_{14}O_{4}) which is a dicarboxylic acid and therefore has a vapor pressure that is 4 order of magnitude lower than cis-Pinonic acid, resulting in its desorption at higher temperature. Interesting feature to note is the double peak structure for 155 Th, 183 Th and somewhat for 169 Th. This is second peak, occurring at a higher temperature, is probably due to the thermal degradation of oligomeric compounds into respective monomers.

**Oligomerization**

Oligomerization is the process in which two or more monomer molecules (smaller molecular weight compounds) combine to form a larger molecular weight compound. One of the key implications of this process is that it can convert volatile compounds, present in gas-phase, to low-volatility compounds that can condensed into particle-phase and increase aerosol particle mass. Oligomerization is also hypothesized to happen through heterogeneous and multiphase reactions in the presence of acids (Jang et al. 2002). Acid-catalyzed reactions such as hydration, hemiacetal/acetal formation, polymerization, and aldol condensation of carbonyls have been reported in aerosol phase, not completely explained by condensation and thermodynamic theories (Jang et al. 2002).
Several studies have observed oligomers during oxidation of monoterpenes in environmental chambers and in ambient fine-mode aerosol-particles (Tolocka et al. 2004; Kalberer et al., 2006; Reinhardt et al., 2007; Gao et al., 2010), but the analytical instruments so far used for their detection are laboratory based techniques such as UPLC-ESI-MS and MALDI-TOFMS. In contrast, MOVI-CI-HTOFMS can detect oligomers in near real-time due to the high-sensitivity and low-fragmentation offered by CI. Figure 4.6 shows the oligomers observed with the MOVI-CI-HTOFMS during a α-pinene ozonolysis experiment. The mass spectral evolution in divided into four different desorption temperatures bins to show the shifting patterns of the peaks probably related to their functionality. The ability to detect oligomeric compounds in the field is one of the major advantages that the MOVI-CI-HTOFMS provides over the other presently available analytical techniques.

4.2 Oxidation of Alkanes by OH radicals

Alkanes are estimated to constitute about a third to half of VOC emissions in urban areas (Lurmann and Main, 1992; Calvert et al., 2008). Major sources are motor vehicle exhaust, and evaporation of liquid fuels and spirits (Calvert et al., 2008). Their reactivity with OH· radicals is lower than that of alkenes and aromatics (Atkinson and Arey, 2003). Therefore, alkanes are important O₃ precursors on a regional scale rather than in urban centers (Calvert et al., 2008). Although their importance in O₃ formation is now known, there have been only few studies to understand their SOA forming potential. Therefore, a series of oxidation experiments were conducted during February and March 2011, in the
Caltech environmental chambers with linear, branched, and cyclic alkanes. Experiments were conducted with low and high-NO_x conditions, low OA mass concentrations and oxidation time scales of 18 and 36 hours. This chapter describes preliminary results from two of these experiments; OH· radical oxidation of Cyclododecane (CDD, C_{12}H_{24}) under (1) high-NO_x conditions for 18 hr and (2) in low-NO_x conditions for 18 hr.

4.2.1 Alkane Oxidation Mechanisms and Products

Reaction pathways and products for various linear, branched and cyclic alkanes have recently been investigated due to their potential as SOA precursors (Lim and Ziemann, 2005, 2009a, 2009b, 2009c; Presto et al., 2009; 2010). Figures 4.7 and 4.8 show the general reaction mechanism for gas-phase alkane oxidation in high and low-NO_x conditions, respectively. The first step in the OH· radical oxidation of an alkane proceeds via a secondary hydrogen (H) atom abstraction to form an alkyl radical, R·. Under atmospheric conditions, the alkyl radical reacts with O_2 to form an alkylperoxy radical, RO_2·. The RO_2· radical has multiple pathways through which it can be lost. Under high-NO_x conditions, the RO_2· radicals predominantly react with NO to form NO_2 and an alkoxy radical, RO', or an alkynitrate (AN), RONO_2. The alkoxy radical can (1) decompose to form a pair of carbonyl and alkyl radicals, which then follow the same steps as above, (2) react with O_2 to form a carbonyl, or (3) isomerize through a (1,4) H-shift to form a δ-hydroxyalkyl radical. The δ-hydroxyalkyl radical then follows the above steps to form other first-generation products. For example, in a polluted atmosphere with significant amounts of NO_x, the corresponding δ-hydroxyalkylperoxy radical can form...
either a 1,4-hydroxynitrate (1,4-HN) or a 1,4-hydroxycarbonyl (1,4-HC). It has been shown in previous studies that the 1,4-HC is one of the major products formed during oxidation of linear C5–C8 alkanes in the presence of NO with a yield of 49 ± 19% (Reisen et al., 2005), and 35 ± 8% (Atkinson et al., 2008).

In low-NOx environments, the reaction pathways and some of the products formed are different. At sufficiently low NO concentrations, RO₂⁻ radicals react instead with (1) hydroperoxyl radicals, HO₂⁻, to form organic hydroperoxides, (2) other RO₂⁻ radicals to form a carbonyl and an alcohol, or an RO⁻ radical. The RO⁻ radical follows some of the steps described above for the high-NOx conditions to form a 1,4-HC, but can also form 1,4-Hydroxyhydroperoxides (1,4-HHP), or 1,4-diols (Russell et al., 2011). Atkinson et al. (2008) observed similar 1,4-HC (5-hydroxy-2-pentanone, 5H2P) in the presence and absence of NO, but with the yield being an order of magnitude lower in the low-NOx case. Thus, in either high or low NOx conditions, the 1,4-HC will be a significant first-generation product, with some combination of 1,4-HN and 1,4-HHP making up the balance.

Once formed, the major product 1,4-HCs can quickly isomerize to cyclic hemiacetals (CHA) which then dehydrate to form dihydrofurans (DHF) on aerosol particles or environmental chamber walls (Dibble, 2007). Using a kinetic model, Lim and Ziemann (2009c) calculated efficient up-take of CHA onto aerosol particles. In addition, they also calculated a timescale of approximately 15 mins for conversion of CHA to DHF. Recent studies have shown that the dehydration of CHA to DHF is dependent on aerosol pH, water concentration, and carbon chain length (Holt et al., 2005; Atkinson et
al., 2008; Lim and Ziemann, 2009a, 2009c). DHFs formed from typical alkane oxidation products are likely volatile and thus evaporate from aerosol particles (Martin et al., 2002; Holt et al., 2005; Lim and Ziemann, 2009a). Because of their unsaturated moiety, DHFs react rapidly once in the gas-phase with OH and NO$_3$ radicals and O$_3$ in the same way as cyclic alkenes forming oxo-carboxylic acids (Russell et al., 2011).

Using 5H2P as a surrogate for 1,4-HCs and dry experimental conditions (<5% RH), Martin et al. (2002) calculated a time scale of 1.1 hr to completely convert 5H2P to 4,5-Dihydro-2-methylfuran which had a lifetime of 1.3 hr, 24 s, and 7 min against OH (10$^6$ molec cm$^{-3}$), NO$_3$ (2.5 x 10$^8$ molec cm$^{-3}$), and O$_3$ (7.2 x 10$^{11}$ molec cm$^{-3}$), respectively. Russell et al. (2011), using a 24-hr OH average of 1 x 10$^6$ molec cm$^{-3}$, calculated the lifetime for first-generation oxidation products of C$_{12}$ and C$_{25}$ alkanes to be 0.8 days and 0.4 days, respectively, and that for second-generation products of C$_{12}$ alkane is 1.6 days (2 lifetimes). The second-generation products formed from the oxidation of DHF thus have low enough vapor pressure to partition more strongly to aerosol particles thereby contributing to SOA (Lim and Ziemann, 2009a).

Secondary organic aerosol yields (ratio of the amount of organic mass formed to the amount of hydrocarbon reacted) of alkanes are higher than previously thought and therefore are now considered to be a significant source to OA mass in aerosol particles. Presto et al. (2010) calculated a yield of 0.51 for n-heptadecane (C$_{17}$) and also observed that, under high-NOx conditions, yields increase with increasing carbon number and organic mass. Other studies using n-pentadecane (C$_{15}$) and n-nonadecane (C$_{19}$) observed
similar results (Chacon-Madrid and Donahue, 2011). These studies suggest the importance of alkanes as precursors for radicals and SOA mass on a regional scale.

4.2.2 Experimental Section

Three different alkanes, CDD, 2-methylundecane, and dodecane were oxidized under low and high-NOx conditions to understand the SOA formation. To investigate the SOA formation of already oxidized VOCs rather than starting with an alkane, 5H2P and (3R,6R)3,6-Octanediol were also oxidized. Table 4.2 lists all the experiments and the chamber conditions. In this section I describe some initial results from CDD oxidation under high and low-NOx conditions.

Caltech Environmental Chamber

Experiments were performed at Caltech in two indoor, 28 m³ Teflon environmental chambers (Cocker et al., 2001; Keywood et al., 2004). The temperature and RH during these experiments were 20 ± 2 °C and <5%. Blacklights (4-foot, 400 Sylvania 350BL) with emission spectra peaking at 350 nm were used to irradiate the chambers. The two chambers were alternated between experiments; while one was used for an oxidation experiment the other was being flushed with zero air. Table 4.3 lists the instruments used during the experiments and the parameters monitored. OH radicals were generated by photolysis of (1) hydrogen peroxide (H₂O₂) during low-NOx experiments and (2) nitrous acid (HONO) during high-NOx experiments. Approximate OH radical concentrations averaged 3 x 10⁶ molec cm⁻³ over the course of the experiment for low-NOx experiments.
In the high-NO<sub>x</sub> experiments, OH concentrations peaked at 1 x 10<sup>7</sup> molec cm<sup>-3</sup> for the first two hours (personal communication, Christine Loza, Caltech). During high-NO<sub>x</sub> experiments, photolysis of HONO produced NO and NO<sub>2</sub> and additional NO was added so that the dominant loss process for the RO<sub>2</sub> radicals was through reaction with NO. Initial NO and NO<sub>2</sub> concentrations were 377 and 359 ppb, respectively. During low-NO<sub>x</sub> experiments, NO and NO<sub>2</sub> were below the detection limit (< 1 ppbv) of the instrument. Ozone concentrations in the chamber were below 5 ppb during the entire course of experiments. Initial CDD concentrations in the bag, as measured with Tenax TA sorption tubes and GC-FID analysis, were 10 ppb in all cases. Multiple Tenax tubes where collected during the course of the experiments to monitor losses of the hydrocarbon precursor.

Dry ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) seed aerosol were generated by atomizing 15 mM solution. Seed aerosol was present during all the experiments. Two TSI differential mobility analyzers along with condensation particle counters were used for number and size measurements. The number-weighted mean diameter of see particles was typically 70 nm. Both chambers were characterized for hydrocarbon and particle wall losses before the experiments (Loza et al., 2010) but the data presented here is not corrected for these losses. Experiments described here are #5 and #14 listed in Table 4.2. SOA mass concentrations are calculated from the SMPS data assuming spherical particles and a density of 1 g cm<sup>-3</sup>.

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For the experiments described here, only mass spectra obtained using H$_3$O$^+$ reagent ion are presented. We decided to use H$_3$O$^+$ chemistry rather than CH$_3$C(O)O$^-$ because (1) during high-NO$_x$ experiments large concentrations of gas-phase HNO$_3$ are formed in the chamber which efficiently reacts with CH$_3$C(O)O$^-$, resulting in substantial titration of the reagent ion and (2) preliminary analysis of other 18hr CDD oxidation experiments showed minimal carboxylic acid signal. For 36hr oxidation experiments CH$_3$COO$^-$ was used for the last 9 hr of the oxidation. The mass range for all the experiments was 5 – 523 Th. Average H$_3$O$^+$ reagent ion counts rates were 1 x 10$^6$ counts s$^{-1}$.

4.2.3 Results and Discussion

SOA Yields

As a first step I assess the differences in the high and low-NO$_x$ experiments by observing the SOA mass formed, changes in the particle size distribution and the evolution of SOA yields as a function of the experiment time. Figures 4.9a and b show the evolution of particle size distribution, SOA mass concentration, and the loss of the hydrocarbon during the entire 18hr experiments under high-NOx conditions. We can clearly see the rapid loss of CDD and corresponding growth in the SOA mass concentration within 1 hr of the chamber lights being turned on. The aerosol particles distribution also shows this dramatic change with increase in both number and size of the aerosol particles. The number mean diameter increases from 70 nm before the lights are turned on to 100 nm within 1 hr and increase up to 105 nm by the end of the experiment. The growth in SOA mass concentration reaches a maximum at 17 µg m$^{-3}$ after 2 hrs and then decreases over
for the rest of the experiment. CDD is rapidly lost within the first 2 hrs and reached approximately 2.5 ppb, which mirrors the increase in SOA mass concentration. After the first 2 hrs the SOA mass concentration decreases slowly and can be explained by the loss of oxidation products and aerosol particles to the chamber walls. The data presented here is not corrected for these losses and future analysis will include this correction.

Figures 4.10a and b are similar to the Figures 4.9a and b but correspond to the CDD oxidation experiment under low-NO\textsubscript{x} conditions. The evolution of particle distribution, SOA mass concentration and the loss of hydrocarbon are very different from the high-NO\textsubscript{x} experiment. Although the increase in particle diameter is same for the high and low-NO\textsubscript{x} conditions, 70 nm to 105 nm in 18 hrs, the change in particle distribution is much more gradual in low-NO\textsubscript{x} conditions compared to that in the high-NO\textsubscript{x}. Similar evolution is also seen in the SOA mass concentration shown in figure 4.10b. Hydrocarbon decreases from 10 ppb to 1 ppb and mirrors the increase in SOA mass concentration over the course of the experiment which reaches 12.5 µg m\textsuperscript{-3} by the end of 18 hrs. The differences in the OH concentration in the two experiments may contribute to observed profiles. OH concentration in high-NO\textsubscript{x} condition is a factor of 3 higher in the first 2 hrs of the experiment compared to that in the low-NO\textsubscript{x} case. Therefore, an appropriate way to analyze the data is by plotting on an OH exposure axis (OH x time, molec cm\textsuperscript{-3} s) and presently efforts are underway to better estimate the OH concentration during the high and low-NO\textsubscript{x} conditions.

Time series of SOA mass yields for both high and low-NO\textsubscript{x} conditions are shown in Figure 4.11. Under high-NO\textsubscript{x} conditions, the highest SOA yield is 0.4 after 2 hrs and
decreases to 0.3 at the end of the experiment. In contrast, the SOA yield under low-NO<sub>x</sub> conditions increases more slowly and reaches a lower yield by the end of the experiment. In experiments by Presto et al. (2005), under high-NO<sub>x</sub> conditions, the OH radical-initiated oxidation of linear alkanes yielded more oxygenated SOA, which generally has lower-volatility, subsequently condensing into particle-phase. Lim and Zeimann (2005) suggested that the higher flux through the alkoxy radical which favors isomerization over fragmentation leads to lower volatility products containing multiple functional groups such as hydroxycarbonyls and hydroxynitrates with the same number of C-atoms but increased oxygen content.

The SOA yield observed here for the C<sub>12</sub> cyclic alkane under high-NO<sub>x</sub> condition is lower than that observed by Lim and Ziemann (2009b), 0.8. This is probably due to the large amounts of organic mass produced in their experiments (more than 2 orders of magnitude compared to that observed here), and it is known that SOA yields increase with increasing organic mass due to increased product partitioning (Presto et al., 2010). Nevertheless, the results presented here and that of Lim and Ziemann (2009b) suggest that alkane oxidation can lead to high SOA yields.

**Mass spectra and time profiles**

We examine the mass spectra obtained in high and low-NO<sub>x</sub> experiments separately. Our goal is to assess whether the molecular speciation capabilities of the MOVI-CI-HTOFMS allow for insights into the oxidation mechanisms and partitioning of products over the course of several generation. As an initial approach to assessing the information yielded
by the CI-HTOFMS, I examine the gas and particle spectra broadly as a function of oxidation time, and then exam the evolution of individual ions to compare against the expected products that should be observed based on existing mechanisms under high and low-NO\textsubscript{x} conditions. As a first cut, the analysis is performed using mass spectra where ion signal has been binned and averaged to unit mass resolution. Analysis of high resolution spectra is ongoing and could be used to confirm final conclusions drawn from the unit mass resolution spectra.

\textit{High-NO\textsubscript{x} Spectra Interpretation}

I begin by examining the mass spectra obtained during “gas-phase sampling” mode in the high-NO\textsubscript{x} experiment. Based on the above mechanism, the spectra should evolve in time with first generation products being composed of hydroxycarbonyls and hydroxynitrates, and later generations should become more oxidized, perhaps increasing molecular weight depending on the balance between fragmentation and functionalization pathways.

Figures 4.12a-d shows the gas-phase mass spectra obtained during high-NO\textsubscript{x} experiments before (a), 1 hr after (b), 8 hrs after (c), and 16 hrs after (d) the lights were turned on in the chamber. Changes in the mass spectra, both in terms of signal intensity and m/Q detected appear with increasing oxidation timescale. The mass spectra before the lights were turned on show some background contamination in the chamber (each bag was flushed for 24 hr before an experiment), especially visible at masses below m/Q 100, and therefore should be subtracted from the other mass spectra to eliminate the background peaks. This subtraction will be performed during future analysis. A
significant increase in specific ion intensity, especially at 183 Th, and 197 Th, is observed just after 1 hr of oxidation. By 8 hrs of oxidation, products are observed across the whole spectrum. Very low signals are even detected up to 400 Th in “gas-phase” mode. In particular, two clusters of ion intensities at 297 - 315 Th and 371 - 385 Th illustrate a slow continuous buildup after 16 hr of oxidation, consistent with the appearance of second and third generation products as shown in the final figure 4.12d.

To investigate this time dependence further, I examine the evolution of the unit mass resolution signals at the m/Q’s that correspond to expected major products based on the reaction mechanism presented by and Ziemann (2009a). Chemical structures of some of these products are shown in Figure 4.13. For example, the signal at m/Q 183 Th likely corresponds to the carbonyl compound that forms from the reaction of the first-generation alkoxy radical (RO) with O₂. The signal at 181 Th is likely composed of a contribution from the corresponding dihydrofuran (DHF) and the cyclic hemiacetal (CHA). The CHA can dehydrate in the chamber (on aerosol or walls) to form the DHF (see above) which has the m/Q of 181 Th, or CHA can dehydrate under ionization by H₃O⁺ to give an ion with an equivalent m/Q as the DHF. Thus, we can think of the signal at 181 Th as a sum of DHF and its relative CHA. As shown in Figure 4.14, the signals at 181 and 183 Th dramatically increase in the first few hours of oxidation consistent with the expectation that these are major first-generation products. Also shown in Figure 4.14 are the signals at m/Q 199 Th and 213 Th, which I tentatively assign to the 1,4-HC or its CHA and the carbonylester, respectively. These first and second generation products are known to
partition to aerosol particles and their relatively low gas-phase signals throughout the experiment is consistent with a strong sink.

The reaction mechanism presented in Lim and Ziemann (2009a), and other alkane oxidation schemes, predict significant yields of alkyl nitrates during oxidation of these high carbon number alkanes. Following the above mechanism, I have assembled structures of the likely first and second generation alkyl nitrate products (Figure 4.15) and then examined the mass spectra to determine whether ions with m/Q consistent with these products are detected. The signal at 246 Th most likely corresponds to the 1,4-hydroxynitrate, a first generation product. Its temporal profile, shown in Figure 4.16 suggests that it is rapidly produced early in the experiment and achieves a steady state. Its profile suggests that it is a first-generation product with very slow losses after initial production. The signals at 260 Th, 276 Th, 291 Th, and 307 Th have m/Q consistent with the second generation mono and di-nitrates. Interestingly, these second generation products show a profile that is consistent with production and then subsequent loss, consistent with consumption of precursors followed by steady loss either to the aerosol or third generation gas-phase products.

As mentioned earlier, there is evidence for later generation gas-phase products being produced, though not necessarily from the second generation nitrates. The pairs of peaks at 297 - 315 Th and 371 - 385 Th were observed to be increasing in intensity with oxidation timescale and are shown in Figure 4.17. Although their structure or elemental composition is not yet known, their temporal profile relative to the other signals discussed above suggests that they are 3\textsuperscript{rd} or 4\textsuperscript{th} generation products.
Figure 4.18 shows an average mass spectrum for a heating cycle after 5 hr of oxidation. The data was binned into four different temperature bins based on the temperature at which they desorb, < 75 °C, 75 – 125 °C, 125 – 175 °C, and >175 °C and figure 4.18 shows the signals observed between 125 – 175 °C. The mass spectrum contains numerous peaks with the most intense signal at 183 Th. Clusters of peaks every 14 and 16 Th suggest the addition of –CH₂ group, N₂ and/or an O₂ molecule. A significant fraction of these could be organic nitrates formed by the addition of NO and NO₂ to the RO₂⁻ and RO⁻ radicals. Similar to Figures 4.14 and 4.16, unit mass resolution signals of the major products observed during CDD oxidation in high-NOₓ conditions, but in particle-phase, are shown in Figures 4.19 and 4.20.

The time evolution of 183 Th is similar in gas and particle-phases. It increases quickly after chamber lights are turned on and then slowly decreases over the entire experiments. In contrast, 181 Th increases slowly in the particle-phase, over the course of several hours, in contrast to that observed in gas-phase where it rapidly increases in the first few hours and then stabilizes. As mentioned previously, if we assume that 181 Th is a sum of DHF and its relative CHA signal, then the particle-phase evolution indicates a constant uptake of 1,4-HC onto aerosol-particles which then cyclizes to CHA, which stays in particle-phase. The difference in evolution in gas and particle-phase also indicates that either (1) the dehydration of CHA to DHF is slower than the production of CHA leading to an increase in 181 Th in particle-phase and/or (2) The loss processes (reaction with OH and wall loss) for DHF are higher in gas-phase than in the particle-phase. Future analysis is required to ascertain the possible causes of this evolution.
Figures 4.20 a and b shows the evolution of possible organonitrates (structures shown in Figure 4.15) for this alkane. The time evolution of these compounds in particle-phase is different than that observed in gas-phase (see Figure 4.16). This suggests that once the products are formed in gas-phase they are rapidly partitioned to aerosol-particles increasing their concentration in particle-phase.

Similar to Figures 4.12a-d, Figures 4.21a-d shows the mass spectral evolution during the low-NO\textsubscript{x} experiment. The spectra in Figure 4.21a show contamination in the gas-phase arising from the chamber walls or the MOVI surfaces. The evolution is different than that observed for the high-NO\textsubscript{x} experiment. We can clearly see the increase in lower m/Q products over the oxidation timescale. These products are probably either too volatile or semi-volatile resulting in the lower and slower SOA mass formation during this experiment. The main peak observed is 183 Th which is probably the carbonyl formed from RO· + O\textsubscript{2} reaction. We can also observe an increase in the higher m/Q signals, especially peaks at 297 - 315 Th and 371 - 385 Th, as observed during the high-NO\textsubscript{x} experiment.

Shown in Figure 4.22 are the 183 Th, 181 Th, 199 Th, and 213 Th signals, similar to that in Figure 4.14. The 183 Th profile is different than that observed during high-NO\textsubscript{x} experiment and also compared to the other m/Qs which show a much gradual increase over the course of the experiment. This profile is unexpected for a first generation product and infact is that of a second-generation products (Lim and Ziemann, 2009a). So, there is a possibility that the signal at 183 Th corresponds to a different product. Figure 4.23 shows a particle-phase mass spectrum from signals in the temperature bin 125 – 175
°C and obtained after 4 hr of oxidation. Comparing to figure 4.18 during the high-NO\textsubscript{x} condition, we observe higher intensity signals at lower m/Qs and also fewer higher m/Q peaks. These differences in mass spectra suggest that the reaction mechanisms are different in the presence and absence of NO\textsubscript{x} and that under high-NO\textsubscript{x} condition a higher percentage of low-volatility products are formed that partition into particle-phase compared to low-NO\textsubscript{x} conditions. Future analysis will focus on high-resolution data and also analyzing the particle-phase products to understand the reaction pathways.

4.3 Summary

Initial characterization of the MOVI-CI-HTOFMS instrument was conducted by sampling SOA generated from the oxidation of (1) α-pine in a flow-through chamber and (2) photo-oxidation of alkanes in a large environmental chamber. The aim of these experiments was to assess (1) the capability of the MOVI in differentiating between gas and particle-phase compounds, (2) the ability of the CI-HTOFMS system in detecting and resolving the hundreds of compounds formed in gas and particle-phases and (3) the usefulness of the thermal desorption in separating compounds based on their volatility.

During the first set of experiment, α-pine was oxidized in a flow through chamber by O\textsubscript{3} and two different OH radical concentrations. Using acetate as the reagent ion and the sensitivity of Azelaic acid, the total carboxylic acid mass fraction was calculated to be 8%, 50%, and 34% for ozone, low RH and high RH experiments, respectively. Formic acid was the dominant product observed in gas-phase and was the highest during high OH radical experiment. This is evident of the C-C bond cleavage
during oxidation resulting in volatile products. Numerous particle-phase carboxylic acid products were also observed, with the concentrations being highest during ozonolysis experiments. Oligomer formation was clearly observed during OH radical experiments. Being able to detect oligomers in the field using the MOVI-CI-HTOFMS will be a significant advantage in understanding their formation and composition.

The instrument was recently part of an environmental chamber study at Caltech to understand the products and SOA formation mechanisms from the oxidation of various alkanes. The experiments were conducted in high and low-NO\textsubscript{x} environments and for 18 and 36 hrs. Positive ion mode using H\textsubscript{3}O\textsuperscript{+} reagent ion was tested for the first time to detect numerous gas and particle-phase products. Preliminary analysis of the Cyclooctadecane oxidation experiments reveal interesting features and differences between reaction mechanism during high and low- NO\textsubscript{x} conditions. 1,4-hydroxycarbonyl along with several organic nitrates were observed in the high- NO\textsubscript{x} case with a clear difference in time evolution of gas and particle-phase profiles of various products. Further analysis is on-going to understand this mechanism and its importance as an SOA source in urban areas.
**Table 4.1** SOA mass collected on the MOVI post and the fraction of particle mass estimated to contain carboxylic acid functionalities using the sensitivities of Azelaic and Palmitic acids. Collection efficiency is assumed to be that of solid particles and particle density = 1.4 g cm$^{-3}$

<table>
<thead>
<tr>
<th></th>
<th>Total SOA mass sampled (ng)</th>
<th>Carboxylic acid mass using AA (ng)</th>
<th>Carboxylic acid mass using PA (ng)</th>
<th>Fraction of total mass AA vs. PA</th>
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<tbody>
<tr>
<td><strong>O$_3$</strong></td>
<td>940</td>
<td>75</td>
<td>240</td>
<td>0.08 – 0.26</td>
</tr>
<tr>
<td><strong>Low OH</strong></td>
<td>670</td>
<td>340</td>
<td>1100</td>
<td>0.5 – 1.6</td>
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<tr>
<td><strong>High OH</strong></td>
<td>760</td>
<td>260</td>
<td>820</td>
<td>0.34 – 1.08</td>
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Table 4.2 Hydrocarbons oxidized and experimental conditions for Caltech experiments

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Date</th>
<th>Hydrocarbon</th>
<th>Conc (ppb)</th>
<th>Exp time (hr)</th>
<th>NO\textsubscript{x} condition</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>02.18.2011</td>
<td>Cyclododecane</td>
<td>10</td>
<td>18</td>
<td>low</td>
<td></td>
</tr>
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<td>2</td>
<td>02.19.2011</td>
<td>Cyclododecane</td>
<td>10</td>
<td>18</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>02.20.2011</td>
<td>Cyclododecane</td>
<td>10</td>
<td>36</td>
<td>low</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>02.18.2011</td>
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<td>10</td>
<td>18</td>
<td>low</td>
<td>Repeat of #1</td>
</tr>
<tr>
<td>5</td>
<td>02.24.2011</td>
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<td>18</td>
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<td>Repeat of #2</td>
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<td>2-methylundecane</td>
<td>30</td>
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<td></td>
</tr>
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<td></td>
</tr>
<tr>
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<td>03.15.2011</td>
<td>(3R,6R)3,6-Octanediol</td>
<td>40</td>
<td>18</td>
<td>low</td>
<td></td>
</tr>
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<td>03.16.2011</td>
<td>Dodecane</td>
<td>40</td>
<td>18</td>
<td>low</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3 List of instruments used to monitor various parameters during alkane oxidation experiments at Caltech

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Parameter</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Licor 1800 portable spectroradiometer</td>
<td>Light spectrum 280-850 nm</td>
<td></td>
</tr>
<tr>
<td>Vaisala HMP 233 hygrometer</td>
<td>Temperature and RH</td>
<td></td>
</tr>
<tr>
<td>Dasibi Environmental</td>
<td>O₃</td>
<td></td>
</tr>
<tr>
<td>Thermo Environmental Instruments Model 42 chemiluminescent NOₓ analyzer</td>
<td>NO, NO₂</td>
<td></td>
</tr>
<tr>
<td>TSI differential mobility analyzer and condensation particle counter</td>
<td>Particle size distributions</td>
<td></td>
</tr>
<tr>
<td>(Model 3081 and 3760)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agilent 6890N GC-FID</td>
<td>VOC concentrations</td>
<td>Tenax TA sorption tubes</td>
</tr>
<tr>
<td>Aerodyne HR-AMS</td>
<td>Organic mass and elemental composition</td>
<td>Alternating between V and W modes</td>
</tr>
<tr>
<td>Chemical Ionization-Quadrupole MS/MS instrument</td>
<td>Peroxides, 1-4HCs and HNO₃</td>
<td>Using CF₂O⁻ as reagent ion. Alternating between negative and positive modes</td>
</tr>
<tr>
<td>MOVI-CI-HTOFMS</td>
<td>Gas and particle phase acids and/or oxygenated VOCs</td>
<td>Using CH₃C(O)O⁻ for low-NOₓ exps and H₂O⁺ for high-NOₓ exps</td>
</tr>
<tr>
<td>Filters for FTIR and UPLC/ESI-MS analysis</td>
<td>Elemental composition and functional groups</td>
<td>Sampled at the end of each experiment</td>
</tr>
</tbody>
</table>
Figure 4.1 Gas and particle phase mass spectra from ozonolysis of α-pinene in low-NO$_x$ conditions
Figure 4.2 Gas and particle-phase mass spectra from OH radical oxidation of α-pinene under low-NOx conditions at an RH of 7%.
Figure 4.3 Gas and particle-phase mass spectra from OH radical oxidation of α-pinene under low-NOx conditions at an RH of 43%
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Figure 4.7 OH radical initiated oxidation of alkanes in high-NO\textsubscript{x} conditions (adapted from Lim and Ziemann (2009a))
Figure 4.8 OH radical initial reaction of alkanes in low-NO$_x$ conditions (adapted from Molina et al. (2004))
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Figure 4.10 (a) Number size distributions and (b) SOA mass and hydrocarbon concentrations during the photo-oxidation of CDD under low-NOₓ conditions for 18 hr
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Figure 4.15 Possible structures of some of the organonitrate products detected during Cyclododecane oxidation by OH radicals under high-NOx conditions (adapted from Lim and Ziemann (2009a))
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**Figure 4.18** Average particle-phase mass spectrum from a heating cycle after 5 hr of Cyclododecane oxidation by OH-radicals under high-NO$_x$ conditions.
Figure 4.19 Particle-phase signals observed during Cyclododecane oxidation by OH radicals under high-NO\textsubscript{x} conditions. Possible structures are shown in Figure 4.13.
**Figure 4.20** Particle-phase organonitrate signals observed during Cyclododecane oxidation by OH radicals under high-NO\textsubscript{x} conditions. Possible structures are shown in Figure 4.15.
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Figure 4.22 Gas-phase signals observed during Cyclododecane oxidation by OH radicals under low-NO$_x$ conditions.
Figure 4.23 Particle-phase mass spectrum from a heating cycle after 4 hr of Cyclododecane oxidation by OH-radicals under low-NO\textsubscript{x} conditions.
5. Conclusions

Understanding the formation and evolution of organic aerosol (OA) in the atmosphere is important to understand the effect of aerosol particles on visibility, cloud formation, and human health. A critical need for this understanding is the availability of fast, and sensitive analytical techniques. Therefore, development of a sensitive and selective technique to identify the gas and particle-phase OA products has been a primary focus of this research. The primary result of my research is the development and characterization of a chemical-ionization, high resolution time-of-flight mass spectrometer (CI-HTOFMS) that is field-deployable and able to detect OA compounds with a 1-hr time resolution at ppt levels in gas-phase, and picograms in particle-phase.

Designing an aerosol collection inlet for the CI-MS instrument was the first project in this research. The inlet is an inertial impactor and is called the micro-orifice volatilization impactor (MOVI). Chapter 2 describes the design features and characterization of the MOVI coupled to a Quadrupole-based MS instrument. The impactor has 100 nozzles each 150 µm in diameter. At a flow rate of 10 L min⁻¹ the cut point diameter was calculated to be 130 nm. At this flow rate, the pressure drop across the nozzles is only 15%, thus keeping the semi-volatile compounds in the particle-phase.

The MOVI process has 3 steps: sample collection and gas-phase analysis, thermal desorption of collected aerosol material, and cooling. During the first step, sample air with aerosols is forced through nozzles and impacted on a flat place, called the impactor plate. Due to inertia, larger particles are collected on the plate whereas smaller particles
follow the streamlines. Simultaneously, portion of the gas is analyzed for gas-phase products. In the second step, the sample air is replaced with dry N\textsubscript{2} flowing at 2 L min\textsuperscript{-1} and simultaneously the impactor plate is heated volatilizing the collected aerosol material. The volatilized compounds are analyzed for particle-phase products. The third step is cooling of the MOVI so it is ready for another sample-desorption cycle.

Using $I^-$ as reagent ion, the detection limit for monocarboxylic acids using the laboratory-based CIMS instrument was estimated to be 80 ± 10 ng. Temperature-programmed desorption experiments using MOVI-CIMS were also conducted to calculate the vapor pressure and thermodynamic parameters of PA, OA, and AA. The $\Delta H^0_{\text{sub}}$ and $\Delta S^0_{\text{sub}}$ obtained were within the range reported by various studies for PA and AA, whereas the $\Delta H^0_{\text{vap}}$ and $\Delta S^0_{\text{vap}}$ for OA agreed very well to the most recent estimate. In addition, the kinetics of the heterogeneous oxidation of OA by O\textsubscript{3} was also investigated using the MOVI-CIMS.

Chapter 3 discusses the modifications to the MOVI and development and characterization of a new CI-HTOFMS instrument. This instrument was developed in collaboration with Aerodyne Research Inc. (Billerica, MA), Tofwerk, AG. (Thun, Switzerland) and University of San Diego, CA. The advantage that the TOFMS has over Quadrupole-based mass spectrometers, when coupled with the MOVI inlet and a soft chemical ionization source, greatly improves our ability to speciate gas and particle-phase OA products. The CI-HTOFMS has high mass resolving powers. At m/Q’s above 250 Th, the mass resolving power obtained in V and W-modes is 4700 Th Th\textsuperscript{-1} and 7300 Th Th\textsuperscript{-1}, respectively.
The instrument sensitivity was tested with CH$_3$C(O)O$^-$ and H$_3$O$^+$ reagent ions in negative and positive-ion modes, respectively. Both, syringe deposition and impaction methods were used to measure the sensitivity of Palmitic, Azelaic and Tricarballylic acids in the negative ion mode. Detection limit of the CI-HTOFMS instrument for organic acids using the CH$_3$C(O)O$^-$ ion and syringe deposition method was calculated to be 90 pg, 100 pg, and 0.95 ng for PA, AA, and TA, respectively. Assuming the same uncertainty in sample peak areas for impaction method as for syringe deposition, the detection limits for PA, AA, and TA, are 270 pg, 240 pg, and 0.65 ng, respectively.

Deployment to the Pasadena, CA ground site during CalNex-2010 helped me understand some of the issues that need to be resolved with the MOVI design. Below are a list of few of the improvements that are either planned or should be considered in future

1. Background contamination: Recent improvements such as coating the MOVI body and post with inert material have helped reduce the background peaks but keeping the MOVI body hot during sampling collection is critical for reducing the background peaks further. With the present design, that is not possible, so future design improvements are planned that will help keep the body at higher temperature.

2. Long cooling times: It takes about 10 min to cool the MOVI to ambient temperature. To minimize this, future design improvements will consider a coolant circulation mechanism that will not only cool the MOVI faster but
also keep the MOVI post at ambient temperature while the MOVI body is maintained at a higher temperature.

3. Lower cutpoint: The present cut-point diameter of 130 nm should be reduced further to collect smaller aerosol particles, especially to understand aerosol growth mechanisms.

4. Different reagent ions: Although CH$_3$C(O)O$^-$ is a unique ion to detect acids, other reagent ions should be studied to increase the capability of the instrument. H$_3$O$^+$ ionization scheme has been extensively studied and some of the experiments described here have proved it usefulness but other positive and negative reagent ions should be tested. Some of the positive ions that are worth considering are O$_2^+$, NO$^+$, and Li$^+$.

5. Data analysis methods: Due to the vast amounts of data collected during each experiment it is nearly impossible to analyze all the data with the present analysis methods. Future analysis methods have to be developed that can process the data faster. Extensive testing of the recently developed high-resolution code of the Tofwerk’s analysis software is needed.

6. Thermogram analysis: The data provided by the MOVI can be used to estimate the vapor pressure of the detected compounds but the method I employed is very slow. Developing a new technique to automate this part of the analysis will greatly aid in data interpretation and provide new insights into the OA composition.
The final chapter describes the application of the CI-HTOFMS to SOA formation studies from oxidation of α-pinene and alkanes. α-pinene is one of the major monoterpenes emitted to the atmosphere and is known to produce significant SOA from ozonolysis and OH oxidation. In this study, I used the CH$_3$C(O)O$^-$ reagent ion to detect organic acids in gas and particle-phases. The total organic acid mass concentration is lower during ozonolysis than during OH oxidation suggesting that the production of SOA stops once all the α-pinene and its products, that have a double bond, are oxidized by Ozone. In the case of OH radicals, the oxidation continues producing low-volatility compounds that form SOA. Also noticeable is the increase in formic acid signal with increasing OH concentration. Significant formation of oligomeric compounds was observed even in the absence of acidic seed aerosol. This aspect of the reaction mechanism needs further study as is the determination of vapor pressures from mass thermogram data.

The second part of chapter 4 describes two alkane photo-oxidation experiments in a large environmental chamber. Cyclododecane, a C$_{12}$ alkane was oxidized by OH radicals under high and low-NO$_x$ conditions for 18 hr. Preliminary analysis of the mass spectra reveal important differences in the reaction mechanism in the presence and absence of NO$_x$. Higher SOA yields were observed under high-NO$_x$ conditions consistent with the formation of higher m/Q products. Future analyses will focus on understanding the formation pathways of these products, estimation of their elemental composition, and their gas-particle partitioning.
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