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Abstract

The aqueous phase photo-oxidation of water soluble organic compounds (WSOC) extracted from α-pinene ozonolysis secondary organic aerosol (SOA) was investigated using high resolution time-of-flight chemical ionization mass spectrometry (CI-ToFMS). The results have shown that WSOC get more functionalized and fragmented as the reaction proceeds. The capabilities of three reagent ions, were assessed; specifically, $(\text{H}_2\text{O})_n\text{H}^+$ ionizes organic compounds with carbon oxidation state $(\text{OS}_C) \leq 1.3$, whereas $\text{CH}_3\text{C(O)O}^-$ and $\text{I(H}_2\text{O})_n^-\text{I}$ ionize highly oxygenated organics with $\text{OS}_C$ up to 4, with $\text{I(H}_2\text{O})_n^-\text{I}$ showing more selectivity.

The aqueous phase OH oxidation of cis-pinonic acid and tricarballylic acid (a surrogate for 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), recognized as a tracer of α-pinene SOA) were also studied. The respective rate constants at 301 K were measured to be $3.4(\pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ at pH=2 and $3.1(\pm 0.3) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at pH=4.6. This work also illustrates possible aqueous phase mechanism for MBTCA formation from cis-pinonic oxidation.
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Chapter 1
Introduction and Overview

1 Organics in the Atmosphere

Organic compounds comprise an important subset of atmospheric constituents and can exist in all atmospheric phases, i.e. gas, particle and aqueous. It is known that organics play important roles in determining the abundance of atmospheric oxidants and influencing the properties of suspended particles and aqueous droplets, affecting climate and human health (Hallquist et al. 2009, Ervens et al. 2011).

Volatile Organic Compounds (VOCs) are emitted in the atmosphere from both biogenic (marine and terrestrial) and anthropogenic sources. It is estimated that biogenic VOCs emissions exceed those from an anthropogenic origin (Kanakidou et al. 2005). Examples of biogenic VOCs are isoprenoid compounds, which are emitted from vegetation. Isoprenoids include isoprene, monoterpenes and sesquiterpenes. Isoprene is a C5 compound, with the highest emission rate by mass among all biogenic VOCs with reported emission rates ranging from 250 and 750 Tg C yr\(^{-1}\) (Kanakidou et al. 2005). Mono-terpenes are C10 hydrocarbons and are the second highest emitted biogenic VOCs with 127 Tg C yr\(^{-1}\) emission rate (Finlayson-Pitts 2000). The most highly emitted hydrocarbons in the mono-terpene family are α-pinene, β-pinene and limonene. Sesquiterpenes are C15 hydrocarbons and account for 7.4% of the total terpene emissions (Kanakidou et al. 2005). Anthropogenic VOCs include alkanes, alkenes and aromatics compounds emitted in the atmosphere by human activity.

In the presence of atmospheric oxidants, such O\(_3\), OH and NO\(_3\) radicals, VOCs react forming oxygenated compounds with a variety of functional groups and degree of oxidation. The oxidation products formed are generally classified based on their volatility. Some products can stay in the gas phase if their volatility is high enough. The rest of the oxidation products are either semi-volatile organics, which have intermediate volatility, or low volatility organics. These compounds with low volatility can condense on pre-existing particles, adding organic mass to the existing particles or nucleate leading to new particles formation. Particulate matter formed by this pathway is referred to as Secondary Organic Aerosols (SOA) (Hallquist et al. 2009).
Particles can also be introduced directly into the atmosphere by several processes such as biomass burning, cooking, volcanic eruptions, fossil fuel combustion and the suspension of mineral dust, biological particles and sea salt created by wind forces (Hallquist et al. 2009). When containing an organic component, these particles are referred to as Primary Organic Aerosols (POA).

Global-scale measurements of aerosol particles have assigned ~50% of sub-micron aerosol mass to be organic (Zhang et al. 2007, Jimenez et al. 2009), with much of this material secondary in nature (i.e. SOA) (Kanakidou et al. 2005, Hallquist et al. 2009, De Gouw and Jimenez 2009). There are thought to be hundreds to thousands of organic compounds within SOA, which may undergo chemical processing in the atmosphere after condensation (Hamilton et al. 2004), in what is referred to as SOA aging. Laboratory studies focused on elucidating the kinetics and mechanisms of gas phase oxidation reactions of VOCs and measuring the yield of SOA are abundant. However, predictions of organic aerosol loading made by advanced global models that include laboratory SOA data tend to underestimate the observed SOA mass and bulk oxidation state in the atmosphere (Heald et al. 2005, Hallquist et al. 2009, Heald et al. 2010). The discrepancy is suggested to be due to the incomplete understanding of SOA formation mechanisms. This raises questions as to whether new SOA formation pathways and chemical processes that lead to changes in SOA composition need to be explored.

### 1.1 Aerosol Aging

Aging is the process by which the composition of the particle phase components changes due to multiphase processing (Rudich et al. 2007). Aging of organics can take place by 1) condensed phase reactions, 2) heterogeneous reactions and 3) changes in the gas phase concentrations of organics, which are in equilibrium with the particle phase (Rudich et al. 2007). In particular, condensed phase reactions of organics are highly dependent on the physical state of the particle. For instance, more viscous and solid particles lead to reduction in the reactivity of condensed phase components due to the reduction in the diffusion rates of reactants into the particles (Ervens et al. 2011).
1.1.1 Aqueous Phase: a Possible Aging Medium

One of the roles particulate matter plays in the atmosphere is acting as cloud condensation nuclei (CCN) in the atmospheric hydrological cycle (Hallquist et al. 2009). Under certain atmospheric conditions (i.e., largely controlled by the relative humidity, RH) the ability of particles to activate into cloud droplet depends on the chemical composition and the size of the particle (Hallquist et al. 2009). According to Köhler theory, if the relative humidity of the surrounding air mass is lower than the particle’s critical super-saturation, then water uptake by the particles takes place forming an aqueous particle without activating into cloud droplet (Hallquist et al. 2009). However, if the critical super-saturation of the particle is reached, then the particle grows into a cloud droplet with a significant increase in the liquid water content (LWC) (Hallquist et al. 2009).

Considering semi-solid or viscous SOA in the atmosphere that is exposed to a wide range of RH, the SOA physical state can transition into the aqueous phase forming an aqueous SOA particle (aqSOA) or activating into cloud droplet depending on where the RH lies with respect to the critical super-saturation (Ervens et al. 2011). In either case, the organic fraction of SOA can potentially be involved in reactions within the aqueous phase. The difference between aqSOA and cloud droplets is in the LWC (the solvent), which subsequently affects the concentration of the organics within the aqueous phase (Ervens et al. 2011). The aqueous phase processing of organics has only recently been considered as a potential SOA aging mechanism (Ervens et al. 2011). Not only can the aqueous phase alter the composition of the original SOA particle, but volatile gas phase organics can be dissolved into the aqSOA or cloud droplets and further processed (Ervens et al. 2011). The first process changes the oxidation state of the organics, while the second process might lead to additional organic mass to the aqSOA or cloud droplet (Ervens et al. 2011). Examples of aqueous phase reactions include 1) radical reactions (e.g., OH and NO₃), 2) photolysis, 3) oligomerization reactions forming high molecular weight compounds (e.g., aldol condensation and acetal formation) and 4) reactions with H₂O₂ forming organic peroxide species (e.g., α-hydroxy hydroperoxides and peroxyhemiacetals) (Hallquist et al. 2009, Ervens et al. 2011, Zhao et al. 2012). Upon water evaporation, the aqSOA and cloud droplets can form SOA with a different chemical composition and mass compared to the original SOA (Ervens et al. 2011). The aqSOA/cloud cycles and the resulting changes in the chemical and
physical prosperities of the particles involved have only recently been considered as part of SOA aging mechanisms (Ervens et al. 2011).

1.2 Analytical Techniques to Study SOA

Due to the role aerosol play in the atmosphere there is growing demand for advanced analytical techniques which allow for the detection and elucidation of condensed phase organic species and to assist in understanding their transformations, sources and sinks (Duarte and Duarte 2011, Pratt and Prather 2012, Pratt and Prather 2012, Laskin et al. 2012). Such techniques can vary in sensitivity, specificity, and time response. In addition, the ability of such techniques to be deployed in the field is highly desirable because a comprehensive understanding of organic processing requires both lab and complementary field measurements.

1.2.1 Spectroscopic Techniques

On the one hand, a wide range of spectroscopic techniques has been utilized to successfully investigate the organic composition of particulate matter (PM) and cloud-, fog- and rain-water, including Nuclear Magnetic Resonance (NMR) (Decesari et al. 2000, Decesari et al. 2007, Duarte et al. 2007, Decesari et al. 2011, Shakya et al. 2012, Cleveland et al. 2012, Finessi et al. 2012, Santos et al. 2012), Fourier Transform Infrared (FT-IR) (Sax et al. 2005, Duarte et al. 2007, Polidori et al. 2008, Takahama et al. 2013) and Ultraviolet–visible (UV-Vis) (Decesari et al. 2000, Duarte et al. 2005, Walser et al. 2007, Moosmueller et al. 2009, Wagner et al. 2009, Shapiro et al. 2009, Bones et al. 2010, Santos et al. 2012, Gyawali et al. 2012). All such spectroscopic measurements provide information on organic aerosol bulk properties with specificity commonly restricted to individual functional groups. For example, proton NMR ($^1$H-NMR) directly provides quantitative information on the amount of aldehydic, hydroxyl and aromatic groups, whereas, ketone and carboxylic acid functionalities can be measured indirectly (Decesari et al. 2007) or via derivatization (Moretti et al. 2008). FT-IR gives more direct quantitative information on the carbonyl functional groups and has been implemented in PM and cloud studies (Sax et al. 2005, Duarte et al. 2007, Polidori et al. 2008, Wagner et al. 2009, Russell et al. 2009, Takahama et al. 2013). However, FT-IR can be prone to inorganic interferences, which are likely to be present in ambient samples (Duarte et al. 2007, Polidori et al. 2008). In addition, better resolution of individual constituents requires chromatographic separation prior to analysis (Polidori et al. 2008). UV-Vis has been used for brown carbon (BrC)
measurements, which is important to understand the radiative forcing influence of PM and clouds (Moosmueller et al. 2009, Wagner et al. 2009). However, the fact that only multi-conjugated functional groups are detected implies the need for complementary analytical techniques in order to characterize the whole organic composition. A common limitation of the spectroscopic techniques NMR, FT-IR and UV-Vis is the requirement of a large amount of sample due to low sensitivity, which subsequently results in low time resolution (Duarte and Duarte 2011).

1.2.2 Mass Spectrometry Techniques

As a complement to spectroscopic techniques, mass spectrometry is increasingly being applied for measurements of condensed phase atmospheric organics because it has the potential to provide quantitative chemical formula information with very high sensitivity. Approaches vary via their means of vaporizing the constituents, in their ionization methods and in the mass analyzers employed. Widely used methods are the Aerodyne Aerosol Mass Spectrometer (AMS), which is based on Electron ionization (EI) with flash vaporization at 600 degrees, and single-particle approaches that use lasers for both particle vaporization and/or ionization (Murphy and Thomson 1995, Gard et al. 1997, Onasch et al. 2012). AMS instruments have emerged as a very powerful tool to study PM (Canagaratna et al. 2007, Zhang et al. 2007, Jimenez et al. 2009) and more recently fog and rain droplets (Ge et al. 2012, Lee et al. 2012). The attraction of the AMS is the ability to derive quantitative information of inorganic and organic constituents in an on-line manner (Canagaratna et al. 2007). In addition, the instruments are field-deployable allowing on-line ambient measurements to be easily obtained. While measurements from the AMS have substantially improved the understanding of PM evolution in the atmosphere, the instrument is limited to elemental analysis of the bulk particle and estimation of functional groups present, while much molecular information is lost due to fragmentation during the hard ionization by EI (Canagaratna et al. 2007).

Electro-Spray Ionization (ESI) Mass Spectrometry (ESI-MS) has also been used in several lab and field studies to elucidate the organic aerosol and fog water composition (Altieri et al. 2008, Perri et al. 2009, Tan et al. 2009, Schmitt-Kopplin et al. 2010, Lim et al. 2010, Mazzoleni et al. 2010, Tan et al. 2010, Kundu et al. 2012). The advantage of ESI-MS is the soft ionization of ESI, in which the analyte ion stays intact; as well, the sample is not heated before ionization. Also,
ESI-MS instruments are sometimes equipped with high resolution Fourier transform ion cyclotron mass spectrometers (FTICR-MS), by which molecular level information for individual species can be drawn from very complex samples (Laskin et al. 2012, Laskin et al. 2013). The application of ESI-MS in aerosol research has substantially improved the understanding of aerosol evolution and processing in the atmosphere (Perri et al. 2009, Tan et al. 2009, Tan et al. 2010, Laskin et al. 2012, Laskin et al. 2013). However, in this technique the sample must be mixed with a solvent that is required to induce ionization, which might lead to unwanted bulk reactions between the analyte and the solvent (Bateman et al. 2008). Most importantly, ESI-MS instruments are not easily field-deployable.

While the technique of Chemical Ionization Mass Spectrometry (CIMS) has been used in atmospheric chemistry for decades, the technique is only now being applied to the study of organic processing that takes place in atmospheric cloud-, fog-, and rain-water, and particles (Thornton et al. 2003, Hearn and Smith 2004, Sareen et al. 2010, Ervens et al. 2011, Zhao et al. 2012). An advantage of the CIMS over other mass spectrometry techniques is the ability to use a variety of reagent ions that induce the chemical ionization in order to selectively detect certain classes of organic compounds of interest. Most importantly, chemical ionization is a relatively soft ionization technique and thus the analyte ion is often not fragmented. This is important if information at the molecular level is desired, such as in mechanistic and kinetic studies. However, as the sample composition becomes more complex, the low resolution quadrupole mass analyzer used with traditional CIMS instruments becomes inadequate to resolve the whole organic composition (Hearn and Smith 2006), and higher resolution instruments are preferred.

Aerosols studies utilizing the CIMS rely on thermal desorption to volatilize the organic constituents of the particles. For instance, a multi-orifice volatilization impactor (MOVI) has recently been developed as an interface to CIMS instruments, which allows for on-line separation of gas and particle phase organics (Yatavelli and Thornton 2010, Yatavelli et al. 2012). While particles are collected on the MOVI, gaseous species are detected by the CIMS. After particle collection ends, the impactor is heated gradually and organics volatilize off depending on their vapour pressures. Thus, it can also provide vapour pressure information of the species being analyzed. Another interface that has been previously employed in aerosol studies is the aerosol-CIMS (or thermal desorption CIMS, TD-CIMS) (Hearn and Smith 2004, Hearn and Smith 2006, Sareen et al. 2010, Zhao et al. 2012). The advantage of aerosol-CIMS is the ability
to detect both gas and particle phase constituents simultaneously on-line by introducing a heated inlet to volatilize particle phase components.

1.3 Objectives and Goals

1.3.1 High Resolution Aerosol-CIMS: a Novel Tool to Study Aqueous Phase Chemistry

This work illustrates the potential of high resolution aerosol-CIMS to study the composition of a complex organic matrix in the atmosphere, namely the water soluble organic compounds (WSOC) of α-pinene ozonolysis SOA. This complex organic mixture and its subsequent aqueous photo-oxidation components were treated as models to highlight the capabilities of high resolution aerosol-CIMS to study organic aerosol composition and processing. This work illustrates how a comprehensive analysis can be achieved by choosing the CIMS reagent ions to selectively ionize certain classes of organic compounds within the WSOC SOA. In particular, three reagent ions: 1) protonated water clusters \((\text{H}_2\text{O})_n\text{H}^+\), 2) acetate anions, \(\text{CH}_3\text{C(O)O}^-\) and 3) iodide \(\text{I}(\text{H}_2\text{O})_n^-\) ions were used to explore the selectivity of each reagent ion for the same change in chemical composition occurring during SOA photo-oxidation. The results are presented as oxygen-to-carbon atomic ratios (O:C), hydrogen-to-carbon ratios (H:C), carbon oxidation state (OS\(_C\)) and numbers of carbon atoms (#C) distributions over the course of aqueous phase oxidation for the three reagent ions. For reference, the data are compared to those obtained simultaneously with high resolution AMS. Furthermore, this work illustrates that different chemical classes, corresponding to monomers and dimers of the α-pinene oxidation products, were observed for the WSOC in all the CIMS spectra. Their differing rates of oxidation illustrate how aerosol-CIMS can be utilized to study chemical change within a chemically complex matrix.

1.3.2 Kinetics and Mechanisms: Aqueous OH Oxidation of Relevant Organic Compounds

cis-Pinonic acid is a semi-volatile compound that is formed by the atmospheric oxidation of α-/β-pinene initiated by OH and ozone (Hallquist et al. 2009, Mueller et al. 2012). It has been shown by Mueller et al. (2012) that gas phase OH oxidation of cis-pinonic acid leads to the formation of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). MBTCA is a low volatility tri-acid compound that has been detected in SOA in previous studies (Szmigielski et al. 2007, Zhang et
al. 2010). In addition, it was suggested that MBTCA is suitable stable tracer for mono-terpene SOA (Szmigielski et al. 2007, Zhang et al. 2010, Mueller et al. 2012).

Due to the presence of acidic and ketone functional groups in the cis-pinonic acid structure, it is expected that gaseous and particulate cis-pinonic acid dissolves in cloud droplets or aqSOA in the atmosphere, as part of the cloud cycle. It is hypothesized that the oxidation of cis-pinnonic acid by OH can take place in the aqueous phase forming highly oxygenated compounds that are less volatile compared to cis-pinonic acid, similar to what has been observed by the gas phase reaction (Mueller et al. 2012). The oxidation of cis-pinonic acid that is from a gaseous source leads to additional SOA mass and cis-pinonic acid oxidation in a particle leads to a change in the overall oxidation state of the particle. The goal of this aspect of the thesis was to obtain kinetics data for the aqueous OH reaction with cis-pinonic acid. In addition, possible reaction mechanisms that could lead to MBTCA formation were also explored. As discussed earlier, MBTCA was selected as a tracer compound for SOA from biogenic origin. However, as it is a particle phase component, it can also be present in the aqueous phase during its transport as part of cloud cycles and activation. Thus, it is thought that MBTCA could be processed while in the aqueous phase. As a result, attempts were made to evaluate the stability of MBTCA in the aqueous phase in the presence of OH. An estimation of the rate constant of the reaction of MBTCA with OH was made and possible mechanisms were suggested using the surrogate compound, tricarballylic acid.
2 Aqueous Phase Photo-Oxidation

2.1 WSOC

The experiments were carried out in the following sequence: 1) SOA generation and collection, 2) Water Soluble Organic Compounds (WSOC) aqueous phase photo-oxidation and 3) detection of photo-oxidation products using high resolution CI-ToFMS and AMS (Aerodyne Inc.).

2.1.1 SOA Generation

The reaction of ozone with α-pinene was used to generate SOA in a continuous manner in the University of Toronto Mobile Oxidation, Concentration and Aging (MOCA) chamber (i.e. FEP Teflon bag, 1 m³ volume). An OH radical scavenger was not added and as a result α-pinene was oxidized by both ozone and OH. No nucleation seed aerosol was employed. The experimental set up is illustrated in Figure 2.1. The chamber was run in the dark at room temperature and pressure. Dry (RH~ <5%), purified, hydrocarbon free air, from an AADCO 737 pure air generator, was the carrier gas and flowed continuously into the chamber before the reagents were introduced. All flows were controlled using MKS mass flow controllers. Ozone was generated by passing 0.1 LPM (Liter per minute) of air over a mercury lamp. α-Pinene (Aldrich, >99%) was injected continuously in 1 LPM of air using a 25 µL syringe (Hamilton) mounted on a syringe pump (Harvard Apparatus, Pump11 Elite) at a rate of 0.1 µL/min. In order to reduce the concentration of α-pinene, 0.1 LPM of the air carrying α-pinene was introduced in the chamber while the rest flowed to the exhaust. A needle valve was placed on the exhaust line to insure sufficient pressure is present to allow 0.1 LPM to flow into the chamber (see Figure 2.1). Makeup air of 10.5 LPM was added in order to dilute the reagents and to give a residence time of ~1.6 hrs in the chamber. A pump was connected to the chamber outlet to pull 8.9 LPM of air through an O₃ denuder to remove part of the ozone.

The reagents and products were monitored using several analytical instruments. An Ozone analyzer (model 49i, Thermo scientific) was used to monitor the O₃ concentration in the
Figure 2.1: Experimental set up used to run a 1 m$^3$ chamber in continuous mode to generate SOA by the gas phase ozonolysis of α-pinene. Air flowing into and out of the chamber was controlled by mass flow controllers. Instruments connected to the outlet of the chamber were used to monitor gas phase and particle concentrations.

Figure 2.2: Time profiles of O$_3$, α-pinene and SOA mass loading evolution in the MOCA chamber, which was run in continuous mode. Dashed red line indicates when SOA collection started.

chamber, α-Pinene concentration was monitored with a PTR-MS (Ionicon) by following mz 137 and 81, and the SOA size distribution was measured using a TSI SMPS (3081 DMA, 3025A
Typical time profiles for the reagents and SOA mass loading (assuming a density of 1.2 g/mL) are shown in Figure 2.2. When the reagents and SOA loading reach a stable level (Figure 2.2), a Teflon filter (Pall life sciences, 47 mm diameter and 2 µm pore size) was placed downstream of the ozone denuder (Figure 2.1). SOA was collected on the filter for 6-8 hours and the mass collected was determined gravimetrically by a balance (Sartorius BP211D) before and after SOA collection. Immediately after SOA was collected (and the mass was measured) the filter was immersed in ~50 mL of purified water (18 mΩ cm, Veolia) in a plastic bottle (Nalgene), which was pre-rinsed with purified water (18 mΩ cm). The immersed filter was shaken for ~15 min and then left in the freezer at -30°C.

2.1.2 WSOC Photo-Oxidation

The aqueous phase photo-oxidation reaction was carried out in a photo-reactor (Rayonet Reactor, RPR-200) equipped with UV-B lamps (RPR-3000, peak emission at 310 nm) mounted in a circular manner such that they are equidistant from the centre. A stirring plate and a fan were added to the photo-reactor to ensure adequate solution mixing and cooling, respectively. The aqueous solutions were placed in a glass bottle (Wheaton) in the centre of the photo-reactor, and thus light of wavelengths greater than 300 nm was transmitted to the sample. The solution temperature when the lamps are on was 28°C. The aqueous phase OH photo-oxidation was initiated by the photolysis of hydrogen peroxide (Sigma-Aldrich, ≥30% in water, TraceSELECT) to form OH. From the decay of species with known rate constants with OH, it was estimated that the average OH concentration is on the order (1.2±0.1) × 10^13 M.

Three frozen WSOC solutions were allowed to thaw at room temperature and combined. Purified water (18 mΩ cm, Veolia) was added to make a 200 mL solution of 10 µg/mL SOA mass in water. The 200 mL solution was divided into 4×50 mL aliquots. 1×50 mL aliquot was used to carry out the OH oxidation and 2×50 mL solutions were used for photolysis (i.e. no H_2O_2) and dark H_2O_2 (i.e. H_2O_2 but no light) control experiments, and 1×50 mL was a backup. A volume of 51.3 µL of hydrogen peroxide was injected in the SOA solution to give a concentration of 1 mM. The oxidation was initiated by the irradiation of UV-B lamps. The photo-oxidation and control experiments were allowed to run for 4 hours.
2.1.3 Detection

The WSOC solution was atomized using a TSI constant output atomizer (model 3076). A fraction of the droplets was diluted by a factor of four with N$_2$ gas (BOC, grade 4.8) or Air (Linde, grade 0.1) before entering the HR- CI-ToFMS (Aerodyne Inc.) (Figure 2.3). In order to volatilize the organics from the droplets, the diluted flow was heated up to 150˚C by passing it through a 70 cm long Siltek-coated stainless steel tubing (Restek). The tubing was heated by wrapping it with a heating tape (Omega, STH051) and the temperature was controlled using a modified temperature controller (Omega, CN1A-TC). The residence time in the heated line was about 1.4 seconds. Temperature ramping experiments were carried out where the temperature of the line was ramped from 100˚C to 250˚C in steps of 50˚C. The line temperature (150˚C) was selected such that the signal for the majority of the ions of interest was maximized.

![Diagram of experimental setup]

**Figure 2.3:** Setup used to run the aqueous phase photo-oxidation of WSOC. The solution was constantly stirred and atomized in the glass bottle while UV-B light was continuously irradiated for 4 hours. The flow carrying the mist from the atomizer was split such that part was introduced to the HR-CIMS and the rest was admitted to the HR-AMS and SMPS. Red line indicates the CIMS heated inlet (150˚C). MFC refers to mass flow controller.

The rest of the unheated droplet flow was diluted by air (Linde, grade 0.1) (see Figure 2.3) and passed through a diffusion dryer. The flow was then introduced to the HR-AMS (Aerodyne Inc.)
and an SMPS (TSI, 3081 DMA, 3776 CPC). A pump was also connected to the manifold downstream of the dryer in order to reduce the residence time of the droplets in the tubing downstream from the atomizer.

### 2.1.3.1 HR-CI-ToFMS

A detailed description of the HR-CI-ToFMS can be found in Bertram et al. (2011). The sample flow rate entering the low pressure ion-molecule reaction (IMR) chamber of the CI-ToFMS was set to 2.0 LPM by a critical orifice.

![CI-ToFMS Diagram](image)

**Figure 2.4:** The setup used to operate the CI-ToFMS. Sample flow was introduced to the IMR through the heated inlet. \((\text{H}_2\text{O})_n\text{H}^+\), iodide and acetate reagent ions were generated by passing a flow of nitrogen gas carrying a) water b) methyl iodide and c) acetic anhydride through a \(^{210}\text{Po}\) radioactive cell, respectively. One reagent ion was used at a time. Bolded circles indicate points of attachment of the reagent ion flows on the right to the manifold on the left. Scmm refers to Standard Cubic Centimeters per Minute.

The reagent ions used in this work were: protonated water cluster \((\text{H}_2\text{O})_n\text{H}^+\), acetate anions \(\text{CH}_3\text{C}(\text{O})\text{O}^-\) and iodide water clusters \(\text{I}(\text{H}_2\text{O})_n^-\). The reagent ion precursors were water (18 mΩ cm), acetic anhydride (Sigma, 539996) and methyl iodide (Sigma, I8507). A fritted glass bubbler was used to bubble the water with 2.2 LPM of nitrogen to create \((\text{H}_2\text{O})_n\text{H}^+\). Acetate reagent ions were generated by a flow of 10 sccm from the acetic anhydride headspace contained in a stainless steel bottle (Swagelok), which was diluted by 2.2 LPM \(\text{N}_2\). A home-built permeation
tube left at room temperature containing methyl iodide was the source required to create the iodide reagent ions. Each reagent ion precursor was passed through a $^{210}$Po radioactive cell (NRD, Model 2031), at a flow of 2 LPM set by a critical orifice, in order to create the ionization reagent ions. The analyte ionization took place in the following chemical ionization reactions:

Water: $(\text{H}_2\text{O})_n\text{H}^+ + \text{M} \rightarrow n(\text{H}_2\text{O}) + \text{MH}^+$  
Reaction 2.1

Acetate: $\text{CH}_3\text{C}(\text{O})\text{O}^- + \text{MH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{M}^-$  
Reaction 2.2

Iodide: $\text{I}(\text{H}_2\text{O})_n^- + \text{M} \rightarrow n(\text{H}_2\text{O}) + \text{I(M)}^-$  
Reaction 2.3

The IMR pressure and temperature were adjusted to 96±1 mbar and 57°C, respectively. The pressure of the collisional dissociation chamber (CDC), the chamber following the IMR containing the short segmented quadrupoles (SSQ), was adjusted to 2.0±0.2 mbar. A nitrogen flow was used to dilute the sample flow in the water and iodide reagent ion experiments (Figure 2.3), while a flow of air was used for the dilution in the acetate reagent ion experiments (Veres et al. 2008). This was essential as the acetate reagent ion concentration is correlated with the amount of oxygen present. Water and iodide reagent ions experiments were run in weak-field while acetate reagent ion experiments were run in strong-field mode, where the field strength controls the amount of gas phase ion clustering and fragmentation. The fields found to be most determinant to ion clustering/fragmentation were 1) the fields between the two quadrupoles (SSQ and BSQ, big segmented quadrupoles), 2) the field across the BSQ and 3) the field across the SSQ. A list of the voltages in the mass spectrometer used to run the experiments is given in Table 1. All experiments were run in V-mode with the time-of-flight mass spectrometer, and data were acquired at 1 s time resolution and averaged to 5 min using the data analysis software, Tofware 2.2.2 (Aerodyne Inc.).
Table 2.1: Voltages (V) applied on the HR-CIMS elements in positive mode for water and negative mode for acetate and iodide reagent ions. These elements are listed from left to right according their order in the mass spectrometer downstream from the sample inlet. A detailed description of the CI-ToFMS can be found in (Bertram et al. 2011). Q1 is SSQ and Q2 is BSQ.

<table>
<thead>
<tr>
<th>Reagent ion</th>
<th>IMR</th>
<th>Nozzle</th>
<th>Q1 entrance plate</th>
<th>Q1 front</th>
<th>Q1 back</th>
<th>Lens skimmer</th>
<th>Skimmer</th>
<th>Q2 front</th>
<th>Q2 back</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)nH⁺</td>
<td>0</td>
<td>-3.3</td>
<td>0</td>
<td>-9.9</td>
<td>-2.1</td>
<td>0</td>
<td>0</td>
<td>-7.6</td>
<td>-9.5</td>
</tr>
<tr>
<td>CH₃C(O)O⁻</td>
<td>0</td>
<td>3.3</td>
<td>6.6</td>
<td>17.9</td>
<td>-8.1</td>
<td>-7.2</td>
<td>-1.4</td>
<td>8.3</td>
<td>7.2</td>
</tr>
<tr>
<td>I(H₂O)n⁻</td>
<td>0</td>
<td>3.3</td>
<td>6.6</td>
<td>17.9</td>
<td>2.1</td>
<td>2.2</td>
<td>5.2</td>
<td>6.6</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Peak fitting and ion assignment was performed for all peaks in the spectra for the three reagent ion up to molecular weight of 300 u. The mass accuracy for all V-mode experiments was ± 5 µTh Th⁻¹ (ppm). The ToF resolving power was 4285 (at m/z 301), 4194 (at m/z 299) and 4186 (at m/z 427) for (H₂O)nH⁺, CH₃C(O)O⁻ and I(H₂O)n⁻, respectively. More details regarding mass accuracy and resolving power of the mass spectrometer can be found elsewhere (Bertram et al. 2011, Yatavelli et al. 2012, Jokinen et al. 2012). Data for the three reagent ions were normalized to reagent ion signal and background subtracted.

2.1.3.2 HR-AMS
The aqueous particles passed through a diffusion dryer and were subsequently analyzed by the HR-AMS for determination of non-refractory components. The working principle of AMS has been reviewed by (Canagaratna et al. 2007). The HR-AMS switched between V-mode (1 min) and W-mode (4 min) during the experiments. The data analysis was performed using Squirrel (version 1.51H) and Pika (version 1.10H). The standard fragmentation table in Pika with the corrected air fragment column for our carrier gas were used. The elemental analysis of W-mode data were performed with the default correction factors for O:C (0.75) and H:C (0.91) in Pika (Aiken et al. 2008).

2.1.3.3 CI-ToFMS Sensitivity Evaluation
To evaluate relative sensitivities of different species, the following organic compounds were used: glyoxal (Sigma, 40 wt. % in H₂O), methylglyoxal (Sigma, 40% in H₂O), formic acid
(Sigma, 50 wt. % in H$_2$O), acetic acid (Fisher, 99.9%), glyoxylic acid (Sigma, 50 wt. % in H$_2$O), pyruvic acid (Sigma, 98%), pinonic acid (Sigma, 98%), oxalic acid (Fisher, 99.9%), malonic acid (Sigma, 99%), succinic acid (Fisher, 99.7%), levoglucosan (Sigma, 99%), citric acid (Sigma, $\geq$99.5%) and L-tartaric acid (Fisher, $>99.5$%). The structures of these compounds are given in table A.1. Three standard solutions of a combination of the thirteen organic compounds were prepared in water (18 mΩ cm). The concentrations of each of the organic compounds were 5, 15 and 25 µM. The standard solutions were sampled as illustrated in Figure 2.3, with the HR-CIMS operating with the three reagent ions separately. The sensitivity of each compound was obtained from the slope of the three-point calibration curve.

### 2.2 Kinetics and Mechanisms: Selected Organic Compounds

The experiments were carried out in order to elucidate possible mechanisms and to determine the rate constant for the reaction of OH radical with cis-pinonic acid (PIN) and tricarballylic acid (TCA) in the aqueous phase. The photo-oxidation of PIN and TCA was carried out in the system described in 2.1.2 but with the diffusion dryer connected directly to the SMPS and without using the AMS. Also, a dilution flow was not added to the droplet stream prior to the dryer for PIN and TCA mechanism experiments and for TCA kinetics experiments (Table 2.2). A dilution of 0.285 LPM was added for PIN kinetics experiments. This dilution was required as sulfuric acid, which was added to adjust the solution pH, generated high concentration of particles. The H$_2$O$_2$ concentration was 1 mM in all experiments. The concentrations of PIN and TCA for the mechanism experiments are given in Table 2.2. The pH of the solution in the mechanism experiment was not adjusted and left free as the reaction progressed. The mechanism experiments were run for 4 hours for both PIN and TCA. The three reagent ions were used to run the PIN mechanism experiments separately. CH$_3$C(O)O$^-$ reagent ions were used to run TCA mechanism experiments.

The relative rates method was implemented to run the kinetic experiments involving rate constant determination. Dimethyl sulfoxide (DMSO) (Caledon Labs) and propanoic acid (Sigma) were the reference compounds chosen for the PIN and TCA relative rate kinetics experiments, respectively. The pH of the solution was adjusted to 2 for PIN rate constant measurement using sulfuric acid (Fisher). This was done in order to ensure that $<99$% of PIN was present in the solution in one form (i.e., not dissociated). The CI-ToFMS was operated with (H$_2$O)$_n$H$^+$. 
Attempts were made to run kinetics experiments for PIN at pH 10 and free pH, however, due to technical problems, the experiments were not successful. TCA kinetics experiments were run at free pH and the CI-ToFMS was operated with the CH$_3$C(O)O$^-$ reagent ion.

**Table 2.2:** The concentration of PIN and TCA for the mechanism and kinetics experiments are listed. The reference compound concentrations and rate constants used in this work are also listed. The rate constant for propanoic acid is the weighted average rate constant at pH 4.6 (see section 4.1.2 for detailed calculations).

<table>
<thead>
<tr>
<th>Organic Compounds</th>
<th>Mechanism</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. (µM)</td>
<td>pH (initial)</td>
</tr>
<tr>
<td>Cis-pinonic acid</td>
<td>20</td>
<td>4.79</td>
</tr>
<tr>
<td>Tricarballylic acid</td>
<td>30</td>
<td>4.48</td>
</tr>
</tbody>
</table>

*(Zhu et al. 2003, Ervens et al. 2003)*
Chapter 3
CI-ToFMS Characterization: Reagent Ions

3 CI-ToFMS Sensitivity and Selectivity Evaluation

3.1 Selected Organic Compounds

The sensitivity of 13 organic compounds with known concentrations in the aqueous phase was assessed using the CIMS with the three reagent ions. This test was performed in order to evaluate the selectivity of each reagent ion towards known organic compounds. The organic compounds were chosen such that a variety of functional groups are presented.

3.1.1 Protonated Water Clusters

Figure 3.1a shows the sensitivities of the 13 compounds using \((H_2O)_nH^+\) reagent ions. The sensitivities obtained for all compounds are relatively low with the exception of pinonic acid and succinic acid. The proton transfer reaction (Reaction 2.1) is governed by the gas phase affinity of the organic compounds to protonation. The reaction proceeds if the gas phase basicity of the analyte is higher than that of the water clusters, \((H_2O)_n\). The reagent cluster ions observed in the spectra were with \(n=3, 2, 4\) listed by descending intensity, although this may not reflect the nature of the cluster distribution in the IMR. The gas phase basicity of the clusters are 730, 694 and 769 kJ/mol, respectively (Arifov et al. retrieved March 30, 2013). It is unknown which combination of the water cluster ions ionizes the analyte. Gas phase basicity data are not available for the majority of the organic compounds, except for formic acid (710 kJ/mol) and acetic acid (753 kJ/mol) (Hunter and Lias 1998). The gas phase basicity of acetic acid is higher than \(n=2\) and 3 water clusters. However, formic acid gas phase basicity is only higher than that of \(n=2\) water cluster. Formic acid was not observed in the \((H_2O)_nH^+\) reagent ion spectra at all concentrations, unlike acetic acid, which was detected. This indicates that the proton transfer reaction from \((H_2O)_nH^+\) to formic acid did not proceed. In addition, according to these observations, \((H_2O)_nH^+\) clusters with \(n\geq3\) appear to be playing a role in the proton transfer reaction. This also suggests the possibility that the actual distribution of \((H_2O)_nH^+\) clusters is with \(n\geq3\) in the IMR. The observation of \(n=2\) cluster in the mass spectra was probably due to
Figure 3.1: The sensitivity of 13 organic compounds in units of CPS (counts per second)/µM in solution. The sensitivities were obtained by operating the CIMS with the three reagent ions a) (H₂O)_nH⁺, giving rise to protonated molecular ions, b) CH₃C(O)O⁻, giving rise to deprotonated species aside from levoglucosan which was detected as a cluster with acetate, and c) iodide I(H₂O)_n⁻, giving rise to clusters with iodide. The error bars reflect the standard error in the slopes of the 3-point calibration curves. Also, the total ion count (TIC) is shown for each reagent ion.
fragmentation of higher order clusters yielding n=2 cluster. However, this interpretation is based on the data from only two organic compounds and more information regarding other compounds is required before a conclusive understanding can be drawn. It appears from Figure 3.1a that all the multi-functional organic compounds have very low sensitivity compared to pinonic acid, malonic acid, succinic acid, levoglucosan and citric acid, all of which contain reduced carbons (–CH₂–). This illustrates the selectivity of \((H_2O)_nH^+\) reagent ions toward compounds that are not highly oxygenated.

3.1.2 Acetate

Details about the \(CH_3C(O)O^-\) ionization method can be found elsewhere (Veres et al. 2008). Ionization takes place if the gas phase acidity of the analyte is higher than that of acetic acid. It has been found that acetic acid has a low gas phase acidity and thus most acids can deprotonate via Reaction 2.2 (Veres et al. 2008). The sensitivity of the CIMS to the organic compounds using acetate reagent ions is shown in Figure 3.1b. All acids were detected in the deprotonated form and all the non-acid bearing compounds were not detected, with the exception of levoglucosan, which was detected as a cluster with \(CH_3C(O)O^-\). Interestingly, the majority of the acids have more uniform sensitivities, with less than a factor of 4 difference, as compared to Figures 3.1a and 3.1c. In addition, small compounds such as formic, glyoxylic and pyruvic acids (C<3) and large organic compounds show similar sensitivities. The results demonstrate that \(CH_3C(O)O^-\) reagent ions are selective to acids in general, in accord with the work of (Veres et al. 2008). However, compounds with non-acid functionality (levoglucosan) were also observed clustering with \(CH_3C(O)O^-\).

3.1.3 Iodide

\(I(H_2O)_n^-\) reagent ions data are shown in Figure 3.1c. The ionization by Reaction 2.3 has been described earlier (Caldwell and Kebarle 1984) and used extensively in atmospheric studies (Thornton and Abbatt 2005, Zhao et al. 2012). The ionization depends on the ability of the organic compounds to hydrogen bond with the iodide anion. In addition, since iodide is a large polarisable anion, compounds with large polarisability, such as compounds with high molecular weight and those containing double bonds, will be better detected. As can be seen in Figure 3.1c, multi-functional compounds with C>3 can be detected with very similar sensitivities. Those compounds are di-acids, tri-acids and alcohols, all of which can participate in hydrogen bonding.
with the iodide and at the same time are more polarisable by size. Glyoxylic acid, which has an aldehydic and an acidic groups, was also detected with a good sensitivity similar to the multi-acids. This is possibly due to the fact the aldehydic hydrogen is slightly electron deficient and thus can form a hydrogen bond with the iodide. The aldehydes, glyoxal and methylglyoxal, were not detected well. These two aldehydes have been previously detected in the hydrated gas phase forms after volatilization from a solution using iodide reagent ions (Zhao et al. 2012). However, these previous measurements using aerosol-CIMS were carried out at lower heated inlet temperatures (110°C). Thus, it is possible that dehydration of the aldehydes was more efficient at 150°C, which was the temperature used in this study. As a result, the ability of binding to iodide is reduced.

3.2 WSOC and Aqueous Photo-Oxidation Processing

Four hour aqueous photo-oxidation experiments of the WSOC were followed using the CI-ToFMS using the three reagent ions. In all cases the control experiments (not shown) conducted with either H₂O₂ present but not light, or vice versa, showed negligible chemical change as compared to the photo-oxidation results arising from when both are present. As a result, data from photo-oxidation experiments are presented.

3.2.1 Raw Mass Spectra

Mass spectra were collected every second for 4 hours of oxidation. The mass spectra obtained for the WSOC before oxidation and after 2 and 4 hours of oxidation are shown in Figure 3.2. As the reaction proceeds, regions where ions decay are shown in the left spectra and regions where ions form are shown in the right spectra. In addition, all spectra before the oxidation was initiated show two humps, monomers and dimers regions, where the monomer region corresponds to ions with molecular weight similar to pinonic and pinic acids i.e. primary oxidation products of α-pinene. Dimeric species are thought to arise via ester, acetal and peroxy-acetal formation. It is clear that the dimer regions in the three reagent ions spectra are decaying during photo-oxidation without any formation observed in that region. In addition, the majority of the products formed after 2 and 4 hours of oxidation lie in a lower molecular weight monomer region. This is one indication that fragmentation (and functionalization) reactions are possibly occurring within the organic species during oxidation. By comparing the time dependent spectra of the dimer to monomer region in the iodide spectra, it is clear that the dimers decay at a much faster rate
compared to the monomers, which show slow decay. This could be due to the fact that dimer reactions lead to monomers (fragmentation), which subsequently appear as if the monomers are slowly reacting.

**Figure 3.2:** Mass spectra of the photo-oxidized SOA using the three reagent ions, water \((\text{H}_2\text{O})_n\text{H}^+\), acetate \(\text{CH}_3\text{C}(\text{O})\text{O}^-\) and iodide \(\text{I}(\text{H}_2\text{O})_n^-\), at time 0, 2 and 4 hours. The spectra on the left show the m/z regions where the intensity decreased indicating loss of signal. The spectra on the right show the m/z regions where the intensity increased for some ions illustrating products formation. Monomer and dimer regions were observed in the spectra of the three reagent ions, most clearly in the iodide spectra.

The observation that the iodide spectra are showing the largest and most clear decay compared to \(\text{CH}_3\text{C}(\text{O})\text{O}^-\) and \((\text{H}_2\text{O})_n\text{H}^+\) spectra may be due to gas phase ion cluster formation for the two latter reagent ions. To illustrate, it was observed (not shown) in the sensitivity test (Section 3.1) the presence of ions for \((\text{H}_2\text{O})_n\text{H}^+\) and in \(\text{CH}_3\text{C}(\text{O})\text{O}^-\) reagent ions, which was not expected based on Reactions 2.1 and 2.2. These ions form by gas phase clustering between ions formed in
Reactions 2.1 and 2.2 and with non-ionized analyte compounds, and thus show up as a high molecular weight ion. These gas phase ion clusters can be a combination of 1) an analyte ion and another analyte or 2) an analyte ion and a reagent ion related species such as H\textsubscript{2}O clusters or Acetic acid/acetic anhydride. Such ions did not show up in the iodide spectra. As a result, the dimer region in (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+} and in CH\textsubscript{3}C(O)O\textsuperscript{−} contains a combination of real aqueous phase dimers, such as those that appear in the iodide spectra, and gas phase ion clusters.

### 3.2.2 Ion Assignment and Speciation

Peak fitting was performed for all three reagent ion spectra covering chemical formulas with molecular weights up to 300 u (m/z 301, m/z 299 and m/z 427 for (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+}, CH\textsubscript{3}C(O)O\textsuperscript{−} and I(H\textsubscript{2}O\textsubscript{n})\textsuperscript{−}, respectively). Peaks higher than 300 u cannot be unambiguously assigned for the (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+}, CH\textsubscript{3}C(O)O\textsuperscript{−} reagent ions. Chemical formulas were assigned for odd m/z based on selection criteria governed by the following chemical formula C\textsubscript{n}H\textsubscript{2n+2}O\textsubscript{x}, where formulas assigned cannot have a number of hydrogen atoms greater than 2n+2 for a given carbon number equal to n. The peaks were fit with the minimum number of ions such that a residual area (un-fitted area) of less than 5% is achieved. Isotopic patterns were used to confirm ion assignments in some cases. The number of ions assigned were 595, 555 and 428 for (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+}, CH\textsubscript{3}C(O)O\textsuperscript{−} and I(H\textsubscript{2}O\textsubscript{n})\textsuperscript{−}, respectively. The smaller number of ions assigned for the same chemical composition with I(H\textsubscript{2}O\textsubscript{n})\textsuperscript{−} compared to the other reagent ions is an indication of the selectivity of I(H\textsubscript{2}O\textsubscript{n})\textsuperscript{−}. The ion chemical formulas were corrected for the proton added when using (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+}, and subtracted in the case of CH\textsubscript{3}C(O)O\textsuperscript{−}, such that the neutral chemical formula of the analytes was used for calculations and plotting. Gas phase ion clusters cannot be separated from non-cluster ions that appear at the same m/z as both could have the same chemical formula.

From the ion lists generated from the spectra, hydrogen-to-carbon ratios (H/C), oxygen-to-carbon ratios (O/C) and the number of carbon atoms (#C) were derived for the individual chemical formulas. The carbon oxidation state (OS\textsubscript{C}) was calculated as described in Kroll et al. (2011) by the approximation OS\textsubscript{C} ≈ 2O/C + H/C. The distribution of the 4 parameters H/C, O/C, OS\textsubscript{C} and #C for the ions lists is shown in Figure 3.3 as percentile box plots. The ions assigned in the (H\textsubscript{2}O\textsubscript{n})\textsuperscript{+} spectra cover noticeably narrower H/C, O/C and OS\textsubscript{C} ranges as compared to CH\textsubscript{3}C(O)O\textsuperscript{−} and I(H\textsubscript{2}O\textsubscript{n})\textsuperscript{−}. In addition, the H/C distribution spans a higher H/C region ranging from 1 to 2 compared to 0.6-2 for the other reagent ions. Lower O/C and OS\textsubscript{C} values for all the
percentiles are also observed for \((\text{H}_2\text{O})\text{nH}^+\). The \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I(\text{H}_2\text{O})n}^-\) percentiles for the 4 parameters are very similar overall. This indicates that the assigned ions in the two reagent ions spectra are similar, although with some selectivity associated with \(\text{I(\text{H}_2\text{O})n}^-\). These results are consistent with the observation in Section 3.1, where highly oxygenated multi-functional organics were detected with high sensitivity with \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I(\text{H}_2\text{O})n}^-\) but not with \((\text{H}_2\text{O})\text{nH}^+\). It is noted also that these two reagent ions (\(\text{CH}_3\text{C(O)O}^-\) and \(\text{I(\text{H}_2\text{O})n}^-\)) can detect some species with extremely high \(\text{OS}_\text{C}\), approaching 3.7 and 4, and \(\text{O/C}\), approaching 2.75 and 3, respectively.

**Figure 3.3:** Box plots showing the 10\(^{\text{th}}\), 25\(^{\text{th}}\), 50\(^{\text{th}}\), 75\(^{\text{th}}\) and 90\(^{\text{th}}\) percentiles for H/C, O/C, OS\(_\text{C}\) and \#C for the pool of ions detected by each reagent ion. The population size was 595, 555 and 428 ions for \((\text{H}_2\text{O})\text{nH}^+\), \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I(\text{H}_2\text{O})n}^-\), respectively.

### 3.2.3 The Van Krevelen Plot

The intensity of each ion together with the H/C and O/C values were used to calculate the intensity weighted average elemental ratios, \(\overline{\text{H/C}}\) and \(\overline{\text{O/C}}\). This allows plotting the time dependent \(\overline{\text{H/C}}\) and \(\overline{\text{O/C}}\) for the photo-oxidation reaction in a Van Krevelen diagram (Heald et al. 2010, Ng et al. 2011). One question of interest is the degree to which Van Krevelen diagram is
similar to data that are derived from the AMS instrument. Figure 3.4b expands the Van Krevelen diagram to emphasize the differences between the data for the CI-ToFMS three reagent ions and the AMS. As a reference point, it is interesting that the slope of the linear fit of the AMS data is -0.48, which is essentially the same as the slope of -0.5 found by (Ng et al. 2011) from a compilation of aerosol ambient data affected by aging. As well, Figure 3.4a illustrates that the CI-ToFMS and AMS data largely overlap in the H/C and O/C spaces, with the CI-ToFMS data lying within the accuracy range of the AMS data. This close agreement is somewhat surprising given the use of uncalibrated CI-ToFMS ion intensity, which is not necessarily a good approximation to the true analyte abundances. As well, the AMS detects only particle phase organics while the aerosol-CI-ToFMS detects both gas and particles phase components.

Figure 3.4: Van Krevelen diagram of the AMS and CI-ToFMS data for the WSOC aqueous phase photo-oxidation using the three reagent ions. The plot on the right is an expanded view of the plot on the left. The time scale covers the 4 hours of photo-oxidation moving from light to dark bolded symbols. The dark blue dashed lines are the parameterized O/C and H/C from the triangle plot compiling a large dataset of ambient and laboratory data as described in (Ng et al. 2011) Note that although AMS measurements were conducted for each experiment, for clarity sake only one set of data is plotted here; the other experiments gave similar results. The linear fit for the AMS data, which is shown in orange, had a slope of -0.48. The error bars of the AMS H/C and O/C are shown in gray obtained from the H/C and O/C accuracies of 10% and 30% reported in (Aiken et al. 2007).

Figure 3.4b highlights the differences between the three CI-ToFMS reagent ions. The data show that the maximum $\overline{O/C}$ obtained with $(\text{H}_2\text{O})_n\text{H}^+$ was 0.53, while CH$_3$C(O)O$^-$ and I(\text{H}_2\text{O})_n$ maxima were 0.75 and 0.71. This illustrates the inability of $(\text{H}_2\text{O})_n\text{H}^+$ reagent ions to efficiently
ionize highly oxygenated organics, especially those present at the end of the oxidation reaction. Correspondingly, the trajectory of the \((\text{H}_2\text{O})_n\text{H}^+ \text{O}/\text{C}\) and \(\text{H}/\text{C}\) data series always lags in time behind those for \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I}(\text{H}_2\text{O})_n^-\). On the other hand, \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I}(\text{H}_2\text{O})_n^-\) follow a similar path in \(\text{O}/\text{C}\) as the reaction proceeds. However, their \(\text{H}/\text{C}\) values slightly diverge at \(\text{O}/\text{C}\) of 0.6, where the \(\text{I}(\text{H}_2\text{O})_n^-\) data stay closer to the AMS data. As discussed in Section 3.1.2, \(\text{CH}_3\text{C(O)O}^-\) reagent ions allow for efficient detection of carboxylic acids in general and show no discrimination in ionizing small acids, which are relatively volatile (or semi-volatile) and are not detected by the AMS. Thus, more volatile species with higher H/C may be detected by \(\text{CH}_3\text{C(O)O}^-\) causing a divergence from the AMS data. On the other hand, \(\text{I}(\text{H}_2\text{O})_n^-\) reagent ions are more efficient in ionizing large acids compared to small acids, and in detecting large, multifunctional organics. Thus, it is reasonable that the \(\text{I}(\text{H}_2\text{O})_n^-\) data converge to those from the AMS, given that the CIMS data are likely dominated by particle-phase species.

3.2.4 The Difference Kroll Diagram

The 2D space of the other two parameters \(\text{OS}_C\) and \#C, the so-called Kroll diagram, can also be used to obtain more informative evidence on the nature of chemical change (Kroll et al. 2011). In a typical Kroll diagram, the \(\text{OS}_C\) is plotted as a function of \#C. Here, the CI-ToFMS is advantageous over the AMS as it provides carbon number information directly for individual ions. This feature of CI-ToFMS arises from the soft ionization ability that frequently retains the ions intact without fragmentation. In addition, the CI-ToFMS provides a means by which bulk or individual compound \(\text{OS}_C\) and \#C values can be obtained. The \(\overline{\text{OS}_C}\) and \(\overline{\#C}\) are the intensity weighted averages of \(\text{OS}_C\) and \#C summed over all individual ions.

In order to observe a change in the \(\text{OS}_C\) and \#C distribution for individual compounds over the 4 hours of photo-oxidation, a difference-Kroll diagram was constructed as shown in Figure 3.5. In the difference-Kroll diagram the intensities of ions with the same co-ordinates on the plot are summed at time 0 and 4 hours. The Kroll diagram information at time 4 hours is subtracted from that at time 0 hours. Coordinates with positive intensity are those that decay away and are marked in light coloured solid circles. Negative intensities indicate coordinates where ions have formed after 4 hours of photo-oxidation and are marked in solid dark coloured circles. The highest \(\text{OS}_C\) in the difference Kroll diagram for \((\text{H}_2\text{O})_n\text{H}^+\) is 1.33. On the other hand, the plots for \(\text{CH}_3\text{C(O)O}^-\) and \(\text{I}(\text{H}_2\text{O})_n^-\) clearly show many occupied coordinates with \(\text{OS}_C\) reaching \(\text{OS}_C\) of
Figure 3.5: Difference Kroll diagrams for the WSOC before oxidation and after 4 hours of oxidation using the three reagent ions; (H_2O)_nH^+, CH_3C(O)O^- and I(H_2O)_n-. Light bolded circles indicate coordinates where ions formed while dark bolded circles indicate ion losses. The average OS_C and #C are also shown over 4 hours of oxidation. The size of marker indicates the magnitude of the subtracted intensity.
4, i.e. very highly oxidized species, with C# well less than 10. All three reagent ion difference Kroll diagrams show that the majority of the ions formed after 4 hours of oxidation have a lower carbon number and higher oxidation state compared to the original state, consistent with a large degree of functionalization and fragmentation occurring in the reaction (Kroll et al. 2009). In addition, the vertical distribution (\(\text{OS}_C\)) of the ions in the \(\text{I(H}_2\text{O)}\) \(\text{I}\) Kroll diagram is narrower compared \(\text{CH}_3\text{C(O)O}^\cdot\), which is consistent with the selectivity observed for \(\text{I(H}_2\text{O)}\) \(\text{I}\) in Section 3.1.3.

The \(\text{OS}_C\) and \(\#C\) reflect how the whole distribution is moving over 4 hours of oxidation. The change in \(\text{OS}_C\) and \(\#C\) is most obvious with \(\text{CH}_3\text{C(O)O}^\cdot\) and \(\text{I(H}_2\text{O)}\) \(\text{I}\) reagent ions while a small change is observed in the \(\text{H}_2\text{O)}\) \(\text{H}^+\) Kroll diagram, in large part because this latter reagent ion is insensitive to many of the more highly oxidized species that are forming. In all three cases, the \(\text{OS}_C\) and \(\#C\) trajectory indicates that both fragmentation and functionalization reactions are taking place. Note that one caveat in comparing overall intensities of one coordinate on the Kroll diagram to another is that the sensitivity may vary from species to species. As illustrated above through our sensitivity analyses, this variation is expected to be much less for \(\text{CH}_3\text{C(O)O}^\cdot\) and \(\text{I(H}_2\text{O)}\) \(\text{I}\) than for \(\text{H}_2\text{O)}\) \(\text{H}^+\).
Chapter 4
Kinetics

4 Rate Constant Determination

4.1 Relative Rate Method

The relative rate method was applied in this work for rate constant determination. The advantage of this technique is that the OH radical concentration need not be monitored. Also, the exact concentration of the reactants does not need to be known accurately (Finlayson-Pitts 2000). The relative rate method can be used when the rate constant for the reaction of OH with a reference compound ($k_{\text{reference}}$) is well known (Finlayson-Pitts 2000). In such experiments, the reference compound and the compound with unknown rate constants are mixed in the same reaction cell with the oxidant OH as illustrated in Reactions 4.1 and 4.2.

\[
\text{OH} + \text{Reference} \xrightarrow{k_{\text{reference}}} P_{\text{reference}} \tag{Reaction 4.1}
\]

\[
\text{OH} + \text{Unknown} \xrightarrow{k_{\text{unknown}}} P_{\text{unknown}} \tag{Reaction 4.2}
\]

The following equations can be written for reactions 4.1 and 4.2.

\[
\ln \left( \frac{[\text{Unknown}]_t}{[\text{Unknown}]_0} \right) = k_{\text{unknown}} [\text{OH}]_0 t \tag{Equation 4.1}
\]

\[
\ln \left( \frac{[\text{Reference}]_t}{[\text{Reference}]_0} \right) = k_{\text{reference}} [\text{OH}]_0 t \tag{Equation 4.2}
\]

Equation 4.2 can be divided by equation 4.1 and then rearranged to give 4.3.

\[
\ln \left( \frac{[\text{Unknown}]_t}{[\text{Unknown}]_0} \right) = \frac{k_{\text{unknown}}}{k_{\text{Reference}}} \ln \left( \frac{[\text{Reference}]_t}{[\text{Reference}]_0} \right) \tag{Equation 4.3}
\]

Equation 4.3 shows that plotting $\ln \left( \frac{[\text{Unknown}]_t}{[\text{Unknown}]_0} \right)$ against $\ln \left( \frac{[\text{Reference}]_t}{[\text{Reference}]_0} \right)$ should yield a straight line with slope $= \frac{k_{\text{unknown}}}{k_{\text{Reference}}}$. The measured slope and the $k_{\text{reference}}$ obtained from the literature allow for the $k_{\text{unknown}}$ to be determined.
4.1.1 cis-Pinonic Acid

 cis-Pinonic acid (PIN) is a mono-acid with a $pK_a = 4.82$ (Howell and Fisher 1958). Thus, it can exist in the protonated form (PIN) or as pinonate anions (PINn) in the aqueous phase. Previous studies have shown differences exist in the measured rate constants for the aqueous OH reaction with mono-acids (e.g., PIN) compared to the dissociated form of the same acids (e.g., PINn) (Ervens et al. 2003). Thus, to determine the rate constant for the reaction of OH with PIN, it was important to control the pH. The fraction of each form (PIN and PINn) is dependent on the pH of the solution and can be calculated by:

$$\alpha = \frac{[AH]}{[AH] + [A^-]} = \frac{[H^+]}{[H^+] + K_a},$$

Equation 4.4

Where $\alpha$ is the ionization fraction, $[AH]$ is the concentration of the mono-acid, $[A^-]$ is the concentration of the dissociated mono-acid, $[H^+]$ is the concentration of $H^+$ and $K_a$ is the acid dissociation constant. Using equation 4.1 to calculate $\alpha$ for PIN at pH = 2, yields $\alpha = 99.8\%$, which indicates that the majority of the PIN is not dissociated at that pH. As a result, sulfuric acid was added to 10 $\mu$M of PIN solution to adjust the pH to 2 for the kinetics experiments. Because sulfuric acid is a strong acid that was present in the solution at high concentration, when the CI-ToFMS was operated in negative mode (Acetate and Iodide reagent ions), large sulfuric acid peaks were observed in the spectra with intensities higher than the reagent ions. For this reason, $(H_2O)_nH^+$ reagent ions were used to run the kinetic experiments at low pH as sulfuric acid peaks were absent.

DMSO was the reference compound selected to run relative rate kinetics for PIN. The rate constant for DMSO with respect to reaction with OH, $k_{DMSO} = 6.9 (\pm 0.1) \times 10^9$ M$^{-1}$ s$^{-1}$ (at 301 K) was obtained from (Zhu et al. 2003). It is important to note here that a database exists for OH reaction rate constants for a wide range of compounds, which could be used as reference
compounds other than DMSO (NIST 2002, Herrmann et al. 2010). However, DMSO is unique in that it cannot be produced as a product from the reaction of PIN with OH. Also, PIN oxidation products do not overlap with DMSO at the same m/z 79 that is used to follow DMSO decay. The oxidation of DMSO also does not interfere with the signal of PIN at m/z 185, which was used to follow the decay of PIN. This was confirmed by carrying out oxidation experiments for DMSO and PIN separately and monitoring m/z 79 and 185 in both experiments. Also, it was assumed that DMSO was not protonated in water at pH=2.

Figure 4.1 illustrates the kinetics data obtained for PIN and DMSO for three runs. It can be seen that highly linear relationships were obtained for the three experiments with a y-intercept close to 0. Using the average slope in Figure 4.1 and $k_{DMSO}$ value from (Zhu et al. 2003) and using equation 4.4, $k_{PIN}$ was measured to be $3.4 \times 10^9$ M$^{-1}$ s$^{-1}$ at 301 K in a solution at pH = 2.

![Figure 4.1](image-url)

**Figure 4.1:** Plot of 36 minutes of kinetics data for PIN rate constant determination using equation 4.4. The different colours represent triplicate runs. The average of the three slopes is shown with the rate constant of the reference compounds (DMSO) and the calculated rate constant for PIN.
The measured rate constant for PIN is within the diffusion limit of aqueous phase reactions of organics with OH ($10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) (Ervens et al. 2011). The measured rate indicates that the reaction of PIN with OH is generally fast in the aqueous phase and is a potential sink for PIN in atmospheric aqueous media.

The same experiments were run at pH = 10 to assess the rate constant for PINn. However, with the same reagent (PIN and H$_2$O$_2$) concentrations as in the pH = 2 experiments, PIN was not detected with CI-ToFMS with the three reagent ions. This problem was possibly due to the presence of the counter ion (Na$^+$) from the base added (NaOH) to adjust the pH in the solution. Na$^+$ either a) formed the salt with PINn in the reaction bottle and thus precipitated out PIN in the form of NaPINn or b) the salt formed in the heated inlet as the droplets from the atomized solution were heated and water evaporated. A solution for this problem would be trying a different base (YOH) to increase the pH, such that the counter ion (Y$^+$) effect is minimized. However, since the concentration of H$^+$ is $10^{-10}$ M compared to $10^{-4}$ M for Na$^+$ (or Y$^+$) under these conditions, PINn would preferentially form the salt with Na$^+$ (or Y$^+$), which is 6 orders of magnitude higher than that of H$^+$. Thus, the choice of YOH (the base) should be such that Y$^+$ forms a salt with PINn (pinonate) with solubility constant ($K_{sp}$) that is 6 orders of magnitude higher than that of NaPINn (the sodium salt of PIN). Another possibility is using ammonium salts or bases. However, the presence of ammonia in high concentration in solution might result in depleting the (H$_2$O)$_n$H$^+$ reagent ions. Thus, acetate or iodide reagent ions need to be used with a reference compound different than DMSO.

4.1.2 Tricarballylic Acid

3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) has recently been identified and used as a tracer for biogenic SOA aged by the chemical reaction with OH (Szmigielski et al. 2007, Zhang et al. 2010, Mueller et al. 2012). However, the stability of MBTCA in the atmospheric aqueous
phase in the presence of OH has not been assessed before. Thus, experiments were carried out in order to estimate the rate constant for OH reaction with MBTCA in the aqueous phase. Since MBTCA was not commercially available, tricarballylic acid (TCA), a surrogate compound similar to MBTCA in structure, was used in this work to determine an estimated rate constant for MBTCA reaction with OH. TCA is a tri-acid with three acid dissociation constants in water, pKa\textsubscript{1}=3.47, pKa\textsubscript{2}=4.54 and pKa\textsubscript{3}=5.89 (Campi et al. 1964). Thus, it can be found in the aqueous phase in four forms that are different in the extent of dissociation, which is dependent on the solution pH. Figure 4.2 shows the distribution of the different forms of TCA at different pH calculated from the given pKa values. It is clearly shown that a minimum of two forms can exist simultaneously in the pH range of ~1-8, which indicates that a single form of TCA cannot be isolated alone. The extreme cases, at pH less than 1 and greater than 8, show that the fully protonated and dissociated forms of TCA can be isolated. However, those pH ranges are not relevant to atmospheric cloud water. Several studies have measured the acidity of ambient cloud water droplets and showed that cloud droplet water is acidic with an average pH ~ 4.5 (Guo et al. 2012, Gioda et al. 2012, Ervens et al. 2012). Thus, under atmospheric relevant condition, several forms of dissociated TCA (or MBTCA, assuming similar pK\textsubscript{a}’s) could exist at once. In addition, according to figure 4.2, at pH = 3.5 to 6, the majority of TCA is found in the first and second dissociated forms, both of which cannot be isolated in solution. As a result, attempts were not

\textbf{Figure 4.2:} fraction of the four dissociated forms of TCA and PRP (propanoic acid) at pH range from 0 to 9. α\textsubscript{1} is the non-dissociated form, α\textsubscript{4} is the fully dissociated form and α\textsubscript{2} and α\textsubscript{3} are the first and second dissociated forms of TCA.
made to adjust the pH and the experiments were run at free pH (4.6) for rate constant determination for the reaction of TCA with OH.

The CI-ToFMS was operated with the acetate reagent ions. This is because TCA was not detected with \((\text{H}_2\text{O})_n\text{H}^+\) reagent ions. Also, DMSO, the reference compound, was not detected with the acetate reagent ions and detected with very poor sensitivity with the iodide reagent ions. Thus, propanoic acid (PRP) was the reference compound used to run the relative rate method to determine TCA. PRP was chosen for several reasons 1) it can be detected with the acetate reagent ions in parallel with TCA, 2) PRP \((\text{C}_3\text{H}_6\text{O}_2)\) shows up as a peak at m/z 73 in the acetate reagent ion spectra, which can be separated from TCA oxidation products appearing at the same nominal m/z 73, 3) PRP oxidation does not lead to products with the same chemical formula as TCA at m/z 175 and 4) TCA oxidation does not lead to products with the same chemical formula as that of PRP. The pK\(\alpha\) of PRP is 4.87 (Ervens et al. 2003) and thus PRP exists in the protonated (PRP) and dissociated (PRP\(n\)) forms as shown in Figure 4.2. The reported rate constant for the reaction of OH with PRP is \(k_{\text{PRP}} = 3.2 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}\) and with PRP\(n\) is \(k_{\text{PRP}n} = 7.2 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}\) (Ervens et al. 2003). At pH = 4.48, \(\alpha_1=0.65\) and \(\alpha_2=0.35\) for PRP. Thus an estimated rate constant for PRP was calculated using \(\alpha\) weighted average rate constant of PRP and PRP\(n\) \((\bar{k}_{\text{PRP}} = 4.6 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1})\). Figure 4.3 shows the data collected for the TCA rate constant using Equation 4.4. As illustrated, the data for two runs yield a straight line with a y-intercept close to 0. \(\bar{k}_{\text{PRP}}\) and the average slope of the two runs were used to calculate the rate constant for the reaction of OH with TCA, which was determined to be \(k_{\text{TCA}} = 3.1 (\pm 0.3) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}\) at 301 K in a solution at pH = 4.6. The measured rate constant is similar to the rate constant reported for the diacid, succinic acid \((k_{\text{succinic acid}} = 1.1 (\pm 0.1) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}\), \(k_{\text{succinate}} = 5.0 (\pm 0.5) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}\)) (Ervens et al. 2003).

Since MBTCA is similar in structure to TCA, it is expected the rate constant for MBTCA to be similar to that of TCA. The difference in the presence of two methyl groups on the MBTCA backbone compared to TCA might alter the reactivity and pK\(\alpha\)’s slightly. Nevertheless, the results show that MBTCA in SOA that is involved in CCN activation or exposed to high relative humidity (RH\%) can be degraded by OH oxidation while in the aqueous phase. After water evaporation takes place, the resultant particle would have a different MBTCA concentration compared to the initial concentration in the particle before water uptake. The results illustrate that the use of MBTCA as a tracer compound for SOA from a biogenic source might need to be
reconsidered, especially in cloudy environments. Most studies assume that MBTCA is stable after being produced in the gas phase oxidation of biogenic organics (Szmigielski et al. 2007, Zhang et al. 2010, Mueller et al. 2012). However, for successful use of receptor models for source apportionment, the atmospheric tracer compounds used to run the model need to be chemically stable from their sources through their transport in the atmosphere to the location where they are detected (Schauer et al. 1996).

**Figure 4.3:** Plot of 55 minutes of kinetics data for TCA rate constant determination using equation 4.4. The different colours represent two runs. The average of the two slopes is shown with the rate constant of the reference compounds (PRP) and the calculated rate constant for TCA.

### 4.2 Steady State OH Concentration

The measurement of the OH concentration is essential as it allows assessment of the relevance of the experimental conditions used in this study to ambient conditions. The concentration of OH was estimated from the rate constants measured for PIN and TCA, assuming that it is in steady

\[
\begin{align*}
    k_{\text{Propanoic acid}} &= 4.6 (\pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \\
    k_{\text{Tricarballylic acid}} &= 3.1 (\pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}
\end{align*}
\]

\[
\begin{align*}
    Y &= 0.62 (\pm 0.02) X + 0.014 (\pm 0.008) \\
    Y &= 0.72 (\pm 0.02) X + 0.027 (\pm 0.009)
\end{align*}
\]

**Average slope** = 0.67017
state throughout the reaction. The pseudo first-order integrated first law was used for this purpose, which is shown below.

\[ \ln \left( \frac{X_t}{X_0} \right) = k [OH_{ss}] t \] \hspace{1cm} \text{Equation 4.4}

Plotting \( \ln \left( \frac{X_t}{X_0} \right) \) as a function of time, should yield a straight line with slope \( = k [OH_{ss}] \). The measured slope from the fitted straight line and the rate constants measured in sections 4.1.1 and 4.1.2 allow for solving for the steady state concentration of OH, \([OH_{ss}]\).

**Figure 4.4:** Steady state OH concentration measurement for the SOA photo-oxidation experiments with the three reagent ions.

**Figure 4.5:** Steady state OH concentration measurement for PIN and TCA oxidation mechanism experiments described in chapter 5.

Figure 4.4 shows the kinetics data used to calculate the \([OH_{ss}]\) for SOA photo-oxidation experiments using PIN decay for calculations. The measured concentration is close to modeled
OH concentration in cloud water studies, which is in the range of $10^{-12} - 10^{-13}$ M. (Jacob 1986, Herrmann et al. 2010). Similar $[\text{OH}_s]$ for PIN and TCA oxidation experiments were also measured with respective values of $1.7 \times 10^{-13}$ M and $3.4 \times 10^{-13}$ M (Figure 4.5).
Chapter 5
Mechanisms

5 Possible Products and Reaction Pathways

5.1 Aqueous Phase OH Oxidation

The mechanisms for aqueous phase photo-oxidation of organics are qualitatively similar to those found in the gas phase with some differences arising from the different intermediates formed and the interference from the aqueous solvent (von Sonntag and Schuchmann 1991, von Sonntag et al. 1997, Herrmann 2003). Generally, reactions are initiated by a hydrogen abstraction by OH, but OH addition to aromatics has also been observed (Herrmann 2003). This is followed by a reaction between the alkyl radical formed and molecular oxygen \((O_2)\) to form peroxy radical \((RO_2)\). Peroxy radicals have several fates in the aqueous phase. As in the gas phase, \(RO_2\) can react with \(HO_2\) or \(RO_2\) in solution to form alkoxy radicals \((RO)\) or carbonyl, alcohol, peroxide compounds (Orlando and Tyndall 2012). This happens via the formation of tetraoxide intermediate, which forms from the bimolecular reaction of \(RO_2\) (or \(HO_2\)) as illustrated in Reaction 5.1 (von Sonntag and Schuchmann 1991, von Sonntag et al. 1997). The fate of the tetraoxide is shown in Reaction 5.2 through 5.5 (von Sonntag and Schuchmann 1991, von Sonntag et al. 1997).

\[
\text{R}_2\text{CH} - \text{O}_2 + \text{R}_2\text{CH} - \text{O}_2 \rightarrow \text{R}_2\text{CH} - \text{OOOO} - \text{CHR}_2 \quad \text{Reaction 5.1}
\]

\[
\text{R}_2\text{CH} - \text{OOOO} - \text{CHR}_2 \rightarrow \text{R}_2\text{C}(O) + \text{R}_2\text{CHOH} + \text{O}_2 \\
\quad \rightarrow 2 \text{R}_2\text{C}(O) + \text{H}_2\text{O}_2 \\
\quad \rightarrow 2 \text{R}_2\text{CHO}^- + \text{O}_2 \quad \text{Reaction 5.3}
\]

\[
\text{R}_2\text{CH} - \text{O}_2 + \text{R}_2\text{CH} - \text{O}_2 \rightarrow \text{R}_2\text{CH} - \text{OOOO} - \text{CHR}_2 \\
\quad \rightarrow 2 \text{R}_2\text{C}(O) + \text{H}_2\text{O}_2 \\
\quad \rightarrow 2 \text{R}_2\text{CHO}^- + \text{O}_2 \quad \text{Reaction 5.4}
\]
\[ \rightarrow R_2\text{CHOOCR}_2 + O_2 \] 

Reaction 5.5

While the tetraoxide chemistry have been observed in previous studies, it is likely that the role it plays in photo-oxidation reactions in this work is minor. In particular, the tetraoxide intermediate has been observed in studies, where the $RO_2$ concentration is greater than 50 µM (vonSonntag and Schuchmann 1991). This limit of $RO_2$ concentration is higher than the total reactants concentrations in this work, i.e., 20 µM for DMSO/PIN and 30 µM for TCA/PRP, which implies that the $RO_2$ concentration must be lower than the 50 µM reported for the appearance of tetraoxide.

In addition, the fact that the reaction takes place in an aqueous medium allows hydration to proceed. For example, aldehydes strongly hydrate in water forming geminal diols (Reaction 5.6).

\[
\begin{align*}
\text{H}_2\text{O} \quad &\quad \text{R} \quad \text{H} \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{R} \quad \text{OH} \quad \text{OH} \\
\end{align*}
\]

Reaction 5.6

In the presence of OH, the geminal hydrogen is abstracted from the hydrated alkyl radical ($\text{RC(OH)}_2\cdot$) (Ervens et al. 2003). The alkyl radical reacts with oxygen to form a hydrated peroxy radical ($\text{RC(OH)}_2\text{OO}\cdot$). The peroxy radical rapidly decomposes to form the corresponding acid and HO$_2^\cdot$.

\[
\begin{align*}
\text{R} - \text{CH(OH)}_2 + \text{OH} &\rightarrow \text{R} - \text{C(OH)}_2\cdot + \text{H}_2\text{O} \\
\text{R} - \text{C(OH)}_2\cdot + \text{O}_2 &\rightarrow \text{R} - \text{C(OH)}_2\text{OO}^\cdot \\
\text{R} - \text{C(OH)}_2\text{OO}^\cdot &\rightarrow \text{R} - \text{C(O)}\text{OH} + \text{HO}_2 \\
\end{align*}
\]

Reaction 5.7, Reaction 5.8, Reaction 5.9

This aldehyde processing pathway is unique to the aqueous phase and does not occur in gas phase oxidations.

The general aqueous phase oxidation pathways discussed here were applied to investigate the oxidation of TCA and PIN. The results are discussed in the next section.
5.1.1 Tricarballylic Acid

As discussed earlier, TCA was used in this study as a surrogate compound to help understand MBTCA oxidation chemistry in the aqueous phase. Figure 5.1 shows the proposed mechanism for TCA oxidation, where products coloured in gray were not observed. TCA is shown in the fully protonated form in Figure 5.1 but it is important to note that multiple dissociated forms of TCA would follow the same pathways. Products that are structural isomers are labeled with the same colour as they appear at the same m/z. The OH radical abstracts a hydrogen atom on the tertiary (pathway 1) or secondary carbon (pathway 2). This is supported by previous observations from dicarboxylic acid reactions with OH (Herrmann 2003). Then molecular oxygen reacts with the alkyl radicals to form two peroxy radicals.

**Figure 5.1:** Proposed reaction mechanism for TCA oxidation by OH radicals in the aqueous phase. The colouring of the compounds follows the time profiles shown in Figure 5.2. Gray compounds were proposed but either were not detected or showed no change in signal.

The peroxy radical on the tertiary carbon must result in a decomposition (pathway 1) of the TCA backbone leading to a carbon-carbon bond breakage. Due to the symmetry of TCA around the
tertiary carbon, two possible C-C bonds can be cleaved (P1.1/P1.2). The resultant products from the cleavage are C5.1 through P1.1 and C4.1/C2.1 through P1.2. These are thought to be the first generation products formed from P1. However, as indicated in Figure 5.1, the C4.1 (gray) product from P1.2 did not show change in signal over the reaction time. This C4.1 compound is also proposed to be produced by several other pathways in the mechanism. This could suggest that pathways leading to C4.1 compound such as P2.1 and P2.1.1 are not favourable or do not proceed in the reaction system. Another possibility is that C4.1 has a low detection efficiency with the C-ToFMS. However, this is unlikely because compounds with similar structure (tartaric acid and succinic acid) were detected efficiently.

**Figure 5.2:** Time profiles for the decay of TCA oxidation and the evolution of selected products plotted over OH exposure. The chemical formulas are for the ions in the deprotonated form. The signal for each ion was scaled by the maximum signal each ion reached. All the product traces start from their minimum signal and the y-axis are not zeroed. Data is plotted in 1 min time resolution. OH exposure was calculated as the product of the time and the OHss measured in section 4.2. Labels in brackets follow Figure 5.1.

P2 in Figure 5.1 has three branches resulting from hydrogen abstraction by OH on the secondary carbon. Two pathways lead to C-C bond cleavage (P2.1 and P2.2) and one (P2.3) is due to O₂ abstraction of a hydrogen. P2.2 leads to the formation of C5.2a, a diacid compound with an aldehyde group. However, it is expected that C5.2b is also produced since both C5.2a and C5.2b both originate from the same pathway P2.2. Even if the aldehyde (C5.2a) was produced alone by P2.2, further reactions of C5.2a should lead to C5.2b. In addition, C5.2b has the same chemical
formula ($C_5H_6O_5$) as C5.1 formed by P1.1 (both labeled in green). This indicates that the signal detected was most likely not that of C5.2a but for C5.1.

P2.1 forms products (C3.2b malonic acid and C2.2 glyoxylic acid), which can also be produced by P1.1 with the exception of C3.2a, which is produced by P2.1 only. Figure 5.2 shows the evolution of C3.2b (purple), C2.2 (red) and C3.2a (pink). The traces for C3.2b and C2.2 show a very similar time profile, while C3.2a peaks earlier. In addition, the C5.1 diacid (green) from P1.1 also shows an earlier evolution compared to C3.1 and C2.1. This suggests that either P1.1 or P2.1 could be plausible pathways that lead to first generation products formation (C5.1 and C3.2a). However, since 1) malonic and glyoxylic acids show similar evolution over time (Figure 5.2) and 2) both appear as second (or later) generation products in Figure 5.2, then this suggests that the majority of malonic acid (C3.1) and glyoxylic acid (C2.1) originate from the same pathway. The common origin supports that pathway P1.1 is most likely the pathway that leads to their formation. Even though P2.1 is proposed to form malonic acid (C3.2b) and glyoxylic acid (C2.2), the two acids are not produced by the same branch in P2.1. To illustrate, C2.2 is produced by P2.1.1 and P2.1.3, while C3.2b is produced by P2.1.2. Also, P2.1.1 and P2.1.3 suggest that C2.2 is a first generation product, which opposes the observation in Figure 5.2, where C2.2 appears as a later generation product. The separate branches leading to the acids suggests that malonic and glyoxylic acids are not produced by P2.1. Figure 5.2 shows that C5.1 (green trace) clearly evolves early. This leads to the conclusion that C5.1 is a first generation product that leads to the formation of both malonic acid and glyoxylic acid simultaneously. However, that does not rule out the fact that P2.1.2 does proceed. The C3.2a early evolution is consistent with P2.1.2 that it is a first generation product. In addition, it can still contribute to malonic acid formation, however, the contribution might be minor as it is unlikely for P3.2a to form glyoxylic acid simultaneously with malonic acid. A confirmation of these conclusions could be drawn by running C3.2a oxidation and monitoring the products. The same applies to the C5.1 diacid.

The C6 products formed from P2.3 were also observed and appeared to form very early in the reaction as shown in Figure 5.2. These two C6 products seem to be very reactive with OH radicals. It is proposed that C6.2a reacts mostly with OH by a hydrogen abstraction on the carbon bearing the electron donating hydroxyl group to produce C6.2b. This is supported by the earlier onset and peak of C6.2a observed in Figure 5.2 compared to C6.2b. Since these two C6 products
seem to be reactive, their potential to produce malonic and glyoxylic acid was investigated as shown in Figure 5.3. As indicated, none of the oxidation pathways lead to the formation of malonic acid. While several pathways lead to glyoxylic acid formation, the parallel product resulting from the same branch were not detected (products in gray). This suggests that the proposed mechanism in Figure 5.3 is not plausible. However, since C6.2 compounds appeared to be forming and reacting in the reaction profile, products must be forming from them. Several reasons could explain this: 1) the C6.2 compounds are formed at low concentrations (both having low signal = 40 CPS) and thus the products formed from their decay are lower in concentration than the detection limit of the acetate CI-ToFMS, 2) some of their degradation products appear on the same nominal m/z as background ions that are high in signal, which makes it hard to detect small changes in the signal of nearby ions.

**Figure 5.3:** Continued proposed reaction mechanism for one of the first generation products formed from TCA aqueous photo-oxidation. The colouring of the compounds follows the time profiles shown in Figure 5.2. Gray compounds were proposed but either were not detected or showed no change in signal.
5.1.2 cis-Pinonic Acid

cis-pinonic acid is a semi-volatile organic that is mostly found in the gas phase (Mueller et al. 2012). The oxidation of PIN was carried out in order to assess the SOA forming potential through aqueous phase oxidation and to elucidate some potential mechanisms for key products.

Figure 5.4: Atomized particle total volume concentration and size distribution (top) as the oxidation of PIN proceeds. Data collected by SMPS at 3 min time resolution. OH exposure was calculated as the product of the time and the OHss measured in section 4.2.

Figure 5.4 shows a particle volume profile as the reaction of PIN with OH radical proceeds. In the presence of PIN, the particle volume is the same as the background level indicating that PIN alone does not contribute to particle volume. However, when the reaction is initiated, the particle volume measured by the SMPS increases significantly higher than the background. This shows that the photo-oxidation of PIN in the aqueous phase results in low volatility products that form...
particles even in the absence of seed inorganic particles. In addition, the total particle volume starts decaying past 2 hours of oxidation. This provides evidence of fragmentation reactions leading to the degradation of the low volatility organics and resulting is small oxygenated compounds that are relatively volatile.

In parallel to particle volume measurements, the reaction products that were formed by the oxidation were followed by the acetate CI-ToFMS. Key products formed from the oxidation reaction, their mechanism and time profiles are plotted in Figures 5.5 and 5.6.

Figure 5.5: Proposed reaction mechanism for PIN oxidation by OH radicals in the aqueous phase. The colouring of the compounds follows the time profiles shown in Figure 5.5.

Figure 5.5 shows the mechanism for PIN adopted from the gas phase experiments reported in (Mueller et al. 2012), where it is has been shown that one of the PIN oxidation pathways leads to MBTCA (shown in pink). The reaction is initiated by a hydrogen abstraction on the 4 membered ring. This is followed by C-C cleavage leading to ring opening. Figure 5.6 illustrates the evolution of the C10 compounds (blue and green) and MBTCA (shown in pink) over OH exposure in the aqueous phase. As proposed by the mechanism in Figure 5.5, the first onset observed is for the C_{10}H_{14}O_5 aldehyde. C_{10}H_{14}O_6 onset is close to that of C_{10}H_{14}O_5 but still lags behind the onset of C_{10}H_{14}O_5. The two C10 compounds can react with OH to form MBTCA as observed by the delayed onset of MBTCA.
Figure 5.6: Time profiles for the decay of PIN oxidation and the evolution of selected products plotted over OH exposure. The chemical formulas are for the ions in the deprotonated form. The signal for each ion was scaled by the maximum signal each ion reached. All the product traces start from their minimum signal and the y-axis are not zeroed. Data is plotted in 1 min time resolution. Chemical formulas are for deprotonated ions. OH exposure was calculated as the product of the time and the OHs measured in section 4.2.

It was assumed that the oxidation of MBTCA would follow the mechanism proposed for TCA in section 5.1.1 after accounting for the two additional methyl groups. The C7 compound (C7H10O5) in Figure 5.5 is the analogue of the C5.1 in Figure 5.1. The initial slow evolution of the C7 compound is similar to what was observed for C5.1 in Figure 5.2. Also, as the reaction proceeds, a decay was observed for the C7 signal. This is likely due to hydrogen abstraction on the –CH2– or the methyl groups. The reaction of the C7 compound with OH is expected to produce glyoxylic acid and the analogue of malonic acid (the C5 blue compound). Glyoxylic is expected to form from multiple pathways from PIN unlike TCA. Thus, it was not shown. However, the C5 product in Figure 5.5 does not follow the mechanism proposed for malonic acid formation from TCA as a delay in C5 evolution was expected. On the other hand, a C6 product (shown in orange) shows a similar delayed evolution that is similar to malonic acid and glyoxylic acid evolution observed from TCA oxidation in Figure 5.2. This suggests that it is a second generation product. A possible pathway that could lead to the C5 compound is pathway 1.1 in Figure 5.1. If OH abstraction takes place as in Figure 5.1 on the –CH2– carbon, then the C5 product can be formed if the C-C bond cleaves between the terminal carboxylic acid group and the secondary carbon (–CH2–). Another pathway is P1.2, where the C5 product can form directly
from MBTCA without going through the C7 compound. While these pathways can lead to the C5 product, other plausible pathways cannot be ruled out.

Overall, the data shown here provide evidence illustrating the instability of PIN and MBTCA in the aqueous phase under conditions similar to those of cloud droplets. In addition, the formation of more oxygenated compounds from PIN that are expected to have low volatility is consistent with the observation earlier from the SMPS. Thus, the aqueous oxidation of semi-volatile compounds such as PIN could possibly be treated as a source of additional mass to SOA.
Chapter 6
Significance and Conclusions

Given the widespread use of CIMS in the atmospheric chemistry community for the study of the gas phase, it is now important to evaluate how well CIMS can be used to assess the chemical nature of aerosol composition, including SOA (Sareen et al. 2010, Yatavelli and Thornton 2010, Yatavelli et al. 2012, Zhao et al. 2012). This work has focused on two aspects of this analysis, taking advantage of new instrumental advances in the field, especially a high resolution time-of-flight that can readily be deployed to the field (Bertram et al. 2011). In particular, this study attempted to address how the composition of a common WSOC SOA material is analyzed using three common CIMS reagent ions, monitoring both the starting material but also the changes that arise during an OH oxidation process. To our knowledge this is the first illustration of the comparative abilities of these common reagent ions to study the composition of complex organic mixtures, such as SOA.

While it was convenient to monitor changes occurring during aqueous phase oxidation in the laboratory, it is important to stress that the same general behavior is likely to be observed from chemical change being driven by gas phase or heterogeneous OH oxidation. It is hoped that these initial characterization experiments will form the foundation for similar analyses of aging processes observed in the field as well. For example, these methods could be used for studying: cloud water oxidation (Lee et al. 2012) or atmospheric aerosol processing as observed using the MOVI interface (Yatavelli and Thornton 2010, Yatavelli et al. 2012).

Finally, this work illustrated the capabilities of a high mass resolution time-of-flight mass spectrometer to analyze a complex organic mixture, given that most aerosol-CIMS studies (Hearn and Smith 2004, Hearn and Smith 2006, Zhao et al. 2012) have worked with quadrupoles and much simpler samples in the past.

Specific findings include:

- Complex organic composition of atmospherically relevant WSOC samples can be resolved with high resolution aerosol CI-ToFMS.
- The monomers and dimer regions of α-pinene SOA WSOC can be resolved and observed with CI-ToFMS, most clearly with I(H₂O)ₙ⁻ reagent ions. The chemical change of these two regions can be followed on-line with the dimers degrading more rapidly than the monomers.

- The simplicity in the switching of the CI-ToFMS reagent ions allows for a more comprehensive understanding of chemical change.

- This also illustrates that care must be taken when choosing the reagent ions with which to operate depending on the targeted analysis. For instance, (H₂O)ₙH⁺ reagent ions are shown to be more selective towards the more reduced organic compounds with WSOC SOA, while CH₃C(O)O⁻ and I(H₂O)ₙ⁻ allow for the detection of more highly oxygenated compounds with I(H₂O)ₙ⁻ being more selective to multifunctional compounds. In general, the range of sensitivities for the latter two reagent ions is far less than with the more selective (H₂O)ₙH⁺.

- Despite these potential differences in sensitivity to different analytes, the data arising from a combination of the (H₂O)ₙH⁺ data and either the CH₃C(O)O⁻ and I(H₂O)ₙ⁻ results yield a van Krevelen analysis that is remarkably similar to that measured simultaneously by high resolution AMS, despite the AMS being only sensitive to particle phase species and the CIMS to both gas and particle phases.

- Aerosol-CIMS clearly can monitor the functionalization and fragmentation processes that occur with SOA as it is oxidized by OH, generally giving rise to more functionalized products that are of lower carbon number and higher oxidation state.

In addition to the instrument characterization, aqueous phase reactions of selected organic compounds, cis-pinonic and tricarballylic acid, were investigated at the molecular level using aerosol-CIToFMS. The results have shown that an additional sink process for cis-pinonic acid exists while in the aqueous phase and that it is initiated by OH. The oxidation of cis-pinonic leads to the formation of more oxygenated organic compounds including MBTCA, a tracer for mono-terpene SOA. These highly oxygenated compounds can add to the SOA mass in the ambient and cause changes to the chemical and physical properties of SOA. As previous studies have investigated the aqueous phase oxidation of organics, this is the first study that illustrates
the additional aqueous sink for first generation products formed in the gas phase oxidation of mono-terpenes. As the oxidation was carried out for selected organics, the results can be used as a model case that applies to compounds with similar properties (i.e., semi-volatile organics). Considering this aging pathway with the measured rate constants, model predictions of SOA mass could be improved.

Furthermore, the results have shown that the surrogate compound of MBTCA (i.e., tricarballylic acid) is likely not stable in particles undergoing cloud activation. MBTCA can be oxidized in conditions similar to those of cloud droplets in the presence of OH. As a result, care must taken when MBTCA is used in receptor models for source apportionment. These models require that the tracer compound be stable throughout the transport from the source to the sampling point. The tracer should not be consumed or formed by chemical reaction during the transport process, which is clearly not the case for MBTCA.

For a complete understanding of the aqueous phase chemical aging, further oxidation experiments are needed to evaluate the significance of different classes of compounds to aqueous phase processing. Pinic acid, norpinic acid and other oxidation products formed by mono-terpene gas phase oxidation can be studied in a similar sitting as pinonic acid to assess their contribution to SOA formation though aqueous phase chemistry. The experiments in this work were carried out in conditions similar to cloud water. However, due to the high concentration of organics in aqSOA, it is expected that additional oxidation pathways constrained by the high RO_2 concentration might exist in aqSOA and had negligible contribution in the experiments carried out in this work. The role of these pathways and the products formed are needed to be investigated for a better understanding of aqSOA processing. Previous studies have shown that oligomer formation takes place by aqueous phase oxidation of methacrolein, pyruvic acid, glyoxal and methylglyoxal under aqSOA conditions (Ervens et al. 2011). Similar experiments could be conducted for cis-pinonic acid and MBTCA to reveal their oligomer-forming potential in aqSOA, which will add to the understanding of the fate of these two acids in the atmospheric aqueous phase.
References


Appendix A

Table A.1: List of the chemicals and structures used to run the sensitivity experiments as described in section 2.1.3.3

<table>
<thead>
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<th>Chemical</th>
<th>Structure</th>
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<tr>
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<tr>
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<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Glyoxal</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Pyruvic Acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Methyglyoxal</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Cis-pinonic Acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
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<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Succinic Acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Malonic Acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
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</tr>
<tr>
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<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
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