The role of aqueous-phase oxidation in the formation of highly-oxidized organic aerosol by
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B.S., Seattle University (2009)
Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Chemistry at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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Abstract

Atmospheric particulate matter (or “aerosol”) is known to have important implications for climate change, air quality, and human health. Our ability to predict its formation and fate is hindered by uncertainties associated with one type in particular, organic aerosol (OA). Ambient OA measurements indicate that it can become highly oxidized in short timescales, but this is generally not reproduced well in laboratory studies or models, suggesting the importance of formation processes that are not fully understood at present. In this thesis, I focus on the potential for chemistry within aqueous aerosol to produce highly oxidized OA. I first use a retrosynthetic modeling approach to constrain the viable precursors and formation pathways of highly oxidized OA, starting with a target oxidized product and considering possible reverse reactions. Results suggest three general formation mechanisms are possible: (1) functionalization reactions that add multiple functional groups per oxidation step, (2) oligomerization of highly oxidized precursors, or (3) fast aging within the condensed phase, such as oxidation within aqueous particles. The focus of the remainder of the thesis involves experiments designed to study this third pathway. To examine the importance of the formation of highly oxidized OA in the aqueous phase (wet particles or cloud droplets), I investigate aqueous oxidation of polyols within submicron particles in an environmental chamber, allowing for significant gas-particle partitioning of reactants, intermediates, and products. Results are compared to those from analogous oxidation reactions carried out in bulk solution (the phase in which most previous studies were carried out). Both sets of experiments result in rapid oxidation, but substantially more carbon is lost from the submicron particles, likely due to differences in partitioning of early-generation products. Finally, OA is formed from the gas-phase ozonolysis of biogenic precursors in the presence of reactive aqueous particles, showing that oxidation within the condensed phase can generate highly oxidized products. The overall results of this thesis demonstrate that aqueous-phase oxidation can contribute to the rapid formation of highly oxidized OA and therefore its inclusion in atmospheric models should be considered, but that experiments to constrain such pathways must be carried out under atmospherically relevant conditions.

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Contents

1 Introduction 9
  1.1 Research Questions .................................................. 12
  1.2 Outline ..................................................................... 12
  1.3 References ................................................................... 13

2 Average chemical properties and potential formation pathways of highly oxidized organic aerosol 19
  2.1 Introduction ............................................................... 19
  2.2 Methodology .............................................................. 21
  2.3 Results ....................................................................... 33
  2.4 Conclusions ............................................................... 49
  2.5 Acknowledgements .................................................... 52
  2.6 References ................................................................... 52

3 Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution 59
  3.1 Introduction ............................................................... 59
  3.2 Experimental Methods ............................................... 62
  3.3 Results and Discussion ............................................... 68
  3.4 Conclusions and Implications ...................................... 79
  3.5 Acknowledgements .................................................... 81
  3.6 References ................................................................... 81
  3.7 Supplement .................................................................. 87

4 Role of aqueous-phase oxidants in SOA formation 91
  4.1 Introduction ............................................................... 91
  4.2 Experimental Methods ............................................... 93
  4.3 Results and Discussion ............................................... 97
  4.4 Conclusions and Implications ...................................... 110
  4.5 References ................................................................... 112

5 Conclusions 115
Chapter 1

Introduction

Aerosols have been shown to play a key role in climate change, air quality, visibility, and human health (Kanakidou et al., 2005). These fine particles can impact global radiative forcing directly (by scattering or absorbing solar radiation) or indirectly (by acting as cloud condensation nuclei and altering cloud formation which in turn affects radiative forcing) (IPCC, 2014). Numerous studies have found a strong correlation between the presence of aerosol particles and adverse human health effects, such as increases in lung cancer rates (Pope and Dockery, 2006). These implications underscore the need for models that can accurately predict the amount and properties of aerosol. However, our ability to model the formation and fate of particulate matter is hindered by uncertainties associated with one type in particular, organic aerosol (OA), which comprises a substantial fraction of fine particulate matter (20-90% of dry mass, Kanakidou et al., 2005). Although OA has been studied in depth in recent years, there is still much unknown about the mechanisms by which it is formed. These uncertainties are due in part to the immense complexity resulting from a large number of reactions and products. Organic particulate matter can be comprised of primary organic aerosol (POA) that is directly released into the atmosphere, or secondary organic aerosol (SOA) that is formed from the oxidation and subsequent condensation of gas-phase organic compounds (Kroll and Seinfeld, 2008). Once formed, SOA products may continue to evolve or “age” via additional reactions in the gas phase and/or condensed phase.
The largest degree of uncertainty surrounds the most oxidized fraction of OA, whose sources and chemistry are largely unknown. This highly oxidized material makes up a significant fraction of OA (~20-70% by mass, Jimenez et al., 2009), and has been shown to form rapidly in the atmosphere (Volkamer et al., 2006). However, its formation has not been well-reproduced in the laboratory. Laboratory chamber experiments of SOA formed from various classes of precursors tend to produce aerosol that is relatively unoxidized (average carbon oxidation state (OSc) ~ -1.1 to 0.1, Heald et al., 2010; Kroll et al., 2011). Several efforts to age OA in laboratory chambers have also fallen short of reaching oxidation levels as high as those measured for ambient aerosol (Donahue et al., 2012; Qi et al., 2010). Those studies that have succeeded in generating highly oxidized SOA have generally been able to do so only with a select few precursors (Bahreini et al., 2005; Chhabra et al., 2011) or at OH exposures substantially higher than those relevant to the formation of oxidized aerosol in the atmosphere (Kessler et al., 2010; 2012; Lambe et al., 2012).

Recent modeling efforts have also attempted to reproduce the amount and degree of oxidation of OA as measured in field studies, by introducing additional aging chemistry to simulate oxidation beyond the initial SOA formation (Cappa and Wilson, 2012; Donahue et al., 2011; Dzepina et al., 2011). However, such models, whether simulating a specific environment (e.g., Mexico City, Dzepina et al., 2011; 2009; Hodzic et al., 2010), or SOA formation from a specific class of precursors (Aumont et al., 2012; Cappa and Wilson, 2012), still tend to be unsuccessful in reproducing the formation of highly oxidized aerosol. They either underpredict OSc at a given loading (Dzepina et al., 2009; 2011; Hodzic et al., 2010) or predict the formation of highly oxidized OA over longer time scales than what is observed (Lee-Taylor et al., 2011). These model-measurement discrepancies suggest that traditionally
considered pathways may not fully represent the formation of highly oxidized OA.

Aqueous-phase oxidation has received considerable attention as a potential formation pathway for highly oxidized OA (Ervens et al., 2011; Lim et al., 2010). It is estimated that particulate liquid water exceeds the total dry aerosol mass by a factor of 2-3, globally (Carlton & Turpin, 2013; Liao and Seinfeld, 2005). The oxidation of organic species in the aqueous phase has recently been investigated in the laboratory for a range of water-soluble species, including small carbonyls (Altieri et al., 2008; Carlton et al., 2007; Kirkland et al., 2013; Perri et al., 2010; 2009; Tan et al., 2010; 2009), isoprene and its oxidation products (Altieri et al., 2006; Kameel et al., 2013; Liu et al., 2012; Renard et al., 2013; Zhang et al., 2010), and phenolic compounds (Smith et al., 2014; Sun et al., 2010). Such bulk-phase studies have clearly demonstrated that aqueous-phase oxidation, when it occurs, can lead to the rapid formation of highly oxidized organic species.

However, because a compound can only undergo aqueous-phase oxidation if it is present in the aqueous phase (cloud droplets or aqueous submicron particles), the atmospheric relevance of these oxidation processes strongly depends on partitioning (Donahue et al., 2014). Gas-aqueous partitioning is determined by a compound's effective Henry’s law constant ($H^*$) and the liquid water content (LWC) of the air mass. Because LWCs are so much lower in the atmosphere (~1 to 100 μg m$^{-3}$ for aqueous aerosol, and ~$10^5$ to $10^6$ μg m$^{-3}$ for cloud droplets, Ervens et al., 2011), than for bulk aqueous solution (~$10^{12}$ μg m$^{-3}$, the density of water), many compounds that are considered to be “water-soluble” for bulk solutions will not actually partition significantly into the aqueous-phase in the atmosphere. This suggests that experiments conducted in a bulk solution may not be fully representative of aqueous processing in the atmosphere.
The overarching goal of this thesis is to determine to what extent aqueous-phase oxidation can aid in the formation highly-oxidized OA under atmospherically realistic partitioning conditions. The specific research questions that are addressed as well as an outline of the thesis are provided in the following sections.

1.1 Research Questions

1) Can highly oxidized organic aerosol be formed from traditional gas-phase oxidation pathways and precursors? (Chapter 2)

2) How does aqueous oxidation within submicron particles differ from oxidation in a bulk aqueous solution? Is oxidation within submicron particles still an efficient pathway for the generation of oxidized organic material? (Chapter 3)

3) How does the presence of aqueous-phase oxidants affect SOA formation? Can oxidized OA be generated from fresh SOA via oxidation within the condensed phase? (Chapter 4)

1.2 Outline

In order to address the first research question (*can highly oxidized OA form from traditional gas-phase oxidation pathways*?), we develop a novel retrosynthetic approach for constraining the viable precursors and formation pathways. This involves starting with the oxidized product and considering the possible reverse reactions, using a set of simple chemical rules. We focus on the formation of low-volatility oxidized organic aerosol (LV-OOA), determined from factor analysis of aerosol mass spectrometer data. The elemental composition and volatility of the aerosol enable the determination of its position in a three-dimensional chemical space (defined by the hydrogen-to-carbon ratio, oxygen-to-carbon ratio, and carbon number) and thus its average chemical formula. Consideration of possible back-reactions then
defines the movement taken through this chemical space, constraining potential reaction pathways and precursors. This work is presented in Chapter 2.

In order to address the second research questions (how does aqueous oxidation differ within submicron particles and bulk solution?), we conduct aqueous oxidation experiments on a set of polyols, which serve as simple surrogates for water-soluble compounds in the atmosphere. Two analogous sets of experiment are carried out: (1) in a bulk aqueous solution, and (2) within aqueous submicron particles in an environmental chamber, allowing for significant gas-particle partitioning of reactants, intermediates, and products. This allows for the first direct comparison of aqueous oxidation under drastically different partitioning conditions. These experiments are presented in Chapter 3.

In order to address the final research question (how do aqueous-phase oxidants affect SOA formation?), we conduct additional chamber experiments with more atmospherically relevant organic precursors and a broader range of condensed phase oxidation conditions. We generate SOA from the gas-phase ozonolysis of biogenic volatile organic compounds with a range of seed types in order to vary the phase and oxidant levels within the particles. Changes to the oxidation state of particulate carbon are directly measured using aerosol mass spectrometry. These experiments are presented in Chapter 4. In Chapter 5, we provide a brief summary of our overall findings, and discuss implications for future research.

1.3 References


Chapter 2

Average chemical properties and potential formation pathways of highly oxidized organic aerosol


2.1 Introduction

As described in Chapter 1, organic aerosol (OA) constitutes a substantial fraction of atmospheric fine particulate matter, and thus a thorough understanding of its formation and evolution is necessary in order to better evaluate the effects of particulate matter on climate and human health (Kanakidou et al., 2005). However, despite substantial research efforts, there remains a great deal unknown about the chemical mechanisms important to OA. Especially uncertain are the sources and chemistry of the most oxidized fraction of OA, sometimes termed “humic-like substances” (HULIS, Graber and Rudich, 2006) (when measured using offline techniques of fractionated filter samples), or low-volatility oxidized organic aerosol (LV-OOA) (when determined from factor analysis of online aerosol mass spectrometer data) (Jimenez et al., 2009). (It is worth noting that as used in the acronym LV-OOA, the term volatility is synonymous with saturation vapor concentration.) This highly oxidized fraction of organic aerosol is ubiquitous in the atmosphere, making up between 20-
70% of total organic aerosol mass (Jimenez et al., 2009; Zhang et al., 2007). It is highly oxidized (with an average carbon oxidation state of approximately 0-1, Kroll et al., 2011), exceedingly low in saturation vapor concentration ($c^* \sim 0.1$ to $<10^{-7}$ µg m$^3$, Cappa and Jimenez, 2010), and generated relatively quickly (over time scales of ~1-3 days, Jimenez et al., 2009; Volkamer et al., 2006). While this highly oxidized OA is presumed to be secondary in nature (formed from chemical transformations of gas-phase organics that subsequently condense as particulate matter), its detailed formation pathways are poorly understood and have not been adequately reproduced either in the laboratory or in atmospheric models. This suggests major gaps in our understanding of the chemistry underlying the formation of highly oxidized organic aerosol. Unfortunately at present we have very little information as to whether these gaps relate to uncertainties in reaction mechanisms, SOA precursors, or both.

Here we present a new approach for constraining the formation of highly oxidized aerosol, involving the use of chemical properties of the aerosol to better understand its possible formation pathways and precursors. In contrast to most modeling approaches that start with potential precursors and simulate their forward evolution in an attempt to generate products chemically similar to those measured in the atmosphere, we start with the known products (highly oxidized OA components) and work backwards toward reactants (SOA precursors). This approach is similar to the retrosynthetic approach of Pun, et al. (2000) for assessing formation pathways of atmospheric water-soluble organic compounds. That approach was highly molecule- and reaction- specific, involving the identification of detailed chemical reactions that link individual precursors to individual aerosol components. Here we take a more generalized view of the chemistry, assessing classes of reactions that could
ultimately lead to the formation of highly oxidized organic products with low saturation vapor concentrations. Such an approach requires knowledge of the chemical properties of the “targets” (molecules representing the oxidized fraction of the aerosol); we define these in terms of the average chemical formulas of their constituent molecules, as determined from properties measured in field studies as well as structure-activity relationships. From these targets, a set of simple, general rules governing possible atmospheric reactions lets us work backwards, allowing for identification of viable reaction pathways and aerosol precursors (which are also defined in terms of their average chemical properties). By focusing on generic processes rather than detailed chemical structures and mechanisms, we can draw general conclusions about the types of processes and precursors that might yield highly oxidized organic species. These can be used to provide guidance in identifying relevant reaction conditions and precursors in future studies.

In the following section we describe this methodology in detail, including the chemical space we use to describe the organics, the characterization of our targets, and the types and characteristics of reverse pathways considered. Results — the chemical characteristics of our targets (constrained by AMS measurements of LV-OOA components) and the possible range of aerosol formation pathways — are then described. We conclude with discussions of implications of this work for our understanding of highly oxidized organic aerosol, as well as potential areas of future work.

2.2 Methodology

We describe molecules in terms of their position in a three-dimensional chemical space, defined by their carbon number ($n_C$), oxygen-to-carbon ratio (O/C), and hydrogen-to-carbon ratio (H/C). O/C and H/C have already seen substantial use in describing the average
properties of atmospheric organic aerosol using the two-dimensional van Krevelen diagram (Heald et al., 2010; Ng et al., 2011); however this provides no information on the size of the molecule (a crucial factor governing saturation vapor concentration). By considering $n_C$ as a third dimension to the van Krevelen space, we can represent any molecular formula $C_{n_C}H_{n_H}O_{n_O}$ as a single, unique point, and can relate its position in chemical space to $c^*$ (Kessler et al., 2010; 2012). This space is equivalent to the three-dimensional space defined by carbon number, hydrogen number, and oxygen number ($n_C$ vs. $n_H$ vs. $n_O$); we choose to use O/C and H/C here since they are also used in the van Krevelen diagram, and are more amenable to visualization and comparison of elemental composition (hydrogen and oxygen content) of molecules of different sizes. A previously proposed alternative three-dimensional space uses molecular weight, heteroatom mass, and double bond equivalents (Wei et al., 2012). While this has advantages for describing certain atmospheric systems, especially those with nitrogen or sulfur containing species, the space proposed here is more conducive to the description of atmospheric reactions in terms of changes to carbon, hydrogen, and oxygen content of the molecules.

The three-dimensional space we use here is closely related to many of the two-dimensional frameworks that have recently been used to describe and/or model organic aerosol. These include the van Krevelen plot (Heald et al., 2010), polarity vs. $n_C$ (Pankow and Barsanti, 2009), $OS_C$ vs. saturation vapor concentration ($c^*$) (Donahue et al., 2011; Jimenez et al., 2009), the $f_{44}$ vs. $f_{43}$ space for plotting AMS data (Ng et al., 2011; 2010), $OS_C$ vs. $n_C$ (Kroll et al., 2011), and $n_O$ vs. $n_C$ (Cappa and Wilson, 2012). Although adding a third dimension introduces complexity to any of these descriptions, it allows for more chemical information to be represented. It explicitly includes the effects of carbon number,
which are missing from functional-group-based frameworks (e.g., van Krevelen and f44-f43), and it requires fewer assumptions about the identity or distributions of functional groups than frameworks that reduce the descriptions of functional groups to a single dimension (polarity- \( n_C \), OSc-\( n_C \), OSc-\( c^* \), nO-\( n_C \)). We note that isomeric species of a given formula \( C_x H_y O_z \) are not distinguished even in this 3-D space, which can lead to errors in the calculation of \( c^* \) when the identity of the functional groups changes, as discussed below. Nonetheless, chemical transformations and properties (e.g., \( c^* \)) can be represented in this space in a straightforward manner.

2.2.1 Characterization of the target.

Our general approach is to start with the product (molecules representative of highly oxidized organic aerosol) and work backwards. We refer to this species as the “target” and the backwards reactions as “transforms”, following the conventions of retrosynthetic analysis (Corey, 1988). Key to this approach is the accurate determination of the chemical formula (position in O/C-H/C-\( n_C \) space) of the target.

Since the target in this case (highly oxidized organic aerosol) is not a single molecule, but rather a complex mixture, we define it in terms of its average properties and average chemical formula. In the present study we determine this from field studies using the Aerodyne High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS, or simply AMS, Canagaratna et al., 2007; DeCarlo et al., 2006) which provides measurements of the elemental ratios of OA (Aiken et al., 2007; 2008). Positive matrix factorization (PMF) of AMS data (Ulbrich et al., 2009) typically yields several factors, of which LV-OOA is the most highly oxidized. We take this to be representative of the most oxidized fraction of organic aerosol, and use measurements of LV-OOA elemental ratios to define the location of
our target in van Krevelen space.

Because the AMS provides no information regarding carbon number (the third dimension of our chemical space), we determine $n_C$ from field measurements of aerosol $c^*$ (Cappa and Jimenez, 2010; Cappa, 2010; Huffman et al., 2009). The carbon number can be estimated from $c^*$ using structure-activity relationships (SARs) for determining vapor pressure. In this work we use SIMPOL (Pankow and Asher, 2008), allowing for the direct determination of $c^*$ from $n_C$ and the functional group abundance, as described below. We focus on partitioning only into the condensed organic phase, as described by $c^*$. Partitioning into liquid water could also be included using this general approach; it would require use of a SAR for estimating the saturation vapor concentration over water (Henry's law constant, e.g. Hine and Mookerjee, 1975), but is beyond the scope of this work.

Key inputs for SIMPOL (and most other SARs for estimating vapor pressures) are the abundances of different functional groups in the molecule (Pankow and Asher, 2008). In order to determine these from our values for $n_C$, H/C, and O/C, we make two assumptions. The first is that functional groups in the molecule are limited to carbonyls, hydroxyls, or some combination of the two (e.g., carboxylic acids), which have been shown to be the major functional groups in ambient organic aerosol samples (Russell et al., 2011). Since each functional group contains only one oxygen atom, their abundances can be related to the oxygen number of the molecule:

$$n_O = n_C \frac{O}{C} = n_{-\text{OH}} + n_{-\text{O}}$$

(2.1)

where $n_O$, $n_C$, and $O/C$ are as defined above, and $n_{-\text{OH}}$ and $n_{-\text{O}}$ are the number of hydroxyl groups and carbonyl groups in the molecule, respectively. While other functional groups are also likely to be present in organic aerosol, several groups can be approximated using this
The second assumption is that all sites of unsaturation (double bond equivalents, DBE) in the molecule arise from carbonyl groups:

\[ n_{\text{sat}} = DBE = 1 + n_c \left( 1 - \frac{1}{2} \frac{H/C}{C} \right) \]  

(2.2)

We therefore assume that our target contains no carbon-carbon double bonds or rings. While this is reasonable for aliphatic \( \text{C} = \text{C} \) bonds, which are highly susceptible to oxidation and unlikely to survive significant atmospheric processing, cyclic (or aromatic) structures may be present in highly oxidized OA. The effect of neglecting any rings present is to overestimate \( n_{\text{=O}} \) and underestimate \( n_{\text{OH}} \), thereby overestimating \( c^* \) somewhat.

The two assumptions above (Eqs. 2.1 and 2.2) allow for the straightforward derivation of expressions relating elemental ratios, functional groups, saturation vapor concentration, and carbon number. The number of hydroxyl groups (\( n_{\text{OH}} \)) can be determined by combining Eqs. 2.1 and 2.2:

\[ n_{\text{OH}} = n_0 - n_{\text{=O}} = n_c \frac{O}{C - \left( 1 + n_c \left( 1 - \frac{1}{2} \frac{H/C}{C} \right) \right)} = -1 + n_c \left( \frac{O}{C} + \frac{1}{2} \frac{H/C}{C} - 1 \right) \]  

(2.3)

The carbon number (\( n_c \)) and functional group abundances (\( n_{\text{=O}} \) and \( n_{\text{OH}} \)) allow for the calculation of \( c^* \) (\( \mu \text{g m}^{-3} \)) using SIMPOL:

\[
\log_{10} c^* = \log_{10} (P_{\text{sat}}) = \log_{10} \alpha + b_0 + b_c n_c + b_{\text{=O}} n_{\text{=O}} + b_{\text{OH}} n_{\text{OH}} \\
= \log_{10} \alpha + b_0 + b_c n_c + b_{\text{=O}} \left( 1 + n_c \left( 1 - \frac{1}{2} \frac{H/C}{C} \right) \right) + b_{\text{OH}} \left( -1 + n_c \left( \frac{O}{C} + \frac{1}{2} \frac{H/C}{C} - 1 \right) \right) 
\]  

(2.4)

where \( P_{\text{sat}} \) is the vapor pressure in atm, \( \alpha \) is the conversion from \( P_{\text{sat}} \) to \( c^* \), and the \( b \) terms are the different group contribution terms for quantifying the contribution of each chemical moiety to vapor pressure: \( b_0 \) is the zero order term, \( b_c \) is the carbon number term, \( b_{\text{=O}} \) is the carbonyl group term, and \( b_{\text{OH}} \) is the hydroxyl group term (for \( MW = 200 \text{ g mol}^{-1} \) and \( T = 293 \text{ K} \), equal to 1.79, -0.438, -0.935, and -2.23, respectively) (Pankow and Asher, 2008). The
conversion factor $\alpha$ is given by $\alpha = 10^6 (\text{MW})/RT$, or $8.314 \times 10^9$ at 293 K, where MW is the average molecular weight (g mol$^{-1}$) of the molecules making up the absorbing phase, R is the ideal gas constant ($8.21 \times 10^{-5}$ atm m$^3$ mol$^{-1}$ K$^{-1}$), and T is the temperature in K. For these calculations we use an assumed MW value of 200 g mol$^{-1}$; the actual value used has little effect on the results. Rearranging Eq. 2.4 to solve for carbon number, and substituting in values of $n_O$ and $n_{OH}$ from Eqs. 2.2 and 2.3, we obtain

$$n_C = \frac{\log_{10} c^* - \log_{10} \alpha - b_0 - b_{nO} + b_{OH}}{b_C + b_{nO}(1 - \frac{1}{2}H/C) + b_{OH}(O/C + \frac{1}{2}H/C - 1)}$$

Equation 2.5 allows for the determination of carbon number from elemental (H/C, O/C) and $c^*$ data. This approach, used in previous descriptions of heterogeneous oxidation systems (Kessler et al., 2010; 2012), is similar to that of Donahue et al. (2011) for estimating carbon number from OS$_C$ (O/C) and $c^*$ alone; however that approach required making assumptions about functional group distribution (specifically that $n_{OH} = n_{O}$). With the explicit inclusion of H/C, we can directly calculate $n_{OH}$ and $n_{O}$, which allows for a more accurate estimation of $n_C$.

Eq. 2.5 relies critically on the assumption that target molecules contain only hydroxyl and carbonyl groups. While molecules containing other functional groups will be less accurately represented, many such functional groups are reasonably approximated as carbonyls, alcohols, or some combination of the two. Because the vapor pressure effect of an acid group ($b_{OH} = -3.58$) is similar to that of a hydroxyl plus a carbonyl ($b_{OH} + b_{O} = -3.165$), treating an acid as the sum of the two introduces only a minor error. Likewise, epoxides are very similar to carbonyls in terms of both bonding and effect on $c^*$: like carbonyls, they contribute one DBE, and the vapor pressure effect of an ether ($b_{O} = -0.718$) is similar to that of a carbonyl. Similarly, nitrate and hydroperoxyl groups are connected to
the carbon skeleton via a single C-O bond and so have similar bonding as a hydroxyl, and also have roughly the same vapor pressure effect (b_{NO3} = -2.23, b_{OOH} = -2.48). These functional groups have additional oxygen atoms, but in the AMS these are likely lost as NO₂ or OH fragments (Farmer et al., 2010) and so it is likely that only one oxygen atom is measured (as is the case for a hydroxyl group). Since these moieties contribute one fewer hydrogen than a hydroxyl group, the measured H/C may not be exactly the same as for the corresponding alcohol, but this will have only a minor effect on results. Unfortunately, not all functional groups are as well-represented in the above treatment. Acyclic ethers have the same bonding (and contribution to O/C and H/C) as hydroxyl groups, but have a substantially smaller effect on vapor pressure (b_{O.} = -0.718 vs. b_{OH} = -2.23). Similarly, esters, like acids, will be treated as a carbonyl plus a hydroxyl group, but their actual effect on vapor pressure is far smaller (b_{-O} = -1.20 vs. b_{OH} + b_{O} = -3.165). While ethers generally make up an insignificant fraction of functional groups in OA, esters (which are predicted to form from the condensed-phase reaction of carboxylic and hydroxyl groups) may account for as much as 20% of functional groups in some organic aerosol (Russell, et al., 2011). There is no good way to account for these errors using elemental ratios alone; direct measurements of functional group abundances in OA (e.g., using FTIR, Maria et al., 2002) would thus greatly aid in this general approach for determining the chemical formula and properties of the target.

We note there are ways to determine the chemical formula (position in a given chemical space) other than the elemental- and c*-based approach described above. One widely-used technique is ultrahigh-resolution electrospray ionization mass spectrometry (UHR-ESI-MS) of filter samples to directly determine exact chemical formulas (Lin et al.,
2012; Wozniak et al., 2008). There are currently far fewer measurements of ambient OA by UHR-ESI-MS than by AMS, but this is another promising technique for characterizing the target. While concerns such as variations in sensitivity toward different compounds, and the possibility of fractionation arising from dissolution in a given solvent, still need to be addressed, estimates of $O_{Sc}$ and $n_c$ from AMS and ESI measurements are generally in good agreement (Kroll et al., 2011).

2.2.2. Transforms

Once the target is well-defined, transforms (the reverse of atmospheric reactions) allow for the formation chemistry to be traced backwards toward potential precursors. Again, the aim is not to identify specific formation pathways and precursor molecules, but rather to examine the key features of viable ones. Here, we consider three reaction classes—functionalization, fragmentation, and oligomerization—each of which is discussed below. Simple chemical rules for each reaction class help constrain their potential role and possible precursors.

a) Functionalization

Functionalization reactions are those that add (or interconvert) functional groups without other changes to the carbon skeleton. They are easily represented in a 2-D van Krevelen plot since they involve no change in $n_c$. Movement through this space has been used previously to describe different functional group additions (Heald et al., 2010; Ng et al., 2011). Reverse functionalization reactions connecting target molecules back to their precursors involve the loss of carbonyl or hydroxyl groups, as shown in Figure 2-1. The exact direction in van Krevelen space depends not only on the functional group involved but also the nature of the precursor, specifically the bond (C-H vs. C=C) being replaced by the
Figure 2-1. Possible transforms (back-reactions) available to a target molecule, assuming functionalization reactions only (with no change to carbon number). Loss of functional groups is illustrated in terms of movement in van Krevelen space, depicting changes in H/C and O/C. The exact trajectory depends on the identity both of the functional group and the bond being replaced. Panel a: functionalization of C-H bonds (saturated case), with slopes of -2 for carbonyl groups and 0 for hydroxyl groups. Panel b: functionalization of C=C bonds or rings (unsaturated case), with slopes of -1 for carbonyl groups and +1 for hydroxyl groups. In either case, changes to more than one functional group (light grey arrows and points) can be described by simple vector addition.

A functional group. Figure 2-1a shows the “saturated” case, in which the functional groups replace C-H bonds, which has been considered previously (Heald et al., 2010). Removing a single functional group decreases O/C by \(1/n_c\), with the effect on H/C depending on the identity of the group. Loss of a carbonyl decreases H/C by \(2/n_c\) (following a slope of -2 on the van Krevelen plot), while removing a hydroxyl has no effect on the H/C ratio (following a slope of 0). These steps are fully additive, such that the loss of multiple functional groups can be described simply by the sum of the vectors associated with the individual groups. For example, removing a hydroxycarbonyl or carboxylic acid (the equivalent of removing one hydroxyl and one carbonyl) decreases O/C by \(2/n_c\) and increases H/C by \(2/n_c\) (thereby
following a slope of $-1$). Figure 2-1b shows the “unsaturated” case, in which the functional group replaces a carbon-carbon double bond (or C-C single bond within a ring). Loss of a functional group still decreases O/C by $1/n_C$, but now removing a carbonyl increases H/C by only $1/n_C$ (slope = $-1$), whereas removing a hydroxyl actually decreases H/C, by $1/n_C$ (slope = $+1$). Note that the oxidation of C=C bonds typically involves changes to two functional groups, so movement through this space can be quite rapid. In either case (saturated or unsaturated), for a given $n_C$, each point in van Krevelen space corresponds to a value of $c^*$, allowing the change in $c^*$ associated with any transform to be easily computed.

We can define the range of potential precursors of our target by providing two fundamental limits on what reverse reactions are possible: (1) a molecule cannot lose more of a given functional group than it actually has; and (2) going backwards, the average carbon oxidation state cannot increase, since reduction reactions are thermodynamically unfavorable. This can significantly narrow the area in chemical space that defines the potential precursors, as discussed in the Results section.

**b) Fragmentation**

Fragmentation reactions decrease the carbon number of the molecule via the cleavage of carbon-carbon bonds. Since these reactions are oxidative, they will involve the addition of functional groups at the site of the bond breakage. (The scission of a single bond within a ring is therefore not considered a fragmentation reaction, and is instead a functionalization reaction, involving the addition of multiple functional groups.) Fragmentation reactions can result in rapid oxidation of the carbon, since they can lead to a high abundance of functional groups on relatively small molecules. However the decrease in carbon number can also lead to a substantial increase in $c^*$. This tradeoff likely limits the importance of fragmentation
pathways for the formation of very oxidized, low-volatility species.

Because \( n_C \) changes during fragmentation, simple 2-D van Krevelen plots are not sufficient to accurately capture these transformations. Furthermore, because of the range of possible precursors (with any number of carbon, oxygen, or hydrogen atoms), there are no simple generic transforms to describe this change. Nonetheless, we can apply constraints that considerably narrow the chemical space associated with the possible transforms and precursors. One approach is to assume that functional groups are evenly distributed across all the carbon in a molecule, and that this distribution is conserved during the fragmentation process (with the exception of any functional groups added during fragmentation). This statistical treatment of fragmentation is similar to that used in the recently-developed Statistical Oxidation Model (Cappa and Wilson, 2012). For the present study, we assume that two functional groups (one hydroxyl and one carbonyl) are added to a given fragment, but this distribution can be altered as necessary. Such assumptions (plus the requirement that \( n_C \) of the precursor must exceed that of the target), give the following constraints: \( n_{C,p} > n_{C,t} \), \( n_{OH,p} = (n_{OH} - 1) \left( \frac{n_{C,p}}{n_{C,t}} \right) \), and \( n_{-O_p} = (n_{-O,t} - 1) \left( \frac{n_{C,p}}{n_{C,t}} \right) \), where subscript “t” refers to the target and subscript “p” refers to the precursor. The subtraction of 1 from \( n_{OH,t} \) and \( n_{-O,t} \) accounts for the addition of the two functional groups upon fragmentation.

An alternative, more exact approach is to allow the functional groups to be localized somewhere on a molecule, rather than distributed evenly across it. This allows for a broader range of potential precursors, since fragments can have varying degrees of oxidation (i.e., one that is more oxidized than the other). In this case, the number of functional groups in the target provides constraints on precursors: after taking into account any new functional groups, the precursor cannot have fewer hydroxyl or carbonyl groups than the target. Again,
if we assume that two groups (one hydroxyl and one carbonyl) are added to the fragment, thereby increasing \( n=O \) and \( n,OH \) each by one, we obtain the following constraints: \( n_{C,p} > n_{C,t} \), \( n_{OH,p} \geq (n_{OH,t} - 1) \), and \( n_{O,p} \geq (n_{O,t} - 1) \).

c) Oligomerization

Oligomerization reactions occur when two molecular species combine to form a larger one. Because of the associated increase in carbon number, oligomerization reactions are an efficient way to lower vapor pressure. However, this type of reaction is typically non-oxidative (Kroll and Seinfeld, 2008) so is not accompanied by an overall change in \( \Delta \)OSC. Therefore the carbon atoms in the precursors must, on average, be as oxidized as those in the target.

As with fragmentation, oligomerization transforms are more difficult to describe than those for functionalization, since any number of changes to \( n_C \), \( n_H \), and \( n_O \) are possible. However, we can still apply basic constraints related to the allowable number of carbons and functional groups to narrow the range of potential precursors. The same statistical method described for fragmentation reactions can be used for oligomerization to constrain the precursor molecules. Here, we require the \( n_C \) of the precursor to be smaller than that of the target, and we assume that the precursor molecules have the same functional group distribution as the target, giving the following constraints: \( n_{C,p} < n_{C,t} \), \( n_{OH,p} = n_{C,p}(n_{OH,t} / n_{C,t}) \), and \( n_{O,p} = n_{C,p}(n_{O,t} / n_{C,t}) \).

As with fragmentation, we can expand the range of precursors further by allowing the functional groups to be unevenly distributed between the two precursors. This allows one of the oligomerization reactants to be more functionalized than the other. While a large number of different oligomerization transformations are possible, we assume that for any
oligomerization reaction each precursor must have at least one functional group. We also allow the total oxygen and hydrogen content to change somewhat by the gain or loss of a water molecule, or by the conversion of a carbonyl to an alcohol (as in a hemiacetal formation). These assumptions, plus the requirement that the precursor $n_C$ be lower than the target $n_C$, yield the following simple rules for the number of oxygen atoms and carbonyl and hydroxyl groups: $n_{O,p} \leq n_{O,t}$, $n_{=O,p} \leq (n_{=O,t} + 1)$, and $n_{OH,p} \leq (n_{OH,t} + 1)$. It should be noted that if ester or ether linkages are formed during the oligomerization reaction, they will introduce an error in the $c^*$ calculation. However, these effects are likely to be relatively small since the change in $c^*$ is governed mostly by changes to the carbon number, rather than by interconversions of functional groups.

2.3 Results

2.3.1 LV-OOA Target.

Table 2-1. HR-ToF-AMS data from measurements at 10 field locations. Elemental ratios are reported for the average of LV-OOA measurements at each site and are used to calculate each average LV-OOA OSc ($\Delta O/C - H/C$).

<table>
<thead>
<tr>
<th>Measurement Location</th>
<th>O/C</th>
<th>H/C</th>
<th>OSc</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverside, CA (2005)</td>
<td>0.72</td>
<td>1.27</td>
<td>0.17</td>
<td>(Docherty et al., 2011)</td>
</tr>
<tr>
<td>Mexico City Aircraft (2006)</td>
<td>1.02</td>
<td>1.12</td>
<td>0.92</td>
<td>(DeCarlo et al., 2010)</td>
</tr>
<tr>
<td>Mexico City Ground (2006)</td>
<td>0.84</td>
<td>1.21</td>
<td>0.47</td>
<td>(Aiken et al., 2008)</td>
</tr>
<tr>
<td>Kaiping, China (2008)</td>
<td>0.64</td>
<td>1.30</td>
<td>-0.02</td>
<td>(Huang et al., 2011)</td>
</tr>
<tr>
<td>Barcelona, Spain (2009)</td>
<td>0.75</td>
<td>1.18</td>
<td>0.32</td>
<td>(Mohr et al., 2011)</td>
</tr>
<tr>
<td>Paris, France (2009)</td>
<td>0.73</td>
<td>1.33</td>
<td>0.13</td>
<td>(Crippa et al., 2013)</td>
</tr>
<tr>
<td>New York City, NY (2009)</td>
<td>0.63</td>
<td>1.29</td>
<td>-0.03</td>
<td>(Sun et al., 2011)</td>
</tr>
<tr>
<td>Hong Kong, China (2009)</td>
<td>0.59</td>
<td>1.26</td>
<td>-0.08</td>
<td>(He et al., 2011)</td>
</tr>
<tr>
<td>Shanghai, China (2010)</td>
<td>0.65</td>
<td>1.49</td>
<td>-0.19</td>
<td>(Huang et al., 2012)</td>
</tr>
<tr>
<td>Sacramento, CA (2010)</td>
<td>0.54</td>
<td>1.32</td>
<td>-0.24</td>
<td>(Setyan et al., 2012)</td>
</tr>
<tr>
<td>Heshan, China (2010)</td>
<td>0.55</td>
<td>1.30</td>
<td>-0.20</td>
<td>(Gong et al., 2012)</td>
</tr>
</tbody>
</table>

Properties of the highly oxidized OA target are determined from HR-ToF-AMS field measurements. Table 2-1 summarizes AMS elemental ratios for studies that report H/C and
Figure 2-2. Van Krevelen diagram showing the reported elemental ratios of LV-OOA from HR-AMS field campaigns (see Table 2-1) in the red circles and elemental ratios after applying the recommended correction of 1.3 and 1.1 to O/C and H/C, respectively (Canagaratna et al., 2014) in the blue circles. The red star is the average reported O/C and H/C from all measurements, with the red ellipse indicating the covariance of the data within 1.96 standard deviations of the uncorrected mean value. The blue star and ellipse are for an average of all the corrected measurements.

O/C for the LV-OOA PMF factor (or, more generally, the most oxidized of multiple OOA factors, which includes factors such as OOA-I (Aiken et al., 2008) or MO-OOA (Setyan et al., 2012)). Figure 2-2 shows the location of these as red circles in van Krevelen space. The degree of oxidation varies widely from study to study, indicating that LV-OOA is not one class of compounds but rather an aged form of SOA with a composition that varies as a function of location, emissions profile, and/or oxidant exposure. For example, LV-OOA from the MILAGRO field campaign in the Mexico City Metropolitan Area (MCMA) (Aiken et al., 2008; DeCarlo et al., 2010) is substantially more oxidized than that measured at the other field sites. Nonetheless, we use the average values of LV-OOA H/C and O/C (1.28 and 0.696 respectively) from these studies as our generic highly-oxidized OA target. This is shown as a red star in Figure 2-2. The ellipse represents the covariance of the data within 1.96 standard deviations of the uncorrected mean value. AMS elemental ratios for ambient organic aerosol are typically corrected using empirical factors to account for biases in ion fragmentation.
(Aiken et al., 2008). Recent calibration studies indicate that the recommended factors result in an underestimation of O/C and H/C values for a range of multi-functional oxidized organic standards, indicating that AMS elemental ratios reported for ambient environments will need to be modified by new correction factors (effectively 1.3 for O/C and 1.1 for H/C, Canagaratna et al., 2014). The average ratios calculated after using these new proposed correction factors are shown as blue circles in Figure 2-2.

Saturation vapor concentration of the aerosol, as measured with thermodenuders, has to our knowledge been reported for only a limited number of field studies (Huffman et al., 2009), and values for $c^*$ have been determined only for the MCMA ground-based data (Cappa and Jimenez, 2010). The decrease in LV-OOA upon heating in the thermodenuder is consistent with a range of $c^*$ values between $10^{-7}$ and $10^{-1}$ µg m$^{-3}$ (Cappa and Jimenez, 2010). However, since the LV-OOA measured in MCMA appears not to be representative of LV-OOA everywhere (Figure 2-2), these $c^*$ ranges may not be widely applicable to other locations. On the other hand, the elemental composition of Riverside LV-OOA is close to that of the overall LV-OOA average (Figure 2-2), suggesting its $c^*$, which is substantially higher than that of LV-OOA in MCMA (Huffman et al., 2009), may be more representative of typical LV-OOA. We choose $c^*$ in the range of $10^{-5}$ to $10^{-1}$ µg m$^{-3}$ as reasonable values based on the reported $c^*$ distribution (Cappa and Jimenez, 2010). From these $c^*$ values, carbon numbers can be calculated (Eq. 2-5): for log$_{10}(c^*)$ of -1, -3, and -5, the corresponding chemical formulas are $C_{9.2}H_{11.8}O_{5.4}$, $C_{10.5}H_{13.4}O_{7.3}$, and $C_{11.8}H_{15.1}O_{8.2}$, respectively, for the reported average, and $C_{6.8}H_{9.5}O_{6.1}$, $C_{7.7}H_{10.9}O_{7}$, and $C_{8.7}H_{12.2}O_{7.9}$, respectively, for the corrected average (Canagaratna et al., 2014). These formulas are not meant to define exact chemical species or specific molecules, but instead represent averages of all the compounds.
in LV-OOA.

The sources of uncertainty considered in evaluating the average number of carbon atoms in the LV-OOA mixture arise from estimated errors in the elemental analysis calculation, the distribution of vapor pressures of the compounds within the mixture, and variation in the elemental ratios measured in the different field studies. The measurement error arising from elemental analysis is estimated to be $\pm 30\%$ of the reported O/C and $\pm 10\%$ for H/C (Aiken et al., 2007; 2008). Because these errors were reported for individual compounds, we expect the measurement error of a large mixture of compounds to be substantially smaller, so that the values given represent the most conservative case. The uncertainty in $c^*$ for the average of all OOA components is taken to be $10^{-3.2}$ $\mu$g m$^{-3}$, as approximated from the distribution of values reported (Cappa and Jimenez, 2010). The variance in elemental ratios for the mixtures is simply the variance of the data presented in Table 2-1, multiplied by $1.96^2$ in order to reflect the range in which 95% of the data is expected to fall. These errors are propagated forward using the sensitivity of $n_C$ to O/C, H/C, and $\log_{10}(c^*)$ as described by Eq. 2-5, to give three separate values of the uncertainty in the carbon number, $\delta n_C$. The contributions from elemental analysis measurement error, variation in $c^*$, and variance are 3.3, 1.3, and 3.8, respectively. An overall uncertainty, $\delta n_{C,\text{tot}}$, is calculated as the square root of sum of squares of each separate uncertainty, to yield a final estimate of $10.5 \pm 5.2$ for the LV-OOA carbon number, with the greatest source of uncertainty being the variance in elemental ratios reported for each field study discussed here.

Figure 2-3 ($O_{Sc}$ vs. $n_C$) shows the location of the different LV-OOA measurements in carbon oxidation state vs. carbon number space (Kroll et al., 2011). Also shown is the
Figure 2-3. Locations of the different LV-OOA measurements in OSc-nc space. Grey circles indicate the possible combinations of average carbon oxidation state and carbon number (Kroll et al., 2011). Numbered points denote LV-OOA from all ten field campaigns (numbers are the same as in Figure 2-2); OSc is determined from elemental ratios, and nc from Eq. 2.5, using a c* of $10^{-3}$ $\mu$g m$^{-3}$. The red star shows the average values for all the measurements, with the red ellipse depicting the uncertainty in its nc and OSc values (see text for details). The blue star shows the position of the average LV-OOA after applying the recommended correction of 1.3 and 1.1 to O/C and H/C, respectively (Canagaratna et al., 2014), with the blue ellipse depicting uncertainty in the corrected nc and OSc values.

average LV-OOA target, with the ellipse depicting the uncertainty associated with its nc and OSc values. The rotated ellipse arises from the covariance between the outputs and reflects the fact that more highly oxidized compounds require a smaller carbon number for a given value of c*. The carbon numbers determined here (nc ~6-15) are slightly larger than those estimated by Donahue et al. (nc ~5-10) using a similar technique and the same general c* range (Donahue et al., 2012). This difference in part results from the lower value of OSc that we use, and our direct determination of the abundance of hydroxyl and carbonyl functional groups individually, rather than assuming the two are equally abundant.
Functionalization.

Taking the LV-OOA target determined using $c^* = 10^{-3}$ μg m$^{-3}$ (C$_{10.5}$H$_{13.4}$O$_{7.3}$), and assuming it was formed via functionalization reactions only (with changes to H/C and O/C but not carbon number), allows us to work backwards toward precursors in van Krevelen space, using the simple rules described in the Methodology section. Figure 2-4 shows the potential formation pathways and precursors, but is different than most other van Krevelen plots used to represent atmospheric OA since it includes gas-phase as well as particulate organics. The black star denotes the target, and the black circles depict the possible transforms associated with functionalization (as depicted in Figure 2-1), with each point corresponding to the loss of an integer number of functional groups. Figure 2-4a shows the fully saturated case in which functional groups replace C-H bonds only, and Figure 2-4b shows the unsaturated case in which they replace only C=C bonds. Figures 2-4c and 2-4d show the corrected values and are discussed at the end of this section.

The parallelograms represent the range of possible transforms and precursors, and are bounded by the requirement that the target cannot lose more hydroxyl or carbonyl groups than it has (so that the dimensions of the parallelogram are given by the number of hydroxyl and carbonyl groups). The left corner of the parallelogram (y-intercept in the van Krevelen diagram) corresponds to the fully de-functionalized hydrocarbon precursor. For the saturated case, this gives a precursor with a formula consistent with an acyclic alkane. For the unsaturated case, it gives an alkene containing n$_0$/2 C=C bonds (or 3.7 for our target). This corresponds to a precursor of formula C$_{10.5}$H$_{15.7}$, which interestingly is similar to that of monoterpenes, a well-studied class of SOA precursors. These two limiting cases bound the H/C of the hydrocarbon precursor to between 1.5 and 2.2.
Figure 2-4. Functionalization transforms available to the LV-OOA target (black star). For the uncorrected O/C and H/C values, these are calculated for $n_c = 10.5$ and $c^* = 10^{-3}$ μg m$^{-3}$, for the fully saturated case (panel a) and the fully unsaturated case (panel b). For the corrected O/C and H/C values (multiplied by 1.3 and 1.1, respectively), these are calculated for $n_c = 7.7$ and $c^* = 10^{-3}$ μg m$^{-3}$, for the fully saturated case (panel c) and the fully unsaturated case (panel d). Potential oxidative transforms and precursors are bounded by the parallelograms, whose dimensions are defined by the number of hydroxyl and carbonyl functional groups in the target. Each black circle depicts an intermediate precursor, formed from the removal of an integer number of functional groups; the leftmost corner of each parallelogram (y-intercept) gives the limiting H/C value of the unfunctionalized hydrocarbon precursor. OSc contours are shown as dashed lines, and shading indicates the predominant phase of the species: gas phase (white, $c^* > 10$ μg m$^{-3}$), semi-volatile (light grey, $c^* = 0.1$ to 10 μg m$^{-3}$), or condensed-phase (dark grey, $c^* < 0.1$ μg m$^{-3}$). Multiple functional groups (including at least one hydroxyl group) must be lost for the immediate precursor of the target to be in the gas phase. Nonoxidative processes (e.g. hydrolysis) may also be important in SOA formation; the open circles indicate immediate hydrolysis precursors.
The areas defined by the parallelograms in Figure 2-4, and movement within them, are not necessarily tied to specific chemistry, but rather describe the range of possible precursors. The dashed lines are carbon oxidation state contours ($\text{OS}_C \approx 20/C-H/C$). From these, it can be seen that replacing C-H bonds with functional groups (Figure 2-4a) moves more directly along the $\text{OS}_C$ gradient than replacing C=C bonds (Figure 2-4b) does, and results in a larger increase in $\text{OS}_C$ per functional group. At the same time, the oxidation of C=C bonds usually involves the addition of two functional groups per oxidation step. It should be noted that the areas bounded by the parallelograms are for oxidation reactions only; non-oxidative transformations (involving movement along lines of constant $\text{OS}_C$) could lead to a wider range of possible precursors. One example is the dehydration of the target molecule (open circles in Figure 2-4a and 2-4b), whose corresponding forward reaction is the hydrolysis of a carbonyl or epoxide group to form two hydroxyl groups, believed to be an important reaction in the formation of isoprene SOA (Paulot et al., 2009).

The shading in Figure 2-4 indicates the saturation vapor concentration (and therefore predominant phase) as a function of location in van Krevelen space: gas-phase (white, $c^* > 10 \mu g \text{ m}^{-3}$), intermediate (light grey, $0.1 < c^* < 10 \mu g \text{ m}^{-3}$), or particle-phase (dark grey, $c^* < 0.1 \mu g \text{ m}^{-3}$). This is similar to the work of Kessler et al. in which $c^*$ cutoffs were calculated as a function of carbon number (Kessler et al., 2010; 2012). While the exact cutoffs will vary with organic aerosol loading, these are reasonable values for most ambient conditions. Values for $c^*$ were calculated using Eq. 2.4, though for Figure 2-4b it was modified to allow for one DBE to be from a C=C bond:

$$\log_{10} c^* = \log_{10} \alpha + b_C n_C + b_{\text{OH}} \left(n_C \left(1 - \frac{1}{2}H/C\right)\right) + b_{\text{H_2O}} \left(n_C \left(O/C + \frac{1}{2}H/C - 1\right)\right)$$

While the timescales of formation of highly oxidized OA are highly uncertain, there is
evidence (based on Mexico City data) that the process is relatively fast, on the order of a day (Jimenez et al., 2009; Volkamer et al., 2006). This is faster than the rate of heterogeneous oxidation (which occurs on the order of several days, George and Abbatt, 2010; Kessler et al., 2010; 2012; Robinson et al., 2006) suggesting that the immediate precursor to highly oxidized OA is likely not in the particle phase. The production of products with low $c^*$ by gas-phase oxidation leads to a “trapping” in the particle phase where the rate of oxidation slows dramatically (Hearn and Smith, 2006; Weitkamp et al., 2008). Thus the rapid formation of highly oxidized OA via functionalization reactions would seem to require gas-phase precursors. Semi-volatile compounds (light grey area in Figure 2-4) may serve as gas-phase precursors, but their oxidation reactions tend to be slow, since they spend some fraction of their time in the particle phase; in addition they are highly susceptible to depositional losses to other environmental surfaces. Thus, in the absence of fast particle phase oxidation reactions, the most likely immediate gas-phase precursors to highly oxidized aerosol are those that are fully in the gas phase; as shown in Figure 2-4, this requires the precursor to have substantially fewer functional groups than the target (at least two fewer hydroxyl groups or three fewer mixed hydroxyl/carbonyl groups). Known routes for the addition of multiple functional groups in a single oxidation step include the oxidation of carbon-carbon double bonds or oxidative ring-opening reactions, both of which add at least two (and possibly more) functional groups to the molecule. In addition, some alkoxy isomerization reactions can add three or more functional groups at a time (Ziemann and Atkinson, 2012); plus there is evidence for other, poorly-understood mechanisms that involve the rapid addition of multiple functional groups (Ehn et al., 2012).

The above discussion assumes that the formation of low-volatility organics is rapid
compared to the rate of heterogeneous oxidation, and also that gas-particle partitioning is essentially instantaneous. In general, the formation kinetics of the most oxidized fraction of OA are not well constrained; if they are substantially slower in most environments than in MCMA, heterogeneous oxidation could play an important role, allowing the immediate oxidative precursors to be in the condensed phase. This uncertainty underscores the need for additional ambient studies of OA at a variety of photochemical ages. Additionally, recent studies of partitioning kinetics suggest that condensable organics may remain in the gas phase longer than predicted by assumptions of thermodynamic equilibrium (Shiraiwa and Seinfeld, 2012). This could potentially allow for additional gas-phase oxidation even when the precursors have volatilities below the semi-volatile/condensed-phase cutoff. On the other hand, several experimental studies suggest a mass transfer limitation to the evaporation of particulate organics (Grieshop et al., 2007; Perraud et al., 2012; Vaden et al., 2011); this would have the opposite effect, enhancing the “trapping” effect and causing the semi-volatile precursors to behave more like the least-volatile species.

The potential formation pathways of highly oxidized aerosol also depend on our knowledge of the physicochemical properties (elemental ratios and $c^*$), which can be uncertain. While the $c^*$ chosen for our target has a relatively minor effect on calculated carbon number, it strongly influences the potential formation processes, most importantly by affecting the phase of the precursors. Decreasing the $c^*$ of the target (for example, from $10^{-3}$ to $10^{-5} \mu g m^{-3}$, increasing the calculated $n_C$ from 10.5 to 11.8), increases the number of functional groups that must be removed in order for the immediate precursor to be in the gas phase. Therefore targets with low $c^*$ are less likely to be formed from functionalization reactions, whereas targets with higher $c^*$ can be easily formed from reactions that add only 1-
2 functional groups.

The elemental ratios used for the target in Figure 2-4a and 2-4b represent the average from a number of studies (Table 2-1), yielding an average chemical formula of $C_{10.5}H_{13.4}O_{7.3}$ (with 2.5 hydroxyl groups and 4.8 carbonyl groups). If we use the corrected values for the elemental ratios (Canagaratna et al., 2014) (blue star in Figure 2-2), but the same $c^*$ as in the base case ($10^{-3} \, \text{µg m}^{-3}$), we obtain a target with a chemical formula of $C_{7.7}H_{10.9}O_{7}$ (3.7 hydroxyl groups and 3.3 carbonyl groups, Figure 2-4c and 2-4d). The higher $n_{\text{OH}}/n_{=\text{O}}$ ratio implies a lower carbon number at a given $c^*$, since hydroxyl groups have a greater effect on $c^*$ than do carbonyl groups. While this has little effect on the number of functional groups separating the target and a gas-phase precursor (since the separation is governed primarily by the $c^*$ of the target), it can affect the overall pathways connecting the oxidized aerosol to hydrocarbon precursors; additional oxidation steps will be required to form a target with a higher number of functional groups.

**Fragmentation reactions.**

In addition to the chemical constraints listed in the Methodology section, the phase of the fragmentation precursor also limits the possible transforms associated with this reaction. As in the functionalization case, we require the precursor to be in the gas phase ($c^* > 0.1 \, \text{µg m}^{-3}$) since heterogeneous oxidation is assumed to be too slow to account for the rate of formation of highly oxidized aerosol.

The overall, average effect of fragmentation reactions on $c^*$ is illustrated in Figure 2-5, which shows the contribution of a single carbon atom (and its associated functional groups) to the $c^*$ of a molecule of $n_C = 10.5$. (Results are only weakly dependent on carbon number above $n_C = 7$.) This is calculated from Eq. 2.4, assuming that the functional groups
Figure 2-5. Contour plot showing the influence of a single carbon atom in a molecule, including its associated functional groups, on the molecule’s saturation vapor concentration ($\delta(\log_{10} c^*)/\delta n_c$), as calculated from Eq. 2.4. These are calculated for $n_c = 10.5$, but do not vary significantly with carbon number above $n_c = 7$. Instead H/C and O/C have the strongest influence on “per-carbon $c^*$”, which is greatest when both ratios are high (top right corner, when hydroxyl groups are abundant) (Kessler et al, 2010; 2012). The discontinuities near the left of the figure reflect the fact that Eq. 2.4 does not always hold at low O/C, where unsaturation arises from C=C double bonds or rings rather than carbonyl groups; thus when DBE > $n_0$, Eq. 2.4 is modified to allow for C=C double bonds. LV-OOA targets used in this study are denoted by markers.

are evenly distributed throughout the molecule (i.e., the number of groups on the carbon atom is equal to the number of groups on the entire molecule divided by $n_c$). For our target (black star in Figure 2-5), each carbon atom decreases the vapor pressure by 1.4 orders of magnitude. This is a full order of magnitude larger than the effect of a non-functionalized carbon (e.g., a CH$_2$ group). This simple view of “per-carbon $c^*$” helps guide assessments of the viability of fragmentation reactions as steps in the formation of highly oxidized organic
aerosol; however, as discussed in the Methodology section, it does not accurately represent all fragmentation reactions, since functional groups generally are not evenly distributed throughout a given molecule. Here we consider potential fragmentation precursors both with and without evenly-distributed functional groups.

Assuming the functional groups are distributed evenly, fragmentation of a gas-phase molecule cannot form highly oxidized, low-volatility OA. This is because the decrease in $c^*$ from the additional functional groups (in this case, one hydroxyl group and one carbonyl group, lowering $c^*$ by 3.2 orders of magnitude) is largely if not completely offset by the $c^*$ increase from the carbon loss (1.4 orders of magnitude per carbon atom). As a result, the large decrease in $c^*$ needed to form a low-volatility target (2 orders of magnitude) is not possible, a conclusion broadly consistent with the findings of Cappa and Wilson (2012). However, when functional groups are not evenly distributed, and reduced carbon can be lost during fragmentation, the formation of the target via fragmentation is possible in some cases. The carbon numbers and elemental ratios of viable precursors are depicted in Figure 2-6 (solid-shaded areas). The allowed precursors are only slightly larger than the target, and are significantly less oxidized, indicating that fragmentation can produce highly oxidized organic aerosol only when the precursor loses a small ($C_1$ or $C_2$) and essentially unfunctionalized fragment. (This exact requirement depends on the identity and number of functional groups added to the fragment). However, molecules that are more volatile than our target are more likely to form via fragmentation, since they may be more easily formed from gas-phase precursors. Similarly, less-oxidized species can also be formed from fragmentation reactions, since the increase in $c^*$ from losing carbon atoms is not as great (top left corner of Figure 2-5). Thus, while fragmentation reactions probably do not lead to the immediate formation of
highly oxidized OA, they might occur as part of the overall reaction mechanism, primarily in the earlier oxidation steps.

**Figure 2-6.** Ranges of possible precursors of fragmentation (solid-shaded areas) and oligomerization (lightly-shaded areas) reactions that can form the LV-OOA target (black star). Three-dimensional chemical space is depicted by showing the range in van Krevelen space available to precursors of different carbon numbers. The numbers correspond to the carbon number change of the reaction; for example "-2" refers to a fragmentation reaction in which the target has two fewer carbon atoms than the precursor. The target can be formed via fragmentation of a gas-phase precursor only if a small (C1-C2) reduced fragment is lost; oligomerization is a more viable channel, though it requires the precursors to be low in c* and thus extremely oxidized. In both cases, the range of possible precursors is considerably narrower if it is assumed that functional groups are evenly distributed on the target and precursor(s).

**Oligomerization reactions.**

Because oligomerization reactions decrease c*, they are generally more viable steps in the formation of oxidized OA components than fragmentation reactions. As with fragmentation reactions, the phase of the precursor introduces constraints beyond those described in the Methodology section: since the probability of two gas-phase precursors reacting is quite low under most conditions, at least one precursor must be present in the
particle phase \( (c^* < 10 \, \mu g \, m^{-3}) \).

Since oligomerization reactions involve changes to \( n_C \), their effects can be visualized similarly to the effects of fragmentation reactions, by treating all carbon as evenly functionalized (Figure 2-5). Assuming that functional groups are evenly-distributed in both the precursors and the targets, the condensed-phase precursor can be smaller than the target by one or two carbon atoms. Precursors with even fewer carbon atoms will be so volatile that they will be present in the gas phase only, and therefore cannot participate in oligomerization reactions. However, a wider range of precursors is possible if the functional groups are not evenly distributed, and instead the two precursor molecules have different levels of functionalization. The range of possible oligomerization precursors are shown as lightly-shaded regions in Figure 2-6; lower carbon numbers are possible when the majority of the functional groups are on the condensed-phase precursor. Thus oxidized organic aerosol could form from the oligomerization of smaller, highly-oxidized molecular species, which themselves may be formed by previous functionalization or fragmentation reactions. This is broadly consistent with the view of formation of SOA from aqueous chemistry (Ervens et al., 2011); even though we do not explicitly model partitioning into the aqueous phase, this work provides some constraints into the chemical nature (\( H/C \) and \( O/C \) ratios) of these smaller species. On the other hand, the target itself (of formula \( C_{10.5}H_{13.4}O_{7.3} \)) is not consistent with the oligomeric species measured in SOA, such as those from monoterpene oxidation (which typically have twenty or more carbon atoms and relatively low \( O/C \) values, Tolocka et al., 2004), isoprene photooxidation, or glyoxal oligomerization (which typically have higher \( H/C \) values, Chhabra et al., 2011). Thus, even though these oligomerization reactions can occur under atmospheric conditions, they do not appear to dominate formation of the most oxidized
fraction of the aerosol.

**MCMA Case Study.**

![Graph](image)

**Figure 2-7.** Functionalization transforms available to the LV-OOA target from the MILAGRO ground site, using \( n_c = 10 \) and \( c^* = 10^{-5} \) µg m\(^{-3}\). (These are different than the values in Figures 2-3 and 2-4 which used \( c^* = 10^{-3} \) µg m\(^{-3}\).) This plot is similar to Figure 2-4, except that the saturated and unsaturated cases are shown together, as black and grey parallelograms, respectively (the \( c^* \) cutoffs are given for the saturated case only). Because of the exceedingly low \( c^* \) of these organics (Cappa and Jimenez, 2010; Huang et al., 2011), their formation from gas-phase precursors can occur only if a large number of functional groups (three or more) are added to the precursor in a single oxidation step.

Although LV-OOA in Mexico City is significantly more oxidized than that measured in other locations (Table 2-1 and Figure 2-2), it has received substantial study and to our knowledge is the only time LV-OOA \( c^* \) and elemental ratios have both been reported. Here, we examine LV-OOA at the T0 ground site at MILAGRO (Aiken et al., 2008; Huffman et al., 2009) as a case study, in order to gain insight into potential formation pathways for this exceedingly highly oxidized organic aerosol. Using a \( c^* \) of \( 10^{-5}\pm2 \) µg m\(^{-3}\) gives a target carbon.
number estimate of 10.0 ± 3.4 with the chemical formula C_{10}H_{12.1}O_{8.4} (3.4 hydroxyl groups and 5 carbonyl groups). The sources of uncertainty studied in this case for the carbon number are the error in computing elemental ratios and the deviations in $c^*$, which give values of $\delta n_C$ of 3.2 and 1.1, respectively. As with the average LV-OOA, the overall error is computed from the sum of the square of the errors. The potential functionalization precursors are shown in Figure 2-7 for the saturated and unsaturated cases. Because the target in this case is so low in $c^*$, the functionalization transforms involve the loss of at least two hydroxyl groups, or all five carbonyl groups, to form precursors that are semi-volatile, and even more for the precursor to be present exclusively in the gas phase. This suggests that gas-phase functionalization reactions would have to be exceedingly rapid to lead to the formation of organic material that is so high in oxidation state and low in $c^*$. Similarly, this class of organics cannot be formed directly from fragmentation reactions (even if the loss of small, reduced fragments are allowed). Again, some fragmentation reactions might occur earlier in the overall oxidation mechanism, but they do not play a role in the last step that forms this target. As in our average LV-OOA target (Figure 2-6), oligomerization could be a viable step in the formation of these compounds, provided highly oxidized organic precursor species are present in the condensed phase.

### 2.4 Conclusions

We have presented a new general approach for assessing the potential pathways and precursors involved in the formation of highly oxidized organic aerosol, which involves starting from the product or “target” and working backwards. We define this target based on thermodenuder measurements of $c^*$ and average elemental ratios of LV-OOA as measured by
the AMS, yielding an average approximate chemical formula of C_{10.5}H_{13.4}O_{7.3}. The utility of our retrosynthetic method for constraining its formation chemistry has been demonstrated for this average LV-OOA target, as well as an exceedingly oxidized case, LV-OOA measured at the MILAGRO ground site. Our results suggest that the most probable LV-OOA-forming reactions are (1) functionalization reactions that add multiple functional groups (including at least one hydroxyl group) at a time, (2) oligomerization reactions of smaller, highly oxidized precursors, and (3) fast oxidation reactions within the condensed phase, such as aging within aqueous particles. While this third pathway was not explicitly modeled in the present study, the first two pathways were determined based on conditions in which fast particle phase oxidation reactions are not allowed. Therefore, allowing for rapid aging within particles reduces the constraints on the system, making it a viable alternative pathway. Fragmentation reactions are only possible as the final step if they involve the loss of a small number of relatively reduced carbon atoms. While the specific aim of this study was to apply this technique to LV-OOA, this approach could be useful for understanding a wider range of targets, including other fractions of the aerosol (e.g., SV-OOA, Jimenez et al., 2009), as well as SOA generated in laboratory studies. However, this requires some information about $c^*$ and/or carbon number of the aerosol of interest.

In the present work, we limited the partitioning of the organic species to only two phases, the gas phase and the condensed-organic phase. Recent work has suggested the importance of the liquid-water phase as a medium for oxidation reactions (Ervens et al., 2011), which could also be included in this treatment. This could be done using existing structure activity relationships (e.g. Hine and Mookerjee, 1975) to estimate saturation vapor concentrations of organics over water (Henry’s law constant) from chemical properties.
(elemental ratios, functional group distributions, etc.). Otherwise the general approach, including the transforms that describe the chemical reactions, is the same as described in this work.

This retrosynthetic approach relies critically on the accurate characterization of the target molecule and key characteristics of its formation. This present work highlights the need for accurate measurements of the elemental ratios and \( c^* \) of organic aerosol. Field measurements of \( c^* \) are limited, hindering accurate estimates of carbon number. If actual \( c^* \) values are higher than those used here, then functionalization pathways would become more feasible since they would require the addition of a smaller number of functional groups to move from a gas-phase precursor to the target. Conversely, ambient organic products with lower \( c^* \) values will be harder to form via functionalization reactions as they will require a larger decrease in \( c^* \). Therefore, better constraints on \( c^* \) of the oxidized aerosol could significantly improve the accuracy of our target carbon number. There is also a need for better constraints on the kinetics of the formation of highly oxidized aerosol. This has been measured only in the outflow from MCMA, which might not be widely representative. This rate is a key constraint on the formation pathway, as it limits the number of oxidation steps that are possible as well as the phase in which those reactions can happen. Additionally, characterization of highly-oxidized OA using techniques other than AMS would be useful. The direct measurement of functional group distributions (e.g., using FTIR, Maria et al., 2002), can provide an alternative, and potentially more comprehensive, description of the relationships between chemical structure, saturation vapor concentration, and formation chemistry. Similarly, direct measurements of \( n_c \) (e.g., using UHR-ESI-MS) would improve the accuracy of the target chemical formula and could provide more detailed information on
the formation pathways of a wide range of molecular compounds.

We have made an effort to demonstrate the utility of this retrosynthetic approach for exploring the possible pathways by which highly oxidized aerosol is formed. By starting at the known endpoint/target, we improve our ability to identify pathways that can actually result in the formation of low-volatility, highly-oxidized organic compounds. This is in contrast to standard forward approaches that require some guesswork as to the starting molecules and pathways that may result in the formation of the target. This general approach could be particularly powerful when applied to rigorous models of oxidation mechanisms, gas-particle partitioning, and aerosol chemistry (Aumont et al., 2012; Cappa and Wilson, 2012; Donahue et al., 2012; Zhang and Seinfeld, 2012). Running such models backwards from well-defined targets may help identify key classes (or even structures) of organic compounds, as well as reaction conditions, that are most likely to lead to the formation of this important class of organic aerosol.

2.5 Acknowledgements

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2.6 References


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Chapter 3

Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution

http://www.atmos-chem-phys.net/14/10773/2014/acp-14-10773-2014.pdf

3.1 Introduction

As explained in Chapter 1, the sources and formation mechanisms for the most oxidized fraction of OA remain highly uncertain. In Chapter 2, we showed that traditional gas-phase oxidation pathways are not able to fully describe the production of this material and therefore non-traditional pathways (e.g. oxidation within aqueous particles) may be important. Aqueous-phase reactions in atmospheric water droplets have been known to play a role in the fate of chemicals in the atmosphere for many years (Faust, 1994); more recently, these reactions have received attention as a possible mechanism for the production and evolution of organic aerosol (Ervens et al., 2011). As described in Chapter 1, a number of laboratory studies have investigated oxidation of organic compounds in the aqueous phase and shown that it can lead to the rapid formation of highly oxidized organic products.

The importance of such oxidation processes relies critically on partitioning (Donahue et al., 2014): a compound will undergo aqueous-phase oxidation only if it is partitioned to the
atmospheric aqueous phase (cloud droplets or aqueous submicron particles), rather than the gas or condensed-organic phase. The partitioning between the gas and aqueous phases is determined by a compound’s effective Henry’s law constant ($H^*$) (or alternatively its saturation vapor concentration over water ($c_{aq}^*$) (Ervens et al., 2011)), as well the liquid water content (LWC) of the air mass, as shown in Eq. 3.1:

$$f_{aq} = \frac{(LWC)H^*RT}{10^{12}+(LWC)H^*RT} = \frac{\text{LWC}/c_{aq}^*}{1+\text{LWC}/c_{aq}^*}$$

(3.1)

in which $f_{aq}$ is the equilibrium fraction in the aqueous phase, LWC is in units of $\mu$g m$^{-3}$, $H^*$ is in units of M atm$^{-1}$, and $c_{aq}^*$ is in units of $\mu$g m$^{-3}$ and is equal to $10^{12} H^* R T^1$ (where $R = 0.0821$ L atm mol$^{-1}$ K$^{-1}$ and $T$ is temperature in K). By Eq. 3.1, the partitioning of a single compound (with a fixed $H^*$ or $c_{aq}^*$) can be very different for different values of LWC. Atmospheric LWCs can span many orders of magnitude, ranging from $\sim 1$ to $100$ $\mu$g m$^{-3}$ for aqueous aerosol, and $\sim 10^5$ to $10^6$ $\mu$g m$^{-3}$ for cloud droplets (Ervens et al., 2011), while a bulk aqueous solution has a

Figure 3-1. The fraction of a compound that will partition to the aqueous phase ($f_{aq}$) as a function of its Henry’s law constant, $H^*$ (or alternatively its saturation vapor concentration, $c_{aq}^*$), and the liquid water content (LWC). Compounds with $0.1$ M atm$^{-1} < H^* < 10^9$ M atm$^{-1}$ will be primarily in the aqueous phase at bulk LWC (blue line), but primarily in the gas phase at aqueous aerosol LWC (green line). Cloud water (teal line) represents the intermediate case, with more partitioning into the aqueous phase than for aqueous particles, but still with far less than for a bulk aqueous solution.
LWC on the order of $10^{12}$ µg m$^{-3}$ (the density of water). Therefore, $f_{aq}$ for a given compound will also vary by many orders of magnitude for these systems, as illustrated in Figure 3-1. Many compounds that are considered to be “water-soluble” for bulk solutions ($H^*$ of 1-1000 M atm$^{-1}$) will not actually partition significantly into aqueous submicron particles, or even into cloud droplets. This could have an important influence on the resulting chemistry, and suggests that a bulk solution may not always accurately represent aqueous processing under atmospheric conditions.

Some recent bulk-solution experiments have begun to examine the role of gas-particle partitioning under lower-LWC conditions, by atomizing or nebulizing the bulk aqueous solution as it undergoes aqueous oxidation (Lee et al., 2011a; 2011b; 2012; Liu et al., 2012b; Ortiz-Montalvo et al., 2012; Zhao et al., 2012). While these studies do indeed show loss of the most volatile species formed, leaving behind only low-volatility condensed-phase products, the chemistry that forms these products still takes place in the bulk aqueous solution, with limited partitioning into the gas phase. To our knowledge, only two studies (Nguyen et al., 2013; Volkamer et al., 2009) have examined oxidation chemistry within aqueous droplets themselves, allowing for gas-particle partitioning that mimics what may occur in the atmosphere. These studies found enhanced uptake and aerosol yield from glyoxal (Volkamer et al., 2009) and glycolaldehyde (Nguyen et al., 2013) in the presence of aqueous submicron particles; results from these experiments have not been explicitly compared to those in which oxidation was carried out in bulk solutions.

Here we describe laboratory studies of the oxidation of water-soluble organic species in the aqueous phase, with experiments conducted both within bulk aqueous solutions and within submicron aqueous particles. The goal of these experiments is to compare the oxidation
chemistry under very different partitioning conditions. We focus on the oxidation of polyols with the chemical formula $C_nH_{2n+2}O_n$ (with one hydroxyl group on each carbon atom). Polyols with four or more carbon atoms have exceedingly high values of $H^* (> 10^{16} \text{ M atm}^{-1}$ (Sander, 1999)), ensuring they will be present in the aqueous phase even at the low LWC in our chamber; thus any observed partitioning will involve reaction intermediates and products only. To our knowledge, this work is the first direct comparison of aqueous oxidation in submicron particles and in bulk aqueous solution.

3.2 Experimental Methods

Two sets of experiments are conducted: (1) bulk oxidation, in which reactions take place within a bulk aqueous solution of $\sim0.5$ L volume, and (2) chamber oxidation, in which reactions take place within submicron aqueous particles in an environmental chamber. Both sets of experiments use dark Fenton chemistry ($\text{Fe}^{2+}$ and hydrogen peroxide) as an aqueous-phase source of oxidants. While there is some uncertainty as to the exact oxidant-forming mechanisms in Fenton systems, in part due to the complex iron speciation, it is likely that hydroxyl radicals ($\text{OH}$) are the predominant oxidant formed in our experiments (Ma et al., 2006; Southworth and Voelker, 2003). $\text{Fe}^{2+}$ reacts with hydrogen peroxide ($\text{H}_2\text{O}_2$) to produce $\text{OH}$ and $\text{Fe}^{3+}$, which is subsequently converted back to $\text{Fe}^{2+}$ via reaction with other species:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH} \quad \text{(R3.1)}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2 + \text{H}^+ \quad \text{(R3.2)}
\]

\[
\text{Fe}^{3+} + \text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad \text{(R3.3)}
\]

Alternatively, $\text{Fe}^{3+}$ can form complexes with water or organic acids; these pathways compete with the regeneration of $\text{Fe}^{2+}$ and can eventually slow the production of $\text{OH}$.
Fe\(^{3+}\) + H\(_2\)O → Fe(OH)\(^{2+}\) + H\(^+\) \hspace{1cm} \text{(R3.4)}

Fe\(^{3+}\) + L \rightarrow Fe(L)\(^{2+}\) (L = organic ligand) \hspace{1cm} \text{(R3.5)}

A more detailed treatment of this chemistry is described elsewhere (Arakaki and Faust, 1998; Faust and Hoigne, 1990; Hoffmann et al., 1996; Ma et al., 2006; Nguyen et al., 2013; Ou et al., 2008). In both sets of experiments, we start with a mixture of a polyol and Fe\(^{2+}\), and initiate the oxidation chemistry with the addition of H\(_2\)O\(_2\). The use of Fenton chemistry to initiate oxidation within aqueous submicron particles was first demonstrated in a recent glycolaldehyde uptake study by Nguyen et al. (2013); the present experiments differ from that work in that we focus on dark Fenton chemistry, using the addition of H\(_2\)O\(_2\) rather than exposure to UV lights to initiate the reaction.

3.2.1 Bulk aqueous oxidation

![Figure 3-2. Experimental setup for (a) bulk experiments and (b) chamber experiments. The atomizer serves as a reactor for bulk oxidation but only as a source of aqueous particles for chamber oxidation. In the bulk experiments, the solution is continuously atomized, with H\(_2\)O\(_2\) added after the polyol and FeSO\(_4\) have been sampled for 1 hour. In the chamber experiments, a solution containing the polyol and FeSO\(_4\) is atomized into the chamber for 1 hour, with gas-phase H\(_2\)O\(_2\) introduced later via the two-neck flask. Humidified make-up air is continuously supplied to the chamber via the bubbler. While the focus of this work is dark Fenton chemistry, UV lights are turned on following oxidation in both setups in order to assess the photo-reactivity of the reaction products.](image-url)
For bulk oxidation experiments, the general technique of Lee et al. (2011a) is used, in which an atomizer serves both as the reactor containing the aqueous solution and as the method for aerosolizing the solution, enabling online analysis by aerosol instrumentation. Figure 3-2a shows a simple schematic of the experimental setup. Reactions are carried out in a 1 L borosilicate reaction bottle, and the solution is continuously atomized using a constant output atomizer (TSI, Model 3076) with a backing pressure of ~30 psi of pure compressed air (Aadco 737-13A/C with methane reactor), giving 2.5-3 LPM aerosol output flow. The atomizer output is passed through an empty 1 L bottle to remove excess liquid water, then through a diffusion dryer, and finally into the aerosol instruments, described in Section 3.2.3.

A major difference between the present experiments and previous bulk oxidation experiments (Lee et al., 2011a; 2011b; 2012; Liu et al., 2012b; Ortiz-Montalvo et al., 2012; Zhao et al., 2012) is the oxidation scheme: here OH radicals are generated via dark Fenton chemistry rather than photolysis of hydrogen peroxide, avoiding the use of 254 nm lights. The initial atomization solution contains iron(II) sulfate heptahydrate (99+%)) and a polyol (glycerol, 99.5+%, erythritol, 99+%, adonitol 99+%), mannitol 98+%, or volemitol, all Sigma-Aldrich) fully dissolved in Milli-Q water; concentrations are given in Table 3-1. Prior to H$_2$O$_2$ addition, this solution is atomized into the AMS (see below) to characterize the reactants and ensure they are inert with respect to each other. To initiate Fenton chemistry, hydrogen peroxide (30% w/w in water, Alfa Aesar) is added and the solution is shaken to facilitate mixing. After ~3 hours, once the reaction appears to have gone to completion, the solution is exposed to UV light for additional oxidation (via photo-Fenton chemistry) and/or direct photolysis, using four external blacklights (Sylvania BL-350 ECO, output 300-400 nm). Photo-Fenton reactions regenerate Fe$^{2+}$ and can produce additional OH:
\[
\begin{align*}
\text{Fe}^{3+} (\text{OH}^-) + \text{hv} & \rightarrow \text{Fe}^{2+} + \text{OH}^\cdot \\
\text{Fe}^{3+} (\text{L}^-) + \text{hv} & \rightarrow \text{Fe}^{2+} + \text{L}
\end{align*}
\]

Table 3-1. Initial concentrations of reactants in the atomizer solutions.

<table>
<thead>
<tr>
<th>Polyol Precursor</th>
<th>Chemical Structure</th>
<th>Bulk Experiments</th>
<th>Chamber Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Polyol] (mM)</td>
<td>[FeSO₄] (mM)</td>
<td>[H₂O₂] (mM)</td>
</tr>
<tr>
<td>Glycerol (C₃H₈O₃)</td>
<td>0.20</td>
<td>0.45</td>
<td>2.0</td>
</tr>
<tr>
<td>Erythritol (C₄H₁₀O₄)</td>
<td>0.20</td>
<td>0.42</td>
<td>2.0</td>
</tr>
<tr>
<td>Adonitol (C₅H₁₂O₅)</td>
<td>0.20</td>
<td>0.41</td>
<td>2.0</td>
</tr>
<tr>
<td>Mannitol (C₆H₁₄O₆)</td>
<td>0.22</td>
<td>0.42</td>
<td>2.0</td>
</tr>
<tr>
<td>Volemitol (C₇H₁₆O₇)</td>
<td>0.19</td>
<td>0.40</td>
<td>2.0</td>
</tr>
</tbody>
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<tbody>
<tr>
<td>(a) Initial concentrations in the atomizer solution; the aqueous particles themselves will be substantially more concentrated (by a factor of ~1000).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Estimated concentrations within the particles, calculated by assuming full evaporation of (\text{H}_2\text{O}_2) into the chamber, with Henry’s law partitioning into the aqueous particles; likely represent an upper limit.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Chamber oxidation

Chamber experiments are conducted to allow for aqueous oxidation in submicron particles, providing partitioning conditions representative of deliquesced atmospheric aerosol. The chamber oxidation setup is shown in Figure 3-2b. The MIT chamber is a 7.5 m³ Teflon (5 mil PFA) bag within a temperature-controlled environmental room. Two banks of 24 blacklights (Sylvania BL-350 ECO) on opposite sides of the chamber provide UV irradiation when needed. The chamber is run as a semi-batch reactor with 5 LPM pure air added to balance instrument...
sample flows. A fraction of this air is sent through a bubbler containing Milli-Q water in order to maintain a relative humidity of between 67% and 79%, ensuring that all sulfate-containing particles are aqueous. Prior to reaction, seed particles composed of iron(II) sulfate (FeSO₄) and a polyol are introduced into the chamber via atomization. The liquid water content in the chamber is not directly measured, but is estimated to be in the range of ~20 to ~150 μg m⁻³ prior to oxidation, based on concentrations of particulate water measured by the AMS. These values are broadly consistent with liquid water contents estimated by assuming the particles have a similar hygroscopic growth factor as particles of ammonium sulfate (Seinfeld & Pandis, 2006).

Concentrations of the atomizer solution are given in Table 3-1; it should be noted that within the aqueous particles themselves, concentrations will be substantially higher than these values, since the solution is concentrated upon atomization by a factor of ~1000 (based on measured mass loadings and estimated LWC).

Seed particles are allowed to mix in the chamber for one hour prior to addition of H₂O₂, which initiates the reaction. H₂O₂ is not added directly to the atomizer solution since this would initiate oxidation in the bulk solution prior to atomization, and so is instead introduced in the gas phase, from which it subsequently partitions into the aqueous phase. Gas-phase H₂O₂ is introduced by sending 1-1.5 LPM air through a two-neck flask containing 6.0 μL of 30% aqueous H₂O₂ solution and into the chamber via a Teflon line; full evaporation of the H₂O₂ takes approximately 30 min. Assuming all the H₂O₂ enters the chamber, and partitions into the aqueous particles according to Henry's law (with $H^* = 10^5$ M atm⁻¹ (Sander, 1999)), this gives 270 ppb H₂O₂ in the gas phase, and 27 mM in the aqueous particles. This aqueous concentration is higher than in the bulk experiments, but the concentrations of Fe²⁺ and polyol are also higher in the particles than in the bulk solution. However, because some H₂O₂ is expected to be lost to
surfaces, such as the Teflon inlet tubing and chamber walls, these H$_2$O$_2$ concentrations likely represent upper limits. After completion of the dark Fenton chemistry, the blacklights are turned on for additional photolytic and/or oxidative chemistry, as in the bulk experiments. Under dark conditions, gas-phase oxidation is unlikely; however, during irradiation the photolysis of H$_2$O$_2$ will lead to the formation of some gas-phase OH; as discussed below, this is unlikely to affect the observed chemistry.

### 3.2.3 Aerosol analysis

Aerosol size distribution, volume, and number density are monitored using a scanning mobility particle sizer (SMPS, TSI, Inc.). Chemical composition of non-refractory particulate matter (here, operationally defined as all material that is instantly vaporized on the 600 °C tungsten heater) is measured using a high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne Research, Inc.). Although the AMS uses electron impact ionization, the resulting mass spectra are also influenced by the heater, and should be compared to standard spectra in the AMS spectral database rather than the NIST database. The AMS allows for the measurement of chemical families, such as total organic, sulfate, and ammonium (Canagaratna et al., 2007; DeCarlo et al., 2006), as well as elemental ratios of the organic species, most importantly oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) (Aiken et al., 2007; 2008). All data reported here was taken with the instrument operated in V mode. Because the amount of sulfate per particle is constant, abundances of all reported ions and families are normalized to sulfate, accounting for possible changes in collection efficiency (CE), variations in atomizer output, dilution in the chamber or atomizer, and loss of particles to surfaces. Some sulfate signal (10-25%) is measured in the “closed” mass spectra, suggesting that FeSO$_4$ does not flash-vaporize at the temperature of the AMS vaporizer (~550-600°C). However, this fraction does not
vary significantly over any experiment, suggesting the AMS “diff” signal is sufficient for this normalization. In most chamber experiments the aerosol is not sent through a dryer prior to analysis, though drying appears to have no effect on measured elemental ratios or sulfate-normalized concentrations. For chamber oxidation experiments, we also monitor temperature and relative humidity (Vaisala), NOx (Horiba, Inc.), and ozone (2B Tech).

3.3 Results and Discussion

A series of control experiments were carried out to verify that aqueous-phase, dark Fenton chemistry was indeed responsible for any chemistry observed. No reaction was observed between the polyols and FeSO₄ in the absence of H₂O₂, nor between the polyols and H₂O₂ in the absence of FeSO₄, confirming that both Fe²⁺ and H₂O₂ are necessary for oxidation to occur. Furthermore, no chemical changes were observed upon addition of H₂O₂ or exposure to UV when a chamber experiment (using erythritol-FeSO₄ particles) was conducted under dry conditions (RH < 4%). The sulfate-normalized organic signal gradually decayed over the course of this experiment, but this is likely a result of gradual evaporation of organic material as the chamber air is diluted. The lack of a reaction under such dry conditions confirms that the chemistry described below indeed takes place only in the aqueous phase.

3.3.1 Bulk oxidation of erythritol

Results for the bulk oxidation of erythritol (C₄H₁₀O₄) are shown in Fig. 3-3. Figure 3-3a shows the aerosol mass spectrum of the aqueous erythritol solution, taken over a 30-minute period immediately prior to the addition of H₂O₂. Figure 3-3b shows the time traces of key AMS ions and species (all normalized to sulfate). Once H₂O₂ is added, oxidation occurs immediately. Key ions associated with erythritol (m/z 29, 61, 73, 91) begin to decay rapidly (initial lifetime
Figure 3-3. Results for the oxidation of erythritol within the bulk aqueous phase: (a) AMS spectra of unreacted erythritol; (b) sulfate-normalized mass concentrations of total organic (Org), ammonium (NH$_4^+$), CO$_2^+$, and key ions associated with erythritol ($m/z$ 29, 61, 73, 91) as a function of reaction time; (c) AMS spectra of oxidation products; and (d) oxygen-to-carbon and hydrogen-to-carbon ratios as a function of reaction time. Results in panels a, c, and d are from high-resolution mass spectrometric analysis. All traces in panel b are from unit mass resolution, except NH$_4^+$ and CO$_2^+$, which are high-resolution traces.

~1.8 min), presumably by reaction with OH. This compares to a lifetime of ~14 hr in the gas phase (assuming a $k_{OH}$ of 2 x $10^{11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ and OH concentration of 1 x $10^6$ molec cm$^{-3}$, Seinfeld & Pandis, 2006). Using a $k_{OH}$ of 1.9 x $10^9$ M$^{-1}$ s$^{-1}$ (Herrmann et al., 2010), this decay is consistent with an initial aqueous OH concentration of 4.8 x $10^{-12}$ M, which is within an order of magnitude of the average OH concentrations estimated for ambient deliquesced particles.
(Herrmann et al., 2010). The OH concentration, estimated from the time dependence of the polyol concentration (see Supporting Information), drops over the course of the experiment, reaching a final OH exposure of $2.7 \times 10^{-9}$ M s. Sulfate-normalized organic signal initially decreases, likely due to the formation and evaporation of compounds that are more volatile than erythritol, but then gradually rises, presumably from the addition of oxygen-containing functional groups that increase the molecular weight and reduce the volatility of the organic species. Ammonium ($\text{NH}_4^+$) also rises, likely due to uptake of ammonia from the laboratory air; this is consistent with acidification of the solution, which is known to occur upon initiation of dark Fenton chemistry (Nguyen et al., 2013). While aqueous ammonia can undergo oxidation by OH to form nitrite and nitrate (which are photosensitizers), this process is expected to be too slow to be important here (with $k_{\text{OH}+\text{NH}_3} = 1 \times 10^8$ M$^{-1}$ s$^{-1}$, ~20 times slower than $k_{\text{OH}+\text{erythritol}}$, Huang et al., 2008). The uptake of $\text{NH}_4^+$ is accompanied by an instantaneous change in the appearance of the atomizer solution from colorless to yellow-orange, consistent with the formation of $\text{Fe(OH)}_2^+$ (Zuo and Hoigne, 1992).

Rapid growth of the $\text{CO}_2^+$ ion in the AMS is observed upon oxidation (Fig. 3-3b). This highly oxidized ion fragment, which typically indicates the presence of carboxylic acids in the AMS, is the most abundant ion in the product mass spectra, shown in Fig. 3-3c. Figure 3-3d shows the elemental ratios of the particulate organic species as a function of time; the rapid rise in O/C and drop in H/C upon addition of H$_2$O$_2$ is also consistent with rapid oxidation of the organic species. It should be noted that the initial H/C and O/C measured by the AMS do not match the true values for erythritol. This is a result of using the default elemental analysis correction factors, which have been determined empirically for an ensemble of species rather than individual compounds (Aiken et al., 2008); however, errors in the absolute elemental ratios
are not expected to affect the observed trends in H/C and O/C, nor the overall conclusions of this work. The rapid oxidation of dissolved organic species observed here is broadly consistent with the findings of other bulk oxidation studies (Altieri et al., 2006; 2008; Carlton et al., 2007; Kirkland et al., 2013; Lee et al., 2011a; 2011b; 2012; Liu et al., 2012a; Perri et al., 2009; Sun et al., 2010; Tan et al., 2009; 2010; Zhang et al., 2010; Zhao et al., 2012).

The AMS mass spectrum of the oxidation products closely resembles that of oxalate ($C_2O_4^{2-}$) (Mensah et al., 2011; Takegawa et al., 2007), which has been shown to be a major product in other aqueous-phase oxidation systems (Carlton et al., 2007; Perri et al., 2009; Tan et al., 2010). A pathway for the formation of oxalic acid from the aqueous oxidation of ethylene glycol (a C2 diol) has been shown by Tilgner & Herrmann (2010) and mechanisms for the formation of oxalic acid from larger diacids have been described by Ervens et al. (2004). We did not observe the formation of organonitrogen compounds, which were major reaction products in the uptake of glyoxal (Galloway et al., 2009; Nozière et al., 2009) and glycolaldehyde (Nguyen et al., 2013). In those studies, imidazoles and other N-containing products were formed via nucleophilic attack of ketones and aldehydes by ammonia (Galloway et al., 2009; Nozière et al., 2009); such reactions are unlikely in the present system given the lack of carbonyl moieties in the polyols studied here.

The formation of oxalate (a highly-oxidized C2 compound) from erythritol (a less-oxidized C4 compound) likely occurs via multiple generations of oxidation. Individual product ions (shown in Fig. 3-4) have significantly different temporal behavior, with some growing in and decaying before others, suggesting complex chemistry with intermediate products formed at different stages of oxidation. The varying rates of decay of erythritol ions in Fig. 3-3b (e.g., m/z 61 vs. 91) provide further evidence that multigenerational oxidation is occurring in this system.
Figure 3-4. Sulfate-normalized concentrations of key ions associated with intermediate products in the bulk oxidation of erythritol.

Upon exposure to UV, the organic ions decay still further, and the total organic signal decreases dramatically, in a short period of time (lifetime ~36 min; see Fig. S1a, Supporting Information). This is likely a result of either further oxidation by OH generated from photo-Fenton chemistry (R3.6) or direct photolysis (R3.7) to form small volatile species that cannot be detected by the AMS. This provides additional evidence for oxalate, since Fe(III) oxalato complexes are known to rapidly photolyze, a process that has been suggested as an important sink of atmospheric oxalate (Sorooshian et al., 2013). Given the abundance of iron in the system, our results suggest that the main condensed-phase oxidation product is oxalate, present as an iron oxalato complex.

3.3.2 Chamber oxidation of erythritol

Results for the oxidation of erythritol in aqueous particles in the chamber are shown in Fig. 3-5. As in the bulk experiment, dark Fenton chemistry within submicron particles in the chamber was found to lead to the rapid decay of erythritol and formation of oxidized products. A maximum OH concentration of $3.5 \times 10^{-12}$ M is reached between 30 and 40 min (where erythritol
lifetime is ~2.5 min), and subsequently decreases to give a final OH exposure of $4 \times 10^9$ M s; these values are similar (within a factor of two) to those of the bulk experiments. The initial organic mass spectrum of unreacted erythritol in the chamber (Fig. 3-5a) closely matches that of erythritol in the bulk (Fig. 3-3a). The observed chemical changes in the two oxidation systems, as described by the time traces of key AMS ions from the chamber experiment (Fig. 3-5b), the
product mass spectrum (Fig. 3-5c), and changes to O/C and H/C (Fig. 3-5d) are also similar to the bulk oxidation results. The primary difference is that the total organic signal decreases substantially more than in the bulk, with no subsequent increase, discussed in detail below. As in the bulk experiment, a rapid loss of organic mass is observed upon UV irradiation (Fig. S1b).

This loss is unlikely to arise from oxidation by gas-phase OH (formed from H₂O₂ photolysis): the rapid loss of the organic species (lifetime ~7 min) would require an OH mixing ratio of > 6 x 10^7 molec cm⁻³ (assuming a k₀H of < 3 x 10⁻¹¹ cm³ molec⁻¹ s⁻¹), far greater than can be produced by H₂O₂ photolysis. Instead, the rapid loss of organic mass probably arises from the direct photolysis of Fe(III) oxalato complexes, as in the bulk oxidation experiment.

Our finding of rapid oxidation by Fenton chemistry in the absence of UV light differs from the results of Nguyen et al. (2013), who found oxidation to occur only upon UV irradiation (photo-Fenton chemistry). In that work, the H₂O₂ was added directly to the atomizer solution (along with FeSO₄), and so dark Fenton chemistry may have gone to completion prior to the introduction of the organic species (glycolaldehyde) in the gas phase. By contrast, in the present experiments, H₂O₂ is added last, so that all OH is produced in the presence of the aerosol-phase organic compound. Because of such differences, and the differences in the organic species studied, results from the two chemical systems are difficult to compare directly. Nonetheless, our results are broadly consistent with those of Nguyen et al., in that they indicate that aqueous-phase oxidation in submicron particles can lead to the rapid formation of highly oxidized organic aerosol.

3.3.3 Oxidation of other polyols

Similar results are seen for the oxidation of most of the other polyols, in both the bulk phase and the chamber. The one exception is the oxidation of glycerol (a C₃ polyol), which
behaved differently in both the bulk and chamber experiments, presumably due to its high volatility. In the glycerol bulk experiments, the measured organic mass actually increased after oxidation, likely because the less volatile oxidation products evaporated less than glycerol upon atomization; and in the chamber experiments, the LWC was too low for any measureable particulate glycerol. However, the C5-C7 polyols (adonitol, mannitol, and volemitol) all behaved similarly to erythritol upon oxidation, with decreases in the intensity of the polyol ions and H/C, increases in the CO$_2^+$ ion intensity and O/C, and product mass spectra resembling that of oxalate (Figs. S2-S4 in the Supplement). Estimated OH concentrations and exposures were also similar between the bulk and chamber cases (see Fig. S5 in the Supplement). As in the erythritol case, exposure to UV led to a rapid decrease in all organic ion signal intensity, as well as a decrease in total organic mass. In each case, the fraction of organic material remaining after oxidation was smaller for the chamber experiment than for the bulk experiment.

Shown in Fig. 3-6 is the fraction of carbon remaining in the condensed phase ($f_C$) after reaction in the bulk solution or deliquesced particles for each polyol (except glycerol, for which meaningful values of $f_C$ could not be determined). This is calculated from the changes in organic mass concentration and elemental ratios:

$$f_C = \frac{[\text{Org}]_f (16O/C_f + H/C_f + 12)}{[\text{Org}]_i (16O/C_i + H/C_i + 12)}$$  \hspace{1cm} (3.2)$$

in which $[\text{Org}]$ is the average high-resolution sulfate-normalized mass concentration of total organic, O/C and H/C are the oxygen-to-carbon and hydrogen-to-carbon ratios, respectively, of the organic species, with the subscripts $i$ and $f$ denoting initial and final conditions (before and after H$_2$O$_2$ addition), respectively. For example, in the case of erythritol oxidation, 51% of the initial carbon remained after bulk oxidation, but only 16% remained after oxidation in aqueous
aerosol in the chamber. For all bulk experiments, between 48% and 58% of the original carbon remained in the condensed phase after oxidation, with no obvious dependence on carbon number. However, a clear trend is observed for the chamber experiments, with $f_C$ increasing with the size of the polyol.

![Graph showing fraction of carbon remaining in the condensed phase after oxidation for bulk and chamber experiments.](image)

**Figure 3-6.** The fraction of carbon remaining in the condensed phase after oxidation ($f_C$) in the bulk solution (blue bars) or in submicron particles (red bars), as calculated from Eq. 3.2, using high-resolution V mode data. Meaningful values could not be determined for the oxidation of glycerol (C3) due to evaporation from the particle phase prior to oxidation.

### 3.3.4 Differences between chamber and bulk experiments

The above observations — that a larger fraction of carbon remains in the condensed phase for the bulk experiments than for the chamber experiments, and that this difference gets smaller with increasing carbon number — can be explained either by differences in reactivity or differences in partitioning between the two systems. The submicron particles in the chamber have higher reactant concentrations and a greater ionic strength than the dilute bulk solution, and also require dissolution of gas-phase H$_2$O$_2$ prior to oxidation; these differences may cause the observed differences in oxidation kinetics. Furthermore, the availability of gas-phase H$_2$O$_2$ in the chamber that can partition into the submicron particles, could allow for a longer production of
OH. However, the ratio of polyol to Fe$^{2+}$ is also greater in the chamber, so the OH may react away more quickly. These complex effects are difficult to quantify, but could result in different chemical reactions and degrees of oxidation between the two systems.

Nonetheless, it is unlikely that differences in reactivity are driving the differences in $f_c$ between the bulk and chamber experiments, given the similarities in mass spectra, changes to individual ions, and elemental ratios in the two cases (as shown in Figures 3-3, 3-5, and S1-4). The final OH exposures for the oxidation of erythritol in the bulk solution ($4.7 \times 10^{-12}$ M s) and in the submicron particles ($2.7 \times 10^{-9}$ M s) agree to within a factor of two. This is true for the larger polyols (C5-C7) as well (Fig. S5), suggesting that differences in oxidant availability are not likely to account for the observed differences between the bulk and chamber results. Furthermore, the variation in $f_c$ for different polyols oxidized in the chamber (Figure 3-6) is also unlikely to result from differences in chemistry, given that the oxidation conditions were the same.

Rather, the difference in total organic mass remaining in the condensed phase appears to be a result of differences in gas-aqueous partitioning of intermediate species (early-generation oxidation products). A general mechanism is illustrated in Fig. 3-7. The polyol is oxidized to form multiple generations of products, ultimately forming oxalate (in the form of an iron (III) oxalato complex). In the bulk aqueous solution, where the liquid water content is very high, the reactants, intermediates, and products remain in the condensed phase. (Some of these species may evaporate upon atomization and not be detected by the AMS, but they still would have been present in the condensed phase during oxidation.) However, in the chamber experiments, in which LWC is low, relatively volatile compounds can partition out of the condensed phase. The polyols and oxalate are sufficiently water-soluble to remain in the particle phase at this low LWC,
Figure 3-7. Simplified mechanism to explain observed differences between oxidation in the bulk and in submicron particles. The polyol reacts to form intermediates with lower $H^*$ (higher volatility over water), which remain fully in the aqueous phase during bulk experiments, but partition to the gas phase (red arrows) during chamber experiments. This partitioning, which occurs to a greater extent for smaller polyol precursors, competes with further aqueous oxidation, and has the effect of lowering the product (oxalate) yield. Upon exposure to ultraviolet light, the Fe(III) oxalato complex photolyzes, forming small gas-phase products.

suggesting that the partitioning of intermediate compounds from the aqueous phase to the gas phase (red arrow in Fig. 3-7) accounts for the increased loss of organic material in the chamber. These early-generation oxidation products are likely to be more volatile (lower $H^*$) than the polyol precursor, due to the oxidative conversion of hydroxyl groups to carbonyl groups (Bethel et al., 2003) and/or the formation of smaller molecular species via fragmentation reactions (Kroll et al., 2009). Evaporation of these species may also be promoted by a decrease in particulate water, which is observed upon $\text{H}_2\text{O}_2$ addition and likely occurs due to a change in the hygroscopicity of iron salts upon initiation of Fenton chemistry. Regardless of the exact mechanism, partitioning of intermediates into the gas phase will compete with further oxidation, as shown in Fig. 3-7, resulting in lower yields of oxalate than were measured in the bulk experiments. This general mechanism also explains the correlation between $f_c$ and carbon number (Fig. 3-6), since the size, and thus the volatility, of the intermediate compounds should be related to the size of the polyol precursor.
3.4 Conclusions and Implications

To our knowledge, this work presents the first direct comparison of aqueous-phase oxidation within submicron particles to that within the bulk phase. In both systems, dark Fenton chemistry leads to the rapid conversion of polyol precursors to highly-oxidized organic material, a result that is broadly consistent with previous aqueous-phase oxidation studies (Altieri et al., 2006; 2008; Carlton et al., 2007; Kirkland et al., 2013; Lee et al., 2011a; 2011b; 2012; Liu et al., 2012a; Nguyen et al., 2013; Perri et al., 2009; Sun et al., 2010; Tan et al., 2009; 2010; Zhang et al., 2010; Zhao et al., 2012). The primary difference between the two systems is that less carbon remains in the condensed phase in the chamber experiments, with the smallest precursors having the greatest differences in $f_c$. As shown in Fig. 3-1, under bulk conditions, any compound with $H^\phi \geq 0.1$ M atm$^{-1}$ should be present primarily in the aqueous phase. However, at the lower LWC of the chamber, compounds with $H^\phi$ as high as $10^9$ M atm$^{-1}$ will instead be present predominantly in the gas phase. Thus, species with $H^\phi$ between these limits will remain dissolved in bulk-phase water, but will partition out of submicron particles into the gas phase. Our results suggest that the reaction intermediates formed from the oxidation of polyols appear to have $H^\phi$ in this range. Therefore, the partitioning of these early-generation products from aqueous aerosol to the gas phase can explain the dramatic differences in $f_c$ observed in the bulk and chamber experiments.

The present results confirm those of previous studies showing that aqueous-phase oxidation is an efficient pathway for the rapid formation of highly oxidized material. However, when oxidation occurs within submicron particles, the fraction of carbon remaining in the condensed phase is substantially smaller than in the bulk oxidation experiments, implying that the formation of highly oxidized OA by aqueous chemistry may be somewhat less important than bulk-phase experiments suggest. Bulk oxidation experiments may not accurately simulate the
chemistry that takes place in the atmospheric aqueous phase, due to large differences in LWC (and therefore partitioning) between the bulk solution and atmospheric droplets or particles. This difference points to the importance of running aqueous-phase oxidation experiments under atmospherically-relevant partitioning conditions. This is analogous to chamber studies of secondary organic aerosol (SOA) formation via partitioning into the condensed-organic phase, which to be representative of atmospheric conditions must be run at low total organic mass concentrations \(c_{\text{OA}}\) (Presto and Donahue, 2006). A major difference between such “traditional” SOA chamber experiments and aqueous-phase oxidation, however, is that LWC can vary by a great deal more than \(c_{\text{OA}}\) between the laboratory and atmosphere. Our results show that even bulk oxidation experiments that allow for evaporation of oxidation products (Lee et al., 2011a; 2011b; 2012; Liu et al., 2012b; Ortiz-Montalvo et al., 2012; Zhao et al., 2012), may not fully simulate atmospheric processing, since they do not include the effects of partitioning of reaction intermediates. Further, the experiments with glycerol oxidation demonstrate that in bulk-phase experiments it is possible to oxidize compounds that would not actually be present in the atmospheric aqueous phase under most conditions. Results from the oxidation of larger polyols indicate that differences in LWC between bulk and chamber oxidation result in significant differences in partitioning, which in turn can affect the chemistry. For experiments like ours with a single product, this affects only the final yield. However, when multiple oxidation products are formed, with intermediates of varying volatility, changing the LWC may also alter the product distributions.

This study underscores the need for conducting oxidation experiments at atmospherically-relevant liquid water contents, and extending the existing suite of bulk experiments to additional partitioning conditions. Oxidizing previously-studied compounds
(small carboxylics, acids, isoprene oxidation products, etc.) within aqueous submicron particles would provide valuable information on the role of partitioning and LWC on the formation of highly-oxidized OA for a wider range of water-soluble organic compounds. Further, the large differences in partitioning between deliquesced particles and clouds (Fig. 3-1) suggest that a similar set of experiments is a useful next step for the accurate study of atmospheric cloud processing. Oxidation experiments involving actual cloud droplets, with LWCs much higher than those of aqueous particles but still far lower than that of the bulk aqueous phase, would improve our understanding of this potentially important source of oxidized organic aerosol.

3.5 Acknowledgements

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3.6 References


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3.7 Supplement

Figure S1. Results (including photolysis) for the oxidation of erythritol (C₄H₁₀O₄), showing sulfate-normalized mass concentrations of total organic (Org), ammonium (NH₄⁺), CO₂⁺, and key ions associated with erythritol (m/z 29, 61, 73, 91) as a function of reaction time for (a) bulk oxidation and (b) chamber oxidation. All data is shown in unit mass resolution, except for NH₄⁺ and CO₂⁺, which are high-resolution traces. Dark Fenton chemistry is indicated by grey shading, and exposure to UV by yellow shading.

Figure S2. Same as Figure S1, but for the oxidation of adonitol (C₅H₁₂O₅).
Figure S3. Same as Figure S1, but for the oxidation of mannitol (C₆H₁₄O₆).

Figure S4. Same as Figure S1, but for the oxidation of volemitol (C₇H₁₆O₇).
Figure S5. Estimated OH exposures for all experiments. These are determined from OH exposure = ln([polyol]_o/[polyol]_t)/k_{OH}, where [polyol]_o and [polyol]_t are the sulfate-normalized mass concentrations of the fastest decaying tracer ion at times 0 and t, respectively, and k_{OH} is the rate constant for aqueous reaction with OH (Herrmann et al., 2010). OH exposures for both bulk and chamber oxidation are shown as a function of time from 30 min prior to adding H_2O_2 until exposure to UV lights for (a) erythritol using m/z 61 as a tracer and k_{OH} = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}, (b) adonitol using m/z 61 as a tracer and k_{OH} = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}, (c) mannitol using m/z 73 as a tracer and k_{OH} = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}, and (d) volemitol using m/z 73 as a tracer and k_{OH} = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}. (Because no k_{OH} has been reported for volemitol, it was assumed to be equal to the k_{OH} for mannitol.)
Chapter 4

Role of aqueous-phase oxidants in SOA formation

4.1 Introduction

As shown in Chapter 2, there are only a few potential pathways for the formation of oxidized organic aerosol (OA), one of which is rapid oxidation within the condensed phase. Further oxidation of SOA within particles is often neglected since heterogeneous oxidation (in which gas-phase oxidants react with condensed-phase molecules at the particle surface) is known to be slow, with lifetimes on the order of several days (George and Abbatt, 2010; Kessler et al., 2010; 2012; Robinson et al., 2006). However, if oxidants are also present within the condensed phase, then oxidation within SOA particles could be an efficient pathway for the production of highly oxidized OA. In Chapter 3, we showed that rapid oxidation of water-soluble organic compounds is possible within aqueous systems.

In this chapter, we investigate whether the presence of condensed-phase oxidants can lead to the production of highly oxidized OA from the oxidation of gas-phase precursors. As described in Chapter 1, SOA is formed from the oxidation and subsequent condensation of gas-phase organic precursors. This can be an efficient pathway for formation of OA, but the organic material is generally not very oxidized. A number of studies have focused on oxidation within the condensed phase as a means for aging this aerosol. As described in Chapter 3, numerous oxidation studies using bulk aqueous solutions have shown aqueous oxidation to be an efficient
pathway for the formation of oxidized organic material (Daumit et al., 2014). Some work has
also been done to examine oxidation within the submicron particles. A couple studies have
examined the role of photoenhanced chemical reactions within aqueous particles containing α-
pinene ozonolysis SOA (Lignell and Hinks, 2014; Wong et al., 2014). Volkamer et al. studied
the formation of SOA from acetylene and glyoxal for a range of seed compositions and RH, and
found that organic photochemistry within aqueous aerosol can accelerate SOA formation
(Volkamer et al., 2009). Several studies have used iron sulfate (FS) seed particles to generate
aqueous oxidants via Fenton-like chemistry in submicron aerosol. Chu et al. observed reduced
yields in photooxidation experiments with FS seed particles (Chu et al., 2012; 2014), and
Nguyen et al. showed that FS seed enhanced the condensed-phase oxidation of glycolaldehyde
(Nguyen et al., 2013). In Chapter 3, we focused on the oxidation of simple single component
systems in deliquesced FS particles, using polyols as surrogates for water-soluble atmospheric
oxidation products. We saw evidence for multiple generations of aqueous oxidation, as well as
partitioning of oxidation intermediates out of the condensed phase, resulting in decreased yields.

In this chapter, we expand our focus to more atmospherically relevant organic
compounds and a broader range of condensed phase oxidation conditions. Rather than starting
with a single organic molecule in the condensed phase, we generate a mixture of condensable
products from gas-phase ozonolysis of biogenic VOCs. We still use deliquesced submicron
particles as the aqueous reactors, which we have shown to be more atmospherically
representative than bulk aqueous solutions. However, we now use a range of seed types
including dry and wet ammonium sulfate and iron sulfate in order to vary the phase and oxidant
levels within the particles, while keeping the gas phase oxidants constant. While we discuss the
effects of this oxidation on aerosol yield (the fraction of carbon that ends up in the condensed
phase) the main focus of this work is the effect of condensed-phase oxidation on chemistry in the aerosol, specifically changes to the oxidation state of particulate carbon. This is the first study, to our knowledge, to directly examine how varying oxidant levels and photochemical processes within aerosol can affect the oxidation state of SOA.

4.2 Experimental Methods

SOA is formed from both ozonolysis of α-pinene and ozonolysis of isoprene under a number of different seed and humidity conditions, in order to systematically vary the oxidant levels within the particles: (1) phase of particles (aqueous vs. dry), (2) added oxidant source (none vs. H₂O₂ vs. Fenton chemistry), (3) irradiation (dark vs. UV lights). As described previously (Daumit et al., 2014), Fenton-type chemistry can produce aqueous-phase hydroxyl radicals (OH) via the cycling of Fe²⁺ and Fe³⁺ in the presence of H₂O₂; in this work we find that other ROS species, such as those formed from alkene ozonolysis, can drive this chemistry as well. The conditions for each experiment are provided in Table 4-1 in the Results and Discussion.

4.2.1 Experimental setup

Much of the experimental setup (shown in Fig. 4-1) was previously described in Chapter 3 (Daumit et al., 2014). Here, we will briefly highlight key features and important changes for this present study. The MIT chamber is a 7.5 m³ Teflon bag run in semi-batch mode at 20°C, with relative humidity controlled by a bubbler containing Milli-Q water. Deliquesced seed particles are introduced by directly atomizing a 1 g L⁻¹ solution of either ammonium sulfate (AS, Sigma-Aldrich, > 99.0%) or iron(II) sulfate heptahydrate (FS, Alfa Aesar, > 99.999% metals basis) into the chamber for 0.5-1 h. This generates a seed volume of between ~55 and 170 nL m⁻³, depending on the RH and seed type. During atomization, 20 ppb of (-)-α-pinene (1.0 μL,
Figure 4-1. Experimental setup.

Sigma-Aldrich, 98%) or 400 ppb of isoprene (13.5 µL, Sigma-Aldrich, 99%) is injected through a septum into a 1/4 inch OD stainless steel line with ~1 Lpm of clean air flow. A non-reactive dilution tracer (2.0 µL of hexafluorobenzene, Sigma-Aldrich, > 99%) is also injected. After at least 20 minutes to allow for mixing, SOA formation is initiated by introducing an excess of ozone (80-100 ppb for α-pinene, ~900 ppb for isoprene), generated by sending 1.5 Lpm of clean air through a corona ozone generator (Enaly). This also generates a small amount of NOx (< 5 ppb for α-pinene, < 25 ppb for isoprene). An OH scavenger was not used in these experiments. As in the previous polyol study, 6.0 µL of 30% w/w H2O2 in water (Alfa Aesar) is added to the gas-phase, giving ~27 mM H2O2 in the aqueous particles, in order to initiate the Fenton-like chemistry once the SOA precursor has reacted away (~3 h for α-pinene, ~5 h for isoprene). However, as described in the Results and Discussion, it was found that H2O2 is not necessary in order to initiate the Fenton-like chemistry, and therefore it was only added for some experiments.
Once the reactions appear to have gone to completion (~6 h for α-pinene, ~10 h for isoprene), two banks of 24 black lights are turned on to assess the photo-reactivity of the reaction products and/or initiate any further condensed-phase photochemistry.

4.2.2 Instrumentation

As described in our previous work, a high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne Research Inc.) and a scanning mobility particle sizer (SMPS, TSI Inc.) are used to measure the aerosol chemical composition and the aerosol size distribution, volume, and number concentration, respectively (Daumit et al., 2014). All reported AMS data was collected in V-mode. Concentrations of α-pinene, isoprene, and hexafluorobenzene are monitored using gas chromatography-flame ionization detection (GC-FID, SRI). We also monitor NOx (Horiba Inc.), ozone (2B Tech), and temperature and relative humidity (Vaisala).

4.2.3 Yield calculation

SOA mass yields \(Y\) are given by eq. 4.1

\[
Y = \frac{\Delta c_{OA}}{\Delta HC}
\]

(4.1)
in which \(\Delta c_{OA}\) is the wall-loss and dilution-corrected increase in organic aerosol mass loading and \(\Delta HC\) is the dilution-corrected decrease in mass concentration of hydrocarbon (α-pinene or isoprene) lost to reaction with ozone. The hydrocarbon concentration is corrected for dilution using the measured hexafluorobenzene decay rate. The GC-FID calibration factors were determined by averaging the peak area across experiments conducted within a given time period and assuming it to be equal to 114 μg m\(^{-3}\) for α-pinene or 1135 μg m\(^{-3}\) for isoprene.

For standard chamber experiments that use dry AS seed, \(c_{OA}\) can be estimated from the AMS organic-to-sulfate ratio (org/SO\(_4\)) and the initial SO\(_4\) mass (which is calculated from the SMPS volume and AS density). However, in the present set of experiments, uncertainties in seed
hygroscopicity, density, and AMS collection efficiency prevent the accurate determination of the initial SO$_4$ mass, and necessitate the use of a more complex approach.

Here, the absolute organic mass loading is determined from SMPS data at a single point in time (2.5-3 h after ozonolysis of α-pinene, 4.5-5 h after ozonolysis of isoprene). The SMPS volume concentration is first corrected for dilution and deposition to the walls using a decay rate fitted over a time period where the AMS data indicate that chemical composition (and density) is not changing. The organic volume concentration is then estimated by subtracting the seed volume from the total wall-loss corrected volume. For most experiments, the seed volume is measured just prior to the addition of ozone. However, for the wet FS experiments, the addition of ozone appears to change the density and/or hygroscopicity of the seed particles, making the initial seed volume a poor measure of the seed volume throughout the experiment. For such experiments, the seed volume is instead estimated from the total volume at the end of the experiment after most of the organic material is lost to the gas phase (as described in the Results). The organic volume is converted to $c_{OA}$ using a density of 1.4 g cm$^{-3}$ (the implications of this assumption are discussed in the Results and Discussion). The time dependence of $c_{OA}$ is then determined from changes to the AMS org/SO$_4$ ratio.

Carbon yield ($Y_c$) is given by eq. 4.2

$$Y_c = \frac{\Delta c_{OC}}{\Delta HC_c} \quad (4.2)$$

where $\Delta c_{OC}$ is the wall-loss and dilution corrected mass of carbon in organic aerosol and $\Delta HC_c$ is the mass of α-pinene carbon that has reacted. $c_{OC}$ is calculated from eq. 4.3

$$c_{OC} = \frac{12c_{OC}}{12 + 16O/C + H/C} \quad (4.3)$$
where O/C and H/C are the oxygen-to-carbon and hydrogen-to-carbon ratios of the organic aerosol.

### 4.3 Results and Discussion

Table 4-1: Reaction conditions and results for α-pinene (Expt. 1-7) and isoprene (Expt. 8-9).

Note that because the data reported here have been rounded to the nearest hundredth place, very small changes are clearer in the figures than in the table (e.g. see Fig. 4-3 for comparison of changes in O/C after UV for Experiments 1-4b).

<table>
<thead>
<tr>
<th>#</th>
<th>Seed</th>
<th>O/C initial</th>
<th>ΔO/C after H₂O₂</th>
<th>ΔO/C after UV</th>
<th>Yield after H₂O₂</th>
<th>Carbon Yield after H₂O₂</th>
<th>Yield after UV</th>
<th>Carbon Yield after UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dry AS</td>
<td>0.55</td>
<td>(0.02)</td>
<td>0.02</td>
<td>0.27</td>
<td>(0.26)</td>
<td>0.25</td>
<td>(0.16)</td>
</tr>
<tr>
<td>2</td>
<td>Dry AS</td>
<td>0.47</td>
<td>0</td>
<td>0.01</td>
<td>0.26</td>
<td>0.26</td>
<td>0.25</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>Aq AS</td>
<td>0.47</td>
<td>(0.02)</td>
<td>0.03</td>
<td>0.19</td>
<td>(0.16)</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>4a</td>
<td>Aq AS</td>
<td>0.51</td>
<td>0</td>
<td>0.08</td>
<td>0.18</td>
<td>0.15</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>4b</td>
<td>Aq AS</td>
<td>0.45</td>
<td>0</td>
<td>0.06</td>
<td>0.16</td>
<td>0.13</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>Dry FS</td>
<td>0.62</td>
<td>0.07</td>
<td>0.06</td>
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<td>0.13</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>Aq FS</td>
<td>0.95</td>
<td>(0.08)</td>
<td>0.04</td>
<td>0.12</td>
<td>(0.12)</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>7</td>
<td>Aq FS</td>
<td>1.06</td>
<td>0.20</td>
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<td>0.12</td>
<td>0.11</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>Dry AS</td>
<td>0.59</td>
<td>(--)</td>
<td>0.02</td>
<td>0.038</td>
<td>(--)</td>
<td>0.036</td>
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<tr>
<td>9</td>
<td>Aq FS</td>
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<td>-0.81</td>
<td>0.020</td>
<td>0.023</td>
<td>0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Experimental conditions and key results for each experiment are provided in Table 4-1. Experiments 1 through 7 used α-pinene; Experiments 8 and 9 used isoprene. The “Seed” column indicates the seed type and humidity conditions (dry experiments were run at RH < 12%, below the efflorescence RH of ammonium sulfate ensuring the seed particles were dry whereas aqueous experiments were run at 70% < RH < 87%, above the deliquescence RH ensuring that seed particles contained liquid water (Seinfeld and Pandis, 2006)). The initial O/C, yield, and carbon yield were measured just prior to the addition of H₂O₂ (t = 3 h for α-pinene, t = 5 h for isoprene). The yield, carbon yield, and change in O/C are also reported after the addition of H₂O₂ (t = 6 h for α-pinene, t = 10 h for isoprene), and after UV irradiation (t = 9 h for α-pinene, t = 15 h for isoprene). Experiments in which H₂O₂ was not added are indicated by parenthesis.
4.3.1 “Traditional” α-pinene SOA (dry AS seed)

Results for Experiment 1 (ozonolysis of α-pinene with dry AS seed) are shown in Figure 4-2. SOA formation in this experiment occurs in the absence of any condensed-phase oxidants and therefore represents the base degree of oxidation against which other experiments are compared. Figure 4-2a shows the mass concentration of organic aerosol and α-pinene, and the O/C and H/C of the organic aerosol, Figure 4-2b shows the organic mass spectrum of the SOA, and Figure 4-2c shows the sulfate-normalized mass concentrations of total organic signal and individual ion fragments. Oxidation begins immediately following the addition of ozone, producing SOA with an O/C between 0.5 and 0.6, and H/C between 1.3 and 1.4. Most of the α-
pinene reaction and SOA formation is completed within ~3 hours. Exposure to UV light does not appear to have any effect, causing no appreciable change to the elemental ratios or organic mass loading. The individual ion fragments all follow the same trend, implying that the composition of the organic material does not change following condensation.

In a similar experiment in which 270 ppb H$_2$O$_2$ was added prior to UV irradiation (Expt. 2), a similar degree of oxidation was observed (Table 4-1), again with no change to O/C upon UV exposure. This indicates that photolysis of gas-phase H$_2$O$_2$ has no measureable effect on SOA.

4.3.2 $\alpha$-pinene SOA formed on aqueous AS seed

![Graph showing O/C for different experiments](Image)

**Figure 4-3.** Effect of UV irradiation on O/C for the different $\alpha$-pinene ozonolysis experiments with AS seed (Expt. 1-3, 4a, 4b).

SOA formed on aqueous AS seed (Expt. 3, 4a, 4b) had a similar degree of oxidation (Table 4-1). However, unlike with dry AS, there was an increase in O/C upon exposure to UV, suggesting that UV irradiation leads to oxidant formation within the aqueous particles. This can be seen in Fig. 4-3, which shows O/C before and after UV irradiation for all the AS seed experiments. The variation in absolute O/C values gives a sense of the reproducibility. Despite
this variability, it is clear that UV causes O/C to increase in the aqueous AS experiments, but has no effect in the dry AS experiments. It is hypothesized that this occurs via photochemical excitation of aqueous-phase SOA molecules, resulting in the production of aqueous oxidants. The increase in O/C was greater when H₂O₂ had been added, likely due to additional oxidant formation from the photolysis of aqueous H₂O₂ to OH. Because H₂O₂ did not enhance oxidation in the dry AS experiment, it is not likely that gas-phase oxidants are responsible for the increase in oxidation upon UV irradiation. This enhancement in the degree of oxidation for irradiated aqueous AS seed but not dry AS seed is consistent with the findings of Chu et al. (2014); however, the results of their FS seed experiments differ from ours as is discussed below.

4.3.3 α-pinene SOA formed on aqueous FS seed

![Figure 4-4](image-url). Results for formation of SOA from ozonolysis of α-pinene in the presence of aqueous FS seed (Expt. 6): (a) mass concentrations of organic aerosol and α-pinene, and O/C and H/C of organic aerosol, (b) average organic mass spectrum prior to UV irradiation, (c) sulfate-normalized total organic mass and fragment ions.
SOA formed with aqueous FS seed (Expt. 6 and 7) is fundamentally different from the SOA formed with AS seed (Table 4-1), with the condensed-phase organics having undergone substantially more oxidation. Figure 4-4a shows the mass concentration of OA and α-pinene, and the OA elemental ratios for Experiment 6. Prior to UV irradiation, the organic material reaches an O/C > 1 and H/C < 1, with a mass spectrum dominated by m/z 44 (CO$_2^+$), a highly oxidized ion fragment which typically indicates the presence of carboxylic acids (Fig. 4-4b). The less oxidized ion fragments (m/z 43 and m/z 55) grow in earlier and gradually decrease as the more oxidized fragments (m/z 44 and m/z 45) gradually increase (Fig 4-4c). UV irradiation leads to a rapid loss of organic material from the condensed phase, likely due to the photolysis of oxidation products to smaller volatile species which partition out of the condensed phase. The initial sharp decline in O/C following UV suggests that the products undergoing photolysis are the most highly oxidized species. Oxalate is one potential product that is both highly oxidized (O/C = 2) and known to undergo rapid photolysis when present as an iron complex (Sorooshian et al., 2013). The organic mass spectrum (Fig. 4-4b) is consistent with the presence of some oxalate (Mensah et al., 2011; Takegawa et al., 2007). Following its initial decline upon UV exposure, O/C begins to rise indicating that UV also leads to increased concentrations of aqueous oxidants, possibly from photo-Fenton chemistry.

For the first 3 h of oxidation, Expt. 6 and 7 had identical conditions. Therefore the differences in initial O/C (0.95 vs. 1.06) are due to random variability between experiments and give insight into the reproducibility. Regardless, the addition of H$_2$O$_2$ in Experiment 7 appeared to accelerate the Fenton-like chemistry, clearly increasing the rate at which O/C rises, leading to a higher degree of oxidation and a greater loss of organic material upon photolysis. Figure 4-5 shows O/C for all the aqueous experiments, highlighting the dramatic enhancement in the degree
of oxidation when SOA is formed in the presence of aqueous oxidants. To our knowledge, no other ozonolysis experiment reported in the literature has ever generated SOA that is as highly oxidized as that generated in Expt. 6 and 7.

**Figure 4-5.** Differences in O/C for α-pinene ozonolysis with aqueous FS (red/pink traces) and aqueous AS seed (green/blue traces).

The immediate production of highly oxidized organic material indicates that aqueous oxidants are generated as soon as SOA formation begins, and that Fenton-like chemistry is initiated without the addition of H$_2$O$_2$. To investigate whether this chemistry is initiated directly by ozone, we re-ran the previously described chamber oxidation of erythritol in aqueous FS particles (Daumit et al., 2014), but with ozone added to the chamber prior to the addition of H$_2$O$_2$. Although ozone dissolved in water can generate OH (von Gunten, 2003), in this study ozone did not lead to any aqueous oxidation of erythritol, indicating that only an insignificant amount of OH was generated from the reaction of ozone with water or ozone with iron. This suggests that the Fenton-like chemistry in the present study is not initiated by ozone itself, but rather by a product of ozonolysis such as HO$_2$, RO$_2$, or ROOH. A proposed general reaction scheme for ozonolysis of α-pinene in the presence of FS seed is shown in Figure 4-6.
Figure 4-6. Proposed reaction scheme for ozonolysis of α-pinene in the presence of aqueous FS seed. Following the gas-phase reaction of ozone and α-pinene, water-soluble organic products and reactive oxygen species (ROS) partition into the condensed phase. ROS react with iron to initiate Fenton-like chemistry and produce aqueous hydroxyl radicals (OH). The organic products then undergo further oxidation by OH within the particles. Some of this oxidation leads to smaller volatile products which partition out of the particles. Upon exposure to UV, the more oxidized organic molecules undergo photolysis to gas-phase products. The addition of H$_2$O$_2$ (which is a ROS) accelerates the formation of OOA by increasing [ROS] and therefore the rate of OH$_{aq}$ production via reactions with iron. An additional experiment was conducted with FS seed and H$_2$O$_2$ at low RH (Expt. 5). This represents an intermediate case, with SOA that is somewhat more oxidized than for dry AS seed, but still substantially less oxidized than for aqueous FS seed (Table 4-1). Similarly to the aqueous FS experiment, UV irradiation led to some loss of organic compounds from the condensed phase, suggesting that some oxidized photolabile products had been formed. However, the lower degree of oxidation relative to the aqueous FS experiments points to the importance of the aqueous phase for the generation of oxidants. The reason for higher oxidation than in the AS experiments is not clear, but could be due to some chemistry at the particle interface and/or the presence of a small amount of water within the particles. These results differ from those of Chu et al. (2014) who observed higher levels of oxidation with aqueous AS than
4.3.4 Additional α-pinene SOA experiments

In order to investigate the ability for SOA generated in the absence of aqueous oxidants to be later oxidized within separate seed particles, α-pinene SOA was initially formed on aqueous AS seed, and FS seed was later introduced. Figure 4-7 shows the time evolution of O/C, H/C, and ammonium-normalized total organic mass and individual fragment ions. (Because the sulfate concentration increases when FS is added, ions are normalized to ammonium instead of sulfate.) The initial SOA resembled that produced in the other aqueous AS experiments (O/C ~0.5, H/C ~1.3). However, as soon as FS seed particles are added, the SOA undergoes further oxidation with m/z 44 growing in as less oxidized ion fragments decay away, generating oxidized OA with a final O/C of ~0.9 and H/C of ~1. As with the other aqueous FS experiments, UV irradiation leads to photolysis of oxidized products and loss of organic material to the gas phase.

These results suggest that SOA products are able to partition out of unreactive aqueous particles and into reactive aqueous particles where they can undergo further oxidation. While it is
possible that some coagulation of unreactive and reactive particles occurs, this is expected to be slow relative to the rates of partitioning. Partitioning timescales for α-pinene SOA products have been estimated to be < 5 min for 80% RH and ammonium sulfate particles with a diameter ≤ 200 nm (Shiraiwa et al., 2013); because our experiments were run under the same conditions, we expect our partitioning timescales to be similar. The theoretical coagulation timescale for the particles in this experiment is ~1 h; the coagulation timescale estimated from the rates of decay of number and volume concentration over the first 20 min after the addition of FS seed stopped is ~2 h (assuming the rates of wall loss for number concentration and volume concentration are the same). Therefore, it appears that partitioning plays a key role.

The primary oxidants in the aqueous FS experiments are likely to be hydroxyl radicals. Therefore, the results should not be unique to iron-containing particles, but instead applicable to deliquesced particles with any OH source. In order to estimate aqueous hydroxyl radical concentrations, a repeat of the aqueous FS + H₂O₂ experiment was run with 2 mM of adonitol (a C₅ polyol) added to the seed particles as an aqueous OH tracer. Based on the rate of decay of adonitol (from tracer ions m/z 61 and 73) maximum [OH]ₐq was measured to be 3.3 x 10⁻¹³ M during ozonolysis and 2.5 x 10⁻¹² M after the addition of H₂O₂, using kOH of 1.6 x 10⁹ M⁻¹ s⁻¹ (Herrmann et al., 2010). However, because adonitol may act as a quencher of OH, the maximum [OH]ₐq during the original experiment is likely greater than this. The mass concentration of adonitol was ~3 times greater than the mass concentration of SOA; if we assume that adonitol and α-pinene ozonolysis products have similar rate constants for aqueous reaction with OH, then [OH]ₐq during the original experiment could be ~4 times as high. This is still within an order of magnitude of the average OH concentrations estimated for ambient deliquesced particles (Herrmann et al., 2010); however, the estimated ambient concentrations are highly uncertain.
In order to determine the contribution from background organic material, a blank was run under the same conditions as the aqueous FS + H₂O₂ experiment, but without the addition of any α-pinene. This resulted in a c_OA of 2.6 μg m⁻³, or ~18% of the SOA in the version containing α-pinene. While this background may seem somewhat high, it likely undergoes the same types of condensed-phase oxidation as the SOA, and therefore does not change our conclusions about the ability of condensed-phase oxidants to produce more highly oxidized OA.

4.3.5 Isoprene SOA experiments

The isoprene experiments gave similar results to the α-pinene experiments. Ozonolysis of isoprene with dry AS seed produced SOA with an O/C of 0.6 and H/C of 1.4 (Expt. 8 in Table 4-1). As with α-pinene ozonolysis, the SOA composition did not change over the course of the experiments and was not affected by exposure to UV. Isoprene SOA formed with aqueous FS seed and H₂O₂ (Expt. 9) was extremely oxidized reaching an O/C of 1.9 and H/C of 0.6, and with a mass spectra that closely resembles that of oxalic acid (not shown, Mensah et al., 2011; Takegawa et al., 2007). This establishes that the enhancement in the degree of oxidation when SOA is formed in the presence of aqueous-phase oxidants is not unique to α-pinene. The time evolution of sulfate-normalized mass concentrations of total organic signal and key ion fragments are shown in Figure 4-8. The rise and decay of different ions at different times (e.g. m/z 29 vs. 45 vs. 55) suggests that multiple generations of oxidation occur. Here, the addition of H₂O₂ has a more substantial influence on the degree of oxidation than it did for α-pinene SOA, and appears to initiate new chemistry (e.g. the divergence of m/z 29 and 43). As with α-pinene SOA, exposure to UV results in the rapid photolysis of organic matter, except here nearly all of the SOA is lost to the gas-phase. This is consistent with all the material having been converted to oxalic acid as implied by the mass spectrum.
Figure 4-8. Sulfate-normalized total organic and fragment ion time traces for ozonolysis of isoprene with aqueous FS seed (Expt. 9).

4.3.6 Yields

As described in the experimental section, an accurate determination of yields is made difficult by uncertainties in particle seed density, hygroscopicity, AMS collection efficiency, and the relative detection of water in the AMS and SMPS. Therefore, the mass yields and carbon yields presented in Table 4-1 are only approximate and should be treated as such. Regardless, we will discuss possible explanations for trends in the reported values.

The dry AS experiments (1 & 2) have the highest reported yields. These are somewhat higher than previously reported yields for α-pinene ozonolysis, but this could be a result of different experimental conditions (e.g. higher seed concentration, no use of an OH scavenger) (Griffin et al., 1999; Hallquist et al., 2009). Based on the similarity in the composition of SOA in the dry and aqueous AS experiments, it would be expected for aqueous AS yields to be similar, but instead they are ~35-50% lower. One possible explanation is if the condensation of organic material decreases the hygroscopicity of the seed particles. This would drive some water out of
the condensed phase, causing an underestimate of yield for the aqueous AS experiments. Cocker et al. (2001) also measured lower yields for α-pinene ozonolysis with aqueous AS than with dry AS. However, they reported total mass yields (mass organic + mass water), so it is also possible their yields were lower due to loss of water rather than less condensed organic material.

On average, the FS experiments have lower yields than the AS experiments, with a greater difference between carbon yields than mass yields (due to the high oxygen content in the organic material formed with FS seed). This suggests that aqueous oxidation results in some fragmentation to smaller products that partition out of condensed phase. These yield comparisons assume that the fresh SOA formed on dry AS has the same density as the oxidized SOA formed on aqueous FS. However, it is likely that the oxidized SOA has a higher density; if we instead use a density of 1.9 g cm\(^{-3}\) (that of solid oxalic acid, so an upper limit for oxalate in solution) for the FS experiments, their yields increase by a factor of 1.4 and are no longer significantly lower than for the aqueous AS experiments. While these uncertainties make it difficult to say conclusively, it is likely that the difference in densities is smaller than this and that the presence of aqueous oxidants does in fact result in the loss of carbon to the gas phase.

Isoprene SOA formed in the presences of aqueous oxidants has a 48% lower yield and 68% lower carbon yield than isoprene SOA formed in the absence of condensed-phase oxidants. However, because the product mass spectrum in the aqueous FS experiment resembles oxalic acid, the SOA may have a density closer to 1.9 g cm\(^{-3}\) than 1.4 g cm\(^{-3}\). Using this higher density gives an initial yield of 0.027 and carbon yield of 0.010. These are both still lower than for the dry AS experiment, further suggesting that aqueous oxidation leads to the loss of carbon from the condensed phase.
4.3.7 Kinetics

Figure 4-9. Comparison of effective oxidation rates in the aqueous phase (blue circles) and gas phase (red squares) in aqueous fine particles (a) and cloud droplets (b) for compounds with varying Henry's law constants.

The atmospheric importance of these results depends in part on how the rates of transformation within aqueous aerosol compare to gas phase transformation rates. Figure 4-9 compares the effective rates of oxidation in the gas phase to those in the atmospheric liquid water phase (aqueous aerosol in panel a, or cloud droplets in panel b) for compounds with varying Henry's law constants. These are calculated for reaction with hydroxyl radicals using an average [OH] of 10^6 molec cm^-3 in the gas phase, 10^8 molec cm^-3 in aqueous aerosol, and 10^7 molec cm^-3 in cloud droplets (Seinfeld & Pandis, 2006, Herrmann et al., 2010). The Henry's law constants and rate constants (k_{OH,aq} and k_{OH,gas}) are compiled or estimated from the literature for each compound (Sander, 1999; Haag & Yao, 1992; Kwok & Atkinson, 1995; NIST Webbook). These estimates suggest that aqueous oxidation can outcompete gas-phase oxidation for compounds with Henry's law constants > 10^8 M atm^-1 for aqueous aerosol and > 100 M atm^-1 for cloud droplets. The oxidation rates within aqueous particles in the experiments discussed here are on the order of 10^{-4} s^{-1} (e.g. rapid decay of m/z 43 in Fig. 4-7b following addition of FS seed),
suggesting that this condensed-phase chemistry could compete with gas-phase oxidation under typical atmospheric conditions.

4.4 Conclusions and Implications

Our previous work showed that aqueous oxidants within submicron particles can lead to the efficient oxidation of simple water-soluble compounds that start out in the condensed phase (Daumit et al., 2014). In the present study, we have shown that this holds true for a more complex, atmospherically relevant SOA system. By directly measuring the degree of oxidation, we found that the presence of aqueous oxidants can have a significant effect on the formation of SOA, and that chemistry within the condensed-phase can lead to the formation of highly oxidized OA. This was observed for SOA formed from the ozonolysis of both α-pinene and isoprene, suggesting that the effects are not unique to a single type of SOA. Furthermore, the partitioning experiment suggests that even SOA initially formed on unreactive seed particles can later undergo further oxidation if it encounters reactive aerosol. Our overall findings are consistent with previous studies that have shown aqueous oxidation to be an efficient pathway for the formation of oxidized organic material (Chu et al., 2014; Daumit et al., 2014; Lee et al., 2011; Nguyen et al., 2013).

We also found that exposure to UV irradiation caused additional significant changes to OA mass loading and composition. For experiments with aqueous AS seed, UV resulted in higher degrees of oxidation, likely via the formation of aqueous oxidants from photolysis of SOA products and/or H₂O₂. For example, organic peroxides have been shown to make up ~20-50% by mass of α-pinene ozonolysis SOA (Docherty et al., 2005; Epstein et al., 2014), and are known to generate OH radicals upon photolysis (Lim et al., 2010; Ng et al., 2011). For the experiments with FS seed, exposure to UV again led to an increased production of aqueous
oxidants (here, presumably via photo-Fenton-like chemistry), but also resulted in photolysis of
the most oxidized products and a loss of organic material from the condensed phase.

A number of other studies have also shown UV irradiation to cause important changes to
SOA. Wong et al. (2014) found that photolysis of SOA from α-pinene ozonolysis resulted in loss
of organic material from the particles and produced more oxidized SOA, both effects that were
greater at higher RH. They attributed the higher degree of oxidation to both the loss of less
oxidized products such as carbonyls, and the formation of additional oxidants. The latter
mechanism is consistent with all of our aqueous experiments. However, in our FS experiments,
we saw a dramatic decrease in OA mass, likely due to the photolysis of the more oxidized
products (presumably photolabile iron-carboxylate complexes) (Sorooshian et al., 2013). Unlike
Wong et al. (2014), in our experiments UV irradiation had no effect at low RH and did not affect
mass yields for any AS experiments; this could be due to experimental differences (e.g. SOA
from filter extracts vs. formed in situ). In another study, SOA from α-pinene ozonolysis was
found to increase the photolysis rate of 2,3-dinitrophenol, suggesting it can enhance indirect
photodegradation (Lignell and Hinks, 2014). A number of low RH studies have found UV
irradiation to result in loss of material from the condensed phase for SOA generated from
ozonolysis of α-pinene (Epstein et al., 2014; Presto et al., 2005), ozonolysis of d-limonene
(Mang et al., 2008), and low-NOx photooxidation of isoprene (Surratt et al., 2006). It is unclear
why we do not observe this loss of organic material in the low RH AS experiments, but it is
likely to be a result of differences between experiments (e.g. Presto et al. irradiated the particles
during SOA formation; Epstein et al. used denuders to remove VOCs and ozone; and the other
studies used different SOA precursors or oxidants). Regardless, our finding that UV effects are
enhanced at high RH suggests that the previously documented UV effects may be even greater for humid systems.

These results demonstrate that the presence of aqueous oxidants can have a dramatic effect on SOA formation. It has been estimated that on a global scale, aerosol water exceeds dry aerosol mass, making it a potentially important phase (Ervens et al., 2011). However, because there is currently great uncertainty regarding the ambient concentrations of condensed-phase oxidants, it is difficult to quantify what effect condensed-phase chemistry may have on overall SOA production. Currently, the only estimates of oxidant concentrations within deliquesced particles come from models (Herrmann et al., 2010). Therefore, direct measurements of concentrations of condensed-phase oxidants in the atmosphere would be extremely valuable for future studies and could help determine the overall importance of oxidation within the condensed phase.

4.5 References


Chapter 5

Conclusions

A thorough understanding of the mechanisms governing the formation and evolution of organic aerosol (OA) is necessary in order to predict the impact of particulate matter on climate change, air quality, and human health. This thesis has aimed to improve our understanding of the formation of highly oxidized OA, with specific attention given to the role of aqueous-phase oxidation. Here, we summarize our key findings, discuss their broader implications, and suggest possible areas for future research.

In Chapter 2, we developed a novel retrosynthetic approach for constraining the potential formation pathways and precursors of highly oxidized OA. This involved starting with the known products (oxidized OA components), and moving backwards toward possible reactants (SOA precursors). The “target” product was defined in terms of an average chemical formula, determined from properties measured in field studies as well as structure-activity relationships. A set of simple, general rules were developed to constrain possible atmospheric reactions and allow for the identification of viable reaction pathways and aerosol precursors. Three general formation mechanisms were found to be possible: (1) functionalization reactions that add multiple function groups per oxidation step, (2) oligomerization of highly oxidized precursors, or (3) fast aging within the condensed phase, such as oxidation within aqueous particles. The accuracy of this approach was somewhat hindered by the limited number of field measurements of OA volatility (which allows for the estimation of carbon number) and formation kinetics (which constrain the
number of oxidation steps). Therefore, additional measurements of these parameters in future field studies could improve this method by allowing for further characterization of the target molecule and better constraints on possible formation mechanisms. While the partitioning of organic species in this study was limited to either the gas phase or condensed-organic phase, this approach could be extended to explicitly include partitioning to and reactions within the liquid-water phase. This could be done using existing structure-activity relationships to determine Henry's law constants from chemical properties (elemental ratios, functional group distributions, etc.), and could be valuable given that aqueous-phase aging was suggested as a possible pathways for oxidized OA formation.

Chapters 3 and 4 focused on experiments designed to study the role of chemistry within the aqueous-phase (wet particles or cloud droplets) in the formation of highly oxidized OA. In Chapter 3, we described experiments designed to directly compare aqueous oxidation chemistry under vastly different partitioning conditions. Polyols (which served as simple surrogates for water-soluble compounds in the atmosphere) were oxidized both in aqueous submicron particles and in bulk aqueous solution. Both sets of experiments resulted in rapid oxidation, but substantially more carbon was lost from the submicron particles, likely due to differences in partitioning of early-generation products. These results confirmed that aqueous-phase oxidation is an efficient pathway for the rapid formation of highly oxidized material. However, they also implied that bulk oxidation experiments may not accurately simulate the chemistry that occurs in the atmospheric aqueous phase, due to large differences in liquid water content (LWC) and therefore partitioning. This underscores the need for future experiments to be carried out within aqueous submicron particles where partitioning conditions are more representative of the atmosphere.
In Chapter 4, we examined the role of aqueous oxidants on the formation of SOA from the gas-phase ozonolysis of atmospherically important biogenic precursors. Shifting the focus to a more complex and realistic SOA system allowed for better insight into the potential effects of aqueous oxidation in the atmosphere. In these experiments the presence of aqueous oxidants was found to dramatically influence SOA formation, leading to substantially higher degrees of oxidation. This demonstrated that chemistry within aerosol particles can result in the formation of highly oxidized material. In some cases, exposure to UV irradiation was shown to enhance the degree of oxidation presumably via increased production of condensed-phase oxidants. These experiments represent the first time organic aerosol with this high a degree of oxidation has been generated from ozonolysis of gas-phase precursors.

This thesis has provided compelling evidence that oxidation within aqueous particles could play an important role in the formation of highly oxidized OA. We have shown that aqueous-phase chemistry, when it occurs, can result in efficient oxidation of organic material. We also demonstrated the need for future studies to be conducted under atmospherically relevant partitioning conditions, since oxidation within bulk aqueous solutions was found to differ from oxidation in aqueous aerosol. Our overall findings suggest that the inclusion of aqueous-phase chemistry in atmospheric models needs to be considered. However, the atmospheric importance of these processes, as well as their integration into models, are both strongly dependent on the concentrations of oxidants within atmospheric particles. These concentrations, which currently only exist as estimations from models, are highly uncertain, largely due to the absence of direct measurements of aqueous oxidants in the atmosphere. Therefore, future measurements of ambient aqueous oxidant concentrations could prove extremely valuable. These could be used along with detailed information regarding liquid water contents to better estimate the relative im-

117
portance of aqueous- and gas-phase chemistry under different conditions. These measurements
together with the results of this thesis would prove a valuable addition to current models.