Chapter 1

Introduction

1.1 Motivation

While the composition of the atmosphere is predominantly gaseous, the atmosphere contains aqueous and solid phase particulate matter (aerosols) with important roles in atmospheric processes that lead to climate and visibility effects.[1] Aerosol particles have both direct and indirect effects on the atmosphere and climate. An example of a direct effect of aerosol particles is their interaction with solar radiation: atmospheric aerosol can absorb and scatter solar radiation, affecting the radiative transfer of energy and influencing climate directly. The scattering of visible light by aerosol particles is commonly recognized as the haze in urban environments, including Los Angeles. An indirect effect of aerosol particles is their role in cloud production: aerosols are known to act as cloud condensation nuclei (CCN) and ice nuclei (IN), which form clouds and thereby affect the global climate.[1] Aerosol particles are composed of organic and inorganic compounds, originate from anthropogenic or biogenic sources, and can become airborne as particles (primary organic aerosol, POA; e.g. pollen) or develop in the atmosphere as the result of chemical and physical processes (secondary organic aerosol, SOA).[2] The chemical compositions of POA and SOA affect their physical properties, which in turn determine their direct and indirect climate effects.

Organic compounds compose 20-90% by mass of ambient aerosol. Volatile organic compounds (VOCs) in the atmosphere originate from both anthropogenic and biogenic sources; the most abundant non-methane hydrocarbon in the atmosphere is isoprene, which is biogenic in origin.[3] The atmosphere contains highly reactive radicals, predominantly OH and NO_3, which drive the oxidation of atmospheric organic compounds. As organic compounds undergo oxidation, they can decrease in volatility through the addition of polar functional groups (e.g. carbonyl and hydroxyl groups) or increase in volatility through decomposition into smaller C-chain compounds. Gas/particle partitioning of these semi- and low-volatility compounds leads to SOA formation. Ambient aerosol is often chemically complex due to the variety of ambient sources of organic compounds and the diverse products from atmospheric photooxidation of these species.[4] Reduction of aerosol burdens and prediction of CCN efficacy and climate effects require identification of major SOA sources; this effort requires understanding of the chemistry leading to SOA formation and measurements of the chemical composition of ambient aerosol to identify the parent organic compounds.

SOA particles exist in a chemical and physical state of flux: the constituent molecules can continue to condense, evaporate, and be chemically transformed through reactions and photochemistry. The dynamic nature of gas/particle partitioning dictates that compounds can freely partition between the phases, driven by concentration gradients and temperature. Chemical reactions and photochemical reactions can occur within the bulk and at the surface of aerosol. Oxidation in the particle-phase can occur at the surface or from unique bulk processes like photo-Fenton reactions. Oligomerization is a key process in particle formation and growth; it has been shown to be important to anthropogenic and biogenic compounds. These transformative processes occur on an atmospherically relevant timescale.

Detailed chemical characterization of SOA composition at a molecular level is typically conducted using solvent extraction and electron impact ionization (EI) in order to conduct a mass spectrometric analysis. These techniques are highly useful in identifying molecules by fragmentation patterns, which indicate structural details. Analysis method artifacts arise with the use of these methods, however; less stable compounds like peroxides, epoxides, and acid-cleavable, high-boiling oligomers are not readily detectable in their native state. Derivatization and gas chromatographic/mass spectrometric (GC/MS) analysis, and liquid chromatography/mass spectrometry (LC/MS) are powerful techniques for the separation of complex mixtures and identification of components, but like all techniques, they need to be used alongside auxiliary techniques to gain a fuller view of SOA chemical composition that includes more fragile or low-volatility species. Recent advancements in ambient ionization methods including direct analysis in real time mass spectrometry (DART-MS) have shown promise in measuring sensitive compounds in complex matrices.

1.2 Research Objectives

The principal objectives of this research are to study the formation of SOA from anthropogenic marker compounds (C_{12} alkanes, toluene, and *o*-, *m*-, and *p*-cresol) under simulated urban and rural atmospheric conditions using comprehensive characterization of SOA composition using GC/MS and DART-MS, and to explore the extent of particle-phase chemistry to SOA chemical composition, specifically the importance of oligomer formation to SOA growth.

1.3 Approach

This section provides an overview of the research presented in the following chapters.

Chapter 2 describes the study of the effect of structure, NO_x conditions, relative humidity, and acidity on the chemical composition of SOA generated from the photooxidation of the C_{12} alkanes *n*-dodecane, cyclododecane, and hexylcyclohexane. Alkanes are an important anthropogenic VOC in urban areas, and known precursors to SOA. The gas-phase oxidation of alkanes is known to lead to peroxide formation and oligomers including hemiacetals and peroxy hemiacetals.[5] The findings presented in Chapter 2 originate from the offline analysis of alkane SOA collected via filtration by solvent extraction and GC/MS analysis paired with on-filter DART-MS analysis. In the GC/MS analysis, electron impact ionization was used along with chemical ionization by methanol to obtain structural and molecular information about the analytes. GC/EI-MS with a high-resolution time-of-flight mass spectrometer was used to obtain accurate mass measurements of the ion fragments. DART-MS analysis was performed on a commercial high-resolution system to obtain accurate mass measurements of the pseudomolecular ions and ion clusters, as well as on an experimental source coupled to an ion trap mass spectrometer to use reactive methods to identify ion clusters and the target analyte contained within the cluster. The products identified in this research show the influence of particle-phase oligomerization, cyclization, and imine formation on alkane SOA chemical composition, as well as the impact of NO_x and parent alkane structure.

Chapter 3 describes the study of toluene SOA formation under low- and high-NO conditions, and explores the influence of the cresol pathway on determining the chemical composition of toluene SOA. Toluene is known to undergo photooxidation through a bicyclic peroxy radical intermediate as well as through a cresol intermediate; those two major pathways account for 83% of the photooxidative fate of toluene. Low and extremely low volatility organic compounds (LVOC and ELVOC) are known to be important to aromatic SOA formation, as well as oligomeric species, particularly those derived from glyoxal. In this research, the extent to which LVOC and ELVOC comprise aromatic SOA is explored, as well as ascertaining the nature of those compounds to determine the contributions of oligomerization and multigenerational photooxidation to the formation of these low-volatility species and toluene SOA. To this end, toluene and *o*-, *m*-, and *p*-cresol were directly photooxidized under comparable conditions to allow for the comparison of SOA chemical compositions and the estimation of the contribution of the cresol pathway to toluene SOA. In this study, chemical analysis of SOA was conducted by using high-resolution aerosol mass spectrometry (HR-AMS) and high-resolution direct analysis in real time mass spectrometry (DART-HR-MS). The mass spectral datasets for toluene and *o*-cresol SOA produced under high-NO conditions were qualitatively analyzed using positive matrix factorization to draw out commonalities and differences between the different growth periods of toluene and cresol SOA. The chemical compositions measured by offline DART-HR-MS analysis were examined in van Krevelen space to identify overall trends in functionalization and fragmentation over the course of the photooxidation experiment.

To close, chapter 4 summarizes the main findings of this research and provides future directions for extensions of this work. Additional applications of offline analysis of SOA to the addressing of major chemical questions involving biogenic SOA, anthropogenic SOA, and ambient SOA are located in the Appendices.

1.4 References

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