CHAMBER STUDIES OF SECONDARY ORGANIC AEROSOL FORMATION

Thesis by

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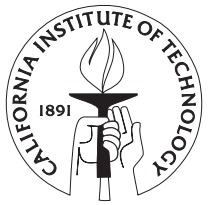

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“Perseverance is the key to learning.” – Chinese proverb

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Abstract

Atmospheric oxidation of volatile organic compounds leads to the formation of secondary organic aerosol (SOA). Laboratory chambers provide a controlled environment for investigating aerosol formation and evolution. This thesis presents results on aerosol formation from a wide range of parent organic compounds under a variety of experimental conditions.

The effect of particle-phase acidity on aerosol formation is explored in a series of alkene ozonolysis experiments. Oligomeric species are detected regardless of the particle-phase acidity, indicating the ubiquitous existence of particle-phase reactions. As acidity increases, larger oligomers are formed more abundantly and aerosol yields also increase. Volatile organic compounds generally not considered to be SOA precursors, including isoprene and glyoxal, have been shown to lead to aerosol formation. Uptake of glyoxal into particles is evidence that small molecules can potentially produce aerosol via reactive absorption. Although there is strong evidence that heterogeneous reactions play an important role in SOA formation, the detailed mechanisms remain poorly understood. In a comprehensive study on aerosol formation from biogenic hydrocarbons, it is found that data on aerosol growth as a function of the amount of hydrocarbon reacted provide important insights into the general aerosol formation mechanisms by identifying rate-determining steps and whether SOA is formed from first- or second-generation products.

The mechanism of aerosol formation by isoprene is specifically investigated over a range of NO_x concentrations. Aerosol yields are found to decrease substantially with increasing NO_x. The same NO_x dependence is observed for monoterpenes (α-pinene), as well as aromatic hydrocarbons (*m*-xylene, toluene, and benzene). It is suggested that

peroxy radical chemistry plays the central role in the observed NO_x dependence. The NO_x dependence for larger compounds is, however, different from that of isoprene, monoterpenes, and aromatics. For sesquiterpenes such as longifolene and aromadendrene, aerosol yields increase with increasing NO_x concentration. The reversal of the NO_x dependence of SOA formation for the sesquiterpenes appears to be the result of formation of relatively nonvolatile organic nitrates, and/or the isomerization of large alkoxy radicals that leads to less volatile products.

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Chapter 1

Introduction

Introduction

Aerosols are suspended solid or liquid particles and they affect air quality, human health and the earth's climate. Aerosols can be classified into two main categories according to their formation processes. Primary aerosols are emitted directly from different sources into the atmosphere, while the oxidation of organic gases leads to the formation of low-volatility products that partition into the condensed phase and result in the formation of secondary organic aerosol (SOA). Biogenic hydrocarbons emitted by vegetation and aromatics from anthropogenic sources are important precursors for SOA formation. The main oxidants in the atmosphere are ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3). SOA contributes significantly to the total ambient organic aerosols in urban areas, as well as regionally and globally.

Laboratory chambers provide a controlled environment to study the formation and evolution of secondary organic aerosol, by isolating specific compounds of interest and controlling the oxidation environment. Since identification and quantification of all oxidation products from parent hydrocarbons are difficult, aerosol yields have been used in the study of secondary precursor organics. Aerosol yields indicate the aerosol-forming potential of various precursor organics. Yield is defined as the ratio of the mass concentration of aerosol formed from the oxidation of a given parent hydrocarbon to that of the hydrocarbon reacted: $Y = \Delta M_o / \Delta HC$, where ΔM_o ($\mu g\ m^{-3}$) is the organic aerosol mass produced for a certain reacted amount of hydrocarbon ΔHC ($\mu g\ m^{-3}$). While yield curves (Y plotted against ΔM_o) have proven to be useful in representing SOA formation, the general mechanisms of SOA formation cannot be readily inferred. In chapter 2 it is shown that this model can be extended for interpretation of laboratory SOA growth data

in terms of underlying chemistry, by plotting experimentally measured aerosol growth, ΔM_o, as a function of the amount of hydrocarbon reacted, ΔHC (growth curve). The growth curve approach is applied in a comprehensive study on aerosol formation from biogenic hydrocarbons to study the general aerosol formation mechanisms.

In chapter 3 the effect of particle-phase acidity on aerosol formation is explored in a series of alkene ozonolysis experiments, including α-pinene and 6 cycloalkenes of various carbon numbers and substitutions. The aerosol yields from α-pinene ozonolysis are systematically studied over a range of initial hydrocarbon concentrations, in the presence of seed particles of differing acidity. The composition of the aerosols formed are presented.

Volatile organic compounds previously not considered to be SOA precursors, including glyoxal and isoprene, are shown to lead to aerosol formation. In chapter 4 the potential for aerosol growth via heterogeneous reactions for a number of small carbonyls is examined by measuring changes in particle volume and composition when inorganic seed and gas-phase carbonyls are introduced into the chambers. Glyoxal is the only single carbonyl that leads to substantial aerosol growth and this reactive uptake is discussed in detail. Chapter 5 presents the results on the first study on secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions in which HONO is used as the OH precursor. In chapter 6 the mechanism of aerosol formation by isoprene photooxidation is comprehensively investigated over a range of experimental conditions, namely isoprene and NO_x concentrations. The effect of NO_x concentration on aerosol yields and composition is discussed. In chapter 7 the effect of NO_x levels on SOA formation from photooxidation of larger biogenic hydrocarbons such as monoterpenes

(α-pinene) and sesquiterpenes (longifolene and aromadendrene) are investigated by performing experiments under two limiting NO_x conditions, as well as varying the amount of NO_x present systematically. The SOA yields and composition under different NO_x conditions is presented.

Besides biogenic compounds, aerosol formation from aromatic hydrocarbons, including *m*-xylene, toluene, and benzene are investigated under different NO_x conditions. The results are presented in chapter 8. Additionally, the effect of seed aerosol acidity on SOA formation is studied under both high- and low-NO_x conditions. The SOA yield parameters obtained at the two NO_x limits allow one to parameterize the NO_x dependence of SOA formation for use in atmospheric models.

Finally, chapter 9 summarizes the findings presented in the previous seven chapters. Appendix A presents results from a kinetic model of the behavior of a semivolatile compound which may undergo irreversible reactions in both the gas and particle phases in addition to partitioning. The effect of such loss processes on aerosol yields is discussed. Appendices B-J present results on studies of SOA composition and formation mechanisms with a wide range of instruments and analytical techniques, including filter sample analysis (Appendices B-E), Aerosol Mass Spectrometer (AMS, Appendices F and G), and Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA, Appendix H). The gas-phase composition from the ozonolysis and photooxidation of various biogenic hydrocarbons are studied in detail with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) and the results are presented in Appendices I and J.