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Introduction

Organic material contributes ~20–50% to the total fine aerosol mass at continental mid-latitudes (Saxena and Hildemann, 1996; Murphy et al., 1998; Peterson and Tyler, 2002; Putaud et al., 2004) and as much as 90% in tropical forested areas (Andreae and Crutzen, 1997; Artaxo et al., 2002). Significant amounts of carbonaceous aerosols are also observed in the free troposphere (Heald et al., 2005). A substantial fraction of the organic component of atmospheric particles consists of water-soluble, possibly multifunctional compounds (Saxena and Hildemann, 1996; Kavouras et al., 1998).

It is critical that we understand how organic aerosols and their precursors are transformed in the atmosphere and the dependence of the transformation on the chemical and thermodynamic conditions of the ambient environment: 1) to accurately forecast how changing emissions will impact atmospheric organic aerosol concentrations and properties on the regional to global scale, and 2) to relate atmospheric measurements to sources. A large (but as yet unquantified) fraction of organic aerosol is formed in the atmosphere by precursor gases. In addition, both primary and secondary organic aerosol interact with other gas and aerosol species in the atmosphere so that their properties (i.e., size, hygroscopicity, light absorption and scattering sphere efficiency) can change significantly with time and distance from their source.

Organic aerosols (OA) are composed of complex mixtures of different organic species from less-polar organics (*n*-alkanes, polycyclic aromatic hydrocarbons, fatty alcohols, fatty acids, etc.) to highly polar organics such as dicarboxylic acids and multi-functional organic acids. Studies employing FTIR spectroscopy and NEXAFS have demonstrated the presence of different functional groups such as ketonic and carboxylic groups. Humic-like substances (HULIS) have been identified in aerosols. Field observation and laboratory smog chamber studies have demonstrated that oxidative reactions of biogenic and anthropogenic precursors in the gas phase produce low molecular weight organic acids such as oxalic and other dicarboxylic acids, dicarbonyls and multi-functional organics. Oxidation reactions in the particle phase may also produce oxygenated species, including aldehydes, organic acids, and large molecules such as HULIS. Despite this progress, a significant fraction of atmospheric OA still remains poorly characterized.

Secondary organic aerosol (SOA), particulate matter formed by the condensation of oxidation products of volatile organic compounds (VOCs), is known to constitute a substantial fraction of fine particulate matter in the lower atmosphere. Considerable effort has been devoted to gaining a detailed, quantitative understanding of the formation and growth of SOA in the troposphere, but this has been hampered by difficulties in identifying the individual chemical components of SOA. Even a single precursor hydrocarbon generally yields a large number of condensable products, many of which may not have been identified in laboratory studies. This lack of speciated aerosol data has made it difficult to model aerosol growth accurately from first principles using detailed treatments of gas-phase chemistry and gas-particle partitioning. The oxidation of terpenes in the troposphere plays an important role in the generation of secondary organic particulate matter (Kavouras et al., 1999; Yu et al., 1999ab). SOA formation from biogenic VOCs has now been amply demonstrated in laboratory chamber experiments (e.g., Palen et al., 1992; Zhang et al., 1992; Hoffmann et al., 1997; Griffin et al., 1999a; Barnes, 2004; Hoffmann, 2001; Jaoui and Kamens, 2003).

A long-standing puzzle associated with the analysis of molecular speciation of SOA has been the presence in the aerosol of species whose vapor pressures are far too high to support significant partitioning into the aerosol phase (Forstner et al., 1997ab; Yu et al., 1998, 1999ab). It was speculated that these relatively small and volatile species might actually be decomposition products of larger, less volatile molecules that were broken apart by the relatively harsh environment of the mass spectrometric methods traditionally used for analysis. Very recently, high molecular weight (and therefore low vapor pressure) products have been identified in the aerosol phase using less harsh analytical techniques. There is now substantial evidence that SOA growth may also be influenced by heterogeneous reactions, so that the condensation of some organics may be reactive as well as absorptive. Such evidence includes the observation of increased aerosol yields under acidic conditions (Jang et al., 2001, 2002; Iinuma et al., 2004; Gao et al., 2004 ab) and the measurement of high-MW oligomers in SOA (Kalberer et al., 2004; Tolocka et al., 2004; Gao et al., 2004 ab). Although the evidence that heterogeneous reactions may contribute to SOA growth is strong, the reactions themselves remain poorly understood. The detailed chemistry (kinetics, thermodynamics, mechanism) is generally poorly constrained, and significant discrepancies exist between the results from experimental and theoretical studies (Barsanti and Pankow, 2004). Oligomer formation following both biogenic and anthropogenic VOC degradation may indeed be responsible for an important fraction of the SOA chemical build up in the troposphere Tolocka et al. (2004) and Gao et al. (2004ab) have identified oligomers as large as tetramers in chamber experiments during α-pinene ozonolysis using acidic inorganic seed aerosol. They conclude that α-pinene ozonolysis is strongly influenced by oligomerization reactions of primary ozonolysis products, most likely by aldol condensation and/or gem-diol formation. The exact mechanisms of the oligomer and/or polymer formation and their significance for the chemical formation and properties of the secondary organic aerosol remain to be determined.

The gas-phase chemistry prior to gas-particle partitioning is believed, in addition, to be significantly more complex than simply the formation of condensable products from a single oxidation step. For example, SOA formed in the photooxidation of aromatic hydrocarbons includes compounds such as cyclic anhydrides, organic acids, and polycarbonyls (Forstner et al., 1997; Yu et al., 1997; Edney et al., 2001; Jang et al., 2001), highly oxidized compounds that are not produced directly in the initial reaction of the parent aromatic hydrocarbon. Instead, they are likely to be formed by photolysis or gas-phase reactions (with OH, NO_3, or O_3) of the first-generation products (Ng et al., 2006). Aerosol growth from first-generation oxidation products may be governed by a complex competition between reaction with those oxidants, reaction with OH, and photolysis. NO_x concentration controls the fate of peroxy radical intermediates by changing the branching between reaction with NO and reaction with HO_2 or RO_2. Reaction with NO produces mostly alkoxy radicals, which may decompose to smaller (and more volatile) compounds, whereas reaction with HO_2 or RO_2 may form acids, peracids, peroxides, and alcohols, which may partition efficiently into the aerosol phase. In this case, the "first-generation products" are not the first set of molecular oxidation products but rather the peroxy radical intermediates formed from the initial OH reaction.

Key questions on secondary organic aerosol (SOA) formation include: (1) How important is SOA formation in the atmosphere (OA vs. inorganics; SOA vs. POA), and how does it influence the properties and environmental effects of atmospheric aerosols? (2) How important are the different SOA formation pathways relative to each other; in particular, how important are aerosol-phase reactions relative to gas-phase oxidation followed by gas-to-particle conversion? (3) What are the molecular mechanisms and kinetics of the chemical and physical processes involved? (4) What are the most important products of SOA formation (organic acids, oligomers/polymers, HULIS, etc.) and what are their physicochemical properties (functional groups, molecular mass, stability, volatility, solubility, hygroscopicity, optical absorption, etc.)?

The following sections summarize results obtained under this grant aimed at addressing the above questions. Each of these sections summarizes results contained in journal publications that are attached to this report as pdf files.

Particle Phase Acidity and Oligomer Formation in Secondary Organic Aerosol

A series of controlled laboratory experiments are carried out in dual Teflon chambers to examine the presence of oligomers in secondary organic aerosols (SOA) from hydrocarbon ozonolysis as well as to explore the effect of particle phase acidity on SOA formation. In all seven hydrocarbon systems studied (i.e., α-pinene, cyclohexene, 1-methyl cyclopentene, cycloheptene, 1-methyl cyclohexene, cyclooctene, and terpinolene), oligomers with MW from 250 to 1600 are present in the SOA formed, both in the absence and presence of seed particles and regardless of the seed particle acidity. These oligomers are comparable to, and in some cases, exceed the low molecular weight species (MW < 250) in ion intensities in the ion trap mass spectra, suggesting they may comprise a substantial fraction of the total aerosol mass. It is possible that oligomers are widely present in atmospheric organic aerosols, formed through acid- or base-catalyzed heterogeneous reactions. In addition, as the seed particle acidity increases, larger oligomers are formed more abundantly in the SOA; consequently, the overall SOA yield also increases. This explicit effect of particle phase acidity on the composition and yield of SOA may have important climatic consequences and need to be considered in relevant models.

Low-molecular-weight and Oligomeric Components in Secondary Organic Aerosol from the Ozonolysis of Cycloalkenes and alpha-Pinene

The composition of secondary organic aerosol (SOA) from the ozonolysis of C_5-C_8 cycloalkenes and α-pinene, as well as the effects of hydrocarbon precursor structure and particle-phase acidity on SOA formation, have been investigated by a series of controlled laboratory chamber experiments. A liquid chromatography-mass spectrometer and an ion trap mass spectrometer are used concurrently to identify and to quantify SOA components with molecular weights up to 1600 Da. Diacids, carbonyl-containing acids, diacid alkyl esters, and hydroxy diacids are the four major classes of low-molecular-weight (MW < 250 Da) components in the SOA; together they comprise 42-83% of the total SOA mass, assuming an aerosol density of 1.4 g/cm^3. In addition, oligomers (MW > 250 Da) are found to be present in all SOA. Using surrogate standards, it is estimated that the mass fraction of oligomers in the total SOA is at least 10% for the cycloalkene systems (with six or more carbons) and well over 50% for the α-pinene system. Higher seed particle acidity is found to lead to more rapid oligomer formation and, ultimately, to higher SOA yields. Because oligomers are observed to form even in the absence of seed particles, organic acids produced from hydrocarbon oxidation itself may readily promote acid catalysis and oligomer formation. The distinct effects of carbon numbers, substituent groups, and isomeric structures of the precursor hydrocarbons on the composition and yield of SOA formed are also discussed.

Secondary Organic Aerosol Formation from the Ozonolysis of Cycloalkenes and Related Compounds

The secondary organic aerosol (SOA) yields from the laboratory chamber ozonolysis of a series of cycloalkenes and related compounds are reported. The aim of this work is to investigate the effect of the structure of the hydrocarbon parent molecule on SOA formation for a homologous set of compounds. Aspects of the compound structures that are varied include the number of carbon atoms present in the cycloalkene ring (C_5 to C_8), the presence and location of methyl groups, and the presence of an exocyclic or endocyclic double bond. The specific compounds considered here are cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-methyl-1-cyclopentene, 1-methyl-1-cyclohexene, 1-methyl-1-cycloheptene, 3-methyl-1- cyclohexene, and methylenecyclohexane. The SOA yield is found to be a function of the number of carbons present in the cycloalkene ring, with an increasing number resulting in increased yield. The yield is enhanced by the presence of a methyl group located at a double-bonded site but reduced by the presence of a methyl group at a nondouble-bonded site. The presence of an exocyclic double bond also leads to a reduced yield relative to that of the equivalent methylated cycloalkene. On the basis of these observations, the SOA yield for terpinolene relative to the other cyclic alkenes is qualitatively predicted, and this prediction compares well to measurements of the SOA yield from the ozonolysis of terpinolene. This work shows that relative SOA yields from ozonolysis of cyclic alkenes can be qualitatively predicted from properties of the parent hydrocarbons.

Secondary Organic Aerosol Formation from Cyclohexene Ozonolysis: Effect of OH Scavenger and the Role of Radical Chemistry

To isolate secondary organic aerosol (SOA) formation in ozone-alkene systems from the additional influence of hydroxyl (OH) radicals formed in the gas-phase ozone-alkene reaction, OH scavengers are employed. The detailed chemistry associated with three different scavengers (cyclohexane, 2-butanol, and CO) is studied in relation to the effects of the scavengers on observed SOA yields in the ozone-cyclohexene system. Our results confirm those of Docherty and Ziemann that the OH scavenger plays a role in SOA formation in alkene ozonolysis. The extent and direction of this influence are shown to be dependent on the specific alkene. The main influence of the scavenger arises from its independent production of HO_2 radicals, with CO producing the most HO_2, 2-butanol an intermediate amount, and cyclohexane the least. This work provides evidence for the central role of acylperoxy radicals in SOA formation from the ozonolysis of alkenes and generally underscores the importance of gas-phase radical chemistry beyond the initial ozone-alkene reaction.

Measurement of Secondary Organic Aerosol (SOA) from Oxidation of Cycloalkenes, Teprenes, and m-Xylene using an Aerodyne Aerosol Mass Spectrometer

The Aerodyne aerosol mass spectrometer (AMS) was used to characterize physical and chemical properties of secondary organic aerosol (SOA) formed during ozonolysis of cycloalkenes and biogenic hydrocarbons and photooxidation of *m*-xylene. Comparison of mass and volume distributions from the AMS and differential mobility analyzers yielded estimates of "effective" density of the SOA in the range of 0.64-1.45 g/cm^3, depending on the particular system. Increased contribution of the fragment at *m/z* 44, CO_2+ ion fragment of oxygenated organics, and higher "Δ" values, based on ion series analysis of the mass spectra, in nucleation experiments of cycloalkenes suggest greater contribution of more oxygenated molecules to the SOA as compared to those formed under seeded experiments. Dominant negative "Δ" values of SOA formed during ozonolysis of biogenics indicates the presence of terpene derivative structures or cyclic or unsaturated oxygenated compounds in the SOA. Evidence of acidcatalyzed heterogeneous chemistry, characterized by greater contribution of higher molecular weight fragments to the SOA and corresponding changes in "Δ" patterns, is observed in the ozonolysis of α-pinene. Mass spectra of SOA formed during photooxidation of *m*-xylene exhibit features consistent with the presence of furandione compounds and nitro organics. This study demonstrates that mixtures of SOA compounds produced from similar precursors result in broadly similar AMS mass spectra. Thus, fragmentation patterns observed for biogenic versus anthropogenic SOA may be useful in determining the sources of ambient SOA.

Cloud Condensation Nucleus Activation Properties of Biogenic Secondary Organic Aerosol

Organic aerosols in general and secondary organic aerosol (SOA) in particular are known to contribute significantly to the atmospheric population of cloud condensation nuclei (CCN). However, current knowledge is limited with respect to the nature of this contribution. This study presents a series of experiments wherein the potential for biogenically derived SOA to act as CCN is explored. Five compounds were studied: four monoterpenes (α-pinene, β-pinene, limonene, and Δ^3-carene) and one terpenoid alcohol (terpinene-4-ol). In each case the aerosol formation was driven by the reaction of ozone with the biogenic precursor. The SOA produced in each experiment was allowed to age for several hours, during which CCN concentrations were periodically measured at four supersaturations: $S = 0.27\%$, 0.32%, 0.54%, and 0.80%. The calculated relationships between particle dry diameter and critical supersaturation were found to fall in the range of previously reported data for single-component organic aerosols; of the systems studied, α-pinene SOA was the least CCN active, while limonene SOA exhibited the strongest CCN activity. Interestingly, the inferred critical supersaturation of the SOA products was considerably more sensitive to particle diameter than was found in previous studies. Furthermore, the relationships between particle size and critical supersaturation for the monoterpene SOA shifted considerably over the course of the experiments, with the aerosol becoming less hygroscopic over time. These results are consistent with the progressive oligomerization of the SOA.

Representation of Secondary Organic Aerosol (SOA) Laboratory Chamber Data for the Interpretation of Mechanisms of Particle Growth

Absorptive models of gas-particle partitioning have been shown to be successful in describing the formation and growth of secondary organic aerosol (SOA). Here the expression for particle growth derived by Odum et al. (Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.,* **1996**, 30, 2580- 2585) is extended to facilitate interpretation of SOA growth data measured in the laboratory in terms of the underlying chemistry, even when details of the reactions are not wellconstrained. Asimple (one-component) expression for aerosol growth (ΔM) as a function of the amount of hydrocarbon reacted (ΔHC) is derived, and the effects of changes to three key parameters, stoichiometric yield of condensable species, gas-particle partitioning coefficient, and concentration of preexisting aerosol, are discussed. Two sets of laboratory chamber data on SOA growth are examined in this context: the ozonolysis of α-pinene and the OH-initiated photooxidation of aromatic compounds. Even though these two systems have a number of significant differences, both are described well within this framework. From the shapes of the ΔM versus ΔHC curves in each case, the importance of poorly constrained chemistry such as heterogeneous reactions and gas-phase reactions of oxidation products is examined.

Chamber Studies of Secondary Organic Aerosol Growth by Reactive Uptake of Simple Carbonyl Compounds

Recent experimental evidence indicates that heterogeneous chemical reactions play an important role in the gas-particle partitioning of organic compounds, contributing to the formation and growth of secondary organic aerosol in the atmosphere. Here we present laboratory chamber studies of the reactive uptake of simple carbonyl species (formaldehyde, octanal, *trans,trans*-2,4-hexadienal, glyoxal, methylglyoxal, 2,3-butanedione, 2,4-pentanedione, glutaraldehyde, and hydroxyacetone) onto inorganic aerosol. Gas-phase organic compounds and aqueous seed particles (ammonium sulfate or mixed ammonium sulfate/sulfuric acid) are introduced into the chamber, and particle growth and composition are monitored using a differential mobility analyzer and an Aerodyne Aerosol Mass Spectrometer. No growth is observed for most carbonyls studied, even at high concentrations (500 ppb to 5 ppm), in contrast with the results from previous studies. The single exception is glyoxal (CHOCHO), which partitions into the aqueous aerosol much more efficiently than its Henry's law constant would predict. No major enhancement in particle growth is observed for the acidic seed, suggesting that the large glyoxal uptake is not a result of particle acidity but rather of ionic strength of the seed. This increased partitioning into the particle phase still cannot explain the high levels of glyoxal measured in ambient aerosol, indicating that additional (possibly irreversible) pathways of glyoxal uptake may be important in the atmosphere.

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