

Chapter 1

Introduction

1.1 Background and Motivation

Organic compounds contribute a large fraction (i.e., 20–90%) towards the total mass of tropospheric fine particulate matter (PM_{2.5}, with aerodynamic diameter < 2.5 μm) (Kanakidou et al., 2005; Hallquist et al., 2009). High concentrations of PM_{2.5} are known to have adverse health effects (Hallquist et al., 2009, and references therein) and play a role in global climate change (Kanakidou et al., 2005; Hallquist et al., 2009). Although there are many sources for organic compounds found in PM_{2.5}, which includes primary emissions (e.g., diesel engine exhaust), SOA formation often accounts for a large, and at times, dominant fraction of the organic mass found in tropospheric PM_{2.5} (Hallquist et al., 2009). SOA has been traditionally viewed to form in the troposphere from the oxidation of volatile organic compounds (VOCs), where the resultant low vapor pressure oxidation products partition between the gas and aerosol phases.

Although the application of both off-line and on-line advanced analytical techniques have increased our understanding of SOA formation pathways, such as the detection of high-molecular-weight species indicating the potential role of heterogeneous chemistry, in recent years (e.g., Docherty et al., 2005; Gao et al., 2004ab; Iinuma et al., 2004; Kalberer et al., 2004; Tobias et al., 2000; Tolocka et al., 2004), current models predict notably less SOA mass than is typically observed in the atmosphere (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). A large source for this underestimation is due, in large part, to the lack of full chemical characterization of organic constituents found in tropospheric PM_{2.5}, likely resulting in significant sources or chemical formation pathways of SOA not being identified or well characterized, and thus, not included in current SOA models (Hallquist et al., 2009; and references therein).

Much of the current efforts in the research community are now focused on trying to identify this missing source of SOA (Hallquist et al., 2009).

Until recently, the formation of SOA from the oxidation of isoprene, the most abundant non-methane hydrocarbon emitted annually into the troposphere, was considered insignificant (Claeys et al., 2004), and as a result, has not been included in SOA models. This was largely due to the known volatility of first-generation gas-phase oxidation products, such as methacrolein (MACR), methyl vinyl ketone (MVK), and formaldehyde, from isoprene oxidation in the presence of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), and a previous chamber study that concluded that isoprene oxidation does not lead to SOA formation (Pandis et al., 1991). Recent field observations of certain organic aerosol compounds, diastereoisomeric 2-methyltetrols (2-methylerythritol and 2-methylthreitol) and 2-methylglyceric acid, attributable to isoprene oxidation, and the experimental observation that isoprene under highly acidic conditions can lead to the formation of polymeric, humic-like substances through heterogeneous reactions, reopened the issue of SOA formation from isoprene (Claeys et al., 2004; Edney et al., 2005; Limbeck et al., 2003; Wang et al., 2005). Subsequent to their ambient identification, Edney et al. (2005) and Böge et al. (2006) detected 2-methyltetrols in SOA formed from laboratory chamber studies of isoprene. Recent work in our laboratory has shown that SOA formation from isoprene oxidation can be significant (Kroll et al., 2005, 2006). More specifically, higher SOA yields from isoprene are observed under low- NO_x (or NO_x -free) conditions (i.e., upwards of 3%); in this regime, peroxy radicals (RO_2) radicals react primarily with HO_2 , a pathway that tends to produce lower-volatility oxidation products than that involving the reaction of RO_2 with NO (Kroll et al., 2005,

2006, 2008, and references therein; Presto et al., 2005). Under high-NO_x conditions, RO₂ radicals react with NO to produce alkoxy (RO) radicals, or as a minor pathway, organic nitrates (RONO₂); for small VOCs ($\leq C_{10}$), like isoprene, these RO radicals generally fragment into smaller more volatile products, resulting in small amounts of SOA (~1% mass yields for high-NO_x SOA) (Kroll et al., 2005, 2006). For isoprene, as well as other VOCs, these differences in SOA yields remain unclear due to lack of understanding of the detailed reaction pathways leading to SOA.

1.2 Organization of Thesis

Although isoprene is now recognized to yield significant amounts of aerosol under low- or high-NO_x conditions, as well as being enhanced with increasing aerosol acidity, the detailed chemical mechanisms of isoprene SOA formation have remained elusive, especially those that are relevant in the Earth's atmosphere. Much of this has been a direct result of the lack of detailed chemical characterization of the isoprene SOA constituents using suitable mass spectrometry techniques. The chemical characterization of individual SOA constituents provides significant insights into the chemical formation pathways of SOA, especially when combined with detailed gas-phase chemical measurements.

Owing to the fact that SOA formation from isoprene oxidation likely contributes significantly to the ambient organic aerosol budget (Carlton et al., 2009, and references therein; Henze and Seinfeld, 2006), its detailed chemical formation pathways need to be fully elucidated so that the research community can accurately include it into global SOA models. In order to elucidate these pathways, many questions about the formation of

isoprene SOA need to be resolved, and thus, are central to this thesis. These include the following:

- 1.) Why is there a difference in the isoprene SOA yields between low- and high- NO_x conditions? Specifically, what oxidation products from isoprene are responsible for forming SOA under both NO_x regimes? What are the subsequent reactions of these oxidation products that lead to isoprene SOA formation? Does heterogeneous chemistry play a major role? Are the reactions we uncover under these different NO_x regimes relevant to the troposphere?
- 2.) Are there ambient tracer compounds that can be used to identify when isoprene SOA forms under low- and high- NO_x conditions in the troposphere, as well as be used in source apportionment efforts?
- 3.) What are the precise acid-catalyzed reactions that cause the laboratory observed enhancements in isoprene SOA mass with increasing aerosol acidity? Are these reactions relevant to ambient organic aerosol formation?
- 4.) For the chemical formation mechanisms we uncover from studying the chemical composition of isoprene SOA, how might these relate to other SOA precursors, such as the monoterpenes (e.g., α -pinene)?

In this thesis, the applications of both off-line and on-line advanced mass spectrometry techniques are used to address these above questions. The reactions we uncover that lead to the formation of isoprene SOA are then evaluated in certain cases for other SOA precursors; for example, the formation of SOA from the photooxidation (i.e., OH-initiated oxidation) of naphthalene, a polycyclic aromatic hydrocarbon (PAH)

emitted from anthropogenic sources, under both low- and high-NO_x conditions is examined in detail in Appendix F. Also, many of the mass spectrometry techniques applied in this thesis are used in the chemical characterization of a new atmospheric tracer (i.e., 3-methyl-1,2,3-butanetricarboxylic acid) for terpene SOA formation in Appendix E.

In Chapter 2, the chemical composition of SOA from the photooxidation of isoprene over the full range of NO_x conditions is investigated through a series of controlled laboratory chamber experiments. Oligomerization was observed to be an important SOA formation pathway in all cases; however, the nature of the oligomers depends strongly on the NO_x level, with acidic products formed under high-NO_x conditions only. We present, to our knowledge, the first evidence of particle-phase esterification reactions in SOA, where the further oxidation of the isoprene oxidation product methacrolein under high-NO_x conditions produces polyesters involving 2-methylglyceric acid (2-MG) as a key monomeric unit. These oligomers comprise ~ 22–34% of the high-NO_x SOA mass. In Appendix A, a detailed discussion of the EI mass spectral behavior of the TMS derivatives of 2-MG, 2-MG dimer and trimers are presented in a complimentary GC/MS study. Under low-NO_x conditions, organic peroxides contribute significantly to the low-NO_x SOA mass (~ 61% when SOA forms by nucleation and ~ 25–30% in the presence of seed particles). The contribution of organic peroxides in the SOA decreases with time, indicating photochemical aging. Hemiacetal dimers are found to form from C₅ alkene triols and 2-methyltetrols under low-NO_x conditions; these compounds are also found in aerosol collected from the Amazonian rainforest, demonstrating the atmospheric relevance of these low-NO_x

chamber experiments. Chapter 2 serves as the foundation for building up our understanding of the detailed formation pathways of isoprene SOA in the subsequent chapters.

In Chapter 3, the chemical composition of SOA from the photooxidations of isoprene and α -pinene, in the presence or absence of sulfate seed aerosol, is investigated through a series of controlled chamber experiments in two separate laboratories. By using electrospray ionization – mass spectrometry, sulfate esters in SOA produced in laboratory photooxidation experiments are identified for the first time. Sulfate esters are found to account for a larger fraction of the SOA mass when the acidity of seed aerosol is increased, a result consistent with aerosol acidity increasing SOA formation. Many of the isoprene and α -pinene sulfate esters identified in these chamber experiments are also found in ambient aerosol collected at several locations in the southeastern United States (also see Appendix B for a study of the composition of atmospheric aerosol collected from this region) and in Europe (also see Appendix C for the characterization of organosulfates of isoprene and unsaturated fatty acids in ambient aerosol collected from K-pusztá, Hungary). It is likely that this pathway is important for other biogenic terpenes, and may be important in the formation of humic-like substances (HULIS) in ambient aerosol.

In Chapter 4, the effect of particle-phase acidity on SOA formation from isoprene is investigated in a laboratory chamber study, in which the acidity of the inorganic seed aerosol was controlled systematically. The observed enhancement in SOA mass concentration is closely correlated with increasing aerosol acidity ($R^2 = 0.979$). Direct chemical evidence for acid-catalyzed particle-phase reactions was obtained from the SOA

chemical analyses. Aerosol mass concentrations for the 2-methyltetrols, as well as the newly identified sulfate esters, both of which serve as tracers for isoprene SOA in ambient aerosols, increased significantly with enhanced aerosol acidity. Aerosol acidities, as measured in $\text{nmol H}^+ \text{m}^{-3}$, employed in the present study are in the same range as those observed in tropospheric aerosol collected from the eastern U.S.

Owing to the results obtained in Chapters 3 and 4, in Chapter 5 the mechanism and ubiquity of organosulfate formation in biogenic SOA is investigated by a comprehensive series of laboratory photooxidation (i.e., OH-initiated oxidation) and nighttime-oxidation (i.e., NO_3 -initiated oxidation under dark conditions) experiments using nine monoterpenes (α -pinene, β -pinene, *d*-limonene, *l*-limonene, α -terpinene, γ -terpinene, terpinolene, Δ^3 -carene, and β -phellandrene) and three monoterpenes (α -pinene, *d*-limonene, and *l*-limonene), respectively. Organosulfates were characterized using liquid chromatographic techniques coupled to electrospray ionization combined with both linear ion trap and high-resolution time-of-flight mass spectrometry. Organosulfates are formed only when monoterpenes are oxidized in the presence of acidified sulfate seed aerosol, a result consistent with prior work. Archived laboratory-generated isoprene SOA and ambient filter samples collected from the southeastern U.S. were reexamined for organosulfates. By comparing the tandem mass spectrometric and accurate mass measurements collected for both the laboratory-generated and ambient aerosol, previously uncharacterized ambient organic aerosol components are found to be organosulfates of isoprene, α -pinene, β -pinene, and limonene-like monoterpenes (e.g., myrcene), demonstrating the ubiquity of organosulfate formation in ambient SOA. Several of the organosulfates of isoprene and of the

monoterpenes characterized in this study are ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. Furthermore, the nighttime-oxidation experiments conducted under highly acidic conditions reveal a viable mechanism for the formation of previously identified nitrooxy organosulfates found in ambient nighttime aerosol samples. It should be noted that Appendix D describes the detailed chemical mechanism resulting in the formation of SOA from the NO_3 -initiated oxidation of isoprene under dark conditions. Overall, we estimate that the organosulfate contribution to the total organic mass fraction of ambient aerosol collected from K-pusztá, Hungary, a field site with a similar organosulfate composition as that found in the present study for the southeastern U.S., can be as high as 30%.

In Chapter 6, we apply our knowledge gained from Chapters 2–5 and identify the role of two key reactive intermediates, epoxydiols of isoprene (IEPOX = β -IEPOX + δ -IEPOX) and methacryloylperoxynitrate (MPAN), that are formed during isoprene oxidation under low- and high- NO_x conditions, respectively. Isoprene low- NO_x SOA is enhanced in the presence of acidified sulfate seed aerosol (mass yield 28.6%) over that in the presence of neutral aerosol (mass yield 1.3%). Increased uptake of IEPOX by acid-catalyzed particle-phase reactions is shown to explain this enhancement. Under high- NO_x conditions, isoprene SOA formation occurs through oxidation of its second-generation product, MPAN. The similarity of the composition of SOA formed from the photooxidation of MPAN to that formed from isoprene and methacrolein (MACR) demonstrates the role of MPAN in the formation of isoprene high- NO_x SOA. Reactions of IEPOX and MPAN in the presence of anthropogenic pollutants (i.e., acidic aerosol

produced from the oxidation of SO₂ and NO₂, respectively) could be a substantial source of “missing urban SOA” not included in current atmospheric models.

Finally, Chapter 7 summarizes the findings presented in the previous five chapters and highlights the unresolved issues needed for future research. In addition, from the work demonstrated in Chapters 2–5, it is concluded that the combination of both gas- and particle-phase chemical measurements are essential in order to fully characterize the chemical mechanisms leading to the formation of SOA from potential precursors. Previous work has relied heavily on deriving chemical formation mechanisms only from particle-phase chemical measurements. This thesis clearly highlights the importance of applying advanced mass spectrometry techniques to the chemical characterization of both gas and aerosol phases.

1.3 References

- Böge O, Miao Y, Plewka A, Herrmann H (2006) Formation of secondary organic particle phase compounds from isoprene gas-phase oxidation products: An aerosol chamber and field study. *Atmos Environ* 40:2501–2509.
- Carlton AG, Wiedinmyer C, Kroll JH (2009) A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmos Chem Phys* 9:4987–5005.
- Claeys M, et al. (2004) Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303:1173–1176.
- de Gouw JA, et al. (2005) Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. *J Geophys Res* 110:D16305.
- Docherty KS, Wu W, Lim YB, Ziemann PJ (2005) Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O₃. *Environ Sci Technol* 39:4049–4059.
- Edney EO, et al. (2005) Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States. *Atmos Environ* 39:5281–5289.

- Gao S, et al. (2004a) Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α -pinene. *J Phys Chem A* 108:10147–10164.
- Gao S, et al. (2004b) Particle phase acidity and oligomer formation in secondary organic aerosol. *Environ Sci Technol* 38:6582–6589.
- Hallquist M, et al. (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos Chem Phys* 9:5155–5236.
- Heald CL, et al. (2005) A large organic aerosol source in the free troposphere missing from current models. *Geophys Res Lett* 32:L18809.
- Henze DK, Seinfeld JH (2006) Global secondary organic aerosol from isoprene oxidation. *Geophys Res Lett* 33:L09812.
- Iinuma Y, Böge O, Gnauk T, Hermann H (2004) Aerosol-chamber study of the α -pinene/O₃ reaction: influence of particle acidity on aerosol yields and products. *Atmos Environ* 38:761–773.
- Kalberer M, et al. (2004) Identification of polymers as major components of atmospheric organic aerosols. *Science* 303:1659–1662.
- Kanakidou M, et al. (2005) Organic aerosol and global climate modeling: a review. *Atmos Chem Phys* 5:1053–1123.
- Kroll JH, Ng NL, Murphy SM, Flagan RC, Seinfeld JH (2005) Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions. *Geophys Res Lett* 32:L18808.
- Kroll JH, Ng NL, Murphy SM, Flagan RC, Seinfeld JH (2006) Secondary organic aerosol formation from isoprene photooxidation. *Environ Sci Technol* 40:1869–1877.
- Kroll JH, Seinfeld JH (2008) Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos Environ* 42:3593–3624.
- Limbeck A, Kulmala M, Puxbaum H (2003) Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. *Geophys Res Lett* 30:1996–1999.
- Pandis SN, Paulson SE, Seinfeld JH, Flagan RC (1991) Aerosol formation in the photooxidation of isoprene and beta-pinene. *Atmos Environ Part A – General Topics* 25:997–1008.

- Presto AA, Hartz KEH, Donahue NM (2005) Secondary organic aerosol production from terpene ozonolysis 2. Effect of NO_x concentration. *Environ Sci Technol* 39:7046–7054.
- Tobias HJ, Ziemann PJ (2000) Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environ Sci Technol* 34:2105–2115.
- Tolocka MP, et al. (2004) Formation of oligomers in secondary organic aerosol. *Environ Sci Technol* 38:1428–1434.
- Volkamer R, et al. (2006) Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. *Geophys Res Lett* 33:L17811.
- Wang W, et al. (2005) Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass spectrometry. *Rapid Commun Mass Spectrom* 19:1343–1351.