Chapter 7

Conclusions

7.1 Conclusions

In most of this thesis, the chemical composition of SOA from the photooxidation of isoprene under both high- and low-NO_x conditions has been thoroughly investigated through a series of controlled laboratory chamber experiments. It is found that the chemical nature of the resultant SOA is significantly different in the two NO_x regimes, which indicates that different chemical formation mechanisms are operating due to the kinds of gas-phase oxidation products favored to form under each NO_x condition.

Under high-NO_x conditions, the SOA constituents are acidic and isoprene SOA formation occurs through oxidation of its second-generation product, methacryloylperoxynitrate (MPAN). The similarity of the composition of SOA formed from the photooxidation of MPAN to that formed from isoprene and methacrolein demonstrates the role of MPAN in the formation of isoprene high-NO_x SOA. More specifically, we confirm that MPAN is the key intermediate in the isoprene and methacrolein systems in the formation of 2-methylglyceric acid, a known high-NO_x tracer compound for the formation of isoprene SOA in the atmosphere, and its corresponding low-volatility oligoesters in the aerosol phase. One key unresolved question is the exact path by which 2-methylglyceric acid and its corresponding oligoesters are formed from the further oxidation of MPAN, which at present is still not fully understood. One possibility is that 2-methlyglyceric acid and its corresponding oligoesters are formed through the further heterogeneous reaction of the C_4-hydroxynitate-PAN product formed from the further oxidation of MPAN; however, we do not have conclusive chemical evidence at this time to support the hypothesis that the C_4-hydroxynitrate-PAN is the main precursor to the isoprene high-NO_x SOA. Thus, it is possible that some other unknown C_4-preserving chemical reaction is occurring when MPAN is oxidized by the OH radical. Further gas- and particle-phase studies on isoprene oxidation under high-NO_x conditions are needed in order to elucidate the details of the oligoester formation.

SOA components formed under low-NO_x conditions, by contrast, are primarily non-acidic, the only exception being with that of the organosulfates, with primary species identified being polyols and organic peroxides. 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 epoxydiols of isoprene (IEPOX = β-IEPOX + δ-IEPOX), which is the key reactive intermediate identified to lead to low-NO_x SOA formation from isoprene under atmospherically relevant organic aerosol loadings (i.e., 5–10 $\mu g\ m^{-3}$), by acid-catalyzed particle-phase reactions is shown to explain this enhancement. Here we have established that the reactive uptake of IEPOX occurs by the acid-catalyzed ring opening of this epoxydiol, followed by the subsequent addition of the following nucleophiles: (1) H_2O; (2) inorganic sulfate; (3) a 2-methyltetrol already formed in the aerosol; and (4) a hydroxy sulfate ester already present in the aerosol; the addition of these four nucleophiles yields either 2-methyltetrols, organosulfate derivatives of the 2-methyltetrols, dimers, or organosulfate derivatives of the dimers, respectively. Importantly, the reactive uptake of IEPOX onto acidified sulfate seed aerosol is clearly demonstrated by the combination of both gas- and particle-phase chemical measurements using mass spectrometry techniques. Organic peroxides (likely dominated by hydroperoxides) contribute significantly to the low-NO_x SOA mass (~ 61% for nucleation experiments and ~ 25% and 30% for dry seeded and acid seeded experiments, respectively) when organic aerosol loadings were much higher (i.e., > 50 μg

m^{-3}), which may not be atmospherically relevant. However, differences in the organic peroxide contribution and the rate of loss in SOA mass for nucleation (seed-free) and seeded experiments are not well understood and require further investigation. The chemical composition changes with time in the low-NO_x case, showing evidence of chemical aging.

The importance of IEPOX and MPAN in forming isoprene SOA under low- and high-NO_x conditions, respectively, provides significant insights into heretofore-unidentified aerosol precursors. In the presence of anthropogenic pollutants, such as NO_2 and acidic aerosol produced from the oxidation of SO_2, SOA mass yields from isoprene under high- and low- NO_x conditions, respectively, increase substantially. As isoprene is estimated to be the largest single contributor to global SOA, these results may help to resolve two existing dilemmas in atmospheric chemistry: (1) radiocarbon (^{14}C) data consistently indicate that well over half of the ambient SOA is of modern (biogenic) origin (Hallquist et al., 2009, and references therein; Schichtel et al., 2008), whereas correlations between water-soluble organic carbon and anthropogenic tracers, such as CO, suggest that much of the SOA is actually of anthropogenic origin (de Gouw et al., 2005; Weber et al., 2007); and (2) comparisons between measured and predicted SOA based on known precursors suggest that there is a substantial amount of "missing urban SOA" not included in current models (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). Revising the chemistry of isoprene in regional and global SOA models could lead to a decrease in this discrepancy; however, the measurement and parameterization of aerosol acidity requires additional work.

Although we mainly investigated the effect of NO_x level on the chemical mechanisms leading to isoprene SOA formation, we also explored the effect of increasing aerosol acidity on the composition of isoprene SOA. In addition to isoprene, we also investigated the effect of increasing aerosol acidity on monoterpene SOA formation. Organosulfates (or sulfate esters) of isoprene and monoterpenes 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. The presence of organosulfates and nitrooxy organosulfates of both monoterpenes and isoprene in ambient samples is confirmed. With the exception of the organosulfates of glyoxal and methylglyoxal, our results indicate that all of the organosulfates characterized in this study should be considered as unique tracers for the occurrence of biogenic SOA formation under acidic conditions. Owing to the fact that glyoxal and methylglyoxal are also oxidation products from anthropogenic VOCs (such as aromatics – e.g. toluene), oxidation experiments of these VOCs under acidic conditions are needed in order to confirm whether they serve as additional sources of organosulfates of glyoxal and methylglyoxal in ambient fine aerosol.

Laboratory studies of isoprene and monoterpene oxidation have tended to employ levels of seed aerosol acidity that exceed those expected in ambient aerosol. These studies have established seed aerosol acidity either by adding sulfuric acid to ammonium sulfate solutions or by oxidizing gas-phase SO_2, resulting in sulfate aerosol mass. These approaches leave it unclear as to whether organosulfate formation is dependent upon either the sulfate aerosol mass concentration or acidity. In this regard, this thesis found that organosulfates and nitrooxy organosulfates of isoprene form in the presence of nonacidified sulfate seed aerosol; however, it was found that as the sulfuric acid concentration increased in the atomization solution, so did the number of organosulfate and nitrooxy organosulfate products. Further work is required to elucidate the extent to which sulfate aerosol mass concentration, level of acidity, and ionic strength affect the organosulfate formation potential from isoprene and monoterpenes in ambient aerosol.

One of the reasons there is so much excitement and interest in studying the formation of organosulfates is the result of this thesis showing that they may contribute significantly to the organic mass fraction in ambient aerosol (i.e., upwards of 30% in certain locations) (Chapter 5). Since numerical models currently underestimate the amount of SOA mass observed in ambient aerosol, organosulfate and nitrooxy organosulfate formation potentially offers one significant missing source of SOA not currently accounted for in models. In order to incorporate organosulfate and nitrooxy organosulfate formation chemistry into models, improvements in our fundamental understanding of the detailed reaction mechanisms are needed. Currently, there is much debate in the literature as to which intermediate gas-phase products (e.g., alcohols, epoxides, hydroxynitrates, or aldehydes) primarily lead to the formation of these compounds in both chamber-generated and ambient organic aerosol. It is possible that only one or all of these reaction intermediates lead to organosulfates; however, this is likely dependent on the reaction conditions employed or present in the atmosphere (e.g., oxidant type, dark vs. light conditions, and seed aerosol conditions). Much of the previous work (including Chapters 3 and 5 of this thesis) has proposed that these compounds form from either the particle-phase esterification of a semivolatile oxidation product containing one or two hydroxyl groups with sulfuric acid, or by a semivolatile oxidation product containing an aldehyde (or keto group) that forms a gem-diol upon partitioning to the aerosol phase followed by the esterification with sulfuric acid. Alternatively, recent work demonstrated that the direct reaction between alcohols and sulfuric acid to form sulfate esters in tropospheric particles is kinetically infeasible, and further proposed and showed that rapid hydrolysis of epoxides under mildly acidic conditions is a more likely favorable formation mechanism for these compounds in the troposphere (Minerath et al., 2008, 2009ab). As shown in Chapter 6, epoxydiols of isoprene (IEPOX) were in fact shown to play a major role in the formation of previously observed organosulfates of isoprene (Chapters 3 and 5), which now suggests that the acid-catalyzed ring-opening reactions of epoxides are likely the more favorable formation pathway (over that of alcohol sulfate esterification) of organosulfates in ambient aerosol. In addition to the latter, recent work has also demonstrated that inorganic sulfate can trigger heterogeneous reactions of VOCs when sulfate radicals are formed in the aqueous phase of pre-existing particles as a result from UV light exposure (Noziére et al., 2010); these sulfate radicals produced organosulfates of the organic compounds investigated with a lifetime of 9 h, and as a result, provides another heterogeneous pathway for the formation of organosulfates that might be more atmospherically relevant than previously proposed mechanisms (such as the alcohol sulfate esterification mechanism proposed in Chapters 3 and 5).

Finally, owing to the tradeoffs that exist with the current set of available analytical techniques, no single perfect instrument/technique with all the ideal analytical characteristics currently exists (i.e., high-time resolution and 100% mass closure of the organic mass fraction at the molecular level) (Hallquist et al., 2009). As a result, new analytical methods need to be developed, incorporated, and applied with existing techniques (on-line and off-line) in order to more fully characterize SOA at the molecular level, and thus, providing a more full chemical understanding of SOA formation pathways. This approach was central to the work of this thesis and should be continued in future studies. More specifically, it is essential in future work that the combination of gas- and particle-phase mass spectrometric measurements be made (as demonstrated in Chapter 6 of this thesis) in order to more fully elucidate chemical formation mechanisms of SOA.

7.2. References

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