Chapter 4

Conclusions and Future Work

4.1 Conclusions

This thesis discusses insights into anthropogenic SOA formation by extensive analysis of SOA chemical composition using complementary mass spectrometry methods. Environmental chamber experiments enable the detailed study of SOA formation from a single parent compound. In this work, the formation of SOA from C_{12} alkanes, toluene, and *o*-, *m*-, and *p*-cresol was studied by applying a combination of mass spectrometric methods to analyze the SOA chemical composition.

Gasoline and diesel fuel contain significant amounts of cyclic, branched, and linear alkanes.[1] Moreover, the combustion and photooxidation products of alkanes are major contributors to urban and transportation-related SOA.[2-4] The effects of parent alkane structure, NO_x conditions, relative humidity, and aerosol acidity on SOA formation and composition were studied in Chapter 2. The composition of alkane SOA produced in these studies was characterized strongly by particle-phase chemistry, including oligomerization reactions. The monomeric species participating in these reactions are chiefly hydroxycarbonyl compounds in linear and cyclized forms (e.g., furans, dihydrofurans). Imines are another monomeric species forming potentially from reactions of carbonyl compounds with ammonia present in the seed aerosol. The oligomers that are formed from these monomers include peroxyhemiacetals, hemiacetals, esters, and aldol condensation products. Peroxyhemiacetals are the major contributor to alkane SOA mass under the low-NO conditions studied here; under high-NO conditions, ether formation is significant to SOA formation, as is the generation of alkyl nitrates. The NO_x effect on alkane SOA composition, specifically oligomer structure and functionality, is shown to be important in Chapter 2. Alkane structure affected the degree of functionalization and fragmentation of the parent compound as it progressed through multigenerational photooxidation; the final outcome of this was a variation in organic aerosol volume produced. Nitrogen incorporation from the ammonium sulfate seed aerosol into the organic fraction by imine formation occurred for all alkane structures studied in Chapter 2. Overall, the composition of alkane SOA is found to be attributable to a large number of oxidation products, each of which is present at a relatively low concentration.

Aromatic compounds are a major component of anthropogenic and biogenic emissions; they appear in fuels as well as in biomass burning emissions, among other sources.[1] Toluene is an important industrial VOC and SOA precursor. Its gas-phase photooxidation and the photooxidation of its early-generation product, cresol, have been studied extensively, as discussed in Chapter 3. Open questions center on the extent to which low- and extremely-low volatility organic compounds (LVOC and ELVOC) comprise toluene SOA, and the proportions of the LVOC and ELVOC which arise from oligomerization and multigenerational photooxidation. Given that glyoxal and other volatile dicarbonyls are major fragmentation products in aromatic systems, the role of relative humidity and seed hygroscopicity is important to determining the chemical composition of toluene- and cresol-derived SOA. The experiments described in Chapter 3 were conducted under dry conditions to promote SOA formation from other channels. Highly oxygenated compounds were found to be the major contributors to toluene SOA under dry low- and high-NO conditions. The NO_x effect was primarily seen in the production of nitro and nitrate compounds that partitioned to the particle phase. Heterogeneous chemistry is implied by the chemical formulae of oligomeric species produced by toluene and all cresol isomers; the range of C number in these molecules is continuous, suggesting small, volatile aldehydes are reacting with highly-oxygenated C_7 compounds already present in the particle phase. This is different to oligomer formation in the alkane systems, where dimerization occurred between C_{12} oxidized species. For toluene- and cresol-derived SOA, the LVOC and ELVOC components arise from both multigenerational oxidation and oligomer formation. Through comparison of SOA chemical compositions, a relative mass fraction of 0.84 of toluene SOA is estimated to be attributable to the cresol pathway, specifically $C_7H_8O_4$ (0.7) and $C_7H_6O_4$ (0.1) species, with the remainder composed of $C_xH_yO_2$, $C_xH_yNO_2$, $C_xH_yNO_3$, and C_xH_yO.

4.2 Future Work: Exploring Heterogeneous Reactions Leading to Oligomerization in Secondary Organic Aerosol

SOA formation is commonly predicted by equilibrium partitioning models, but there is evidence in certain chemical systems that reactive uptake can be important to SOA formation. Reactive uptake as a phenomenon involves the collision of a gas-phase molecule with a surface, resulting in the incorporation of that molecule into the surface because of a chemical reaction. Some examples of reactive uptake include isoprene epoxydiols, glycolaldehyde, and glyoxal and simple carbonyl compounds.[5-8]

There is evidence for oligomerization, in some cases, occurring in the manner of reactive uptake as opposed to equilibrium partitioning and condensed-phase reactions.[5, 9] If monomer abundance in the particle phase, leading to oligomerization through equilibrium reactions, was driven by equilibrium partitioning, there would be a correlation between monomer abundance and vapor pressure. In the case of SOA formed from α-pinene ozonolysis, Hall and Johnston used a Fourier transform ion cyclotron resonance mass spectrometer with an electrospray ionization (ESI) interface to identify over 1000 distinct oligomer elemental formulae, and find independence between monomer abundance and vapor pressure.[10] The classes of oligomers included in that study included aldol condensation products, hemiacetals, ethers, esters, and carboxylic acid anhydrides; this system covers all major oligomer types one would find, with, perhaps, the exception of the peroxyhemiacetal, which is known to be important under low-NO conditions in some cases.[10-11]

Table 4.1. Compounds measured in SOA formed from isoprene nitroxy epoxydiol uptake onto $(NH_4)_2SO_4$ seed aerosol by filtration and extraction in methanol for analysis by reverse-phase ultra-high performance liquid chromatography/(-)ESI-MS. Compounds are indexed by retention time (t_R).

t_R (min)	Measured *m/z* (Da)	Calculated *m/z* (Da)	Error (mDa)	Formula $[M\text{-}H]^-$
2.61	346.007	346.008	1.0	$C_8H_{12}NO_{12}S^-$
2.61	283.0111	283.0124	1.3	$C_8H_{11}O_9S^-$
2.68	241.9962	241.9971	0.9	$C_5H_8NO_8S^-$
2.88	304.9921	304.9927	0.6	$C_5H_9N_2O_{11}S^-$
2.95	304.9921	304.9927	0.6	$C_5H_9N_2O_{11}S^-$
3.02	304.9916	304.9927	1.1	$C_5H_9N_2O_{11}S^-$
3.1	304.9916	304.9927	1.1	$C_5H_9N_2O_{11}S^-$
3.15	304.9924	304.9927	0.3	$C_5H_9N_2O_{11}S^-$
3.4	302.9757	302.9771	1.4	$C_5H_7N_2O_{11}S^-$
3.52	365.9716	365.9727	1.1	$C_5H_8N_3O_{14}S^-$
3.61	318.9702	318.972	1.8	$C_5H_7N_2O_{12}S^-$
3.61	493.024	493.0248	0.8	$C_{12}H_{17}N_2O_{17}S^-$
3.69	390.9918	390.9931	1.3	$C_8H_{11}N_2O_{14}S^-$
3.89	327.9962	327.9975	1.3	$C_8H_{10}NO_{11}S^-$
3.89	390.9919	390.9931	1.2	$C_8H_{11}N_2O_{14}S^-$
3.89	448.9969	448.9985	1.6	$C_{10}H_{13}N_2O_{16}S^-$
3.97	349.9767	349.9778	1.1	$C_5H_8N_3O_{13}S^-$
4.06	349.9763	349.9778	1.5	$C_5H_8N_3O_{13}S^-$
4.06	138.9684	138.9701	1.7	$C_2H_3O_5S^-$
4.14	349.9771	349.9778	0.7	$C_5H_8N_3O_{13}S^-$
4.14	138.9686	138.9701	1.5	$C_2H_3O_5S^-$
4.34	372.9789	372.9825	3.6	$C_8H_9N_2O_{13}S^-$

Evidence from recent experiments to study SOA formation from isoprene nitroxy-epoxydiols as well as that presented in Chapter 3 shows that the reaction of small, gas-phase carbonyl compounds and alcohols with particle-phase species to form oligomers is possible (Table 4.1). This is expected, based on what is known about the reactivity of these compound types, but it would be compelling to explore the limits of the SOA mass contribution of this kind of reactive uptake, as well as its sensitivities to relative humidity, seed hygroscopicity, seed composition, and parent compound type.

A fundamental chamber experiment would be to atomize a solution of a functionalized alkane sulfonate and introduce into the gas phase a compound proposed to react with that functional group. This experiment would simply target reactive uptake without accounting for any photochemistry or diverse range of products. An example of this type of experiment would be to use sodium dodecanal sulfonate as the seed aerosol and to introduce a hydroperoxide, such as cumene hydroperoxide or tert-butyl hydroperoxide, into the chamber by blowing clean air through a tube containing the peroxide. Peroxyhemiacetal formation should occur in the particle phase between the aldehyde functionality on the surfactant seed and the gas-phase peroxide. The vapor pressures of cumene and tert-butyl hydroperoxides (5.5×10^{-6} and 7.4×10^{-3} atm, respectively) are such that they should not condense onto the particles significantly. Control experiments measuring the partitioning of cumene and tert-butyl hydroperoxide to the chamber walls and to an inert seed such as NaCl would also need to be conducted.

A common question in SOA compositional analysis is on the origin of high-volatility compounds detected in offline analysis of SOA. Some have explained the modest concentrations of high-volatility species through equilibrium partitioning: when these are present in high concentration in the gas phase, they are driven into the particle phase, and as oxidation proceeds in the gas phase and these species are consumed, they partition back into the gas phase and are reacted away. A small amount remains in the particle, perhaps due to the presumed glassy nature of SOA.[12] Another scenario is that these high-volatility species are present in the particle-phase as oligomers, but revert back to their monomeric state during sample preparation for analysis. Given the invasiveness of solvent extraction, it is not implausible that oligomers were reverted back to monomeric species, but there is no means at present to verify this scenario in the suspended aerosol. A potential means of tagging the surface-available reactive organic compounds is to conduct a photooxidation experiment on a well-known system (e.g. dodecane or toluene), stop the photooxidation by turning off the black lights initiating OH generation, and introduce a unique marker compound that is not known to occur naturally in the system at a ppb-level mixing ratio. A volatile, halogen-labeled aldehyde (e.g. trifluoromethyl butyraldehyde) would be a potential tag for hemiacetal and peroxyhemiacetal formation, as well as aldol condensation. The tag molecule concentration would be monitored by either GC or gas-phase chemical ionization mass spectrometry, and any change in particle composition and volume would be measured by online aerosol mass spectrometry and differential mobility analyzer. SOA samples would also be collected by filtration and analyzed using noninvasive, soft ionization methods like direct electrospray ionization (DESI) or DART coupled to a high-resolution mass spectrometer, as well as by complementary techniques that provide structural information (e.g. GC/MS or LC/MS).

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