

## **Chapter 9**

### **Conclusions**

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Laboratory chamber studies provide the basis for evaluating SOA formation mechanism and chamber data are the foundation for predicting SOA formation. This thesis presents chamber study results on aerosol formation from a wide range of parent organic compounds under a variety of experimental conditions.

Over the last two decades, yield curves have been widely used to represent the aerosol-forming potential of different hydrocarbon precursors, providing the important yield parameters for use in atmospheric models. In chapter 2 it is shown that this two-product model can be extended to infer the general mechanisms of SOA formation, by plotting aerosol mass formed versus the amount of hydrocarbon reacted and we refer to this as the “growth curve”. In studying aerosol formation from ozonolysis and photooxidation of a series of biogenics hydrocarbons, it is found that for compounds with only one double bond, the first oxidation step is rate-limiting and aerosols are formed mainly from low volatility first-generation oxidation products; whereas for compounds with more than one double bond, the second oxidation step may also be rate-limiting and second-generation products contribute substantially to SOA growth. This behavior is characterized by a vertical section in the growth curve, in which continued aerosol growth is observed even after all the parent hydrocarbon is consumed. The growth curve approach has been shown to be useful in interpreting SOA growth mechanism in different systems (chapters 7 and 8).

The effect of seed particle acidity on SOA yield and composition is demonstrated in chapter 3. The ubiquitous presence of oligomers in SOA suggests that in addition to gas-phase reactions and gas-particle partitioning, particle-phase reactions are important

processes in the formation of secondary organic aerosol. As seed particle acidity increases, oligomers are formed more abundantly and the aerosol yield increases; for  $\alpha$ -pinene mixing ratios ranging from ~10-140 ppb, aerosol yield increases by 10-40% in the presence of acidic seed particles.

Chapters 4 and 5 demonstrate the aerosol-formation potential of glyoxal and isoprene, compounds previously not thought to be aerosol precursors because of volatility considerations. Glyoxal is observed to partition into the aerosol phase much more efficiently than its Henry's Law constant would predict, possibly due to the presence of particle-phase reactions. The reactive uptake of glyoxal indicates that small molecules with vapor pressures far too high to qualify as semivolatile can produce SOA via reactive absorption. Given the large emissions of isoprene, the discovery of the aerosol-forming potential from isoprene photooxidation has significant impacts on predicting SOA formation from biogenic hydrocarbons. SOA yield is found to increase substantially as the  $\text{NO}_x$  level decreases (chapter 6). The proposed mechanism for this effect is the competitive chemistry of peroxy radicals between  $\text{NO}$  and  $\text{HO}_2$ , with the  $\text{HO}_2$  reaction route producing products of lower volatility and hence a higher SOA yield

Given the importance of  $\text{NO}_x$  dependence on SOA formation, this effect is examined in detail for other biogenic hydrocarbons in chapter 7. The  $\text{NO}_x$  dependence of  $\alpha$ -pinene photooxidation follows the same trend as that of isoprene, in which SOA yield decreases as  $\text{NO}_x$  levels increases. The  $\text{NO}_x$  dependence of SOA yield for the sesquiterpenes, longifolene and aromadendrene, however, differs from that determined for isoprene and  $\alpha$ -pinene; the aerosol yield under high- $\text{NO}_x$  conditions substantially exceeds that under low- $\text{NO}_x$  conditions. The reversal of the  $\text{NO}_x$  dependence of SOA

formation for the sesquiterpenes is consistent with formation of relatively nonvolatile organic nitrates, and/or the isomerization of large alkoxy radicals that leads to less volatile products. Analysis of the aerosol chemical composition confirms the presence of organic nitrates under high-NO<sub>x</sub> conditions. Consequently the formation of SOA from certain biogenic hydrocarbons such as sesquiterpenes may be more efficient in polluted air.

The SOA formation from aromatic hydrocarbons is presented in chapter 8. The photooxidation of *m*-xylene, toluene, and benzene follows the same NO<sub>x</sub> dependence as smaller biogenic hydrocarbons, such as isoprene and  $\alpha$ -pinene, in which aerosols yields under low-NO<sub>x</sub> conditions substantially exceed those under high-NO<sub>x</sub> conditions, suggesting the importance of peroxy radical chemistry in SOA formation. The SOA yield parameters obtained under high- and low-NO<sub>x</sub> conditions allow one to parameterize the NO<sub>x</sub> dependence for atmospheric models. In contrast to the  $\alpha$ -pinene ozonolysis system (chapter 3), experiments carried out in the presence of acidic seed aerosol reveal no change of SOA yields from the aromatics as compared with those using neutral seed aerosol.

With the above findings concerning the ubiquitous existence of particle-phase reactions, the SOA-forming potential of volatile compounds, as well as the profound dependence of NO<sub>x</sub> on SOA formation, it is necessary to revise the modeling basis to incorporate these new understandings on SOA formation. In light of the aerosol formation from isoprene photooxidation, it is important to evaluate the SOA-forming potential of unstudied classes of VOCs, including ones previously thought not to be able to produce SOA because of volatility considerations. Classes of VOCs already known to

form SOA should also be restudied to establish fully the  $\text{NO}_x$  dependence of SOA formation and to determine the role of particle-phase reactions, including the effect of particle-phase acidity.