Chapter 14

Summary

The emphasis of this thesis has been to summarize the results from field and laboratory measurement studies using the Aerosol Mass Spectrometer (AMS), in an effort to understand the atmospheric processes that lead to aerosol formation and growth. Size-resolved, chemical composition measurements of non-refractory components of submicron aerosols by the AMS, with high time resolution, make it a powerful instrument in probing ambient aerosol properties, especially airborne measurements since highly variable plumes are usually encountered during flights. On the other hand, laboratory chamber experiments provide the opportunity to study a specific system in a more controlled environment.

AMS observations during laboratory photooxidation experiments of diiodomethane (CH_2I_2) provided evidence that nucleated particles contain iodine oxides and oxyacids. In these experiments, nucleation was observed at CH_2I_2 concentration levels down to 15 ppt, which is comparable to total ambient gas-phase iodine species measured in coastal areas, indicating that biogenically emitted iodine-containing species may contribute to a great extent to particle formation and growth in coastal areas.

During the ACE-Asia field study, the AMS measured distinct layers of sub-micron aerosols, mainly composed of sulfate, ammonium, and organics, from the boundary layer up to ~3700 m. Back trajectory analysis indicated that these pollution plumes originated from urban and industrial areas of China and Korea. The mass distribution measurements of sulfate and ammonium showed little variation from day to day and layer to layer, with mass distributions centering at ~400-500 nm.

Sulfate and organic measurements of the AMS during CRYSTAL-FACE field campaign were used in a cloud-aerosol closure study. In this study, measured droplet concentration in adiabatic cloud regions was within 15% of the predictions, based on a cloud activation parcel model, which predicts cloud drop concentration using observed aerosol concentration, size distribution, cloud updraft velocity, and thermodynamic state.

The laboratory chamber experiments of oxidation of cycloalkenes and terpenes provided the opportunity to study the different aspects of SOA formation under controlled conditions. The influence of hydroxy radical scavenger on SOA yield-- through HO_2 radical production and consequent reactions to form acids that can partition into the aerosol phase-- was studied in dark ozonolysis experiments of cyclohexene. Effect of the parent hydrocarbon structure, such as position of the double bond or a methyl substituent, on SOA yield were also studied in the experiments of dark ozonolysis of series of cycloalkenes. It was determined that the SOA yield increased with increasing carbon number, as well as with the presence of a methyl group located on a double-bonded carbon. However, the yield decreased in the presence of an exocyclic double bond compared to the equivalent methylated cycloalkene.

Detailed chemical composition of SOA formed in ozonolysis experiments of cycloalkenes and α-pinene, determined by LC-MS and ion trap MS, indicated that diacids, carbonyl-containing acids, diacid alkyl esters, and hydroxy diacids are the most dominant types of low-molecular-weight components of the SOA. Evidence of increased SOA yield and increased contribution of higher-molecular-weight oligomers was observed in experiments in the presence of acidic seed particles. Estimates of effective density of the SOA were determined by comparison of mass and volume distributions from the AMS and DMA. Ozonolysis experiments of cycloalkenes in the absence of seed particles resulted in SOA that were denser and had a higher contribution of oxygenated organics to the total mass compared to seeded experiments. Ion series analysis of AMS organic mass spectra showed dominance of negative “delta” values, indicative of terpene derivative structures or cyclic or unsaturated oxygenated compounds, in the SOA formed during ozonolysis of biogenics, as opposed to positive “delta” values as observed in oxidation of cycloalkenes and *m*-xylene. Greater contribution of higher molecular weight fragments to the SOA and corresponding changes in “delta” patterns were observed in the presence of acidic seed, indicating the evidence for acid-catalyzed heterogeneous chemistry in the ozonolysis of α-pinene. The mixtures of SOA compounds produced from similar precursors studied resulted in broadly similar AMS mass spectra. Thus, fragmentation patterns observed for biogenic vs. anthropogenic SOA can be potentially useful in determining the sources of ambient SOA.

Because of the high-temperature vaporization (650 °C) in the AMS, greater fragmentation of organic molecules is observed when compared to the mass spectra obtained by other instruments that apply electron impact ionization. Thus, it would be an interesting exercise for future laboratory chamber experiments to ramp the vaporizer temperature up/down during the experiment in order to obtain more compound-specific information from the mass spectrum as it is evolving. This will also provide the opportunity to relate the appearance of different fragments in the mass spectra to their vapor pressure based on the temperature of the vaporizer.