Chapter 5

Conclusions and future directions

The study of organic aerosols will likely remain an active, complex, and evolving field. While this work, encompassing just a small selection of the field's analytical tools and current problems, has provided potentially important insights, it has also created many new questions deserving of further study.

In Chapter 2 we show the importance of ROOR dimers to SOA formation in laboratory studies. These compounds have generally been considered insignificant in the past, but their discovery motivates new avenues of research, in particular because SOA comprises a minor portion of VOC oxidation products, so even minor reaction pathways may be important. As ROOR dimers are novel compounds, the kinetics and mechanism of their formation are unknown even under controlled laboratory conditions, which makes predictions about their atmospheric relevance purely speculative. More studies focusing on ROOR are necessary to characterize their importance in atmospheric chemistry. Ultimately, it would be ideal to develop robust correlations between ROOR yields and measureable parameters (e.g., temperature, pressure, peroxy radical structure) for use in atmospheric models.

Even if ROOR formation were fully characterized, its full impact in the atmosphere will not be understood without knowledge of its subsequent reaction pathways. Although ROOR dimers are important SOA precursors in the laboratory, they do not lead exclusively to SOA. For many organic compounds, oxidation can either add mass and polarity, increasing the likelihood of SOA formation, or break carbon-carbon bonds, increasing volatility and decreasing the likelihood of SOA formation. Not reported in Chapter 2 is the formation of C_7 compounds in experiments where second generation chemistry is possible, i.e., where the concentration of NO_3 radical exceeds that isoprene. These likely come from the breaking of carbon-carbon bonds of first generation C_{10} ROOR compounds. Performing analyses of multiple oxidation steps is non-trivial because the variety of first generation products, each with their own unique second generation chemistry, leads to extremely complicated chemical evolution in the chamber. Thus, obtaining complete VOC oxidation mechanisms will require systematically stepping through single oxidation steps, which is time consuming and difficult, especially because many intermediates in the overall oxidation mechanism are not easily synthesizable or quantifiable.

Studies on ROOR formation will center on RO_2-RO_2 reactions, but as shown in Chapter 3, the current suite of experimental data provide inadequate proxies for explaining the product yield of RO_2-RO_2 (and RO_2-HO_2) reactions in the isoprene-NO_3 system, even for non-ROOR products. Flow tubes have been effective for characterizing reactions of small peroxy radicals, but the study of more complex radicals is limited by the challenges of their synthesis. It is also unclear at the moment if the conditions and analytical techniques typically employed in flow tube studies are appropriate for forming or detecting ROOR.

These fundamental studies are only a first step, because the atmosphere is a complex mixture where diverse hydrocarbons react with multiple oxidants (OH, NO_3, O_3, halogen atoms). If conditions favor RO_2-RO_2 reactions, they are likely to be cross-reactions (i.e., reactions between different peroxy radicals) rather than self-reactions (i.e., reactions between identical peroxy radicals). Peroxy radical cross-reactions are even less well understood than self-reactions.

While our work on isoprene-NO_3 is too recent for its impact to be assessed, studies addressing the issues posed in our analysis of aerosol sinks (Chapter 4) suggest that while volatilization of ambient organic aerosol does occur, it does not occur at a rate that is significant for organic aerosol budgets, or, likely, OVOC budgets. Murphy et al. (2007) report that tropospheric aerosols that reach the stratosphere, with an estimated age of ~ 4-6 months, show loss of organic matter with respect to sulfate, consistent with volatilization by heterogeneous oxidation ($\gamma > 0.1$, considering only oxidation by OH radical). The age of the particles, however, is significantly longer than the lifetime against oxidation proposed in Chapter 4 (~ 10 days), which can be explained by our key assumptions ($\gamma = 1$ and the volatilization of 6 carbons per OH collision) being overly favorable to volatilization, and the larger particles detected by the authors (> 300 nm) having lower surface area to volume ratios than fine particles and thus being more resistant to volatilization. The particle lifetimes in the study are also significantly longer than that of most tropospheric aerosol, ~ 5-10 days against deposition (Kanakidou et al., 2005). Recent laboratory and field studies of aerosol oxidation over these timescales show minor loss of carbon, and negligible loss of total mass due to increasing oxygen content in the aerosol (Capes et al., 2008; DeCarlo et al., 2008; George et al., 2008; Dunlea et al., 2009). Although heterogeneous oxidation may not be relevant to OVOC production or aerosol abundance, its impacts on aerosol chemical composition still make it worthy of further study.

Besides its exploration of scientific theories, this work also exemplifies the importance of having a diverse array of analytical techniques for addressing the complex problems of organic aerosols. In addition to the importance of ROOR dimers, recent experiments at the Caltech environmental chamber have combined insights from CIMS and aerosol measurements to elucidate the role of peroxy acetyl nitrates and epoxydiols in SOA formation (Surratt et al., 2009; Chan et al., 2010), while field measurements with the CIMS have shown that biomass burning is at times the dominant source of organic aerosols in the Mexico City airshed (Crounse et al., 2009). Where definitive conclusions have not been achieved in this work (e.g., the parameters determining ROOR formation, how the fate of isoprene nitrooxyalkoxy radicals depends on their formation mechanism, or what the accommodation coefficient of oxidants on an organic aerosol is), it is generally due to the limitations of our analytical tools, and more studies expanding the suite of techniques and perspectives analyzing the problem may lead to more concrete explanations.

Applying the CIMS in its current configuration to study a wider variety of systems will likely produce more useful data, but in the future the CIMS will not be limited to gas-phase measurements. With a custom aerosol inlet currently under development, we will be able to apply the CIMS to direct measurements of aerosol-phase composition, enhancing the instrument's capabilities and its contributions to understanding organic aerosol chemistry.

While this work has focused on applications of the CIMS to organic aerosol studies, the instrument's qualities make it useful to address a range of other outstanding problems in atmospheric chemistry. In particular, its high time resolution makes it ideal for airplane sampling, allowing for high spatial resolution for studying small scale processes, for example the interaction of trace gases with liquid and ice cloud particles during vertical transport. Convection and frontal lofting transport surface emissions (and their oxidation products) to the upper troposphere, where their fate and global impacts may be significantly different than in their source regions (e.g., Lacis et al., 1990). As air parcels rise, liquid and possibly ice clouds will form, providing additional media for gas scavenging or heterogeneous reactions. Of particular interest is what happens to dissolved gases when a liquid hydrometeor freezes. Thermodynamically, gases are less soluble in ice than liquid water, which implies that they would be released at the level of freezing, but kinetically, the mass transfer to the gas phase may be slower than freezing, in which case the gases will be carried with the ice and released at the elevation the ice sublimes or evaporates (Stuart and Jacobson, 2003). Although there have been numerous campaigns aimed at understanding the chemical consequences of deep convection, these campaigns have relied on traditional methods for measuring soluble acids and peroxides, which lack the resolution to reveal the detailed structure of air masses, which is important because encounters with cloud influenced air may be of short duration in an airplane.

Many challenges remain, some known, many waiting to be revealed by new discoveries or creative disruptions. No tool, no instrument – or instrument user – is perfect, and fully understanding the atmosphere and mankind’s impacts on it will require continued diligent and multifaceted efforts filled mostly with dead ends and misdirections, but also, occasionally, triumph, and, always, enlightenment. It is left to future researchers to determine if this work is a dead end, a triumph, or something in between, but regardless of history’s judgment it has been a worthwhile journey.

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