# Chapter 1

## Introduction

Aerosols, liquid or solid particles suspended in air, are important components of the Earth's atmosphere. They affect the Earth's radiative balance both directly, through shortwave scattering and longwave absorption, and indirectly, through cloud formation, with consequences for global climate. Clouds in turn also impact atmospheric chemistry through their role in affecting photolysis reactions and mediating aqueous phase reactions that significantly alter the fate and distribution of trace gases (Cohan et al., 1999; Mari et al., 2000; Tie et al., 2003; Ervens et al., 2004; Sorooshian et al., 2006). Aerosols have also been implicated in respiratory and cardiovascular disease (Harrison and Yin, 2000; Davidson et al., 2005; Pope and Dockery, 2006).

Fully assessing aerosols' impact on the environment, and predicting future impacts driven by changes in emissions and climate, requires an understanding of aerosol sources, sinks, and composition that is currently lacking. Models of global aerosol burdens routinely underpredict field measurements (de Gouw et al., 2005; Heald et al., 2005; Volkammer et al., 2006), while analytical techniques have identified only ~ 10% of the mass of organic aerosols (Hallquist et al., 2009). Although aerosols are complex mixtures of inorganic (primarily sulfate) and organic components (Murphy et al., 2006; Zhang et al., 2007), most of the current uncertainties surrounding aerosol are probably linked to the organic portion, which is the more abundant fraction. Sulfur budgets have fewer uncertainties – estimates of global sufur budgets are constrained to a factor of 2 (Barrie et al., 2001) – and less variation in chemical speciation than organic carbon.

Organic aerosol can be catergorized as either primary (POA), i.e., directly emitted into the atmosphere, or secondary (SOA), i.e., formed from gaseous precursors, with SOA believed to be dominant (Goldstein and Galbally, 2007; Robinson et al., 2007;

Donahue et al., 2009; Hallquist et al., 2009). Currently, models apply laboratory determinations of SOA yields (aerosol mass formed divided by mass of precursor reacted) and precursor emission inventories to predict aerosol burdens. The significant underestimation by models can thus be due to many factors, including missing or underestimated precursor volatile organic compounds (VOCs) (Lewis et al., 2000; Di Carlo et al., 2004; Holzinger et al., 2005; Hamilton et al., 2009), missing SOA formation pathways such as heterogeneous esterification and polymerization reactions (Iinuma et al., 2004; Surratt et al., 2006, 2007ab, 2008), or that laboratory conditions are not representative of the atmosphere with respect to certain crucial parameters (Kroll and Seinfeld, 2008; Hallquist et al., 2009).

Increased understanding of SOA formation processes will help resolve the current discrepancy between models and measurements. Experimental studies of SOA typically fall into one of three complementary categories: flow tube studies, environmental chamber studies, and field studies. Flow tube studies are useful for isolating individual reaction pathways and quantifying fundamental parameters such as rate constants and accommodation coefficients, but are typically performed on too short a time scale (~ seconds) to capture the chemical aging processes relevant to SOA formation. Field studies represent real atmospheric conditions, but important conditions such as emissions, wind patterns, and temperature are uncontrolled, which complicates data interpretation, and important species in both the gas and aerosol phases are often at low concentrations, which presents analytical challenges. Environmental chambers bridge these two scales, facilitating studies under conditions that are more atmospherically relevant than those of flow tubes and more controlled than those of field studies. Chamber studies also have limitations; for example, they are usually performed at reagent concentrations that are higher than ambient, which can affect both the thermodynamics and kinetics of SOA formation (Odum et al., 1996; Presto and Donahue, 2006; Chan et al., 2007; Kroll et al., 2007), and most chambers can only run experiments that last about 1 day, which may not capture all processes relevant to SOA formation and loss. Nonetheless, in concert with other experimental and modeling techniques, they can provide important insights into SOA formation.

When performing chamber studies, the complexity of SOA precursors, components, and formation mechanisms necessitates having a wide suite of instrumentation to provide multiple, complementary perspectives on the evolution of gas and particle phase species during an experiment, as there is no single instrument that is capable of providing a complete characterization. A recent addition to the instrumental suite of the Caltech environmental chamber is a chemical ionization mass spectrometer (CIMS) (Crounse et al., 2006), which utilizes the $CF_3O^-$ ion to selectively cluster compounds with high fluorine affinity. Two characteristics of the CIMS make it particularly suited for SOA studies. First, unlike common ionizing agents such as electrons or protons, $CF_3O^-$ ionizes "softly," i.e., with minimal fragmentation of the analyte, so that the analyte's mass can be determined unambiguously. Second, polar compounds, such as acids, peroxides, and multifunctional carbonyls, have high fluorine affinity and are thus detectable by the CIMS. As VOCs are oxidized, they tend to gain polarity which in turn lowers their vapor pressure. Therefore, the CIMS provides previously missing information about the sources and fate of polar compounds which are important components of VOC degradation mechanisms and key intermediates to SOA formation.

The selectivity, versatility, and time resolution of the CIMS makes it a good alternative to other techniques that measure a similar set of compounds. Acid and peroxide measurements typically involve collecting samples in water, which are then analyzed with chromatographic separation (Cofer et al., 1985; Lee et al., 1995). These techniques involve significant sample handling, which increase the chance of artifacts, and have poor time resolution. Nitrates, which are important VOC oxidation products in anthropogenically influenced environments, are often measured with Fourier transform infrared (FT-IR) (Barnes et al., 1990; Skov er al., 1992; Bernt and Böge, 1997), or thermal dissociation-laser induced fluorescence (TD-LIF) (Perring et al., 2009; Rollins et al., 2009), which measure only total nitrate, but don't speciate between different nitrate compounds.

The following work demonstrates insights into SOA formation and VOC degradation mechanisms that have been gained by coupling the CIMS to the Caltech environmental chamber. It focuses on studies of the reaction between the nitrate radical ($NO_3$) and isoprene ($C_5H_8$). Isoprene is a highly reactive VOC and is the most abundant VOC in the atmosphere after methane. Because of its reactivity and abundance, it is an important compound in atmospheric oxidation chemistry, and in the last decade it has also been recognized as an important source of SOA during photooxidation (i.e., daytime oxidation by OH, the hydroxyl radical). Its nighttime chemistry has been studied less extensively, so studies with the $NO_3$ radical, an important nighttime oxidant, are important to fully understand its fate and impact in the atmosphere.

In the following chapter, we demonstrate that the $NO_3$-initiated oxidation of isoprene can produce a significant yield of SOA, and that a key parameter in determining the yield is the fate of the peroxy radical ($RO_2$) that forms in the initial oxidation step. In particular, if an $RO_2$ reacts with another $RO_2$, it can dimerize into an ROOR compound, which is an efficient pathway for lowering vapor pressure.

Next, we perform a detailed gas-phase product study of $RO_2$-$RO_2$ reactions in the isoprene-$NO_3$ system. Despite the potential importance of $RO_2$-$RO_2$ reactions, only a limited suite of these reactions has been studied due to experimental challenges. In these studies, the $RO_2$ are typically small ($< C_3$) and are alkyl-, hydroxy-, acetyl-, or halogenated peroxy radicals. No studies of large, nitrooxy, or allylic peroxy radicals, such as those in the isoprene-$NO_3$ system, have been performed, and our study shows that these peroxy radicals lead to a significantly different product distribution than what is suggested by previous work, indicating that more studies on a greater variety of peroxy radical reactions are necessary to produce accurate chemical models.

Finally, the fate of organic aerosols after emission or formation are also important, so we speculate on organic aerosol sinks using data from the airborne NASA INTEX-NA field campaign. Specifically, we examine heterogeneous oxidation by OH, $O_3$, and $H_2O_2$ as a potential source of oxygenated VOC into the upper troposphere, which is another current controversy in atmospheric chemistry.

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