The Aging of Organic Aerosol in the Atmosphere: Chemical Transformations by Heterogeneous Oxidation

by

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The immense chemical complexity of organic particulate matter (“aerosol”) has left the general field of condensed-phase atmospheric organic chemistry relatively under-developed when compared with either gas-phase chemistry or the formation of inorganic compounds. In this work, we endeavor to improve the general understanding of the narrow class of oxidation reactions that occur at the interface between the particle surface and the gas-phase.

The heterogeneous oxidation of pure erythritol ($\text{C}_4\text{H}_{10}\text{O}_4$) and levoglucosan ($\text{C}_6\text{H}_{10}\text{O}_5$) particles by hydroxyl radical (OH) was studied first in order to evaluate the effects of atmospheric aging on the mass and chemical composition of atmospheric organic aerosol, particularly that resembling fresh secondary organic aerosol (SOA) and biomass-burning organic aerosol (BBOA). In contrast to what is generally observed for the heterogeneous oxidation of reduced organics, substantial volatilization is observed in both systems. However, the ratio of the decrease in particle mass to the decrease in the concentration of the parent species is about three times higher for erythritol than for levoglucosan, indicating that details of chemical structure (such as carbon number, cyclic moieties, and oxygen-containing functional groups) play a governing role in the importance of volatilization reactions. The kinetics of the reaction indicate that while both compounds react at approximately the same rate, reactions of their oxidation products appear to be slowed substantially. Estimates of volatilities of organic species based on elemental composition measurements suggest that the heterogeneous oxidation of oxygenated organics may be an important loss mechanism of organic aerosol.

As a continuation of the heterogeneous oxidation experiments, we also measure the kinetics and products of the aging of highly oxidized organic aerosol, with an aim of better constraining such atmospheric aging processes. Submicron particles composed of model oxidized organics—1,2,3,4-butane-tetracarboxylic acid ($\text{C}_8\text{H}_{10}\text{O}_8$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), and Suwannee River fulvic acid—were oxidized by gas-phase OH in the same flow reactor, and the masses and elemental composition of the particles were monitored as a function of OH exposure. In contrast to our previous studies of the less-
oxidized model systems, particle mass did not decrease significantly with heterogeneous oxidation. Carbon content of the aerosol always decreased somewhat, but this mass loss was approximately balanced by an increase in oxygen content. The estimated reactive uptake coefficients of the reactions of all compounds studied range from 0.3 to 1.0 and indicate that chemical transformations occur at rates corresponding to 1–2 weeks in the atmosphere, suggesting the importance of heterogeneous oxidation in the atmospheric lifecycle of most organic particulate matter.

Lastly, the immense complexity inherent in the formation of SOA—due primarily to the large number of oxidation steps and reaction pathways involved—has limited the detailed understanding of its underlying chemistry. In order to simplify this inherent complexity, we give over the last portion of this thesis to a novel technique for the formation of SOA through the photolysis of gas-phase alkyl iodides, which generates organic peroxy radicals of known structure. In contrast to standard OH-initiated oxidation experiments, photolytically initiated oxidation forms a limited number of products via a single reactive step. As is typical for SOA, the yields of aerosol generated from the photolysis of alkyl iodides depend on aerosol loading, indicating the semivolatile nature of the particulate species. The aerosol was observed to be somewhat higher in volatility and less oxidized than in previous multigenerational studies of alkane oxidation, suggesting that additional oxidative steps are necessary to produce properly oxidized semi-volatile material in the atmosphere.

The system in which the photolytic SOA is formed is also repurposed as a generator of organic aerosol for input into a secondary reaction chamber, where the organic particles undergo additional aging by the heterogeneous oxidation mechanism already discussed. Particles exiting this reactor are observed to have become more dramatically oxidized than comparable systems containing SOA formed by gas-phase alkanes undergoing “normal” photo-oxidation by OH. The physical and chemical characteristics of the photolytic SOA are nonetheless very similar to other observations of traditional SOA, suggesting simultaneously the utility of gas-phase precursor photolysis as an effective experimental platform for studying directly the chemistry involved in atmospheric aerosol formation and also the possibility that heterogeneous processes may play a more significant role in the atmosphere than what is predicted from chamber experiments. Consideration is given for the application of these results to larger-scale experiments, models, and conceptual frameworks.