Analysis of the Chemical Composition of Atmospheric Organic Aerosols by Mass Spectrometry

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To My Parents, Matt, Megan, and Alan

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Abstract

Although secondary organic aerosol (SOA) makes up a substantial fraction of the organic mass observed in tropospheric fine particulate matter, there remain significant uncertainties in the true impact of atmospheric aerosols on climate and health due to the lack of full knowledge of the sources, composition, and mechanisms of formation of SOA. This thesis demonstrates how the detailed chemical characterization of both laboratory-generated and ambient organic aerosol using advanced mass spectrometric techniques has been critical to the discovery of previously unidentified sources (i.e., role heterogeneous chemistry) of SOA.

The focal point of this thesis is given to the detailed chemical characterization of isoprene SOA formed under both high- and low-NO_x conditions. Until recently, the formation of SOA from isoprene, the most abundant non-methane hydrocarbon emitted into the troposphere, was considered insignificant owing to the volatility of its oxidation products. In conjunction with the chemical characterization of gas-phase oxidation products, we identify the role of two key reactive intermediates, epoxydiols of isoprene (IEPOX) and methacryloylperoxynitrate (MPAN), that are formed during isoprene oxidation under low- and high-NO_x conditions, respectively. Increased uptake of IEPOX by acid-catalyzed particle-phase reactions is shown to enhance low-NO_x SOA formation. The similarity of the composition of SOA formed from the photooxidation of MPAN to that formed from isoprene and methacrolein demonstrates the role of MPAN in the formation of isoprene high-NO_x SOA. More specifically, the further oxidation of MPAN leads to SOA by particle-phase esterification reactions. Reactions of IEPOX and MPAN in the presence of anthropogenic pollutants could be a substantial source of "missing urban SOA" not included in current SOA models.

Increased aerosol acidity is found to result in the formation of organosulfates, which was a previously unrecognized source of SOA. By comparing the tandem mass spectrometric and accurate mass measurements collected for both the laboratory-generated and ambient aerosol, previously uncharacterized ambient organic aerosol components are found to be organosulfates of isoprene, α-pinene, β-pinene, and limonene-like monoterpenes, demonstrating the ubiquity of organosulfate formation in ambient SOA. We estimate that the organosulfate contribution to the total organic mass fraction in certain locations could be substantial (upwards of 30%).

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