

Unraveling the complexity of organic aerosol chemistry through the study of simple heterogeneous reaction systems

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The formation and processing of atmospheric organic aerosol particles involves gas phase, heterogeneous, and multiphase chemical reactions, which alter particle composition and thus affect particle chemical and physical properties such as hygroscopicity, cloud nucleating activity, and light scattering and absorption. These properties have major effects on chemical lifetimes and transport, visibility, the hydrological cycle, and climate. The mechanisms of these reactions are complex and not yet well understood. Reactions with atmospheric oxidants, primarily OH radicals, O₃, and NO₃ radicals, usually either add functional groups to molecules or cause molecular fragmentation, whereas reactions with other organic molecules form larger oligomeric species. Whereas the mechanisms of radical-initiated reactions of organic compounds have much in common, regardless of the oxidant or whether they occur in the gas phase or via heterogeneous or multiphase mechanisms, there are also differences that can significantly alter reaction kinetics and products. Elucidating these mechanism can be a challenge, because of the great complexity of many reaction systems and the large numbers of products that can be formed. Studies on reactions systems with more tightly constrained and simpler chemistry can often provide much more detailed information that can be used to understand more complex systems. In this talk I will discuss results of extensive studies we have conducted over a few years using the reaction of oleic acid aerosol particles with NO₃ radicals and N₂O₅ as a model system for radical-initiated heterogeneous/multiphase reactions. I will demonstrate that by using a diverse array of measurement techniques including mass spectrometry, nuclear magnetic resonance spectroscopy, gas and liquid chromatography, spectrophotometry (with and without compound derivatization), traditional elemental analysis, pycnometry, temperature-programmed thermal desorption, and scanning mobility particle sizing to investigate reaction kinetics and products that it is possible to develop a full chemical reaction mechanism for this system, and that the results provide interesting insights into gas phase, heterogeneous, and multiphase and chemistry.