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Highly Oxygenated Molecules from Aromatic Compounds and Their Role in Formation of Secondary Organic Aerosols

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Aromatic hydrocarbons, primarily emitted by anthropogenic sources, account for a big fraction of the volatile organic compounds in the urban atmosphere and play a significant role in the formation of secondary organic aerosols (SOA). However, the detailed gas-phase oxidation mechanism of multiple aromatic compounds is not fully understood.

In this work, we investigate hydroxyl radical (OH) multigeneration oxidation chemistry of three aromatic hydrocarbons: toluene, 1,2,4-trimethylbenzene (1,2,4-TMB) and 1,3,5-trimethylbenzene (1,3,5-TMB) under moderate, urban-relevant NO_x levels (30-70 ppbv). Laboratory experiments were conducted at the MIT environmental chamber over approximately 1 day of atmospheric-equivalent oxidation. We used a comprehensive suite of chemical ionization mass spectrometry (CIMS) techniques to characterize and quantify oxidation products including two proton-transfer reaction time-of-flight MS (PTR3 and VOCUS PTR) and two high-resolution time-of-flight chemical-ionization MS (NH_4^+-CIMS and I^--CIMS) for the gas-phase measurements. As for measuring particle-phase organics, we deployed an aerosol mass spectrometer (AMS), a FIGAERO-I^--CIMS and a second NH_4^+-CIMS equipped with an aerosol inlet comprising a gas-phase denuder and a thermal desorption unit. Additional measurements were taken using optical, gas chromatographic, and mass spectrometric techniques. Using this extensive suite of instrumentation, we were able to quantify a large fraction of the reactive carbon in multiple generations of oxidation.

Hydroxyl radicals are known to react with aromatic hydrocarbons to form peroxy (RO_2) radicals which can isomerize by intramolecular hydrogen abstraction and lead to the formation of highly oxygenated molecules (HOMs). Here, we report the elemental composition and concentration of HOMs in the gas and condensed phases. We show that under urban conditions, in the presence of NO, the reaction of RO_2 radicals with NO competes with the autooxidation pathway and leads to the formation of highly oxygenated nitrates which we quantify in the gas and particle phases. We also determine the kinetics of the formation of HOMs and other major oxidation products using a best-fit kinetic parametrization which can provide information on the generation and reactivity of products. We show that although HOMs comprise only a small portion of the gas phase oxidation products, they contribute to a significant fraction of SOA mass. Information on the molecular level provided by the particle phase NH_4^+-CIMS and FIGAERO-I^--CIMS reveals insights into the range of volatilities and oxidation states of the compounds in the condensed phase.