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Characterization of organic aerosols by online CI-Orbitrap MS: Laboratory studies of biogenic SOA formation and size-dependent aerosol chemistry

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Atmospheric aerosols are an important part of Earth's climate system. Further, they have great influence on air quality and human health. Secondary organic aerosols (SOA) generated from the oxidation of volatile biogenic precursors are an important contributor to the global aerosol budget. Therefore, understanding new particle formation and their subsequent growth is critical for our ability to predict the atmospheric aerosol composition and global climate change.

The coupling of a chemical ionization source with an Orbitrap mass spectrometer provides soft ionization and a high mass resolution for the on-line measurements of laboratory-generated SOA. Through heating of the aerosol, it is possible to measure both the gas phase and the vaporized particle phase. We use this technique to compare the chemical composition of particles produced from the oxidation of α -pinene and α -carene. Although exhibiting a very similar chemical structure, they differ greatly in their resulting SOA, in terms of particle size and number concentration when oxidized with ozone in smog-chamber experiments.

These differences lie in their abilities to form characteristic SOA precursors, which depending on their chemical structure, promote either new particle formation or the growth of existing ones. The extremely low volatile organic compounds (ELVOCs) required for these processes are generally believed to be formed by gas phase chemistry. However, newly formed particles provide a unique nanoscale chemical environment that affects chemical reactions in the condensed phase and heterogeneous reactions on their surface, making them a potential source of ELVOCs as well. The increasing pressure inside the particles with decreasing diameter (Laplace pressure) favors bond-forming reactions. The lower viscosity in nanometer-sized particles further promotes reactions within the particle and increases reactivity at the particle surface such as heterogeneous oxidation. We show the particle size-dependent heterogeneous oxidation in a model system and ongoing work on other size-dependent reactions.