Secondary organic aerosol (SOA) formation from \( \alpha \)-pinene:
Chamber studies of kinetics, yield and aerosol composition

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Abstract
Ozonolysis of alpha-pinene is an efficient route to condensable oxidized organic compounds. We have conducted a series of SOA formation experiments in both a 430 L Teflon bag chamber and a 200 L steel drum chamber, monitoring oxidants, particle size distribution, and particle composition at the functional group level using FTIR spectroscopy. We present experimental results from daytime and nighttime simulations, with varying levels of NOx. In addition, kinetic modeling gives insights into gas-phase and heterogeneous reaction rates, aerosol nucleation and growth dynamics, and SOA yields.

Atmospheric Chambers

200 L steel drum: Chamber experiments were carried out in a 208 L steel drum. Reactants enter through the port on the right side of the barrel, while air is sampled from the left valve. To keep the barrel at atmospheric pressure, a source of clean dry air is constantly available to the barrel. Excess air bypasses the barrel and flows out a bubbler. Black circles denote ball valves.

430 L Teflon Bag: Chamber experiments were carried out in a 430 L Teflon bag. The bag is hung in chamber fitted with fluorescent lights, allowing for experiments to be carried out with either day or night time conditions. As with the steel drum, oxidants and hydrocarbons enter at one side of the chamber, while instrumentation samples air from the other. Experiments involving NOx were also carried out in this chamber. A constant volume in the bag was maintained by replacing sampled air with air from a clean, dry air generator.

Hydrocarbon Injection: A three-way stopcock is first purged with nitrogen gas. A gas tight syringe filled with a few milliliters of \( \alpha \)-pinene is attached (1). Nitrogen gas is used to fill the syringe, and then the stopcock is closed so that the \( \alpha \)-pinene can equilibrate between the gas and liquid phases (2). To inject, the stopcock is oriented such that when the syringe plunger is depressed, the headspace above the liquid \( \alpha \)-pinene is injected into the chamber (3). After the desired amount of headspace has been delivered by the syringe, the stopcock is twisted to allow nitrogen gas through the lines connected to the chamber, flushing out any \( \alpha \)-pinene still in the lines (4).

3D plots show different phases of particle formation and growth for an experiment (dark, low NOx). \( \frac{dN}{d\log Dp} \) (left) ranges from 0 (purple) to 1.4 x 10^11 cm^-3 (red). \( \frac{dV}{d\log Dp} \) (center) ranges from 0 (blue) to 4.6 x 10^11 cm^-3 (red). \( \frac{dN}{d\log Dp} \) (right) ranges from 0 (purple) to 1.4 x 10^11 cm^-3 (red). Particle number growth via nucleation dominates through the first 11 minutes of the experiment. Blue areas on the right-hand figure show particles below 100 nm in diameter are lost after 4 minutes, indicating that particles of this size quickly coagulate to form larger particles. The particle number concentration reaches its maximum value while the volume concentration is still growing, indicating that in this interval (11 to 20 min post injection), condensation is the dominant reaction occurring. From 20 to 34 minutes post injection, the particle number concentration is decreasing while the volume concentration is increasing slightly, indicating that both coagulation and condensation are occurring. Stabilization occurs around 50 minutes post injection.

Aerosol Composition

The top spectrum shows ATR-FTIR analysis of an aerosol sample collected from a dark, low NOx experiment, while the bottom spectrum was collected from aerosol produced in a light, high NOx experiment. As would be expected from the oxidation of \( \alpha \)-pinene, both samples showed strong absorbance in the aliphatic (C-H), carbonyl (C=O), and hydroxyl (O-H) regions. As indicated in the bottom spectrum, the aerosol formed in the high NOx experiment showed the characteristic absorbanices of organic nitrate at 860, 1280, and 1630 cm^-1.

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