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

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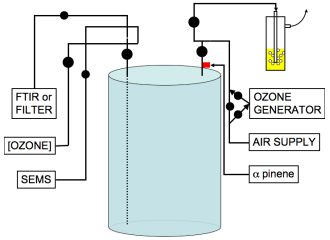
Abstract

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.

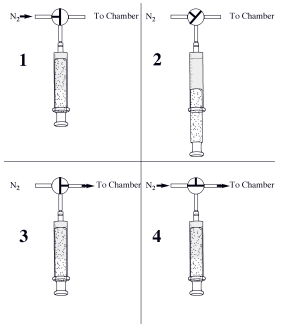
Atmospheric Chambers

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 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.

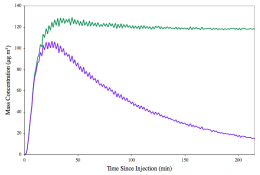


430 L Teflon Bag: Chamber experiments were carried out in a 430 L Teflon bag. The bag is hung in chamber fitted with fluorescent lights, allowing for experiments to be carried out with either day or night time conditions. As with the steel drum, oxidants and hydrocarbons enter at one side of the chamber, while instrumentation samples air from the other. Experiments involving NO_x 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.

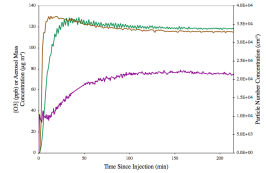
Hydrocarbon Injection: A three-way stopcock is first purged with nitrogen gas. A gas tight syringe filled with a few milliliters of α pinene is attached (1). Nitrogen gas is used to fill the syringe, and then the stopcock is closed so that the α pinene can equilibrate between the gas and liquid phases (2). To inject, the stopcock is oriented such that when the syringe plunger is depressed, the headspace above the liquid α 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 α pinene still in the lines(4).



Data Workup

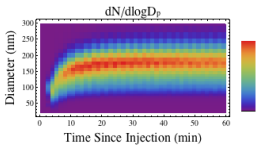


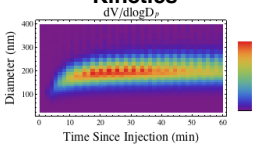
Dilution Correction: Because air is constantly being sampled from the chambers, the data must be corrected for dilution. The blue line shows the mass concentration at time t, $M_{o,t}$ during an experiment (μg m^{-3}). $M_{o,t}$ reaches a maximum concentration of 106.6 μg m^{-3} at 26 minutes, and then begins to fall due to dilution. $M`_{o,t}$, the mass concentration corrected for dilution is shown in green, and represents to total mass concentration of aerosol formed since time t. $M`_{o,t}$ reaches a maximum of 128.9 μg m^{-3} at 44 minutes.

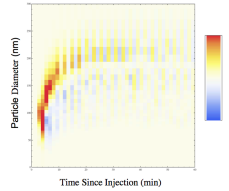


Quantification of α-pinene Consumed: The above graph shows the dilution corrected values for mass concentration (μg m^{-3}) (green), number concentration (cm^{-3}) (brown), and ozone reacted (ppb) (purple). In calculating the amount ozone reacted, both the rate of dilution and the rate of wall loss are taken into account. The reacted ozone is assumed to be consumed only in the ozonolysis of α-pinene in a one-to-one ratio. Because ozonolysis of α-pinene gives the hydroxyl radical in a yield of 0.77, and because the hydroxyl radical reacts with α-pinene much faster than ozone does, the amount of α-pinene consumed in an experiment (dark, low No_x) is calculated as 1.77 times the amount of ozone consumed.

Kinetics

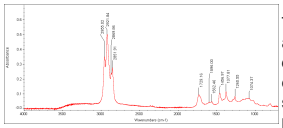


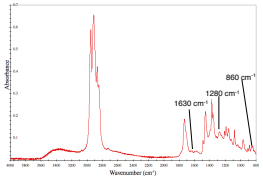




3D plots show different phases of particle formation and growth for an experiment (dark, low NO_x). $dN/dlogD_p$ (left) ranges from 0 (purple) to 1.4 x 10^5 cm^{-3} (red). $dV/dlogD_p$ (center) ranges from 0 (blue) to 4.6 x 10^{11} nm^3 cm^{-3} (red). $\Delta dN/dlogDp\ /\Delta t$ for the same experiment. The plot ranges from -25,000 (blue) to 25,000 (red) cm^{-3} min^{-1} , with 0 cm^{-3} min^{-1} shown as the cream color prevalent throughout the plot. The growth of aerosol occurs through the stages of oxidation, nucleation, condensation, coagulation, and finally deposition. 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

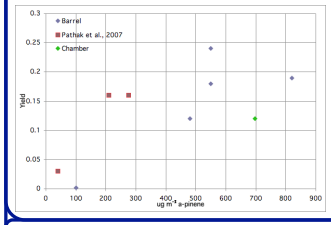




The top spectrum shows ATR-FTIR analysis of an aerosol sample collected from a dark, low NO_x experiment, while the bottom spectrum was collected from aerosol produced in a light, high NO_x experiment. As would be expected from the oxidation of α-pinene, both samples showed strong absorbance in the aliphatic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

Yield

$$Y = \frac{\Delta M_o}{\Delta \alpha \text{ pinene}}$$



Yields from experiments conducted in the Barrel chamber are shown in blue, while the pink circle shows the yield from an experiment carried out in the Teflon bag. Red squares denote yields reported by Pathak et al. (JGR 112, 2007). All experiments were carried out in low light and low No_x. Pathak et al report higher yields than this research, possibly due to the use of an OH scavenger.

Acknowledgments

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