

Aging of α -pinene first-generation ozonolysis products formed under low- and high-NO_x conditions

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Secondary organic aerosol (SOA) is produced by the transfer of the lower volatility oxidation products of volatile, intermediate volatility, and semi-volatile organic compounds (VOCs) to the particulate phase. SOA may contribute up to 70% to the total aerosol organic carbon mass (Hallquist et al., 2009) and most of it in a global scale is believed to be due to the oxidation of biogenic VOCs. Secondary organic aerosol (SOA) formation from volatile organic compounds in the atmosphere can be thought of as a succession of oxidation steps. The production of later-generation SOA via continued oxidation of the first-generation products is defined as chemical aging. Previous studies have explored various forms of aging, including heterogeneous reactions of oxidants and aerosol particles, oligomerization, photolysis of either gas or condensed-phase products, and homogeneous gas-phase oxidation by OH (Donahue et al., 2012). Homogeneous gas-phase oxidation reactions appear to be in general much faster than heterogeneous reactions, due to diffusion limitations of the latter. The first-generation oxidation reactions of most SOA precursors convert much less than 50% of the precursor to SOA, leaving more than half of the carbon still in the gas-phase. Additional oxidation of these vapors can potentially contribute additional and more oxygenated SOA components. These later generation reactions have been proposed to be a major missing step connecting chamber studies to field measurements (Donahue et al., 2012).

Our work investigates the hypothesis that while first-generation monoterpene SOA mass yields are generally lower at high-NO_x (largely because formation of organonitrates terminates oxidation sequences), later-generation (aging) SOA formation could be enhanced. This could be due to three reasons: increased radical cycling, less fragmentation of later-generation SOA products, and reduced photolysis of SOA species.

A series of experiments was conducted in the environmental simulation chambers of Carnegie Mellon University and of FORTH in Greece. SOA was first formed through reaction of α -pinene and ozone under low and high NO_x conditions respectively. During the second step, the first-generation products were allowed to react further with hydroxyl radicals (OH) generated via H₂O₂ and HNO₂ photo-dissociation. The SOA was characterized by a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS). Attenuated total reflectance (ATR-FTIR) was also employed to identify and quantify organonitrate

functional groups. A second-generation aerosol mass yield was defined to quantify the aging effects. Potential hydrolysis effects of organonitrate compounds were also explored by performing experiments at low and high RH.

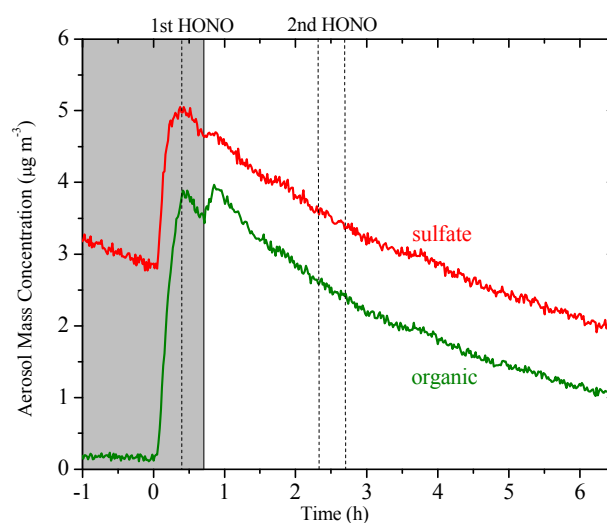


Figure 1. AMS-measured mass concentrations for both organics and sulfate for a typical aging experiment. α -pinene was added into the chamber at time 0. The grey and white backgrounds indicate UV lights off or on in the chamber. The dashed lines indicate the two times when HONO were added.

The results from our chamber experiments show that the first-generation products from α -pinene ozonolysis age with OH. Additional SOA was formed and a more oxygenated product distribution was observed. These increases in SOA yields and O:C for the different conditions will be discussed.

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