

Chemical characterization of SOA formed from α -pinene and 1,3,5-trimethylbenzene during the POLYSOA experiment.

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A significant fraction of ambient fine particle mass is composed of secondary organic aerosol (SOA). A considerable amount of data on the SOA forming potential of individual gaseous precursors has been obtained so far, however the elucidation of SOA chemical composition has proven to be more difficult. A number of recent studies have shown that organic molecules in SOA can polymerize, forming high-molecular weight compounds (i.e., oligomers). Here we present results obtained in the frame of PolySOA EU-project (1) where various state-of-the-art analytical techniques were employed to characterize the chemical composition of chamber-produced SOA particles with emphasis on the oligomeric mass fraction. SOA were produced at PSI smog chamber facility from photooxidation or ozonolysis of anthropogenic (1,3,5-trimethylbenzene, TMB) and biogenic (α -pinene) precursors. Measurements performed with an Aerodyne Aerosol mass spectrometer (AMS) showed that the aerosol produced at low precursor concentrations exhibit a higher oxidation state with a better overlap with the composition observed for ambient particles in aged continental air masses (2). Other on-line mass-spectrometric measurements performed with an ATOFMS showed a molecular distribution reaching 750 Da, providing evidence for the formation of oligomers. The formation of dimers was clearly observed using on-line atmospheric pressure chemical ionization mass spectrometry (APCI-MS) during the α -pinene photooxidation experiments. The combination of APCI-MS measurements with off-line liquid chromatography electrospray ionisation mass spectrometry (LC/ESI-MSⁿ) support the esters formation as important oligomer formation pathway (3). Polymeric substances with acidic properties (polyacids, or humic-like substances, HULIS) were analyzed using a series of liquid chromatographic methods coupled to TOC analysis. Most of the organic carbon was apportioned into neutral compounds or monoacids, with a secondary contribution from diacids. Polyacid concentrations were often below the detection limit, although HULIS were occasionally found during the TMB photooxidation experiments. In summary, SOA oligomers were identified as formed by the chemical condensation (with esterification as plausible route) of a few monomers, providing hydroxycarboxylic and dicarboxylic acids, whereas HULIS were not detected in the large amounts observed in ambient particles. Finally, the actual chemical composition of SOA in the low concentration regime awaits to be fully explored.

- (1) Baltensperger et al., 2008. Combined determination of the chemical composition and of health effects of secondary organic aerosols: the POLYSOA Project, *J. Aerosol Medicine*, 21, 145-154.
- (2) Duplissy et al., 2008. Cloud forming potential of secondary organic aerosol under near atmospheric conditions. *Geophys. Res. Lett.*, 35, L03818, doi:10.1029/2007GL031075.
- (3) Müller et al., 2008. Unambiguous identification of esters as oligomers in secondary organic aerosol formed from cyclohexene and cyclohexene/ α -pinene ozonolysis. *Atmos. Chem. Phys.*, 8, 1423-1433.