Geophysical Research Abstracts Vol. 16, EGU2014-13340, 2014 EGU General Assembly 2014 © Author(s) 2014. CC Attribution 3.0 License.



High Molecular Weight Dimer Esters in α -Pinene Secondary Organic Aerosol

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Monoterpenes, such as α -pinene, constitute an important group of biogenic volatile organic compounds (BVOC). Once emitted into the atmosphere α -pinene is removed by oxidization by the hydroxyl radical (OH), reactions with ozone (O₃), and with nitrate radicals (NO₃) resulting in the formation of first-generation oxidation products, such as semi-volatile carboxylic acids. In addition, higher molecular weight dimer esters originating from the oxidation of α -pinene have been observed in both laboratory-generated and ambient secondary organic aerosols (SOA). While recent studies suggest that the dimers are formed through esterification between carboxylic acids in the particle phase, the formation mechanism of the dimer esters is still ambiguous.

In this work, we present the results of a series of smog chamber experiments to assess the formation of dimer esters formed from the oxidation of α -pinene. Experiments were conducted in the University of North Carolina (UNC) dual outdoor smog chamber facility to investigate the effect of oxidant species (OH versus O_3), relative humidity (RH), and seed aerosol acidity in order to obtain a better understanding of the conditions leading to the formation of the dimer esters and how these parameters may affect the formation and chemical composition of SOA. The chemical composition of α -pinene SOA was investigated by ultra-performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-Q-TOFMS), and a total of eight carboxylic acids and four dimer esters were identified, constituting between 8 and 12 % of the total α -pinene SOA mass.