Production of Highly Oxygenated Organic Molecules During The Later Oxidation Stages of Various Sesquiterpenes

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Abstract

The oxidation of biogenic volatile organic compounds is an important pathway for the atmospheric formation of secondary organic aerosol (SOA). The contribution of sesquiterpenes to biogenic SOA remains uncertain, with field studies based on tracer compounds suggesting low values and some modelling studies suggesting that they can be more important than isoprene. Laboratory studies of sesquiterpene ozonolysis suggest high SOA yields, but the formed SOA has relatively low O:C and is inconsistent with biogenic SOA observations. In an effort to explain these inconsistencies we follow a different approach. We perform atmospheric simulation chamber experiments starting from three first generation sesquiterpene ozonolysis products ($C_{10}H_{16}O_4$, $C_{13}H_{20}O_5$, $C_{15}H_{24}O_4$) and investigate their aging chemistry with the OH radical. The compounds were synthesized for the purposes of this work. The gas and particle phase composition was characterized with a high-resolution PTR-ToF-MS/CHARON system and an aerosol mass spectrometer (AMS). The investigated sesquiterpene SOA components are semivolatile (C^* of a few μg m^{-3}) based on our volatility measurements and the SOA within approximately one hour is oxidized to compounds with an average O:C approaching 0.7. The SOA AMS spectrum changes significantly as it ages. The functionalization reactions dominate over the fragmentation pathways and there is net increase in the SOA concentration. A physicochemical mechanism is proposed and tested for the description of the later generation gas-phase reactions converting the SOA to highly oxidized compounds. We estimate that around two thirds of the carbon follow the functionalization pathways. This suggests that quantification of the sesquiterpene SOA under ambient conditions based on the ozonolysis tracers can seriously underestimate its levels. Later generation products identified in this study can be more useful. The parameterizations developed in this work can be used in future modelling efforts to revisit the sesquiterpene contribution to SOA.

Early Career Scientist

YES, I am an early career scientist.