Online measurements and modeling of SOA formation from isoprene photooxidation: insights from multiple chamber experiments and field campaigns.

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Abstract:

Isoprene, the most abundantly emitted non-methane volatile organic compound globally, has the potential to produce large quantities of secondary organic aerosol (SOA) with implications for climate, air quality and human health. However, much remains unknown about the mechanisms and processes that lead to isoprene derived SOA, as well as its chemical and physical properties. We present measurements and modeling of a suite of newly detected compounds from isoprene oxidation during laboratory studies at the Pacific Northwest National Laboratory (PNNL) as well as in the atmosphere during the Southern Oxidant and Aerosol Study (SOAS) field campaign. In both cases, measurements were made with a high resolution time of flight chemical ionization mass spectrometer utilizing iodide adduct ionization coupled to the Filter Inlet for Gas and AEROsol (FIGAERO) for the simultaneous sampling of the gas and aerosol phases. In chamber experiments, isoprene photo-oxidation with dry neutral seed, and, separately isoprene-derived epoxy diol (IEPOX) multiphase chemistry on aqueous particles, were investigated at a variety of atmospherically relevant conditions. Isoprene photo-oxidation under high HO$_2$ and low NO conditions produced unexpectedly large amounts of SOA, at a yield similar in magnitude but from a distinctly different mechanism than that from IEPOX uptake. Aging experiments in both cases show clear evidence for particle phase chemistry such as hydrolysis and oligomerization altering the chemical and physical properties of the SOA. Indeed, oligomerization was inferred by observations of composition and thermal desorption characteristics to be a dominant feature in NOx-rich isoprene photochemical SOA formation, although at lower overall SOA yields. Using observations and a new MCM-based gas-particle partitioning model, we assess the degree to which the different mechanisms are operable in the atmosphere and other independent chamber experiments.