Rapid Formation of Sulfate Aerosols through Aqueous Aerosol Oxidation by Isoprene Hydroxy Hydroperoxides (ISOPOOH)

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Abstract

Isoprene is the most abundant non-methane volatile organic compound (VOC) emitted globally. Isomeric isoprene hydroxy hydroperoxides (ISOPOOH), key photooxidation products of isoprene, likely comprise the second most abundant class of peroxides in the atmosphere, following hydrogen peroxide. Studies have shown that hydrogen peroxide plays important roles in the formation of inorganic sulfates in cloud water mimics. However, the potential for ISOPOOH to play a role in sulfate formation in wet aerosol oxidation from reduced sulfur species (such as inorganic sulfite) is not well understood. This study systematically investigates the reaction kinetics and products of ISOPOOH reacting with particle phase inorganic sulfite and discusses implications to the sulfate aerosol budget.

In order to examine the reaction kinetics of ISOPOOH with aqueous sulfite, ammonium bisulfite particles were injected into the UNC indoor environmental chamber under dark conditions with 70% RH. After the inorganic sulfite concentrations stabilized, selected concentrations of gas-phase 1,2-ISOPOOH was injected into the chamber to initiate the multiphase reaction. The gas-phase ISOPOOH and particle-phase species were sampled with online instruments, including a chemical ionization mass spectrometer (CIMS), an aerosol chemical speciation monitor (ACSM), and a particle-into-liquid sampler (PILS), and also collected by Teflon filters for offline molecular-level analyses by an ultraperformance liquid chromatography coupled to an electrospray ionization high resolution quadrupole time-of-flight mass spectrometry (UPLC-ESI-HR-QTOFMS). Results show that a significant amount of inorganic sulfite was converted to inorganic sulfate and organosulfates in the particle phase at relatively fast reaction rates, altering the chemical and physical properties of the particles including phase state, pH, reactivity, and composition. Given the high abundance and water solubility of ISOPOOH in the ambient environment, the multiphase reactions examined in our study indicate significant impacts of ISOPOOH on the atmospheric lifecycle of sulfur and the physicochemical properties of ambient particles.

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