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Synergistic Multiphase Chemistry of Isoprene Hydroxy Hydroperoxides (ISOPOOH) with Sulfur Dioxide in Acidic Sulfate Aerosols Leading to Secondary Inorganic and Organic Aerosol Formation.

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Isoprene is the most abundant non-methane volatile organic compound (VOC) emitted globally. 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 and ISOPOOH play important roles in the formation of inorganic sulfate in cloud water mimics. However, there is limited information on the role of ISOPOOH in SOA and sulfate formation in wet aerosol oxidation of dissolved reduced sulfur species such as sulfur dioxide and inorganic sulfite.

In order to examine the reaction products, kinetics, and implications of ISOPOOH with aqueous sulfite, ammonium bisulfate particles were injected into the UNC 10-m³ indoor environmental chamber under humid (i.e., 72% RH) and dark conditions. After the inorganic sulfate concentration stabilized, selected concentrations of gas-phase 1,2-ISOPOOH were injected into the chamber, and aerosols showed a minimal mass increase. Gaseous SO₂ was subsequently injected into the chamber and a significant amount of aerosol mass was produced. 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), a particle-into-liquid sampler (PILS) for analysis by ion chromatography analysis (IC), and filter samples were analyzed by an ultra-performance liquid chromatography coupled to an electrospray ionization high resolution quadrupole time-of-flight mass spectrometry (UPLCESI-HR-QTOFMS) to obtain offline molecular-level information. Results show that a significant amount of inorganic sulfate and organosulfates were formed rapidly after injecting SO₂, altering the chemical and physical properties of the particles including phase state, pH, reactivity, and composition. Multifunctional C₅-organic species that were previously measured in atmospheric fine aerosol samples were also reported here as reaction products, including 2-methyletrols and 2-methyltetrol sulfates that were previously thought to be only produced from the reactive uptake of isoprene-derived epoxydiols (IEPOX). Such results indicate that the multiphase reactions of ISOPOOH could have significant impacts on the atmospheric lifecycle of organic aerosols and sulfur, as well as the physicochemical properties of ambient particles.