Effect of Aerosol Acidity on the Kinetics and Products of Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-Derived Secondary Organic Aerosol

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Abstract Number: 267
Working Group: Aerosol Chemistry

Abstract
We recently demonstrated that the heterogeneous hydroxyl radical (·OH) oxidation is an important aging process for isoprene epoxydiol-derived secondary organic aerosol (IEPOX-SOA) that alters its chemical composition, and thus, aerosol physicochemical properties. Notably, dimeric species in IEPOX-SOA were found to heterogeneously react with ·OH at a much faster rate than monomers, suggesting that the initial oligomeric content of freshly-generated IEPOX-SOA particles may affect its subsequent atmospheric oxidation. Aerosol acidity could in principle influence this aging process by enhancing the formation of sulfated and non-sulfated oligomers in freshly-generated IEPOX-SOA. Many multifunctional organosulfate (OS) products derived from heterogeneous ·OH oxidation of sulfur-containing IEPOX-SOA have been observed in cloud water residues and ice nucleating particles and could affect the ability of aged IEPOX-SOA particles to act as cloud condensation nuclei. Hence, this study systematically investigated the effect of aerosol acidity on the kinetics and products resulting from heterogeneous ·OH oxidation of IEPOX-SOA particles.

Gas-phase IEPOX was reacted with inorganic sulfate particles of varying pH (0.5 to 2.0) in an indoor smog chamber operated under dark, steady-state conditions to form freshly-generated IEPOX-SOA particles. These particles were then aged at a relative humidity of 60% in an oxidation flow reactor (OFR) for 0-15 days of equivalent atmospheric ·OH exposure. Aged IEPOX-SOA particles were sampled by an online aerosol chemical speciation monitor (ACSM) to measure real-time aerosol mass and chemical changes of the SOA particles, and were also collected onto Teflon filters and into PILS vials for molecular-level chemical analyses by hydrophilic liquid interaction chromatography method interfaced to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS), ion chromatography, and total OS mass amounts.

AAAR 2022