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

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. We reacted gas-phase IEPOX with inorganic sulfate particles of varying pH (0.5 to 2.5) in an indoor smog chamber operated under dark, steady-state conditions to form freshly-generated IEPOX-SOA particles. These particles were aged at a relative humidity of 65% in an oxidation flow reactor (OFR) for 0-21 days of equivalent atmospheric OH exposure. Through molecular-level chemical analyses by hydrophilic interaction liquid chromatography method interfaced to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS), we observed that highly acidic aerosol has higher oligomer ratio and exhibit much slower mass decay with OH oxidation (pH=0.5, lifetime = 56 days) as compared to less acidic aerosols (pH=2.5, lifetime=17 days). Based on atomic force microscopy (AFM) analysis, aerosol acidity could also affect the morphology and viscosity of IEPOX-SOA during OH oxidation process.