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Kinetics and Products of Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-Derived SOA.

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In isoprene-rich regions, acid-catalyzed multiphase reactions of isoprene epoxydiols (IEPOX) with inorganic sulfate ($Sulf_{inorg}$) particles form secondary organic aerosol (IEPOX-SOA), extensively converting $Sulf_{inorg}$ to lower volatility particulate organosulfates (OSs), including 2-methyltetrol sulfates (2-MTSs) and their dimers. Recently, we showed that heterogeneous hydroxyl radical (OH) oxidation of particulate 2-MTSs generated multifunctional OS products. However, atmospheric models assume that OS-rich IEPOX-SOA particles remain unreactive towards heterogeneous OH oxidation, and limited laboratory studies have been conducted to examine the heterogeneous OH oxidation kinetics of full IEPOX-SOA mixtures. Hence, this study investigated the kinetics and products resulting from heterogeneous OH oxidation of freshly-generated IEPOXSOA in order to help derive model-ready parameterizations. First, gas-phase IEPOX was reacted with acidic $Sulf_{inorg}$ particles under dark conditions in order to form fresh IEPOX-SOA particles. These particles were then subsequently aged at RH of 56% in an oxidation flow reactor at OH exposures ranging from 0~15 days of equivalent atmospheric exposure. Aged IEPOX-SOA particles were sampled by an online aerosol chemical speciation monitor (ACSM) and collected onto Teflon filters for off-line molecular-level chemical analyses by hydrophilic liquid interaction chromatography method interfaced to electrospray ionization high-resolution quadrupole time-offlight mass spectrometry (HILIC/ESI-HR-QTOFMS). Our results show that heterogeneous OH oxidation only caused a 7% decay of IEPOX-SOA by 10 days exposure, likely owing to the inhibition of reactive uptake of OH as fresh IEPOXSOA particles have an inorganic core-organic shell morphology. A significantly higher fraction of IEPOX-SOA (~37%) decayed by 15 days exposure, likely due to the increasing reactive uptake of OH as IEPOX-SOA become more liquid-like with aging. Freshly-generated IEPOX-SOA constituents exhibited varying degrees of aging with 2-MTSdimers being the most reactive, followed by 2-MTSs and 2-methyltetrols (2-MTs), respectively. Notably, extensive amounts of previously characterized particle-phase products in ambient fine aerosols were detected in our laboratory-aged IEPOX-SOA samples.