Isoprene Epoxydiol-Derived Sulfated and Non-Sulfated Oligomers Suppress Particulate Mass Loss during Oxidative Aging of Secondary Organic Aerosol

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Abstract

Acid-driven multiphase chemistry of isoprene epoxydiols (IEPOX) with inorganic sulfate aerosols contributes substantially to formation of secondary organic aerosol (SOA), which constitutes a large mass fraction of atmospheric fine particulate matter ($PM_{2.5}$). However, atmospheric chemical sinks of freshly generated IEPOX-SOA particles remain unclear. We examined the role of heterogeneous oxidation of freshly-generated IEPOX-SOA particles by gas-phase hydroxyl radical (•OH) under dark conditions as one potential atmospheric sink. After 4 h of gas-phase •OH exposure (~$3x10^8$ molecules cm^{-3}), chemical changes in smog chamber-generated IEPOX-SOA particles were assessed by hydrophilic interaction liquid chromatography coupled with electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS). Comparison of molecular-level compositional changes in IEPOX-SOA particles during aging with or without •OH revealed that decomposition of oligomers by heterogeneous •OH oxidation acts as a sink for •OH and maintains a reservoir of low-volatility compounds including monomeric sulfate esters and oligomer fragments. We propose tentative structures and formation mechanisms for previously uncharacterized SOA constituents in $PM_{2.5}$. Our results suggest that this •OH-driven renewal of low-volatility products may extend atmospheric lifetimes of IEPOX-SOA particles by slowing production of low-molecular weight, high-volatility organic fragments, and likely contributes to large quantities of 2-methyltetrols and methyltetrol sulfates reported in $PM_{2.5}$.

This abstract has supplementary material available. Click PDF icon to download.

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