Unexpected Stereochemical Specificity for Organosulfates Formed from Isoprene-Epoxide Ring Opening Reactions as a Function of Aerosol Acidity

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Abstract Number: 127
Working Group: Aerosol Chemistry

Abstract
Chirality is a central property of organic molecules that plays a key role in chemical properties and biological impacts of molecules with only a slight difference at a single stereocenter within a molecule. In secondary organic aerosol (SOA) species with different stereoisomers are assumed to be present equally within racemic mixtures, unless there is an initial stereospecificity of the condensing or reacting oxidized VOCs. Unexpectedly, we found that certain stereoisomers of organosulfates are formed preferentially from isoprene epoxydiols without initial stereospecificity. In addition, we see a pH-dependent shift in the mechanism of reaction from an SN1 dominating the lowest acidities studied to an increase in the concerted SN2 mechanism at higher pH values. These findings were supported by computational chemistry analysis of underlying reaction pathways that reveal the origins of selectivity. These results were enabled through a combination of advanced analytical methodologies, specifically hydrophilic interaction liquid chromatography coupled with mass spectrometry (HILIC/ESI-HR-QTOFMS) that can separate the MTS diastereomers and computational chemistry studies using advanced sampling methods to explore the reaction mechanisms. Identifying this unexpected chirality from racemic precursors and connecting it to mechanisms occurring within atmospheric aerosols has broad importance for SOA chemical composition, physicochemical properties, and potentially human health after inhalation. Further studies are needed to determine the breadth of this chirality within aerosols and its potential implications.