

Formation of (nitrooxy)organosulfates from organic peroxides and S(IV) via daytime and nighttime chemistry

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Abstract

Sulfur and nitrogen containing organic compounds, such as organosulfates (OSs) and nitrooxy organosulfates (NOSs), are recognized to be ubiquitously present in secondary organic aerosol (SOA). However, little is known about the chemical mechanisms or the required conditions for the formation of these compounds in the ambient atmosphere. Earlier studies have commonly suggested that OSs are predominantly formed through the reaction of organic gaseous epoxides with acidic sulfate particles. However, this epoxide pathway often fails to explain the formation of (N)OSs from monoterpenes. Moreover, recent studies highlight the potential role of gas-phase SO₂ and organic peroxides for the formation of OSs, which might serve as predominant precursors for OSs and NOSs from atmospheric monoterpene oxidation.

Here, we conducted a series of chamber experiments to elucidate the formation mechanisms of (N)OSs from α -pinene oxidation during daytime and nighttime conditions. In particular, we focused on the role of organic peroxides and S(IV) (i.e., gas-phase SO₂ and particulate SO₃²⁻) in contrast to organic epoxides and isotope-labelled particulate sulfate (i.e., S(VI)). SOA particles were analyzed online by extractive electrospray ionization coupled with high-resolution Orbitrap mass spectrometry (EESI-Orbitrap MS) allowing an unambiguous identification of OS and NOS species with a high time resolution. Additionally, filter samples were collected and analyzed by liquid chromatography (LC) coupled with Orbitrap MS to determine the presence of isomeric compounds.

Consistently, online and offline Orbitrap MS analysis showed that particulate sulfate played a minor role in the formation of OSs and NOSs. In contrast, (N)OSs were rapidly formed upon addition of either gaseous SO₂ or particulate SO₃²⁻, suggesting S(IV) to react with organic peroxides that were formed through monoterpene oxidation. Based on these experiments, we identified specific NOS species that are formed only through either daytime or nighttime chemistry, and thus, might serve as marker molecules. Moreover, we present complete formation pathways for these species. Our study indicates that in contrast to previous work, the formation of OSs and NOSs does not require acidic sulfate particles, but rather involves the reaction of organic peroxides with S(IV) in the gas phase or the particle phase.