

Formation of Organosulfates and Nitrooxy Organosulfates from Monoterpene Oxidation via Daytime and Nighttime Chemistry

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Organosulfates (OS) and nitrooxy organosulfates (NOS) are recognized as ubiquitous constituents of secondary organic aerosols (SOA) (Iinuma, 2007; Riva 2019; Brüggemann 2019). Nonetheless, knowledge on their formation mechanisms in the ambient atmosphere is still connected to larger uncertainties. Mostly, OSs are assumed to form primarily by the reaction of organic gaseous epoxides with acidic sulfate particles (Surratt 2008). In contrast to isoprene-derived OSs, it seems however unlikely that this epoxide pathway alone can explain the ubiquity of monoterpene-derived (N)OSs in ambient aerosol particles. Moreover, recent studies suggest additional formation pathways through reactions of SO₂ and organic (hydro-)peroxides, which might even dominate OS and NOS formation in monoterpene oxidation (Ye 2018; Wang 2019).

Here, we have conducted a series of experiments at the TROPOS ACD chamber (ACD-C) to elucidate the formation mechanisms of OSs and NOSs from α -pinene oxidation under daytime and nighttime conditions at different particle acidities and medium NO_x levels. In particular, we focused on the role of organic (hydro-)peroxides and S(IV) (i.e., SO₂ in the gas phase) in contrast to organic epoxides and particulate sulfate (i.e. S(VI)). The SOA particles were analyzed online by extractive electrospray ionization in combination with high resolution Orbitrap mass spectrometry (EESI-Orbitrap MS), which allows an unambiguous identification of OS and NOS species with high time resolution. In addition, filter samples were collected and analyzed by liquid chromatography (LC) coupled with Orbitrap MS to determine concentrations and the presence of isomeric compounds.

Under highly acidic conditions, the formation of known OSs was readily observed in photooxidation experiments. However, at lower particle acidities, the online and offline analysis of Orbitrap MS showed consistently that OS formation rates decreased significantly. Furthermore, formation of NOS was mainly observed in nighttime chemistry experiments, questioning the well-established epoxide pathway for the formation of these species. Based on these experiments, we identified specific NOS species that are formed only by day or night chemistry, and therefore, could serve as marker molecules in source

apportionment studies. Furthermore, we present complete formation pathways for these species. Remarkably, for both online and offline analysis, detected OS abundances were significantly affected by the presence of gas-phase SO₂ during particle collection and analysis. So far, this potential source of artificially enhanced OS formation is commonly neglected and should be thoroughly considered in future studies on OS detection to allow an accurate determination of these species.

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