

Experimental study of organosulfates formation at the gas-particle interface from oxidation products of α -pinene

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Within the highly complex organic fraction of atmospheric aerosol, organosulfates have recently been the subject of particular attention. Indeed, these compounds may account for up to more than 10 % of atmospheric particulate organic matter (Surratt *et al.*, 2008; Tolocka and Turpin, 2012). Furthermore, terpene-derived organosulfates may be good tracers of anthropogenically enhanced biogenic secondary organic aerosols (Hoyle *et al.*, 2011). Although organosulfate precursors and formation pathways are only beginning to be explored, these compounds are believed to be formed secondarily in the atmosphere.

In this context, the objective of this study was to provide kinetic and mechanistic data describing heterogeneous organosulfate formation, to improve our understanding of multiphase reactions and assess the potential of these reactions in transferring organic matter from gaseous to particulate phase.

In this work, organosulfate formation was investigated using a new and fully dedicated experimental set-up (quasi-static reactor). The original approach proposed here is based on the chemical analysis at the molecular level of both the gaseous and the particulate phases. This approach allows to study elementary reactions in highly controlled and repeatable conditions. Model particles were generated from the nebulisation of ammonium sulfate/sulfuric acid solutions and deposited on a filter. Particles were exposed to a gaseous flow of a single volatile organic compound. A set of α -pinene oxidation products (or proxies) such as α -pinene oxide, myrtenal, pinanediol and isopinocampheol was selected to investigate the influence of the functional group on the reactivity with sulfated particles. The gaseous phase was characterised on-line using a Proton Transfer Reaction Time of Flight Mass spectrometer (PTR/TOF-MS). Particles were extracted in acetonitrile and organosulfates were analysed by Liquid Chromatography coupled to Mass spectrometry (LC/MS). Structures of the organosulfates were determined by high resolution tandem mass spectrometry (LC/Q/TOF-MS). A series of aerosol chamber experiments (CESAM, LISA) (Wang *et al.*, 2011) was also performed to investigate the formation of organosulfates from reactive uptake of monoterpene

oxidation products in experimental conditions closer to ambient air (suspended particles, lower concentrations, longer time scales, higher relative humidity).

New organosulfate products were detected and identified for the first time in this study and mechanistic pathways for the reaction between α -pinene, α -pinene oxide, isopinocampheol or pinanediol with acidified ammonium sulfate particles are proposed. The role of relative humidity on organosulfate formation yields and product distribution is specifically examined. Organosulfate concentrations were found to decrease with increasing relative humidity. Acidity conditions were found to increase notably the amounts of organosulfates formed in quasi-static reactor. Nevertheless, in chamber experiments, it was found that the mass concentration of organosulfates depends on the available sulfate in the particulate phase. Finally, first kinetic data on heterogeneous formation of organosulfates are provided. Atmospheric implications of these results will be discussed.

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