

Structural elucidation of α -pinene originating $C_{10}H_{17}O_6S$ organosulfates from CCS values derived from ion mobility mass spectrometry and theoretical structural modelling

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Organosulfates (OS) are recognised as one of the important classes of marker compounds for atmospheric oxidation of biogenic volatile compounds (BVOCs) as it can account as high as 30% of the organic mass fraction in PM_{10} (Brüggemann et al., 2020). While a number of studies report the presence of OS in laboratory generated and ambient biogenic SOA based on LC/MS data, little is known about their formation mechanism and exact structures owing to a wide variety of possible formation mechanisms and structures. Nevertheless, several formation mechanisms are accepted in the community based on laboratory experimental data. These include the reaction of BVOC oxidation products with acidic sulfate or sulfoxy radical anion in the particle phase, and the reactions of unsaturated hydrocarbons and SO_2 in the gas phase (Brüggemann et al., 2020). The structural elucidation of OS species remains challenging owing to lack of authentic standard compounds.

In this work, we present the results from the structural elucidation experiments of m/z 265 ($C_{10}H_{17}O_6S^-$) organosulfates originating from the photo-oxidation and ozonolysis of α -pinene in the presence of neutral and acidic seed particles at two different temperatures. The resulting SOA were collected on Teflon filter, and extracted in acetonitrile, dried using a centrifugal evaporator, and reconstituted in a 50/50 (v/v) acetonitrile/water solution. The samples were analysed using high-performance liquid chromatography coupled to ion mobility spectrometry tandem time-of-flight mass spectrometry (Agilent 1290 HPLC and Bruker TimsTOF) to obtain collision cross section (CCS) values of m/z 265 organosulfates. To further evaluate the structures of m/z 265 compounds, the theoretical CCS value of a previously reported structure for m/z 265 organosulfate, specifically sulfated pinonaldehyde, was calculated with MobCal-MPI (Ieritano et al., 2019), and compared to the measured CCS values. The measured CCS values of m/z 265 compounds are in the range of 154 to 158 $\text{\AA}^2$ that are much smaller than the theoretical CCS value of 164.7 $\text{\AA}^2$. The theoretical CCS values of positional isomers of sulfated pinonaldehyde (i.e. a sulfate group is attached at a different position than the previously reported structure) are also greater than those of measured CCS values, indicating that m/z 265 organosulfates likely have closed shell structures rather than open shell structures. To support this, theoretical CCS values of two of $C_{10}H_{17}O_6S^-$ compounds that are analogous to closed shell m/z 249 ($C_{10}H_{17}O_5S^-$) organosulfates were calculated and compared to measured values. The theoretical CCS values of both the closed shell m/z 265 compounds are in the order of 156 $\text{\AA}^2$, suggesting that they are likely structures of m/z 265 organosulfates.

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