



Reactions of S^{IV} species with organic compounds: formation mechanisms of organo-sulfur derivatives in atmospheric aerosols

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Secondary organic aerosol (SOA) have an important impact on climate, air quality and human health. However the chemical reactions involved in their formation and growth are not fully understood or well-constrained in climate models.

It is well known that inorganic sulfur (mainly in oxidation states (+IV) and (+VI)) plays a key role in aerosol formation, for instance sulfuric acid is known to be a good nucleating gas. In addition, acid-catalyzed heterogeneous reactions of organic compounds has shown to produce new particles, with a clear enhancement in the presence of ozone (Iinuma 2013).

Organosulfates have been detected in tropospheric particles and aqueous phases, which suggests they are products of secondary organic aerosol formation process (Tolocka 2012). Originally, the production of organosulfates was explained by the esterification reaction of alcohols, but this reaction in atmosphere is kinetically negligible. Other formation pathways have been suggested such as hydrolysis of peroxides and reaction of organic matter with sulfite and sulfate radical anions (SO_3^- , SO_4^-) (Nozière 2010), but it remains unclear if these can completely explain atmospheric organo-sulfur aerosol loading.

To better understand the formation of organo-sulfur compounds, we started to investigate the reactivity of S^{IV} species (SO_2 and SO_3^{2-}) with respect to specific functional groups (organic acids and double bonds) on atmospherically relevant carboxylic acids and alkenes. The experiments were carried out in the homogeneous aqueous phase and at the solid-gas interface. A custom built coated-wall flow tube reactor was developed to control relative humidity, SO_2 concentration, temperature and gas flow rate. Homogeneous and heterogeneous reaction kinetics were measured and resulting products were identified using liquid chromatography coupled with an orbitrap mass spectrometer (LC-HR-MS). The experiments were performed with and without the presence of ozone in order to evaluate any impact on the S^{IV} oxidation and product formation.

Preliminary results reveal that oxidation of S^{IV} species can occur under a variety of atmospherically relevant conditions. Furthermore, LC-HR-MS analysis confirms the formation of organo-sulfur compounds that could derive from sulfate and/or the sulfite radical anion. These results elucidate the role of organo-sulfates aqueous and interfacial chemistry, important for our scientific understanding of atmospheric SOA formation.

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