

MODEL SOA DERIVED FROM CATECHOL AND GUAIACOL AND ITS HALOGENATION PROCESSES

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Secondary organic aerosol (SOA) was produced from the aromatic precursors catechol and guaiacol by reaction with ozone in the presence and absence of simulated sunlight and humidity and investigated for its properties as a proxy for Humic-Like Substances (HULIS). Beside a small particle size, a relatively low molecular weight and typical optical features in the UV/VIS spectral range, HULIS contain a typical aromatic and/or olefinic chemical structure and highly oxidized functional groups within a high chemical diversity. Various methods were used to characterize the secondary organic aerosols obtained: Fourier transform infrared spectroscopy (FTIR) demonstrated the formation of several carbonyl containing functional groups as well as structural and functional differences between aerosols formed at different environmental conditions. UV/VIS spectroscopy of filter samples showed that the particulate matter absorbs far into the visible range up to more than 500 nm. Ultrahigh resolved mass spectroscopy (ICR-FT/MS) determined O/C ratios between 0.3 and 1 and observed m/z ratios between 200 and 450 to be most abundant. Temperature-programmed-pyrolysis mass spectroscopy (TPP-MS) identified carboxylic acids and lactones/esters as major functional groups. Particle sizing using a condensation-nucleus-counter and differential-mobility-particle-sizer (CNC/DMPS) monitored the formation of small particles during the SOA formation process.

Reactive halogen species (RHS), such as X·, X₂ and HOX containing X=chlorine and/or bromine, are released by various sources like photo-activated sea-salt aerosol or from salt pans, and salt lakes. Despite many studies of RHS reactions, the potential of RHS reacting with secondary organic aerosol (SOA) and organic aerosol derived from biomass-burning (BBOA) has been neglected. Such reactions can constitute sources of gaseous organohalogen compounds or halogenated organic matter in the tropospheric boundary layer and can influence physicochemical properties of atmospheric aerosols. Model SOA from -pinene, catechol, and guaiacol was used to study heterogeneous interactions with RHS. Particles were exposed to molecular chlorine and bromine in an aerosol smog-chamber in the presence of UV/VIS irradiation and to RHS, released from

simulated natural halogen sources like salt pans. Subsequently, the aerosol was characterized in detail using a variety of physicochemical and spectroscopic methods. Fundamental features were correlated with heterogeneous halogenation, which results in new functional groups (FTIR spectroscopy), changes UV/VIS absorption, chemical composition (ultrahigh resolution mass spectroscopy (ICR-FT/MS)), or aerosol size distribution. However, the halogen release mechanisms were also found to be affected by the presence of organic aerosol. Those interaction processes, changing chemical and physical properties of the aerosol are likely to influence e.g. the ability of the aerosol to act as cloud condensation nuclei, its potential to adsorb other gases with low-volatility, or its contribution to radiative forcing and ultimately the Earth's radiation balance.