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Formation, ageing and thermal properties of secondary organic aerosol

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Abstract

In order to properly represent and predict the effects of aerosol in climate systems, an accurate description of their formation and properties is needed. This thesis describes work done to increase the knowledge of processes and properties of atmospherically relevant secondary organic aerosol (SOA) from both biogenic and anthropogenic origin. The common theme for these projects is the use of a Volatility Tandem Differential Mobility Analyser (VTDMA) setup, which in combination with other observations has generated insight into both detailed chemical mechanisms and physical processes that eventually could be suitable for testing in air quality or climate models. During the course of this work, the experimental facility the Gothenburg Flow Reactor for Oxidation Studies at low Temperatures (G-FROST) and the VTDMA setup, as well as a corresponding data evaluation methodology, have been improved and refined.

Thermal properties could be linked to both formation and ageing processes of SOA. Using a VTDMA setup, where the thermal characteristics of SOA were measured at a range of evaporation temperatures, a sigmoidal fit to the data enabled parameterisation of their volatility properties. The parameters extracted were e.g. the temperature corresponding to a volume fraction remaining of 0.5 ($T_{\text{VFR}0.5}$) and the slope factor (S_{VFR}), which are measures of the general volatility and the volatility distribution of the condensed phase products, respectively. A higher $T_{\text{VFR}0.5}$ indicates lower volatility, while an increase of S_{VFR} states a broader distribution of vapour pressures. The response of these parameters from changes in experimental conditions could be linked to processes occurring both in the gaseous and the condensed phase. In photo-chemical experiments, the change in $T_{\text{VFR}0.5}$ and S_{VFR} could be described using the OH dose.

The gas phase processes were found to be very important for SOA ageing, driven mainly by OH radical exposure in the outdoor chamber SAPHIR. However, processes in the condensed phase, such as plausible non oxidative ageing processes and non-liquid behaviour of SOA particles, were also observed.

Detailed studies of ozonolysis of the boreal forest monoterpenes β -pinene and limonene were enabled by precise control of reaction conditions using the G-FROST. The experimental findings in response to e.g. water and radical conditions emphasized the difference in ozonolysis reaction paths between endo- and exocyclic compounds. The results support the recently suggested decomposition of the stabilized Criegee Intermediate via the hydroperoxide channel in ozonolysis of β -pinene.

Keywords

volatile organic compounds, biogenic, anthropogenic, secondary organic aerosol, troposphere, volatility, ozone