Characterization of selected compound classes in secondary organic aerosol from biogenic VOCs by HPLC/MS

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Abstract

The formation of secondary organic aerosol (SOA) plays an important role in earth’s aerosol budget and can affect climate and health. SOA is formed by the reaction of volatile organic compounds (VOCs) from anthropogenic and biogenic sources with reactive atmospheric species like ozone, NOx radicals or OH radicals. Some efforts were made to reveal the structure and chemical composition of the formed aerosol, to get a closer look at formation pathways and mechanisms. Unfortunately, a large fraction of formed products are still ambiguous. However, a general understanding exists about the most important VOC precursors, the fundamental underlying gas-phase chemistry and the major particle-phase products. During the first years of SOA research attention was paid to the carbonyl and carboxylic oxidation products, both important compound classes formed in the photodegradation and ozonolysis of biogenic VOCs. Recent studies show that also other product classes with different functionalities, such as esters, peroxides or organosulfates, have to be considered in order to understand the detailed chemical mechanisms leading to SOA as well as to predict the aerosol mass loadings. For the identification and quantification of these three compound classes as well as for carbonyl SOA compounds, LCMS is the most appropriate analytical methodology. This contribution tries to shortly summarize the work that has been done for the determination of SOA related carbonyl acids as well as present new LC/MS/MS results on the characterization of esters, peroxides and organosulfates, if necessary, supported by on-line MS. In contrast to earlier work, the mass spectrometric characterization of the individual compounds is always based on the comparison with authentic reference compounds.

Motivation

• Characterization of organic compound classes by HPLC-MS
• Applying the results to different SOA systems
• Identification of the characterized substance classes in SOA
• Clarification of the underlying formation mechanisms
• Connecting laboratory studies to ambient SOA samples

HPLC-ESI(-)-MS

• HPL system (Agilent Technology GmbH, Germany)
• Column: Vanian Pursuit XRs 3 CB
• Electrospray ionization MS, HCTplus (Bruker Daltokin GmbH, Bremen, Germany)

Table 1: Synthesized ester structures and retention times in LC-MS/MS chromatograms

Table 2: Organosulfates: structures and retention times in LC-MS/MS chromatograms

Table 3: Organic peroxides: structures and retention times in LC-MS chromatograms

Conclusions / Outlook

Substance classes show characteristic fragmentation patterns: esters, organic peroxides and organosulfates.

Esters: formation of quasi-molecular ion of SO2OH and neutral loss of organic moiety.

Organosulfates: formation of quasi-molecular ion of SO2OH and neutral loss of corresponding dicarbonyl acid and neutral loss of alcohol moiety.

Organic peroxides: neutral loss of hydrogen peroxyde (H2O2) during ionization step.

Identification of esters in cyclohexene SOA.

Complete structural clarification of the unknown oligomers.

Clariﬁcation of the reaction mechanism in the atmosphere.

References:

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