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*Analysis of Secondary Organic Aerosol from Isoprene and Butadiene with Hyphenated Mass Spectrometry*

## **Abstract**

Atmospheric aerosol (AA) originates from direct emissions or transformation of various volatile organic compounds (VOCs) emitted by biogenic and anthropogenic sources, and resides in the lowest layer of the atmosphere – the troposphere. Chemical reactions of volatile organic compounds with oxidizing reagents present in the atmosphere, like hydroxyl radicals ( $\bullet\text{OH}$ ), ozone ( $\text{O}_3$ ), and nitrate radicals ( $\text{NO}_3\bullet$ ), are driven by solar radiation and play a significant role in the chemistry of the troposphere. Therefore, the troposphere can be perceived as a chemical reactor where thousands of gas-phase, heterogeneous and aqueous-phase reactions produce a complex mixture of products. Fine aerosol particles ( $\text{PM}_{2.5}$ ) of primary and secondary origin are a significant constituent of AA as they influence weather and climate directly by scattering incoming solar radiation and indirectly by acting as cloud condensation nuclei (CCN) in clouds formation and ice nuclei (IN) in ice crystals formation. They affect human health and cause respiratory, cardiovascular, infectious, and allergic diseases, as they are efficiently transported into the thoracic and tracheobronchial regions of the respiratory system. Secondary organic aerosol (SOA) is a substantial part of  $\text{PM}_{2.5}$  particles, however only 10–15% of the organic species in SOA have been successfully and reliably identified so far (Prather et al., 2008; Noziere et al., 2015; Glasius and Goldstein, 2016).

In my Ph.D. thesis, I focused on the identification of unrecognized SOA components in the  $\text{PM}_{2.5}$  fraction formed from two different aerosol precursors – isoprene (2-methylbuta-1,3-diene, ISO) and buta-1,3-diene (13BD) – using UPLC–MS techniques. The studies conducted can be divided into five stages: (1) investigation of the chemical composition of aerosol formed in the smog-chamber experiments from two precursors – isoprene and 1,3-butadiene; (2) determination of the influence of relative humidity and acidity on the formation of identified ISO and 13BD SOA components; (3) comparison of smog-chamber results with

ambient aerosol samples collected in rural (Diabla Góra, Zielonka) and polluted sites in Poland (Godów, Kaskada); (4) proposal of molecular structures for identified novel SOA components based on product ion mass spectra and high-resolution MS measurements (when authentic standards were unavailable), and confirmation of other compounds (organic hydroxy acids) with commercially available or synthesized standards; (5) quantification of significant and novel components of isoprene and butadiene SOA in field samples with reference to smog-chamber results on the influence of RH and acidity on SOA formation in the atmosphere.

The two investigated compounds – ISO and 13BD – are homologs, however, they are emitted into the atmosphere from totally different sources. Isoprene is the most abundant and widely studied biogenic VOC, while 1,3-butadiene is a VOC of anthropogenic origin. The formation of SOA from ISO and 13BD was examined in collaboration with the U.S. Environmental Protection Agency (EPA) in a series of experiments conducted in an in-door smog chamber. The effect of relative humidity and acidity of seed aerosol on the formation of ISO and 13BD components was investigated. Contrary to other studies, the concentrations of the majority of ISO and 13BD compounds detected and the total yields of secondary organic carbon (SOC) decreased with increasing RH level, more sharply in experiments with acidic seed than non-acidic. Thus, the increase of the liquid water content of an aerosol system did not promote the formation of ISO and 13BD organosulfates (OSs), nitrooxy- (NOSs) and nitrosooxy- organosulfates (NSOSs). Under acidic conditions and low RH levels, the formation of isoprene and butadiene products containing sulfate moieties was enhanced comparing to non-acidic conditions at the same RH level.

The observed ISO- and 13BD-derived products were thoroughly characterized using UPLC–ESI–HRMS technique followed by the interpretation of obtained analytical data, including product ion mass spectra with accurate mass measurements. All mass spectrometric analyses were performed in the negative ion mode, as the investigated compounds had reasonable ionization efficiencies to deprotonated ions ( $[M-H]^-$ ). The molecular structures of newly identified compounds were elucidated. Several novel SOA components were discovered i.a.: 3-methylthreonic acid organosulfate (MW 230), 2-methylthreonic acid nitrooxy-organosulfate (MW 275), and 2-methyltartaric acid organosulfate (MW 244) in ISO SOA; and glyceric acid organosulfate (MW 186), malic acid organosulfate (MW 214), threonic acid organosulfate (MW 216), and 1,2,3,4-butanetetrol nitrooxy-organosulfate (MW 247) in 13BD SOA. Those compounds were also found in ambient aerosol from trace to substantial amounts. The chemical structures proposed for highly oxygenated acids formed

from ISO and 13BD were based on the product ion mass spectra and confirmed against appropriate synthesized or purchased standard compounds. The syntheses of novel ISO hydroxy organic acids – 2-methyltartaric acid (2-MTA) and 2- and 3-methylthreonic acids (2-, 3-MTrA) were performed. The compounds were proposed as highly oxygenated molecular (HOM) tracers of aged isoprene aerosol as they were also found in ambient aerosol samples in amounts ranging from 0.8 to 2.8 ng m<sup>-3</sup> on average.

In order to prove the link between smog-chamber experiments and ambient atmospheric processes, the UPLC–ESI–HRMS analyses of fine ambient aerosol (PM<sub>2.5</sub>) samples collected at four various sites in Poland were conducted. High concentrations and diversity of isoprene SOA components detected in Zielonka (Bory Tucholskie) and Diabla Góra (Puszcza Borecka) sampling sites revealed a large share of terrestrial vegetation in local emissions. The total amount of detected ISO-derived organosulfates and nitrooxy-organosulfate at those sampling sites were 474.9 ± 149.3 ng m<sup>-3</sup> and 324.0 ± 76.0 ng m<sup>-3</sup>, which accounted for approx. 7.9% and 7.1% of the total OC mass, respectively. The most abundant compounds were 2-methyltetrol NOS (MW 261) and 2-methyltetrol OS (MW 216), which contributed significantly to the mass of ISO SOA. Moreover, Zielonka ambient aerosol was the richest one in 13BD SOA components containing sulfate moieties, although not as chemically diverse as in ISO SOA. The total amount of detected compounds was 14.0 ± 5.3 ng m<sup>-3</sup>, which accounted for 0.24% of the OC mass. Besides, malic acid organosulfate (MW 214) was the most abundant OS detected (13.3 ± 5.0 ng m<sup>-3</sup>). Moreover, malic acid, a known secondary organic aerosol tracer was a highly abundant 13BD-derived component at all investigated sites. The greatest amounts of those compound was detected in Zielonka at the level of 93.7 ± 31.7 ng m<sup>-3</sup>. The sources of two mentioned compounds in the atmosphere could be direct 1,3-butadiene emission and biomass burning in nearby households. 1,2,3,4-butanetetrol OS (MW 202) was not detected in ambient aerosol, while its analogue 2-methyltetrol OS (MW 216) formed from isoprene was a highly abundant key tracer of ISO SOA.

This Ph.D. thesis presents results of the comprehensive studies on the chemical composition of isoprene and 1,3-butadiene SOA, which forms in the troposphere, the lower part of the Earth's atmosphere. Advanced research tools, including smog chambers and hyphenated mass spectrometry techniques were used for that purpose. The influence of relative humidity and acidity on the formation of individual 13BD and ISO SOA components was examined. Revealing ISO and 13BD SOA composition under laboratory conditions enabled the firm identification of the complex composition of ambient aerosol. The results

presented may fill the gaps in understanding of chemical transformations of isoprene and butadiene in the atmosphere and the formation of secondary organic aerosol from those precursors. Several significant and novel <sup>13</sup>BD- and ISO-derived components were identified and their concentrations were determined both in smog-chamber experiments and ambient fine aerosol. Moreover, organosulfates and other SOA components detected in this study are expected to enhance the capacity of ambient aerosol as cloud condensation nuclei (CCN) impacting the air quality. The data obtained in this study will pave the way for better description of the complex and time-varying chemical composition of SOA and may improve the performance of air quality models.