

Impact of initial reactants concentrations and reaction time on secondary organic aerosol (SOA) composition produced by ozonolysis of limonene

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Atmospheric aerosols have significant impact on both climate and human health and the organic compounds can compose up to 90% of the mass of atmospheric particulate matter. It is well known that oxidation of natural volatile organic compounds (NVOC) leads to secondary organic aerosols (SOA) formation.¹ Biogenic VOC emission account for 90% of the global non-methane VOC emission. The main NVOCs introduced into the atmosphere are isoprene together with monoterpenes and limonene accounts for approx. 20% of the total monoterpene emission. Limonene is present in significant quantities in both ambient atmosphere as well as in the indoor environment^{1,2} and due to presence of two double bonds this monoterpene has a high SOA-forming potential when reacted with atmospheric oxidants.³

The presented work had two main goal: development of the analytical method for studying limonene SOA composition and subsequently apply this new methodology to analyze composition of aerosol formed under different conditions in the flow reactor. This study was carried out in order to gain insights into formation mechanism of SOA formed during ozonolysis of limonene.

Reaction of limonene (1-10 ppm) with ozone (0.1-2 ppm) under dark and dry conditions (RH \approx 5%) was carried out in the flow reactor and the reaction time was varied from approx. 3 min to 30 s; no OH radicals scavenger was used. This experimental setup is a significantly more advanced system as compared to the reactor used in our previous study.⁴ It was possible to precisely control the reaction conditions, therefore SOA formation in the new reactor was highly reproducible.

Aerosol composition was studied with liquid chromatography (LC) coupled to the negative electrospray ionization tandem mass spectrometry (triple quadrupole mass analyzer) and to the high resolution MS (time-of-flight mass analyzer). By carrying out LC/MS analysis it was possible to separate several structural isomers, elucidate the structures of the detected aerosol components and unambiguously distinguish between dimers and non-covalently bonded clusters formed during widely used direct-infusion ESI analysis.⁵ Presented results include elucidation of the initial stages of particles formation and possible formation mechanisms of the detected oligomers.

References

- (1) Walser, M. L.; Desyaterik, Y.; Laskin, J.; Laskin, A.; Nizkorodov, S. A. *Physical Chemistry Chemical Physics* **2008**, *10*, 1009-1022.
- (2) Nazaroff, W. W.; Weschler, C. J. *Atmospheric Environment* **2004**, *38*, 2841-2865.
- (3) Hoffmann, T.; Odum, J. R.; Bowman, F.; Collins, D.; Klockow, D.; Flagan, R. C.; Seinfeld, J. H. *J. Atmos. Chem.*, *26*, 189-222.
- (4) Witkowski, B.; Gierczak, T. *Atmospheric Environment* **2014**, *95*, 59-70.
- (5) Kundu, S.; Fisseha, R.; Putman, A. L.; Rahn, T. A.; Mazzoleni, L. R. *Atmos. Chem. Phys.* **2012**, *12*, 5523-5536.