Review doctoral thesis of M. Sc. Kumar Sarang, entitled:

Atmospheric Secondary Organic Aerosol: Kinetic and Chemical Studies of in-Cloud Reactions of Selected Plant Volatiles

General comments:

The doctoral thesis research addresses an important gap in our knowledge of the role that volatile organic compounds (VOCs) play in the formation of secondary organic aerosol (SOA). It is well established by now how the major VOCs, including isoprene and monoterpenes, contribute to biogenic SOA (BSOA) formation, but the role of other VOCs, such as green leaf volatiles (GLVs), has remained rather unclear. However, GLVs may be emitted into the atmosphere in specific circumstances of plant stress and should not be ignored. This work is thus inspired by a real need for enhancing our knowledge on the role of GLVs, knowledge which is needed to improve climate models and support environmental policy. Three plant volatiles were selected, i.e., 1-penten-3-ol (PENTOL), (Z)-3-hexe-1-ol (HEXOL), and (E)-2-hexen-1-al (HEXAL), a choice which is very appropriate, as the latter is formed from an abundant polyunsaturated fatty acid, i.e., α-linolenic acid, which is released from plant cell membranes and converted through the lipoxygenase/ hydroperoxide lyase pathway, and the other GLVs, HEXOL and PENTOL, are derived from it. To explore the role of these plant volatiles and their participation in the formation of aqueous-phase biogenic SOA, the research strategy consisted of performing kinetic as well as chemical studies. The kinetic studies involved studies of the aqueous-phase reaction of the GLVs with sulfate, hydroxyl and nitrate radicals, whereas the chemical studies dealt with product studies on the OH-radical-mediated aqueous-phase oxidation of GLVs. The analytical methodology employed in the work, capillary gas chromatography/mass spectrometry (cGC/MS) and reversed phase liquid chromatography/mass spectrometry (rpLC/MS) is state-of-the-art and selected rationally. Below, I will provide additional detailed general and specific comments on the various chapters of the thesis, but I can only comment on the chapters that are within my area of expertise.

Chapter 1. Introduction to atmospheric aerosols and their chemistry

This chapter provides a thorough review of atmospheric aerosol, including aerosol formation, tropospheric aerosol chemistry, biogenic organic compounds as precursors of secondary organic aerosol, atmospheric oxidants, kinetics of atmospheric reactions, reactions of BVOCs with oxidants, formation of radicals, etc.

Specific comment: Page 27 – line 3 from bottom: The author writes: “Their sources are usually anthropogenic, e.g., vehicular and industrial emissions, ….”. I do not agree with this statement and correction is needed. Fine particle formation has been very well documented above forests on warm sunny days resulting in the

phenomenon of “blue haze” formation. See, for example, the article by C. Went (Nature 1960, 187, 641-643) and more recent articles by M. Ehn and coworkers.

Chapter 2. Research background and objectives

This chapter provides necessary research background information, and reviews the current state-of-the-art of atmospheric chemistry and significance of green leaf volatiles. However, I missed in this chapter important background information on the generation of GLVs from plants. A major leaf volatile, HEXAL, covered in this thesis, is formed from a polyunsaturated fatty acid, i.e., α-linolenic acid, which is released from plant cell membranes and converted through the lipoxygenase/ hydroperoxide lyase pathway. See, for example, the article by Hatanaka. The biosynthesis of green odor by green leaves, Phytochemistry 1993, 34, 1201-1218.

Chapter 3. Instrumentation, techniques, and methods

In this chapter, the various experimental techniques used throughout the research are well documented. With regard to the parts on mass spectrometry techniques, the techniques selected, i.e., cp-GC/MS and rp-LC/MS are state-of-the-art and properly selected for applications in atmospheric chemistry. With regard to terminology, I recommend to follow the IUPAC recommendations for terms relating to mass spectrometry; see article by K. K. Murray, R. K. Boyd, M. N. Eberlin, G. J. Langley, L. Li, Y. Naito. Definitions of terms relating to mass spectrometry. IUPAC Recommendations 2013. Pure Appl. Chem., 85, 1515-1609, 2013. For example, the abbreviation “MS” is reserved for “mass spectrometry” and should not be used to refer to the instrument.

Chapter 4. Physical properties of green leaf volatiles (GLVs)
Chapter 5. Aqueous-phase reaction of green leaf volatiles with sulfate, hydroxyl and nitrate radicals in troposphere: kinetics and atmospheric implications
Chapter 6. Evaluating bias of the experimental rate constants determined for the aqueous-phase reactions of selected GLVs with NO_3

These three chapters are fine with me and contain a wealth of relevant kinetic data, but they are beyond my expertise.

Chapter 7. Product studies on the OH radical-mediated aqueous-phase GLV photooxidation

This chapter deals with product studies on the OH radical-mediated aqueous-phase oxidation of GLVs, using a combination of mass spectrometric techniques and theoretical calculations to unravel the very complex photo-oxidation chemistry. This approach is very sound and well chosen. Many studies have been undertaken in the past but much less thoroughly than in the present study. Relevant reactions have

been examined in detail, i.e., the reactions of PENTOL, HEXAL and HEXOL with the OH radical, thereby using the cp-GC/MS technique for detecting reaction products of the alcohol type and carbonyls, HPLC-PDA/UV for detecting UV-sensitive reaction products, and rp-ESI-MS for detecting polar reaction products. The proposed reaction schemes are very informative and are nicely presented in Schemes. The characterization of the polar product $C_6H_{10}O_2$, formed upon photo-oxidation of HEXAL, has been investigated in great detail, including DFT calculations.

Chapter 8. Summary and future perspective

The summary and future perspectives are fine with me.

Technical comments:

The thesis is well structured, the tables and figures are fine, but it does not read fluently because of the English usage, which makes it difficult for a reader not to be distracted and to focus on the scientific content. A thorough language-edited revision is recommended for correct English style and grammar. There is especially a problem with the correct use of both definite and indefinite articles, hyphens, commas, tenses, terminology, consistent use of US English, etc. In the attached annotated manuscript I have provided numerous suggestions for corrections. A very useful reference that I have used as a bible throughout my entire career is: The American Chemical Society Style Guide: A Manual for Authors and Editors. I have used an old (1986) edition but recent editions are available.

Conclusions

This doctoral thesis work is of high scientific quality and contains a very valuable and comprehensive dataset, which will be appreciated by the international atmospheric community. Proof for this is that part of the work has already been published in leading international journals and thus has been reviewed by peers. Based on the high scientific content of this thesis, I recommend that this work can be defended in public and deserves a high grade.

Waasmunster, 4 March 2022

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