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Review of the doctoral dissertation by Kumara Sarang: **Atmospheric Secondary Organic Aerosol: Kinetic and Chemical Studies of in-Cloud Reactions of Selected Plant Volatiles**

The doctoral dissertation presented by Mr. Kumar Sarang, M.Sc., titled: Atmospheric Secondary Organic Aerosol: Kinetic and Chemical Studies of in-Cloud Reactions of Selected Plant Volatiles presents experiments and quantum-mechanical calculations whose main goal was to test the hypothesis that three selected green leaf volatile compounds (GLV) could be a missing source of secondary organic particles (SOA) in the atmosphere through in-cloud reactions with radical species. To verify this hypothesis, the author investigated the kinetics of aqueous-phase reactions of three GLV compounds with hydroxyl (OH), sulfate (SO_4^-), and nitrate (NO_3) radicals. Additionally, the mechanism of the reaction of GLV compounds with hydroxyl radicals was experimentally investigated. To get more insights into the reaction mechanism and structures of identified oxidation products, the density functional theory (DFT) was used for quantum calculations. Mr. Kumar Sarang chose the following green leaf volatile for his research: 1-penten-3-ol (PENTOL) (Z)-2-hexen-1-ol (HEXOL) and (E)-2-hexene-1-ol (HEXAL).

The subject investigated by Mr. Kumar Sarang is very relevant, and at present, it is an area of major incompatibilities in atmospheric chemistry. Secondary organic aerosol accounts for a significant fraction of ambient tropospheric aerosol and detailed knowledge of the formation, properties, and transformation of SOA is therefore required to evaluate its impact on atmospheric processes, climate, and human health. Meanwhile, the attempt to establish a realistic SOA budget in the atmosphere encounters a significant discrepancy. The SOA

estimation using the bottom-up approach and the comparison with the top-down approach is not matching. The difference is large. Therefore, it is necessary to find new additional formation processes to the already known processes of SOA formation. One of such processes may be the formation of so-called $_{aq}$ SOA, as a result of GLV compounds oxidation. Mr. Kumar Sarang in his work investigates the importance of these processes, which may potentially lead to the explanation of the discrepancy.

The reviewed dissertation is very extensive, 309 pages long, including an appendix and a list of references (504 positions). In my opinion, the work is unnecessarily long, and some fragments could be removed from it. The results of Mr. Kumar Sarang's experiments and calculations are presented in 8 chapters. The work begins with information about the author's achievements, then the abstracts (in English and Polish) are followed by an introduction, research background, and objectives with a short one-page presenting the aim of this work (key objectives). Then the author describes the experimental methods and techniques and physical properties of some GLV compounds. The next four chapters contain the main information on kinetic measurements, product studies, including theoretical calculations. The dissertation ends with chapter "Summary and future perspective" followed by an appendix and a list of references.

Chapter 1 "Introduction to atmospheric aerosol chemistry" is short, only 24 pages. It is a text that briefly and clearly presents basic information on aerosols, the main precursors of secondary aerosols (Biogenic Volatile Organic Compounds), and gives a brief lecture on the basics of chemical kinetics. This short introduction is followed by Chapter 2, "Research background and objectives", which is much longer (40 pages). A large part of this chapter contains a description of the gas-phase oxidation reactions of GLV compounds, which is not the subject of the author's research. This part of the dissertation could be significantly shortened and rather placed in the introduction. Especially that the information presented therein is described in an excellent review publication, co-authored by Kumar Sarang (Kumar Sarang, Krzysztof Rudzinski, Rafal Szmigielski, Green Leaf Volatiles in the atmosphere - properties, transformation, and significance, Open access, Atmosphere 2021, 12 (12), 1655). Chapter 2.5 is a very important part of the dissertation. Firstly, the author presents a short but convincing

explanation of the choice of GLV compounds taken for consideration. Secondly, the author formulates the goal of his work.

In the next extensive chapter (chapter 3; 33 pages), the author describes the experimental techniques, details of experiments performed, and the computational methods used (COPASI and DFT). The chapter is clearly written, although some information, for example, on the UV-Vis spectroscopy (see e.g. Fig. 3.2, Fig.3.3, Table3.1, etc.) as well as the description of other instrumental techniques are quite general and could rather be included in the introduction, or even omitted. On the other hand, much more details should be given to the description of kinetic experiments carried out. The description of the kinetic measurement technique used, the laser flash-photolysis long path absorption (LFP-LLPA) is very sparse. It is a pity since two different kinetic approaches used in this work: absolute kinetic measurement of the rate coefficients and the relative rate kinetic technique are state-of-art methods. The rate coefficients for reaction of $\text{SO}_4^{\cdot-}$ and NO_3 radicals were measured differently than the rate coefficients for the reaction of GLV compounds with OH radicals. In the case of kinetic measurements of the reaction of hydroxyl radical with GLV compounds, a very clever approach was used, and in fact, it was a relative rate method measurement.

In chapters 4, 5, 6, and 7, the results of measurements and theoretical calculations carried out in this work are described (112 pages).

Chapter 4 presents estimates of the fundamental physicochemical constants needed for later calculations of atmospheric lifetimes and GLV compounds removal rates. Here, the results of the UV-Vis spectra of the series of GLV compounds (not only the spectra of three selected by author GLV compounds) were presented. These measurements include additionally: (Z) - 3-hexenyl acetate, methyl salicylate and 2-methyl-3-buten-2-ol. The spectra of GLV compounds are very important information, both necessary for kinetic experiments and, as well as for the understating of GLV compound's pathways of removal from the atmosphere.

Chapter 5 describes one of the major achievements of this work - kinetic experiments in the aqueous phase. The results of kinetic measurements presented in Chapter 5 and the thermodynamic values calculated on their basis are extremely valuable experimental materials. However, I would like to state once again that this part of the work is sparse in the details of

kinetic experiments. Additionally, the results for COPASI modeling of NO_3 reactions with GLV compounds should be rather presented in chapter 5.3.3, not in a separate chapter. (Whole chapter 6 is not necessary.) The experiments presented in chapter 6 convince the reader that the rate coefficients for reactions of NO_3 with GLV compounds are not biased due to the additional, unwanted chemical reactions in the experimental reaction system. This information is necessary to quote the final values of rate coefficients for NO_3 experiments. The reaction rate coefficients presented in chapter 5 are fundamental for the calculation of atmospheric lifetimes and removal rates of GLV compounds. The calculated atmospheric lifetime of reactions of GLV compounds with investigated radicals allowed the author to propose that the reaction with hydroxyl radicals is the main sink for GLV compounds in the aqueous phase. This conclusion prompted the author to investigate this reaction in more detail. To understand well the role of chemical transformations of GLV compounds in the atmospheric waters, not only kinetic parameters are needed, but also the knowledge of the reaction mechanism and the product yields are necessary. These processes were investigated by the author and are described in the next chapter.

Considerations on the mechanism of the reaction of the hydroxyl radicals with GLV compounds, and calculations supplementing these experiments, are presented in chapter 7. The author exposed OH radical precursor and GLV compounds to light simulating the sunlight. The resulting products were determined using GC/MS or LC/HRMS techniques. The detected products allowed to propose the reaction schemes for the reaction of GLV compounds with the hydroxyl radicals. Additionally, the author performed calculations using the group contribution method (GCM) and density functional theory. In general, the GCM and DFT calculations confirmed the correctness of the author's conclusions of the experimental findings of the reaction mechanisms. Particularly interesting and important is the determination of the place of the hydroxyl radical attack on GLV compounds; whether it joins a double bond or whether the reaction is a hydrogen atom abstraction from the C-H bond. These are very essential mechanistic considerations that make a significant contribution to modern knowledge in the field of oxidation reactions of unsaturated organic compounds in atmospheric chemistry. On the other hand, in the reappearing chapter, atmospheric implications (chapter 7.4), the lifetimes of GLV compounds in the reaction with the hydroxyl radical presented in Table 7.6 are in some

contradiction to those shown in Figure 5.9. (Urban aerosols; $[\text{OH}]_{\text{aq}} = 3.5 \times 10^{-15} \text{ mol L}^{-1}$ according to Table 5.8). Moreover, in chapter 7.4 reader may find a description of the “flux analysis” calculations. What is the difference between flux analysis and removal rates, the calculations described in chapter 5.5.2? Is there any difference between these chapters? It seems that it would be much clearer if there is only one chapter in the dissertation describing Atmospheric Implications.

Chapter 8 - Summary and future perspective. The author presents briefly and clearly the results of his extensive work and forecasts further trends in the aqueous chemistry of GLV compounds.

In conclusion, I would like to state that the bimolecular rate coefficients for reaction of GLV compounds with OH, NO₃, and SO₄⁻ presented in this dissertation, their temperature dependencies, the obtained thermochemical parameters, and information on the mechanisms of OH reactions, constitute fundamental information necessary to understand the issue of participation of GLV compounds oxidation processes in atmospheric waters in the possible formation of secondary organic aerosols. All the information gathered in this dissertation is of high value. It is safe to say that Mr. Kumar Sarang is a mature scientist with extensive experience.

The work has also some shortcomings. It is too large and, on the other hand, there is a lack of details relating specifically to kinetic experiments. Also, the Atmospheric Implications should be collected and discussed in one chapter.

Therefore, I conclude that the doctoral dissertation of Mr. Kumar Sarang meets all the conditions for doctoral dissertations specified in art. 187 ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz.U. z 2018 r., poz. 1668 ze zm.) and I request the author to be admitted to further stages of the procedure.