Atmos. Chem. Phys. Discuss., 14, C12671–C12678, 2015
www.atmos-chem-phys-discuss.net/14/C12671/2015/

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on "Formation and chemical aging of secondary organic aerosol during the β-caryophyllene oxidation" *by* A. Tasoglou and S. N. Pandis

A. Tasoglou and S. N. Pandis

spyros@chemeng.upatras.gr

Received and published: 17 March 2015

This manuscript by Tasoglou and Pandis presents detailed aerosol physical and chemical results obtained from smog chamber experiments examining the formation and chemical aging of secondary organic aerosol (SOA) during the beta-caryophyllene oxidation. Specifically, this study generated SOA from the ozonolysis of beta- caryophyllene and the OH-initiated oxidation of beta-caryophyllene under low-NOx (no NOx added where H2O2 photolysis was employed to generated OH) and high-NOx (where HONO photolysis was employed to generated OH) conditions. In this study, the authors ambitiously set out to measure the SOA yields (and thus derive fitting parameters us-

ing the VBS approach that could be used in chemical transport models), examine the effect of UV light and temperature on these SOA types, examine the volatility and the effective vaporization enthalpy of these SOA types, and then conduct chemical aging of the SOA as it continues to react with OH radicals.

1. *In the abstract and even in the main text, it wasn't always clear how exactly the chemical aging was performed. From carefully looking through all the details, it appears that only the SOA generated from beta-caryophyllene ozonolysis was aged with OH radicals. This is fine, but I think this should be more clearly written in the abstract.*

We have clarified in the revised abstract that we study the aging of the beta-caryophyllene ozonolysis products with OH radicals.

2. *In the opinion of this reviewer, there is a lot of territory the authors are trying to cover and not much time is spent on each item to carefully discuss the details of how some of the data were interpreted exactly. For example, deriving SOA fitting parameterizations from these experiments using VBS could be its own paper, especially if the authors more carefully address how the SOA yields are corrected for vapor wall losses. Since their stated objective for this paper "is to measure the amount of aerosol produced by reaction of beta-caryophyllene with ozone and hydroxyl radicals and suggest aerosol yield parameterizations for atmospheric chemical transport models" then I think the authors have to seriously consider the potentially important wall losses of vapors, especially since there is not seed aerosol used in these experiments. How can the authors be justified that vapor wall losses from large beta-caryophyllene oxidation products are negligible when determining SOA yields? Have the authors tried measuring select vapors by PTR-MS or CIMS to see how large these can be? I can imagine if you used substantial seed aerosol to compete with the wall of your chamber, you would find that aerosol yields would even be higher, as observed by Kroll et al. (2007) for aromatic VOCs. I don't think this effect can be neglected, especially for potentially*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

large and sticky oxidation products produced from beta-caryophyllene oxidation. This issue is one of the main reasons I suggest major revision for this paper.

This is a fair point. We have provided additional information in the revised paper about the calculation of particle and vapor wall losses. Please also see our responses to comments 7 and 8 of the previous reviewer. More specifically we have performed additional experiments with various amounts of seeds to estimate the magnitude of the vapor wall losses to the Teflon walls. We have also tried different reaction timescales (the longer the timescale the higher the corresponding losses). Our conclusion is that there are such losses in the beta-caryophyllene system, but they are modest (less than 30 percent in most cases) due to the fast kinetics of the system. These additional results and the corresponding analysis are included in the revised paper.

3. *In addition, I have several specific comments below that need to be considered in a revision below. Overall, I do find these experiments very interesting and important to have published in the literature, and certainly Atmospheric Chemistry and Physics would be an appropriate venue for such information once these issues are carefully considered by the authors.*

We do appreciate the constructive criticism of our work.

Specific Comments:

4. *Acronym usage: Be consistent with acronyms or chemical formulas. If you define it earlier in the text, then why not use it instead of spelling it out again? I noticed this for several acronyms and formulas used. For example, VOCs and ozone.*

We have improved the use of acronyms throughout the revised text.

5. *Introduction: Why not reference work by Chan et al. (2011, ACP) and Offenberg et al. (2009, EST), that showed that beta-caryophyllene SOA can be enhanced due to*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

aerosol acidity? Since aerosol pH is now known to be lower than pH 2 in southeastern U.S. (Guo et al., 2014, ACPD, and other recent work from the GA Tech groups), the effect of aerosol acidity on beta-caryophyllene SOA formation is worthy of mention in the introduction since this effect is explained in part due to the increased formation of organosulfates and other hydrolysis reaction products. It now appears that particle-phase reactions cannot be neglected.

We do mention in the revised introduction that aerosol acidity can enhance the SOA formation in this system together with the corresponding references. This effect was not investigated in the current work.

6. *Experimental Section: Were any experiments done to confirm that OH + 2-butanol doesn't contribute to any measurable SOA, especially in the presence of some sort of low-volatility seed (like sulfate aerosol)?*

We have tested the possibility of formation of aerosol from the reaction of OH and 2-butanol in the presence of ammonium sulfate seeds. There was no detectable organic aerosol formation for the conditions used in our experiments. This information has been added in the experimental methods section.

7. *Should the authors explain more how the HONO was collected and stored from the combination of the H2SO4 solution and sodium nitrite solution? How was it then handled upon injection into the chamber?*

We have added the corresponding information. A fresh solution of HONO was produced and used in each experiment so there was no need for storage.

8. *I'm curious why the authors didn't consider the effect of seed aerosol on the SOA yields, and thus, the potential importance of vapor wall losses that could affect the yields. Work by Ehn et al. (2014, Nature Letters) recently showed that extremely low-volatility organic compounds (ELVOCs) were produced from alpha-pinene + O3 and*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

OH and found that seed aerosols could help prove their existence. I think a careful treatment like this could help to better constrain the SOA yields.

We have followed the reviewer's suggestion and performed four additional ozonolysis experiments in the presence of high concentrations of ammonium sulfate seeds. The results of these experiments were added in Table 1 and Figures 2 and 3. The corresponding yields were consistent with the yields of the non-seeded experiments but at the high range of the corresponding variability. The SOA O:C in the seeded experiments was the same as in the non-seeded ones. We are using these results together with those of experiments where we tried to expose the ozonolysis products to OH as fast as possible to estimate the magnitude of these vapor losses. These losses appear to be modest (less than 30 percent) possibly because of the rapid reaction rates leading to fast nucleation and growth of particles as soon as the reactants are both in the chamber.

9. *Results and Discussion - Oxidation by OH: The authors should note that Chan et al. (2011, ACP) did observe nitrated products, such as nitrated organosulfates in beta-caryophyllene SOA providing evidence of the NOx effect.*

In the revised document we have added a sentence about the formation of nitrated organosulfates and their effect on the SOA yield together with a reference to Chan et al. (2011).

10. *Results and Discussion - Chemical Aging of beta-caryophyllene SOA: The test of RH seems weak if you are only considering 2 RH conditions and only conducting 1 experiment at each condition. Shouldn't this be repeated to confirm re-producibility of this result? How does the DMA/SMPS system behave at high RHs like 90 percent? Is the sheath air from the chamber or is it dried sheath air and can this affect the sizing measurement? How will the latter affect your SOA yield measurements? For the high-RH experiments, I wonder if the authors used ammonium sulfate seed aerosol if they* *would contain higher liquid water contents (LWCs) than the pure SOA they generated via nucleation? That is, would you have LWCs with sulfate seed aerosol that would more directly mimic conditions like that commonly found in the S.E. USA? How would this aerosol water affect chemical aging?*

We agree that the small number of experiments at high RH limits the generality of their results. We have qualified the corresponding conclusions in the abstract and the conclusions sections stating that these were based on a limited number of high yield experiments.

The SMPS sheath air flow was not dried and therefore the SMPS measurements were at a RH similar and a little lower of that in the chamber chamber. The hygroscopic growth of beta-caryophyllene SOA has been investigated by Alfarra et al. (2012). The corresponding water uptake even at 90 percent RH was low (diameter growth factor of 1.03 on average) and therefore any increase in the volume of the particles should be less than 10 percent. This is no mentioned in the revised paper in the discussion of the corresponding experiments.

Our experiments with ammonium sulfate seeds were all at low RH. The interactions of aerosol water and the SOA compounds in this system requires an additional detailed study.

11. *Even if the SOA mass didn't change, how confident are the authors from just AMS data that nothing in terms of functionality changed in the SOA upon exposure to UV light and OH under low NOx conditions? For example, how stable are the potential organic peroxides produced in this system? I always worry when conclusions are only being made with AMS data, which typically is used for measuring bulk chemical properties of SOA and not detailed changes in SOA composition. For the latter, techniques like GC/MS, LC/MS or even FTIR might be useful to consider.*

This is a fair point. In the revised manuscript we state clearly that there was no change

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

in the AMS spectra of the corresponding SOA. This stability of the spectra does not necessarily prove that there were no chemical changes in the particles. Unfortunately, we did not use other analytical techniques in the specific experiments.

12. *Finally, one thing I think needs to be stressed here more clearly is are the authors trying to examine heterogeneous oxidation of SOA by OH or both aging of particles and gases? This needs to be made more clear and if the former was the goal is the current setup the best approach for that? I wonder if flow tube studies would be warranted if the goal was to examine chemical aging due to heterogeneous oxidation by OH radicals?*

Oxidation of gas-phase compounds are contributing to the changes in SOA mass concentration and O:C ratios. However, we cannot eliminate the possibility of OH oxidation taking place at the same time and contributing to the changes. Studies in which the gas-phase organic compounds were not present (or were present at much lower levels) are needed to separate the effects of homogeneous and heterogeneous reactions in this system. We now make this point explicitly in the revised manuscript.

13. *Results and Discussion - Vaporization Enthalpy of beta-caryophyllene SOA: If the authors are hoping that the vaporization enthalpies measured could be used by modelers, why not provide error bars on these estimates?*

We have added in the manuscript the estimated uncertainties of the effective enthalpies of vaporization for each system.

14. *In general, can the authors make sure to provide error bars for their reported data?*

We have added a discussion of the uncertainties of the estimated yields. The major source of uncertainty appears to be the correction due to wall losses of vapors for the fresh SOA and vapors and particles for the aging experiments and not the uncertainty of the various instruments and measurements. We prefer not to add explicitly the error bars in the diagrams to avoid misleading the reader about our understanding of these uncertainties. We believe that published yield uncertainties of less than 10 percent in past smog chamber experiments have proven to be unrealistic. The variability of our experimental results (e.g., Figure 2) does suggest uncertainties of the order of 30 percent.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28919, 2014.