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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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Overall Comments and Recommendation:

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 parame-

ters using 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. 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. 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 parametrizations 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 parametrizations 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 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. 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.

Specific Comments:

1.) 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.

2.) Introduction:

Why not reference work by Chan et al. (2011, ACP) and Offenberg et al. (2009, ES&T), that showed that beta-carophyllene SOA can be enhanced due to 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-caropyhllene 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.

3.) Experimental Section:

a.) 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)?

b.) 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?

c.) 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 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.

4.) 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.

5.) Results and Discussion - Chemical Aging of beta-caryophyllene SOA:

a.) 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 reproducibility of this result? How does the DMA/SMPS system behave at high RHs like 90%? 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?

b.) 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.

c.) 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 flowtube studies would be warranted if the goal was to examine chemical aging due to heterogeneous oxidation by OH radicals?

6.) 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?

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

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