Atmos. Chem. Phys. Discuss., 14, C12643–C12655, 2015
www.atmos-chem-phys-discuss.net/14/C12643/2015/

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: 16 March 2015

This study investigates the SOA formation from -caryophyllene ozonolysis and photooxidation. A series of perturbation experiments were conducted to test the effects of UV, continuous aging with OH, and relative humidity on SOA yield and composition, which are important and relevant. My main concern is that the wall-loss correction method introduced by Pathak et al. (2007) might not be applicable for this multi-generation system. A kinetic model is needed to understand the time scale of gas-phase oxidation steps. Moreover, although the paper is well organized, details about the experimental results are not well explained. Comparisons to previous stud-

ies are needed and inconsistencies need to be explored. I think this article requires substantial revision before considering for publishing.

The issue of the wall loss corrections is addressed in our responses to comments 7 and 8 below. We have provided the necessary evidence to justify our use of the Pathak et al. (2007) correction method for this fast reacting system. We have also performed a number of additional experiments (discussed in comment 8) to quantify the magnitude of vapor losses to the Teflon walls in this system and we have found them to be similar or lower to our experimental variability. We have added the necessary text providing additional experimental details and also improving the comparisons with previous work.

Specific comments

1. *Abstract, Line 6-8: The SOA yield highly depends on reaction conditions (residence time, oxidant level, temperature, RH, etc.). Loading is not the only determinant. The information listed here seems a bit misleading.*

We have added the rest of the conditions of the experiments (room temperature, very low RH, and excess of oxidants) to the abstract for completeness.

2. *P28921, Line 9: BVOC also include some oxygenated compounds (Atkinson and Arey, 2003).*

We have rephrased this sentence adding the oxygenated biogenic compounds (methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, etc.) to the list of biogenic VOCs.

3. *P28921, Line 15: β-caryophyllene is not always the most abundant sesquiterpene. Many sesquiterpenes remain unidentified. Emissions from different trees/environment are also different.*

We have rephrased the sentence. We now just state that β-caryophyllene is often one of the most abundant sesquiterpenes.

4. *P28922, Line 2-3: Chen et al. (2012) reported a range of SOA yields depending on the ozone level. Why is there only one value (24.3 percent at 10 μg/m3) used when comparing to other studies? Also, how did the authors obtain this value of 24.3 percent? This value is not reported in Table 2 of Chen et al. (2012).*

The corresponding value was calculated by interpolation of the data provided by Chen et al. (2012) to facilitate comparison with other studies. We have replaced this with a sentence explaining better the findings of Chen et al. (2012), discussing the SOA dependence on the ozone level, and then mentioning the measured values for different ozone levels.

5. *P28922, Line 3-5 and Line 10-11: Ng et al. (2006) and Lee et al. (2006a, b) reported the results from the same set of experiments, which should not be considered as two independent studies. I also cannot find the value of 53 percent yield in Ng et al. (2006).*

Indeed the studies of Ng et al. (2006) and Lee et al. (2006a, b) used the same experimental data. In the revised manuscript we describe them together as one study. We have deleted the reference to the Ng et al. (2006) study from this second paragraph.

6. *P28922, Line 19-24: The authors should include many other important reasons that explain the different SOA yields observed in different studies. For example, ozone concentration is insufficient for first-generation products to continue oxidation in Winterhalter's study, leading to lower yields. Relative humidity and temperature also affect the yield.*

This is a valid point. In the revised manuscript we explain that other differences among the various studies including the relatively low ozone levels used by Winterhalter et al.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

(2009), temperature, and relative humidity can explain, at least partially, the different yields reported.

7. *P28923, Line 10-15: In this study particle wall losses are calculated by Pathak et al (2007)'s method that assumes size-independent loss rate and is developed for monoterpene ozonolysis with seed injection. However, it is known that particle wall losses depend on size (VanReken et al., 2006; Pierce et al., 2008). Are the studied populations (without seed) similar to those in Pathak's study? At least the wall-loss rate for smaller particles formed at the beginning is expected to be greater than that for larger particles. As the size of the studied population changes, especially after perturbations (e.g., temperature change in Fig.1), how would the wall-loss rate change? Moreover, unlike monoterpene, sesquiterpenes have two double-bonds that involve multi-generation reactions in prolonged timescale. The SOA mass concentration is a balance between wall losses and the production. The production may take hours (especially for photooxidation experiments) depending on the conditions. How do the authors pick "no chemical-production periods" (Pathak et al., 2007) to derive the wall loss rate constant? The authors need to clarify the difference and convince the readers that Pathak's method is still applicable here. If not, a new method (maybe a multi-step kinetic model) is needed to derive the wall losses under assumptions.*

We agree with the reviewer that the wall loss corrections (probably the Achilles heel of smog chamber experiments) deserve additional discussion and justification.

The first important point is that relatively high oxidant levels are used in this study and therefore the reaction times are short resulting in relatively low losses to the walls during these periods. For example, for all our ozonolysis experiments the time for the first reaction step is of the order of tens of seconds, while the second around 20 minutes. To ensure that these reactions were completed the particle wall loss rate constants were estimated at least one hour after the beginning of the reactions. For example, the corresponding wall loss rate constants estimated for all the ozonolysis experiments were 0.31± 0.11 h^{-1}.

A second issue was the stability of these rate constants with time during each experiment. To test this we estimated them for different sub-periods of each experiment. For example, for Exp. 6 we calculated a wall loss rate constant of 0.29 h^{-1} for the 50-100 min period (with R^2=0.98), also 0.29 h^{-1} for the 100-150 min period (with R^2=0.99), and 0.28 h^{-1} for 150-200 min (with R^2=0.99). Similar results were obtained for other experiments during periods in which the reactions in the system were assumed to be completed.

To ensure that the rate constants were estimated during periods in which the reactions rate were very low or zero we used three different criteria. The first was the theoretical estimates of the reaction times described above. The second was the use of periods in which the AMS O:C ratio was ratio. The third was the testing of sub-periods to make sure that there was change in the corresponding constant.

The use of a time-independent value for the correction (even if sub-100 nm particles are lost in general faster than larger particles as the reviewer correctly notes) is justified by the fact that particles in our experiments grew to sizes above 100 nm in less than 20 minutes. Therefore the period during which losses may have been different was small and the resulting uncertainty also small. We are estimating for this fast reacting system that the uncertainty in the yields introduced by the particle wall loss correction is of the order of 20 percent.

Changes in temperature do result in significant changes of the loss rate constants in our chamber. For example, in Exp. 1 when the temperature was increased from 20 to 40 degrees C the particle loss rate constant increased from 0.26 to 0.46 h^{-1}. This increase is due to the increased ventilation outside the chamber which leads to increased turbulence inside the chamber and thus increased losses. We have estimated and used different loss rate constants for periods with different temperatures in the same experiment.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

We have added a new paragraph in the revised manuscript summarizing the various issues related to particle wall loss corrections in our experiments and also providing the necessary justification for our use of the relatively simple Pathak et al. (2007) correction method for this fast reacting system.

8. *P28923, Line 22-23: The gaseous semi-volatile products, especially second generation products present for much longer lifetime than precursors in the chamber system. I am not convinced that "negligible wall loss of organic vapors" can be assumed. Maybe this sentence is just misplaced because in Table 1 and 3, yield are reported for w=1.*

We have corrected for vapor losses to the particles deposited on the chamber walls using the w=1 approach of Hildebrandt et al. (2011). This approach assumes that mass transfer from the chamber to the walls is fast and the particles on the wall behave as if they were suspended in the chamber. However, we have assumed that direct losses of vapors to the Teflon are low in this system and can be neglected.

To test this hypothesis we have performed four additional experiments using ammonium sulfate seeds. The use of the seeds increases the surface area of the aerosol in the chamber and should reduce any artifact related to vapor losses to the Teflon. The yields of these experiments (shown in the revised Figure 2) are not different from the rest of the yields. This suggests that the magnitude of losses of vapors to the walls for this fast reacting system are of the same order as the variability of the yields calculated in the rest of the experiments.

We have added a paragraph discussing the losses of vapors to the walls of our chamber and also the additional experiments performed to investigate the potential magnitude of these losses in this system.

9. *P28925, Line 1-2: This procedure confuses me. A figure is helpful to understand exactly how the reactant concentration is achieved. If the injection of β-caryophyllene takes an hour, how could the injection affect your results and wall-loss correction (with* *dilution and addition of reactant)? Particularly for Exp. 31 (Fig. 7), adding HONO starts before 30 minutes, i.e., before finishing the purge of β-caryophyllene injection line.*

Indeed, mentioning the 1 hr purge time that was used in a couple of test experiments in which we injected the ozone first and the β-caryophyllene next is making this part of the experimental description rather confusing. We have rewritten this paragraph clarifying that the purging time was 10-20 min for most experiments (with the exception of the test experiments where we kept purging for an hour). We also clarify that the injected air volume was less than 0.3 cubic meters (less than 3 percent of the chamber volume) so the dilution effect was minimal. The accuracy of the estimated concentration based on the injected β-caryophyllene amount was checked in selected experiments with the PTR-MS.

10. *P28926, Line 6: See my comment above (9), should "at time zero" be "at time zero to 1h"?*

The injection of the reactants was completed in approximately fifteen minutes in this experiment with the ozone injection first. Time zero corresponds to the completion of the injection of both reactants. This is now explained in the revised manuscript.

11. *P28926, Line 13-21: The reported density and O:C are much lower than the values reported in Chen et al. (2012). Chen et al. (2012) also showed that the SOA density and O:C ratios vary with SOA concentration, which seems not shown in this study (values are rather constant for a wide range of SOA concentration). Why? For the derived density, how big is the uncertainty? Also, H:C should be reported. The AMS O:C and H:C ratios are biased low (Chen et al., 2011; Canagaratna et al., 2014). Are the reported ratios corrected? Has the elemental analysis considered organonitrates (Farmer et al., 2010), especially for high NOx experiments?*

The difference in O:C between this study and Chen et al. (2012) is partially due to the use of the Aitken et al. (2008) fragmentation table in this study, while the Chen et al.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

(2011) approach was used in the latter. This is now explained in the revised manuscript and the effect of the fragmentation table choices is discussed.

The densities that we estimated for the ozonolysis experiments are lower than the Chen et al. (2012) values and their uncertainty was approximately 0.1 g m^{-3} so it can only explain part of the discrepancy. The approaches that were used for the density estimation are different (we matched the full distributions of the AMS and the SMPS while Chen et al. (2012) relied on the corresponding mass mode diameters). The variation of composition with size (seeds were used and there could be more organics condensing on the smaller and less on the larger particles) could introduce some additional uncertainty in the Chen et al. (2012) approach. We do mention in the revised manuscript these differences in the findings of the two studies.

We have added in the paper the H:C values for the different SOA types. They were all close to 1.5. Their values for the aging experiments are now included in Table 3. We also mention that the organonitrates were not included in the elemental analysis.

12. *P28926, Line 22, Fig. 2, and Table 2: Chen et al. (2012) reported three sets of yield, which differ in the fraction of first- to second-generation conversion. Only data at 200 ppb ozone are considered as close to "ultimate" yield. It seems inappropriate to use all of them together. While comparing to Chen et al. (2012), what are the estimated mean conversions of first- to second-generation for each of your experiments? The data in Fig. 2 are quite scattered. Can the reaction timescale explain some of the scattering? Does temperature and RH lead substantial difference (25 C, 40 percent RH in Chen et al. (2012) vs 20 C, dry in this study)? If temperature does, the authors should convert data based on the measured enthalpy.*

We have followed the reviewer's suggestion and excluded from Figure 2 and the analysis leading to Table 2 the Chen et al. (2012) which may not correspond to the "ultimate" yield. The excluded data points are those with SOA concentrations above 10 μg m^{-3} and ozone concentrations less than 200 ppb. The results of the analysis do not change substantially (a few percent).

For the conditions used in our experiments (ozone equal to 300 ppb or more and 293 K) the lifetime of β-caryophyllene is less than 15 seconds while the lifetime of its first generation products should be less than 20 minutes. Given that all our experiments covered periods much longer than these timescales, the incomplete reactions cannot explain the observed scatter in the yields. We performed a few experiments at higher RH and the yields did not appear to be substantially different from the low RH experiments. Finally the small temperature difference can explain only a few percent of the difference. Uncertainties in losses of vapors and particles and the reacted VOC are probably responsible for most of the scatter in Figure 2.

We have updated Figure 2 and Table 2 in the revised paper and we have also added a brief discussion of the uncertainty of the results and the corresponding scatter.

13. *P28927, Line 17 and 26 (also P28926, Line 15): The reported CE values are low. Chen et al. (2012) reported a CE of 1. Can you explain why? What are the CE values for high relative humidity experiments?*

We estimated a CE=0.58±0.12 for the ozonolysis experiments under low RH conditions. Docherty et al. (2013) reported an even lower AMS CE of 0.36 ±0.01 for β-caryophyllene ozonolysis SOA under dry conditions. The CE in our higher RH experiments (Exp. 30 and Exp. 31) was around 0.5 similar to the experiments under dry conditions. We believe that the difference between our study and Chen et al. (2012) is probably due to AMS instrument differences.

14. *P28927, Line 26: Has ozone concentration been measured during those experiments? Would the combination of ozone (generated) and OH pathways contribute to the difference as well?*

The ozone formed in these experiments was a few ppb so its contribution to the SOA formed was small. This is consistent with the differences in the AMS spectra of the SOA formed during the ozonolysis and the OH experiments.

15. *Figure 4: It is difficult to look at the ion markers through the dotted spectra. I suggest plotting the mass spectra separately. The fact that SOA produced by ozonolysis has lower peak at m/z 43 and greater peak at m/z 44 is consistent with the observed greater O:C. However, the O:C ratio for high-NOx SOA is greater than the ratio for low-NOx SOA when the spectra look similar. Why? I think it is better to show high-resolution spectra which may provide more information about various ions.*

We have redrawn Figure 4 so that now the ion markers can be seen clearly. The apparent discrepancy was due to the selection of spectra from specific experiments. In the revised paper we include the average spectra and now the differences in O:C can be seen.

16. *P28928, Line 25-28 and P28929, Line 4: Is first paragraph misplaced? I am confused about which experiments have used OH scavenger. Several in Table 1? Or Just Table 3. Please clarify (maybe add OH scavenger information in the tables.)*

The OH scavenger was used only in experiments 1-14 summarized in Table 1. We refer to these as simple ozonolysis experiments. The order of the paragraphs is probably creating the confusion. We have changed their order in the revised manuscript and also stated clearly in the Tables using the appropriate footnotes the use of OH scavenger.

17. *P28929, Line 1: Higher by what percent? Please be specific.*

We now clarify that this yield can be as much as a factor of two higher than that of the ozonolysis reaction depending on the conditions.

18. *P28929, Line 8-11: What is the definition of "no change"? What does this result mean?*

We have rephrased this sentence. We now state the angle between the two mass spectra was less than 2 degrees indicating that they were practically the same.

19. *P28930, Line 1-10: What reaction leads the increase of SOA mass concentration? Gas-phase oxidation of semi-volatile products (first- or second- generation) or heterogeneous oxidation? The discussion of Exp. 29 ended hastily. Do you conclude that the increase of SOA mass concentration in Exp. 29 support the wall loss of organic vapors (i.e., the negative artifacts)? Please be specific about the reasoning.*

Gas-phase oxidation and transfer of the corresponding later generation products to the particulate phase can probably explain the increase in SOA mass concentration and the change in O:C. However, we cannot eliminate the possibility of existence of heterogeneous processes that also contribute to this increase. We have added a sentence making this point in the revised manuscript.

The results of Experiment 29 do support the wall loss of organic vapors to the walls (an artifact of around 30 percent). We have tried to address this point further performing several additional experiments with different amounts of seeds. The results do suggest such artifacts of the order of 20-30 percent. These are similar to the uncertainty of our experiments but they do appear to be present. We describe the additional experiments and analyze these artifacts in the revised paper.

20. *P28930, Line 14-16: Is this result consistent with other's finding? Winterhalter et al. (2009) showed elevated yield when RH increased. How would you compare the scavenging of reactive Criegee intermediates in your system to other studies? Why the maximum reached so earlier in Exp. 31 compared to other experiments in Fig. 1 and Fig. 5?*

Our results are not consistent with those of Winterhalter et al. (2009) regarding the effect of RH as we did not see a significant effect on either the SOA yield or the O:C for the ozonolysis experiments. However, there are numerous experimental differences in the two studies so it is difficult to draw any firm conclusions about what is causing this discrepancy. We do mention the difference in the conclusions in the revised paper.

The earlier maximum in experiment 31 is mainly due to a much higher wall loss rate constant for this experiment compared to the others. It was 0.42 h^{-1} compared to 0.28 h^{-1} for Exp. 1. These faster losses led to an earlier decline of the concentrations by 15 min or so compared to other experiments.

Technical corrections:

21. *P28294, Line 25: What is "organic volume"? Liquid volume? Please clarify.*

We have clarified this by stating that it is the organic mass injected.

22. *P28925, Line 22: Brief descriptions about AMS data analysis (e.g., RIE) and elemental analysis are needed.*

We have added the recommended brief description of AMS data and elemental analysis.

23. *P28926, Line 1: Add "Table 3".*

Done.

24. *Figure 2: "solid line" instead of "dashed line"?*

Corrected.

25. *P28928, Line 5: NO3 should be the nitrate ion form. Add one sentence about why organonitrates being detected as nitrate signal by the AMS and reference Farmer et al. (2010).*

We added the explanation and the reference.

26. *P28928, Line 20-21: "lower m/z 43" should be "lower relative intensity of m/z 43 (i.e., f43)". What is θ angle? Please explain.*

We have made the suggested correction and added the definition of the angle theta at this point together with a reference.

27. *Figure 4: Add label for y axis.*

We added the missing label.

28. *P28929, Line 23: Add "at" before "m/z 43".*

Done.

29. *P28930, Line 11: Revise "SOA corrected mass" (wall-loss corrected SOA mass concentration?). Similarly, P28930, Line 26.*

Done.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper