

Interactive comment on “Chemical and isotopic composition of secondary organic aerosol generated by α -pinene ozonolysis” by C. Meusinger et al.

Anonymous Referee #1

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Chemical and isotopic composition of secondary organic aerosol generated by alpha-pinene ozonolysis by Meusinger et al.

The paper reports a study for secondary organic aerosol (SOA) produced in a large continuous-flow chamber by ozonolysis of α -pinene. SOA was produced by the chemical reaction(s) of α -pinene with ozone in the gas-phase, and the produced SOA was sampled on fiber filters, and followed by analysis using a thermal desorption (TD) system coupled with a proton-transfer reaction ionization mass spectrometry (PTR-MS) for product identification/quantification of fragment ions from SOA components and with a stable isotope ratio mass spectrometry (IRMS) for their stable carbon isotope ratios ($d_{13}C$). SOA substances on the filter samples were heated to six (or seven) different

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temperatures in the TD apparatus to desorb the SOA components, and the evaporated substances/fragments of SOA components at each isothermal stage were analyzed by PTR-MS. Independently, $d_{13}C$ of the evaporated organic carbon at each stage was analyzed by the TD apparatus coupled with the IRMS. The study for isotope fractionation possibly provides valuable information to elucidate veiled production/sink processes of ambient SOA, which is one of hot topics in the subject of atmospheric science. Therefore, I think the topic is appropriate for an article of ACP.

General comments

After reading the manuscript, I had impression that points the authors argued were unclear: pieces of discussions seemed to be fragmented. I also had impression that some information and discussion (e.g., already studied C:O ratios and natural processes with isotope fractionations) were very detailed, and some (e.g., chemical reactions that lead to formation of low volatility products, calculation for predicted $d_{13}C$ in Table 5) were insufficient. In addition, the authors may want to make more focus on what they can conclude from the data they gained. For example, the position-specific isotope analysis (PSIA) sounded a key achievement in the abstract. However, if my understanding is correct, the PSIA was performed only on the unreacted α -pinene. I did not get what conclusion the authors were going to draw from the comparison of this information with $d_{13}C$ of step-wisely evaporated OCs, each of which is still possibly a complex mixture of multiple substances as indicated by more than 400 of fragment ions in the table in S4 of SI. If the authors could identify a specific product possessing enriched/depleted ^{13}C atom at a specific position, which may have originated from a specific position of α -pinene, they should make discussion with the observed evidence (e.g., the difference in $d_{13}C$ between the different samples). Lack of reaction mechanism for production of SOA from ozonolysis of pinene was also a problem to follow the discussions. At last, I was impressed that the goal of this study the authors state at the end of introduction was not convincing to me. The authors may want to thoroughly revise the manuscript, including these points. The followings are specific comments.

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Specific comments

P3I2-3: the statement "Typically. . ." does not sound right. As long as I know, the direction of condensation/evaporation isotope fractionation depends on substances.

P3I10: The authors may want to use a symbol of alpha instead of epsilon for the expression of fractionation factor.

P4I20-29: The objective the authors seems to be available without PSIA. The authors should state more clearly why they need PSIA. Referring to the PSIA study for isotope fractionations by NMR, Singleton et al. (1995, JACS, doi: 10.1021/ja00141a030) should be included. I recommend to reorganize this paragraph.

Section 2.1: α -pinene from different suppliers presented in Table 1 should be stated. Also, I recommend to present a figure for the chemical structure with carbon number for α -pinene here.

P5I10: the published year of the reference is missing.

P5I13: What did they feed through the flange?

Section 2.2.: I recommend to present an experimental scheme for flow chamber experiment.

P6I6: Provide the information of sampling flow rate. The information may give readers some idea of magnitude of artefact.

P6I20: The authors may want to rewrite the sentence like "Experiments were performed with two different OH scavenger: Experiment A with 1-butanol and Experiment B with cyclohexane."

Section 2.3.: The information presented here is the initial condition. It is preferable to present the information of extent of reaction of pinene because SOA's O:C and d13C possibly depends on it.

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P7I13: delete "with time-of-flight detector" because PTR-MS is already defined as PTR-time of flight MS.

P7I20-12: Why did the authors combine the data from the front and back filter analysis together? Please state a reason using a sentence or so.

P8I30: Equation (3) seems to use inconsistent acronym used in Table 1. Please make those consistent.

P9I1: Present the size and the supplier's name for tin capsules used.

P9I16: replace "mix" with mixture.

P10I3: "(1/e)" does not make sense. Readers will appreciate if the authors define the lifetime more specifically.

P10I12: replace "is" with was. Also "Fig.S1 and S2 in the SI" probably means the two figures in Fig. S1. Please check.

P10I13: state more specifically what "that point" is.

P10I13-14: The sentence with "good agreement" should be discussed with numbers: do they agree within their own uncertainties or standard deviations?

Section 3.1.: The authors may want to present an example time series plot of ozone mixing ratios and pinene concentrations.

P10I19: What is "(#41)"?

P10I31: replace "contain" with contained.

P11I3-16: The discussion in this paragraph is critical. Possible problem(s) causing the discrepancy between the mass conc. by filter sample/PTR-MS and by SMPS may be narrowed down using the references the authors referred. The authors should present the recovery of filter/PTR-MS measurements here.

P11I17-24: the discussion is confusing. I do not get the point of argument in this para-

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graph. Additionally, the digits of masses presented are inconsistent. Please correct those.

P11I25-31: Similarly to the previous paragraph, I do not understand the point of this paragraph. The statements are kind of common sense within chemists.

P11I32: replace “significantly” with appreciably or considerably. If you use stats in your argument, significantly would be more appropriate.

P12I11-12: “The reaction of OH. . .” seems to suggest contribution of scavenger to SOA or SOA reactions. Any discussion with references?

Section 3.2.3: I am not sure how important the results of back filter analysis are. Figure 1 tells the amount in the back filters was very small relative to the front. How will the manuscript be without the section 3.2.1? If the results are necessary to justify a point of the authors’ argument, they should write the point explicitly.

P16I10-19: The calculations for prediction of d13C are not described, although the heading of Table 5 state “details in the text”. Please provide the way to calculate those as well as factors (i.e., epsilons) used in the calculations. In addition, according to Fig 7a, OC at 100 degree Celsius (~ 7% of TC) has the largest difference of -3 permil in d13C. Any discussion for this difference? Does this difference attribute to different isotopic composition of different chemical species? This is the part the authors should make deeper discussion, I think.

P16I2033: There are papers discussing site specific isotope fractionations. Why do the authors argue with reactive isotope fractionations using the reference of sorption isotope fractionation of vanillin?

P17I1-4: As long as I read, the authors never measured d13C of residual pinene and products in the gas-phase. The statements sound too speculative.

Section 3.3.2: The section seems to discuss possible phenomena of isotope fractionations that products the authors observed may have undergone. But many of them are

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speculations. The authors may want to write the section more concisely.

Comments on Figures

The figure captions for Figure 1 and Figure 2: I do not know the difference between these figures by reading the figure captions. Please state what these are more specifically.

Figure 1: Why do the authors present the results for two back filters only? Likewise the front filters, the authors may want to present the results for all the back filters or to state a reason why not showing the rest of the results.

The figure caption for Figure 3: I don’t understand the sentence “The allows highlight. . .”. Please rewrite it.

Comments on Tables

I do not see a point presenting Table 3 because the authors do not argue with the information in this table.

Comments on Supplementary information

The authors may want to organize the SI more concisely. Please keep minimum to present extra figures and description even in SI.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-98, 2016.