

I checked the revised manuscript. The authors responded to our comments in professional manner, and attempted to reorganize the manuscript along the comments. It is intriguing to see what products the ozonolysis of alpha-pinene produces and how carbon isotopes are balanced between the gas-phase and condensed phase products. Furthermore, application of PSIA to reaction mechanism study seems to have potential to fingerprint its products in general. After reading the manuscript carefully, however, it was found that the corrections and modifications were not satisfactory and the manuscript has writing issues that need to be solved. Overall, the manuscript still needs substantial revision. The followings are some examples of writing issues I encountered.

There were many sentences that it was hard to understand. For example, in the sentence in P4L29, “If...”, I didn’t know what “depletion of the gas-phase” means, and I didn’t get the logic why depletion of ^{13}C at C9 position leads to it. For the sentence in P7L26, I could not understand what kind of correction the authors have made. The authors should make a message in every sentence clear as writing. There were also unnecessary sentences and paragraphs (I was impressed that those were unnecessary, but those may turn to be valuable, depending on for what the authors are going to explain using those sentences and paragraphs). For example, a paragraph in P3L9-18 defines a KIE and an epsilon value. However, any KIE and epsilon value for the pinene reaction never came out in the text. Those definitions may not be necessary, if the authors are not going to use the KIE in the interpretation. It is also not clear how the authors are going to discuss the observed isotope fractionation with functionalization, fragmentation, and oligomerization introduced in P3L27-P4L15. This paragraph impressed me at the beginning that the authors would discuss isotope fractionation at these reactions later to interpret the own data, but actually those were not discussed. If those are not available from own data or references, statements for combinational use of “isotope” and “functionalization (or oligomerization, fragmentation)” using one or two paragraphs may want to be avoided. Many of these things were piled up, and, at the end, I was not sure what I gained by reading the manuscript. The way to refer Supplementary Information, Tables, and Figures, also needs to be checked with the author’s guide. Many figure captions and table headings also included unnecessary description, which can be inserted in the text. For these reasons, I regret to say, but the manuscript

does not seem to be ready to be published. Thorough revision is still needed. It may be the best to revise the manuscript with professional editors for expression in English, but this does not secure to turn the manuscript well organized. It is still the authors' responsibility that the order of explanations (sentence by sentence) and discussion (paragraph by paragraph and subsection by subsection) need to be well organized prior to the English check in order to make the flow of context smooth in the final form.

It is a minor thing, but the column containing "t/h" in Table 2 has also the information of "V/m³". Those are different information and should be shown in different column. I also recommend the authors to show units in brackets instead of slash in this table for consistency (i.e., the slash of "micro g / m³" is meant a division, while the slash of "V/m³" is meant for unit.

Besides the writing issues, the followings are my responses (underlined) to the authors' comments (Italic) to my previous comments (bold). Please note that I am responding to only the authors' comments that I have opinions on. For those that I am not responding to, it is either of that I am satisfied with the changes or issues are overlapping with those I am already responding to.

General comments

After reading the manuscript, I had impression that points the authors argued were unclear: pieces of discussions seemed to be fragmented.

The discussion was overhauled and there is now a separate section 'Discussion' to allow a clearer distinction between results and discussion. Furthermore, a reaction scheme (new Figure 1) was added as suggested and used to guide the reader through the paper.

Thanks for attempting to revise along my advice, but this change is not satisfactory. I wanted the authors to focus on the important messages that the authors want to tell readers, and logically justify the arguments stepwise using own experimental results and references. The current form seems that the discussion section in the previous manuscript was just divided. The contents and arguments were still confusing. In addition, the "Results"

section in the current manuscript substantially includes authors' interpretation and discussion. It is okay to separate the "Results" and "Discussion" sections, but please give only the observed results in the "Results", and analyze and evaluate own data with references in "Discussion".

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 d13C in Table 5) were insufficient.

We have shortened the former and expanded the latter. The calculations leading to the numbers shown in Table 5 are now illustrated with an example and Table 5 was overhauled. The new reaction scheme highlights the reaction pathways that lead to the calculations in Table 5.

I was a bit confused to find "example" illustration for the calculation of position specific d13C of Dgas and Daerosol in Table 5, but the authors probably meant S5 in the Supplementary Information. I understood that the calculations were based on NMR data, which are for unreacted alpha-pinene. From the revised manuscript, however, I could not retrieve important information to explain the d13C of product Dgas and Daerosol in Table 5 using the position specific d13C of unreacted alpha-pinene.

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 a-pinene. I did not get what conclusion the authors were going to draw from the comparison of this information with d13C of stepwisely 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 13C 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 $\delta^{13}\text{C}$ between the different samples).

Thank you for your comment. It is correct that PSIA was performed on the unreacted α -pinene only. PSIA on single components of the SOA mixture is not possible at this moment. The argument is that if one dominant reaction channel prefers a certain reaction site on the α -pinene, then the position specific isotope distribution might govern the overall isotope signature. However, we cannot fully conclude that. PSIA on α -pinene was performed for the first time and we believe that this is an important result for future research and therefore chose to leave it in the abstract. Other parts of the abstract and large parts of the introduction were rewritten. A reaction scheme was added to better guide the reader in the introduction specifically when it comes to the idea that PSIA could play a role in the 'bulk' isotopic composition. This part reads now as:

“The position-specific isotope composition could yield unexpected isotopic fractionation in atmospheric aerosol. For example, the C9-atom in α -pinene is found in many small, volatile ozonolysis products as it is expelled preferentially solely due to its position during fragmentation reactions (see blue squares in Fig.1). If for example the C9-position was depleted in ^{13}C this could lead to depletion of the gas phase not caused by kinetic fractionation.”

Biased ^{13}C distribution in intra molecular carbons of pinene is interesting, and I am not going to be offensive against this finding. However, again, my point is that it is not clear how this PSIA is related to the product analysis presented in this paper. It is reasonable that the authors will combine this result with results of future compound-specific product study to explore isotope balance between the products, but those are not available at this moment. The presentation of the result here may be justified if D_{gas} and D_{aerosol} in Table 5 were calculated based on the measurement results of PSIA with reasonable assumptions. However, the assumptions (i.e., “maximum expected enrichment” and “branching ratios do not influence the isotopic composition of products”) do not sound. According to Hoefs (1997), the initial isotope ratio, the degree of processing, and the fractionation factor are needed to calculate the isotope ratio of a processing substance or product at any arbitrary time. Presumably, the authors assumed $\sim 100\%$ of degree of

alpha-pinene oxidation (“completion” in the text probably suggests this), however, this does not secure that the complex subsequent reactions also completed, depending on relative reaction speeds (relative to the speed of ozonolysis of alpha-pinene) of subsequent reactions leading to the production of formaldehyde, acetone, CO, and other products. That is, branching reactions significantly influence product isotopic composition, unless otherwise there is no isotope fractionation (i.e., KIE = 0 permil) at all of these reactions. If even only one of these branching reactions had a significant KIE, which seems more reasonable assumption according to Fisseha et al. (2009), this KIE will significantly influence the isotopic composition of remaining alpha-pinene or intermediate(s) as reactions proceeded. This varying isotopic composition of precursors will then influence the isotopic composition of products from other branching reaction channels because all or a part of products originate from the same precursor.

In the text, it is not clear what substances are defined as “aerosol” and “gas-phase”, what number of KIEs and branching ratios were used for the calculation. I am not sure what “the maximum expected enrichment” is, but if the authors assume zero of KIEs at all branching reactions and no branching reactions, I disagree with the assumptions. From the text I could not retrieve those information.

Lack of reaction mechanism for production of SOA from ozonolysis of pinene was also a problem to follow the discussions.

Thank you for your comment. We made a new figure (Fig. 1) that identifies how the site-specific α -pinene $d_{13}C$ values propagate through the reaction mechanism highlighting some key arguments of our paper. The following text was added:

“The ozonolysis of α -pinene is often used as a test system for formation of SOA; it is fairly well studied. Figure 1 shows a reaction scheme for α -pinene ozonolysis, based on the Master Chemical Mechanism (MCMv3.1) as described by Camredon et al. (2010). In the first step ozone adds into the double bond of the molecule resulting in two branches depending on the usual Criegee mechanism. These two branches proceed by stabilisation, and subsequent fragmentation and isomerization, and subsequent reaction with RO_2 , HO_2 and H_2O to yield a wide range of oxidation products from CO ,

HCHO and acetone, to many larger oxidised low volatile molecules like pinic acid and pinonic acid and pinonaldehyde. The figure shows only formation of first generation products. Further reactions including dimer formation (Kristensen et al., 2016) and oligomerization reactions are not shown.”

Thanks for providing the reaction scheme. This will definitely make readers easier to follow the discussion. However, the scheme is incomplete and not reader-friendly to follow the reaction steps producing high and low volatility products. For example, taking a look at the production mechanism of pinonic acid and pinoaldehyde in Fig. 1, I don't know what was changed after the second processing step, “stabilization”. I see that the red star mark on the carbon disappeared after the step, but what does this mean? I also don't get how “H₂O” was involved in the subsequent reaction after the “stabilization”. The same problem for the reaction with RO₂ and HO₂. The authors may want to check how other papers are presenting those reaction schemes. Second point is that the figure also does not show important elemental steps for the production of small products shown in the boxes in Fig. 1. The hidden reaction channels seem to involve reactions with C atoms, thus, must be key steps to explain the results of d¹³C calculations. Third point is that it is helpful for readers to see branching ratios in the figure.

Specific comments

P3110: The authors may want to use a symbol of alpha instead of epsilon for the expression of fractionation factor.

We rewrote the section in question and now describe the Kinetic Isotope Effect (KIE) using ϵ values, as is common practice. We believe this makes the explanation easier to follow and more clear. The replacement of ϵ by α does not change the manuscript as they are simply related by $\epsilon = \alpha - 1$ which is common knowledge within the field of isotope research (see for example Coplen, 2011). The new text now reads as:

“Kinetic fractionation results from isotope-dependent differences in reaction rates. Let ^{12}k denote a reaction rate constant for a reaction involving a compound containing only ^{12}C and let ^{13}k denote the reaction rate constant for the reaction involving a single-substituted ^{13}C isotopologue; the kinetic isotope effect (KIE) can be written as $\epsilon = ^{13}k/^{12}k - 1$. It is common to

distinguish "normal" and "inverse" KIEs."

Regarding the definition of kinetic isotope effects, Colpen (2011) defines a kinetic isotope effect as $^{12}\text{k}/^{13}\text{k}$, while Hoefs (1997) defines a fractionation factor as $^{13}\text{k}/^{12}\text{k}$. The authors may want to stick to either of these.

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

Among authors we discussed providing a plot of the ozone mixing ratios but decided against it. The main reason against it being an interference of organic vapours on the ozone detection system yielding spikes of the ozone mixing ratios. This was tested and confirmed in extra experiments, but with no conclusion / suggestion on how to resolve the issue or how to correct our data for it. An example plot is given here (Experiment B):

In order to avoid an extended discussion on operation and detection mechanisms of ozone monitors, we opted to leave the plot out. The pinene concentration was not measured.

It is very important to have information of pinene concentration change over time at least. Is it possible to present such info based on MCM calculation with given experimental condition?

In addition, according to Fig 7a, OC at 100 degree Celsius (\square 7% of TC) has the largest difference of -3 permil in d^{13}C . 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.

We suspect the reviewer was commenting on panel b of that Figure and will give our answer accordingly. The second last paragraph of section 3 discusses the strong enrichment observed at 100 C. However, the discussion has to stay vague as no clear conclusions can be drawn from the data. Unfortunately, no species or group of species could be assigned to this enrichment. We omitted the last part of the paragraph which dealt with the back filters and added another consideration based on oligomerisation. The text was changed to:

“The reason behind the enrichment in material desorbing from front filters at 100 · C cannot be unambiguously identified. The chemical analysis did not allow to identify single compounds or groups of compounds that contributed significantly more to the total aerosol concentration at 100 · C than at 150 · C and therefore could lead to the observed enrichment. Isotope effects associated with sampling artefacts, which are generally not well known, provide room for speculation on how to interpret the enrichment at 100 · C. During the negative sampling artefact, isotopically light isotopologues re-volatilise from the ensemble of sampled compounds preferentially leading to an overall isotopic enrichment in compounds that are left on the filter. Re-volatilisation should have it’s largest effect at 100 · C. Another explanation can be based on oligomerisation. Hall and Johnston (2012) observed significant evaporation of oligomers in a thermodenuder already at desorption temperatures below 100 · C. The effect of oligomerisation on isotopes is not known, but if it leads to enrichment, the fragments of decomposed oligomers could be enriched and explain our observations.”

Sorry for confusion. It is correct that I was pointing on the panel b. I think it is not necessary to deeply argue with speculation, if there is no reasonable scientific explanation for the difference. However, it is important to point out the difference explicitly and briefly state possible reasons for the difference so that others can hint for future studies to progress the science.

P16l20-33: 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?

There is not much literature available on the topic as the analysis technique is rather new. However, we now included the Botosoa et al., 2009b reference in the text and omitted speculations about bond length variations. The full paragraph reads now as:

“A more realistic set of possible explanations for the observed fractionation of SOA relative to α -pinene should include isotope-dependent changes in branching ratios in the reaction mechanism (Fig. 1) and incomplete reactions. These effects complicate the analysis significantly as new factors come into play, including most notably, kinetically-derived position-dependent isotopic fractionation. It has been shown previously in simple systems (e.g.

evaporation of solvents and sorption of vanillin) that each carbon position can have its own isotopic fractionation and that different positions can show normal and inverse isotope effects at the same time (Höhener et al., 2012; Julien et al., 2015). In chemical reactions, the substitution of a ^{12}C atom by ^{13}C will affect isomerisation and stabilisation dynamics by changing vibrational frequencies with an associated change in zero point energies. Therefore, positions that are not reaction sites can also show isotope effects, which have been termed non-covalent isotope effects (Wade, 1999), as has been observed during the chain-shortening reaction for the bioconversion of ferulic acid to vanillin (Botosoa et al., 2009b). It is generally difficult to predict which position has which isotope effect, but it has been shown that isotopic substitution in ring structures at positions that carry functional groups leads to stronger position-specific isotope effects compared to positions that have no functional groups attached (Höhener et al., 2012; Botosoa et al., 2009b). Similarly, the C-atoms in α -pinene that are not part of the ring structure might have large position-specific isotope effects. However as Höhener et al. (2012) note for the case of vanillin, and as we also show in Table 5 in a simplified scenario, such effects leave the bulk isotopic composition largely unchanged, making the use of PSIA in SOA studies beyond what has been done here potentially challenging.”

I am not sure if we are misunderstanding our comments each other, but I can find references for position specific carbon isotope fractionation at different types of chemical reactions (not for physical phenomena), such as Singleton and Szymanski (1999, JACS) and etc. Because the authors are discussing “carbon isotope fractionation” there, it is not necessary to compare only with the results obtained by NMR measurements. Carbon KIEs for elemental reactions obtained by different techniques have been studied for long, some of those may be comparable. Of course, the current reference is also okay, I think.

References

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