**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Second-generation products of $\vec{\beta}$-caryophyllene ozonolysis are the dominant contributors to particle mass concentration" *by* Y. J. Li et al.

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We thank the reviewers for the helpful comments. We address the comments below. The comments from the reviewer are labeled with [C], our response labeled with [R], and the modified text labeled with [M].

Response to Reviewer 1

[C]: While this paper is well-organized and well-written, it seems that the authors could add more materials to this paper to make it more substantial. For instance, including some gas-phase data from the PTR-MS measurements could strengthen their discussion on product volatility. Also, adding some HR-ToF-AMS data could help provide

insights into whether the 15 identified products represent substantial fraction of all the particle-phase products etc. (more specific comments below)

[R]: We understand the reviewer's broad interest in the additional data sets from the PTR-MS and the HR-ToF-AMS to complement the results presented in the manuscript from the UPLC-MS. Each of these techniques provides different information. The PTR-MS characterizes the gas phase with weak molecular resolution. The HR-ToF-AMS characterizes the average composition of the particle. The UPLC-MS provides molecular level speciation of the composition. The reviewer's call is then related to a decision about the scope of a single manuscript.

In regard to the PTR-MS, this instrument was operated in a monitoring mode at 20 m/z values so that the available scientific characterization of the gas phase is in principle limited. In the submitted manuscript, the PTR-MS was made use of as a monitoring instrument for the precursor concentration.

As indicated in the reference (Chen and Martin, manuscript in preparation), we are in the process of working on a complementary study related to the HR-ToF-AMS analysis. The analysis of the high-resolution AMS data, including detailed and new treatments of the water peaks in the mass spectrum, is an ongoing extended scientific project. We think a layout of two manuscripts is better for the readership, the first which is the present one and is focused on molecular analysis. Our judgment is that a single manuscript, including extensive treatment of the AMS water peaks, would be unhelpfully less focused for a reader. We do understand that our thinking is one of judgment and that different authors approach the topic in different ways. To be clear, we also wish to avoid subdividing all results into too many small manuscripts so that a reader is not sure which manuscript to choose and read. In the present circumstances, the science and the proposed complementary manuscripts are clearly not in this category.

Based on the reviewer's feedback, we must conclude that the manuscript as written has not communicated its major results clearly enough because the reviewer has written:

"beta-caryophyllene is one of the most well-studied sesquiterpenes and many of the oxidation products have been identified previously. In this work, 3 new products are identified. While this paper is well-organized and well-written, it seems that the authors could add more materials to this paper to make it more substantial." We therefore modified the abstract, introduction, and conclusions to highlight what are the main and important scientific results that a reader should take home from this manuscript. These include: new products and new mechanism for second-generation products; product formation under ozone-rich conditions; and a major new product with low enough vapor pressure to participate in new particle formation. New particle formation is a major intellectual challenge in the atmospheric sciences, and this manuscript's results are a key scientific result in the discussion, i.e., identification of a real and plausible organic molecule to participate in the germ event.

[C] Page 17703, line 15-25. One of the main points the authors made is that this study employs excess ozone while the previous studies are ozone-limited. With this in mind, the readers may expect the products found in this study to be quite different from the previous studies. However, among the 9 second-generation products identified in this study, 6 of them have already been identified in the previous studies even though those studies may not be considered as ozone-rich. The authors should change the wordings of this paragraph so as to avoid sounding misleading.

[R]: Of the nine second-generation products, six have been identified with the same molecular formula (isomers) in previous studies. However, in those previous studies that were performed under ozone-limited conditions, a maximum of three such second-generation products were reported. Among the nine second-generation products we observed, other than the three new ones (we call them new because the molecular formulas have not been reported before), five of them (viz. P254-2, P254-3, P270-1, P270-2, and P270-3) were isomers of those small number of second-generation products found in the literature. To clarify this point, line 18-25 in page 17703 has been revised as follows:

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[M]: ...double bonds associated with beta-caryophyllene exceeded the stoichiometric ozone equivalence. Comprehensive product characterization was performed in several previous studies regarding beta-caryophyllene ozonolysis. These studies, however, focused on first-generation products formed under conditions for which ozone concentrations were at approximately stoichiometric quantities with respect to reactions of the first double bond (Jaoui et al., 2003; Kanawati et al., 2008).

[C] Page 17704, line 21 onwards. The authors should add a table of experimental conditions in the manuscript, such as initial b-caryophyllene concentrations, ozone concentrations etc. It is not clear now how much excess ozone is present in the experiments. Also, do the 50ppb, 100ppb, and 200pb refer to b-caryophyllene concentration or ozone concentration?

[R]: The 50 ppb, 100 ppb, and 200 ppb refer to the concentrations of ozone (in excess as we controlled ozone concentration by feedback control). In one set of experiments, we fixed ozone concentration (50 ppbv) and varied the beta-caryophellene concentrations (1.7, 6.7, 13.3, and 46.4 ppbv). In another set of experiments, we fixed the beta-caryophyllene concentration (13.3 ppbv) and varied the ozone concentration (50, 100, and 200 ppbv). In this manuscript, we focused on semi-quantification results using 50 ppbv ozone and 1.7-46.4 ppbv beta-caryophyllene, which generated organic mass concentrations from 0.5 to 30 μg/m^3.

We added a table of experimental conditions (as shown in Fig. 1 in this document) in the Supplementary Materials (Table S1) and revised the corresponding description in the main text (line 22-23 in page 17704), as follows:

[M]: The ozone concentration was set to 50, 100, or 200 ppbv and was maintained constant by feedback control. Because of the feedback control, the ozone concentrations refer to the excess ozone in addition to that consumed by the reactive chemistry. For example, the feedback control maintained an ozone concentration of 50 ppbv (in excess) inside the chamber even as 46.4 ppbv beta-caryophyllene (constantly supplied

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by syringe pump injection) was reacted. We focus on the results of experiments at 50 ppbv. Same products were observed at 100- and 200-ppbv ozone conditions.

[C] Page 17708, structures of the products. According to Winterhalter et al. (2009) and Kanawati et al. (2008), secondary ozonide is a major reaction product. In this work, secondary ozonide is not observed (according to Supp. Info). It is true that the presence of water would decrease the formation of secondary ozonide. However, Winterhalter et al. (2009) performed some experiments at RH=36% which is comparable to the RH of this study (RH=40%), and still observed the formation of secondary ozonide. Do the authors have an explanation for the lack of observation of secondary ozonide in their study?

[R]: The secondary ozonide observed by Winterhalter et al. (2009) was based on FTIR observations. The C-O stretching vibration of secondary ozonides (and also likely in organic peroxides) was detected in the gas phase. We do not exclude the possibility that secondary ozonides exist in the gas phase, but gas-phase products are outside the scope of the current manuscript, which focuses on the particle-phase products. In our experiments, we did not observe secondary ozonides in the particle phase, possibly because of the following two reasons. First, the "endo" secondary ozonide (1,2,4-trioxolane), if any formed unimolecularly, should mainly exist in the gas phase in our study. The estimated vapor pressure of an "endo" secondary ozonide is 0.34 Pa, one order of magnitude higher than that of the most volatile compound we observed in the particle phase, P236 (0.042 Pa). Second, the experimental conditions of low hydrocarbon concentrations and moderately high RH in our study do not favor intermolecular reactions that form high-molecular-weight secondary ozonides in the gas phase via collision and reactions of two gas-phase molecules. We added related discussion (in line 20, page 17710), as follows.

[M]: Some other structures reported in the literature were not observed by us. In particular, secondary ozonides were inferred from infrared spectra of gas-phase reaction products (Nguyen et al., 2009; Winterhalter et al., 2009). In our results, we did not ob-

serve any mass spectral feature of secondary ozonides in the particle phase. Possible explanations are several. First, the infrared signature of secondary ozonides and organic peroxides might be similar and difficult to discriminate from each other. Second, the unimolecular reaction forms an endo secondary ozonide (1,2,4-trioxolane), which has an estimated vapor pressure of 0.34 Pa and should therefore remain mainly in the gas phase. Third, the experimental conditions of low hydrocarbon concentrations and moderately relative humidity of our study do not favor bimolecular reactions that form high-molecular-weight secondary ozonides. Without any evidence in our data for their formation, we do not consider secondary ozonides further in our continuing discussion, yet we do not exclude the possibility of their formation.

[C] Page 17710, line 8 onwards. The authors should also compare their results to other published data, including Calogirou et al. (1997) and Jaoui et al. (2003), and summarize them in the table.

[R]: The comparison shown in our manuscript (Table 1) is based mainly on the comprehensive table from Winterhalter et al. (2009), in which the results from three important studies concerning caryophyllene ozonolysis have been summarized, including the two mentioned by the reviewer. Adding the comparison of these two studies, which has been very well done by Winterhalter et al. (2009), may not add too much valuable information to the current manuscript. We have cited these three important papers (Calogirou et al., 1997; Jaoui et al., 2003; Kanawati et al., 2008) carefully in the manuscript.

[C] Page 17711, line 22. (a) By how much does the sum of the surrogate concentrations exceed that measured by the HR-ToF-AMS? This should be stated in the manuscript, otherwise the authors cannot justify that "Overestimates by the UPLC-MS method compared to the AMS method are in agreement are in agreement once these uncertainties are taken into account" and "The comparison therefore suggests that a substantial fraction of the total organic particle mass concentration is represented by the 15 identified products". (b) What are the mass fractions of each of the products identified? Do the

mass fraction of each individual product change as a function of the aerosol loading? (c) The HR-ToF-AMS data can probably provide further insights into whether these 15 identified products constitute a majority of the aerosol mass. The H:C and O:C of the 15 identified products are known, and with HR-ToF-AMS the H:C and O:C of the aerosols formed can be determined explicitly. By comparing the H:C and O:C of the 15 products (weighted by their mass fractions) and the H:C and O:C determined by the HR-ToF-AMS, the authors can then comment on whether these 15 identified products represent majority of the particle-phase products. (For reference, in Chhabra et al. (ACP 2010) it has been shown the H:C and O:C calculated from the mass-weighted average of the products agree well with those from HR-ToF-AMS measurements for a-pinene ozonolysis system).

[R]: (a) The sum of organic mass concentrations measured by the UPLC-MS method varies from two to five times higher than that measured by the AMS for the different experiments. Variance up to a factor of ten can be largely accounted for by two types of systematic errors, including the surrogate approach and the filter sampling artifact, as mentioned in the manuscript. This general agreement supports our statement that the identified 15 compounds represent a substantial part of the organic particle mass. To state this point, we revised line 8, page 17711-line 3, page 17712 as follows:

[M]: Variance up to a factor of ten between the UPLC-MS and HR-ToF-AMS can be largely accounted for by these two types of systematic errors. The conclusion, given that (2 to 5) < 10, is that a substantial fraction of the total organic particle mass concentration is represented by the 15 identified products.

[R]: (b) The mass fractions of typical second-generation products (e.g., P238 and P254-2+P254-3) decreased as the organic particle mass concentrations increased. In the caption of Fig. 6 of the revised manuscript, we clarify that the mass fraction of the first- and second-generation products are normalized by the total mass measured by the UPLC-MS method, while the mass concentrations are AMS results (Page 17726, caption of Fig. 6).

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[M]: The abscissa of organic particle mass concentration was measured using the AMS. The ordinate of mass fraction represents the mass concentrations of the first- and second-generation products divided by the sum of mass concentrations, all as measured by UPLC-MS.

[R]: (c) The results of elemental analysis will be discussed in the other manuscript (Chen and Martin, 2010).

[C] Page 17712, product volatilities. In the experimental section, the authors mentioned that a PTR-MS is employed in the experiments. Yet, no PTR-MS data have been presented in this paper (other than measuring the b-caryophyllene concentration). Including gas-phase measurements here could provide further insights to the volatility of the products and make this paper more substantial. For instance, do the gas-phase data agree well with the vapor pressure calculations (i.e., did the authors observe more of the volatile products in the gas phase?)? Also, did the authors observe any of the second-generation products in the gas phase?

[R]: As explained in greater detail above, the data of PTR-MS are not included in this manuscript. The purpose of the discussion of product volatility is to roughly compare the overall trends in volatilities of the observed first- and second-generation products. Given the available data, we cannot yet examine the absorptive partitioning theory.

[C] Page 17713, discussion about Figure 6. (a) What are the initial b-caryophyllene concentrations for these experiments? (b) How are these mass fractions estimated? Based on the surrogate approach? If so, as stated by the authors the errors should be pretty large (Page 17711). It has been shown that a substantial amount of the aerosol growth from b-caryophyllene ozonolysis is from second-generation products (Ng et al., 2006) and it is reasonable that the second-generation products will be more dominant in experiments with lower loadings based on partition theory, however, I am not sure if the authors can come to this conclusion based on the data in Figure 6 (if the errors from the surrogate approach is included in the error bars, it would make the errors

much larger).

[R]: (a) The initial beta-caryophyllene concentrations were varied (1.7, 6.7, 13.3, and 46.4 ppbv) but the ozone concentration was fixed at 50 ppbv. In this way, the different organic particle mass concentrations represented in this figure were achieved. (b) The mass fractions were estimated by the surrogate approach. Firstly, the possible errors mentioned earlier in the manuscript are systematic, and the trend of mass fractions still holds although we believe the absolute concentrations of products (both first-generation and second-generation) were over-estimated, as discussed above. Secondly, the observed trend of relative abundance in this study supports the findings in the literature that second-generation products are increasingly dominant at low loadings.

The beta-caryophyllene concentrations are included in the caption of Fig. 6. Clearer statements have been added in the paragraph of line 1-8 on page 17713 and in the caption of Fig. 6 (Page 17726).

[M]: (In page 17713, line 1-8)

The mass fractions of first- and second-generation products are shown in Figure 6 for increasing organic particle mass concentration from 0.5 to 30 μg/mˆ3. The mass fractions are calculated by dividing the individual mass concentrations of the products by the sum of their concentrations, all as determined by the UPLC-MS method using the surrogate approach. Across this range, the second-generation products are dominant by a factor of approximately 10. Toward the low-end of the concentration range, the second-generation products are increasingly dominant. This observation is consistent with the representation in Figure 5 that second-generation products are typically of lower volatility than their first-generation precursors.

(In the caption of Fig. 6, page 17726)

In these experiments, the beta-caryophyllene concentrations varied from 1.7 to 46.4

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ppbv, generating particle organic mass concentrations from the low to high values represented in the figure. The ozone concentration was 50 ppbv.

Response to Reviewer 2

Main Comments:

[C]: The authors emphasized the point that providing excess ozone relative to beta-caryophyllene was key in terms of achieving atmospherically relevant conditions, allowing second generation products to form. Is this really what happens in the atmosphere? It is well established that ozone reacts very quickly with beta-caryophyllene, however whether the available ozone molecules will go on and react with the first generation products to produce second generation products (as illustrated in this study) will certainly depend on the reactivity of ALL available VOCs towards ozone. The conclusion that the second generation products are the dominant contributors to particle mass concentration may be correct for a single precursor compound under conditions of excess ozone, but is it really correct in the real atmosphere in the presence of a huge number of reactive VOCs? The authors should discussion this point in the revised manuscript and justify their main conclusion in this regard.

[R]: We agree with the reviewer that the reactions between ozone and all available VOCs under ambient conditions are extremely complex, not to mention the influences of oxidation by other oxidants such as OH and NOx. The statement of ozone in excess under ambient conditions is made for two reasons. First, it has been widely observed that ozone concentrations even at "background" sites range from 10 to 30 ppbv (Fiore et al., 2003), and in urban areas it can be over 100 ppbv in many locations (Solomon et al., 2000). The concentrations of BVOCs, however, are normally less than 10 ppbv in forested environments (Helmig et al., 1998). Particularly in forested environments, the ozone concentration is further complicated by ozone production from the reactions of the hydrocarbon/NOx/photochemistry cycle. With more anthropogenic influence, the ozone concentration in some forested environments is observed to be highly affected

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by pollutant transport and the ozone production mechanisms (Sun et al., 2010). Second, the estimated reaction rate constant for the second double bond is higher than that of first double bond of some monoterpenes (Atkinson and Arey, 2003; Winterhalter et al., 2009). For example, the average rate constant for the second double bond to react with ozone for b-caryophyllene is estimated to be $11 \times 10\text{-}17$ moleculeˆ-1cmˆ3sˆ-1 (Winterhalter et al., 2009), while the rate constants for a number of monterpenes with ozone are less than $10 \times 10\text{-}17$ moleculeˆ-1cmˆ3sˆ-1 (Atkinson and Arey, 2003). The revised manuscript has included this discussion in line 23-25, page 17703, as follows:

[M]: In contrast, atmospheric ozone concentrations are in excess of the possible consumption by VOCs. Ozone concentrations range from 10 to 30 ppbv at background sites (Fiore et al., 2003) to over 100 ppbv in urban locations (Solomon et al., 2000). The concentrations of BVOCs, however, are normally less than 10 ppbv in forested environments (Helmig et al., 1998). Ozone is also continuously renewed in the atmospheric column whereas VOC concentrations are limited by their surface emissions.

[C]: My other main concern with this study is the use of pinic and pinonic acids as calibration compounds for the semi-quantification mode (Page 17707, lines 4-8). The authors have not really discussed the rational for this choice in any detail. This obviously has a large implication on the quantitative nature of the study.

[R]: The rationale behind using pinic acid and pinonic acid as surrogate compounds is that these two compounds contain similar functional groups (COOH and C=O) as those in the products. The ionization efficiency under electrospray ionization depends on (1) the pKa value and (2) the molecular volume of an analyte (Oss et al., 2010). The first depends on the functional groups of a molecule and the second on the carbon skeleton and functional groups. We used pinic acid and pinonic acid, which contain similar types of functional groups but different carbon skeleton, because the oxidation products from sesquiterpenes are not commercially available. These two acids have also been widely used for semi-quantification of secondary organic material from BVOC oxidation, including those from sesquiterpenes (Glasius et al., 1999; Glasius et al., 2000; Jaoui et

al., 2003; Jaoui et al., 2007). In terms of carbon skeleton, the products possess a four-member ring and two methyl groups on the ring, and the selected surrogates share these structures. The major difference is the carbon number of the carbon branches between the products and the surrogates.

[C]: How representative are those typical monoterpene oxidation products of the range of first and second generation molecules identified in the produced SOA? In addition, it is not really clear in the manuscript, whether the estimated contribution of the second generation products (_90%) to the total SOA mass is calculated using these calibrations or not? This needs to be clarified. Again, this has a direct impact on the major conclusion of the study as summarised in its title.

[R]: As stated in the response to the comment above, these two monoterpene oxidation products are structural analogues of sesquiterpene oxidation products and have been used as surrogates for quantifying products from beta-caryophyllene oxidation (Jaoui et al., 2003; Jaoui et al., 2007). The estimated contribution of the second generation products was estimated from the responses of these two surrogates. We clarified this point in the paragraph of line 2 in page 17713, as follows:

[M]: The mass fractions are calculated by dividing the individual mass concentrations of the products by the sum of their concentrations, all as determined by the UPLC-MS method using the surrogate approach.

[C]: Related to the previous point is the discussion comparing the surrogate method to the AMS measurements (page 17711 – 17712). I believe that the conclusion that the identified 15 compounds quantitatively account for most of the SOA mass is not convincing due to the following reasons:

1- The error associated with the use of pinic and pinonic acids as calibration standards (_30% as mentioned in the manuscript)

2- Artifacts related to filter sampling (_60% as mentioned in the manuscript)

3- The comparison with the AMS is not really conclusive giving that the AMS absolute concentration could change by a factor of 2 or so if the collection efficiency is not determined correctly. The discussion of the AMS data is not provided in this paper and only referenced as "in-preparation". Hence, I am not in a position to evaluate this aspect of the data.

The current version of the manuscript is not really clear on the quantitative capabilities of the analysis methods and therefore, the claim that the second generation products are responsible for most of the SOA mass is not supported enough. The revised version of the manuscript needs to address this point and either make a stronger case for it or change the emphasis of the paper to focus on the product identification and their formation mechanisms.

[R]: We agree with the reviewer that, given the possible errors and artifacts acknowledged, it is difficult to conclude at a quantitative level what fraction of the organic particle mass was measured by the UPLC-MS. As we stated in the response to reviewer 1, although the UPLC-MS method does not take into account of every single particle-phase product formed, higher but in the same order of magnitude of mass concentrations measured by the UPLC-MS method compared to the AMS method suggest that a substantial fraction of the total organic particle mass concentration is represented by the 15 identified products. In line with the reviewer's thinking, we revised the manuscript (line 28, page 17711) as follows:

[M]: Variance up to a factor of ten between the UPLC-MS and HR-ToF-AMS can be largely accounted for by these two types of systematic errors. The conclusion, given that (2 to 5) < 10, is that a substantial fraction of the total organic particle mass concentration is represented by the 15 identified products.

Other Comments:

[C]: Page 17702, Lines 17-19: What are the global emission estimates of sesquiterpenes and how do they compare to monoterpenes? i.e. how important are they as a

source or SOA?

[R]: The global emission estimate of sesquiterpenes is about 15 Tg/yr, while it is about 180 Tg/yr for monoterpenes (Seinfeld and Pankow, 2003). Monoterpenes are no doubt significant contributors of SOA and they are extensively studied. Sesquiterpenes are also important contributor to SOA formation because of their high reactivity hence high yields in SOA formation (Hoffmann et al., 1997). In a recent study, it was shown that the modeled SOA concentration doubled by including sesquiterpenes into the CMAQ model used to predict SOA formation from BVOCs, bring the prediction one step closer to the measured values (Sakulyanontvittaya et al., 2008). A sentence addressing this point is added in line 1 in page 17702.

[M]: The high particle-mass yields during oxidation have led to suggestions that this family of molecules can make important contributions to total organic particle mass concentrations (Hoffmann et al., 1997; Jaoui et al., 2003; Ng et al., 2006), perhaps even the dominant contribution near sources such as in- and above-canopy of forests (e.g., contributing to new particle formation and dominating growth of fresh particles) (Martin et al., 2010).

[C]: Page 17702, Lines 21-29: This section of the introduction mentions what other researches studied in regard to beat-caryophyllene SOA but it does not really provide any brief summary of the importance of the findings. For example, the authors mention that studies on mass yield were conducted. I think it would be a lot more informative to provide a one or two lines on the findings so that the motivation for this study becomes clear.

[R]: This section (line 26 onwards, page 17702) is modified as follows:

[M]: A particle-phase product (beta-caryophyllinic acid) first identified in the laboratory (Jaoui et al., 2003) was later found in the atmosphere (Jaoui et al., 2007) and subsequently used as a tracer of beta-caryopyllene oxidation (Hu et al., 2008). A particular focus of laboratory studies has been SOA particle mass yield, defined as

the particle mass concentration after reaction divided by the mass concentration of beta-caryophyllene consumed (Grosjean et al., 1993; Hoffmann et al., 1997; Griffin et al., 1999; Jaoui et al., 2003; Lee et al., 2006; Ng et al., 2006). The reported yields have ranged from 40% (Jaoui et al., 2003) to 100% (Hoffmann et al., 1997). The oxidation reaction mechanism has also been investigated, especially as related to the first-generation products (Jaoui et al., 2003; Nguyen et al., 2009; Winterhalter et al., 2009). The contributions of different reaction pathways to particle mass yield have been analyzed using a kinetics-based approach (Nguyen et al., 2009).

[C]: Page 17704: The introduction came to an abrupt ending. The authors should state the scope of the paper here and provide a summary of what will be presented.

[R]: The sentences as below are added to the last paragraph of the introduction.

[M]: Products formed for conditions of excess ozone were elucidated with a focus on second-generation products. Product volatilities and implications for particle formation and growth are discussed.

[C]: Page 17704, Line 9 -12: Why dry and not wet ammonium sulphate seed was used? Have the authors compared results under dry and wet conditions? Also, I think the authors should comment on the rational of their choice of quasi-monodisperse particles (50nm).

[R]: The dry ammonium sulfate particles serve as seeds for condensation of oxidation products. All experiments were conducted at 40% RH under which ammonium sulfate particles do not deliquesce to form wet particles. The influence of aqueous phase chemistry and the influence of water vapor (by using high RH) in the gas-phase chemistry are not the intention of the current study. Therefore, only 40% RH was used throughout all the experiments. The seed particle size is not anticipated to influence the results because its purpose is to serve as an inert substrate. A seed size of 50 nm is convenient because the particles grow (by condensation of organic material) to a size of several hundred nm that is amendable to the analytical instrumentation.

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[C]: Page 17704, Line 21 - 24: The initial beta-caryophyllene concentration ranged from 1.47 to 46.4ppbv, and ozone concentration was kept at 50ppbv. This means that the experiments at the high end of beta-caryophyllene concentrations were at approximately stoichiometric quantities with respect to the first double bond and unlikely to be leading to much second generation products (as per your discussion when reviewed previous work on b-caryophyllene). This potentially has an effect on the results presented in Figure 6 and should be discussed.

[R]: Ozone concentration was fixed to a desired level (50 ppbv, or 100 and 200 ppbv for other experiments) by feedback control, meaning that the ozone concentration represented the excess ozone, i.e., the amount of ozone entering the chamber must compensate for all chemistry that occurs during the experiments. So with 50 ppbv ozone concentration it refers to the conditions that ozone is in excess by 50 ppbv, instead of at approximately stoichiometric quantity with high HC concentration (46.4 ppbv). The statement that ozone is in excess in all experimental conditions is valid, and we believe that this is a unique feature of our experimental approach to ensure that the reactions were carried under more realistic conditions. The issue of ozone concentration has been clarified in the revised manuscript (line 22-24, page 17704) as below and a table (shown in this document as Fig. 1) has been added to the Supplementary Materials (Table S1), as suggested by Reviewer 1.

[M]: The ozone concentration was set to 50, 100, or 200 ppbv and was maintained constant by feedback control. Because of the feedback control, the ozone concentrations refer to the excess ozone in addition to that consumed by the reactive chemistry. For example, the feedback control maintained an ozone concentration of 50 ppbv (in excess) inside the chamber even as 46.4 ppbv beta-caryophyllene (constantly supplied by syringe pump injection) was reacted. We focus on the results of experiments at 50 ppbv. Same products were observed at 100- and 200-ppbv ozone conditions.

[C]: Page 17705: Has the sample preparation and analysis methodology described in section 2.2 been evaluated previously? i.e. has this procedure been described

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elsewhere? If it can not be referenced, then a brief discussion of the suitability of the procedure for the type of organic mixture being analysed should be provided.

[R]: The procedures of solvent extraction, SPE purification, and nitrogen concentration have been used in other studies for the preparation of organic aerosol samples and have been described elsewhere (Glasius et al., 1999; Gao et al., 2004). In the updated manuscript, a citation is included in line 20, page 17705.

[M]: For sample preparation for analysis by UPLC-ESI-ToF-MS, a modified procedure of Glasius et al. (1999) and Gao et al. (2004) was followed. The filters were extracted...

[C]: Page 17710, lines 8 - 20: The comparison to the results of the study by Winterhalter et al. (2009) attributed the differences to either detection limit or low yield. Could these differences by attributed, instead, to differences in the experimental conditions between the two studies? i.e. precursor concentration, ozone levels, aging times, humidity, etc.

[R]: We agree with the reviewer that other factors possibly contribute to the differences between the products observed in our study and those of Winterhalter et al. (2009). The attributed reasons are mainly based on a theoretical study performed by the same group (Nguyen et al., 2009). Without further information, we choose not to speculate on other reasons that cause these differences.

[C]: Page 17712, section 3.3: The authors used one method for the estimation of vapor pressure for molecular structures (Hilal et al., 2003) and concluded that compound P302 has an estimated saturation vapor pressure low enough to make it a candidate compound for involvement in atmospheric new particle formation. Barley and McFiggans (2010) have recently shown that there can be a huge range of variability in the estimated vapour pressure depending on which method is used. Has these estimates been compared to any other methods?

REFERENCE: Barley, M. H., and G. McFiggans (2010), The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric

organic aerosol, Atmos. Chem. Phys., 10(2), 749-767.

[R]: Most of the methods for vapor pressure estimation reviewed in Barley and McFiggans (2010) require critical temperature (Tc) or pressure (Pc), which are not readily available for the products of this study. Therefore, a different approach was used. A group contribution method, SIMPOL (Pankow and Asher, 2008), was used to estimate the saturation vapor pressures of the products. The estimated saturation vapor pressures do vary significantly, as investigated by Barley and McFiggans and shown in the figure below (Fig. 2 in this document). However, a general agreement within two orders of magnitude was observed for compounds from terpene oxidation (Compernolle et al., 2010) using a number of estimation methods. The same is true for the products observed in this study, whose vapor pressures are estimated by the group contribution method SIMPOL and the group contribution/interaction method SPARC. Therefore, the conclusion that P302 can be a candidate compound for nucleation is valid because the estimated saturation vapor pressure is three orders of magnitude lower than the suggested value.

This point is clarified at line 13, page 17712, as follows:

[M]: Because estimates of saturation vapor pressures can vary significantly depending on the method used (Barley and McFiggans, 2010), we also used the group contribution method SIMPOL for comparison (Pankow and Asher, 2008). The estimates of vapor pressure by these methods can differ by two orders of magnitude. Nevertheless, Fig. 5 represents 15 orders of magnitude. We restrict ourselves to conclusions that can be reached keeping in mind the uncertainties of the vapor-pressure estimates.

[C]: Page 17713, lines 16 - 18: It is suggested that most first-generation products of sesquiterpene ozonolysis are sufficiently volatile to remain in the gas phase. This appears to contradict the observations of extremely fast (i.e. within a couple of minutes) nucleation of new particles in beta-caryophyllene oxidation experiments as reported by a number of studies.

[R]: The first-generation products are volatile and are expected to be present in the gas phase. But they also partition to the particle phase to some extent and are observed in the particle phase of this study. In the manuscript, we emphasized the fact that those first-generation products that do not partition to the particle phase can react with excess ozone to form less volatile second-generation products. As suggested by Hoffmann et al. (1997), ozonolysis of beta-caryophyllene can generate volatile first-generation products that are present in the gas phase and undergo further oxidation. Using this scenario to explain the aerosol formation, Hoffmann et al. (1997) can match the modeled and observed features of aerosol evolution perfectly. The non-volatile products are very likely formed from further reactions and are possibly responsible for the nucleation and new particle formation in beta-caryophyllene oxidation.

[C]: Page 17726, Figure 6: The mass fraction for the first and second generation products (shown in Figure 6) has not been explained. Is this a fraction of the sum of the total 15 products, a fraction of the total mass collected on a filter, or a fraction of the mass measured by the AMS?

[R]: The mass fraction shown in Figure 6 is a fraction of the sum of the total 15 products. This aspect is modified in the revised manuscript.

[C]: Minor comments: Page 17705, line 19: replace 3d with 3 days. Page 17706, line 19: replace "and another" with "and the third mode"

[R]: Revised as suggested by the reviewer.

[M]: Samples were stored at 4 °C and analyzed by UPLC-ESI-ToF-MS within 3 days.

[M]: The three modes of ToF-MS measurements included a first directed to the determination of the accurate mass of the parent ion and hence its molecular formula, a second to the fragmentation of the parent ion for structure determination, and a third to the semi-quantification of the products.

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Expt	ΔHC (ppbv)	O_3 (ppbv)
1	1.7	50
2	6.7	50
3	13.3	50
4	46.4	50
5	1.7	100
6	6.7	100
7	13.3	100
8	46.4	100
9	1.7	200
10	6.7	200
11	13.3	200
12	46.4	200

Table S1. Experimental conditions. ΔHC is the concentration of β-caryophyllene consumed by reactions inside the chamber. O_3 concentration (in excess) is maintained constant by feedback control.
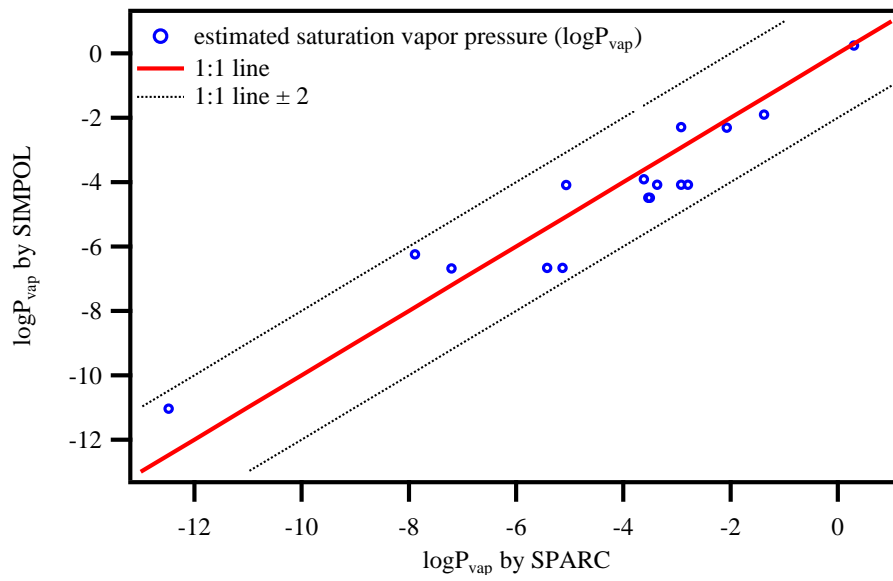
Fig. 1.

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Fig. 2.

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