Authors' response to the reviewers' comments (egusphere-2024-2454)

We are very grateful to the reviewers for their helpful comments. We have incorporated all the comments in the revision. Please see our point-to-point response to the reviewers' comments.

Briefly, we have made the following major revisions, based on the review: (1) we conducted sCI (stabilized Crigee intermediate) scavenger experiments, (2) revised possible molecular structures and chemical reactions for the C19 dimer OOM isomers based on the sCI scavenger experiment results, (3) we reconsidered C16 dimer isomer structures, (4) recalibrated our FIGAERO (filter inlet for gas and aerosol) thermogram which is now more consistent with the literature values, and (5) updated the calculated VBS-based volatilities using *Stolzenburg et al.* [2018] parameterization, which is more appropriate for pure bio-OOMs including dimers. Based on the reviewers' comments, we also refined our writing substantially.

Review 1.

The study utilizes a flow tube to generate aPinene SOA formed from oxidation by both O3 and OH radicals. The authors used 2 mass spectrometers (FIGAERO-CIMS and LC-MS) to evaluate the composition of the formed SOA and species present in the gas-phase. The manuscript is broken down into sections describing the measured composition by the mass spectrometers, a comparison of the log C* measured by the FIGAERO and a (undefined) volatility parameterizations, and LC-MS analysis of specific molecular formula which were thought to be associated with particle phase reactions. The authors desired to connect their measurements to the need to have isomer resolved C* measurements and the need to take into account particle phase reactions into new particle formation parameterizations.

I did not find the manuscript framed and connected the disparate sections effectively. I believe this draft is still very preliminary and the manuscript at this stage needs clear work to use correct terminology, connect their C* results to those of others, and provide adequate evidence of the mechanisms proposed.

RESPONSE: Agreed, we refined our writing to meet the higher standards. We have corrected the C* terminology now and recalculated C* based on *Stolzenburg et al.* [2018] parameterization, which is more appropriate for pure bio-OOMs system including dimers. We have also recalibrated our FIGAERO-thermogram. And these updated results are shown in Figure 4. and made the following revisions:
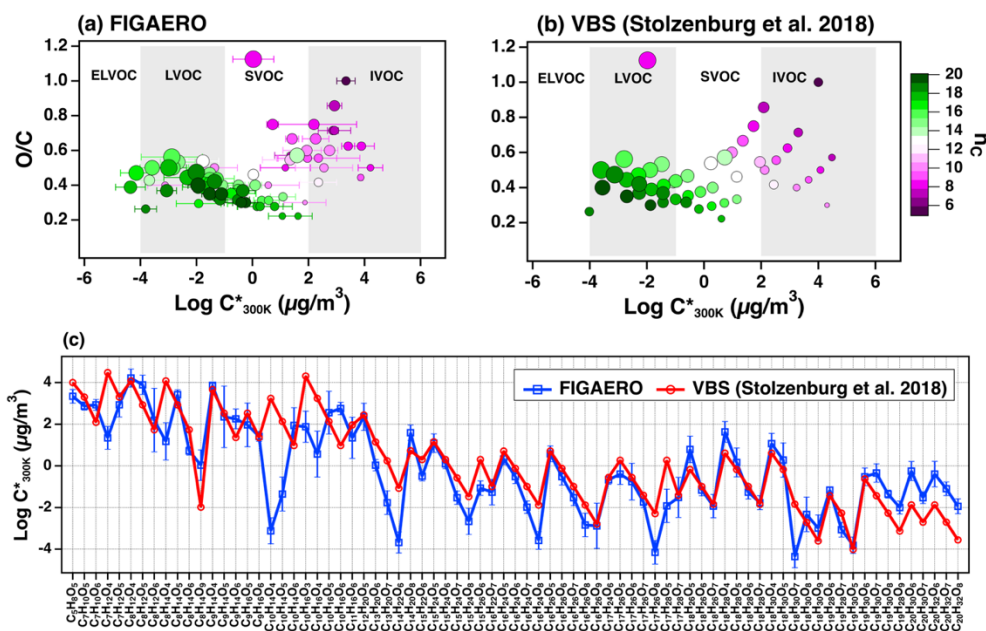

Figure 4. The O/C ratios in OOMs versus $Log_{10}C^*_{300k}$ of OOMs measured with the FIGAERO thermogram (a) and estimated from VBS based on *Stolzenburg et al.* [2018] (see Eq. 2 in the text) (b). The color scale represents the number of carbons in the compound and bubble size represents the oxygen numbers. The O/C vs. $Log_{10}C^*_{300k}$ space is classified into different bins as extremely low volatility organic compounds (ELVOC), low volatility organic compounds (LVOC), semi-volatile organic compounds (SVOC), and intermediate volatile organic compounds (IVOC). (c) Comparison of $Log_{10}C^*_{300k}$ of OOMs obtained from the VBS and FIGAERO. Vertical bars in the FIGAERO-measured volatilities indicate one standard deviation of the data from replicate experiments.

"Volatility basis set (VBS) parameterization

The volatility basis set (VBS) is a simplified parametrization to estimate the saturation vapor concentration of organics and grouping them into volatility bins based on their elemental chemical composition [*Donahue et al.*, 2011]. The saturation vapor concentrations of the organic compounds are projected in the two-dimensional $log_{10}C_i^0 - O{:}C$ space. In this study, we used the VBS parametrization by *Stolzenburg et al.* [2018] which was refined to accommodate the autoxidation reaction for OOMs formation that leads to hydroperoxide, peroxide, or peroxy-acid functional groups:

$$log_{10}C^* = \left(n_C^0 - n_c\right)b_c - n_o b_o - 2\frac{n_C n_o}{n_C + n_o}b_{CO} \qquad (2)$$

Where $n_C^0 = 25, b_C = 0.475, b_{CO} = -0.3$; n_c and n_O are the number of carbon and oxygen, in the OOMs, respectively. The adjusted effect of oxygen b_o was determined separately for monomers ($b_{o,mon} = 1.4$) and dimers ($b_{o,dim} = 1.17$), because dimers include peroxide bonds, thereby lowering the effect on volatility per oxygen atom." (L215)

"Figure 4 shows the saturation vapor concentrations at 300 K (C*) of the OOMs derived from FIGAERO thermogram measurements and VBS parameterizations [*Stolzenburg et al.*, 2018]. The Log_{10} C* derived from both the methods range from -4 to 4, within the extremely-low-volatility organic compounds (ELVOC) and intermediate-volatile organic compounds (IVOC) ranges (Figure 4a and 4b)." (L378)

We note that the discrepancies in the measured Tmax shown in the previous manuscript are due to a different calibration technique. Previously, we applied the calibration compounds dissolved in acetonitrile and flow from an atomizer and directed them through the FIGAERO filter[16]. The re-calibration we carried out involved dissolving the compounds in acetonitrile and directly depositing them on the FIGAERO filter with a syringe[15,16]. As discussed in other studies in detail, these different calibration methods can result in different Tmax values[26].

Major comments:

There is no specific volatility basis set parameterization. The volatility basis set is a simplification to be able to reduce the 1000s of molecules formed into discrete C* bins and to use that as a way to estimate partitioning of organics between the gas and particle phase. This reduces the 1000s of molecules into 3-10+ volatility bins. There are many volatility parameterizations that exist[1-5] and they are correct in the description of how they work, because this is a simplification to take molecular formula measurements to extract C* values. Therefore, in the labels of "VBS" in Figures 2B and C are incorrect (and the corresponding discussion around it). What should be included is what actual parameterization is used (and cite it in the main text), and to note that in the figures. Further, there needs to be a discussion about the inherent uncertainties of the parameterizations, at the moment they are presented as base truth (hence no error bars in parameterization extracted C*), which is not the case. There is a discussion in Donahue (2011) about what the uncertainties are on the parameterization.[1]

RESPONSE: Please see the above response.

Regarding the implications that such particle phase processes are needed to understand new particle formation (NPF) and growth, I would agree with only one of the two statements. For growth I would agree, while for NPF I would not agree. My reason for disagreement comes from what is required to have new particle formation, which is a supersaturation of organic vapors because no pre-existing particle exists. Meaning, the important components are formed in the gas-phase. Also, the prerequisite for a particle-phase

reaction is not present (i.e. particles). Therefore, I don't believe the abstract and implication sections are framed correctly.

RESPONSE: Agreed. We revised the relevant statements as the following:

"Our study demonstrates that particle-phase formation pathways of OOMs should also be considered for the growth of new particles in the atmosphere." (Abstract)

"This study highlights the importance of particle-phase reactions that are currently not considered in the growth of biogenic new particles." (Synopsis)

"The current NPF parameterizations only consider the volatilities of chemical precursors [*S-H Lee et al.*, 2019], but our results demonstrate that the growth of newly formed particles should also consider possible particle-phase reactions." (L418)

"Different isomers may have different volatilities, thus they may affect differently the growth of nanoparticles." (L424)

Given the loading dependent and thermal decomposition effects in the thermogram of the FIGAERO, how did the authors take care to mitigate against these effects when extracting C* values? Related to this, please compare the C*s extracted here to those from other papers because these values are very low and to be quite honest are not realistic. For instance, these results would suggest that all monomers observed are basically LVOCs. (see other minor comments related here below).

RESPONSE: Please see our earlier response related to C*. We also added this in the revision:

"The FIGAERO T_{max} is subject to variability depending on the filter mass loading and thermally driven particle-phase chemistry as discussed in detail by [*Huang et al.*, 2020]; however, the present study did not take into consideration of these effects." (L188)

In the discussion surrounding the mechanisms proposed, my feeling is there is lack of basis for the proposed mechanisms without citations providing rationale for why things like the SOZ are the likely species formed, especially when another study proposed a very different structure with similar fragmentation pathways (as the authors discuss). The importance of the stabilized Criegee Intermediate is based on previous work which found this to be true, but there is no directly evidence to be able to assess if that is also true within this study for these specific molecules without experiments specifically designed to test this hypothesis or standards to demonstrate this. Other measurements used a Criegee and/or OH scavenger to elucidate the dimers forming from the stabilized Crigee Intermediate and found that the C19H30O5 was specifically not impacted by the presence of the Criegee scavenger.[6] Other dimers were impacted (e.g. C20H30Ox dimers). This leads me to question the proposed reaction mechanism.

RESPONSE: Based on this comment, we conducted sCI (stabilized Crigee intermediate) scavenger experiments, (2) revised possible molecular structures and chemical reactions for the C19 dimer OOM isomers based on the sCI scavenger experiment results. We have made the following revisions:
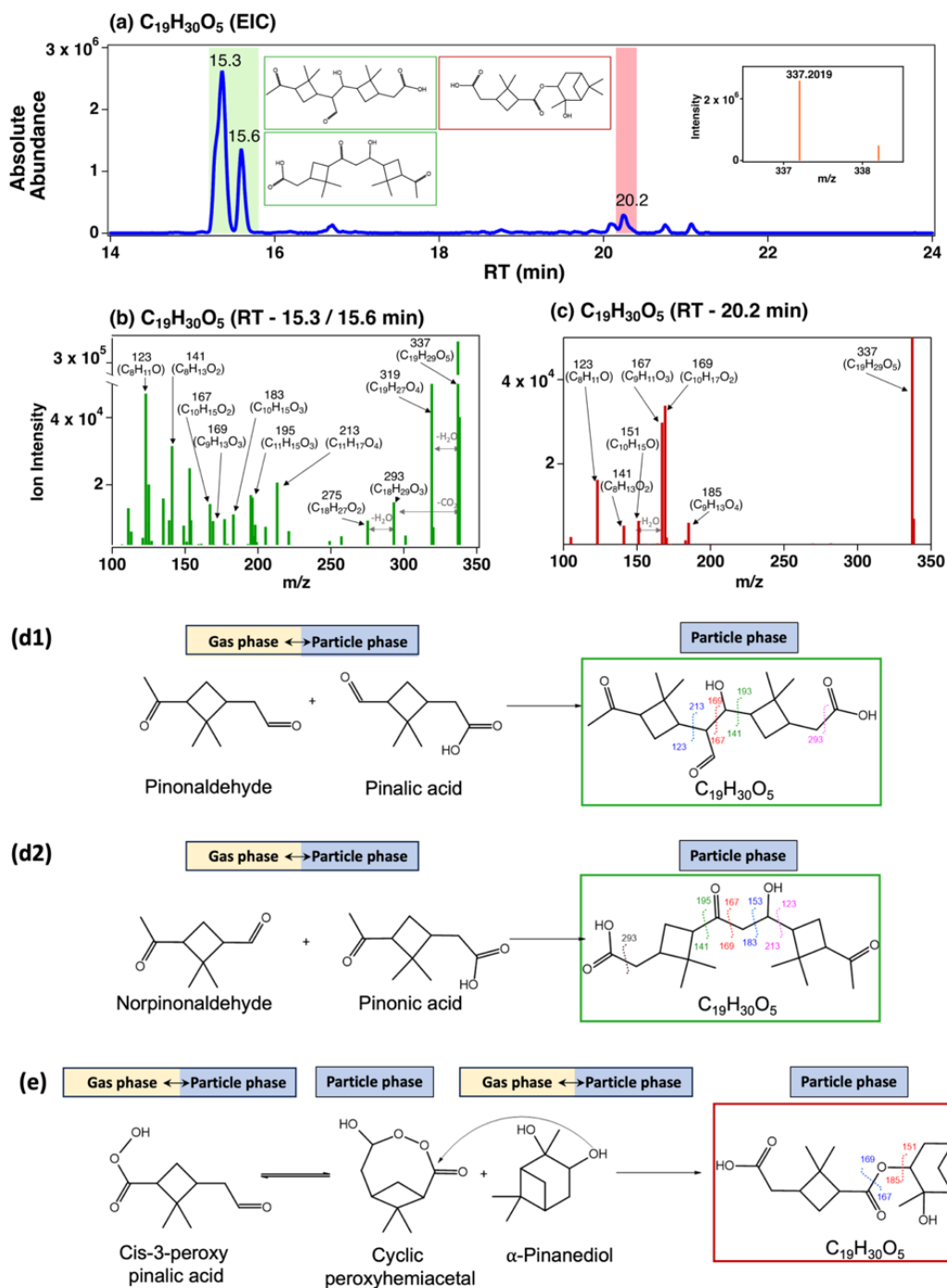
Figure 2. (a) EIC of $C_{19}H_{30}O_5$ (m/z = 337.2019). The inset MS spectrum shows the mass peak of the $C_{19}H_{30}O_5$ at RT of 15.3 min. (a) MS/MS spectra of the isomers with RT of 15.3 min and (c) RT of 20.2 min. MS/MS spectra for RT of 15.3 and 15.6 nm are nearly the same. (d) A proposed reaction and molecular structure for the isomer $C_{19}H_{30}O_5$ (RT = 15.3 min). (e) The reaction and molecular structure for the isomer $C_{19}H_{30}O_5$ (RT = 20.2 min), adapted from [*Kenseth et al.*, 2023]. The numbers indicated in the molecular structures are the corresponding nominal m/z values of [M-H]$^-$ fragment ions in the MS/MS spectra; same in Figure 3.

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"To understand the chemical reaction pathways involving stabilized Criegee Intermediate (sCI), we also performed experiments by introducing 10 ppm formic acid as the sCI scavenger." (L117)

"$C_{19}H_{30}O_5$ ([M-H]$^-$ = 337.2019) is one of the major dimers produced from α-pinene ozonolysis, as detected in boreal forests [*Kristensen et al.*, 2016] and laboratory studies [*Kenseth et al.*, 2023; *Y Zhao et al.*, 2018b]. Figure 2a shows the EIC of $C_{19}H_{30}O_5$, indicating isomers that eluted at 7 different retention times when detected in the negative mode. Figures 2b and 2c show the MS/MS spectra of two isomers, $C_{19}H_{30}O_5$ (RT = 15.3 min) and $C_{19}H_{30}O_5$ (RT = 20.2 min). The isomer eluting at RT = 15.6 min has similar MS/MS spectra as that of RT = 15.3 min. The distinctive MS/MS fragmentation ions of $C_{19}H_{30}O_5$ with RT of 15.3 (or 15.6) and 20.2 min) indicate that these two isomeric compounds have different molecular structures. The fragmentation spectrum of $C_{19}H_{30}O_5$ (RT = 15.3) is in good agreement with that shown by *Witkowski and Gierczak* [2014], where the dimer is proposed as the aldol condensation product of pinalic acid and pinonaldehyde. We made a detailed structural analysis using possible monomer building blocks as illustrated in Table S3. Only the aldol condensation product of pinalic acid and pinonaldehyde [Table S3 (4E.1)] and cis-pinonic acid and norpinonaldehyde [Table S3.(7D.2)] could yield the MS/MS fragments observed. The presence of these reactant monomers in the gas phase, were simulated by the GECKO-A model from α-pinene ozonolysis (Table S4), except the pinalic acid structure (Table S4, Monomer 6). Thus, we excluded the possible pathway of aldol condensation from pinalic acid and pinonaldehyde. Additionally, the secondary ozonide (SOZ) structure formed from the reaction of a stabilized Cregiee intermediate (sCI) with norpinonaldehyde (Table S3. 2D.1) has similar fragments to that observed; however, we did not observe any reduction in the $C_{19}H_{30}O_5$ signal when introducing sCI scavenger to the α-pinene ozonolysis system. Thus, aldol condensation from cis-pinonic acid and norpinonaldehyde is mostly likely (Figure 2d) and consistent with the MS/MS analysis. As shown in Figure 2d, the parent ion (m/z 337) loses H_2O to form the fragment ion with m/z 319 and CO_2 to form m/z 293, which in turn loses another neutral H_2O molecule to form m/z 275. The parent ion then undergoes bond cleavages to form ions with m/z 213/123, 169/167, and 193/141." (L281)

Lines 423 – 424: Why is isomer resolution needed for volatility estimation? I think that there would need to be a discussion focused in this direction.

RESPONSE: We rephrased the relevant to statements as the following:

"As shown in the present work, OOMs often contain isomers with different molecular structures, and future studies are required to understand how isomers affect the volatilities of complex OOMs." (L408)

Minor comments: (some of which are used to generate the major comments)

CHO-1 and CHO-2 (I don't understand their graphical abstract at a first look, and after the reading the manuscript, I see it applies to label present in the manuscript. I would recommend improving this.)

RESPONSE: We removed this illustration.

Line 43: This is the first molecular level analysis??? This paper cited many other papers that have done a similar thing.

RESPONSE: We removed this sentence.

Line 117: Does GECKO-A actually verify the molecular structures? In my mind it helps suggest possible pathways, but does not provide a ground truth.

RESPONSE: GECKO-A does not directly verify molecular structures. Instead, it predicts potential oxidation products that are considered chemically reasonable based on chamber experimental data and validated structure-activity relationships (SARs). As one of the most advanced atmospheric mechanism generators currently available, GECKO-A has been used in a number of peer-reviewed studies, with its α-pinene mechanisms being particularly well-studied and compared against observations (e.g., McVay et al., 2016; Afreh et al., 2021;Galeazzo et al., 2021; Gu et al., 2024).

In this manuscript, we intended to highlight that GECKO-A serves as a valuable tool to support the assignment of OOM structures but does not independently verify those molecular structures. To clarify, the revised manuscript has the following description of the GECKO-A:

"GECKO-A model simulations

To support interpretation of the chemical reactants and products of a-pinene ozonolysis reactions in the gas phase, as well as their molecular structures, we generated an explicit α-pinene degradation mechanism using GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) ([*Aumont et al.*, 2005; *Camredon et al.*, 2007; *Valorso et al.*, 2011], updated per [*Jenkin et al.*, 2020; *Jenkin et al.*, 2019; *Jenkin et al.*, 2018]). GECKO-A is an automated tool that generates explicit atmospheric oxidation schemes for organic compounds based on experimental data and structure–activity relationships (SARs) in the absence of experimental data. The GECKO-A generated mechanisms have been used in many studies to investigate species formed during oxidation under atmospheric conditions (e.g., [*Afreh et al.*, 2021; *Galeazzo et al.*, 2024; *He et al.*, 2024; *Peng et al.*, 2021]). In this study, a five-generation α-pinene oxidation mechanism was generated using GECKO-A and was employed to verify the proposed molecular structures of monomer building blocks (as discussed in detail in Section 3). The generated scheme includes 870,343 reactions and 152,162 species. Since GECKO-A currently does not include particle-phase reactions, the search and selection processes focused on C10 and C9 reactant isomers identified from flow tube experiments. The gas-particle partitioning is treated dynamically based on Nannoolal et al. [*Nannoolal et al.*, 2008] to calculate saturation vapor pressures." (L228)

Lines 125 – 136: What fraction of α-pinene reacted with O3 vs OH?

RESPONSE: Based on the GECKO-A simulations show that fraction of α-pinene reacted with ozone versus OH by the end of flow tube experimental setup is ∼ 68:32.
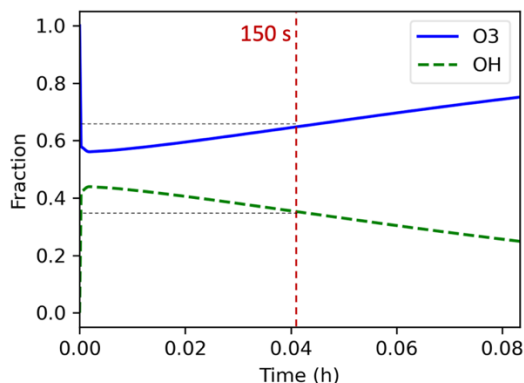

Figure R1: Fraction of a-pinene reacted with O₃ and OH.

We added the following in the revision:

"While both ozone and OH oxidize α-pinene, this is an ozone-oxidation dominant system due to exceedingly higher concentrations of ozone." (L116).

Lines 150-151: I agree with this statement, what was done to take this into consideration?

RESPONSE: Please see our earlier response related to C*.

Methods 2.1: Were any background desorptions performed to determine the "noise" associated with the FIGAERO measurement? (i.e. is 0.1 #/s in Figure 1 really statistically significant?) (the same can also be asked for the LC-MS analysis)

RESPONSE: We now corrected the mass spectra using the correct data (ie. ions/s) as shown in Figure 1. We also rephrased this statement more clearly:

"For the OOMs FIGAERO-HrTOF-CIMS, we used the 50% most abundant OOMs, which contributes about 99% of all the ions detected. For the OOMs with UPLC/(-)ESI-Orbitrap MS, we used data that had the S/N > 3." (L251)

Line 227: shouldn't the full sentence on this line go after the next sentence. How much does 50% of the most abundant species make up of the total signal for each of the instruments?

RESPONSE: Please see the above revision.

Lines 226-242: It would be helpful to report fractions of "monomers" and "dimers" rather than relying on qualitative statements.

RESPONSE: We clarified this sentence:

"In the gas phase, the ratio of monomers over dimers was 91:9, whereas in the particle phase, the ratio is 81:19 (both measured with HrTOF-CIMS), indicating that dimers, in general, are more favorable for gas-to-particle conversion due to relatively lower volatilities, consistent with previous observations [*Lee Tiszenkel and Lee*, 2023]." (L254)

Lines 243 – 255: Perhaps there should be a discussion about the comparability between the FIGAERO-CIMS and the LC-MS data, because there are clear differences in sampling collection time between the instruments. What artefacts can this result in?

RESPONSE: Agreed. We add this paragraph:

"Combining these two independent high-resolution mass spectrometer techniques, HrTOF-CIMS and UPLC/(-)ESI-Orbitrap MS, provides a very powerful tool for analyzing the particle-phase chemical composition of OOMs and, for identifying molecular structures of different isomers. So far, only a few studies have combined these two methods to make molecular-level chemical speciation of OOMs (e.g., [*Du et al.*, 2022; *Huang et al.*, 2020; *Mehra et al.*, 2020]). However, these two methods have advantages and disadvantages. The FIGAERO HrTOF-CIMS measures the real-time particle-phase chemical composition after 20 minutes of filter collection on FIGAERO. There is the possibility that chemical species (such as

dimers) are thermally decomposed during the desorption process from the FIGAERO [*Lopez-Hilfiker et al.*, 2014a]. On the other hand, UPLC/(-)ESI-Orbitrap MS is an offline technique. While this high-resolution MS/MS analysis can provide detailed chemical structure information, artifacts can occur during the filter collection and storage, and sample extraction processes. There are also matrix effects due to a relatively higher amount of particle mass [*Trufelli et al.*, 2011]. It is noted that HrTOF-CIMS (iodide ionization) and UPLC/(-)ESI-Orbitrap MS may have different ionization efficiencies and detection efficiencies for different chemical compounds. As will be discussed in detail in this study, they show very similar chemical compositions of OOMs (e.g., Figure 1), despite these differences." (L199)

Line 254-255: The species in Table 2 (which refers to specific isomers and their distinct RT and MS/MS) were chosen because of their reproducibility in the FIGAERO thermograms? Is this different from the 50% mentioned on line 227?

RESPONSE: We revised as the following:

"For the OOMs FIGAERO-HrTOF-CIMS, we used the 50% most abundant OOMs, which contributes about 99% of all the ions detected. For the OOMs with UPLC/(-)ESI-Orbitrap MS, we used data that had the S/N > 3." (L251)

"In total, 437 OOMs were identified in the gas phase with the HrTOF-CIMS, 405 OOMs were identified in the particle phase with the FIGAERO -CIMS, and 167 OOMs were identified with UPLC/(-)ESI-Orbitrap MS (Figure 1h). As shown in Figure 1g, each OOM detected by LC-Orbitrap MS had 2-8 isomers. Table S1 shows particle-phase OOMs detected in HrTOF-CIMS (gas- and particle-phase) and UPLC/(-)ESI-Orbitrap MS (particle phase). There were 124 OOMs that were detected only in the gas phase; 12 OOMs that were detected only in the particle phase (by the FIGAERO-CIMS and UPLC/(-)ESI-Orbitrap MS) but not in the gas phase. There were 96 OOMs detected in both the gas and particle phases, suggesting that these are OOMs that likely undergo gas-to-particle conversion.

Table S2 lists the select 77 particle-phase OOMs, along with their distinct retention time (RT) in the liquid chromatograms (indicating isomers) and tandem MS/MS fragmentation ions for each isomer. These 77 compounds were detected in the particle phase both by the FIGAERO-CIMS and UPLC/(-)ESI-Orbitrap MS and showed high reproducibility in the FIGAERO thermogram and LC chromatogram. Using the liquid chromatogram and MS/MS fragmentation ions, we identified the possible molecular structures of isomers and their formation reaction pathways. Here, we show our identification processes and proposed structures for $C_{19}H_{30}O_5$ ([M-H]$^-$ = 337.2019) and $C_{16}H_{26}O_6$ ([M-H]$^-$ = 313.1677)." (L264)

Lines 266-269: I would argue the teeth-like shape references is really only apparent for the C15+ molecular formula.

RESPONSE: With the recalibrated FIGAERO measurements and with the *Stolzenburg et al.* [2018] VBS parameterization (Figure 4c), the teeth-like characteristics is now more apparent throughout the study range with few exceptions.
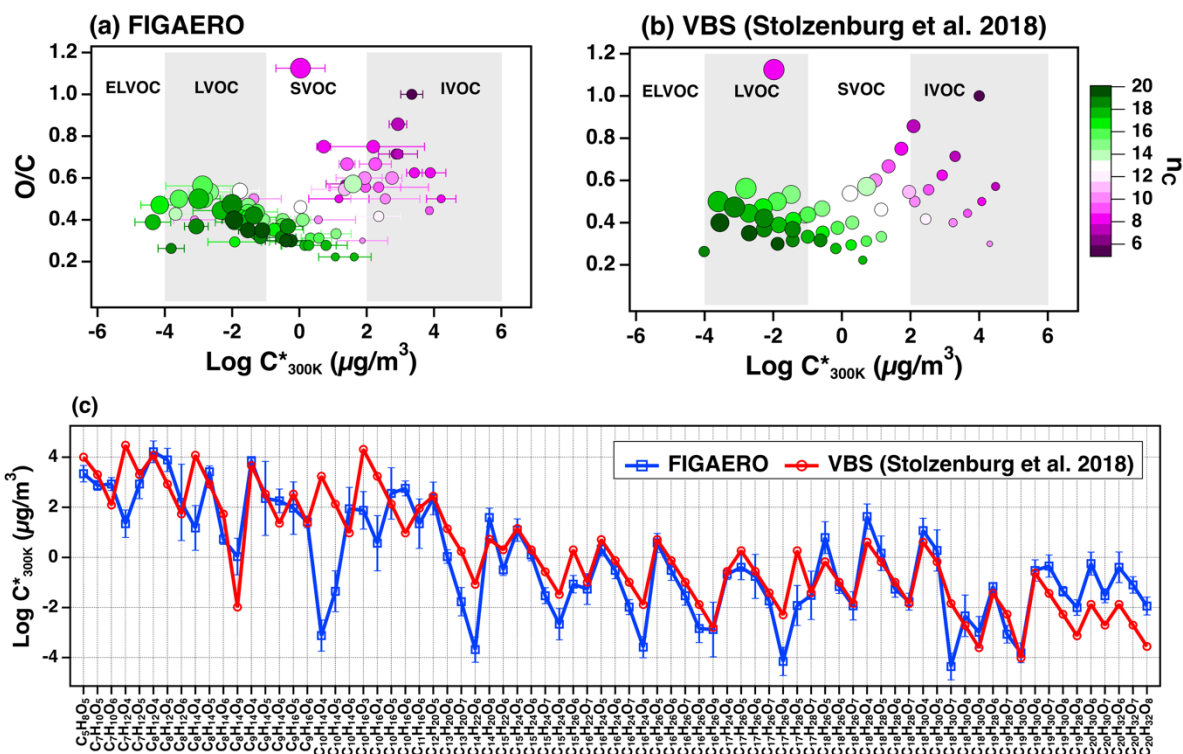
Figure 4. The O/C ratios in OOMs versus $Log_{10}C^*_{300k}$ of OOMs measured with the FIGAERO thermogram (a) and estimated from VBS based on *Stolzenburg et al.* [2018] (see Eq. 2 in the text) (b). The color scale represents the number of carbons in the compound and bubble size represents the oxygen numbers. The O/C vs. $Log_{10}C^*_{300k}$ space is classified into different bins as extremely low volatility organic compounds (ELVOC), low volatility organic compounds (LVOC), semi-volatile organic compounds (SVOC), and intermediate volatile organic compounds (IVOC). (c) Comparison of $Log_{10}C^*_{300k}$ of OOMs obtained from the VBS and FIGAERO. Vertical bars in the FIGAERO-measured volatilities indicate one standard deviation of the data from replicate experiments.

Figure 2a and b are missing the units on the x-axis.

RESPONSE: Corrected.

Figure 2c where do the error bars come from? I don't believe the units on the y-axis are correct. μ / cm^3???

RESPONSE: Corrected.

Line 283: I believe that there should be a comma instead of a dash in the molecular formula, since a $C_8H_{13}O_6$ is not a closed shell species. (same comment about commas on line 285).

RESPONSE: Corrected.

Line 288: "make them more stable in the gas-phase" isn't an important distinction then the activity coefficient (or effective saturation vapor concentration) not the C*.

RESPONSE: We clarified this as the following revision:

"These observations are consistent with the hydron effects on the saturation vapor pressures predicted from the COSMOtherm [*Hyttinen et al.*, 2021; *Kurtén et al.*, 2016]. The COSMOtherm shows that in the case of monomers, an increase in intermolecular hydrogen bonding by hydrogen-donor functional groups likely decreases the volatility, while dimers with more hydrogen donor groups can favorably form intramolecular hydrogen bonds that exceed the effect of the increasing number of carbon or oxygen on saturation vapor pressures." (L400)

Lines 291-295: Aren't these also attributed to thermal decomposition of species on the filter? I would treat this with caution. On the note of thermal decomposition, how do the authors know that the C* extracted for a specific molecular formula is actually for that specific formula? For instance, when I see the C10H14O4 in Figure 2C (Log C* ~ -6) it has a C* similar to 'dimers'. To me that would suggest this should be attributed to decomposition. Further, if there is thermal decomposition of dimers, how would that impact the extracted C* of dimers? Wouldn't this be biased in someway?

RESPONSE: Agreed, thermal decomposition is a limitation of FIGAERO-thermogram Some of the monomers showing unreasonably high Tmax may be due to decomposition of dimers. And in this case, they may show up as multimodal peaks. In the case of C10H14O4, there was one single peak.

Without any oxygen containing an OH functionality, is it reasonable for H2O loss to be a dominate pathway?

RESPONSE: Please see our earlier response to this C19 compound assignment (revised reactions and structures are shown in Figure 2).

Isn't it also possible to have an RO2 + RO2 pathway to form C19H30O5?

RESPONSE: The RO2 + RO2 pathway is an option (as shown Table S3, 1A and 1B). However, the ROOR product structure cannot be explained by the observed MS/MS ions.

Are there citations for SOZ fragmentation pathways? Without providing some evidence for these fragmentation pathways, I do not see why this is reasonable. (e.g. do you have standards where these fragmentation pathways have been observed for model compounds?)

RESPONSE: Please see our earlier response regarding this compound reassignment.

What is the organic aerosol mass concentration in the flow tube for all of the experiments?

RESPONSE: We included the following in the revision:

"Figure S2 shows the measured aerosol size number distribution with a mean diameter of approximately 70 nm during the typical experimental conditions. The aerosol mass concentrations were 135 ± 23 µg cm^{-3}." (L247)

"The mean number size is approximately 70 nm. And the mass concentration is 135 ± 23 μg m^{-3} assuming the density of particles is 1 g/cm^3." (Figure S2 caption)

Line 316-325: This section is pure conjecture since there is no clear evidence that the stabilized Criegee intermediate is actually involved in its formation. To prove that the stabilized Criegee intermediate is important experiments with a Criegee scavenger would be necessary.

RESPONSE: Please see our earlier response regarding this compound reassignment.

Line 346-357: shouldn't this change in oxidants also be reflected in the methods section? How do these changing conditions change the aerosol mass concentrations in the flow tube?

RESPONSE: We have removed this result in the revision.

Line 386: the RO2+RO2 reaction proposed does not work because they are actually closed shell molecules. C8H14O6 + C9H14O4 (did they detect the radicals in the gas-phase?) I guess the authors mean C8H13O6 and C9H13O4. Have these radicals been reported elsewhere in the literature?

RESPONSE: Yes, they should be C8H13O6 and C9H13O4 radicals. To respond to this comment, we revised as the following:

"(2) It is also possible that $C_{16}H_{26}O_6$ forms from particle-phase decarboxylation of the diacyl dimer $C_{17}H_{26}O_8$, which forms from the gas-phase RO$_2$-RO$_2$ dimerization from $C_8H_{13}O_6$· (a diaterpenylic acid precursor RO$_2$ radical [*Sato et al.*, 2016]) and $C_9H_{13}O_4$· (the second generation RO$_2$ radical from α-pinene ozonolysis) as shown in Figure 3e1)." (L367)

Lines 382 – 390: Is there specific evidence that the C16H26O6 comes from a C17H26O8, unique to this study, that would suggest this reaction pathway? Or is this solely based on a mechanism from Zhang et al (2015)?

RESPONSE: We have revised as the following, regarding this dimer:

"The EIC of $C_{16}H_{26}O_6$ ([M-H]$^-$ m/z of 313.1677) shows five RT indicating the presence of isomers (Figure 3a). The two most abundant isomers with distinctive fragmentation mass spectra are those with the RT of 16.6 and 18.4 min, respectively (Figures 3b and c). The fragmentation of $C_{16}H_{26}O_6$ (RT = 16.6 min) is in good agreement with those shown by *Kristensen et al.* [2016]. It yields daughter ions with nominal m/z values of [M−H]$^-$ of 185, 167, 141, 123, 71 and 57. The pattern of daughter ions observed here is similar to that of pinic acid fragmentations ($C_9H_{14}O_4$, MW = 186), suggesting that the monomer building blocks consist of $C_9H_{14}O_4$ and $C_7H_{12}O_2$. While $C_7H_{12}O_2$ was not detected in the negative mode ([M-H]$^-$), in positive mode [M+Na]$^+$ MS/MS spectrum, $C_7H_{12}O_2$ there were both $C_9H_{14}O_4$ and $C_7H_{12}O_2$ (Figure S5a). These fragmentation ions suggest that this $C_{16}H_{26}O_6$ isomer has the same molecular structure and forms from particle-phase diacyl peroxide decomposition as previously shown by *Zhang et al.* [2015] (Figure S1). As stated above, $C_{16}H_{26}O_6$ was not detected in the gas phase. However, $C_{17}H_{26}O_8$ was detected both in the gas- and aerosol-phase. Thus, it is possible that $C_{16}H_{26}O_6$ forms in the particle phase from a diacyl peroxide ($C_{17}H_{26}O_8$) via diacyl peroxide decomposition (Figure 3d). The precursor $C_{17}H_{26}O_8$ can form in the gas phase from $C_9H_{13}O_5$· acetylperoxy radical and a ring-opening acetylperoxy radical ($C_8H_{13}O_5$·) via the RO$_2$ + RO$_2$ dimerization, and then subsequently partition into the particle phase. These monomer building blocks for $C_{17}H_{26}O_8$ were identified by GECKO-A simulations (Table S4, Monomers 15 and 16).

As shown in Figure 3c, fragmentation of the $C_{16}H_{26}O_6$ (RT = 18.4 min) isomer yields daughter ions with nominal [M−H]$^-$ m/z of 171 ($C_8H_{11}O_4^-$), 141 ($C_8H_{13}O_2^-$), 127 ($C_7H_{11}O_2^-$) and 109 ($C_7H_9O^-$). The fragmented ions with m/z 171, 129 and 109 can be attributed to two of the most abundant monomers: diaterpenylic acid ($C_8H_{14}O_5$, MW 190) and cis-norpinic acid ($C_8H_{12}O_4$, MW 172) produced in the α-pinene ozonolysis system [*Kenseth et al.*, 2018; *Yasmeen et al.*, 2010]. The ions with m/z of 127 and 109 are the subsequent fragments of m/z = 171 formed by the loss of CO_2 and H_2O, respectively. The daughter ion $C_8H_{13}O_2^-$ ([M-H]$^-$ = 141) forms by the loss of CO_2 from $C_9H_{14}O_4$ (MW = 186) as discussed previously. Therefore, the possible monomer building blocks for $C_{16}H_{26}O_6$ are $C_8H_{13}O_2$ (m/z 141), which is a pinic acid's fragmentation ion, and $C_8H_{11}O_4^-$ (m/z 171) which can be a fragmentation ion of either *cis*-norpinic acid or diaterpenylic acid. *cis*-norpinic acid have two carboxylic acid moieties, so it can either undergo esterification reaction or react with sCI in gas-phase to form α-acyloxyalkyl hyderoperoxides [*Hall and Johnston*, 2012]. However, the esterification reaction for $C_{16}H_{26}O_6$ is lees likely, because another closed shell monomeric building block $C_8H_{16}O_3$ was not detected. Reaction with sCI is also ruled out, because we did not observe any signal reduction for $C_{16}H_{26}O_6$ (RT = 18.4 min) when the sCI scavenger was added. Thus, the monomer with m/z of 171 is more likely diaterpenylic acid (m/z of 171). Based on the above analysis, we propose two possible structures for $C_{16}H_{26}O_6$ (RT = 16.6 min) that can yield the above MS/MS fragmentation ions. First, $C_{16}H_{26}O_6$ may be a peroxyhemiacetal product from norpinalic acid ($C_8H_{12}O_3$) and $C_8H_{14}O_3$ which has a hydroperoxide moiety (Figure 3e). Second, it is also possible that $C_{16}H_{26}O_6$ forms from particle-phase decarboxylation of the diacyl dimer $C_{17}H_{26}O_8$, which forms from the gas-phase RO_2-RO_2 dimerization from $C_8H_{13}O_6^{\cdot}$ (a diaterpenylic acid precursor RO_2 radical [*Sato et al.*, 2016]) and $C_9H_{13}O_4^{\cdot}$ (the second generation RO_2 radical from α-pinene ozonolysis) (Figure 3f). The second proposed structure is also in agreement with the HrTOF-CIMS detection of the RO_2/HO_2 termination products of $C_8H_{14}O_5$ and $C_9H_{14}O_3$ from $C_8H_{13}O_6^{\cdot}$ and $C_9H_{13}O_4^{\cdot}$ RO_2 radicals, respectively. The GECKO-A model simulated the monomer building blocks required in the above two proposed reactions (Table S4, monomers 17 - 20). Both structures can explain the observed negative mode MS/MS spectra of $C_{16}H_{26}O_6$ (RT = 18.4 min). The positive mode MS/MS spectra of this isomer show an additional peak of $C_8H_{14}O_5$ ([M+Na]$^+$ m/z of 213.0732) (Figure S5b), which could be a fragmented ion from the above proposed molecular structures of $C_{16}H_{26}O_6$. " (L331)
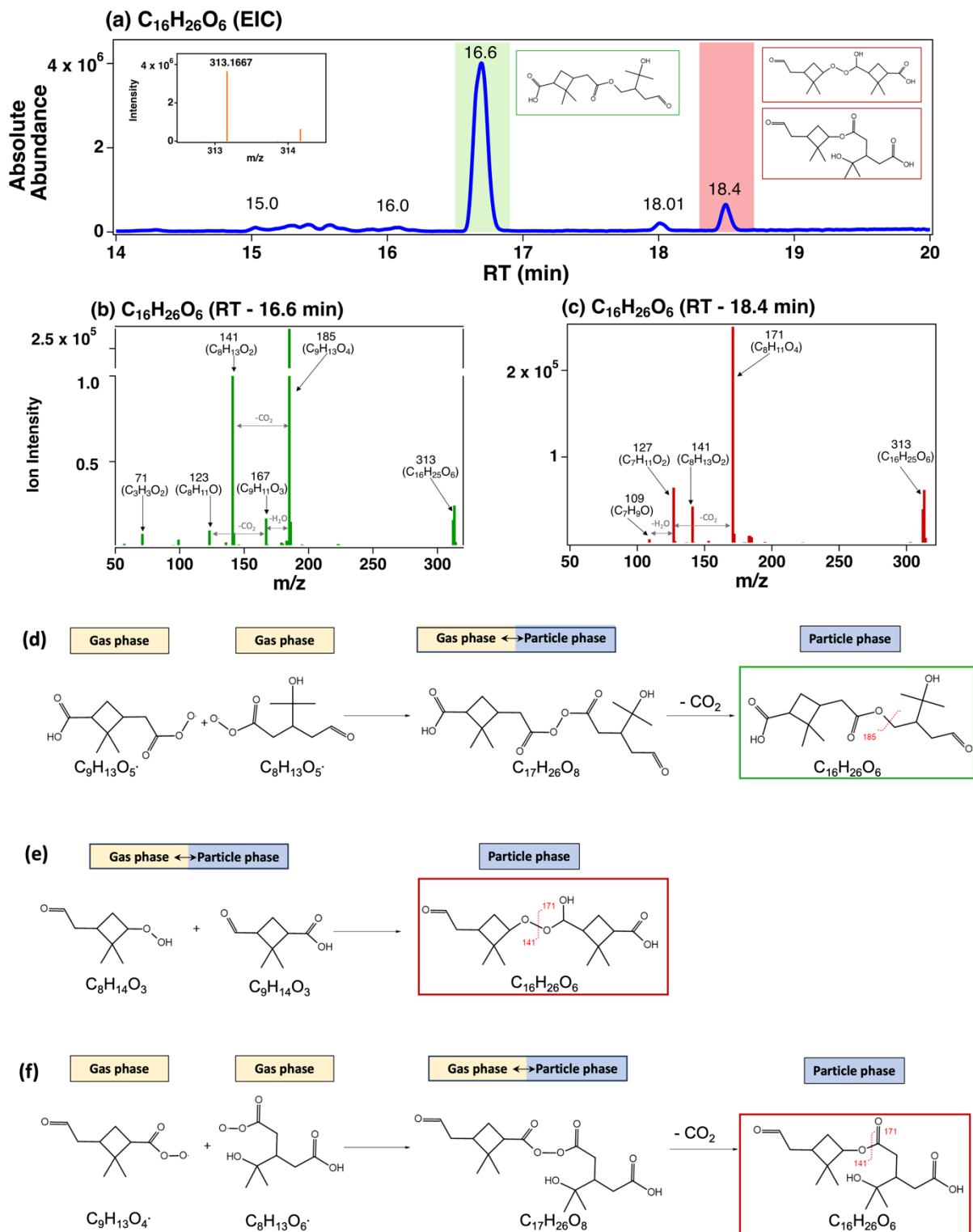
Figure 3. (a) EIC of $C_{16}H_{26}O_6$. The inset MS spectrum shows the mass peak of $C_{16}H_{26}O_6$ at RT = 16.6 min. MS/MS spectra of two isomers for $C_{16}H_{26}O_6$ with RT of 16.6 min (b) and RT of 18.4 min (c). The proposed

the reactions and molecular structures for $C_{16}H_{26}O_6$ (RT = 16.6 min) (d) and $C_{16}H_{26}O_6$ (RT = 18.4 min) (e and f).

Lines 391 – 398: Is this a bias in the fact the filters were collected for 24hrs and then allowed to sit for some amount of time allowing reactions to continue both during and after collection? When considering the Pospisilova et al. (2020) At short time scales (similar to the flow tube in this study) the dimers were dominated by C20 molecules so I don't believe that this is necessarily a fair comparison.

RESPONSE: Agreed, we removed this discussion.

Reviewer 2.

Summary

This manuscript investigated gaseous and particle phase molecular composition from ozonolysis of a-pinene in the absence of seed aerosols. The gas phase analysis is done by an iodide CIMS. The authors applied two complementary MS (FIGAERO CIMS and LC-Orbitrap MS) for particle phase analysis, which are usually not often when both are available. Therefore, it is expected to provide some promising new information of SOA molecular composition, especially LC-Orbitrap MS is likely to provide isomeric speciation as well as structural info from MS2, which is the key focus of this study. However, my feeling is mixed after fully reading the manuscript. I will try if my comments can help the authors to improve their work, but my conclusion is clear that the current form of this manuscript really needs substantial revision and there are many problems I found.

Major concerns

(1) The authors emphasize their study as the first identification of particle-formation pathways in newly formed biogenic particles. This gives me a first feeling that this could not be true actually. Of course, new compounds and new chemistry in SOA can always be identified and proposed, but I strongly believe some SOA particle phase chemistry are already known, and these proposed particle phase mechanisms (even very uncertain) in this study are based on existing knowledge. The below reference is just one of the review papers summarizing some oligomer formation pathways.

It is true that aerosol nucleation and SOA growth occur in this study because of no seed particle, but basically the authors investigate very traditional a-pinene SOA composition that have been done for decades. This manuscript is NOT a typical NPF and aerosol nucleation study and the focus is NOT on composition of very fresh aerosol nucleation processes, e.g. sub-10nm. Therefore, it should have very limited implication that able to extrapolate to the so-called new particle formation. These over extrapolations to NPF processes should be revised and toned down throughout the entire manuscript, to avoid overselling.

Ref: Hall IV W A, Johnston M V. Oligomer formation pathways in secondary organic aerosol from MS and MS/MS measurements with high mass accuracy and resolving power[J]. Journal of the American Society for Mass Spectrometry, 2012, 23(6): 1097-1108.

RESPONSE: In response to this comment, we removed these over-statements in the revision.

(2) The structural characterization for some selected OOMs is the key focus of this study. Unfortunately, this is highly challenging but also highly uncertain based on MS2 alone. There are different levels of identification confidence for communication. I am not sure the authors are aware of this or not, but usually should be deeply discussed when interpret the proposed structures, e.g. see below reference. From my knowledge, the authors proposed four structures of four OOMs, which are all at level 3. This means that these are tentatively assigned structures and highly uncertain.

Ref: Schymanski E L, Jeon J, Gulde R, et al. Identifying small molecules via high resolution mass spectrometry: communicating confidence[J]. ES&T. 2014.

RESPONSE: Agreed, we rephrased in the manuscript to reflect this Level 3 kind of structure analysis. We mainly use words "propose" "possible" or "potential." Please see our response in other comments below. We also added the following:

"We note that our proposed structures contain substantial uncertainties (based on the [*Schymanski et al.*, 2014] definition), as we did not utilize any standard or synthesized chemical compounds, rather only based on the two high-resolution mass spectrometer analysis." (L102)

(3) These structures are proposed without designing targeted experiments to validate the proposed structures, e.g. introducing SCI and RO2 scavengers, which is one of my biggest concerns of this study. The authors mentioned they performed another experiment by varying ozone concentration (250-1000ppb, as shown in Fig. S5). It is not clear to me how many different expts involved, and are they normalized to same mass loading? Line 353-355 this is something vague, and this argument certainly does not convince me. A compound showing same peak area at different ozone concentrations does not justify that this compound is formed via particle phase reaction. By the way, the EICs of blank sample should be added. Again, the best way to test the proposed reaction is to introduce different scavengers rather than change ozone concentration.

RESPONSE: Based on this comment, we conducted sCI scavenger experiments, (2) revised possible molecular structures and chemical reactions for the C19 dimer OOM isomers based on the sCI scavenger experiment results. We have made the following revisions:

"To understand the chemical reaction pathways involving stabilized Criegee Intermediate (sCI), we also performed experiments by introducing 10 ppm formic acid as the sCI scavenger." (L117)

"$C_{19}H_{30}O_5$ ([M-H]$^-$ = 337.2019) is one of the major dimers produced from α-pinene ozonolysis, as detected in boreal forests [*Kristensen et al.*, 2016] and laboratory studies [*Kenseth et al.*, 2023; *Y Zhao et al.*, 2018b]. Figure 2a shows the EIC of $C_{19}H_{30}O_5$, indicating isomers that eluted at 7 different retention times when detected in the negative mode. Figures 2b and 2c show the MS/MS spectra of two isomers, $C_{19}H_{30}O_5$ (RT = 15.3 min) and $C_{19}H_{30}O_5$ (RT = 20.2 min). The isomer eluting at RT = 15.6 min has similar MS/MS spectra as that of RT = 15.3 min. The distinctive MS/MS fragmentation ions of $C_{19}H_{30}O_5$ with RT of 15.3 (or 15.6) and 20.2 min) indicate that these two isomeric compounds have different molecular structures. The fragmentation spectrum of $C_{19}H_{30}O_5$ (RT = 15.3) is in good agreement with that shown by *Witkowski and Gierczak* [2014], where the dimer is proposed as the aldol condensation product of pinalic acid and pinonaldehyde. We made a detailed structural analysis using possible monomer building blocks as illustrated in Table S3. Only the aldol condensation product of pinalic acid and pinonaldehyde [Table S3 (4E.1)] and cis-pinonic acid and norpinonaldehyde [Table S3.(7D.2)] could yield the MS/MS fragments observed. The presence of these reactant monomers in the gas phase, were simulated by the GECKO-A model from α-pinene ozonolysis (Table S4), except the pinalic acid structure (Table S4, Monomer 6). Thus, we excluded the possible pathway of aldol condensation from pinalic acid and pinonaldehyde. Additionally, the secondary ozonide (SOZ) structure formed from the reaction of a stabilized Cregiee intermediate (sCI) with norpinonaldehyde (Table S3. 2D.1) has similar fragments to that observed; however, we did not observe any reduction in the $C_{19}H_{30}O_5$ signal when introducing sCI scavenger to the α-pinene ozonolysis system. Thus, aldol condensation from cis-pinonic acid and norpinonaldehyde is mostly likely (Figure 2d) and consistent with the MS/MS analysis. As shown in Figure 2d, the parent ion (m/z 337) loses H_2O to form the fragment ion with m/z 319 and CO_2 to form m/z 293, which in turn loses another neutral H_2O molecule to form m/z 275. The parent ion then undergoes bond cleavages to form ions with m/z 213/123, 169/167, and 193/141.

The MS/MS spectrum for $C_{19}H_{30}O_5$ (RT = 20.2 min) (Figure 2c) shows fragmentation ions, which were shown previously by other studies [*Kenseth et al.*, 2023; *Kristensen et al.*, 2016; *Witkowski and Gierczak*, 2014]. *Witkowski and Gierczak* [2014] proposed this dimer as the aldol condensation product of cis-pinonic acid and norpinonaldehyde; however, the cited study has misinterpreted the fragment ion with m/z of 169as $C_9H_{13}O_3^-$ (m/z 169.0868) instead of $C_{10}H_{17}O_2^-$ (m/z 169.1234). Using the synthesized standard compounds, *Kenseth et al.* [2023] showed that this dimer forms from nucleophilic addition of α-pinanediol ([M+Na]$^+$ =

193) to cyclic acylperoxyhemiacetal formed by the isomerization of *cis*-3-peroxy pinalic acid ([M-H]$^-$ = 185) followed by Baeyer-Villiger decomposition (Figure 2e). And our MS/MS spectrum is well in agreement with the structure shown by this cited study. As illustrated in Figure 2e there are two main fragmentations near the ester function group, leading to fragmentation ions with m/z of 169/167 and 151/185. The m/z of 185 undergoes subsequent fragmentations by losing CO_2 and H_2O (neutral loss) to form m/z of 141 and 123, respectively. These two monomeric building blocks were identified in the particle phase with UPLC/(-)ESI-Orbitrap mass spectrometer. The GECKO-A model also predicted the formation of *cis*-3-peroxy pinalic acid and α-pinanediol in the gas phase (Table S4, Monomers 13 and 14), with the same molecular structures as shown in Figure 2e. Therefore, it is likely the $C_{19}H_{30}O_5$ (RT = 20.2 min) isomer forms in the particle phase via esterification reactions as shown by *Kenseth et al.* [2023]." (L281)
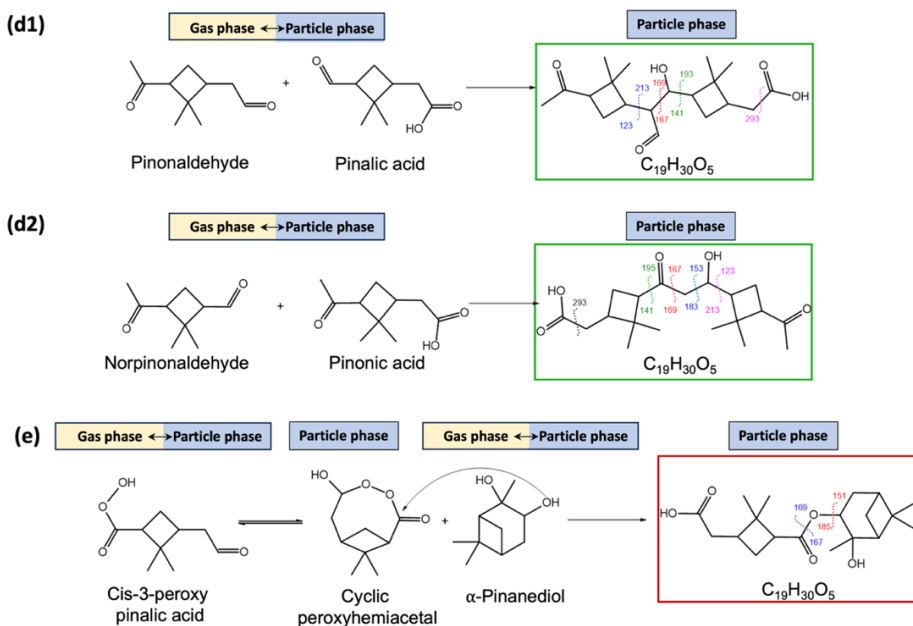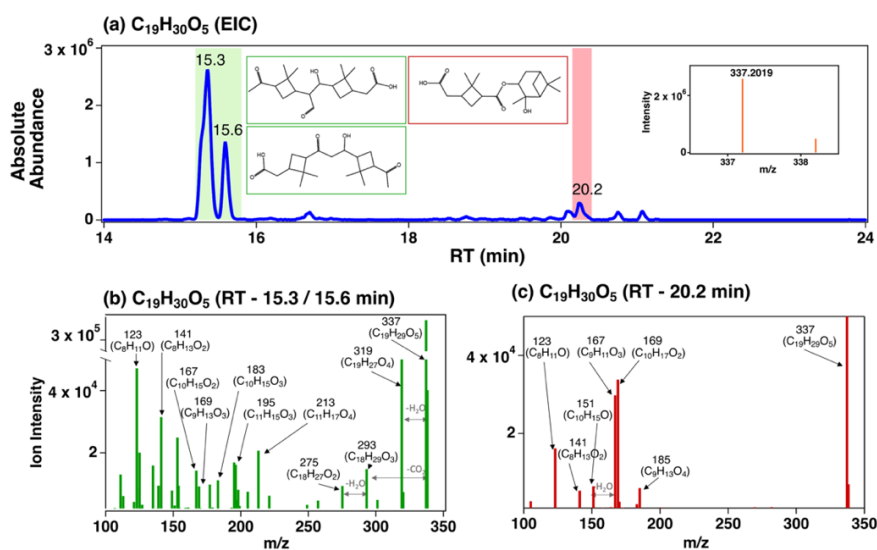
Figure 2. (a) EIC of $C_{19}H_{30}O_5$ (*m/z* = 337.2019). The inset MS spectrum shows the mass peak of the $C_{19}H_{30}O_5$ at RT of 15.3 min. (a) MS/MS spectra of the isomers with RT of 15.3 min and (c) RT of 20.2 min. MS/MS spectra for RT of 15.3 and 15.6 nm are nearly the same. (d) A proposed reaction and molecular structure for the isomer $C_{19}H_{30}O_5$ (RT = 15.3 min). (e) The reaction and molecular structure for the isomer $C_{19}H_{30}O_5$ (RT = 20.2 min), adapted from [*Kenseth et al.*, 2023]. The numbers indicated in the molecular structures are the corresponding nominal m/z values of [M-H]⁻ fragment ions in the MS/MS spectra; same in Figure 3.

(4) Do the authors first get the SOZ structure from MS2 analysis and then propose the SCI+C9 aldehyde reaction? Or in a reverse way that first assume there is such SCI+C9 aldehyde reaction occurring to get the SOZ structure and then interpret MS2 data following the pre-assumed SOZ structure? This is another concern regarding the structural analysis, especially the MS2 based structure is highly uncertain. I notice that the authors mentioned another study in line 324 by Witkowski and Gierczak [2014] that they showed similar MS2 and suggested the particle-phase aldol condensation route leading the formation of C19H30O5. It is not clear for me that how this possibility can be ruled out without other complementary experimental evidence?

RESPONSE: Pleases see the above response related to SOZ and sCI.

(5) For Fig. 3d, there is a clear mistake of the structure of a-pinene SCI, as the C=O of a-pinene SCI is missing. There should be at least two SCI (I/II) structures (not considering cis- and trans-) due to the two decomposition pathways of a-pinene POZ. At the same time, C9H14O2 has two C=O bonds and therefore should at least result in four different SOZ structures of C19H30O5. Even though I do not believe this C19H30O5 at RT=15.3min is SOZ (see my later following comment 6).

In addition, in Fig. 3, there are two clear isomers at ca. 15.3 min, and why specifically chose the one eluting at 15.3min not the other one at ca. 15.5min? By contrast, two isomers found at ca. 20.2min and it seems both are chosen for MS2, which is a bit strange to me. It is not clear what collisional energy condition - HCD of the MS2 for these MS2 spectra in Fig. 3-4.

RESPONSE: Our revision reads:

"Non-targeted tandem mass spectrometric (MS/MS) analyses were performed using higher-energy collisional dissociation (HCD) with a stepped normalized collision energy of 20%, 40%, and 60% for those compounds detected with an ion intensity threshold of 5×10^3." (L163)

(6) I have a very close look at the two isomers of C19H30O5, as shown in Fig. 3, which is one of the two main OOMs in this study. Firstly, I strongly believe the isomer of C19H30O5 at RT=15.3 min is not SOZ, but might be the other dimer involving a-pinanediol (note that other possibility cannot be excluded here). Just simply looking at the proposed SOZ structure of C19H30O5, it is very unlikely to get a deprotonated ionization and result in a form of [M-H]-. The caption of Fig. 3 is not clear but I think the authors mentioned EIC of m/z = 337.2019 referring to [C19H30O5-H]-. Another reason is from Fig. S4, where the EIC of [C10H18O2+Na]+ shows two peaks, and the first one eluting at ca. 11.3 min, and the second peak eluting at 15.3 min. From my experience, this second peak at 15.3 min is an in-source fragmentation and likely from C19H30O5. The first peak eluting at ca. 11.3 min is almost for sure the α-pinanediol because it should be eluting at similar monomeric region to these monomer compounds (e.g. pinic acid C9H14O4 at 9.28min, C10H16O3 at 10.98 min as I found Table S2). This means that the entire structural analysis for C19H30O5 is likely wrong and therefore the interpretation should be re-done and re-written. I did not have further close

look at the two isomers of C16H26O6, but my assessment is that the proposed structures and reaction mechanism are highly uncertain, if no other evidence provided.

RESPONSE: Thank you for the comment on in-source fragmentation. Based on this comment, we revised the Table S2. We also revised as the following, regarding this isomer:

"The EIC of $C_{16}H_{26}O_6$ ([M-H]$^-$ m/z of 313.1677) shows five RT indicating the presence of isomers (Figure 3a). The two most abundant isomers with distinctive fragmentation mass spectra are those with the RT of 16.6 and 18.4 min, respectively (Figures 3b and c). The fragmentation of $C_{16}H_{26}O_6$ (RT = 16.6 min) is in good agreement with those shown by *Kristensen et al.* [2016]. It yields daughter ions with nominal m/z values of [M−H]$^-$ of 185, 167, 141, 123, 71 and 57. The pattern of daughter ions observed here is similar to that of pinic acid fragmentations ($C_9H_{14}O_4$, MW = 186), suggesting that the monomer building blocks consist of $C_9H_{14}O_4$ and $C_7H_{12}O_2$. While $C_7H_{12}O_2$ was not detected in the negative mode ([M-H]$^-$), in positive mode [M+Na]$^+$ MS/MS spectrum, $C_7H_{12}O_2$ there were both $C_9H_{14}O_4$ and $C_7H_{12}O_2$ (Figure S5a). These fragmentation ions suggest that this $C_{16}H_{26}O_6$ isomer has the same molecular structure and forms from particle-phase diacyl peroxide decomposition as previously shown by *Zhang et al.* [2015] (Figure S1). As stated above, $C_{16}H_{26}O_6$ was not detected in the gas phase. However, $C_{17}H_{26}O_8$ was detected both in the gas- and aerosol-phase. Thus, it is possible that $C_{16}H_{26}O_6$ forms in the particle phase from a diacyl peroxide ($C_{17}H_{26}O_8$) via diacyl peroxide decomposition (Figure 3d). The precursor $C_{17}H_{26}O_8$ can form in the gas phase from $C_9H_{13}O_5 \cdot$ acetylperoxy radical and a ring-opening acetylperoxy radical ($C_8H_{13}O_5 \cdot$) via the RO$_2$ + RO$_2$ dimerization, and then subsequently partition into the particle phase. These monomer building blocks for $C_{17}H_{26}O_8$ were identified by GECKO-A simulations (Table S4, Monomers 15 and 16).

As shown in Figure 3c, fragmentation of the $C_{16}H_{26}O_6$ (RT = 18.4 min) isomer yields daughter ions with nominal [M−H]$^-$ m/z of 171 ($C_8H_{11}O_4^-$), 141 ($C_8H_{13}O_2^-$), 127 ($C_7H_{11}O_2^-$) and 109 ($C_7H_9O^-$). The fragmented ions with m/z 171, 129 and 109 can be attributed to two of the most abundant monomers: diaterpenylic acid ($C_8H_{14}O_5$, MW 190) and cis-norpinic acid ($C_8H_{12}O_4$, MW 172) produced in the α-pinene ozonolysis system [*Kenseth et al.*, 2018; *Yasmeen et al.*, 2010]. The ions with m/z of 127 and 109 are the subsequent fragments of m/z = 171 formed by the loss of CO_2 and H_2O, respectively. The daughter ion $C_8H_{13}O_2^-$ ([M-H]$^-$ = 141) forms by the loss of CO_2 from $C_9H_{14}O_4$ (MW = 186) as discussed previously. Therefore, the possible monomer building blocks for $C_{16}H_{26}O_6$ are $C_8H_{13}O_2$ (m/z 141), which is a pinic acid's fragmentation ion, and $C_8H_{11}O_4^-$ (m/z 171) which can be a fragmentation ion of either *cis*-norpinic acid or diaterpenylic acid. *cis*-norpinic acid have two carboxylic acid moieties, so it can either undergo esterification reaction or react with sCI in gas-phase to form α-acyloxyalkyl hyderoperoxides [*Hall and Johnston*, 2012]. However, the esterification reaction for $C_{16}H_{26}O_6$ is lees likely, because another closed shell monomeric building block $C_8H_{16}O_3$ was not detected. Reaction with sCI is also ruled out, because we did not observe any signal reduction for $C_{16}H_{26}O_6$ (RT = 18.4 min) when the sCI scavenger was added. Thus, the monomer with m/z of 171 is more likely diaterpenylic acid (m/z of 171). Based on the above analysis, we propose two possible structures for $C_{16}H_{26}O_6$ (RT = 16.6 min) that can yield the above MS/MS fragmentation ions. First, $C_{16}H_{26}O_6$ may be a peroxyhemiacetal product from norpinalic acid ($C_8H_{12}O_3$) and $C_8H_{14}O_3$ which has a hydroperoxide moiety (Figure 3e). Second, it is also possible that $C_{16}H_{26}O_6$ forms from particle-phase decarboxylation of the diacyl dimer $C_{17}H_{26}O_8$, which forms from the gas-phase RO$_2$-RO$_2$ dimerization from $C_8H_{13}O_6 \cdot$ (a diaterpenylic acid precursor RO$_2$ radical [*Sato et al.*, 2016]) and $C_9H_{13}O_4 \cdot$ (the second generation RO$_2$ radical from α-pinene ozonolysis) (Figure 3f). The second proposed structure is also in agreement with the HrTOF-CIMS detection of the RO$_2$/HO$_2$ termination products of $C_8H_{14}O_5$ and $C_9H_{14}O_3$ from $C_8H_{13}O_6 \cdot$ and $C_9H_{13}O_4 \cdot$ RO$_2$ radicals, respectively. The GECKO-A model simulated the monomer building blocks required in the above two proposed reactions (Table S4, monomers 17 - 20). Both structures can explain the observed negative mode MS/MS spectra of $C_{16}H_{26}O_6$ (RT = 18.4 min). The positive mode MS/MS spectra of this

isomer show an additional peak of $C_8H_{14}O_5$ ([M+Na]$^+$ m/z of 213.0732) (Figure S5b), which could be a fragmented ion from the above proposed molecular structures of $C_{16}H_{26}O_6$." (L331)
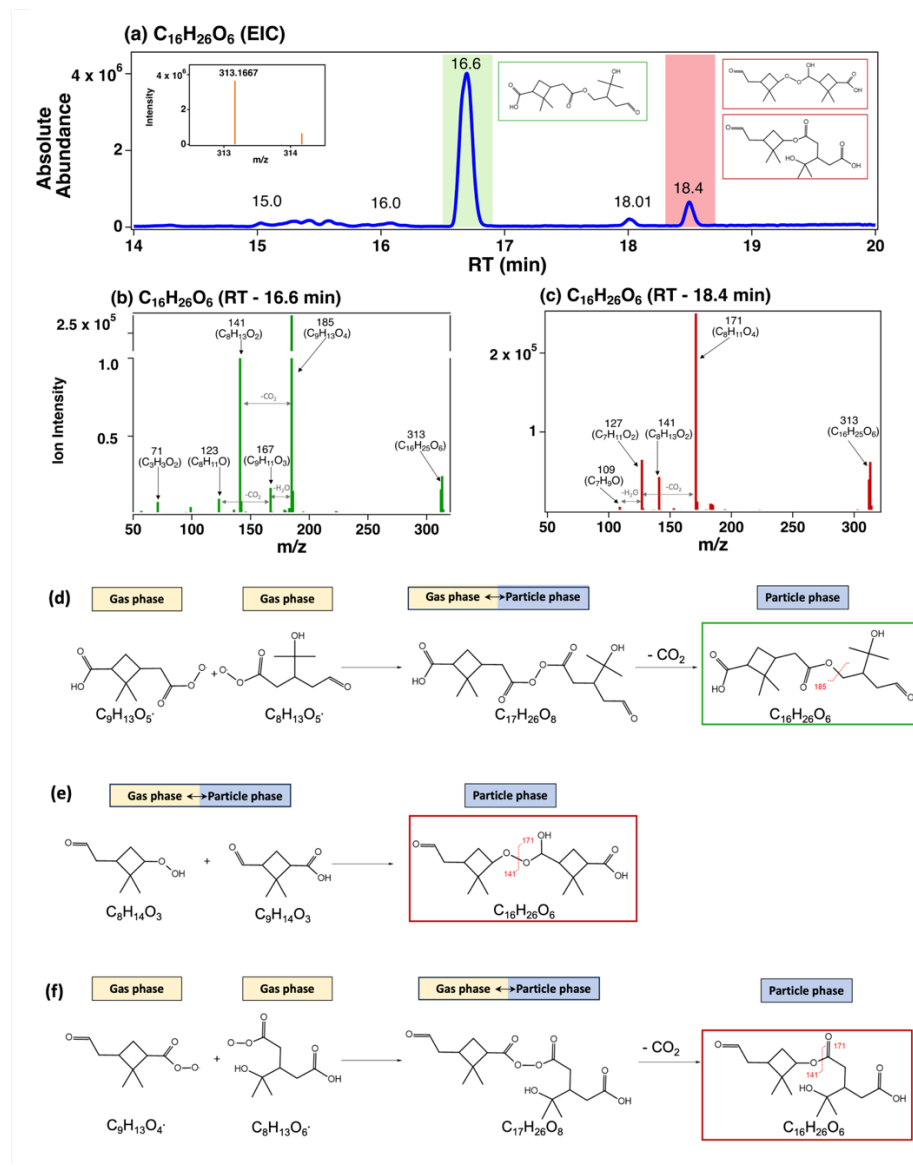

Figure 3. (a) EIC of $C_{16}H_{26}O_6$. The inset MS spectrum shows the mass peak of $C_{16}H_{26}O_6$ at RT = 16.6 min. MS/MS spectra of two isomers for $C_{16}H_{26}O_6$ with RT of 16.6 min (b) and RT of 18.4 min (c). The proposed the reactions and molecular structures for $C_{16}H_{26}O_6$ (RT = 16.6 min) (d) and $C_{16}H_{26}O_6$ (RT = 18.4 min) (e and f).

(7) Speaking of in-source fragmentation, it seems the authors are totally not aware of this issue, but this is a very common issue in LC-ESI Orbitrap MS and can result in misleading data interpretation. There are clearly many wrongly assigned monomer compounds that eluting at dimeric regions in Table S2, e.g. C10H16O3-2 eluting at 20.8 min must be a fragment from a larger molecular. By looking at Table S2, the monomer eluting region seems to be RT<12 min and dimeric eluting region is likely RT>12min. It seems that the authors need some basic HPLC knowledge and polar analysis to understand the eluting orders in

reverse phase C18 HPLC. Otherwise, I would assume the authors are not yet ready to handle such complex LC-Orbitrap MS dataset for complex SOA composition. This is especially for non-targeted analysis where the authors cannot simply rely on the output of Compound Discovery software, which usually needs further refinement of post data analysis and manual adjustment. In addition, pos mode usually has better ionization for dimers than neg mode. Comparing both negative and positive LC Orbitrap data are usually helpful for more accurate formula assignment, especially for positive mode where [M+Na]+, [M+NH4]+, [M+H]+, [M+K]+ as well as H2O neutral loss are common adduct forms and usually can ionize some compounds that not easily being ionized in negative mode, e.g. the structure of the proposed C19 SOZs is likely observed in pos mode (but very hard to identify since other possible structures cannot be excluded). However, the study focuses on negative mode, and it would be better to have pos mode results in these EICs.

I think the authors need to spend a bit of efforts to re-analyze their entire data to make the results and interpretation as accurate as possible.

RESPONSE: We have revised as the following:

"The parent molecules were deprotonated using (-)ESI and were detected as [M-H]$^-$ ions, also protonated by (+)ESI, and were detected as [M+H]$^+$ and [M+Na]$^+$ ions. This study is mostly based on the negative ionization results to compare with the particle-phase OOM chemical composition measured with the iodide HrTOF-CIMS. (L160)

Positive mode ionization mass spectra were also used additionally as shown in Figure S5 for $C_{16}H_{26}O_6$ isomers.
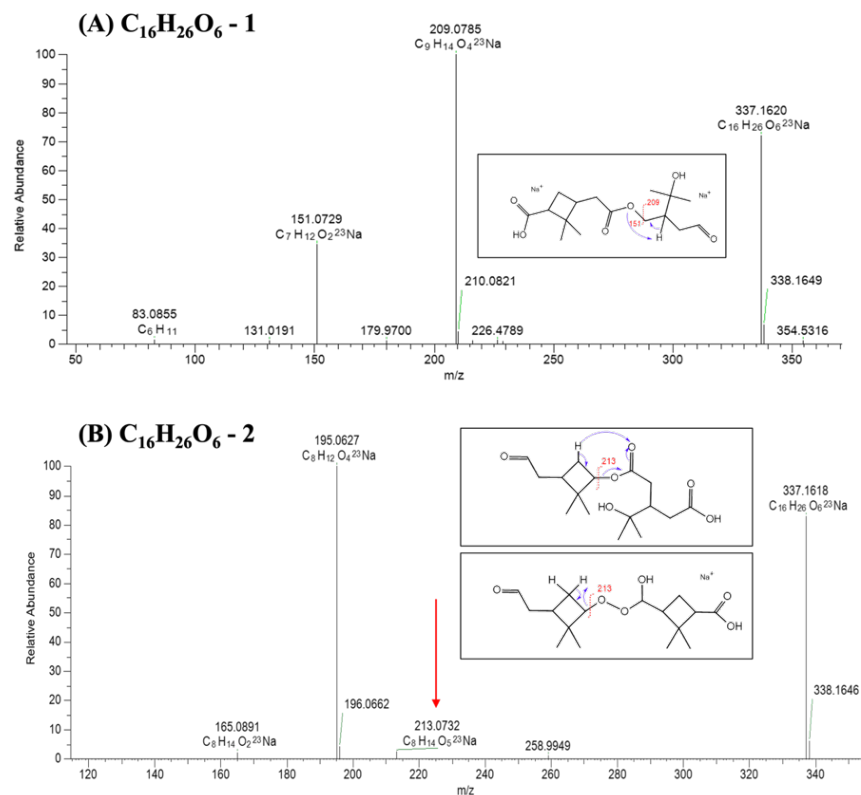

Figure S5. (a) The Na$^+$ adduct positive mode MS/MS spectrum of $C_{16}H_{26}O_6$-1 (RT = 16.6 min) (m/z = 337.1620) isomer showing the two monomeric units $C_9H_{14}O_4$ (m/z 209.0785) and $C_7H_{12}O_2$ (m/z 151.0729) fragmented by remote hydrogen rearrangement [*Demarque et al.*, 2016] as shown in inset. (b)

The Na$^+$ adduct positive mode MS/MS spectrum of $C_{16}H_{26}O_6$-2 (RT = 18.4 min) isomer showing the monomeric units $C_8H_{12}O_4$ (m/z 195.0627). $C_8H_{14}O_2$ (m/z = 165.0891) and $C_8H_{14}O_5$ (m/z 213.0732) could be fragmented from the two products following McLafferty rearrangement and remote hydrogen rearrangement respectively as shown in the inset.

(8) For writing, the authors should spend some efforts to improve the writing and results interpretation of the entire manuscript, especially these text in results and discussion are not in good quality and some logics behind the interpretation are not clear.

RESPONSE: Agreed, we extensively edited the revised manuscript.

Other comments:

Line 81-85: when refereeing CxHyOz, it is typically using MW= xxx rather than m/z of the same MW. If you are refereeing accurate m/z, it must be defined an adduct form. If you are referring one of the isomers of same formula, then RT must also include.

RESPONSE: Agreed, we added MW values or indicated the ionization mode together with m/z values throughout the manuscript.

Line 162: Such long filter sampling of 28h is expected cause some evaporation of SOA, and not sure this is the same filter for FIGAERO CIMS? If not the same filter, then might have further concern with the comparability between LC-MS and FIGAERO CIMS

RESPONSE: LC and FIGAERO use entirely different filters (as described in the manuscript). For clarification for the comparison of the two instruments, we revised the manuscript as the following:

"Combining these two independent high-resolution mass spectrometer techniques, HrTOF-CIMS and UPLC/(-)ESI-Orbitrap MS, provides a very powerful tool for analyzing the particle-phase chemical composition of OOMs and, for identifying molecular structures of different isomers. So far, only a few studies have combined these two methods to make molecular-level chemical speciation of OOMs (e.g., [*Du et al.*, 2022; *Huang et al.*, 2020; *Mehra et al.*, 2020]). However, these two methods have advantages and disadvantages. The FIGAERO HrTOF-CIMS measures the real-time particle-phase chemical composition after 20 minutes of filter collection on FIGAERO. There is the possibility that chemical species (such as dimers) are thermally decomposed during the desorption process from the FIGAERO [*Lopez-Hilfiker et al.*, 2014a]. On the other hand, UPLC/(-)ESI-Orbitrap MS is an offline technique. While this high-resolution MS/MS analysis can provide detailed chemical structure information, artifacts can occur during the filter collection and storage, and sample extraction processes. There are also matrix effects due to a relatively higher amount of particle mass [*Trufelli et al.*, 2011]. It is noted that HrTOF-CIMS (iodide ionization) and UPLC/(-)ESI-Orbitrap MS may have different ionization efficiencies and detection efficiencies for different chemical compounds. As will be discussed in detail in this study, they show very similar chemical compositions of OOMs (e.g., Figure 1), despite these differences." (L199"

Line 166-175: after the filter extraction with methanol, do these extracts injected into LCMS immediately? Methanol extraction is known to creates artifact, e.g. usually leading methyl ester formation

RESPONSE: Yes, all the injections were done immediately after extraction.

RESPONSE: Agreed, we removed this sentence.

RESPONSE: Thank you. You are correct and verify is not the best word choice. GECKO-A is intended to support the interpretation. GECKO-A does not directly verify molecular structures. Instead, it predicts potential oxidation products that are considered chemically reasonable based on chamber experimental data and validated structure-activity relationships (SARs). As one of the most advanced atmospheric mechanism generators currently available, GECKO-A has been used in a number of peer-reviewed studies, with its α-pinene mechanisms being particularly well-studied and compared against observations (e.g., McVay et al., 2016; Afreh et al., 2021Galeazzo et al., 2021; Gu et al., 2024). In this manuscript, we intended to highlight that GECKO-A serves as a valuable tool to support the assignment of OOM structures but does not independently verify those molecular structures.

To improve clarity and accuracy, we have revised the GECKO description as follows:

"GECKO-A model simulations

To support interpretation of the chemical reactants and products of a-pinene ozonolysis reactions in the gas phase, as well as their molecular structures, we generated an explicit α-pinene degradation mechanism using GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) ([*Aumont et al.*, 2005; *Camredon et al.*, 2007; *Valorso et al.*, 2011], updated per [*Jenkin et al.*, 2020; *Jenkin et al.*, 2019; *Jenkin et al.*, 2018]). GECKO-A is an automated tool that generates explicit atmospheric oxidation schemes for organic compounds based on experimental data and structure–activity relationships (SARs) in the absence of experimental data. The GECKO-A generated mechanisms have been used in many studies to investigate species formed during oxidation under atmospheric conditions (e.g., [*Afreh et al.*, 2021; *Galeazzo et al.*, 2024; *He et al.*, 2024; *Peng et al.*, 2021]). In this study, a five-generation α-pinene oxidation mechanism was generated using GECKO-A and was employed to verify the proposed molecular structures of monomer building blocks (as discussed in detail in Section 3). The generated scheme includes 870,343 reactions and 152,162 species. Since GECKO-A currently does not include particle-phase reactions, the search and selection processes focused on C10 and C9 reactant isomers identified from flow tube experiments. The gas-particle partitioning is treated dynamically based on Nannoolal et al. [*Nannoolal et al.*, 2008] to calculate saturation vapor pressures." (L228)

RESPONSE: We have rephrased this as the following:

"In all mass spectra, clearly, monomers (C_5-C_{10}) and dimers (C_{15}-C_{20}) were resolved. In the gas phase, the ratio of monomers over dimers was 91:9, whereas in the particle phase, the ratio is 81:19 (both measured with HrTOF-CIMS), indicating that dimers, in general, are more favorable for gas-to-particle conversion due to relatively lower volatilities, consistent with previous observations [*Lee Tiszenkel and Lee*, 2023].

Line 277: "We chose only the 50% most abundant OOMs in the present study". This 50% is sorted by which measurements? This is also making me confused as in line 254-255 "These compounds were selected by considering the reproducibility of their desorption thermograms". Are these same?

RESPONSE: We made the following revisions for clarity:

"For the OOMs FIGAERO-HrTOF-CIMS, we used the 50% most abundant OOMs, which contributes about 99% of all the ions detected. For the OOMs with UPLC/(-)ESI-Orbitrap MS, we used data that had the S/N > 3." (L251)

"In total, 437 OOMs were identified in the gas phase with the HrTOF-CIMS, 405 OOMs were identified in the particle phase with the FIGAERO -CIMS, and 167 OOMs were identified with UPLC/(-)ESI-Orbitrap MS (Figure 1h). As shown in Figure 1g, each OOM detected by LC-Orbitrap MS had 2-8 isomers. Table S1 shows particle-phase OOMs detected in HrTOF-CIMS (gas- and particle-phase) and UPLC/(-)ESI-Orbitrap MS (particle phase). There were 124 OOMs that were detected only in the gas phase; 12 OOMs that were detected only in the particle phase (by the FIGAERO-CIMS and UPLC/(-)ESI-Orbitrap MS) but not in the gas phase. There were 96 OOMs detected in both the gas and particle phases, suggesting that these are OOMs that likely undergo gas-to-particle conversion.

In total, 437 OOMs were identified in the gas phase with the HrTOF-CIMS, 405 OOMs were identified in the particle phase with the FIGAERO -CIMS, and 167 OOMs were identified with UPLC/(-)ESI-Orbitrap MS (Figure 1h). As shown in Figure 1g, each OOM detected by LC-Orbitrap MS had 2-8 isomers. Table S1 shows particle-phase OOMs detected in HrTOF-CIMS (gas- and particle-phase) and UPLC/(-)ESI-Orbitrap MS (particle phase). There were 124 OOMs that were detected only in the gas phase; 12 OOMs that were detected only in the particle phase (by the FIGAERO-CIMS and UPLC/(-)ESI-Orbitrap MS) but not in the gas phase. There were 96 OOMs detected in both the gas and particle phases, suggesting that these are OOMs that likely undergo gas-to-particle conversion.

Table S2 lists the select 77 particle-phase OOMs, along with their distinct retention time (RT) in the liquid chromatograms (indicating isomers) and tandem MS/MS fragmentation ions for each isomer. These 77 compounds were detected in the particle phase both by the FIGAERO-CIMS and UPLC/(-)ESI-Orbitrap MS and showed high reproducibility in the FIGAERO thermogram and LC chromatogram. Using the liquid chromatogram and MS/MS fragmentation ions, we identified the possible molecular structures of isomers and their formation reaction pathways. Here, we show our identification processes and proposed structures for $C_{19}H_{30}O_5$ ([M-H]$^-$ = 337.2019) and $C_{16}H_{26}O_6$ ([M-H]$^-$ = 313.1677)." (L264)

In Fig. 1, LC-MS has many isomers and is the m/z peak area referring sum of multiple isomers? Fig. 1 caption, c and d are from FIGAERO-CIMS, not e and f. Fig.1(g) should be LC-Orbitrap data, am I right?

RESPONSE: Figure caption is revised now:

"**Figure 1.** High-resolution spectrometer analysis of OOMs detected from α-pinene ozonolysis flow-tube experiment with α-pinene of 240 ppb, ozone of 1.2 ppm, a temperature of 298 K, RH < 10 %, [OH] of 1.6 ppt and residence time of 150 s. (a) Mass spectrometer and (b) mass defects of particle-phase OOMs measured with UPLC/(-)ESI-Orbitrap MS. (c) Mass spectrometer and (d) mass defects of particle-phase OOMs measured with FIGAERO iodide HrTOF-CIMS. (d) Mass spectrometer and (b) mass defects of gas-phase OOMs measured with iodide HrTOF-CIMS (g) The number of isomers identified for each detected OOMs in the particle phase. For clarity, only every other OOMs are shown with their chemical formulas here (see Figure 4c for the entire formulas for all OOMs). (h) Venn diagram showing the number of compounds detected from the gas phase (red) and particle phase (green) with FIGAERO HrTOF-CIMS, and in the particle phase with UPLC/(-)ESI-Orbitrap MS (blue)."