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Atmospheric Chemistry and Physics Discussions

Interactive comment on "High molecular weight SOA formation during limonene ozonolysis: insights from ultrahigh-resolution FT-ICR mass spectrometry characterization" *by* S. Kundu et al.

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This manuscript describes the molecular composition of secondary organic aerosols derived from dark ozonolysis of limonene using FT-ICR-MS. Limonene SOA is generated in a Teflon bag in the absence of light, seed aerosol, and hydroxyl radical scavenger. The authors use RO2 and RO chemistry to describe the formation of low molecular weight monomer products. The formation of high molecular weight products are explained by a combination of non-condensation reactions (hemi-acetal reactions, hydroperoxide reactions and Criegee radical reactions) and condensation reactions (aldol reactions and esterification reactions), with conflicting results depending on analysis

technique. The manuscript is well written and easy to follow. The work is an extension on already published work on SOA derived from limonene ozonolysis, with only minor new scientific contributions, which are not very well emphasized. I recommend the authors focus and enhance the sections that provide new scientific insight into the molecular composition of limonene SOA. I support publication in ACP after these comments are considered.

Response: We thank the reviewer for carefully reviewing the manuscript and providing insightful comments. We revised the manuscript to emphasize our contributions; however the previous contributions are essential to the overall understanding of the limonene ozonolysis SOA composition. Our confirmation of the previous findings using independent experiments and methods is also a valuable contribution to the literature.

The major new findings of this study are:

(1) A high number of molecular formulas (n = 1197) were determined in this study compared to previous work. This may be due to the increased sensitivity of the LTQ FT Ultra (Thermo Scientific) with the co-addition of 200 transients.

(2) The observed homologous series in the low MW region are better predicted by a combination of functionalization (multistep oxygen-increasing-reactions) and fragmentation (bond scission) of alkoxy radicals and reactive uptake of gas phase carbonyls.

(3) An integrated approach involving the evaluation of the elemental ratios, DBE, reaction matrix and fragmentation studies was applied in this study to interpret the formation of high MW compounds.

(4) This study demonstrates that most of the high MW compounds are accretion products of multiple pathways .

Major Comments:

1) Page 2170 line 5-7: The authors state that "Low MW compounds were not fully explained. This suggests a need to characterize…", and that this is part of the purpose of

this paper. In addition, Figures 2a and 3 and the oxygen increasing reactions were proposed by Walser et al. 2008. While the authors indicate the formation of products not included explicitly in Walser et al. 2008, there is no explanation of the new chemistry that is presented. Walser et al. 2008, uses this same scheme you are presenting here to explain the presence of homologous series. What new chemistry have you included to further the explanation of the low MW compounds? Can you quantify to some extent how your new chemistry scheme allows you to better predict the low MW region, such as Walser et al. Figure 8. Does your scheme account for more low MW products and thus necessitate an additional pathway to be considered?

Response: This work presents both the assigned low and high MW limonene ozonolysis SOA components with an emphasis on the formation of the high MW products. Since the low MW SOA components are considered to be building blocks of the high MW SOA components, it is important to revisit the details of their composition. In the work of Walser et al. (2008) they explained the low MW SOA formation with consideration of the isomerization and scission of alkoxy radicals. They mentioned the following in their work.

(1) “The mechanistic understanding of the relationship between different members of CH2-families is not as straightforward as for the members of O-families” (Page 1020 of Walser et al., 2008). We observed that if we consider either (a) multistep isomerization of alkoxy radicals followed by scission of alkoxy radicals or (b) scission of alkoxy radicals followed by multistep isomerization and (c) reactive uptake of carbonyl compounds on the aerosol phases, most of the CH2-homologous series formation can be explained. Some of these representative reaction schemes are provided in Figures 2, 3, S4a and S4b.

(2) Figure 8 of Walser et al., (2008) shows the predicted compounds following their reaction mechanisms and observed compounds are not identical in many cases. Consideration of functionalization (multistep oxygen-increasing-reactions) and fragmentation (bond scission) of alkoxy radicals and reactive uptake of gas phase carbonyls can

better explain most of the observed low MW compounds. To illustrate this, we plotted the observed and predicted compounds in the Kendrick analysis plot like Walser et al. It shows better overlap between the observed and predicted low MW compounds. This is described in the revised manuscript (lines 228-240).

Specifically we wrote, “The diverse homologous series with carbon atom numbers of 7-15 and with oxygen atom numbers 3-9 (Figure 1) cannot be explained with only by the oxygen-increasing-reactions and single scission of alkoxy radicals as proposed by Walser et al., (2008). In the oxygen-increasing-reactions, the alkoxy radical (I, $C_{10}H_{15}O_3$) resulting from the limonene ozonolysis converts to another alkoxy radical (II, $C_{10}H_{15}O_4$) with one more oxygen atom following the isomerization, oxygen addition and RO2 radical reactions (Figure 2a). In the scission step, carbon number is decreased with the decrease/no change of oxygen number. There must exist a process which can increase the carbon number of the low MW compounds since we observe several highly abundant compounds with carbon atom number > 10. Hence, we explain the CH2 homologous series formation by: (a) the multistep oxygen-increasing-reactions of alkoxy radicals followed by scission of alkoxy radicals and (b) scission of alkoxy radicals followed by its multistep oxygen-increasing-reactions and (c) reactive uptake of the gas phase carbonyls.”

2) Figure 2b and c are potentially important pathways that have not been fully explored using HR-ESI-MS techniques. Further analysis of compounds with 16 > C > 10, which could not form from oligomer formation of limonene ozonolysis products, could be interesting. Perhaps MS/MS on these fragments would suggest either formaldehyde or glyoxal as the major contributor to this pathway. Why do you choose a partially hydrated gloxal? What about using your Kendrick analysis to look for homologous series of glyoxal? How many of these peaks could be explained by this formation process, from either uptake or formaldehyde or glyoxal?

Response: Thank you for pointing out this potential misunderstanding. The presence of homologous series does not confirm a reaction pathway. Consider the consistently present CH2 homologous series, does the CH2 homologous series suggest CH2 addition? Instead, it appears to be a coincidence of the variety of ways that the molecules can be built. Likewise, formaldehyde (HCHO) series are consistently present in complex organic matter (Mazzoleni et al., ES&T 2010). As expected, a majority of the low MW components were associated with HCHO homologous series. We did not find significant evidence of glyoxal homologous series, however the lack of homologous series does not negate the possibility of glyoxal uptake. Furthermore since the carbonyl functional groups are reactive, it is not clear how we should find them. MS/MS studies did not clarify the reactive uptake question since we did not find sufficient evidence of CH2O or C2H2O2 elimination in the MS/MS spectra. We have clarified these points in the revised manuscript (lines 376-379).

3) The authors state that there is evidence of isomers present in MS/MS. Why then would you propose a structure as in Figure 7, seems to be totally arbitrary. Page 2180, line 20-21. Is there a reference to who previously proposed this structure, or just the structure you proposed in Fig. 2b? There are a number of structures proposed for C9H14O3 and this is not one of them, limonalic acid (Glasius et al., 2000), norlimononic acid (Warsheid et al., 2001, Glasius et al., 2000), keto-limononaldehyde (Leungsakul et al., 2005).

Response: We have proposed a group of structural isomers with chemical formula C11H18O6, not C9H14O3 to explain the observed fragment ions of m/z 245 . This peak is the most dominant in the full scan FT-ICR mass spectra and could result from the reactive absorption of HCHO as shown in the Figure 2b. The exact masses of the predicted fragments from the structures shown in Figure 7 (a-e) are similar to that of observed major fragments. These suggest that the structure of C11H18O6 could be related with the proposed structural isomers.

4) Figures 2 and 3, S4 (a) and (b) could be easier to follow if the final neutral molecules you detect were boxed. In addition, the separation by DBE is somewhat confusing, why would these OIR reactions conserve DBE, as you seem to imply from your separate

mechanisms based on DBE? Perhaps this is a point you should emphasize if it is true, or state that this is just the way you arranged the mechanisms to explain the products.

Response: Thank you for the suggestion; we boxed the final neutral molecules in Figures 2, 3, S4 (a) and S4 (b) as suggested. The reaction between RO2 radicals can generate alcohol and ketone (RO2 + RO2 → Alcohol + Ketone + O2). The DBE of an alcohol is 1 less than that of the ketone. That is why the mechanisms were explained based on DBE. We have stated this point in the revised manuscript. Please see the lines 272-274

5) How will the uptake of gas-phase carbonyls change the DBE in the low MW region? Can this help explain the presence of DBE = 4 and 5 compounds observed in the low MW region? What about the uptake of gas-phase carbonyls to the Group II, III and IV?

Response: The reactive uptake of glyoxal may explain the presence of DBE 4 and 5 compounds. Formaldehyde addition can't explain it because the double bond is not retained in the reactive uptake. We did not find significant evidence for HCHO or glyoxal homologous series in the Group II-IV compounds. We mentioned these points in the revised manuscript (lines 284-285).

6) Page 2177 line 20-21: This statement seems to suggest artifacts from the sample work-up and not from ozonolysis of limonene? Are there any control experiments with extraction in only acetonitrile? Were compounds of DBE = 2 detected in Bateman et al., 2009, or Walser et al., 2008, where water was not used to extract the SOA? Were these potential artifact peaks used to estimate the contribution of reactions for the oligomers?

Response: Thank you for pointing out this misunderstanding. We revised our comments to suggest although hydration of carbonyls was possible other studies without aqueous extraction saw similar compounds. We observed 44 compounds with DBE 2. To determine if the compounds resulted from sample prep, we compared our data with the Bateman et al., 2010 and Walser et al., 2008 where water was not used for extraction procedure. Bateman et al. observed 15 compounds. Walser et al. observed

35 compounds in the positive mode and 18 compounds in the negative mode. Several molecular formulas were common between this study and the studies of Bateman et al., 2010 and Walser et al., 2008. This result suggests that the DBE 2 compounds are not likely artifacts of the water extraction procedure. This has been mentioned in the revised manuscript (lines 274-282).

7) There is no definition of how one calculates DBE included in the introduction or experiment, please include this.

Response: The equation for DBE has been added to the revised manuscript (lines 102-104).

8) Page 2178 line 12-13: I do not see an example of 3 DBE increase by Criegee radical reactions as mentioned in Fig S5 or S6. Figure S6 (b) Esterification pathway has an "(a) DBE increase by 2" label that is confusing. The important point is the change in DBE, not the total increase. For example the examples you provide in Figure S6a and S6b both show that in these channels DBE is additive, that is, DBE of Compound 1 + DBE compound 2 = DBE oligomer, this is true in all the cases you show in Figure S6, just that the channels in red, one of the compounds has a DBE of 2. The important consideration is how prevalent are compounds with DBE =2? Will they out compete compounds with DBE =3 for reaction? It is suggested that they (DBE=2 compounds) occur via artifacts from use of water during extraction (Pg 2177 line 20-21). The difference in DBE for Criegee radical, hemiacetal and peroxide pathways is, DBE of compound 1 + Compound 2 = DBE oligomer -1. Thus, because the majority of low-MW monomer compounds have DBE of 3, the fact that the majority of Group II compounds have DBE =5, indicates the channels that are non-additive are responsible for oligomer formation.

Response: The label "DBE increase by 2" in Figure S6 (b) was a mistake. We have deleted this phrase. It is true that the reaction of DBE 2 compounds can't out compete that of DBE 3. We also agree that since the majority of low MW compounds have DBE

of 3, the majority of Group II compounds have DBE =5, indicating the channels that are non-additive are responsible for high MW formation. We have modified our manuscript accordingly (lines 288-298).

9) The inclusion of the hydroperoxide channel is definitely unique and should be emphasized, if you can find evidence in MS/MS of their fragmentation that would greatly strengthen this paper. This would be a good starting point and should definitely be cited. (Sadezky et al., ACP, 2008).

Response: We went through the paper of Sadezky et al., 2008. In our hydroperoxide channel, hydroperoxides react with neutral molecules formed during the limonene ozonolysis. Sadezky et al. observed hydroperoxide oligomers by the linking of Criegee radicals. These products were considered to form in gas phase. The structure of Sadezky et al. oligomer is X-(CI)n-Y, where X stands for gaseous molecules of parent hydrocarbon and Y stands for capped CI radicals and CI stands for Criegee radicals. Thus it appears that our idea and the idea at Sadezky et al. paper are different. We agree that it could be interesting to look for Sadezky et al. type products in future studies. We have mentioned the Sadezky et al. formation process in the introduction section of the revised manuscript (lines 82-42).

10) Page 2179 line 4-5: This suggests that your laboratory limonene ozonolysis SOA should be similar to ambient aerosol, which I would argue against.

Response: We removed the sentence.

11) Page 2179 lines 20-21: How did you determine the functional group make-up of the Group 1 compounds? For example, what molecules have alcohol, carbonyl and/or carboxylic acid groups? This should be included in the SI.

Response: Most of Group I analytes (71 of 74) have 4 or more oxygen atoms and fragmentation analysis has suggested the presence of structural isomers. We have also observed loss of 44 (CO2), 28 (CO) and H2O elimination from adjacent OH groups.

Please see the Figure 7. Hence, it was assumed that each building unit in Group I has the structure/structural isomers involving alcohol, ketone and carboxylic acid. This point has been mentioned in the revised manuscript (lines 329-332).

12) Page 2179 line 27 – page 2180 line 3: What percentage of the total group II and group III compounds were covered? What about the % of overlap between the different reaction pathways?

Response: The numbers of compounds detected in this study are 193 for Group II and 158 for Group III compounds with relative abundances >1%. The Criegee channel can explain 58% of Group II compounds while hydroperoxide, hemiacetal, and condensation channels can explain 78%, 79% and 74%, respectively. Criegee, hydroperoxide, hemi-acetal and condensation channels can explain 58%, 64%, 71% and 66% of Group III compounds. The percentage of overlap between the reaction pathways is significant. For example, 88 of 193 predicted compounds in Group II and 91 of 158 Group III compounds can be formed by all 4 of the proposed channels. All these points have been mentioned in the revised manuscript (lines 343-348).

13) Page 2180 line 5-8: Could this be because there are more alcohol and carbonyl containing molecules in group 1, than peroxides and Criegee radicals? Is there a possible way to constrain some of these potential reactions? Possibly by weighting by abundance for the group I compounds, or some form of general rate constants for each reaction pathway, or anything that includes some form of the chemistry involved will be more informative than direct counting.

Response: The higher matching probability could be related with the higher number of building units for hemi-acetal and condensation reactions than for Criegee and hydroperoxide reactions. To address this issue, the contribution of peak intensities were calculated for predicated Group II-III compounds formed via the proposed reaction channels. Although the matching probability is low for Criegee and hydroperoxide reaction channels, they can account for more than 85% of total Group II peak intensity

and more than 78% of total Group III peak intensity. We have mentioned these points in the revised manuscript (lines 352-358).

14) Page 2180 line 20-21: Is there any evidence of losing glyoxal during the fragmentation? This is never explicitly mentioned.

Response: We did not see losses of glyoxal in the fragmentation processes. Previously, glyoxal was included in the reaction scheme as a representative reaction scheme for reactive uptake reaction process.

15) The authors have used fragmentation of only 5 molecules to try and elucidate at the formation processes. It seems that the statistics on this approach are not that great. Perhaps if many molecules were fragmented, the picture would become more clear and conclusions easier to draw from the fragmentation of the oligomers.

Response: We focused the fragmentation analyses on the highly abundant peaks to avoid the simultaneous fragmentation of several precursors. We agree with the referee that more work would clarify and strengthen the conclusions. We have mentioned this uncertainty in the conclusion section of manuscript.

16) Page 2183 lines 9 -26: Conclusions offer no new insights into the formation of high MW compounds. The authors should rework the data analysis of the reaction matrix as previously suggested. In addition, several topics mentioned above could be expanded upon.

Response: We reworked the data and modified the conclusions to emphasize the new insights. As described above, the main new insights of this study are: (1) A high number of molecular formulas (n = 1197) were determined in this study compared to previous work. This may be due to the increased sensitivity of the LTQ FT Ultra (Thermo Scientific) with the co-addition of 200 transients. (2) The observed homologous series in the low MW region are better predicted by a combination of functionalization (multi-step oxygen-increasing-reactions) and fragmentation (bond scission) of alkoxy radicals and reactive uptake of gas phase carbonyls. (3) An integrated approach involving the evaluation of the elemental ratios, DBE, reaction matrix and fragmentation studies was applied in this study to interpret the formation of high MW compounds. (4) This study demonstrates that most of the high MW compounds are accretion products of multiple pathways .

Minor Comments: Page 2169 line 15-17: "other monoterpene ozonolysis" is awkward Response: Revised to "alpha-pinene".

Page 2170 line 29: insert "with increasing MW" between "ratios" and "in" Response: Done.

Page 2172 line 5: insert "thick" after 5 ml Response: Done.

Page 2174 line 21: insert "of" between "20%" and "ions" Response: Done.

Page 2178 line 20: delete extra space between "vs." and "O:C" Response: Done.

Page 2179 line 16: insert comma after "Criegee radicals" Response: Done.

Page 2180 line 16: insert "a" between "on" and "singular" Response: Done.

Page 2181 line 5: It seems from the figure that the other dominant ion is "m/z 183" not "m/z 185" Response: We didn't find m/z 183 to be taller than m/z 185 in any of our mass spectra.

Page 2181 line 9 and line 12: Should reference "Fig. 8a" not "Fig. 7a" Response: Done.

Page 2181 line 20: Please label which panels you refer to Fig S7 b, c, and d Response: Done.

Page 2182 line 5: Reference Fig S7e Response: Done.

Page 2183 line 8-9: insert "in" between "trends" and "O:C"; change "group" to "groups" C780 Page 2191 Figure 2 text, line 3: Arrows are confusing, it should have an arrow

with O2 above it, not an arrow pointing to O2, as this leads to RO2 Response: We have changed (isomerization → O2 addition → RO2) to (isomerization of alkoxy radical → O2 addition with alkyl radicals → reaction between RO2 radicals) for clarification. Please see the Figure 2 caption.

Page 2192 Figure 3 text, line 3: Same comment as above for Figure 2. Response: Done.

Page 2196 Figure 7 text line 3: Reference subpanels, insert "(a) – (e)" after "panel". Response: Done. Please see the figure 7 caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2167, 2012.

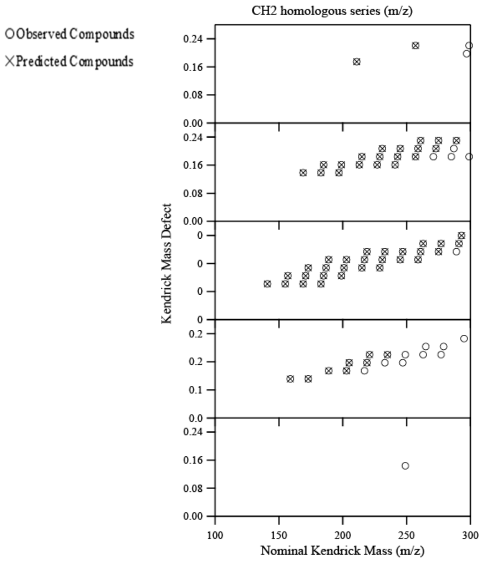

Fig. 1. Observed vs. Predicted Low MW Compounds