Atmos. Chem. Phys. Discuss., 12, C776–C781, 2012
www.atmos-chem-phys-discuss.net/12/C776/2012/

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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.

Anonymous Referee #2

Received and published: 20 March 2012

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

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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.

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?

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 of 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?

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

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the structure you proposed in Fig. 2b? There are a number of structures proposed for $C_9H_{14}O_3$ 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).

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.

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?

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?

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

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 outcompete

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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.

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).

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.

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.

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?

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.

14) Page 2180 line 20-21: Is there any evidence of losing glyoxal during the fragmen-

tation? This is never explicitly mentioned.

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.

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.

Minor Comments:

Page 2169 line 15-17: “other monoterpene ozonolysis” is awkward

Page 2170 line 29: insert “with increasing MW” between “ratios” and “in”

Page 2172 line 5: insert “thick” after 5 ml

Page 2174 line 21: insert “of” between “20%” and “ions”

Page 2178 line 20: delete extra space between “vs.” and “O:C”

Page 2179 line 16: insert comma after “Criegee radicals”

Page 2180 line 16: insert “a” between “on” and “singular”

Page 2181 line 5: It seems from the figure that the other dominant ion is “m/z 183” not “m/z 185”

Page 2181 line 9 and line 12: Should reference “Fig. 8a” not “Fig. 7a”

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

Page 2182 line 5: Reference Fig S7e

Page 2183 line 8-9: insert “in” between “trends” and “O:C”; change “group” to “groups”

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

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

Page 2196 Figure 7 text line 3: Reference subpanels, insert “(a) – (e)” after “panel”.

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