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Atmospheric
Chemistry
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Discussions

Interactive comment on "Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions" *by* O. Vesna et al.

Anonymous Referee #1

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This manuscript describes a new finding of a water dependent channel in the condensed phase ozonolysis of the unsaturated fatty acids. (Oleic acid and ploy-unsaturated arachidonic acid AR were used as model compounds). Hygroscopic growth measurement were used to detect the degree of reaction at different ozone exposures and at different RH during the reaction. In the case of AR where the particles became more hygrospcopic, a functional group analysis was performed. COOH/CH ratio followed quite well the hygroscopic growth factors at 90%RH, both increasing with increasing RH during the reaction. The interpretation of the data is highly speculative. This must be because, no speciation was performed during the study. It would be possibly tolerable, but the essential part of the interpretation, the reconstruction of the observed GF90 from expected products and measured COOH/CH ratios, was difficult to follow. This left the impression that somewhat more work is needed to round up the manuscript. The paper could be published in ACP after major revision i.e. clarification of the interpretation. There are also some minor points,

Major concern:

Page 15659 ff

I cannot easily follow your argumentation during this paragraph. I understand that you end up with 3:1 MA/GA (moles), if you formally split the AR double bonds and assume formation of carboxylic groups on both ends. I also understand that you assume for the non-reacted rest and possible oligomers etc AR like composition.

One difficulty: on p 15 658 you determined the ratio of the acidic and aliphatic protons. This ratio is plotted in Fig. 2b and is named COOH/CHn in the axis legend. (I calculate a H-COO/H-C of about 0.04-0.05 (1 COOH, 21 beta-CH, 2 alpha-CH) commensurable with your observation of 0.055 in the dry case.) In the paragraph starting on p. 15569 you obviously argue now with COOH/CH group ratio (!?), but you use a similar notation, COOH/CH, as in the figure. This introduces some confusion, since I expect values compatible with Figure 2b. As a consequence, for example, the target number, which you use to construct the mixture, is nowhere in the manuscript. Moreover, I still do not fully understand the numbers you produced. Why has AR a COOH/CH ratio of 0.12, I calculate about 0.1? Why do specify a RH=83% for this ratio? How do you treat MA, it has no beta H-C. How do treat GA (4 alpha, 2 beta CH)? I cannot reconstruct your COOH/CH ratio of 0.4 for a 3:1 mole mixture of MA and GA from the information given.

I suggest that the authors reformulate the text and give more clarifying information for each step. I also strongly suggest that you use only one ratio either the proton ratio or the groups ratio in both this paragraph and in the Figure 2b. Overall, I find this part highly speculative, and indeed the result does not match the finding very well. This might be due to the fact that malonic acid evaporates or that the species under discussion are not formed to the extent as assumed.

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Minor points

Page 15 654, line 7f

At least the number of C-atoms of arachidonic acid must be given. Better, if the structure formula would be also given. This would help e.g. the understanding of the "expected products"; (p. 15659f)

Page 15 654, line 15

There is only one reference Hasson et al. 2001.

Page 15556, line 1f

The fact that you varied the relative humidity as a parameter should be added here. It is mentioned in the introduction, but is part of the experimental procedure.

Page 15655, line 6

Is the Teflon reactor a laminar flow tube or a batch reactor ? Please, clarify ? If it is a batch reactor, information on mixing behavior is needed.

Page 15655, line 16

I guess the measurement of 20 -250 nm particles is the potential range of the HTDMA. You selected 100 nm and 68 nm particles only ? Please, clarify.

Page 15656, line 3f and Figure 1

Dehydration curves only make sense if the particles were deliquesced before dehydration. Was that the case? My impression, the particles did not show deliquescence at the available range of RH. Therefore the dehydration measurements do not really add new information. Figure 1 shows that hydration or dehydration mode lead to the same results. Since the Figure 1 is difficult to read, you better use filled and hollow symbols for processed and non processed aerosols.

Page 15656, line 8

I wonder at which particle diameter the volume size distribution has its maximum. Is the composition of the filter samples representative for the particle sizes selected for the hygroscopic growth studies ? Could size dependent composition have influenced the analysis on p. 15659 ff. Smaller particles tend to deplete in semivolatiles faster than larger particles.

Page 15656, line 8, 15, 18

Samburova et al. 2007 !

Page 15657, line 6

The text refers to Figure 1a, not to Figure 2a.

Page 15658, line 15ff

How much is really known about the ozonolysis products of AR? Please, add references here or clarify your rationale. Prenni et al. investigated merely the hygroscopic growth of MA and GA, they did not study the ozonolysis of AR. This misleading.

Page 15658, line 15ff

It is kown that e.g. GA evaporates from particles. The difficulty to match such HG measurements from different groups is e.g. discussed in Koehler et al. ACP, 2006 and was attributed to uncontrolled evaporation. Malonic Acid maybe even more affected. Bilde et al. used this phenomenon to determine vapor pressures of dicarboxlic acids. Did you have any means to estimate a possible evaporation, e.g. by comparing the size distribution before and after processing with O3? Or by measuring the selected size after the passing the diffusion dryer ?

Page 15658, line 29 ff and Figure 2b

Why don't you show the quality of the correlation by plotting GF90 vs COOH/CH. What are possible reasons for the outliers ?

Page 15 659, line 8f

Who’s current understanding of CI fate do you mean. Please, add reference or state clearer that it is your interpretation and on what it is based.

Page 15 659, line 18f

Do you have any indication (H.NMR e.g.) that the water dependent mechanism is operating also in the OA case. What would you expect? Are these expectations in accordance with your GF measurements ?

Page 15660, line 24

The ozone exposures are still high compared to the atmosphere. Moreover, the particles were single component particles. Thus higher order processes may contribute more than in the case of lower exposure over longer time scales. This limits somewhat direct transfer to the atmosphere.

Figure 2b

You plotted the GF90 calculated from the measurements. This not a correction to 90% RH. Please, note that in the legend of the left hand y-axis as GF90.

Figure 3

The scheme is somehow difficult to read. The aldehyde on second level is formed together with the CI. So the arrow should be replaced by a plus-sign. There should be arrows from the CI to products 2,3,4 and the reactants with a plus-sign noted besides the arrows. In total you would have 5 arrows, one to acid (1), 3 with reactants added to product 2,3,4, and one with plus sign and water to the intermediate (5) which than decays in the two channels.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15651, 2007.