

Interactive comment on “Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of $\vec{\alpha}$ - and $\vec{\beta}$ -pinene” by F. Yasmeen et al.

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We thank anonymous reviewer #1 for constructive comments which helped to improve our manuscript. Our responses to the specific comments raised by the reviewer are as follows:

p.10869, line 26 The smog chamber SOA samples were generated in the presence of highly acidic seed. What is the pH of the seed particles? What is the influence of sulphuric acid on the chemistry proposed in the reaction schemes. Would the postulated dimers also form in more neutral conditions? This aspect should be considered throughout the manuscript.

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Re: The pH of the solution used to generate the highly acidic seed particles was about 1. The sulfuric acid present in the seed particles has definitely an influence on the formation of dimers of the ester type, since acid is needed to catalyze ester formation. Therefore, the dimers are not expected to be formed with high abundance under neutral conditions. A previous IfT study (Iinuma et al., 2004) explored dimer formation upon ozonolysis of alpha-pinene in the presence of sulfuric acid and neutral ammonium sulfate seed particles and found evidence for enhancement of dimer formation using sulfuric acid seed particles.

p.10870, line 6 Filter samples were extracted with methanol. In a recent paper Bateman and co-workers (Environ. Sci. Technol. 2008, 42, 7341–7346) showed that extracting organic aerosols with methanol might lead to artefacts induced by the solvent (i.e. ester formation). At least a respective remark of caution should be added in the manuscript.

Re: A word of caution will be added: “With regard to extraction with methanol, it was verified that this procedure could be applied. Using a dicarboxylic acid as a model substance [i.e., 1,4-cyclohexanedicarboxylic acid (Sigma-Aldrich); 100 ng] we have examined in prior tests whether extraction with methanol and further sample workup under our conditions (i.e., solvent removal) results in artifacts such as methyl ester formation; the results show that the mono-ester of 1,4-cyclohexanedicarboxylic acid was formed with a yield of less than 5%. Since the present study was mainly qualitative, possible artifact methyl ester formation due to extraction with methanol was not considered.”

p.10872, line 18 It is difficult to follow the argument that interpreting the MS3 spectrum leads unambiguously to the identification of a dicarboxylic acid. Could the fragment m/z 71 not be explained by a structure without a carboxylic functional group?

Re: We write here: “It is likely that in previous work terpenylic acid has often been misassigned to cis-norpinic acid, owing to the fact that its mass spectrometric fragmentation is consistent with the presence of two carboxyl groups and thus rather misleading.” The precursor ion (deprotonated terpenylic acid) at m/z 171 loses 44 units

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resulting in m/z 127, which fragments further through loss of 44 units resulting in m/z 83. The loss of a neutral fragment with 44 units corresponds to CO_2 , characteristic of a carboxylic acid; since twice 44 units are lost the fragmentation is consistent with a dicarboxylic acid. Please, note that the unambiguous identification of the major MW 172 compound as terpenylic acid is not based on the interpretation of MS data but on the comparison of its MS and chromatographic behaviors with that of a synthesized reference compound. The product ion at m/z 71 noted in the case of deprotonated cis-norpinic acid can be readily explained through the loss of 56 units from m/z 127, as shown in Scheme S1. However, to firmly support this fragmentation scheme accurate mass measurements of the product ion would be necessary. We do not see how m/z 71, which is a product ion of m/z 127, can be explained with a structure that does not contain a carboxylic acid group.

p.10874, line 25 Acid-catalyzed hydrolysis reactions are mentioned. Are these suggested due to the acidic seed particles used in the smog chamber experiments investigated here? Would they be similar important in SOA formed under other (less acidic) conditions?

Re: As already argued above we do not think that acid-catalyzed hydrolysis and esterification reactions are important in the absence of sulfuric acid seed particles.

p.10876, line 25 A rather vague reference is made to ambient samples. Could this be described in more detail?

Re: the pertaining sentence has been clarified as follows: "Furthermore, the major MW 344 compound could also be detected in the ambient samples of the warm period of the 2006 summer field campaign conducted at K-puszt (not shown)."

p.10877, line 8 See comment above.

Re: the pertaining sentence has been clarified as follows: "Similar data were also recorded for the ambient samples of the warm period of the 2006 summer field cam-

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paign conducted at K-puszt (not shown)."

p.10877, line 27 It is argued that esterification reactions are important to generate higher molecular weight compounds in ambient aerosol. This main atmospheric conclusion should be discussed in more detail.

Re: It will be emphasized more that esterification reactions are important to generate higher MW compounds; the pertaining sentence will be extended as follows: "Our study is in line with previous studies (Hamilton et al., 2006; Müller et al., 2008) that provided evidence for esterification being an important route to dimer formation, and moreover demonstrates that esterification reactions are important to generate higher MW compounds in ambient aerosol."

p.10878, line 3 Why were the dimers only observed in the night time samples and not in the day time samples? This interesting finding should be commented.

Re: We have commented the findings as follows: "It is shown in the present study that the dimeric alpha-/beta-pinene SOA tracers with MWs 358 and 344 could only be detected in the nighttime samplings of the warm period of the 2006 K-puszt summer field campaign. This suggests that their formation in the ambient atmosphere occurs at a relatively high temperature (daily maximum temperature >24 °C) and a long time-scale." We have no other explanation for the absence of dimers in the daytime samples, and do not expect that the stability of the dimers is so low that we would lose them during sample workup.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10865, 2010.

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