

Interactive comment on “Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols” by K. Kristensen et al.

K. Kristensen et al.

glasius@chem.au.dk

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We would like to thank the reviewers for their thorough reviews and suggestions. We have considered all comments carefully and our replies are listed below. It is our feeling that this process has contributed to improve and clarify the manuscript.

Sincerely, Kasper Kristensen and Marianne Glasius on behalf of all authors

Reply to reviewer #2

This manuscript reports the investigation of dimer esters formed by oxidation of pinene. The results of various chamber studies and two field campaigns (BEARPEX 2007

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and 2009) are presented. The focus of these studies is the pinyol-diaterpenyl (MW 358) and the pinonyl-pinyol dimer ester (MW 368). Both compounds seem to be formed very rapidly within 30 min in chamber experiments. However, as a consequence of the low time resolution of the analytical methodology no specific evidence was delivered. Likewise, no conclusive evidences for the formation pathway (particle vs. gas phase formation mechanism) were reported. The field studies took place in the Sierra Nevada Mountains in September 2007 and July 2009. While the pinyol diaterpenyl ester was found in both campaigns, the pinonyl pinyol ester was only found in the 2009 campaign. A much higher concentration of the first one was found but also a relatively good correlation between them, therefore a similar formation pathway could be suggested. The pinyol diaterpenyl ester concentration could not be correlated to the pinic and terpenyl acid (TA) concentration, which are possible precursors. But some correlation between the ester and diaterpenylic acid acetate (DTAA) was observed for the 2009 campaign. It was observed that higher temperatures increase the concentration of the esters (field and chamber studies) and also nighttime concentrations are observed to be higher than daytime concentrations. The publication is recommended after some revisions.

Remarks and revisions: 1. The method how the authors quantify especially the esters is highly uncertain. The authors neither use calibration standards nor a chemically similar substance, they just use their precursors – a method that can lead to large errors. Certainly it would be nice to have absolute concentration values for the esters, however, it is certainly better to make only a relative quantification. Actually, for the main conclusions of the manuscript, the absolute concentrations are not necessary and relative values are appropriate.

Reply: We agree that the quantification procedure is uncertain, which is also stated in the manuscript. But we would also argue that use of surrogate standards, here the supposed precursors, better reflects the sample preparation and analytical conditions. In addition, if the dimer esters are synthesized at some point, it will be possible to go

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back and recalculate the concentrations presented here. Furthermore, the quantification of dimer esters by the use of a known surrogate allows for comparison with other data independent of the applied instrumentation. Therefore we prefer to keep the use of quantification in the manuscript.

2. The higher tendency of artifact dimers to form sodium adducts can also result from a higher sodium concentration in this kind of sample than in "normal" air samples.

Reply: Re-analysis of the data showed that artefact dimer esters were in fact artefacts formed from the acid precursors in the MS system. These artefact dimer esters were identified based on retention times matching that of the precursor acids, in contrast to the real dimer esters formed in air. The sentence now reads: "Very low concentrations of artefact dimer esters were observed. Since they have the same retention times as the acid precursors, these dimer ester are identified as artefacts formed in the MS system in contrast to aerosol dimer esters which tend to have longer chromatographic retention times than their suggested precursors. "

3. It is reported that pinyl diaterpenyl ester shows a better correlation with DTA and DTAA then with TA. Although the formation of the latter two compounds is different (Claeys et al. (2009)), there is probably a mainly pH-dependent relation between DTA and TA. Also the reaction of DTTA to DTA or terpenylic could be a simple also pH-dependent reaction. Can a better correlation be found with all three compounds combined?

Reply: We thank the reviewer for the suggestion. We have looked into this and it turns out that combining all three compounds does not result in better correlation.

4. In section 3.2.3. it is mentioned for the first time that the α -pinene concentration is much higher in 2009 than in 2007. This should be done earlier and mentioned during the discussion of the different quantities of the oxidation products.

Especially Figure 6 would be easier to comprehend if the values were normalized.

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Reply: The α -pinene concentrations are now mentioned earlier in the manuscript as suggested by the reviewer.

It is not clear to us, what the reviewer suggests that the data in figure 6 should be normalized with. We prefer to keep the present format but have added new figures to the supplementary showing TM normalized data from the four smog chamber experiments along with OA normalized concentrations of dimer esters during the two campaigns.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 22103, 2012.

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