

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

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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 1

The authors present a study in which concentrations of some dimer esters are measured from (1) smog chamber oxidation experiments of the reaction between O₃ and

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a-pinene without OH scavenger present and (2) ambient observations of SOA composition from a region in which a-pinene is a major SOA source. They observe the chamber dimer esters in the ambient samples. They provide some arguments regarding formation mechanisms of the ester dimers. I find many of the arguments being advanced to be weak in that they are not strongly supported by the available observations, but are really more speculative in nature. In some cases, I believe that the authors have gone beyond the available data in their conclusions (in particular in the “photochemical aging” discussion). I believe that this manuscript requires substantial revision before it is to be acceptable for publication.

P22112, L5: The authors mention that artefact dimer esters can be formed, but that these tended to form sodium complexes whereas “natural” dimer esters. Why do they think this is the case? It is not clear (to me at least). Certainly, their point that time from extraction to analysis should be minimized is important.

Reply: The sentence has been removed. 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 dimer esters from aerosols. 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. "

P22113, L13: The authors note that concentrations of pinonic acid are higher in low T experiments due to the increase in vapor pressure of this compound with temperature. However, wouldn't this be the case for all non-Ådimer species considered? Why is this discussion specific to pinonic acid? Further, how can this volatility (partitioning) effect be separated from the oxidation effect of having greater OH concentrations at higher temperatures and thus greater chemical loss to MBTCA (which is noted in the next sentence)?

Reply: We thank the reviewer for this comment and have rewritten the paragraph. It now reads: “The concentration of pinonic acid is lower in warm experiments compared to cold while pinic acid (also a first generation oxidation product) tends to show the opposite behavior. The second generation product MBTCA shows higher particle-phase concentrations at higher temperatures. While the vapour pressure of the first generation products are expected to increase with temperature (Bilde and Pandis 2001) gas-particle partitioning is also regulated by chemical reactions in the gas or condensed phase. For example greater OH concentrations at higher temperature results in increased oxidation of pinonic acid to MBTCA in the gas phase followed by condensation (as observed by Muller et al 2012). The observations in Figure 1 reflects the complexity of gas-particle partitioning and we are not able to separate the temperature effect on vapour pressure from the effects of chemical reactions in the gas and condensed phase.”

P22113,L20: The authors state “If condensed-phase reactions were important for initial ester formation at chamber conditions, a delay in the occurrence of esters compared to precursors would also be expected,” right after concluding that the dimer esters are formed rapidly (with “rapidly” being limited to the 30 minute time resolution of the experiments). It is not abundantly clear to me why condensed phase reactions would require a delay in the dimer ester formation, especially given the limited time resolution of these experiments. This conclusion presumes something (unstated) about condensed phase reaction rates. Presumably, the authors are assuming that condensed phase reactions are slow compared to the gas-phase formation, but it is not clear to me how they justify this assumption and whether it is based on previous (or new) observations. I do not believe that the Muller reference necessarily provides support, as the Muller results only show that the “intensity of esters increased even faster than the intensity of their monomer precursors in freshly nucleated aerosol” but cannot directly elucidate which phase (gas vs. particle) the esters were actually formed in. What if, and this is speculation, the monomer species reacted rapidly in the condensed phase to form esters? This is not to say that gas-phase processes do not lead to ester formation, only that

it is not clear, as presented, that this gas-phase pathways are the only possibility.

Further, in discussing what is needed to form a nucleating species, the authors only discuss pinic acid, but not any of the 2nd generation products, which would presumably have lower vapor pressures than pinic acid due to the addition of functional groups. This would be true whether or not dimer esters were formed. Would, for example, MBTCA have a sufficiently low vapor pressure to act as a nucleating species?

Reply: We agree with the reviewer, that the data presented are not sufficient to confirm that the esters are formed in gas-phase and not in the condensed phase. The statement was intended as a suggestion. We have now modified and significantly shortened it to reflect the considerations of the reviewer. The text now reads: "Both dimer esters were observed within 30 minutes of addition of α -pinene, indicating that they are formed within the same timeframe as the formation of their structural precursors, at our time-resolution"

Both dimer esters were observed within 30 min of addition of alfa-pinene (Figure 1). This indicates that they are formed simultaneously with the formation of their structural precursors or shortly after. At our time-resolution it is however not possible to determine the nature of the nucleating species or whether the dimers are formed in the gas or condensed phase.

One could speculate that the vapour pressure of MBTCA is lower than pinic acid, but it is not relevant to consider MBTCA as the nucleating species here, since it is not observed above the detection limit within the first 30 min.

Fig. 1: The authors present a time-series of absolute concentrations of different species. However, looking at the total particle mass time-traces for each experiment, it is clear that different amounts of aerosol form for each experiment. I wonder whether it might be useful to in addition present normalized results (i.e. concentration of each species divided by the total SOA)?

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Reply: This is an interesting suggestion, which we have looked into. The normalized data from the smog chamber experiments show somewhat similar trends as the non-normalized data shown in Figure 1. We have therefore chosen to keep the original Figure 1, but have added the normalized data in the supplementary figures.

P22115: The authors argue that the variations in the CCN activity and differences between the different temperature experiments might be a result of differing concentrations of the dimer esters, which have larger MW and thus lower CCN activity. However, I find this argument weak given that the time evolution of the dimer concentrations was very similar in the low vs. high T experiments, despite their different absolute concentrations. Related to my previous comment, I wonder whether considering the behavior in the context of the relative composition (i.e. normalized to the total SOA mass) would be useful. The authors also mention that the slight increases in the hygroscopicity at longer times could be due to “oxidative ageing” leading to higher O:C ratios. However, as the concentration of α -pinene decreases (due to oxidation by O₃ and OH) the concentration of OH will decrease substantially because only oxidation of α -pinene, and not its 1st and 2nd generation products, will lead to efficient OH production. Thus, the “ageing” would really involve only ageing by O₃, not OH, which is an inefficient method to change the already formed particle properties. See, for example, Tritscher et al. (2011). Ultimately, I find that this section adds very little to the current study.

Reply: We have shortened the section significantly. It now reads: “The difference between ccn activity of particles formed under cold (15C) and warm (24C) conditions is very small with the particles formed at the colder temperature being slightly more ccn active during the first 150-200 minutes of the experiments. CCN activity displays only modest variation during the course of experiments and there is some indication in Figure 3 that the rate of the changes depends on chamber temperature. At the higher temperature (24C), k decreases (i.e. CCN activity decreases) by a small but perceptible amount during the first 150-200 min of the experiment, whereas CCN activity remains relatively constant during this same time period at the lower temperature (15C). Fol-

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lowing the initial decrease in CCN activity there is an increase in in the activity under warm conditions and there is a suggestion of an increase under cold conditions.”

P22115,L24: The authors conclude here that “the rapid formation coincident with precursor formation suggests a gas phase mechanism possibly involving Criegee intermediates,” although add the caveat “although due to the low time resolution of the filter samples no direct evidence was observed.” I do not find that they have provided a convincing case that condensed phase reactions are not the primary source of the dimer esters observed in this study, as discussed above. Again, simply finding that the esters are “rapidly” formed does not, in my opinion, demonstrate that the predominant formation pathway is through the gas phase. In fact, I don’t believe that even with higher time resolution this question would adequately be resolved. If, instead, the authors had gas phase measurements in which dimer esters were observed that would be strong evidence. Of course, given the low volatility of these species, they might not be readily observable in the gas phase.

Reply: We understand the concerns of the reviewer and we have removed the statement.

P22116: The authors begin by discussing how absolute concentrations of the various dimer esters vary with time of day. How does this compare with what the total OA does? Is this predominately driven by changes in the boundary layer height or in flow patterns (and SOA sources) during day vs. night? Previous work from the Goldstein group, and others, has shown that the Blodgett forest site is impacted by pretty consistent flow patterns that shift from day to night. The authors simply seem to point out that the concentrations of pinyl diester perenyl ester is higher during night than day, but they provide little discussion of why this might be.

Reply: Diurnal variation of dimer esters concentrations have been normalized to the total OA and added to supplementary. Normalization did not change the diurnal variation significantly. A general higher dimer ester concentration is still present at night

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verifying that the observed diurnal variation shown in figure 4 and 5 are not predominately driven by changes in the boundary layer height. The following sentence has been added to the manuscript: “Normalization of the dimer ester concentrations to OA (Figure 6S) resulted in similar diurnal variation as shown in Figure 4 and 5, with a general higher ester concentration during night compared to day-time samples, indicating that the diurnal changes in the dimer ester concentration are not driven by changes in the boundary layer height.”

P22117, L22: In stating “The higher conversion of DTAA into diaterpenylic acid could also be related to the higher aerosol acidity observed in the 2009 campaign (Zhang et al., 2012),” I assumed that this reference would actually say something about the acidity of the particles at the Blodgett site during 2009. This is not the case, as the Zhang (2012) reference does not discuss any measurements made at Blodgett and further discusses behavior in an isoprene dominated region, not even a monoterpene dominated region. I find this sentence to therefore be misleading. Do the authors actually have evidence of more acidic aerosol in 2009 compared to 2007? Nothing is presented. This seems like unsubstantiated speculation.

Reply: The reference should be corrected to this one, which do indeed calculate aerosol acidity during the same campaigns. H. Zhang, D.R. Worton, M. Lewandowski, J. Ortega, C.L. Rubitschun, K. Kristensen, P. Campuzano-Jost, D.A. Day, J.L. Jimenez, M. Jaoui, J.H. Offenberg, T.E. Kleindienst, J. Gilman, W.C. Kuster, J. de Gouw, C. Park, G.W. Schade, A.A. Frossard, L.M. Russell, L. Kaser, W. Jud, A. Hansel, L. Cappellin, T. Karl, M. Glasius, A. Guenther, A.H. Goldstein, J.H. Seinfeld, A. Gold, R.M. Kamens, and J.D. Surratt (2012) Organosulfate Formation from 2-Methyl-1,3-Buten-2-ol (MBO) as a Secondary Organic Aerosol (SOA) Tracer in the Atmosphere. *Environmental Science and Technology*, 46, 9437-9446. Sorry for the confusion.

Sections 3.2.1/3.2.2: The authors observe lower concentrations of the dimer esters during 2007 compared to 2009 and are unable to explain this difference. Do the authors know for a fact that the dimer ester compounds are stable on the filters over the

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many years in between sampling and measurement? Is it possible that the lower concentrations during 2007 are a result of loss of these species during their storage? I am not proposing that this did occur, only wondering if the authors have considered this possibility and, if so, what evidence led them to discard it.

Reply: All samples were actually analyzed within 1-2 years after their collection, and we thus do not expect considerable differences between the two campaigns. Since no authentic standards are available for these compounds, we have not investigated their stability during storage. But this is of course an important point that should be kept in mind, and if possible, be investigated further.

P22119: The authors propose “more efficient conversion” into esters as an explanation for the difference in the 2007 vs. 2009 concentrations of e.g. pinonic acid and cis-pinonic acid. And indeed, they observe higher concentrations of the dimer esters during 2009 compared to 2007. However, there is very little provided that would actually allow one to understand the reason for this “more efficient conversion,” besides the unsubstantiated postulation that in 2009 the aerosol was more acidic. And the chamber experiments seem to rule out a strong enough sensitivity to temperature. Given this lack of any mechanistic explanation being advanced, I find this discussion to overall be quite weak.

Reply: We agree with the reviewer, that the magnitude, hence importance of the proposed conversion of first generation oxidation products into dimer esters are still unknown, but merely suggest that this might help explain the observed lower than expected concentration of oxidation products in 2009. The mentioned statement has been modified to better reflect this. It now reads: “A suggestion for this lower than expected concentration of cis-pinonic acid and DTAA in 2009 could be a more pronounced conversion of these compounds into esters, such as the pinyl-diaterpenyl and pinonyl-pinyl esters and other oligomers.”

P22119, L21: Here, the authors argue that there is “some correlation ($R^2 = 0.40$)”

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between pinyldiaterpenyl ester and photochemical age. However, earlier in the manuscript the authors state there is “no significant linear relationship” when $R^2 = 0.35$ (p. 22116). Is the difference really so large between $R^2 = 0.35$ and $R^2 = 0.40$ so as to go from having “no significant” to “some” correlation? Can the authors clarify what they take to mean “significant” (or not significant) and apply it consistently throughout the manuscript?

Reply: We agree with the reviewer and have changed the “no significant” correlation for the $R^2 = 0.35$ to “some correlation”

Section 3.2.4: I find this section to be confusing and a bit misleading. The authors state that the “photochemical age of the collected aerosols... was estimated,” and that ester “content” was compared with photochemical age in Figure 6. Figure 6, in my opinion, shows no such thing. There is, for example, no axis that says “photochemical age.” And their estimate of photochemical age is too crude to be useful. Most photochemical age markers rely on the measurement of a ratio between concentrations of two substances, such as NO_x/NO_y or toluene/benzene. The ratio is key, as it helps to remove differences that result from absolute changes in concentrations, which depend on a lot more than just photochemical age. Here, the authors use absolute concentrations MBTCA as an indicator of gas-phase OH photochemical processing. First, they never actually convert this to photochemical age (because they can't) and thus do not compare the ester content to photochemical age. Second, use of the absolute concentration is not a good metric for photochemical age, since it depends on absolute concentrations of the precursors, which is sensitive to changes in both emissions and dilution. The authors take no account of changes to boundary layer heights, only mentioning changes in flow patterns. I do not completely disagree that the MBTCA concentration might provide some indication of photochemical processing, but I believe it is too crude to use here for the purposes of the discussion and arguments that are being advanced. I believe that this section needs to be either removed or completely changed, since the authors are not actually comparing their dimer ester concentrations vs. “photochemical

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age” as they purport to be doing. Aren’t NO_x and NO_y concentration measurements available from the Cohen group for both campaigns? Might this not (perhaps) provide a better indication of photochemical age? Or, perhaps, try looking at ratios of MBTCA to other species? Again, I come back to the idea that consideration of ratios (e.g. relative fractions) might help to provide additional/greater insights than consideration of concentrations alone.

Reply: In this work we have used MBTCA as a rough estimate of the degree of photochemical oxidation of relevant precursors and aerosols. Since the Blodgett forest site is affected by NO_x emissions from the Sacramento area transported uphill during daytime and local/regional biogenic VOC emissions, the aging of BVOC and their reaction products is not well described by the NO_x/NO_y ratio or toluene/benzene for this site. We agree that the MBTCA concentration is a very rough estimate and have also considered to use the MBTCA/pinonic acid ratio, but this would be affected by e.g. changes in temperature affecting aerosol phase pinonic acid concentrations.

We have revised the discussion to better reflect the considerations of the reviewer. It now reads: “Since the Blodgett forest site is affected by NO_x emissions from the Sacramento area transported uphill during daytime, the aging of locally and regionally emitted BVOC and their reaction products is not well described for this site by the NO_x/NO_y or toluene/benzene ratios typically used in photochemical aging studies. However, since the OH-initiated gas-phase oxidation of pinonic acid has been suggested to be the rate-limiting step in formation of the second generation product 3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) (Zhang et al., 2010; Müller et al., 2011), the concentration of MBTCA indicates the degree of gas-phase OH photochemical processing.”

P22120, L20: I do not see how the acidity from Zhang et al. (2012) has anything to do with the current study. The Zhang et al. measurements took place in a different part of the country. So how exactly do the authors look for correlations between individual esters and acidity in the current study? It is entirely unclear.

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Reply: Sorry for the confusion. The reference should be corrected to this one, which does indeed calculate aerosol acidity during the same campaigns. H. Zhang, D.R. Worton, M. Lewandowski, J. Ortega, C.L. Rubitschun, K. Kristensen, P. Campuzano-Jost, D.A. Day, J.L. Jimenez, M. Jaoui, J.H. Offenberg, T.E. Kleindienst, J. Gilman, W.C. Kuster, J. de Gouw, C. Park, G.W. Schade, A.A. Frossard, L.M. Russell, L. Kaser, W. Jud, A. Hansel, L. Cappellin, T. Karl, M. Glasius, A. Guenther, A.H. Goldstein, J.H. Seinfeld, A. Gold, R.M. Kamens, and J.D. Surratt (2012) Organosulfate Formation from 2-Methyl-1,3-Buten-2-ol (MBO) as a Secondary Organic Aerosol (SOA) Tracer in the Atmosphere. *Environmental Science and Technology*, 46, 9437-9446.

P22121, L2: I don't understand how the ester formation is "in contrast to the second-generation product MBTCA" in the smog chamber experiments. When I look at Fig. 1, I see that both MBTCA and ester concentrations are > 0 in the first sample taken at 30 minutes. So what exactly is "in contrast?"

Reply: Firstly, we apologize for the somewhat blurry quality of Figure 1 and hope the new improved version will allow the reviewer to note that the ester concentrations are in fact > 0 in the first sample taken at 15 min, while MBTCA is below the limit of detection in the first samples. In addition, a figure showing normalized data of the four smog chamber experiment has been provided in the supplementary. From this it is clearer that concentrations of the esters are in fact > 0 after only 15 min.

P22122, L1: The sentence here discussing the relationship between "OH ageing" and ester concentrations should be removed because, as discussed above, the authors do not convincingly compare ester concentrations to photochemical age.

Reply: Based on the reply above explaining the use of MBTCA as indicator for photochemical aging, we argue that this comparison is valid.

Other Comments: Fig. 1 is relatively blurry.

Reply: The quality of Fig. 1 has been improved.

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