Review of Kristensen et al.

The authors present a study in which concentrations of some dimer esters are measured from (1) smog chamber oxidation experiments of the reaction between O_3 and α-pinene without OH scavenger present and (2) ambient observations of SOA composition from a region in which α-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 aretefact dimers 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.

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-dimer 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)?

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?

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)?

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 O_3 and OH) the concentration of OH will decrease substantially because only oxidation of α-pinene, and not it’s 1st and 2nd generation products, will lead to efficient OH production. Thus, the “ageing” would really involve only ageing by O_3, 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.

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.

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-diaeterpenyl ester is higher during night than day, but they provide little discussion of why this might be.

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.

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 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.

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-pinic 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.

P22119, L21: Here, the authors argue that there is "some correlation ($R^2 = 0.40$)" between pinyl-diaterpenyl 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?

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 NOx/NOy 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 age” as they purport to be doing. Aren’t NOx and NOy 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.

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.

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?”

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.

Other Comments:

Fig. 1 is relatively blurry.

References:

Tritscher, T., Dommen, J., DeCarlo, P. F., Gysel, M., Barmet, P. B., Praplan, A. P., Weingartner, E., Prévôt, A. S. H., Riipinen, I., Donahue, N. M., and Baltensperger, U.: Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber, Atmos. Chem. Phys., 11, 11477-11496, doi:10.5194/acp-11-11477-2011, 2011