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Interactive comment on “Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber” by T. Tritscher et al.

Anonymous Referee #2

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General:

The manuscript reports results of a smog chamber study on formation and ageing of SOA generated from α -Pinene under various conditions. The ageing is induced by OH radicals either formed as a side product of ozonolysis in the dark and or by a photolytical source. Besides total mass and O:C ratio derived from AMS data, volatility and hygroscopicity are the parameters chosen as diagnostic quantities to follow the chemical evolution of the SOA particles. These measurements were taken by tandem DMA setups, where the Volatility TDMA was newly developed. The VTDMA and its performance is also described in the paper. The manuscript clearly reports interesting and important results, however the presentation has some weakness. In my opinion this is owed to the fact that either the chemical changes are subtle themselves or are

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represented rather in a subtle than a in an obvious fashion in the diagnostic quantities. Figure 7 is indicative for that. Exception is the distinct decrease of the volatility during the OH induced condensation phase, which is an important finding. To summarize my impression, the authors in many case observe small effects, which are pointing in the expected direction, but the changes are subtle, often at the edge of significance and difficult to grab. This is actually in contrast to the summary statement of diagnosis value of kappa and VFR for complex processes, which is a bit optimistic. Nevertheless, hygroscopicity and volatility together support classification of formation and ripening processes as described by the authors. The question arises if the observation and categorization have predictive power. Since the effects are often subtle it is important to have a good structured manuscript with quantified statements including errors. The latter are often missing and instead only qualitative statements are used of the type "similar but somewhat higher". Moreover, the manuscript is difficult to read and formulations are unclear. Despite the good experimental work, the extensive studies and interesting results, I cannot suggest to publish this manuscript in ACP as it is. The manuscript needs mayor revisions.

Mayor comments:

page 2, line 8 "possible mechanism of chemical changes": I find the notation mechanism misleading, since you don't discuss chemical mechanisms. Essentially you observed and classified gross processes, which comprehend several types of chemical mechanisms. This should clarified throughout the manuscript. Moreover, there is unclerness about two processes of chemical composition change: chemical reactions like oligomerization or (heterogeneous) oxidation and replacing or condensing molecules. The latter are physical processes.

page 9, line 1 The authors claim that the walls of the thermodenuder are sufficient to remove the vapors. Is that effect quantitative ? Is there experimental data on the efficiency of the thermodenuder? In the setup, especially, if the temperature sensor in the center of the inner tube (see Fig. 1) controls the heater temperature, walls must

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be warmer than the center line. This should reduce the absorbing effect of the walls. The absence of nucleation is no proof, since the supersaturation that would be needed for nucleation may not be achieved, especially if the walls have some absorbing effect. Moreover, the residual particles may act as condensational sink. In this context: is it possible that HTDMA and VTDMA do not see the same aerosols, because vapors are lost differentially in the two branches of the TDMA ?

page 12, 2nd paragraph This paragraph should not be here. It describes in the same way what you claim as findings in the abstract and in the summary section. Here you mix hypothesis/concept with discussion and interpretation. In any case none of this should be in the experimental section. This regards also Figure 3. Here the legend describes already what you are going to show by your results. This introduces circularity in your manuscript. The way how conduct your experiments, formation by ozonolysis and ageing with OH in a second step is self-evident. You don't need to justify this here. Alternatively you could introduce a section like "concept of the study" where you formulate your concept. But this became sufficiently clear in the introduction section.

page 13, line 23ff This paragraph about the clocks looks complicated too me. What is the sense of physical time? Is there any other time (in natural science)? I guess what you want to say is: The progress of the experiment is described by either "time since SOA formation" or "time since OH initiation". In addition two chemical clocks are introduced, O₃ exposure and OH exposure, which are defined as time x concentration(time) of the oxidant. Please change the manuscript accordingly.

page 14, line 2 Above you mentioned addition of Pentanol as OH tracer, now you use Pinonealdehyde. This must be commented. Why didn't you use the Pentanol ? Could show in one of the figures an OH curve ?

page 14f, section 3.1 and Figure 4 The first two paragraphs of section 3.1 are confusing. Throughout the manuscript you claim that volatility is a good parameter to detect progress of processes. Here you state the data are "similar within these uncertainties",

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but not comparable in detail. What does this mean ? Then you fit a common curve to your data. If I take your approach here serious, you show that all thermograms look the same and you can fit it with one mathematical expression. The variability within an experiment (multiple measurements) is about the same as the variability from experiment to experiment (for different conditions !). In my opinion multiple measurements (how many per experiment ? 2, 5, 10?) automatically mean that you were looking at particles with different chemical evolution. Why averaging them then? Because they are similar enough ? But then thermograms are NOT a good diagnostics for processes, because everything seems to look about the same.

The comparison to VTDMA results of other groups is also not a real comparison, because you eventually argue with non-comparable experimental conditions or thermodenuder performance to explain the differences to your observations. Actually I trust your thermodenuder performance from what you presented in Sect. 2.2, although it maybe imperfect as all others in the sense that you are not reaching thermodynamic equilibrium but are limited by kinetic effects. The proof of performance via comparison to other VTDMA cannot performed with SOA systems which are so variable in themselves. Here it would be more helpful if you could compare your thermograms for the reference compounds to thermograms for the same compounds measured by other groups.

page 17, line 25 and Figure 5 One reason to use kappa was to compare particles selected at different diameters, thus to unify results. Why GF (Figure 5E) has a smaller variability than kappa (Figure 5D). Please, comment on that in the manuscript.

page 21, line 27 and Figure 8 The increase of volatility during the OH induced condensation phase is an interesting and important finding. This should be worked out nicely and not lapidary kept buried in the scatter plot. You need to mark the (anti-)correlation of VFR and kappa during the OH condensation phase, as this is the most significant finding.

page 26, Conclusions Does your finding implicate there is not much ageing by OH in the atmosphere, since the volatile would evaporate as soon as the chemical source stops? Can you comment on implications of your findings for the atmospheric aerosols?

Figures Figure 10 and Table 2 give a very good overview. In Figure 5 and Figure 7 it is probably better to reduce the data to one or two typical or extreme cases, but then with error bars to show the significance of the changes. (The symbols of same color are difficult to distinguish.) In the text changes of VFR, GF (and O:C) over the four phases should always be stated quantitatively with error bars. A table with average / median of distinguished VFR and GF, which describe the time evolution, over all experiments with standard deviations, percentiles etc. could serve to show the variability from experiment to experiment.

Minor Comments:

page 2, line 7 "sensitive physical parameters" what means sensitive in this context?

page 4, line 11 Jimenez et al. (2009) do not treat oligomers, they are mentioned only in conceptual context. Please, remove or replace reference.

page 4, line 14 The phrase "Aerosols, including SOA but also inorganic and other organic substances, have an influence on global climate ..." sounds strange to me. The qualifier "but also inorganic and other organic substances" is misleading. Are you referring to SOA mixed with other substances or are referring to aerosols in general which are composed of inorganic and organic substances, including SOA components?

page 4, eq 1 This equation for kappa is not from Petters and Kreidenweis 2007.

page 6, line 18 What is exactly meant by "chemical quantification"? AMS does allow for chemical quantification of inorganic components, but not of organic mixtures, like SOA.

page 7, line 7 AP for α -Pinene is not correctly introduced.

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page 9, line 20 What do mean here with "very stable" ? What are the typical RH fluctuations ? You obviously had data outside the range 93-97% RH, which you discarded. How many data points you had to discard ?

page 9, line 24 You probably mean "optimized" not "minimized"

page 10, line 3 You probably mean "selected" not "measured"

page 10, line 4 "...and high AP precursor concentrations range from 75 to 250 nm." Here is something wrong.

page 10, line 5 "D0 had to be changed if the number size distribution in the smog chamber changed in a way that the D0 of the V/H-TDMA was out of the range or had too few counts." This sounds complicated: D0 was adjusted to have sufficient particles, thus signal.

page 10, line 23f Is 3% volume loss a very small effect? Very small compared to what? What is meant by reorientation? Is NaCl able to form needle-like structures ? 3% impurities seems to be quite a bit; how pure was your NaCl substrate, how pure was the water used for the solution? Could it be that the shrinkage was due to imperfect drying ?

page 11, line 11 The sentence starting with "Compared..." does not sound grammatically right.

page 11, line 18f The sentence starting with "In contrast..." sounds odd.

page 11, last paragraph This whole paragraph sounds complicated. I guess you wanted to say that your instrument works well and comparable to other VTDMA in high temperatures ranges, but you also tested it with citric acid in the temperature range you are going to apply.

page 12, line 25 Neither 40 nor 10 ppb a-Pinene are atmospheric relevant concentrations. Nevertheless it is a merit to approach low concentrations as close as possible

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within the experimental abilities. Please, change the text accordingly.

page 13, line 2 Unprecise formulation. Ozonolysis proceeds also with the residual 10% α -Pinene, thus last as long as there is precursor.

page 13, line 6 Too many brackets in this sentence. Please split.

page 13, line 13 I think you wanted to say that are using the same setup as described by Taira and Kanda, (1990)? Or did you describe your setup elsewhere ?

page 15, line 6, Do you want to say that thermograms of the single reference compounds are steeper than thermograms of SOA?

page 15, line 8 "The SOA produced purely by ozonolysis tends to be slightly more volatile than after aging with OH." What do want to say: it is the same or it is different. Maybe you (always) give numbers and errors with such statements(see comment above). This statement is symptomatic for many others in the manuscript.

page 15, line 18 Does this comparison really helps ? Huffmann et al. have about the same residence time as you have. So if at all you should match Huffmann et al. data. The simultaneous agreement with Jonsson et al. could indicate that some other parameters are important. E.g. what happens to the vapors in the selecting DMA? Is it possible that some of the vapors are lost here. The same argument which you used for not-needing a charcoal denuder could apply here?!

page 17, line 19f and Figure 5 "plotting GF and kappa allows for better comparison" ... of what.

page 18, line 4ff and Figure 10 If this is an important information, why do place it in the appendix ?

page 18, line 22 In which sense is the wall loss estimate conservative ?

page 18, line 24 On which basis you defined the cut between the regimes?

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page 18, line 27 What do mean by GF increases slightly ? It increase by about 20% ?! Isn't that in significant ?

page 19, line 8 You quote ZSR. In my understanding, the idea of ZSR is to explain e.g. a non-ideal ternary mixture, by an ideal mixture of non-ideal binary sub-systems, wherein the non-ideality of the binary systems is considered at the the total ionic strength of the ternary solution. I guess you did not try to estimate activities for your systems. So I think what you did apply is a simple, linear mixing rule. This is fully ok, but has not much to do with the ZSR approach.

page 19, line 22ff This is a highly speculative approach with large uncertainties. Therefore the statement "The results are very similar if we assume a constant VFR (0.72, 0.69)" is not enough. Please, give the numbers and discuss the errors.

page 20, line 4 If this statement is true, wouldn't the presence of a new class of smaller molecules be reflected in the steepness or the shape of the thermograms ? Did you see such an effect ?

page 20, line 21 "During the second phase, the OH mediated ripening kappa increases just slightly but stays almost constant." This is an unclear statements. Does it mean a small but significant increase or no change ? If the first, how much increase ?

page 21, line 11 This first sentence of the paragraph signals to me not to expect too much from these correlations of VFR and GF. Was that the intention ? Does the correlation analysis help to understand the evolution of the aerosols or not?

page 21, line 14 Where can I see this anti-correlation in Figure 8 ?

page 21, line 17 What is meant with "the correlation with $R^2 = 0.8$ is fair" ? Do you a priory expect the same functional change of VFR and kappa when the particles are formed or ageing ? Does your result imply that with exception of the OH condensation phase, kappa and VFR are linerally correlated. What would that mean ?

page 21, line 22 "Lights on" experiments were not introduced in the experimental

section. Please, do so.

page 22, section 3.4.1 This experiment was not introduced in the experimental section. Please do so. How did you determine the increased OH production ? Could photolytic processes cause the changes observed in the gas phase or the particulate phase ?

page 22, line 27 What do you mean with "Usually several D0, not too different from each other, are selected in.."?

page23, line 23 Did you detect the increased OH levels ? How much was the increase ?

page 23, line 24 "Thus, VFR stays constant." Probably you wanted to say something different. Increase of OH induced SOA production should decrease VFR, does it ?

page 23, line 29 typo "as"

page 24, line 3 kappa decreased by more than 10%. Is that "slightly" ? **page 25, line 13** There is no thermogram of Qi et al. 2010 in Figure 4. What do you mean by slightly lower VFR ? The same within the errors ?

page 26, line 9f A lot of weak qualitative statements in this sentence, as mentioned several times above. Please, be precise. Does e.g. "more or less stable" means constant with in the errors of +/-xy?

page 26, line 17 NOX independence is a result not a conclusion. It was neither shown nor discussed in the result section.

page 34, Table 1 hygroscopicity "/" k ?

page 37, Figure 2 "[-]" in axis label? Can you compare with VTDMA results of other groups for these compounds ?

page 38, Figure 3 Does O3 also drops in case of photolytical OH production ? **page**

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39, Figure 4 caption Shift "(circles)" to the end of the first sentence

page 40, Figure 5 Legend: Please, omit to name the colors. Captions: What is meant by "The vertical lines indicate roughly the 90%-AP-reacted value..." ? Please, give a range like e.g. 85-95%?

page 41, Figure 6 According table 2 the experiments 4 and 7 are also different in NO. Could that have an effect ?

page 42, Figure 7 This figure signals me that the variation from experiment to experiment is about the same as the variation within the experiments, but overall the effects on VFR and kappa are small. How significant are the changes. It would be helpful to indicators the errors of measurements.

page 44, Figure 9 I suggest to skip the size dependence in the Figure. The analysis in section 3.5 shows that it is a kinetic effect. The different symbols are difficult to distinguish, anyhow. Then the "light on" effects will become clearer. The O:C ratio in panel D for this Figure is not discussed in the text. It looks constant within the errors for both cases. How comes that the processing does not reflect in in the O:C ratio.

page 45, Figure 10 I think this is an important Figure and should not appear in the appendix. It gives the most clear overview about your experiments (see comment above).

Typos and Corrections:

Equations should be indented.

Units are given in smaller font size ?!

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