**Atmospheric
Chemistry
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Discussions**

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

Anonymous Referee #1

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Overall Assessment: Tritscher et al. present measurements of the changes in hygroscopicity and volatility of laboratory secondary organic aerosol particles as they age in a chamber. I believe that this manuscript has a lot of potential, as the measurements are novel and cover a wide range of conditions. However, I find the paper overall includes insufficient analysis and discussion; it reads more as simply data presentation without consideration of the broader context and implications of these results. As one prime example, the authors refer fairly often to how composition must be playing a role, yet they never plot their kappa or VFR results vs. the particle O:C. And it is really only in the "Summary and Conclusions" that any real discussion gets going (and here it is very brief). Some of their results are quite intriguing, yet I don't think sufficiently explained. Occasionally, hypotheses are given, but they tend to not be justified. Many of the figures I find to be difficult to read, due to the many different lines and points shown on

individual plots. Given the wealth of data presented, I would like to see this manuscript published. But it is my opinion that significant revision will be required, with a focus on discussion and analysis, before this manuscript is acceptable for publication. Specific questions and comments are given below.

Comments and Questions:

Abstract, Line 11: I find the language "or by an exchange of molecules in the SOA by other molecules with different properties" to be a bit ambiguous. Does this mean that molecules react to turn into other molecules, or that individual molecules are replaced by other, distinct molecules?

Abstract, Line 15: What is meant by "a substantial change in the aerosol mass"? Many of the "exchange" processes indicated would lead to incorporation of oxygen, and thus mass increase.

Abstract, Line 19: Please use a different word than "phase." This could be confused for the actual phase of the particles.

P. 7427, L. 6: The authors state "Only a small increase, if at all, is expected for Ms and rho_s, and thus changes of rho_s/Ms will be small," where rho_s is density and Ms is molecular weight. This statement should be justified, as it can certainly be wrong. For example, fragmentation will clearly lead to a change in Ms. See, for example, Kroll et al. (2009). Also, fragmentation can certainly have an influence on solubility, in contrast to what is stated. Consider that for a homologous series of compounds solubility tends to vary with Ms.

P. 7431, Line 5: Although nucleation is a clear indicator of re-condensation, the absence of nucleation can by no means rule out the possibility of re-condensation on the suspended particles.

P. 7431, Line 22: The authors should state explicitly how the GF data were "corrected to 95.0%."

P. 7432, Line 13: The authors state that "A Kappa of 0 corresponds to GF=1. The use of Kappa allows for direct comparison with other studies or measurements e.g. from a cloud condensation nucleus counter." However, it is well known that there are difficulties in connecting sub-saturated hygroscopicity measurements to super-saturated (e.g. CCN) hygroscopicity measurements, c.f. Prenni et al., 2007; Duplissy et al., 2008; Wex et al., 2009; Massoli et al., 2010. This statement should acknowledge this fact, as should any discussion to follow.

P. 7432, Line 16: The authors state that the reason for testing the V-TDMA system with reference particles is for comparison to other systems. However, if this is the goal their choice of citric acid is strange, since it has not been the focus of any V-TDMA or thermodenuder studies that I am aware of, and thus does not serve as a good reference compound at all.

P7436, Line 2: Just wondering why the OH concentration was calculated from pinonaldehyde decay instead of from pentanol decay, which was supposedly added as a specific OH tracer.

p. 7437, Line 12: Do the authors think that the erf function has any physical meaning, or is it simply used because it can represent the observations well?

Section 3.1: The authors may want to also include the alpha pinene VFRs from Meyer et al. (2009) and from Cappa and Wilson (2011). Also, it would be helpful to explicitly include the residence times for each of the literature experiments in the figure so that the reader can quickly know which experiments are/are not directly comparable.

P. 7438, Line 2: It is, in my opinion, completely unrealistic to think that the slightly longer RT for the An et al. (2007) experiments explains the difference in the SOA thermograms between their study and this one [An et al., 2007]. Note that An et al. (2007) also presented a 3 second RT thermogram, which shows a VFR of around 50% at 100 C, which is in line with the observations here.

P. 7438, Line 7: The authors state, "With our long RT we are able to use low temperatures in the heater and minimize kinetic limitations of evaporation and hope to be close to equilibrium, even though this might be not the case as suggested recently (Riipinen et al., 2010)." I recommend the authors look at the results from Vaden et al. (2011) and Cappa and Wilson (2011), which indicate that the alpha pinene system evaporates extremely slowly and is very far from equilibrium in a V-TDMA or thermodenuder system and likely would require excessively long RT's to ever reach equilibrium. Also, I do not see how these results "show" the importance of residence time. Really only the An et al. (2007) results are quite different and, as pointed out above, are anomalous. Of course, RT is important, I'm just not sure that these measurements really show this.

Section 3.2: I find it particularly surprising that the VFR increases with time. Conventional wisdom tells us that low-volatility products will condense first, followed later by high-volatility products as the aerosol mass increases (or course, the conventional wisdom could be wrong). Further, it has been shown experimentally, both here and previously (e.g. [Shilling et al., 2009]) that O:C decreases as the particle mass increases. Again, I would think that O:C and volatility should be anti-correlated. Perhaps my assumption is incorrect, but I believe that an explanation for the observations needs to be put forward.

P. 7439, Line 13: The reference to Duplissy et al. (2008) is out of place [Duplissy et al., 2008]. Yes, Duplissy saw a "mass concentration dependence", but their experiments were for photo-oxidation experiments, not ozonolysis experiments. The evolution of, e.g. O:C will likely be very different between these two types of experiments. Further, they find that the GF is lowest when mass is highest, exactly the opposite of what is seen here (although I suppose the Duplissy results are not wall-loss corrected, so perhaps my interpretation of the GF vs. mass relationship is off). Nonetheless, the photo-oxidation vs. ozonolysis difference remains, making these two experiments not particularly comparable. The authors do acknowledge this distinction, but it is my opinion that this distinction is key and makes the statement "Other studies found. . ." to be

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irrelevant.

P. 7440, line 4: It is not clear to what Figure this paragraph is referring. I think it should be "A1" not "A". (I find the A1 to be confusing given all the panel A's.) Also, not clear why this is in an appendix. I recommend making a two graph figure so Fig. 5 and A1 can be compared more easily.

Section 3.2: Why should there be any "ripening" during the O3 experiments. Presumably, this has nothing to do with O3, since it is extremely unreactive towards compounds without double bonds. Calling this the "O3 ripening" stage is a bit misleading. . .it is really just a "ripening" stage. In other words, had the experiments been done with excess alpha pinene instead of excess O3, the results may have been the same.

P. 7441, Line 3: An explanation, or at least a hypothesis to explain the following statement is needed: "The O:C ratio is constant or slightly decreasing during the O3 mediated phase, while it correlates well with Kappa during the OH mediated phase." This seems to run counter to some recent observations, e.g. [Jimenez et al., 2009; Massoli et al., 2010].

Section 3.3: An attempt to explain the anti-correlation between O:C and volatility needs to be made.

Page 7441: The connection between the ZSR equation and volatility is not clear. Instead, just state that a volume mixing assumption is being made. Also, I'm not convinced that a mixing rule can be used on VFR values. VFR is defined as the amount remaining divided by the total amount of "stuff". Thus, the new VFR is (remaining_old + remaining_new)/(total_old + total_new), which does not separate easily. Further, the extrapolation of the "O3 ripening" data into the OH oxidation region needs to be justified. Finally, I would like to see "VFR_new" values for all of the experiments, not just the two selected here. Do they all give similarly highly volatile "new" material? From Figure 7, it would seem that e.g. experiment No. 11 is completely different.

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Section 3.4: The meaning of the statement "The correlation is governed by the chemistry. . ." is unclear. By "chemistry", do the authors mean "composition of the particles"? And if so, then shouldn't O:C be an important parameter?

Figure 8: I am confused by the differences between the two panels. A quick look at e.g. Figure 6 suggests that during the O3 period(s) VFR and kappa are correlated, but during the OH period(s), they are anticorrelated (eventually both becoming flat, i.e. no correlation). Yet this doesn't seem to be what is shown in Figure 8b? Am I missing something? Or is this what is meant by "It should be cautioned here that the opposing trends of VFR and kappa during the OH mediated condensing phase are buried in the scatter plot." Also, why are only the TME experiments shown? Why not the HONO experiments? Are they the same? Different?

Section 3.5: This section begins "In the following we present results from the second part of the experiments where OH mediated ripening was investigated." However, ripening experiments have already been discussed in the previous sections. This section focuses on ripening and size, not ripening as a general phenomenon.

Figure 9: The authors need to figure out a different way to present this data. It is extremely difficult to see how, e.g. "In experiment No. 14 the smaller particles tend to have a higher Kappa and lower VFR (higher volatility); this is not observed in experiment No. 5." The data need to be succinctly summarized, perhaps as a mean difference between the different sizes. However, the figure as is I do not find useful.

P. 7445, Line 5: The assumption made here is poor. A single component aerosol will not give robust or correct results. Also, reporting the saturation concentration without reporting the enthalpy of vaporization is not useful to the interpretation of thermodenuder results; these are coupled parameters in a thermodenuder model [Riipinen et al., 2010; Saleh et al., 2010; Cappa, 2010]. The mass accommodation coefficient for alpha pinene SOA has been shown to be far from unity [Vaden et al., 2011; Cappa and Wilson, 2011], thus making this a bad assumption because this affects the kinetics, and

thus the inferred size dependence and conclusions. Finally, I don't see how "The SOA was assumed otherwise to have similar properties as the theoretical AP SOA modeled in Riipinen et al. (2010)" since the important properties (saturation concentration, number of compounds, mass accommodation coefficient) have all been chosen here. Finally, the authors are only explaining one experiment here; the other one mentioned in this section does not show the same behavior. The authors need to explain this discrepancy.

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