

Interactive comment on “Lower than expected volatility of secondary organic aerosols formed during α -pinene ozonolysis” by Kei Sato et al.

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Received and published: 11 November 2017

Note: I am a referee for the paper but am posting my review with my name as much of my response is informed by a highly related (and complementary) paper that a former student and I published on a similar topic (Saha and Grieshop 2016). It appears that the authors of this paper may not be aware of our paper, and I wished to be transparent so thought it most appropriate to post this review under my name.

This paper presents results from a series of chamber experiments in which α -pinene was oxidized with ozone and OH and the resulting aerosol measured in-situ and via measurements of particulate matter. α -pinene ozonolysis is a well-studied system, but a number of open questions remain, with the product distribution (typically quanti-

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fied in terms of volatility) and phase-partitioning kinetics being among two of the most pressing ones. This paper adds to the literature discussing this system by including cutting-edge chemical analyses of particles formed from both ozonolysis and particles thus formed and then perturbed via OH oxidation and additional dilution. A number of different experimental arrangements – e.g. use of thermodenuder (TD), analysis of PTR-MS measurements of gas-phase and vapors driven off a filter, ESI-MS analysis of filter samples and multi-chamber dilution studies – provide valuable data sets by which the partitioning and chemical composition of this SOA can be probed. This is a system and a topic of great interest to ACP readers, and as such I believe this is highly appropriate venue for this analysis. This is an interesting and creative set of experiments resulting in data collected with cutting edge techniques. However, while the data appear to be carefully collected, I find some of the interpretation of these data could be improved and that some of the resulting conclusions are insufficiently supported by the analysis. Therefore, I suggest that this paper be substantially revised before publication is considered.

A number of specific points are included below, but the main concerns I have are:

1) The title and tone of discussion don't give proper weight to previous work that has shown that the partitioning of a-pinene SOA is not well-represented by 'traditional' yield experiments. As the other reviewer suggested, this is not a 'new' insight, and so more effort should be made to put the present results into the proper context, including that provided by our paper and others with more detailed chemical analyses that well preceded ours.

2) Inter-experiment variation is an important theme that should be explored. There is relatively little comparison between sets of experiments conducted at similar conditions to establish repeatability of efforts (which seem to be good for TD results, based on Runs 2, 3 and 4 in Fig. 4c) and also to more systematically explore the influence of different experimental conditions (e.g. OH scavenger, RH) on the measurements. One complication, especially to interpreting TD results is that OA concentration varies quite

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substantially (Table 1). Our paper showed that smog chamber OA concentration has a systematic effect on its observed evaporation. These data are collected at a range of concentrations, though a number of other parameters were simultaneously changed and so it's difficult to say whether the effect of individual changes can be extracted. In addition to inter-experimental variability, I'm also curious about possible explanations for the quite substantial variation in volatility distributions from different methods (Fig. 4 panels) – are there any cases in which experiments show better or worse agreement? What might explain these differences?

3) I have some major concerns about the collection and analysis of the room-temperature evaporation data. In considering these results, I'd ask the authors to take a careful look at our paper (Saha and Grieshop 2016) and also work by Saleh et al. (Saleh et al. 2011, 2013), especially their chamber experiments considering time scales of equilibration. An important point is that equilibration rates cannot be readily separated from volatility in this type of experiment, and so the authors should not compare the assumed equilibrium of particles calculated based on yield experiment data (horizontal lines in Fig. 5) with dynamic equilibration data unless the consistency is somehow proven (e.g. the actual equilibrium state of the system is known). This disconnect especially stands out here because the authors have presented volatility distributions showing much lower volatility, so it is strange to compare 'equilibrium' dictated by another experimental approach (yield experiments) when other parts of your paper are essentially arguing that these are wrong. A better way to compare equilibrium properties is by comparing volatility distributions. Normalized time scales (see Saleh et al. papers referenced above) can be used to compare equilibration time scales for such experiments. As it is, this figure suggests that equilibration time scales for the low and high RH experiments are very different, but this difference may be due to differences in volatility or other experimental conditions. If this is the case, the volatility distributions in Fig. 4 may be able explain this difference. As both our paper and (Saleh et al. 2013) point out, if you assume the wrong volatility you can easily conflate 'slow' evaporation due to a kinetic limitation (as you suggest), when it's really just that

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(as your chemical analyses suggest) the aerosol is much less volatile than yield data suggest. This is an assumption that we show may be at play in the 'kinetic limitation' ascribed to slow evaporation by Vaden et al. (2011). In addition, since different chambers (Teflon-coated steel vs. FEP membrane) were used for the different experiments, it's impossible to say what influence different wall characteristics may have of on the observed evaporation. As it is, there is far too little evidence to support the statements on Line 279-284 about 'irreversible' partitioning and the RH-dependence of evaporation and viscosity. There is good evidence elsewhere that RH dependencies may be important, but I don't find what is presented here convincing. For example, the data don't support the statement (L282-283) that that 'gas/particle partitioning was virtually irreversible'. This level of dilution is insufficient to probe the irreversibility of partitioning for compounds with C^* less than 10^{-1} or 10^{-2} $\mu\text{g}/\text{m}^3$, which comprise the majority of the material in your distribution (Fig. 4) but not the Lane et al. (2008) distribution used to calculate equilibrium partitioning.

Specific points

L42-43 – Discussion of dilution results is limited, and the body of literature lumped as 'later research' should be further discussed. This is a logical place to discuss Saleh et al. (2013).

L90 – It would be helpful to compare density numbers determined here with those from other studies. In general, more comparison of results with the wealth of other studies of this model aerosol system would help to place this study in its proper context relative to the literature.

L97-98 - Discussion of the use of pinonic acid as a reference for the thermodenuder (TD) measurements should be discussed, along with more generally the approach used for interpreting TD measurements to yield Fig 4c. Is the T₅₀ method of Faulhaber et al. (2009) used with only a single 'calibration' compound (pinonic acid) to develop the calibration? Or were more calibration compounds used? Was the cali-

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bration from Faulhaber used directly? If so, do the results for your single calibration compound match well with that from their calibration? It is not clear if your TD has exactly the same residence time as the one used there, which would be an important pre-requisite for applying this calibration.

Line 102-104 – I would be curious to see how wall losses of vapors might affect the determination of the distribution of gas-phase constituents in the chamber at the end of the experiment and how this, and also sampling/storage conditions might affect what was sampled on the chamber walls. Also, during the desorption of the filters, was the PTR-MS signal observed to return to background? In both your and our work, we find materials that remain in the particle phase (not on filters) in a TD to up to 120 C (393 K) with substantial residence times, so I'd be curious to see how PTR-MS-identified products evolve during desorption and if everything was actually desorbed from the filters. In general, no PTR-MS data are shown apart from the points shown in Fig. S2 in the supplement. Is there any reason these data are not further discussed?

Line 109 and 152-153 – A brief description of the analytical method would be helpful. For example, some mention of the source/significance of sodium adducts would be helpful, especially for those (like me) unfamiliar with this quirk of ESI analysis.

Line 241 – Error of +/- 2 – it is not clear what units this error is reported in? Possibly a factor of 2?

Line 212-215 – While a line can be drawn through these data points, and shows a reasonably high R^2 value, there seems to be a discontinuity in this relation at a $\log C^*$ of around -3 or -4, with the clusters of data at either side of this showing a much shallower relationship between MW and $\log C^*$. For example, if you exclude the lower volatility data, you would have a much different dependence. How does this affect your results? Is there any reason for this discontinuity, perhaps due to the oxidation state or other properties of the compounds in these two clusters?

L221-223 – This may be a very normal assumption to make for a TOF-MS, but I would

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like to see it justified, either with a reference or calibration data. How sensitive are results (e.g. volatility distributions) to any uncertainty in this?

L242-244 – I don't quite understand this statement. How were 2D function results 'adjusted'? I'm assuming this is referring to the range of compounds fit by the 2D function? This statement and its implications should be clarified.

Line 250-255 – The level of agreement should be better described (perhaps by comparing others' data to yours). Also, I note that there is quite a bit of scatter in observed evaporation, especially at 50 deg. C, where there is nearly a factor of 2 range in VFR (~ 0.4 to 0.7) for the alpha-pinene SOA systems. It is stated that data were similar 'to within experimental uncertainties', but these uncertainties are not stated or discussed. As noted above, comparing results collected for experiments at the same conditions (Coa, scavenger, RH, etc.) can constrain inter-experiment variability and then be used to discuss whether any observed differences may be ascribed to these conditions or uncontrolled variability in the experiments.

Line 291 – Our study and various others that our paper discussed and cited, many of which were also cited here (e.g. (Ehn et al. 2014; Zhang et al. 2015)) have pointed towards the prevalence of very low volatility compounds in pinene SOA in contrast to existing yield-experiment-based parameterizations. It may be true that you are the first who arrived at the results via application for ESI-MS, but that is not how I read this sentence.

Line 293-294 – Since a VBS model by itself doesn't assume an evaporation rate, it's hard to make this comparison. Also, as noted, volatility and evaporation kinetics are conflated in the comparison in this paper, so insufficient evidence is presented to make this claim. In chemical transport models, the assumption is that frequently made that equilibrium partitioning adequately describes what happens within time steps of on the order of a \sim hour. Our paper argues that this is probably a fine assumption for alpha-pinene SOA produced in our lab under atmospheric conditions, though the assumption

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cannot be made in interpreting thermodenuder measurements.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-860>, 2017.

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