

Interactive comment on “Temperature and VOC concentration as controlling factors for chemical composition of alpha-pinene derived secondary organic aerosol” by Louise N. Jensen et al.

Anonymous Referee #1

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Review of Jensen et al.: Temperature and VOC concentrations as controlling factors for chemical composition of alpha-pinene derived secondary organic aerosol

Summary This paper investigates the effects of temperature and alpha-pinene concentration on the chemical composition of SOA particles formed via dark ozonolysis in a series of chamber studies. Experiments were performed in the dark at two concentrations, 10 ppb and 50 ppb, in the presence of ozone. Three constant temperatures were analyzed (20, 0, and -15 C), and several temperature ramps were induced at various points during the ozonolysis. Chemical composition was investigated in real-time using an HR-ToF-AMS, and offline chemical composition of filter samples was performed via

C1

LC-MS. The authors apply PMF to the AMS data in order to determine controlling factors behind the chemical composition. They discuss a four-factor solution, where two of the factors correspond to temperature and two factors correspond to alpha-pinene concentration. The authors argue that the temperature at which particles initially form is more important for determining particle composition than changes in temperature after the initial formation. However, they do find that temperature ramps lead to slight changes in oxidation levels. The authors also compare AMS derived estimates of organic acid content to off-line LC-MS analysis of filters and find good agreement. They conclude that high temperatures and low initial alpha-pinene concentrations are associated with more oxidized SOA.

General Comments This paper is not suitable for publication in its present form. In general, a more rigorous and thorough discussion of results with consideration of context would be helpful. There is a tendency in this manuscript to state results and not interpret them. I also take issue with some of the findings.

The second to last sentence of this manuscript is “This work confirms that the particle chemical composition is dependent on precursor concentration and particle mass loading.” This is not explored in the manuscript.

The authors state that “Factor 1” is a temperature factor, however this does not seem to be the case. Comparing experiment 1.4 to 3.1 (same constant temperature) Factor 1 appears to change more than a factor of 10 for a factor of 5 change in precursor VOC concentration. Further, Factor 1 does not change during the lower VOC (10ppb) temperature ramp experiments. Factor 1 is essentially the same for experiments 1.4 vs. 1.5, though this is a little hard to discern because the y-axes are different. The authors admit that a five- or six-factor solution provides a better explanation for the data than the four-factor solution presented in the manuscript, but do not adequately explore why the higher-order factor solutions are discarded. Ramp start-to-end RH is presented in Table 1, but it is not explored in the manuscript. RH values change drastically during the temperature ramp, but this information is not used in the analysis. Is it possible

C2

that the ignored factors from the PMF solution are instead factors relating to RH? If so, they should be included in the analysis and their importance should be discussed, or a more adequate reason for discarding them should be addressed.

Atmospheric Chemistry and Physics is an applied journal and it surprises me the authors provide no atmospherically relevant context for the selected temperatures, initial hydrocarbon concentrations, etc. The authors state early in their manuscript that oxidation levels of SOA from α -pinene ozonolysis decrease with increased particle mass loadings. The authors' findings do not seem to be consistent with this. Why?

Specific comments and line numbers follow: Page 2, Line 6: SOA is also formed through the uptake of water-soluble organic gases into condensed-phase water.

Page 2, Line 7: The 1995 Guenther manuscript describing a biogenic emissions model is not the right reference for "SOA forms from biogenic and anthropogenic precursors".

Page 2, Line 10: Hydroxyl radical (OH) should have a dot, not a minus sign.

Page 3, Line 28-32: Why were different precursor concentrations chosen for the temperature-ramp experiments? If precursor concentration is playing an important role in chemical composition, then why aren't all the temperature-ramp experiments performed using the same initial α -pinene concentration? Here, some are done with 10 ppb and some with 50 ppb. Why are these conditions relevant?

Page 4, Line 36 – Page 5, Line 1: According to Table 1, these experiments also saw a wide range of RH, which could lead to the condensation of water onto the particles and subsequent aqueous-phase reactions. Is it possible that Factors 5 and 6 are related to RH? If so, please address this in the manuscript, or provide a justification for why these factors and the large range of RH values can be ignored.

Page 5, starting at Line 14: The authors state, "Under all conditions (i.e. in all experiments), the AMS derived SOA densities are in the range of 1.1 to 1.3 g cm⁻³. Figure 1 indicates that SOA density is < 1.1 for the first 0.5 hour.

C3

Page 5, Line 32-35: Please provide a reasoning for using only some of the temperature ramp experiments in the PMF analysis.

Page 6, Line 29-30: What contributions from f44 and m/z ratios do Factors 5 and 6 have?

Page 7, Line 12-14: Please provide a discussion regarding why it makes sense to have less-oxidized SOA at low temperatures and high α -pinene concentrations. It is interesting that this is the case, but a scientific justification is missing and should be discussed. Is this a matter of kinetics and competition for oxidants?

Page 7, Line 31: Why is no OH scavenger used, and how does potentially changing [OH] confound interpretation of O:C ratios and factors? The authors provide some speculation on Page 7, but the context is insufficient.

Page 8, Line 18-24: A lot of time and energy is spent on discussing the reasons behind changes in the O:C and H:C ratios during temperature ramps in previous paragraphs. However, here it is stated that the changes are small and not very important. If that is the case, then why discuss the changes to the O:C and H:C ratios so extensively? It seems this section could be more focused.

Page 8, Line 39 – Page 9, Line 9: Please provide a reasoning for why a lower precursor concentration leads to more highly oxidized SOA. Is this because there is less competition for oxidants?

Page 10, Line 9-12: The authors state that organic acids with heavier backbones are formed at lower temperatures. Why does this make sense? Is this due to volatility reasons?

Figures and Tables: Table 1: Do I understand correctly that no experiment was repeated and there is no demonstrated repeatability?

Figure 1: Particle density is presented with four significant digits and no estimate of uncertainty. There should be uncertainty bars or some other representation.

C4

Figure 4: In panel b, what is the black line? It is not labeled.

Figure 6: In panel b, the black line is not defined. Why is the black line in panel b different from panel a, if they are both based on Heald and Ng? In panel a, it is unclear how this figure supports the author's conclusions regarding the oxidation level of SOA in each experiment.

Supplemental Information: Figures S5 and S7. Could these extra factors be attributable to RH? They seem to play a consequential role in mass loading.

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