Yee et al. report mass spectral measurements of laboratory SOA formed from the OH oxidation of alkane precursors under low-NO_x conditions. The authors use C_{12} alkanes spanning a range of molecular structures (linear, branched, cyclic, branched-cyclic) to investigate the role of alkane structure on SOA chemical composition. A specific focus of this manuscript is on the characterization of peroxyhemiacetals (PHAs), which are formed in the condensed phase from reactions of organic peroxides and aldehydes. Selected gas-phase oxidation products are monitored with a chemical ionization mass spectrometer, and condensed-phase chemistry is measured with an Aerodyne time-of-flight aerosol mass spectrometer.

The authors report formation of PHAs in all four types of alkane SOA. PHAs are identified from pairs of high-molecular weight ion fragments that are separated by 32 amu and correspond to O-O peroxide bonds: for example, $m/z = 183$ ($C_{12}H_{23}O^+$) and $m/z = 215$ ($C_{12}H_{23}O_3^+$) in dodecane SOA. In general, measurements seem to support the proposed oxidation mechanism outlined in Figure 1 of this manuscript. Yields of PHAs are highest in SOA produced from OH oxidation of hexylcyclohexane, then decrease in the order: dodecane SOA > 2-methylundecane SOA > cyclododecane SOA. The authors propose that the cyclic structure of cyclododecane may hinder interactions between peroxide and aldehyde functional groups, resulting in lower PHA yields. Additionally, they suggest that the branched structure of 2-methylundecane favors fragmentation reactions relative to the other SOA types, which may resul in lower PHA yields than in dodecane and hexylcyclohexane SOA.

This manuscript addresses an important issue in the atmospheric sciences regarding the characterization of SOA formation and aging mechanisms over multiple generations of oxidation. It also represents a unique application of the AMS to measure high-molecular weight PHA species, which to my knowledge, has not previously been performed systematically or extensively. However, in my opinion there are several issues that need to be addressed before I can recommend publication in ACP. In general, I think that the manuscript would be significantly improved by:

(1) Additional background and motivation for their characterization of PHAs.
(2) Rewriting/restructuring of most of Section 3 – particularly Sections 3.2.3 and 3.2.4.
(3) Identifying whether additional analyses/figures, such as the Van Krevelen diagram in Section 3.2.5, supports the proposed mechanisms leading to PHA formation and/or the different PHA yields across the four types of alkane SOA.

COMMENTS

1. In my opinion, the importance of PHAs is not sufficiently motivated in this manuscript. Further, the potential atmospheric implications of this study are not detailed in the conclusions. For example, what is currently known (or unknown) about PHAs, and why are they of specific interest as opposed to other species formed from condensed-phase accretion reactions? What conditions might favor or inhibit PHA formation in the atmosphere? Based on the results reported in this manuscript, is there any indication whether other SOA precursor classes (e.g. aromatics, terpenes) might form PHAs with lower or higher yields than the alkanes studied here?

A previous paper suggesting PHAs are a "key component of initial aerosol growth" (Yee et al., 2012) is cited partway through Section 3.1, but the measurements from that paper that led to this conclusion are not discussed here. Given the theme of this manuscript, I think that more background on PHAs and more specific discussion of potential atmospheric implications of PHAs in the conclusion is needed.

2. Section 3.1 provides useful context for interpretation of measurements. However, as far as I can tell, the proposed mechanism is not derived from the new results presented in this paper; rather, the measurements are used to support this mechanism. I suggest incorporating parts of this section into the introduction and possibly moving Figures 1 and 2 to an Appendix at the end of the paper or to an online supplement, because it seems out of place in Section 3.

3. I suggest filling out Section 3.2.2 with discussion of other features of the AMS spectra and how these might relate to the precursor structure. Most of the discussion is focused on mass spectral features from $m/z = 100$ to 270, but there are other interesting features at $m/z < 100$ – where the majority of the signal is present – that appear to be related to the precursor structure. For example, the abundance of alkyl ions and cycloalkyl ions appears to vary as a function of the precursor, and I think it would be worth adding a brief discussion that compares the relative intensities of these characteristic ion series and how they relates to the precursor structure. Section 3.2.2 may also be a better place to introduce and discuss the Van Krevelen diagram (Comment #10 below).

4. I found it hard to follow the discussion in Section 3.2.3. Here, I think that the authors are trying to show evidence that supports the proposed PHA formation mechanism outlined in Figures 1 and 2. However, there are two apparent inconsistencies in this section, outlined in Comments #4 and #5 below, that obscure the discussion in this section.

5. I think that organic peroxide levels should decrease at some point in the experiment, after their rates of formation from alkane + OH are offset by their rate of decay from peroxide + aldehyde and peroxide + OH reactions. Thus, maximum peroxide levels should precede maximum PHA levels (occur at lower OH exposures). However, Figure 8a does not support this. In fact, the dodecane "CARBROOH" appears to peak at later OH exposures than the dodecane PHA tracers ($m/z = 183$ and 215). How do the authors reconcile this apparent discrepancy with the proposed mechanism shown in Figure 1?

6. The text in Section 3.2.3 (and Figure 8) implies that gas-phase organic acids are precursors to PHA formation. If I understand the proposed mechanism correctly, this is not true. The authors state that they are using the acids as surrogates for the aldehyde coproducts which cannot be measured with CIMS. However, statements such as "the presence of gas-phase acid indicates that peroxyhemiacetal formation may commence" and "in each system, the CARBROOH PHA ions grow in the particle phase when gas-phase acid forms, as indicated by the C_6 carboxylic acid,

C6CARBACID" significantly confused this issue to me. The CARBACID signals shown in Figure 8 increase continuously as a function of OH exposure, and don't show obvious correlations with the peroxide or peroxyhemiacetal signals.

7. It's unclear why the authors describe the dodecane + tridecanal experiment in detail (p. 10871, lines 16-22), but don't show it graphically. This described experiment suggests direct correlation between peroxides, aldehydes, and PHAs. I suggest that the authors add a figure showing results from the dodecane + tridecanal experiment, because this would seem to serve as more convincing evidence/conformation of the proposed PHA formation mechanism.

8. I also found the presentation in Section 3.2.4 confusing. Here, I think that the authors are attempting to relate the structure of the alkane precursor to the yields of different types of PHAs. However, the discussion that starts on p. 10873, line 2 and ends on p. 10875, line 5 (including Figure 9) is very difficult to follow, as the text shifts quickly from discussion of isolated features of individual SOA types, such as 2-methylundecane SOA versus dodecane SOA (p. 10873, line 2-10) to hexylcyclohexane SOA (p. 10873, lines 11-27) to the OHDICARBROOH PHA (pp. 10873-10874, lines 28-29, 1-13) to cyclododecane SOA (p. 10874-10875, lines 14-29 and 1-5). It isn't until the authors compare and contrast trends across all four SOA types (starting on p. 10875, line 6; including Figure 10), that I felt any clear attempt was made to relate alkane structures to PHA yields. In my opinion, this section should start by examining trends across the four SOA types (as is done in Figure 10 and related text), and then expand upon other precursor-specific features as needed, though perhaps in less detail than the current manuscript.

9. In general, it seems that yields of hexylcyclohexane-derived CARBROOH, DICARBROOH, and OHCARBROOH PHAs are higher than those derived from dodecane, 2-methylundecane, and cyclododecane. Further, to the extent that PHA yield is correlated with level of alkane substitution (dodecane > 2-methylundecane > cyclododecane), hexylcyclohexane seems to be an outlier. This should be discussed somewhere in Section 3.2.4, perhaps near the explanation for low cyclodecane-derived PHA yields at the bottom of p. 10875.

10. I think that the Van Krevelen diagram can provide useful information in this manuscript. However, at the moment its inclusion (and Section 3.2.5 in general) seems disjointed, particularly after the preceding sections that focus explicitly PHAs. The main utility of this section is to (1) illustrate the oxidation state "phase space" attained in these experiments, and (2) illustrate the higher degree of unsaturation in the cyclododecane SOA system. I suggest that the authors consider whether this material is more synergistic with earlier discussion in Section 3.2.2.

11. Can the alkane SOA Van Krevelen slopes be used to infer the PHA yield trends formed across the four SOA types? If so, this should be discussed. The authors note that the O/C ratio of dodecane SOA is similar to the O/C ratio of dodecane-derived peroxides and PHAs, but unless they can show that PHAs comprise a significant

amount of the aerosol mass and/or demonstrate a similar correlation with the O/C ratio of other SOA types, this observation seems to have limited application.

12. **p. 10861, line 29**: Typo ("special")

13. **p. 10862, line 26**: The relative humidity dependence of cyclic hemiacetal formation appears to be significant (Lim and Ziemann, 2009), but is not mentioned in this manuscript. There should be a brief discussion of how the relatively dry chamber conditions (RH<10%) may influence the kinetics of PHA formation relative to atmospheric conditions at higher RH.

14. **p. 10864, lines 3-18**: What is the temperature of the AMS vaporizer in these experiments? I assume that the O-O peroxide bonds are prone to decomposition at higher temperatures, were any modifications made to typical AMS operating conditions (e.g. $T_{vap} \sim 600^{o}C$) to minimize decomposition?

15. **p. 10865, lines 20-22**: The relative importance of $RO_2 + RO_2$ self-reactions is not mentioned. I suggest the authors mention any calculations that led them to the conclusion that $RO_2 + RO_2$ reactions are negligible compared to $RO_2 + HO_2$ reactions.

16. **p. 10868, lines 4-6**: The authors state: "Assuming that the CIMS sensitivity to certain functionalized species within the same mode of operation are comparable despite difference in structure (straight, branched, cyclic + branched, cyclic)…":

This type of statement might fit better somewhere in the Methods section.

17. **p. 10868, lines 22-24**: The authors state: "The 2nd-generation carbonyl (CARB) formation is compared across the systems in Fig. 3, middle panel. The trends are consistent with faster gas-phase oxidation for hexylcyclohexane."

I didn't understand this observation. If the kinetics of hexylcyclohexane CARB formation and decay are related to the faster OH-hexylcyclohexane rate constant (Table 1) wouldn't the hexylcyclohexane-derived CARB peak at lower OH exposures than in the other systems, as is observed for ROOH shown in Fig. 3a?

18. **p. 10869, lines 8-22 (last paragraph of Section 3.2.1):** This discussion seems somewhat speculative and of minor importance; I would consider removing it.

19. **p. 10870, line 14**: The word "chaos" is confusing because it implies that the mass spectra are not reproducible under controlled conditions. Calling it a hybrid of the other types of SOA spectra seems sufficient.

20. **p. 10871, line 10**: Typo ("molecular").

21. **p. 10872, line 17:** Should "$C_{12}H_{19}O_5^+$" be "$C_{12}H_{19}O_3^+$", since $C_{12}H_{19}O_5^+$ is not plotted in Figures 9a or b?

22. **p. 10877, lines 1-11:** Somewhere this section, it is worth comparing elemental ratios and Van Krevelen slopes to those measured by Tkacik et al. (2012) in addition to the results of Lambe et al. (2012) discussed in the preceding paragraph and any other previous studies that might be relevant.

23. **p. 10878, lines 12-14**: The authors state: "2-methylundecane exhibits the least extent of chemical processing relative to the other systems, likely a result of gas-phase fragmentation that leads to a product distribution consisting of relatively higher volatility intermediates."

    However, cyclodecane SOA has the lowest O/C ratio of the four SOA types (Figure 11). Perhaps the authors can clarify what they mean by "chemical processing"?

24. **p. 10878, lines 16-18**: The authors state: "Of the systems studied, hexylcyclohexane behaves in terms of SOA chemistry somewhere between 2-methylundecane and cyclododecane."

    In general, I disagree with this statement, for the following reasons:
    1. Hexylcyclohexane has the lowest gas-phase peroxide (ROOH) and carbonyl (CARB) yields of all four alkanes (Figure 3).
    2. Hexylcyclohexane SOA has a similar CARBROOH PHA yield as dodecane SOA, and in general, its PHA yields are significantly higher than 2-methylundecane and cyclododecane (Figure 10).
    3. Hexylcyclohexane is characterized by a higher O/C ratio than the other two SOA types (Figure 11).
    It may the case that specific features of its AMS spectra (Figure 6) are similar to a combination of AMS spectra corresponding to 2-methylundecane SOA (Figure 5) and cyclododecane SOA (Figure 7), but those features need to be explained in more detail.

25. The authors use the word "organic" throughout the paper to describe organic aerosols measured by the AMS. This word choice is confusing to me because "organic" implies a single organic species. I suggest designating AMS-measured organic aerosols with any one of several more conventional, straight-forward labels, such as "organics", "organic aerosols", "OA", etc.

26. **Figure 3**: To highlight the different peak OH exposures for 1st, 2nd, and 3rd-generation oxidation products, it might be useful to add an arrow pointing to the OH exposures at which maximum ROOH, CARB, and CARBROOH levels were attained.

27. **Figures 4-7**: To draw the reader's attention to the PHAs in these spectra, the authors might consider coloring the m/z's corresponding to PHAs that are listed in Tables 5-7. Also, these figures are somewhat busy. Are the "middle" spectra needed? It doesn't seem as though they are discussed much.

28. **Figure 8**: the colors of the ion time series traces don't match the colors of the labels in the figure legends.

29. **Figures 9a and 10(top panel):** Why does the maximum CARBROOH signal for dodecane (m/z = 183) appear to peak at ~$7*10^{-3}$ in Figure 9a but only at ~$3*10^{-3}$ in Figure 10?

30. Figures 9 and 10 seem to mostly repeat the same results. In my opinion, Figure 10 is a lot more useful than Figure 9. A composite figure (of the sort shown below), with addition of subpanels for TRICARBROOH and OHDICARBROOH PHAs to the current CARBROOH, DICARBROOH, and OHCARBROOH PHA time series, could potentially combine the relevant content from Figures 9 and 10:
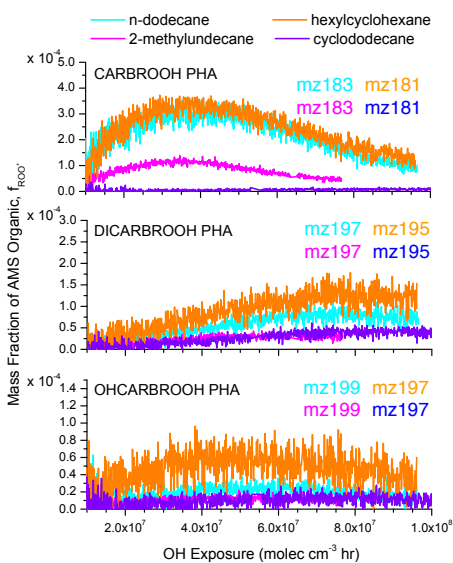
31. **Figure 11**: The application of a single set of Van Krevelen lines with origin of (O/C, H/C = 0, 2.0) is incorrect: the H/C ratio of each alkane precursor is different, ranging from 2.0 (cyclododecane) to 2.17 (dodecane). Depending on how Comment #22 is incorporate, I suggest also adding some sort of representation of literature data for 2-methylundecane SOA from Tkacik et al. (2012) and possibly other alkane SOA types from Lambe et al. (2012). This could be accomplished with a new subpanel in Figure 11 or as a separate figure.

REFERENCES

Lim, Y. B. and Ziemann, P. J. (**2009**). Kinetics of the heterogeneous conversion of 1,4-hydroxycarbonyls to cyclic hemiacetals and dihydrofurans on organic aerosol particles, *Phys. Chem. Chem. Phys.*, 11, 8029–8039.

Tkacik, D. S., Presto, A. A., Donahue, N. M., and Robinson, A. L. (**2012**): Secondary organic aerosol formation from intermediate-volatility organic compounds: cyclic, linear, and branched alkanes, *Environ. Sci. Technol.*, 46, 8773–8781.