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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Effect of chemical structure on secondary organic aerosol formation from C_{12} alkanes” *by* L. D. Yee et al.

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The authors would like to thank both referees for their time and comments that have aided in improving the current manuscript. All referee comments have been addressed. Note: All page, line, and figure references have been made according to that used in the discussion version of the manuscript.

We thank Referee #1 for offering suggestions on improving the presentation of the particle-phase analyses and on restructuring some of the paper's organization.

Response to Referee #1 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.

Thank you for this suggestion. The manuscript has been revised to focus the introduction on better motivating the importance of PHAs and the potential atmospheric implications of this study in the conclusions. This includes more discussion of the following points: 1) observations/previous study of PHAs (Tobias et al., 2000; Tobias et al., 2003) and peroxide formation in biogenic SOA (Docherty et al., 2005; Capouet et al., 2008; Surratt et al., 2007) and anthropogenic SOA systems (Sato et al., 2007), and controlling factors in their formation (Jang et al., 2002) 2) specific measurements in Yee et al., 2012 that suggests PHAs to be a “key component of initial aerosol growth” 3) the general importance of accretion reactions and their potential to act as catalysts for SOA growth (DePalma et al., 2013) 4) the use of controlled studies, such as those presented here, for modelling particle-phase chemical processes relevant for understanding controlling processes in SOA growth (Shiraiwa et al., 2012)

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.

The authors feel that these mechanisms are central to understanding new chemistry derived from the observations described in the manuscript. To our knowledge, measurement of the several intermediate multifunctional compounds presented in Figures 1 and 2 for these specific alkane systems has not been achieved, and the trend information presented for these compounds elucidates the chemical mechanisms behind SOA formation in these systems. We feel that the chemical mechanisms themselves, especially the dynamics of intermolecular and intramolecular reactions presented in Figure 2, are new results themselves, and as such should be kept in the results portion of the manuscript.

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 may also be a better place to introduce and discuss the Van Krevelen diagram (Comment #10 below).

The discussion beginning on p. 10870, line 10 has been modified to highlight other features of the AMS spectra at m/z < 100 as follows:

In the m/z <100 amu range, several of the dominant CxHy+ ions are shared across all systems, though there is greater relative contribution of cycloalkyl ions compared to alkyl ions in the case of hexylcyclohexane and cyclododecane. For example, there is greater signal of the ion C6H7+ compared to C6H9+ for these systems compared

to those of n-dodecane and 2-methylundecane. The highest signal is attributed to the same ions for n-dodecane and 2-methylundecane (Figures 4 and 5); however, the fraction is higher for n-dodecane than in the 2-methylundecane case. This observation is consistent with more fragmentation in the 2-methylundecane oxidation, as compared to n-dodecane. 2-methylundecane oxidation also exhibits a higher fraction of C2H3O+ in the <100 amu range. C2H3O+ has been proposed as an ion tracer for non-organic acid oxygenates (Chhabra et al., 2011). This ion also tends to dominate during hexylcyclohexane oxidation (Figure 6) in the 40-45 amu ion cluster range, though it never dominates in the case of cyclododecane (Figure 7). In the cyclododecane system one ion tends to predominate within a cluster of ions. For example, C4H7+ at m/z 55 dominates during initial aerosol growth (Figure 7) in the 50-60 amu region, whereas in the n-dodecane system, ions at m/z 55 and m/z 57 are present at similar mass fractions (Figure 4). At initial growth, they are reduced ions, whereas at maximum growth, the two ions are more oxidized, and the oxidized ion (C3H5O+) at m/z 57 is higher. For cyclododecane, the m/z 55 ion also shifts from the reduced ion (C4H7+) to the more oxidized ion (C3H3O+) and remains predominant in the 50-60 amu range throughout the oxidation. The fraction of mass at C3H3O+ at m/z 55 is also high for the entire duration of the hexylcyclohexane oxidation, whereas in the other systems, the reduced ion (C4H7+) at m/z 55 is high, and then C3H3O+ grows in. The mass spectrum from the hexylcyclohexane system . . . While the authors agree that many of the mass spectral features in Figures 4-7 are crucial in describing the Van Krevelen diagram (Figure 11), key analyses of the diagram are revealed via complementary ion trends presented in Figure 9. The corresponding text (p. 10877, lines 5-22) to describe these features of the Van Krevelen diagram cannot be introduced in the 3.2.2 Particle-phase composition section without first introducing these ion trends described in Section 3.2.4. Please also refer to our address of Referee #1, Comment 10.

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. Please see Referee #1, Comment 5 below.

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? Thank you for bringing this to the attention of the authors. The authors agree with the kinetic argument presented by Referee #1, and a similar figure with kinetic modelling and measurements that supports this argument was presented in Yee et al., 2012 (Figure 8a). It has come to the attention of the authors that Figure 8a in the current manuscript is incorrect, and it has been revised.

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 C6 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.

Yes, the authors are using the acids as surrogates for the aldehyde co-products, and we do not believe them to be precursors to PHA formation. The text in Section 3.2.3, p. 10871, lines 25-27, has been modified to clarify this point. It now reads, "The presence of gas-phase acid indicates that aldehyde is present in the system, and that peroxy-

hemiacetal formation may commence, as observed in Yee et al. (2012)." The text p. 10872, lines 1-3, have also been corrected to read, "In each system, the CARBROOH PHA ions grow in the particle phase when gas-phase aldehyde forms, as proxied by a measured co-product, C6 carboxylic acid (C6CARBACID), in Fig. 8." Figure 8 serves to show that acid grows in the system coincident with the point at which PHA grows in the system. It is intended to convey that if acid is present in the system, then the co-product aldehydes must also be present, and therefore PHA formation from aldehyde + hydroperoxide reaction can occur. There is no intention to draw correlations of the trends from the gas-phase acid and the particle-phase PHA tracer ions, as they would not be expected to necessarily correlate throughout the duration of the experiment.

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.

The requested figure has been recently published in Shiraiwa et al., (2013), so we have added this reference in the text to refer the reader to additional details presented in that study that provide plausible evidence for the proposed PHA formation mechanism. The text p. 10871, lines 15-16 have been modified to read, "Since these initial studies, another n-dodecane experiment (Shiraiwa et al., 2013) involved intentional injection of tridecanal…"

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.

The authors have reorganized section 3.2.4 to begin with the text describing Figure 10 (p. 10875, line 6 through p. 10876, line 11). The specific ion trend information presented p. 10872, line 11 through p. 10875) systematically goes through each alkane structure and describes how specific ions in the AMS can be used to infer structural effects that control PHA formation (i.e. the schemes for PHA formation and competitive multi-functional hydroperoxide intramolecular reactions in Figure 2). However, we agree that this information is detailed and quite specific, and as such can be presented in support of the features following the discussion of Figure 10. The conclusion of this discussion, p. 10876, lines 10-11, has been modified to read, “This may suggest that these structures may undergo intramolecular reactions that result in the variety of ions and chemical development discussed in further detail below.” We have modified the text to then follow with an additional subsection titled, “Indicators of competitive chemistry with peroxyhemiacetal (PHA) formation)” that follows with the text describing Figure 9. We have also added more introductory and transition sentences as we step through each system to discuss the time trends of the relevant high m/z ions in each system and how these trends lead to inferences that there exists competitive chemistry to PHA formation.

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 cor-

related 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.

The authors appreciate this observation. We assume that the referee is referring to level of alkane “substitution” as to increasing branched and cyclic nature, as neither of these starting hydrocarbons are substituted (contain functional moieties). We have added the following text to describe our interpretation of the hexylcyclohexane ion trends in Figure 10, following p. 10875, line 22, “Hexylcyclohexane may seem like an outlier since the contribution of PHA ions generally decreases in the order of branching or cyclic character (i.e. n-dodecane < 2-methylundecane < cyclododecane), though it is notably higher than or on the same order of n-dodecane. This may be a result of hexylcyclohexane chemistry having the unique mix of many features typically individualized to the other systems. That is, while hexylcyclohexane is branched like 2-methylundecane, even if C-C scission is favored at the branch point, the presence of the cyclohexane ring means that gas-phase fragmentation can still result in preservation of the C12 backbone unlike 2-methylundecane. This means certain aspects of hexylcyclohexane's chemistry will be alike to that of n-dodecane, supporting continued functionalization and higher MW species. While hexylcyclohexane is also cyclic in nature like cyclododecane, the hexyl-chain may still afford it many sites of reaction without the potential of disrupting the stability of the C6 ring. In the case of cyclododecane, any reaction affects a ring-bound carbon, and as such may impact the resulting chemistry.”

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.

While the authors agree with (1) and (2) as raised by the referee, we also strive to (3) connect the proposed oxidation pathways as informed by analyses in Sections 3.2.3-3.2.4 with the trends presented in the Van Krevelen diagram. If presented in Section 3.2.2, the AMS mass spectra and Van Krevelen diagram inform us on the measured ions and associated bulk O/C and H/C ratios, but this does not mechanistically validate the oxidation state and "phase space" nor the slopes indicating functionalization without discussing the evidence for the proposed compounds (and their functionalities) that are present in each system. We use the Van Krevelen diagram to collect the chemical understanding derived in this study, hence there are references back to specific ion tracers that are described in Figure 9 and discussed in Section 3.2.4.

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. While the SOA Van Krevelen slopes do trend in the same way that the PHA yield trends, that is with increasing negative slope (hexylcyclohexane > dodecane > 2-methylundecane > cyclododecane) there is a lower "yield" of PHA from that system, we choose not to speculate if this relationship exists. Since these slopes represent an overall average of the phase space within each system, it is difficult to infer the dynamics of the chemistry unique to each system specifically affecting the PHA yield. That is, we do not mean to suggest that the more that the SOA is characterized by carboxylic acid groups and/or ketone/aldehyde with alcohol functionality, the higher the PHA yield within that system. The statement about the O/C ratio of dodecane SOA was based on analysis in Yee et al., 2012 that placed the proposed species in the chemical mechanism in O/C and volatility space. Based on the expected volatilities and inferred contribution to the

particle-phase, the multi-functional hydroperoxides and PHAs did have O/C ratios that were within the range of the observations. This provided a chemically feasible explanation of the O/C observations in this system, and we expect many of the predicted multifunctional intermediates to be isomeric in the other alkane systems such that similar O/C ranges might be observed as shown in Figure 11 (i.e. hexylcyclohexane and 2-methylundecane both have similar O/C ranges to that of n-dodecane). In this study we recognize that cyclododecane's chemistry has nuances to it that make it unique compared to the other C12 alkanes considered, so the main SOA constituents are likely to include other compounds (with greater degrees of unsaturation). We do, however, acknowledge the difficulty in demonstrating that PHAs comprise a significant amount of the aerosol mass, as we observe that the majority of the AMS signal is not dominated by these PHA tracer ions (Figures 4-7). This is expected as the multifunctional hydroperoxides and PHAs will be harder to keep intact using electron impact ionization techniques, in line with Referee #1, Comment 14 and the associated response from the authors. This is a challenge that cannot be addressed without additional quantitative molecular level techniques that can shed light on the issue.

12. p. 10861, line 29: Typo ("special") Thank you for pointing this out. The manuscript has been revised accordingly.

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. The manuscript has been revised to include discussion of the effect of water on PHA formation in the conclusions section.

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. Tvap $\sim$ 600oC) to minimize decomposition?

The AMS vaporizer was operated using the standard T=600°C during these experiments. We do believe that the O-O peroxide bonds can be prone to decomposition at such temperatures and hence there are associated challenges with using the standard AMS technique to measure such compounds. This effect was mentioned in Yee et al., 2012, and we have added similar discussion to the current manuscript p. 10871, line 14, to accompany discussion on the hydroperoxide and PHA tracer ions. The text has been modified to read, "...for the following discussions. We note that because the typical vaporizer temperature in the AMS is operated at 600°C, as employed in these experiments, that the signals from these m/z > 150 amu R+ and ROO+ ions are small. After running the experiments presented here Craven et al., 2012 explored the effect of lowering the vaporizer temperature for the case of C18 hydroperoxide in the particle phase and found that greater signal from the hydroperoxide ion tracer could be achieved by doing so. This suggests that future studies exploring hydroperoxide and peroxides in the particle-phase may benefit from modification of standard AMS operation. While small in signal for the current experiments, these ions are still crucial indicators of the particle-phase chemistry. These ions are listed in tables ..."

15. p. 10865, lines 20-22: The relative importance of RO2 + RO2 self-reactions is not mentioned. I suggest the authors mention any calculations that led them to the conclusion that RO2 + RO2 reactions are negligible compared to RO2 + HO2 reactions.

The authors have added the following sentence p. 10865, line 22, to address the calculation of the contribution of RO2 + RO2 reactions, "This calculation is based on analogous photochemical simulations as presented for n-dodecane in Yee et al., 2012, which also demonstrate that the time constant by which RO2 + RO2 reactions become significant is greater than 9 days, not relevant for the current experiments."

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.

This statement has been moved to the Methods section, p. 10863, following line 21, and modified to read, "The gas-phase analyses presented here assume 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)." The introductory sentence to Section 3.2.1 has been modified to read, "Comparisons of the several analogous gas-phase species across systems help elucidate the chemical development by structure. Associated CIMS signals are normalized..."

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?

Yes, we agree with this assessment. The hexylcyclohexane CARB does peak at lower OH exposures than the other systems, though it is difficult to tell from the current scaling of Figure 3, middle panel.

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. Thank you for the suggestion. This paragraph has been removed.

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. The sentence has been modified to read, "Since hexylcyclohexane exhibits alkyl, cyclic, and branched features in its structure, this may be interpreted as a unique hybrid of chemical features in the aerosol

spectrum."

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

Thank you for catching this. The typo has been corrected.

21. p. 10872, line 17: Should "C12H19O5+" be "C12H19O3+", since C12H19O5+ is not plotted in Figures 9a or b?

Yes, that is correct. The line has been corrected to reflect this change.

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. We have added the following comparison to results in Tkacik et al. (2012) starting p. 10877, line 5, "…and hexylcyclohexane. In the presence of NOx, Tkacik et al., (2012) found steeper slopes (approaching -2) for the n-dodecane and 2-methylundecane systems, attributed to a combination of carboxylic acid addition and added ketone and alcohol moieties. This was also achieved under a much lower total OH exposure (∼6 x 106 molec cm-3 h) than that used in the current experiments, providing contrast between the more efficiently (in terms of OH exposure) achieved higher O:C ratios with fragmentation pathways in the presence of NOx compared to the proposed functionalization and accretion schemes in the low-NOx regime presented here. In comparison to the average slope of -1.3 in the O:C range 0 to 0.3 from OH-initiated oxidation of alkanes in the absence of NOx by Lambe et al. (2012), many of the systems here show comparable behavior. The fact that many do not reach an O:C much higher than 0.3 with a less negative slope as observed in Lambe et al. (2012) is also consistent with these experiments remaining in the functionalized-dominated regime, and not having yet transitioned to a fragment-dominated regime." As a result of adding this analysis, we have also restructured this section to follow with a sentence introducing p. 10877, lines 6-22 to focus on specific chemical features (in terms of the AMS ions that give more molecular level information)

that support the slopes exhibited by each system in the Van Krevelen diagram. This reads, "This functionalized-dominated regime is supported by the proposed chemical mechanisms and AMS ions found in each system. Cyclododecane SOA has the slope closest to …"

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"?

Yes, it was interesting to us that the highest O/C does not indicate most "chemically processed" (i.e. having undergone several generations of chemistry with OH). Because the products formed may not result in a bulk O/C measurement that is high, the extent of generational development can be masked by this proxy. We mean to say that 2-methylundecane does not undergo as much "chemical processing" in terms of variety and extent of functionalization that the other systems exhibit. This is not reflected in the O/C ratio, as cyclododecane does achieve the lowest O/C ratio, yet the AMS mass spectra show that this system is more rich in the variety of CxHyOz+ ions present, many of them not explained by analogous oxidation pathways as in n-dodecane and 2-methylundecane. We have clarified this terminology, p. 10878, lines 12-14, "2-methylundecane exhibits the least extent of chemical processing in the particle phase (in terms of the least variety of CxHyOz+ ions observed in the mass spectra) relative to the other systems, likely a result of gas-phase fragmentation that leads to a product distribution consisting of relatively higher volatility intermediates."

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. For the points raised, 1. While these figures are plotted to compare time trends of the analogous gas-phase species across systems, it is difficult to infer absolute gas-phase yields of the ROOH and CARB within each system without knowing the true effect of structural differences on CIMS sensitivity. Hence, we did not attempt to derive these yields here as stated p. 10868 lines 10-12. 2. Again, it is difficult to say for certain that these are absolute representations of PHA yields, as structural differences may also cause the AMS fragmentation pattern of functionally analogous species to be different. However, if these can be proxied for PHA yields, we agree that this does mean hexylcyclohexane SOA chemistry is similar to that of n-dodecane. This makes sense based on C-C scission of the C6 ring at the branching point resulting in a linear C12 backbone and subsequent chemistry similar to that of n-dodecane. 3. The O:C for hexylcyclohexane is unique, though it seems as though higher O:C ratios are achieved with transitions to fragmentation processes, which may be attributable to the branching of the molecule. Thus, it seems as though hexylcyclohexane SOA chemistry has attributes from all three systems (linear straight-chain, branched, and cyclic).

As such, we have revised the line to read, “Of the systems studied, hexylcyclohexane behaves in terms of SOA chemistry as a hybrid of the other systems. It exhibits the rapid formation…”

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. Thank you for the suggestion. We have modified the term “organic” to “organic aerosol (OA)” throughout the manuscript.

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.

We appreciate this suggestion, however, the OH exposure at which maximum ROOH, CARB, and CARBROOH levels were attained differs by system, so it would be less visually clear to include 4 arrows per panel to denote this time for each system.

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.

Thank you for the suggestion. We have modified the mass spectra to include coloring of the labels of ions corresponding to the PHA tracer ions listed in Tables 5-7. The middle spectra do highlight tracer ions that dominate mid-experiment and are not obvious during initial growth and at the end of the experiment, so we would prefer to keep these in.

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

Thank you for bringing attention to this error. Figure 8 has been modified to correct the colors of the traces according to those used in the mechanisms and 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?

There are two different ions being plotted in Figure 9a and 10 (top panel). In Figure 9a, the CARBROOH/CARBROOH PHA R+ ion at m/z = 183 is plotted. In Figure 10 top panel, the CARBROOH PHA ROO+ ion at m/z = 215 is plotted. The magnitudes of signal at these two ions are expected to be different, as contributions to the m/z = 183 ion may include the CARBROOH and CARBROOH PHA and CARBROOH PHA is expected to only contribute to the m/z = 215 ion.

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: Figures 9 and 10 show completely different things. Figure 9 shows tracer ions for multi-functional species as well as some R+ PHA ion tracers relevant for comparing the chemical development across systems, whereas Figure 10 shows only ROO+ ions, stronger indicators of particle-phase development attributed to PHA formation within each system.

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. The application of a single set of Van Krevelen lines with origin of (O/C, H/C = 0, 2.0) while displaying the oxidation space of organic aerosol originating from several different organic precursors (laboratory data) or those unknown (ambient data) with unique H/C ratios has been commonly applied in the presentation of Van Krevelen diagrams (Heald et al., 2010; Ng et al., 2011; Chhabra et al., 2011;, Lambe et al., 2012; Tkacik et al., 2012). The guiding lines indicating the functionalization associated with slopes of 0, -1, and -2, are not meant to imply that

data points falling on these lines are evidence of this type of functionalization. Rather the averaged slopes of the data points from each experiment are meant to be compared to the slopes of these guiding Van Krevelen lines to infer functionalization. We have not included initial data points to indicate the O/C, H/C of the starting gas-phase hydrocarbons, which are certainly different for cyclododecane and n-dodecane, as we choose to show just the AMS organic aerosol data. In addition, we have incorporated textual comparison of the measurements of Lambe et al., 2012 and Tkacik et al., 2012 in addressing Referee #1, Comment 22, but we choose not to add additional data to the same Van Krevelen space in Figure 11, as experimental differences in OH exposure and chemical regime (presence/absence of NOx) can lead to visual interpretations that would detract from the focus of this paper (comparing SOA formation from four highly related C12 alkane hydrocarbons under the same experimental conditions).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10859, 2013.