

Interactive comment on “Effect of chemical structure on secondary organic aerosol formation from C₁₂ 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 #2 for their insights into the proposed chemistry and their constructive comments for improving the writing in this manuscript. Response to Referee #2 Comments

1. Page 2, line 8: Does “structures” refer to the two hydrocarbons with rings or only to the cyclic part of these two hydrocarbons.

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This is meant to refer to the two hydrocarbons with rings.

2. Page 2, line 10: “Product identifications reveal [that reactions forming PHAs] initiate SOA growth” These reactions presumably occur in the aerosol phase, so perhaps it would be good to change “initiate” to something like “are key to SOA growth to detectable size”. Otherwise, “initiate SOA growth” could be misread as “initiate SOA formation”.

We have rephrased this portion to read, “Product identifications reveal that particle-phase reactions involving peroxyhemiacetal formation from several multi-functional hydroperoxide species are key components of initial SOA growth in all four systems.”

3. Page 4, line 20: “ μm ” should be “ μm^3 ”

Thank you for catching this typo. The text has been revised.

4. Page 5, line 1. It is interesting the RH grew to 20% in one experiment. Is this due to elimination of water in DHF formation?

This rise in RH is not timed with any chemical development in the gas-phase indicating so, rather it is actually an unintended artifact in which reactor air became depleted due to a leak so the RH crept up towards the end of the experiment.

5. Section 2.2 The Paulot 2009 paper states that ketones and aldehydes not detectable with CF₃O- CIMS. This should be stated explicitly here or page 13, line 25. We have added this explicitly in Section 2.2, p. 10863, line 18, “The CIMS cannot detect ketones and aldehydes in this mode unless a molecule is additionally-functionalized with hydroperoxy or sufficient acidic groups (e.g. –OH, –(O)OH) that it is sensitive to.” What blind spots result from this failure?

It would be ideal to have a direct aldehyde measurement in these systems, though it is inherently difficult in these systems to track distinct signals from the various C1-C12 aldehydes that can be produced. Hence, we have to rely on the photochemical simulations presented in Yee et al., 2012 for n-dodecane to aid in testing the pro-

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posed mechanism and the validity of using the co-product acid tracers as indicators of aldehyde presence in these alkane systems. We also focus on the later generation multi-functional species that provide plausibility for the proposed mechanisms. The second-generation CARB (ketone) was monitored using the positive mode operation of the CIMS since the CF₃O- CIMS is not sensitive to ketones. In the specific tridecanal injection experiment mentioned, the GC-FID was used to monitor the tridecanal levels and is described in a recent publication (Shiraiwa et al., 2013).

What uncertainties result in assigning ion peaks in AMS as a result?

The AMS ions generated from the portion of a PHA molecule that is derived from a various length C1-C12 aldehyde in these systems will not be unique and certainly provides a challenge for certifying that aldehyde is present in the particle phase. Hence, we rely on the larger m/z AMS ions that retain “more” of the molecule and can be reasonably explained using known EI fragmentation pathways and those established with by testing model compounds in the AMS. For example, Craven et al., 2012 confirmed from testing particle-phase C18 hydroperoxide in the AMS that the resulting ions of [M-33]⁺, resulting from loss of the hydroperoxy group, is a reasonable fragmentation pathway for a hydroperoxide.

6. Page 7, line 21. What is the basis for reporting that more than 90% of ROO react with HOO? (This could be part of the Supporting Information).

We have addressed this as part of our response to Referee #1, Comment 15, by adding additional text describing the application of the photochemical simulations performed in Yee et al., 2012 to arrive at this calculation.

7. Page 8, lines 6-8. Regarding the formation of OHCARBOOH: In addition to the pathway indicated here, OHCARBOOH could also form by at least one channel not shown. That is, if the CARB formed in Channel 1 loses a hydrogen atom from carbon separated by 3 or more methylene groups from the carbonyl carbon. I would think this more probable than α -CARBROOH along channel 1a if not also more probable

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than the CARB formed in Channel 1 being transformed to the CARBROOH formed in Channel 2.

We appreciate the referee's commentary and suggestions for the mechanism we present, though we are unclear on the suggested pathway. For this particular pathway, how does the referee propose that a hydrogen atom is lost from a carbon separated 3 or more methylene groups from the carbonyl carbon? Is this due to H-abstraction via reaction with OH? If so, this is implied by the conversion of CARB to CARBROOH along Channel 1 and Channel 2. We definitely acknowledge that the hydroperoxy group in CARBROOH can be located at another carbon alpha to (Channel 1), beta to (Channel 2), or on a carbon greater than 2 methylene groups away from the carbonyl carbon. Channel 1 is highlighted to show how the unique alpha position of the hydroperoxy group to the ketone in CARBROOH results in an important aldehyde and acid-forming channel. Channel 2 is highlighted to show the more likely placement of the hydroperoxy group at least two carbons away from the ketone containing carbon. If the particular beta-placement of this hydroperoxy group is confusing, we have added a sentence to the text to clarify that additional isomers would exist with other numbers of methylene carbons separating the ketone and hydroperoxy containing carbons. We have added the text following p. 10866, line 3, “The formation of the α -CARBROOH is expected to be minor, as several other isomers would result with the hydroperoxy group located at any of several other possible positions along the carbon chain. It could be located beta to the ketone containing carbon as shown in Channel 2 or at positions greater than 2 methylene carbons away (not explicitly shown).” As to the formation of OHCARBROOH, we are not clear how the proposed hydrogen loss can ultimately result in the gain of both a hydroperoxy and hydroxy group to the CARB molecule without additional radical (RO₂ + HO₂) reactions or additional steps of photolysis/generation of an alkoxy radical to get the hydroxyl group.

8. Page 8, line 13. The authors assume that ROO + HOO reactions form exclusively ROOH + O₂. However, they must be aware that there is evidence for a minor channel

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forming RO + OH + O₂ for some systems. The effect of this channel is identical to the mechanism discussed here (ROOH photolysis) except for the timing.

Yes, we are aware of this minor channel as it has been employed in the proposed mechanism for the fate of the acylperoxy radical generated from the decomposition scheme in Channel 1a. Simple acylperoxy radicals were observed to participate in this minor RO₂ + HO₂ channel (Hasson et al., 2004). We agree that the effect of the minor RO₂ + HO₂ channel is the same as ROOH photolysis (i.e. RO is generated), and we pondered this when proposing the chemical mechanism. However, we have not found definitive gas-phase evidence in the current measurements or literature evidence (e.g. Orlando and Tyndall, 2012 and references therein) that would suggest that simple alkyl peroxy radicals also undergo the minor RO₂ + HO₂ → RO + OH + O₂ channel.

9. Page 10, line 8. It would be good to provide plots of total reacted hydrocarbon (and HOOH!) versus time as Supporting Information.

We have added this to a supporting information section.

10. Page 10, line 15-16. "The OH concentration is inferred from the initial hydrocarbon decay. . . The OH concentrations. . . is constant" It is not clear to me how one obtains the OH concentration at long times from the initial [rate] of hydrocarbon decay. Also, does photolysis of hydroperoxides produce significant concentrations of OH?

The authors acknowledge the inherent confusion with these statements and have clarified by adjusting this text to read, "The OH concentration is inferred from the parent hydrocarbon decay using the known reaction rate coefficient with OH." The source of confusion may be that we originally refer to the parent hydrocarbon as the "initial hydrocarbon", and we do not mean to say that the OH concentration for the duration of the experiment is inferred from an "initial rate" of hydrocarbon decay. The OH concentration is calculated using the time trace of the parent hydrocarbon. As it decays over time, knowing its concentration and its reaction rate constant with OH (k_{OH}), we calculate the OH concentration at all times during the experiment. Based on the experimental

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setup (4ppmv H₂O₂, the chamber lighting conditions, and the starting concentration of initial organic), the OH concentration is approximately constant (~ 2 x 10⁶ molec cm⁻³) over the entire duration of the experiment. This is also found using similar photochemical simulations as performed for the case of n-dodecane in Yee et al., 2012, also showing that hydroperoxide photolysis does not produce a significant concentration of OH.

11. Page 11, line 5 "similar trends" should be something like "similar trends across systems"

This change has been incorporated into the text.

12. Page 11, line 16 "experimental design" Does this refer to the present paper or Yee et al?

This refers to the experimental design employed in the present paper, as Yee et al., 2012 covered only n-dodecane. Due to the recommendation of Referee #1, Comment 18, this paragraph p. 10869, lines 8-22, has been removed from the manuscript.

13. Page 11, lines 19-22. Unpack this sentence for those unfamiliar with structure effects on rate constants for fragmentation of alkoxy radicals. Note, fragmentation and decomposition are used here to refer to the what is more generally called the "β C-C scission" reaction. For all alkoxy radicals from cyclododecane and alkoxy radicals on the ring of hexylcyclohexane, "β C-C scission" does not decompose the structure into smaller fragments.

Yes, we appreciate this suggestion for using more precise language to describe this chemistry. While we have removed the paragraph containing these lines, p. 10869, lines 8-22, according to the recommendation of Referee #1, Comment 18, we have incorporated this nuance in description of hexylcyclohexane chemistry as in Referee #1, Comment 9.

14. Page 12, line 9. The mass resolution would be good to state, either here or in

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the experimental section, with reference to earlier papers showing how peaks at one nominal mass spanning two exact masses are decomposed into exact intensities for the exact masses.

The text describing the AMS has been modified, p. 10864, lines 1-6, to include the mass resolution information, "An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (DeCarlo et al., 2006), hereafter referred to as the AMS, was operated at 1 min resolution switching between the lower resolution (up to ~2100 at m/z 200), higher sensitivity "V-mode", and the high-resolution (up to ~4300 at m/z 200), lower sensitivity "W-mode". This section also includes information on the analysis tools and associated references used for exact mass ion fitting (p. 10864, lines 6-12).

15. Page 12, line 10: "A few observations of the spectra are noted here" is confusing. "observations" → "comments" and "noted" → "made"

Thank you for this constructive text change. Though, in light of suggestions from Referee #1, Comment 3, we have deleted this sentence as we have filled in the section with additional details (more than "a few observations") describing the mass spectra.

16. Page 12, line 13 "realized" is probably meant to be "rationalized"

This line has been revised in accordance with our response to Referee #1, Comment 19. The line 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."

17. Page 12, line 14 "unique 'chaos'" might be better expressed as "enhanced chaos"

This comment has been addressed in Referee #1, Comment 19 and Referee #2, Comment 16 above.

18. Page 12, line 17-18 "fragments decreasing in the particle phase" should be "fragments decreasing in AMS signals from the particle phase"

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This revision has been made.

19. Page 12, line 18 "Several ions... have been proposed" References?

We have included the references Yee et al., 2012 and Craven et al., 2012.

20. Page 12, line 19-20 "more molecular information" Than what?

We have modified this line to read, "Several ions in the >150 amu range have been proposed as tracers for particle-phase chemistry (Yee et al., 2012; Craven et al., 2012), as, though low in signal, they retain more molecular information than lower mass ions that are only small fragments of the original molecule."

21. Page 12 The sentence that runs from lines 11-13 seems to duplicate the meaning of the first sentence in the paragraph.

We believe the referee may be referring to the sentence on page 13 (p. 10871) lines 11-13, and as such, we have modified this sentence to read, "However, the distinct pattern of similarly trending R+ ions and those at m/z 32amu higher suggests that this mass difference may result from the peroxide O-O bond of a peroxyhemiacetal."

22. Page 14 line 3. "organic" Here this should be "SOA" or "organic aerosol" but in at least one place "organic" is used to refer the mass of SOA. Also, this sentence seems relevant to Figure 9, which is not discussed for sentences.

With this suggestion and that in Referee #1, Comment 25, we have adjusted this and additional references to the SOA from "organic" to "organic aerosol".

23. Page 14 lines 23-26. The molecular formulas of the ions will differ between the cyclic and acyclic hydrocarbons. Specify which are being referred to here.

We have included this specification to further clarify in this paragraph discussing the ions within the acyclic systems. The sentence beginning at the end of p. 10872, line 22 now reads, "Generally for these acyclic systems, the CARBROOH is initially incorporated..."

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24. Page 15 lines 20-21. It is not clear to me why hexylcyclohexane could undergo another (two, one more than the other hydrocarbons) 1,4 cyclization due to its C6 branch. Do you mean making a second ring structure (hydrofuran + cyclohexane)?

Yes, this is what we are referring to. Thank you for helping us make this language more accurate. We have adjusted these lines to read, "The proposed reaction is consistent with the hexylcyclohexane structure undergoing another 1,4-cyclization along its C6 branch to form a bicyclic structure (cyclohexyl and cyclic hemiacetal). The cyclic hemiacetal portion of the molecule can then dehydrate to form a dihydrofuran-like structure of higher volatility."

25. Page 17 lines 25-27. It is not clear to me why the cyclododecane would be less apt to form PHAs. The aldehyde resulting from cyclododecane would not be cyclic, although the hydroperoxide would be.

Yes, this is an issue for further investigation into stereochemistry. We hypothesize that depending on the particular conformation of the C12 ring and the location of the hydroperoxide group, it may be less accessible for intermolecular reaction with the aldehyde (which we agree would be non-cyclic in this system). It may also be that with additional functionalization (e.g. a carbonyl hydroperoxide that maintains the C12 ring) that intramolecular reaction between the carbonyl group and the hydroperoxy group is more easily facilitated. We have evidence for additional degrees of unsaturation being achieved in this system compared to the other alkanes (perhaps a result of a bicyclic or multi-ring structure being produced via intramolecular reactions), but we leave definitive conclusions on this topic for further study. For the present manuscript, we have added text to this sentence as follows, "Since PHA formation relies on the intermolecular reaction of two condensing species, aldehyde and a hydroperoxide, it may be that the cyclic structure of the cyclododecane hydroperoxide is less apt for this reaction depending on the hydroperoxy group accessibility on the C12 ring. It may also be possible that there are competing intramolecular reactions of more highly-functionalized hydroperoxides within the C12 ring that are more easily facilitated."

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26. Page 20, lines 26-29. These sentences do not make logical sense as written.

We have revised these sentences to read, "Ideally, standards of different structure, but analogous functionality would be available for generating mass spectral standards that can be used to better interpret the mass spectra in this region. Ionization schemes need to be better elucidated to see if observed ions can be explained by particle-phase chemistry that involves species of cyclic structure and/or those undergoing cyclization followed by dehydration."

27. Figure 1: Channel 1b is not discussed in the text. Channel 3: I do not see how the OHROOH will react with OH to form the OHCARB shown. See the schemes at right for more likely reactions.

Thank you for pointing this out. We realize that the source of confusion here is the explicit depiction of the OHCARB structure which correctly places the ketone and hydroxyl groups for the photolysis reaction scheme of the OHROOH, but for reaction of OHROOH with OH, the placement of the surrounding alkyl groups (including R1 and R2) are not correct. We mean for the OHCARB to represent a general structure and we acknowledge there are several other isomers, all of which cannot be included in the mechanism for visual clarity (including the suggested scheme for generating another conformer of the OHROOH from the OHCARB). To allow for these possibilities, we have modified text describing the mechanism starting p. 10866, line 18, "This results in the formation of a 1,4-hydroxy hydroperoxide (OHROOH) which has sufficiently low volatility to partition into the particle-phase or undergo reaction with OH or photolyze. Reaction with OH can result in the formation of a carbonyl hydroperoxide (pathway not shown) or a hydroxy carbonyl. The particular carbonyl hydroperoxide and hydroxy carbonyl generated would be different isomers of the generalized CARBROOH and OHCARB shown in the mechanism."

28. Figure 2. Most of the ions indicate as being formed from the Isomerization reactions are also formed in PHA formation. Does that mean most of the ions on the left-hand

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side should also be in dashed boxes? Because PHA ionization forms two ions 32 amu apart, this, by itself, does not affect the interpretation of PHA formation. It might be possible to infer something about the occurrence of Isomerization from the relative peak heights from pairs of R^+ and ROO^+ .

Yes, there is overlap in the ions between those potentially representative of isomerization reactions and those of PHA formation. We initially elected to not place dashed boxes around these structures as we could not confirm the relative contribution of signal at a single ion to a structure formed via isomerization vs. that in PHA formation. We believe that there is greater evidence in some systems (e.g. the acyclic compounds) for favored PHA formation because of the similar time trends suggesting a similar source for the two ions. Visually marking the isomerization-derived structures might imply that this competitive pathway is generalized to all systems, though we believe it to be more applicable for the cyclic systems. We also did initial comparisons of the relative peak heights from pairs of R^+ and ROO^+ ions to try to infer contributions of isomerization and PHA formation, however there are in some cases R^+ and ROO^+ ions that can be explained by structures derived in both isomerization and PHA schemes. We also cannot rely on peak height to be an absolute quantitative metric, as structural biases in ionization schemes and ionization efficiency in the instrument may exist.

29. Figure 8. The first sentence of the caption is worded awkwardly- the labels (a)-(d) would be better placed at the end of the sentence. The color scheme in the legend of panels (c) and (d) do not match those in the panels, themselves. In (d) the straight lines in the data for CARBROOH and C6CARBACID suggest a gap in the actual data, similar to but longer than the gap shown for the AMS ions. If my analysis is correct, please explicitly show the gap for CARBROOH and C6CARBACID or mention it in the Figure caption.

This sentence in the caption has been revised according to the referee's suggestion. The figure has also been corrected to modify the mismatch in color scheme of the legends and the data, also according to Referee #1, Comment 28. Yes, there is a gap

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in CIMS data in (d) and a shorter gap in the AMS ions. We have corrected the figure to explicitly show the gap.

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