This manuscript contains a lot of interesting data on an important topic very relevant to ACP. The quantity of data and complexity of the systems presents writing and analysis challenges for the authors that they did not meet in this version of the manuscript, but I expect it to ultimately be acceptable.

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

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".

Page 4, line 20: "μm" should be "μm^3"

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?

Section 2.2 The Paulot 2009 paper states that ketones and aldehydes not detectable with CF_3O^- CIMS. This should be stated explicitly here or page 13, line 25.

What blind spots result from this failure?

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

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).

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

Page 8, line 13. The authors assume that ROO+ HOO reactions form exclusively ROOH + O_2. However, they must be aware that there is evidence for a minor channel forming RO + OH + O_2 for some systems. The effect of this channel is identical to the mechanism discussed here (ROOH photolysis) except for the timing.

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

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?

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

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

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.

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

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

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

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

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

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

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

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

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.

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.

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)?

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.

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

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.

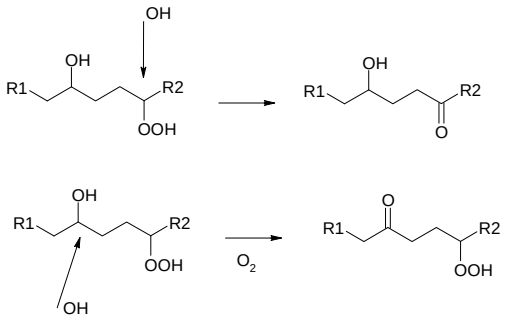

Figure 2. Most of the ions indicate as being formed from the Isomerization reactions are also formed in PHA formation. Does that mean most of the ions on the left-hand side should also be in dashed boxes? Because PHA ionization forms two ions 32 amu apart, this, by itself, does not affect the interpretation 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+.

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.