General Notes

During the revision, it was discovered that the calculation factor used to measure the initial concentration of C10 was wrong. This factor has been corrected and the initial concentrations for C10 have been updated. To improve the model prediction, the coefficient of reaction SR1 (Table S4), and analogous reactions for C9, C10, C11, have been updated in revised manuscript.

Response to Reviewer 1

Thank you for reviewing this paper. We hope we have appropriately addressed all of your concerns below.

1. *This work is a development of a previous work by some of the same workers (Zhou et al 2019), and it is not always immediately apparent what is new work and what is a restatement of that previous work. The text should clarify the distinction. The restated sections should be condensed and appropriate reference should be made to the prior work.*

   Where possible, the model description has been condensed. In other instances, appropriate references to previous work has been added early in each section to make this more clear.

2. *This study should add at least one sensitivity test that attempts to model the morning spike seen in the chamber observations, to support the authors' assertion about its origin.*

   Unfortunately, the model is unable to capture this phenomenon and thus, a sensitivity test to model this spike is not possible. A reference to a previous work which also shows the same morning spike for another precursor has been added as further support.

3. *Line 300: discussion of Figure 3. I agree that C9D, C10D and C11C show good model-data comparisons. Comparisons C9C and C10B are not so good, and look more like comparisons C11A and C11B, which are said to be poor. The text should be clearer about this distinction. This comment des not detract from the paper's overall conclusions.*

   These simulations have been updated with the new rate constant as noted previously, which has improved the model predictions for C9C, and C10B.

4. *Section S4, Table S2: It is unfortunate that the accommodation coefficient alpha_w,i, and the polarizability alpha_i have such similar symbols, and that these could be confused with the mass-based stoichiometric coefficient alpha_i introduced in section 3.2. It might be appropriate to change one of these symbols, or at least to explicitly acknowledge the possibility for confusion.*

   This similarity has been explicitly addressed within the text. Line 259: "Note that this α_i used to represent polarizability is different from the α_i used to represent the mass-based stoichiometric coefficient introduced in section 3.2."

5. *Line 131-132, 197, 215 etc: This reviewer finds the abbreviations "or" and "in" confusing in the text because they can be mistaken for ordinary words. Please spell out the words "organic" & "inorganic" unless the abbreviations are used in combination with other symbols? Or, at a minimum, give them bold italic font to differentiate them from normal text.*

This has been addressed by replacing with "or" and "in" with "org" and "inorg", respectively.

6. *Line 142: Pye 2019 and Xavier 2019 are not appropriate references for the identification of auto-oxidation reactions: they are modeling papers. It would be better to cite an early lab study (e.g. Sahetchian et al, Combust. Flame 1991; Crounse & Nielsen. J. Phys. Chem. Lett., 2013)*

The more appropriate citations have been added. The Pye 2019 and Xavier 2019 papers have been acknowledged as modeling papers.

7. *Tables S4, S5: please provide a key to or explanation of the chemical compound code names?*

The key for explanation for the chemical names are found immediately following table S4 (previously table S5) at the end of section S10.

8. *Line 158: Please briefly discuss the conceptual movement of the reaction products between reactivity levels in your 51-box matrix. What does this represent, in a chemical-physical sense? Are there any constraints on the sum of all the dynamic alpha_sub_i values?*

This discussion has been added. Line 155 : "As gas products originating from the precursor HC are atmospherically aged, they become more oxidized, which leads to the addition of functional groups. This atmospheric aging can augment the product distribution, forming more reactive, less volatile, or photolytic products." The sum of the alpha values represent the total amount of oxidation products produced (excluding radicals and species with vapor pressures higher than lumping group 8 in the matrix) in a unit mass per unit mass of precursor consumed. Generally the sum of alpha values is near 1. It can be greater than 1 as the attachment of functional groups can increase the mass of the products.

9. *The following works are cited in the text but are missing from the reference lists: Line 198: Pankow (1994); Line 272: Yap (2011); SI: Roldin (2019)*

These works have been added to the citations.

10. *Line 45: please correct the reference (Robinson et al., 2007)*

This reference has been corrected.

11. *Lines 46-73: Please mention the names of the models used in Hodzic (2010), Cappa (2013), Zhang & Seinfeld (2013)*

The model names have been added to the text

12. *Line 50: Note that, since Lee-Taylor et al used the larger linear alkanes as surrogates for all larger species, the fact that the majority of SOA precursors in their model were linear alkanes is a logical outcome of those SOA species having larger carbon numbers.*

This has been noted in the text.

13. *Lines 61-65: Perhaps "neglect" would be kinder than "fail to consider"? The previous authors are likely well aware of the limitations of their approaches, and (at least in one case) mention those limitations explicitly.*

    The language has been updated. This now reads: "Lee-Taylor et al. notes that their reasonable agreement for SOA predictions with field data is not necessarily realistic as they do not include alternative pathways for SOA formation such as particle-phase reactions"

14. *Line 86: "... the typical ozone mechanisms.." This seems vague. Did this study use several ozone mechanisms or just one?*
    Only one ozone mechanism was used. This now reads: "In order to increase the feasibility of the model, UNIPAR was also integrated with the carbon bond mechanism (Emery et al., 2015)"

15. *Line 133: "OMAR" needs subscripts.*

    Subscripts have been added

16. *Lines 272-274: This sentence is confusing. Please rearrange it?*

    This sentence has been rearranged. It now reads: "The value of $K_{w,i}$ is used along with the $k_{on,i}$ to predict intermediate product wall loss using an analytical equation from the study by Han and Jang (2020) as follows"

17. *Line 305: Do you mean "from" instead of "form"?*

    Yes. This has been corrected.

18. *Line 321, 323: Do you mean figure 5 instead of fig 6?*

    Yes. This has been corrected.

19. *Line 322: Do you mean figure 4 instead of fig 5?*

    Yes. This has been corrected.

20. *Line 341: why is it notable that previous experiments used H2O2 as a low-NOx OH source? What are the implications? Please discuss.*

    The main difference is that their low NO_x conditions had much lower concentrations of NO_x compared to our experiments. This sentence has been removed and the respective low NO_x concentrations for each of the other studies has been noted within the text.

    Line 339: "Zhang and Seinfeld (2013) found that SOA yields for Dodecane (C12) were higher in lower NOx conditions (<6 ppb). Cappa et al. (2013) found significant differences in SOA yields between high and low NOx conditions after 10 hours of oxidation, with higher yields for the low NOx condition (<1 ppb)."

21. *Line 357: please specify whether you mean the relative or absolute contribution of OMAR?*

The relative contribution. This has been specified within the text.

22. *Line 370: do you mean Figure S6 instead of Fig 5?*

Yes. This figure number has been corrected (Now figure S8 instead of S6).

23. *Line 625, 655: "OCEC is missing its "/"*

This has been corrected.

Response to Reviewer 2

Thank you for reviewing this paper. We hope we have appropriately addressed all of your concerns below.

1. *The use of an outdoor chamber to conduct systematic tests of NOx and particle seed type on SOA yields was a flaw in the experiment design. The day-to-day variability in conditions, namely temperature and light, clouded the very impact of these variables the authors sought to test on SOA yields.*

While we agree that the day-to-day variability can cause some uncertainty in the experimental data, the use of an outdoor chamber can allow for the testing of the model in ambient-like conditions. Temperature and light are both recorded and are input to the model. Conclusions regarding NO_x and seed impact are drawn from model sensitivity testing rather than the experimental data. The model's ability to predict the experimental data well lends credibility to the conclusions derived from the sensitivity tests.

2. *The explanation of the observed morning SOA burst in some of the experiments that the model fails to capture was seriously lacking*

A reference to a previous paper which also observed the same phenomenon with another precursor has been added as support to the explanation. Line 329: "A similar trend of rapid SOA formation early in the morning has been observed previously in chamber studies for highly concentrated d-limonene (Yu et al., 2021), which can be rapidly oxidized and form low volatility products."

3. *The discussion on the effect of NOx on autoxidation, the main driver of SOA formation they report, is thin. What is the implemented rate of autoxidation for each alkane precursor? A sensitivity test of the rate of autoxidation on SOA yield is reported on line 370 to be shown in Figure 5, which does not show that at all (only the sensitivity results of wall loss rates). What are the levels of HOx and NOx in the chamber for the duration of each experiment? Both would undoubtedly affect RO2 fates and lifetimes, neither of which is discussed in the section of NOx impact on autoxidation.*

The implemented rates of autoxidation are the same of each of the precursors. Table S4 shows the reactions and rates present in the autoxidation mechanism for C12. Mechanisms added for C9, C10, and C11 have the analogous reactions for those respective compounds with the same rate

constants. This reference to Figure 5 was inappropriate and has been corrected (Now Fig. S8). Two figures have been added to the SI. The first figure (Fig. S4), which replaced the table in section S7, shows the fraction of autoxidation mass created at several different NO_x values and two different carbon numbers using data from the NO_x sensitivity tests. The second figure (Fig. S5) displays the time profiles of HO_2 and NO_x compared to Integrated reaction rates of selected RO_2 species. Fig. S5 shows that the autoxidation reaction of the respective RO_2 species were insignificant to reactions with NO in both the high and low NO_x conditions. Thus, the addition of autoxidation reactions did not have a significant impact on RO_2 fates. Additionally, the autoxidation reaction rate of the RO_2 species was somewhat increased in the low NO_x condition compared to the high NO_x condition. This discussion has been added to section 4.4 (Line 343)

4. *Figure 6 shows that SOA yields increase with decreasing NOx. However, Figure 2 shows that the model underestimates SOA loading at high NOx and overestimates at low Nox. This, as a result, possibly undercuts the key model results of SOA yield vs Nox shown in Figure 6. Proper explanation of glaring caveats is not discussed.*

   As explained in the "General Notes" section, the initial HC concentrations of the C10 simulations were wrong and have now been updated to the correct values. In addition, the change in the rate constant has improved predictions.

5. *Authors go on to attribute the decrease in SOA yield with Nox to the partitioning of non-autox products, but that explanation is unclear and buried in a Table in the SI. A clearer demonstration with a graphic is needed.*

   Fig S4 has been added to improve the explanation.

6. *I would have like to have seen optimization of model parameters (volatility, reactivity, and/or aging) using the suite of observations made. Or at the very least, show Figures 6 and 7 (which are the key figures) but with observations shown as well. This would ground the model and allow the authors to make conclusions that currently seem like extreme extrapolations. For instance, the levels of SOA in the chamber are beyond atmospherically relevant. The high loadings most likely affected the relative contribution of gas partitioning versus heterogeneous chemistry to SOA loading. Additionally, the authors conclude from this modeling exercise that straight chain alkanes are important for urban SOA - without showing much evidence. This is not backed up by the results shown.*

   Unfortunately, the addition of observations to Figures 6 and 7 would not be appropriate as those figures are simulated under specific conditions (specific sunlight profile, constant temperature and RH) and relatively low concentrations compared to the outdoor chamber experiments. A sentence has been added to the paper which caveats our conclusions regarding OM_{AR} fraction in relation to particle loadings. Line 359 : "Notably, the levels of SOA loading found in the chamber experiments are much greater than those observed in the ambient environment. Lower SOA loadings may change the relative distribution of OM_P and OM_{AR}." An additional reference to a study regarding origins of SOA in industrial cities has been added to support our conclusion that long-chain alkanes are important in urban environments (Line 406).

7. *Line 153: Why 51 species? Where is this from?*

6 levels of volatility and 8 levels of reactivity = 48 species + 3 species lumped explicitly = 51 species

8. *Line 24: symbol in front of C15 did not render*

   This issue has been corrected

9. *Line 125: multiplication symbol did not render properly*
   This issue has been corrected.

10. *Line 128: the "i" in alpha_i needs subscript*

    This has been corrected.

11. *Figure S1. Is that starting from an alkoxy radical? Initial compound is blurry. How does the hydroperoxy group convert to a carbonyl? Please explain in the caption.*

    Image has been updated. Figure explanation has been added.

12. *Instead of "or" for organic phase, "in" for inorganic, consider using "org" and "inorg" for clarity*

    This update has been made.

13. *Figure 2. Consider not using black and grey for MCM and MCM+autox. Something more different.*

    Grey line has been replaced with dashed, black line

14. *Line 321. Should cite Fig 5 not Fig 6?*

    This has been corrected.