Response to the Referee2 (Manuscript Ref. NO.: acp-2022-327)

We would like to thank the reviewer for their time, and useful comments. Their comments are repeated below, followed by our response.

Comment on "Modeling Diurnal Variation of SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons" Anonymous Referee #2

General Comments

Han et al present a series of experiments conducted in a rooftop chamber examining the oxidation of three biogenic hydrocarbons (isoprene, a-pinene, b-caryophyllene) during both daytime and nighttime conditions. They examine the role of four different oxidants (OH, O_3, NO_3, $O(^3P)$) and a series of environmental conditions, including hydrocarbon to NOx levels, relative humidity, temperature, and particle seed composition.

The major emphasis of the paper is on a gas-particle partitioning model, UNIPAR, that is first fit to the experimental data and then used to make predictions about the variation in SOA yields with different parameters. Major conclusions are that there is a strong positive NO_x dependence to SOA yield during nighttime conditions and a weaker negative NO_x dependence during daytime, and that there is a modest negative temperature dependence.

Overall, the paper is in line with other studies of these systems in the recent literature, but offers some new insights based on the explicit gas-particle partitioning model. Some aspects of the presentation should be clarified prior to publication, however, as outlined in the more specific comments below.

Specific Comments:

1. Line 43: Give the total SOA budget for reference. Also add the caveat in this line that these are models of global SOA, and that the cited work is just one of several estimates of this quantity.

   Response: To clarify this point, global SOA production rates and additional citation were added in the revised manuscript.

   L43: "Furthermore, the SOA from the oxidation of biogenic HCs is a considerable source of a global budget of SOA (Kelly et al., 2018; Hodzic et al., 2016;Khan et al., 2017). For example, Kelly et al. (2018) reported that the more than 50% of the annual global SOA production rates (48.5-74.0 Tg SOA yr^{-1}) is from monoterpenes (19.9 Tg SOA yr^{-1}) and isoprene (4-19.6 Tg SOA yr^{-1})."

2. Line 54: Not clear what is meant by a sustainable NO_3 radical – perhaps this refers to production of NO_3 radicals being sustained?

   Response: This sentence refers to the production of NO_3 radicals being sustained as referee commented. The manuscript has been revised.

   L51: "The O_3 generated in daytime is not rapidly consumed at nighttime and can react with NO_2 to form a NO_3 radical that can also be sustain in nighttime."

3. Line 58: There are more recent references to the organic nitrate yield from NO_3 + isoprene. See for example:

Brownwood, B., A. Turdziladze, T. Hohaus, R. Wu, T.F. Mentel, P.T.M. Carlsson, E. Tsiligiannis, M. Hallquist, S. Andres, L. Hantschke, D. Reimer, F. Rohrer, R. Tillmann, B. Winter, J. Liebmann, S.S. Brown, A. Kiendler-Scharr, A. Novelli, H. Fuchs, and J.L. Fry, Gas-Particle Partitioning and SOA Yields of Organonitrate Products from NO3-Initiated Oxidation of Isoprene under Varied Chemical Regimes. ACS Earth and Space Chemistry, 2021. 5(4): p. 785-800.

Perring, A.E., A. Wisthaler, M. Graus, P.J. Wooldridge, A.L. Lockwood, L.H. Mielke, P.B. Shepson, A. Hansel, and R.C. Cohen, A product study of the isoprene+NO3 reaction. Atmos. Chem. Phys., 2009. 9(1): p. 4945-4946.

Response: Those works were added to the revised manuscript.

“For example, the oxidation of isoprene with the NO3 radical can rapidly produce nitrate containing products, resulting the increase in the SOA formation, up to 80% of gas products from the isoprene-NO3 oxidation (Kwok et al., 1996; Barnes et al., 1990;Perring et al., 2009;Brownwood et al., 2021).”

4. Line 97: The definitions of high and low NOx seem arbitrary and as though they might both be high NOx. Was the fate of RO_2 radicals considered in defining the high and low NOx conditions – i.e., the rate of RO_2 + NO compared to other RO_2 losses?

   Response: The high NO_x and low NO_x condition has been defined based on the HC/NO_x ratio as HC/NO_x < 5 ppbC/ppb and HC/NO_x > 5 ppbC/ppb, respectively (in Sect. 2). The fate of RO_2 radicals is covered by the explicit gas mechanism and the resulting stoichiometric coefficient arrays, which are function of HC/NO_x ratios and aging (Sect. 3.1).

5. Line 145: Inclusion of $O(^3P)$ is relatively unusual and not normally important in the lower atmosphere (also a conclusion of this study). What motivated the inclusion of this oxidant rather than other minor oxidants such as chlorine radicals or Criegee intermediates?

   Response: To increase the simplicity and the applicability of UNIPAR model in regional scale, SAPRC07TC has been integrated with the UNIPAR model. In the SAPRC07TC, the oxidation processes of biogenic HCs were treated with 4 different oxidants (i.e., O_3, OH radicals, $O(^3P)$, and NO_3 radicals). Thus, four different oxidation paths with those oxidants were considered in this study. To make it clear, a sentence below has been added in L140.

   L140: “Furthermore, the oxidation process of biogenic HCs by $O(^3P)$ (Paulson et al., 1992;Alvarado et al., 1998) was included to synchronize with the oxidation path in the current regional model.”

6. Line 214: At what rate was N_2O_5 hydrolysis included, and how efficiently does this compete with gas phase NO_3 reactions?

   Response: The hydrolysis rate constant of N_2O_5 was set as 10^{-2} s^{-1}, by simulating the chamber generated SOA data. The hydrolysis rate constant of N_2O_5 has been reported as in a range of 10^{-7}~10^{0} s^{-1} (Wagner et al., 2013;Wood et al., 2005). The sentence below has been added to the revised manuscript.

L207: “The hydrolysis rate constant of N_2O_5 has been reported as in a range of 10^{-7}~10^{0} s^{-1} (Wagner et al., 2013;Wood et al., 2005) and thus, the hydrolysis rate constant of N_2O_5 was set to 10^{-2} s^{-1}in this study.”

7. Figure 2: The abbreviations NS, SA, wAS, etc. are not defined in the figure or the caption and not easy to find in the text. Clarify the meaning of these abbreviations in the figure.

   Response: To make it clear, the definitions of seed condition in the chamber has been added in the figure captions.

   “NS, SA, wAS, and dAS indicate non-seeded, sulfuric acid seeded, wet ammonium sulfate seeded, and dry ammonium sulfate seeded experiment, respectively.**”**

8. Line 230: Conclusion not clear in this sentence. Is this stating that in the presence of aerosol there is no NO_3 reaction with the biogenic hydrocarbons?

   Response: There was an insignificant seed effect in nocturnal SOA formation in the presence of NO_x due to the removal of NO_3 radical via heterogenous hydrolysis of the N_2O_5. However, a small increase in SOA mass was shown in several experiments and it could be a result of the aqueous phase reaction of the ozonolysis products. To clarify this point, the manuscript has been revised as below:

   L222: “However, the impact of inorganic seed on nocturnal SOA formation can be insignificant in the presence of NO_x because N_2O_5 undergoes heterogeneous hydrolysis reaction on the surface of wet aerosol particles to form nitric acid (HNO3) (Brown et al., 2006;Hu and Abbatt, 1997;Galib and Limmer, 2021). The small increase in SOA formation by inorganic seed is mainly caused by the aqueous phase reaction of the ozonolysis products.”

9. Line 248: The biogenic mixing ratios used in the simulations are unrealistically large does this also bias the SOA yields high?

   Response: Possibly, yes. To see the sensitivity of the SOA model prediction associated with the environmental parameters, consumption of biogenic HC is needed to be high enough. Based on the referee’s comment, the sensitivity of the biogenic SOA formation to the initial HC concentration has been tested and added to the SI section 5. A paragraph has been added in L352.

   “For the chamber study, concentrations of HC and NO_x are generally higher than those in ambient air due to the detection limit of analytical instruments. Additionally, the chamber-generated SOA data can be influenced by vapor-wall deposition and the particle-wall loss. Fig. S4 illustrates the influence of the initial concentration of biogenic HCs on SOA formation at a given NOx level (high NO_x condition). Regardless of initial HC concentrations, the sensitivity of SOA yields to different light conditions (day vs. night) or seed conditions (non-seed vs. wAHS) is consistent at a given biogenic hydrocarbon.”

10. Line 254: SOA yields from NO_3 said to be low during daytime, but Figure 4 shows them to be larger than OH? Is this correct? The description of isoprene SOA beginning in this line does not appear consistent with what appears in the figure.

Response: Figure 4 illustrates the potential SOA formation when the same amount of HC is consumed by each oxidation path. In the daytime, SOA yield is still high if the isoprene is consumed by NO_3 radical as seen in Fig. 4. However, the rapid photolysis of NO_3 radical can reduce the contribution of oxidation path through the biogenic HC + NO_3 radical. To clarify this point, the manuscript has been revised as below:

L237: "The atmospheric process of biogenic HCs is complex because of their multi-generation oxidations by the combination of various oxidation paths. To investigate the impact of product distributions of each oxidation path on SOA growth in day and night, SOA yields are simulated under the constrained oxidation path with a fixed amount of HC consumption as seen in Fig. 4."

L245: "For isoprene, the efficient pathways to form SOA are the NO_3-initiated oxidation (6-17%) and OH-initiated oxidation (3 - 4%) in both day and night at given conditions of Fig. 4."

11. Line 279: This paragraph contains a series of qualitative statements about the roles of different mechanistic pathways in forming SOA. Presumably, all of these could be quantified with the model and shown as a figure?

    Response: The UNIPAR model can quantify SOA formation at a given mechanism under the controlled environmental condition. Figure 4 was simulated SOA yields under the constrained oxidation path with a fixed amount of HC consumption. In order to provide better understanding of the manuscript to the reader, the section 4.2 was modified in the revised manuscript. The 1st paragraph of section 4.2 reads now,

    "The atmospheric process of biogenic HCs is complex because of their multi-generation oxidations by the combination of various oxidation paths. To investigate the impact of product distributions of each oxidation path on SOA growth in day and night, SOA yields are simulated under the constrained oxidation path with a fixed amount of HC consumption as seen in Fig. 4. SOA yields simulated under varying environmental conditions including two different NO_x levels ((a) high NO_x: HC/NO_x = 3 ppbC/ppb and (b) low NO_x: HC/NO_x = 10 ppbC/ppb) and three different seed conditions (no seed, wAS, and wet ammonium bisulfate (wAHS)). To simulate the impact of aerosol acidity, the SOA formation is simulated in the presence of AHS seed, which is often found in ambient air. The reported acidity of the ambient aerosol is in the range of pH:-1~5 (Pye et al., 2020). Overall, biogenic SOA formation from the $O(^3P)$ reaction path is negligible."

12. Line 362: What is the chemical composition of gasoline fuel? Presumably this is in the gas phase? Is the high mixing ratio used here realistic to ambient conditions?

    Response: US commercial gasoline fuel (octane number: 87) was used. Its composition has been reported previously (Han and Jang, 2022). Around 30% of gasoline fuel were aromatic compounds.

    Both α-pinene and gasoline fuel were introduced to the chamber in the form of gas (Section 2). Both α-pinene and gasoline concentrations were higher than those in ambient air. As discussed in the response to question 24 from reviewer 1, the concentrations of chamber experiments are limited by detection of instruments. For our chamber studies, gasoline total carbon concentrations were nearly 3000 ppbC and those of α-pinene were about 800 ppbC (80 ppb). In the urban aera, the emissions are dominated by anthropogenic sources.

13. Line 403: Suggest removing the reference to “government agency” and preferring instead to NOx control measures.

    Response: The manuscript has been revised based on this comment as below:

    “The NO_x emission from anthropogenic sources has gradually decreased, and it impacts the NO_3 concentrations.”

14. Line 415: The term “electrolytic” appears out of place here.

    Response: “electrolytic” has been removed from the revised manuscript.

References

Han, S., and Jang, M.: Prediction of secondary organic aerosol from the multiphase reaction of gasoline vapor by using volatility–reactivity base lumping, Atmospheric Chemistry and Physics, 22, 625-639, 2022.

Wagner, N., Riedel, T., Young, C. J., Bahreini, R., Brock, C. A., Dubé, W., Kim, S., Middlebrook, A., Öztürk, F., and Roberts, J.: N2O5 uptake coefficients and nocturnal NO2 removal rates determined from ambient wintertime measurements, Journal of Geophysical Research: Atmospheres, 118, 9331-9350, 2013.

Wood, E., Bertram, T., Wooldridge, P., and Cohen, R.: Measurements of N 2 O 5, NO 2, and O 3 east of the San Francisco Bay, Atmospheric Chemistry and Physics, 5, 483-491, 2005.