# Modeling Day and Nighttime SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons (Manuscript Ref#: acp-2022-327)

#### **Response to the Referees and editor**

We would like to thank the referees and editor for their time and thoughtful comments on this manuscript. Their comments are repeated below followed by our response to each comment.

#### **Comment from Anonymous referee #1**

The revised manuscript has improved a lot from the previous version, and merits publication in ACP.

However, before publication the authors should still address a few issues.

1. I recommend replacing the term "explicit mechanism" with "extended semi-explicit mechanism" and to detail the extension/changes/additions made to the mechanism in the manuscript (e.g., "using the semi-explicit Master-Chemical-Mechanisms extended by ... "). A real "explicit mechanism" would include all possible reactions and pathways (including minor channels) and thus result in millions (if not billions) of calculations.

**Response:** The word "explicit mechanism" has been replaced with "extended semi-explicit mechanism" in the revised manuscript.

2. Minor comment: in L240, rev. manuscript: "SOA yields simulated ...": This sentence is missing a verb. Maybe a final proof reading of the manuscript might be helpful. **Response:** This sentence has been modified in the revised manuscript.
"SOA yields are simulated under varying environmental conditions including two different NO<sub>x</sub> levels ((a) high NO<sub>x</sub>: HC/NO<sub>x</sub> = 3 ppbC/ppb and (b) low NO<sub>x</sub>: HC/NO<sub>x</sub> = 10 ppbC/ppb) and three different seed conditions (no seed, wAS, and wet ammonium bisulfate (wAHS))."

#### **Comment from Anonymous referee #3**

# **Overall Comment:**

This manuscript uses both chamber experiments and modeling to explore photochemical and nocturnal production of SOA from three different biogenic VOC precursors. The approach and questions asked are scientifically relevant to the readership of ACP. However, I have several concerns about the manuscript's readability, overstatement of some conclusions, and missing methodological details that should be addressed before publication.

# **General remarks:**

Understanding the mechanistic processes that contribute to SOA yields is an important question for the atmospheric chemistry community. The authors use a nice general approach of using chamber experiments to validate their model and then using their model to explore mechanistic details of the chemistry.

However, the results/discussion section is very hard to follow. As Referee 1 noted in their remarks, "some parts of the manuscript seem to be more a review paper than an original work." I think this sentiment still applies to the results/discussion section. The original conclusions of this work are deeply buried and hard to follow in this section. I recommend revision of this section to make the conclusions more easily identifiable to the reader. Moreover, many of the mechanistic conclusions stated in the paper are backed up only by previous literature, rather than a detailed analysis of the authors' modeling work. Including some process-level modeling results to support the stated conclusions would greatly improve the science presented (some specific examples of this are listed below as "specific comments").

**Response:** Please find the responses for the specific comments below.

Similarly, the abstract is very long-winded and makes it hard to understand the science question that the authors are trying to answer. I recommend revising the abstract to focus more on the big picture impact of this work rather than a list of detailed conclusions.

**Response:** The abstract has been revised based on the referee's comment.

Some methodological details are missing, including: Was the chamber filled with outdoor air or zero air prior to perturbation by VOC, seed,  $NO_x$ , and  $O_3$  injections? If filled with outdoor air, how did the composition vary between experiments? How was the chamber cleaned between experiments?

**Response:** The chamber was cleaned for 2 days after ventilation with outdoor air. Thus, the background is near zero air after cleaning. This point has been added to the revised manuscript.

L86: "Before experiment, chamber was cleaned by using clean air generator for 2 days after ventilation process."

Figure S2 seems like an important figure that would be worth considering moving to the main text since it relates to some of the main conclusions about the work involving the interaction of different oxidants.

Response: Figure S2 has been moved to the main body based on the referee's comment.

Because the chamber used in this study is outside, the experiments presented here are not explicitly 'controlled experiments,' i.e., multiple variables change between each experiment. This variability is fine when using these experiments to validate their model since the variability is captured in the model inputs, and a framing that emphasizes that the model can capture the observed variability is useful. However, it does become problematic when drawing process-level conclusions in Section 4.1 since variation in multiple

variables could be contributing to the observed trends. As such, I think some of the conclusions in Section 4.1 are overstated.

Response: Based on the referee's comment, some conclusions were moved to the sections 4.2.

Lastly, the paper contains numerous grammatical errors that inhibit its readability. I recommend thorough proofreading.

**Response:** The manuscript has been revised.

# **Specific comments:**

- Lines 15-19: These three sentences are hard to understand and should be rewritten for clarity.
   **Response:** These three sentences are modified in the revised manuscript.
   L13: "The resulting oxygenated products were then classified into volatility-reactivity based lumping species. The stoichiometric coefficients associated with lumping species were dynamically constructed under varying NO<sub>x</sub> levels and aging scales and they were applied to the UNIPAR SOA model."
- 2. Lines 39-41: This sentence contains redundant statements about the dominance of biogenic HC emissions.

**Response:** This sentence has been removed.

- Lines 51-52: Note that O<sub>3</sub> titration is possible in some environments.
   Response: A sentence has been added to the revised manuscript.
   L48: "In the presence of O<sub>3</sub>, NO is titrated to form NO<sub>2</sub>."
- 4. Line 54: It's unclear what the quoted 80% refers to. **Response:** To make it clear, the sentence has been modified in the revised manuscript.
  L50: "For example, the oxidation of isoprene with the NO3 radical can rapidly produce nitrate-containing products (up to 80% of total gas products) resulting the increase in the SOA formation (Kwok et al., 1996;Barnes et al., 1990;Perring et al., 2009;Brownwood et al., 2021)."
- 5. Section 2: Referencing Table 1 in this section would be helpful to the reader.

**Response:** A sentence below has been added to the end of this section to refer the Table 1. L98: "The detail information of the chamber experiments is summarized in Table 1."

- 6. Line 101: What was the CCl<sub>4</sub> from? **Response:** CCl<sub>4</sub> was injected into the chamber with HCs to measure the chamber dilution. L 97: "CCl<sub>4</sub> was also introduced to the chamber to measure chamber dilution."
- Line 124: What process does the "stoichiometric coefficient" refer to? Is it for each lumped bin?
   Response: Yes, stoichiometric coefficients are for each lumped bin. These stoichiometric coefficients were obtained by using oxidation products predicted from the semi-explicit mechanism and they are applied to the SOA model.

L121: "The stoichiometric coefficient ( $\alpha_i$ ) and physicochemical parameters of lumping species (*i*) are estimated by using the products predicted from extended semi-explicit mechanisms at a given oxidation path for each precursor. In the model,  $\alpha_i$  values are dynamically constructed with a mathematical

equation as a function of  $NO_x$  levels and gas aging. The predetermined mathematical equation and physicochemical parameters for lumping groups are applicable to the conventional gas mechanisms. In order to support the atmospheric oxidation of biogenic HCs in complex ambient air, these model parameters were integrated with the HC consumption predicted by the Statewide Air Pollution Research Center (SAPRC07TC) (Carter, 2010) gas mechanisms and then applied to produce SOA mass"

8. Line 141-142: What model does "the current regional model" refer to?

**Response:** Here, the regional scale models refer to the regional scale models, such as CMAQ, CAMx, Geos-Chem, and WRF-Chem, which utilize conventional ozone model (Carbon Bond (CB) mechanism or SAPRC) to simulate the HC consumption. Those CB or SAPRC mechanisms treat the oxidation process of biogenic HCs with major atmospheric oxidants. To make it clear, the sentence has been modified in the revised manuscript

L144: "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 SAPRC."

9. Line 148: It could be helpful to include the C\* saturation vapor pressure equivalents for the vapor pressures listed here.

**Response:** The saturated concentration (C\*) of each lumping species can be estimated from vapor pressure of each lumping species by the following equation

$$C^* = \frac{MW_{or}\gamma_{or,i}p_{L,i}^{\circ}}{RT}$$

In the absence of inorganic seed aerosol, gas-partitioning of gas products is processed in organic phase. In general, the activity coefficient of organic species to SOA is nearly 1 (1998 Jang) and the MW<sub>or</sub> is not much changed at a given precursor system. However,  $\gamma_{in,i}$  (activity coefficient of organic species or lumping species in salted aqueous seed) varies with lumping species and thus, C\* is not interchangeable with vapor pressure. Equally saying that C\* cannot be constant. In the UNIPAR model, C\* is dynamically estimated by using the fixed vapor pressure and the estimated activity coefficient.

10. Line 149: Can you give quantitative descriptions for the reactivity scale?

**Response:** We reported the mathematical description of model parameters including reactivity scales and physicochemical parameters, and mathematical equations for stoichiometric coefficients in the recently published paper by Yu et al (Supporting Information of ACP, 2022). In this manuscript, same reactivity scale has been used, and the physicochemical parameters and mathematical equations for stoichiometric coefficients are extended to biogenic HCs at four major oxidation paths to simulate day and night SOA mass as seen in Sect. S7.

11. Section 3.4 and Figure 1: I'm confused by which parts of the model mechanism uses MCM gas phase chemistry and which parts use SAPRC chemistry. Please clarify.

**Response:** Please find the response to comment 7. The model parameters and the predetermined mathematical equations for stoichiometric coefficients for lumping bins were derived by using the product predicted from the semi-explicit mechanisms for the atmospheric oxidation of biogenic HCs. The model parameter and the equations are integrated to the predicted hydrocarbon consumption from any gas mechanisms. In order to support SOA formation in complex ambient air, model parameters and equations for stoichiometric coefficients were integrated with SAPRAC07TC. The hydrocarbon consumption predicted with both semi-explicit mechanisms and SAPRAC07TC well accords with that observed in chamber studies.

12. Fig. 2 (a): Why isn't there a line for  $OM_P$  here?

**Response:** There is as line for  $OM_P$  in Fig. 2 (a) but it is too small to see. Isoprene SOA is mainly produced via aerosol phase reaction and thus, there is only a small amount of SOA produced via gas-particle partitioning.

13. Fig. 2: An indication of when t=0 is (e.g., injection time at night or sunrise in the daytime) would be helpful in these plots. Additionally, I recommend noting in the caption that meteorological parameters (e.g., temperature, relative humidity) varied between these cases in addition to the chemical parameters already noted. It might also be more appropriate to label the middle and right columns as "VOC + O3 + NO3" instead of just "VOC + O3".

**Response:** In order to response to the reviewer, the x-axis and the label of the plots for the nocturnal SOA formation (Fig. 2) has been revised. For the daytime experiments in outdoor chamber, the use of local time is reasonable because gas oxidation and aqueous reactions of organic species are sensitive to local time closely associated with environmental conditions (i.e., temperature, humidity, and sunlight intensity). The environmental conditions are summarized in Table 1. The example of environmental conditions has been updated in the supporting information of the revised paper (Fig. S1).

14. Line 225: This conclusion about an increase in SOA formation because of aqueous reactions of ozonolysis products is unsupported. Can you include a figure that shows process-level detailed analysis of the model to support this?

**Response:** The description of the role of aqueous reactions on SOA growth has been moved to section 4.2, which is related to sensitivity test of SOA model to various variables (Figure 4).

L303: "In Fig.4, nocturnal SOA formation from the  $\alpha$ -pinene ozonolysis increases by including acidic seed (wAHS). Thus, the small increase in chamber-generated SOA formation (Fig. 2(e) and (f)) by inorganic seed is mainly caused by the aqueous phase reaction of the ozonolysis products."

- 15. Line 242-243: Reporting the atmospheric range of pHs would be more useful if the manuscript also included information about the pH of the seeds used in the experiments. **Response:** The pHs of ammonium hydrogen sulfate (AHS) is influenced by humidity. Thus, pH of the wAHS in our simulation conditions has been added in the revised manuscript.
  L243: "To investigate the impact of aerosol acidity, the SOA formation is simulated in the presence of wAHS seed at pHs -1.5 and 0 corresponding to RHs 45% and 80%, respectively."
- 16. Line 248-250: The sentence beginning with "Evidently..." is redundant.

**Response:** The sentence beginning with "Evidently..." has been merged with the next sentence in the revised manuscript

L267: "Evidently, our simulation suggested that the averaged molecular weight of  $\beta$ -caryophyllene oxidation products in highly reactive groups (VF or F) is 183.01 g mol<sup>-1</sup>, while that from isoprene and  $\alpha$ -pinene is 116.65 g mol<sup>-1</sup> and 143.29 g mol<sup>-1</sup>, respectively."

17. Lines 258-259: The conclusion about the impact of photolysis of isoprene and  $\alpha$ -pinene oxidation products on SOA production is unsupported.

**Response:** The simulated properties (O:C ratio) of oxidation products from isoprene and  $\alpha$ -pinene are added to the revised manuscript

L261: "The UNIPAR model estimates the activity coefficient of lumping species in inorganic-salted aqueous phase by using lumping species' physicochemical parameters. Unlike isoprene (Beardsley and

Jang, 2016) or aromatic products (Han and Jang, 2022;Im et al., 2014;Zhou et al., 2019),  $\alpha$ -pinene gas products are relatively hydrophobic and thus, their solubility is low in the aqueous phase with their large activity coefficients. Evidently,  $\alpha$ -pinene SOA yields the lower O:C ratio (~0.56) than isoprene SOA (~ 1.1) in the model."

18. Lines 261-263: Why is the high reactivity relevant here?

**Response:** In general, photolysis products are multifunctional and highly reactive for heterogeneous reaction. In our model, oligomerization of products are governed by the  $2^{nd}$  order reaction. The reaction rate of aerosol phase reactions increases with increasing concentrations in aerosol phase. In general, the product with a higher molecular weight has a low volatility and increase the concentration in aerosol phase due to a greater partitioning constant. According to the molecular weight of the  $\beta$ -caryophyllene oxidation products, the reaction rate of products in highly reactive group can efficiently yield SOA. Unlike  $\beta$ -caryophyllene, isoprene or  $\alpha$ -pinene photolysis products are more volatile with a low molecular weight and thus, the low product concentration in aerosol phase can be inefficient to form SOA.

19. Lines 283-285: The speculation presented here can be supported by the modeling work in this paper. Including supporting plots/calculations would be useful. **Response:** In order to response to the reviewer, Figure S1 has been added to the revised manuscript. L294: "Figure S1 illustrates the stoichiometric coefficients of the two lumping species (low volatility species in group 2S and the medium reactivity species (one aldehyde group) in group 4M), which increase with increasing NO<sub>x</sub> and can significantly contribute to SOA mass. These two species originate from the reaction of a nitrate radical with the ozonolysis products."

20. Line 316: Is the difference between nighttime and daytime SOA for the same amount of initial VOC? Does this statement account for variation in emissions / PBLH between day and night?

**Response:** The sentence has been revised to provide clear point.

L326: "Figure 5 shows that isoprene and  $\alpha$ -pinene produce more SOA mass by nighttime chemistry than daytime chemistry."

The objective of Figure 5 is to show the sensitivity of biogenic SOA to temperature. SOA yields were simulated under the same amount of HC consumption in the box model.

- 21. Line 320: Note that NO<sub>3</sub> can also be lost at night by reaction with fresh NO emissions. **Response:** As referee mentioned, NO<sub>3</sub> can react with NO and produce NO<sub>2</sub>, which can react with O<sub>3</sub> to reproduce NO<sub>3</sub> radical again. Thus, this information has been added to the revised manuscript. L329: "At night, NO<sub>3</sub> radicals can react with NO to form NO<sub>2</sub>, but NO<sub>3</sub> radicals can be regenerated via the reaction of NO<sub>2</sub> and O<sub>3</sub>. In daytime, the role of NO3 on SOA formation can be minimal owing to its rapid photolysis (e.g., lifetime = 5s) (Magnotta and Johnston, 1980)."
- 22. Lines 371-373: How does the ratio of alpha-pinene to gasoline correspond to that in the atmosphere?

**Response:** For our chamber studies, gasoline total carbon concentrations were nearly 3000 ppbC and those of  $\alpha$ -pinene were about 800 ppbC (80 ppb). In the urban aera, the emissions are dominated by anthropogenic sources.

23. Lines 383-385: Can you provide a plot to support the conclusion of this sentence, or at least a quantification of the conclusion presented here?

Response: To response to the referee, Figure S7 has been added to the revised manuscript.

- 24. Fig 3(f): Why is there no dotted black line in Figure 3(f)? **Response:** A black dotted line is overlapped with a red dotted line in Fig. 3(f). This information has been added to the revised manuscript.
  L233: "In Fig. 3(f), the difference in OM<sub>P</sub> between NS and SA conditions was not appeared."
- 25. Fig 4: Because RH=45% is right around the efflorescence point for ammonium sulfate, do these high and low RH cases actually probe significant differences in aerosol liquid water content? Also, for clarity, I recommend noting in the caption that this figure presents modeling results.

**Response:** In order to simulate the impact of RH on SOA formation in the presence of wet-inorganic aerosol, RHs were higher than ERH. RHs at 45% and 80% were chosen to have a large gap. In the UNIPAR model, the aerosol water content is estimated for a wide variety range of RH under varying seed compositions. Below ERH, the aerosol water content turns to be zero allowing no aqueous reactions.

A sentence in the figure caption has been modified to clarify that the Fig.4 is the simulation result. "The simulated potential SOA yield from each oxidation path from the given HC consumption under (a) high NO<sub>x</sub> level (HC/NO<sub>x</sub> = 3 ppbC/ppb) and (b) low NO<sub>x</sub> level (HC/NO<sub>x</sub> = 10 ppbC/ppb)."

26. Fig 7: What is driving the oscillations in the fraction of SOA from alpha pinene (solid red line)? **Response:** Please attention to the y-scale for the  $\alpha$ -pinene SOA mass fraction of total SOA. The window of the y-scale was narrow down between 0.9 and 1.0. The actual size of oscillations is nearly negligible. The tiny change in OM<sub>P</sub> (SOA mass from partitioning) is caused by the small change in temperature and humidity inside the UF-APHOR chamber during the nighttime experiment.

#### Comments to the author:

Dear authors,

After revision, the manuscript has improved. The second round of referee comments, however, reveals that the following criteria for publication in ACP are not met:

- The scientific methods are not clearly outlined.
- Not all conclusions are adequately supported by material presented in the manuscript.

I would like to highlight two comments by Anonymous Referee #3, which I find most critical regarding these two criteria.

[1] Anonymous Referee #3: "[...] many of the mechanistic conclusions stated in the paper are backed up only by previous literature, rather than a detailed analysis of the authors' modeling work" and "including some process-level modeling results to support the stated conclusions would greatly improve the science presented".

> Editor's comment: I agree with the referee with this assessment. In the following, I am listing further references to text in the manuscript, which I think could benefit from showing how the conclusion was derived from the material presented in this manuscript.

**1-1. L.224:** "The small increase in SOA formation by inorganic seed is mainly caused by the aqueous phase reaction of the ozonolysis products" – Please indicate how this conclusion was derived from the material presented in this manuscript (e.g. in a sensitivity analysis regarding the aqueous phase chemistry).

**Response:** Please find the response to comment 14 from reviewer 3. This sentence has been moved to the sensitivity section to indicate that the increase of nocturnal SOA formation by acidic seed is due to the aqueous phase reaction of ozonolysis products.

L303: "In Fig.4, nocturnal SOA formation from the  $\alpha$ -pinene ozonolysis increases by including acidic seed (wAHS). Thus, the small increase in chamber-generated SOA formation (Fig. 2(e) and (f)) by inorganic seed is mainly caused by the aqueous phase reaction of the ozonolysis products."

**1-2. L.251:** "Low volatile products form from the autoxidation of ozonolysis products as reported in the previous studies." – Please indicate how this conclusion was derived from the material presented in this manuscript (e.g. by showing and comparing the concentration of autoxidation products over time).

Response: Please find the sentence below,

L225: "The importance of autoxidation products on terpene SOA formation has been demonstrated in the previous study by Yu et al for daytime chemistry (Yu et al., 2021). At night, the contribution of autoxidation on ozonolysis SOA depends on the concentration of  $\alpha$ -pinene. For example, the attribution of autoxidation on SOA mass in experiment AP01 (Table 1) was nearly 15%, but it can increase due to gas-particle partitioning of non-autoxidation products onto SOA mass originating autoxidation products."

**1-3.** L. 257: "...  $\alpha$ -pinene gas products are relatively hydrophobic and thus, less soluble in the aqueous phase" – Please indicate how this conclusion was derived from the material presented in this manuscript (e.g. by providing a list of physicochemical parameters).

**Response:** Please find the response for the comment 17 from the referee 3. The simulated properties (O:C ratio) of oxidation products from isoprene and  $\alpha$ -pinene are added to the revised manuscript

L261: "The UNIPAR model estimates the activity coefficient of lumping species in inorganic-salted aqueous phase by using lumping species' physicochemical parameters. Unlike isoprene (Beardsley and Jang, 2016) or aromatic products (Han and Jang, 2022;Im et al., 2014;Zhou et al., 2019),  $\alpha$ -pinene gas products are relatively hydrophobic and thus, their solubility is low in the aqueous phase with their large activity coefficients. Evidently,  $\alpha$ -pinene SOA yields the lower O:C ratio (~0.56) than isoprene SOA (~ 1.1) in the model."

**1-4. L. 259:** "In case of  $\beta$ -caryophyllene, even after the photodegradation the product volatility is still low enough to significantly partition to the aerosol phase and heterogeneously form SOA." – Please indicate how this conclusion was derived from the material presented in this manuscript (e.g. by providing physicochemical parameters of  $\beta$ -caryophyllene photodegradation products). **Response:** As an example of the physicochemical parameters of  $\beta$ -caryophyllene photodegradation products, averaged MW of reactive groups were given in the following sentences.

L268: "In case of  $\beta$ -caryophyllene, even after the photodegradation the product volatility is still low enough to significantly partition to the aerosol phase and heterogeneously form SOA. Evidently, the simulated molecular weight of  $\beta$ -caryophyllene oxidation products with high reactivity is generally higher than that in isoprene or  $\alpha$ -pinene products. For example, the averaged molecular weight of  $\beta$ caryophyllene oxidation products in highly reactive groups (VF or F) is 183.01 g mol<sup>-1</sup>, while that from isoprene and  $\alpha$ -pinene is 116.65 g mol<sup>-1</sup> and 143.29 g mol<sup>-1</sup>, respectively."

**1-5. L296:** "The large molecules originating from  $\beta$ -caryophyllene oxidation might have a poor solubility in aqueous phase, weakening the impact of aerosol acidity on OMAR." – As this is a model result, speculation is not needed. Please indicate how this conclusion was derived from the material presented in this manuscript (e.g. by providing physicochemical parameters of  $\beta$ -caryophyllene oxidation products).

**Response:** As an example of the physicochemical parameters of  $\beta$ -caryophyllene products, averaged MW of reactive groups were given in the following sentences.

L307: "The large molecules originating from  $\beta$ -caryophyllene oxidation might have a poor solubility in aqueous phase, weakening the impact of aerosol acidity on OM<sub>AR</sub>. For example, the simulated O:C of  $\beta$ -caryophyllene SOA is estimated as ~0.27 under the chamber conditions in Fig. 2 (i)."

# [2] Anonymous Referee #3: "Section 3.4 and Figure 1: I'm confused by which parts of the model mechanism uses MCM gas phase chemistry and which parts use SAPRC chemistry. Please clarify."

>Editor's comment: I agree with the referee with this assessment. To remedy this comment, I would suggest that the authors provide a more complete description of the model. In addition to the specific comments of Anonymous Referee #3, I added specific comments below, which I hope will prove helpful.

**2-1. L. 78:** "Lumping species and their stoichiometric coefficient and physicochemical parameters from the explicit gas mechanisms were individually obtained from the four different oxidation pathways with OH radicals,  $O_3$ ,  $NO_3$  radicals, and  $O({}^{3}P)$ ." – How was lumping achieved?

The authors state that gas-oxidation chemistry was "explicitly processed" (l. 135) and MCM gas-phase chemistry was used by "individually processing" (l. 143). This explanation seems insufficient to evaluate the scientific method. Please indicate the detailed actions and methods used. See also the most recent comments by Anonymous Referee #1 regarding explicitness of the mechanism.

**Response:** The more information about the lumping species are added in the Sect. S7. Reactivity scales of the oxidation products are determined according to the number of reactive functional groups in their chemical structure. The reactivity bins used in UNIPAR are very fast (VF,  $\alpha$ -hydroxybicarbonyls and tricarbonyls), fast (F, 2 epoxides or aldehydes,), medium (M, 1 epoxide or aldehyde), slow (S, ketones), partitioning only (P) and multi-alcohol (MA, 3 or more alcohols) (Beardsley and Jang, 2016;Yu et al., 2021;Zhou et al., 2019). The explicit chemical structures of oxidation products from isoprene,  $\alpha$ - pinene, and  $\beta$ -caryophyllene are summarized in Table S5-S7 as examples.

**2-2.** Can the authors list all lumping species, stoichiometric coefficients and physicochemical parameters in the supplement? Can the authors add more detail how these were obtained (e.g. fitting by hand, fitting algorithm)? **Response:** The physicochemical parameters of lumping specie and the equations to estimate stoichiometric coefficients has been included in Sect S7. Additionally, examples of the products in lumping bins have also been represented in Table S5-S7 of the revised manuscript.

**2-3.** The additional mechanisms (Section S1.2, Schemes S1-S4) seem not included in Table S1. What are the rate coefficients of the additional reactions in schemes S1-S4? I would suggest to provide a full list of all chemical reactions of the model in Table S4. The gasoline oxidation mechanism is also absent from Tab. S1.

**Response:** Please find the response to comments 7 and 11 from reviewer 3.

"The model parameters and the predetermined mathematical equations for stoichiometric coefficients for lumping bins were derived by using the products predicted from the semi-explicit mechanisms for the atmospheric oxidation of biogenic HCs. In this study, semi-explicit gas mechanisms were improved to predict low volatility products by the addition of autoxidation mechanisms and the combination of nitrate-originating peroxy radicals to the preexisting explicit gas mechanisms. Those additional mechanisms were illustrated in Schemes S1-S3 of Section S1.1. The model parameter and the equations are integrated to the predicted hydrocarbon consumption from any gas mechanisms. In order to support SOA formation in complex ambient air, model parameters and equations for stoichiometric coefficients were integrated with SAPRAC07TC (Table S4 in Section S1.2)." (see Sect. S1)

In order to respond to the comment, the mechanisms associated with Schemes S1-S3 were summarized in Table S1-S3. The format of mechanisms follows in those in the MCM. The oxidation mechanisms of aromatic HC which is related to the gasoline composition are added to the Table S4.