Response to the comments of Reviewer #1

This manuscript presents the SOA production from individual anthropogenic VOC precursors (i.e., n-dodecane and 1,3,5-trimethylbenzene) versus the system of mixed VOCs. Enhanced SOA yields were observed with mixed VOC precursors compared to the linear addition of SOA yields derived from individual VOC precursors, indicating the significance of chemical interactions between intermediate products from these two precursors. Overall, this study provides useful information and highlights the complexity of SOA chemistry in the mixture of VOCs representative of real atmosphere.

Response: We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

Major Comments:

1. *One major comment is that although ESI-TOF-MS data were presented (in Table 2), the molecular composition of SOA unique for each system was not discussed in detail to probe the underlying chemical processes. More in-depth discussion is required.*

   We thank the reviewer for pointing this out. The discussion on the underlying chemical processes and the proposed reaction mechanism of the mixture AVOCs system are added in the manuscript.

   Page 8, line 232-244: "The gas phase products of OH-initiated oxidation of 1,3,5-TMB in the presence of NO_x are mainly 3,5-dimethyl benzaldehyde ($C_9H_{10}O$), 3,5-dimethylbenzoic acid ($C_9H_{10}O_2$), 2-methyl-4-oxo-2-pentenal ($C_6H_8O_2$), 2-methyl-4-oxo-2-pentenoic acid ($C_6H_8O_3$), 2,4,6-trimethylphenol ($C_9H_{12}O$), and 3,5-dimethyl-2-furanone ($C_6H_8O_2$) (Huang et al., 2015), which contain carbonyl or hydroxyl groups that are formed within 1h photochemical reaction. The intermediate products of OH-initiated oxidation of n-dodecane in the presence of NO_x are also compounds containing carbonyl and hydroxyl groups, and more alcohol can be formed due to RO_2 + NO reaction compared to low NO_X condition (Fahnestock et al., 2015). These compounds tend to undergo acetal reaction and/or esterification reaction in the particle phase. When the photochemical reaction is initiated, the intermediate products produced by 1,3,5-TMB and n-dodecane exist in the same reaction system, acetal and esterification reactions are more likely to occur in the particle phase due to higher concentration of aldehydes, ketones, alcohols, and carboxylic acids. The proposed reaction mechanism of the mixture AVOCs system is shown in Figure 5. As an example, the $C_{16}H_{24}O_5$, which has a much higher intensity in the mixed AVOCs system (as shown in Table 2 and discussed above), might be an ester from the reaction of an acid and an alcohol from 1,3,5-TMB and n-dodecane, respectively."

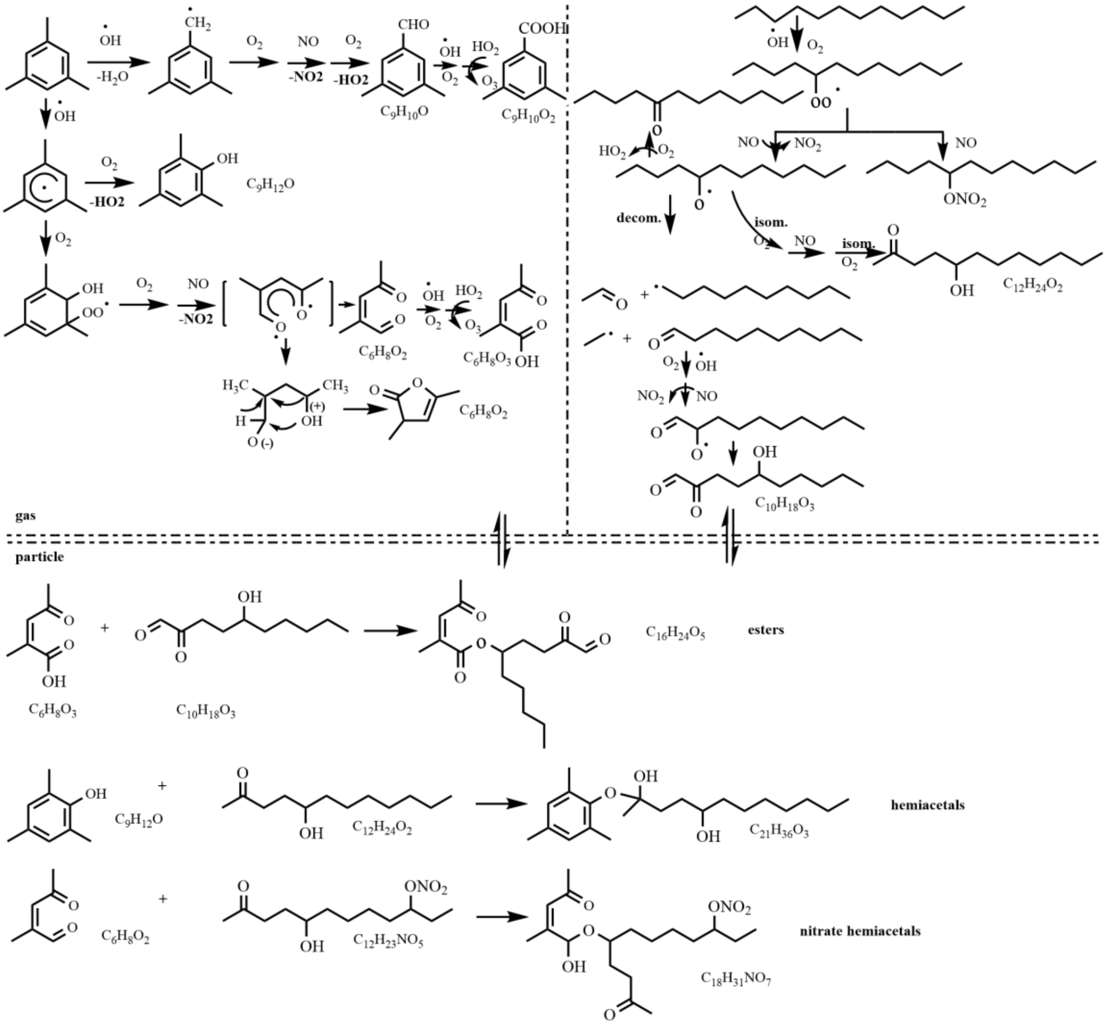

Figure 5. Proposed reaction mechanism of mixture AVOCs system in the presence of NO_X. (**Page 26, line 645-646**)

2. *The difference between measured m/z and theoretical m/z of proposed molecular formula should also be reported for appropriate QA/QC of accurate mass fittings.*

The ESI-ToF-MS used in this study has very high mass resolution, and the mass error between measure *m/z* and theoretical *m/z* of the proposed formula was below 5 ppm. We have added the “Quality Assurance and Quality Control” section in the Supporting Information.

Supporting Information, Page 2, line 28-34: “The collections and analysis of SOA samples were under strict quality control. The Teflon tube in the sampling device was purged with zero air before sampling, and the membrane holder was cleaned with methanol. Glassware used in the experiments was washed with water and methanol, and then dried under high temperature conditions. Before each injection, the micro syringes were cleaned with methanol to prevent cross-contamination among different samples. The blank PTFE filter analysis showed that there was no serious contamination. The typical mass resolving power of the applied ESI-ToF-MS was > 80000 at *m/z* 1222. The absolute mass error between the measured *m/z* and theoretical *m/z* was below 5 ppm.”

Specific Comments:

3. *Line 166: 5.0 × 10ˆ7 nmˆ2/cmˆ3 (please correct the superscripts here)*

   We have corrected this in the manuscript.

   Page 6, line 173: “5.0 × 107 nm2/cm3 → 5.0 × 10^7 nm^2/cm^3”.

4. *Line 219: What are the repeating units (i.e., monomers) of oligomers detected in the range of m/z 500-700? Are they related to the reactive intermediates of individual VOC precursors? More information is needed to directly support the chemical interactions between two precursors.*

   As each precursor can generate intermediate products with smaller carbon numbers, and these intermediate products can oligomerize, the reactions are very complex. The compounds at *m/z* 500-700 have carbon numbers of C_{27}-C_{41}. Concerning the high carbon numbers of these compounds and the complexity of the reaction system, it is infeasible to determine the monomers. Nevertheless, we believe our response to the 1st comment has provided more information to support the chemical interactions between two precursors.

5. *Line 244-247 and 301-303: To determine the potential functional groups in SOA extracts, it would be best to acquire complementary IR spectra. It seems premature to reach these conclusions based*

on the UV-Vis spectra shown in Figure 5.

We thank the reviewer for the helpful suggestion. We have added the ATR-IR analysis in the manuscript. In Section 2.1, we added:

Page 3-4, line 96-100: “The Attenuated Total Internal Reflection Infrared (ATR-IR) analysis was applied to determine the potential functional groups in SOA extracts; an FTIR spectrometer (Bruker, Tensor 27) equipped with a RT-DLaTGs detector was used. The SOA extracts were deposited and dried directly on the Diamant crystal of an ATR-IR cell. The spectra of the dry SOA extracts were recorded by using a background spectrum obtained with no samples as the reference (100 scans, 2.4 cm^{-1} resolution).”

In Section 3.2 “Light absorption of secondary organic aerosol”, we added the following contents:

Page 9, line 259-267: “To further determine the potential functional groups in SOA extracts, ATR-IR spectra were acquired (Figure 6b). In order to eliminate the influence of water, experiments were conducted under dry conditions. As shown in Figure 6 (b) and Table S3, the bold peak at 3360 cm^{-1} corresponds to the characteristic peak of C-OH in alcohol. The peak at 3192cm^{-1} originates from O-H stretching vibration of carboxylic acid. The two characteristic peaks at 2921 cm^{-1} and 2850 cm^{-1} corresponds to the C-H stretching vibration of alkane. The peaks at 1660 cm^{-1} and 1633 cm^{-1} originate from C=O stretching vibrations. The signal at 1465 cm^{-1} and 1415 cm^{-1} represent the deformation vibrations of methyl and methylene groups. The peak around 1268 cm^{-1} corresponds to the vibration of nitrate groups in nitrate ester. The results above suggest that the SOA extracts are dominantly composed of carbonyl compounds, carboxylic acid, nitrate ester, and alcohol. This is consistent with previous studies (Huang et al., 2015; Fahnestock et al., 2015). ”

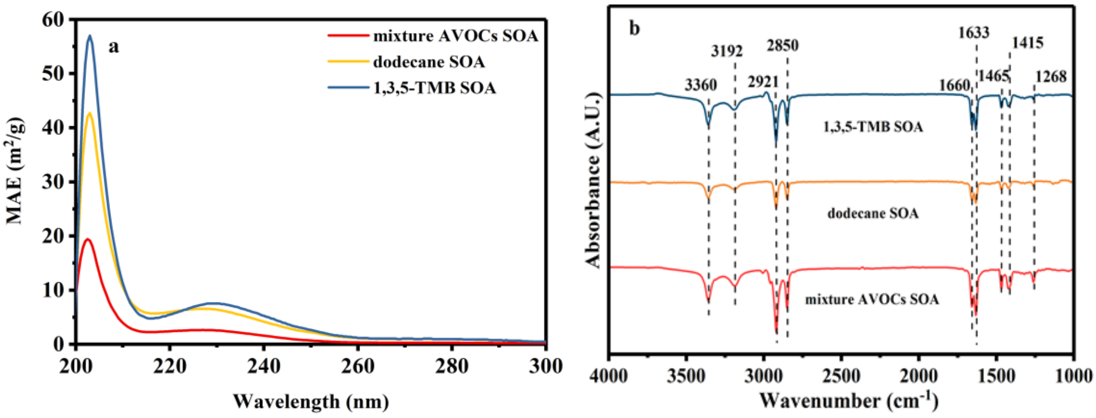

Figure 6. (a) UV-Vis spectra (MAE) of the *n*-dodecane, 1,3,5-TMB, and mixture AVOCs SOA. As the absorbance at wavelengths >300 nm is negligible, we only show the range from 200 to 300 nm. (b) ATR-IR spectra for the *n*-dodecane, 1,3,5-TMB, and mixture AVOCs SOA by using a background spectrum obtained without a sample as the reference. (**Page 27, line 650-652**)

Table S3. List of functional groups in SOA extracts. (**Page 4, line 70, Supporting Information**)

Functional groups	**Wavenumber (cm^{-1})**
C-OH in alcohol	3360
O-H stretching vibration of carboxylic acid	3192
C-H stretching vibration of alkane	2921, 2850
C=O stretching vibrations	1660, 1633
deformation vibrations of methyl and methylene groups	1465, 1415
nitrate groups in nitrate ester	1268

6. *For Figure 5, the absorbance is proportional to the concentration of SOA extracts. What are the mass concentrations of SOA solutions for samples presented in Figure 5? It would be better to present the mass absorption coefficients (MACs) to understand their light absorption properties.*

The mass concentrations of SOA solutions for samples presented in Figure 5 (now is Figure 6a) are 0.03626 g/m^3 (dodecane SOA), 0.0235 g/m^3 (1,3,5-TMB SOA), and 0.1127 g/m^3 (mixture AVOCs SOA), respectively. To better present the light absorption properties of SOA extracts, the mass absorption efficiency (MAE) has been added in the manuscript.

Page 8-9, line 251-258: "Based on the light absorption spectra, the mass absorption efficiency (MAE, m^2/g) of the SOA in the extracts is calculated using the following equation (Chen et al., 2016):

$$MAE(\lambda) = ln(10)\, Abs\ (\lambda)/C_{OM} \tag{7}$$

where $Abs(\lambda)$ is the light absorption coefficient (m^{-1}), and C_{OM} is the SOA mass concentrations in the extracts. The MAE of the SOA extracts in Figure 6 (a) was calculated from 200 to 300 nm. The MAE at 205 nm were in the order: 1,3,5-TMB SOA (56.8 m^2/g) > dodecane SOA (42.5 m^2/g) > mixture AVOCs SOA (19.5 m^2/g). The MAE in the 210-250 nm band also show the same pattern. This indicates that the SOA generated by the mixture AVOCs contains less light-absorbing substance per unit mass relative to dodecane SOA and 1,3,5-TMB SOA."

7. *Line 299: interaction "occurs".*

Page 10, line 317: "occur" → "occurs".