Reviewer #2

This paper studies the formation of secondary organic aerosol from photo-oxidation of α-pinene reacting with NOx. Experiments were conducted in batch mode in a simulation chamber. The SOA yields were investigated under varying concentrations of α-pinene and NOx. The authors discussed the SOA yields as a function of organic aerosol mass concentration from the site of aerosol/gas-phase distribution ratio of semi-volatile products. In addition, SOA chemical composition at the bulk level for different NOx concentrations was also studied.

There is merit to the topic of SOA formation from monoterpene oxidation in the presence of NOx. However, several major and minor comments need to be addressed before the manuscript can be considered for publication.

General comments:

1.

As the authors mentioned in the manuscript, this study uses unrealistically high VOC and NOx concentrations which are much higher than in the general atmosphere. I am therefore wondering how the resulted chemical regime of the experiments could have affected the results presented and their implication to the real atmosphere. Can authors discuss more about the atmospheric implication of the results?

Author reply:

We are very grateful to the reviewer for this comment.

We add the sentences of "Though the initial concentrations of VOCs were higher than that in the atmosphere and the SOA mass loadings was vastly overrated, this study could provide new insights for the nonlinear relationship of NOx with SOA yield, and may be informative to future studies with more atmospheric-relevant concentrations of reactants. And then, according to the changes in the aerosol/gas-phase partition ratio for semi-volatile products with changing VOC concentrations, the ratio of semi-volatile oxidation products distributed in the gas phase would be much higher, but the ratio of that in particulate phase is lower in the real atmosphere than that in our study. The identification of semi-volatile oxidation products in both aerosol and gas phase would further promote the understanding on the process of SOA formation. In addition, the

higher ratio of semi-volatile oxidation products distributed in the gas phase in the atmosphere leads to a more pronounced influence of environmental factors on SOA formation, such as acid-catalyzed heterogeneous reactions, liquid-phase reactions, compared to the laboratory studies." in the end of Section 3.3.

2.

Also, there have been a large amount of investigations on the SOA formation from α-pinene oxidation during the past decades. What is the novelty of this study?

Author reply:

We are very grateful to the reviewer for this comment.

In previous studies, the SOA yield, which used for the analyzation, is obtained in the end of the photooxidation. Odum model simulations in the previous studies were based on multiple sets of experiments. The simulation of SOA formation process in a single set of experiments at different times were relatively rare. Therefore, the effect of aerosol/gas-phase distribution in the SOA formation processes is often overlooked. In this study, we analyzed the dynamic changes of SOA formation based on a variety of online instruments.

Additionally, although the SOA yield increases initially and then decreases as the NOx concentration increases is often mentioned, but the reason for the increase of SOA yield in low NOx conditions have not been well explained. Sarrafzadeh et al. (2016) and Qi et al. (2020) pointed out that the promotion of NO_2 on SOA yield was due to the increase of OH concentration in the chamber (Sarrafzadeh et al., 2016;Qi et al., 2020). Based on this explation, the increased oxidizing ability with initial NOx concentration would lead to a greater consumption of VOCs. The increased consumption of VOCs VOC emissions lead to an increase in the formation of SOA, but it cannot effectively explain why the SOA yield was increased accordingly. In addition, as far as we know, some studies on SOA yield have found that NOx has only an inhibitory effect on SOA yield (Jiang et al., 2019;Sarrafzadeh et al., 2016;Zhao et al., 2018). The different trends in SOA yield with NOx also suggest that the study on the influence of NOx on SOA formation is not complete.

In our study, the dynamic evolution of SOA yield in each photooxidation process single experiment, the aerosol/gas-phase distribution ratio of semi-volatile products can effectively explain the phenomenon of increasing SOA yield with rising NOx levels, and also identify the reasons for different trends of SOA yield with NOx concentration in the previous studies.

3.

The effect of 'Aerosol/gas-phase distribution ratio of semi-volatile products' is one of the major points in this work. However, there is a lack of clear identification and quantification of 'Aerosol/gas-phase distribution ratio of semi-volatile products' in the manuscript. Can the authors explain it in more detail in the manuscript/supplement? Besides, the identification of 'semi-volatile products' is also not clear. Do they refer to the compounds in any range of saturation vapor pressures, or any range of partitioning coefficients, or other specific identification in this work? Or did I miss anything?

Author reply:

We are very grateful to the reviewer for this comment.

We identified the volatile of SOA based on the "triangle plot" of f_{43} and f_{44} which obtained by AMS in Line 336-339: "In our study, the f_{43} and f_{44} of α-pinene SOA ranged from 0.160 to 0.175 and from 0.069 to 0.074, respectively. According to the "triangle plot" of the AMS, the SOA derived from α-pinene photooxidation mainly fell in the lower area designated semi-volatile oxygenated organic aerosols (SV-OOA) (Singh et al., 2019;Reyes-Villegas et al., 2016;Hao et al., 2014;Ng et al., 2010). The AMS results suggested that the α-pinene SOA formed through NOx photooxidation exhibited semi-volatile characteristics."

According to the Odum two-product model, the fitted curves for each experiment gradually moved to the lower position with the increase of NOx, which indicated that the volatility of photooxidation products increases with the increasing initial NOx concentration. At the same time, the higher NOx concentration enhances the RO reaction path, which also indicates the formation ability of SOA was inhibited by NOx. But in low NOx conditions, the consumption of VOCs and the SOA mass concentration was increased with initial NOx concentrations. Based on the nature of Odum model,

the SOA yield was increases with increasing SOA mass concentration in each photooxidation experiment through the gradual increase in the gas-particle partition coefficients of photooxidation product (Odum et al., 1996). We have described the change of gas-particle partition coefficients of photooxidation products for each experiment as "However, the gas-particle partition coefficients of semi-volatile substances are directly related to their concentrations, and the partition coefficients of semi-volatile substances into the particulate phase are larger at higher concentrations (Akherati et al., 2019;Odum et al., 1996). Hence, the increasing partition ratios of semi-volatile organic products between aerosol and gas phases at high M_0 were responsible for the increasing SOA yields with increasing photooxidation time (Takeuchi et al., 2022;Kolesar et al., 2015;Valorso et al., 2011)."

The inhibition of SOA formation by the roles of chemical processes (the branching of RO2 react with RO2/HO2 or NO) and facilitation of SOA formation by the physical processes (aerosol/gas-phase distribution) jointly effect the SOA yield. With the increase of NOx concentration, more SOA was formed. The SOA mass concentration was increased from 26.0 μg m^{-3} to 54.3 μg m^{-3} as the initial NOx concentration increased from 12 ppb to 68 ppb. Hence, we believe that the increased SOA yield with increasing NOx concentration is responsible by the aerosol/gas-phase partition of semi-volatile products.

In addition, the relative content of different classes volatile products in both gas and particulate phase observed in the studies of Chen et al. (2022c) also show an increasing aerosol/gas-phase partition of semi-volatile products with the increasing VOC consumption and SOA yield.

4.

The whole section of '3.2 SOA chemical composition at different NOx concentrations' is based on the calculation of N-containing compounds (NOCs). The authors use a constant RON value of 10 to quantify the NOCs by the equations 4 and 5. This value is from Takeuchi and Ng (2019). However, the VOC and NOx concentrations in this work are largely different from the concentrations in the study of Takeuchi and Ng (2019). This may lead to different chemical composition of generated SOA between two works, which may affect the RON value (Xu et al., 2015). Also, the chemical

compositions of SOA in different experimental conditions are mentioned to be different in this work. Thus, using a constant RON value for all experiments may lead to uncertainties in the quantification of NOCs. Can the authors discuss how the resulted chemical composition could have affected the quantification of NOCs (especially the major results showed in Figure 5)?

Author reply:

We are very grateful to the reviewer for this comment.

For the NO_x^+ ratio method, considering the large variation in NO^+/NO_2^+ ratio for different organic nitrates, the largest uncertainty is associated with the value of RON. this is challenging to determine the RON value for every organic nitrate species. Based on the previous studies, the RON values of 5 and 10 likely correspond to upper and lower bounds of the $NO_{3,org}$ concentrations estimated by the NO_x^+ ratio method.

The sentence of "and RON was assumed to be about 10 referring to the study by Takeuchi and Ng (2019)." in Line 372 is fixed as "Considering the large variation in NO^+/NO_2^+ ratio for different organic nitrates, the R_{ON} values were assumed to be 5 and 10 as the upper and lower bounds referring to the previous studies (Takeuchi and Ng, 2019;Xu et al., 2015)." in the revised manuscript in Line 187-190.

The Figure 5 is changed as
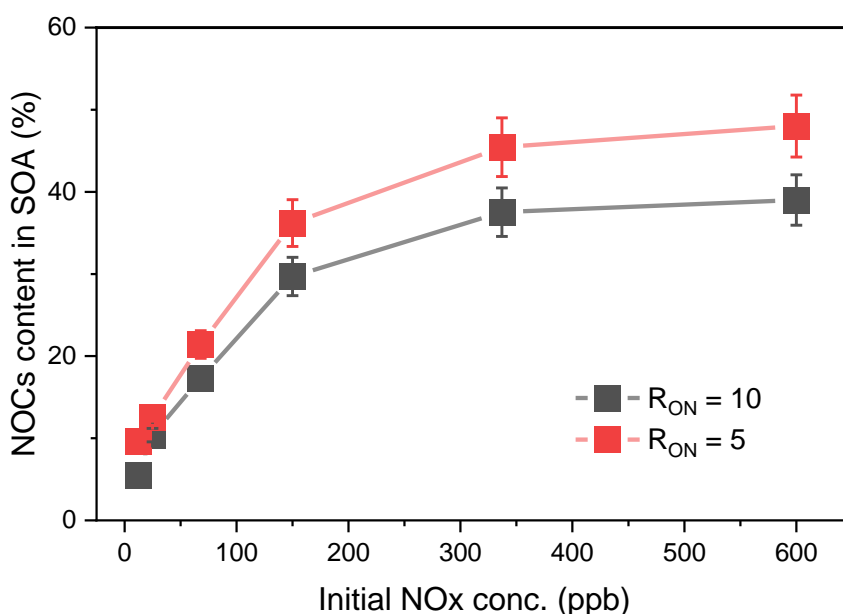
The sentence of "During this stage, the growth in NOC content gradually slowed while approaching the maximum value. Based on the nonlinear fit between NOx concentration and NOC content, the maximum value of NOCs content in SOA was predicted to be about 39 ± 3.8%." in Line 388-391 is fixed as "During this stage, the growth in NOC content gradually slowed while approaching the maximum value. Based on the nonlinear fit between NOx concentration and NOC content, the maximum value of NOCs content in SOA was predicted to be in the range of 39% to 48%." in the revised manuscript in Line 419-422.

5.

I would suggest authors to proofread the manuscript and check the grammar in English. Especially, terminology should be correctly used. Self-identified terms will need to be fully explained at the first time.

Author reply:

We are very grateful to the reviewer for this comment. This manuscript was proofread.

Specific comments:

1.

Line161. The calculation of yields belongs to the section of Experimental Methods.

Author reply:

The SOA yield in Line 160-161 "Here, SOA yield was calculated as the SOA mass concentration divided by the reacted VOCs." is fixed as "Here, SOA yield was defined as the ratio of the maximum SOA mass concentration ($\mu g\ m^{-3}$) to the concentration of reacted α-pinene ($\mu g\ m^{-3}$) in the end of each experiment.", and moved to the section of Experimental method in the revised manuscript in Line 144-146.

2.

Line 200. What is the unit of decay ratio?

Author reply:

The unit of decay ratio is "ppb min^{-1}".

3.

Are the results corrected by the effect of dilution?

Author reply:

We are unsure which part of this manuscript is this this comment corresponds to.

As far as I know, there is no dilution involved in this manuscript.

4.

The quantification of the particle concentration is important in this work. Can authors show the simultaneous measurements of SMPS, and state also the collection efficiency used for AMS measurement? What is the uncertainty of the yields in Table 1?

Author reply:

The SMPS result and AMS result is compared based on the previous expreriments. The comparation of the SOA mass concentration observed by SMPS and the signal of AMS is shown in below. The AMS results are consistent with that of SMPS. The following figure was added in the SI.
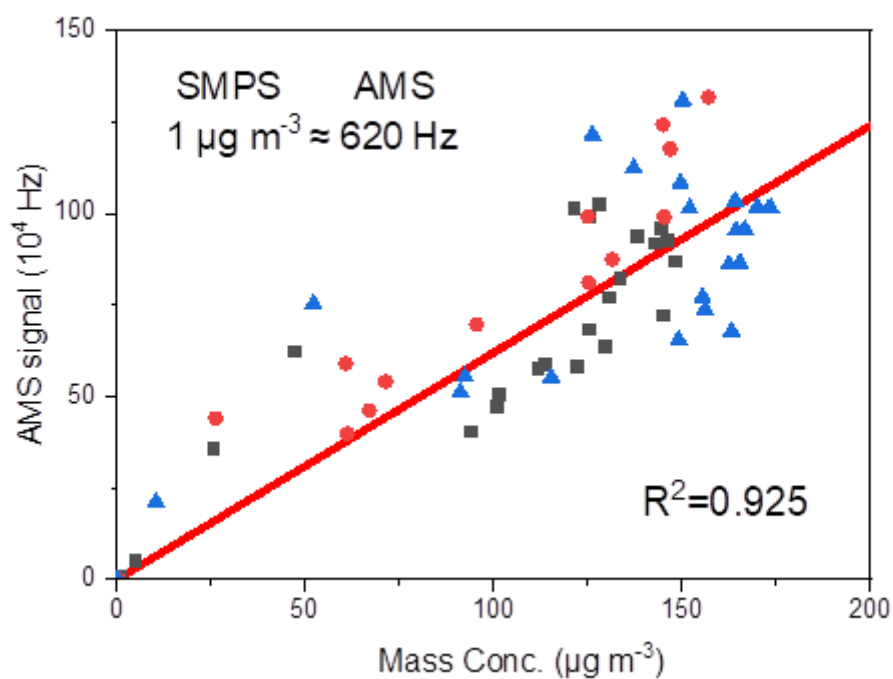
The uncertainty of SOA yield was based on the system error of AMS. We added the error bars in the Fig. 1, and it is changed as below.
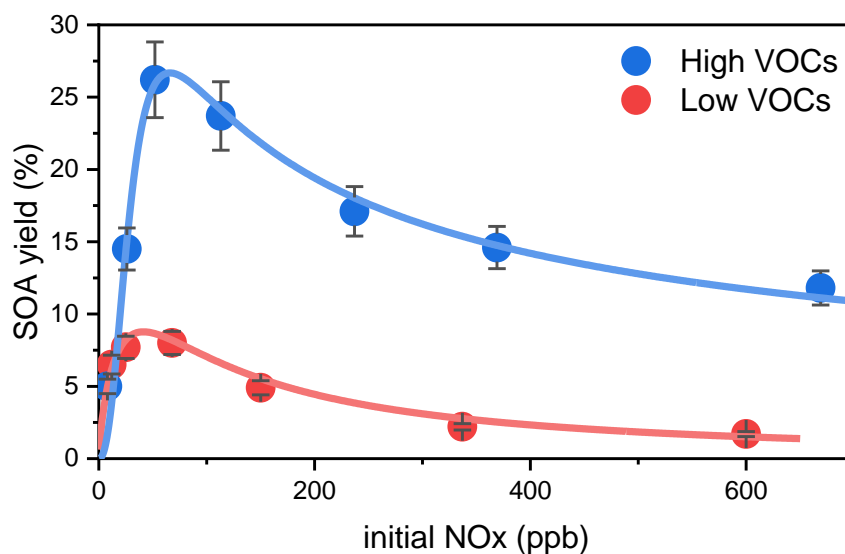

Figure 1. SOA yield from α-pinene photooxidation with different initial NOx concentrations under two levels of VOCs. The error bars were determined on the system error of AMS.

Line230. Does 'gas-particle distribution coefficients' mean gas-particle partition coefficients?

Author reply:

We are very grateful to the reviewer for this comment. The "gas-particle partition coefficients" is more accurate. The "gas-particle distribution coefficients" in the manuscript have been changed as "gas-particle partition coefficients".

6.

The period in each experiment for yields determination is not clear. This could be important when comparing the different SOA in batch-mode studies.

Author reply:

The SOA yield was calculated based on the maximum SOA mass concentration. The photooxidation time for each group of experiments is 3 h in this study. For the low NOx condition of Exp. 1, 2, 7, 8, and 9, the α-pinene was not fully consumed in the end of the photooxidation, and the SOA mass concentration still increase in the end of the photooxidation. For the other experiments, the SOA mass concentration remain constant at the end of each experiment after the SOA wall loss corrected. But it should be noted that the maximum SOA mass concentration is equal to the final SOA mass concentration in the end of each experiment.

As the response to Specific comments #1, The SOA yield was defined in Line 160-161 "Here, SOA yield was calculated as the SOA mass concentration divided by the reacted VOCs." To clarify the statement, it is fixed as "Here, SOA yield was defined as the ratio of the maximum SOA mass concentration (μg m^{-3}) to the concentration of reacted α-pinene (μg m^{-3}) in the end of each experiment.", and it was moved to the section of Experimental method.

7.

Line232. 'into the aerosol phase are larger at higher concentrations' of particle phase? The statement is not clear.

Author reply:

The "aerosol phase" is changed as "particulate phase".

The calculation of the two-product model (line237-248, equation 1, Tabe 2) should be moved into the section of Experimental Methods.

Author reply:

We are very grateful to the reviewer for this comment. The two-product model used in this study is a data analysis method. We think the calculation of the two-product model is reasonable in the section of discussion. In addition, some previous studies also described the calculation of the two-product model in the Discussion, i.e. Yang et al., (2020); Joo et al. (2019); Boyd et al. (2017); Chen et al. (2016).(Yang et al., 2020;Joo et al., 2019;Boyd et al., 2017;Chen et al., 2016)

9.

Line259-261. The sentence is not clear. The results do not show any change of the volatility. How can it be concluded that 'the volatility of semi volatility products produced through α-pinene photooxidation increased with initial NOx concentration'?

Author reply:

We are very grateful to the reviewer for this comment. Here, the $K_{om,2}$ (m^3 μg^{-1}) are the gas-particle partitioning equilibrium constants for semi-volatility products. The decreased value of $K_{om,2}$ illustrates the volatility of semi volatility products was decreased.

For the illustration more clearly, this sentence is changed as "The decreased value of $K_{om,2}$ meant that the volatility of semi-volatility products produced through α-pinene photooxidation increased with initial NOx concentration." in the revised manuscript in Line 299-301.

10.

Line266-275 repeat that yields increase with increasing NOx concentration. Please get them streamlined and delete the unnecessary repeats. Further, why the increasing

yields with increasing NOx are interpreted to be the contribution of higher contributions of semi-volatile products? Do authors mean higher NOx concentrations lead to a higher fraction of semi-volatile products among total products than at lower NOx concentrations?

Author reply:

We are very grateful to the reviewer for this comment.

According to the Odum two-product model the fitted curves for each experiment gradually moved to the lower position with the increase of NOx, which indicated that the volatility of photooxidation products increases with the increasing initial NOx concentration. At the same time, the higher NOx concentration enhances the RO reaction path, which also indicates the formation ability of SOA was inhibited by NOx. But in low NOx conditions, the consumption of VOCs and the SOA mass concentration was increased with initial NOx concentrations. Based on the nature of Odum model, the SOA yield was increases with increasing SOA mass concentration in each photooxidation experiment through the gradual increase in the gas-particle partition coefficients of photooxidation product. The inhibition of SOA formation by the roles of chemical processes (the branching of RO2 react with RO2/HO2 or NO) and facilitation of SOA formation by the physical processes (aerosol/gas-phase distribution) jointly effect the SOA yield. With the increase of NOx concentration, more SOA was formed. The SOA mass concentration was increased from 26.0 μg m^{-3} to 54.3 μg m^{-3} as the initial NOx concentration increased from 12 ppb to 68 ppb. Hence, we believe that the increased SOA yield with increasing NOx concentration is responsible by the aerosol/gas-phase partition of semi-volatile products.

In order to express more clearly, the manuscript in Line 266-275 is fixed as "Due to the lower consumption rate of VOCs and low AOC, α-pinene was not completely consumed at the end of the photooxidation period under low-NOx conditions, and the consumption of α-pinene was increased with the increasing NOx concentration. The increased VOC consumption resulted in higher concentrations of photooxidation products generated in the chamber. Consequently, when the initial NOx concentration increased from 12 ppb to 25 ppb and further to 68 ppb, the mass concentration of SOA increased from 26.0 μg m^{-3} to 43.8 μg m^{-3} and eventually reached 54.3 μg m^{-3}. Because of the positive correlation between SOA yield and SOA mass concentration, although

a gradual downward shift in the fitting curve of the two-product model was observed with increasing NOx levels, the higher SOA mass concentration still resulted in an increase in SOA yield from 6.5% to 8.0% when the initial NOx concentration increased from 12 ppb to 68 ppb." in the revised manuscript in Line 305-316.

We do not mean the higher NOx concentrations lead to a higher fraction of semi-volatile products among total products than at lower NOx concentrations. We want to express the aerosol/gas-phase partition ratio was increased with increasing formation of semi-volatile products. For clarify, The sentence of "The enhancement of the SOA yield with increasing NOx concentrations can be attributed to the increased ratio of the aerosol/gas phase partition resulting from higher concentrations of semi-volatile photooxidation products." in Line 277-280 is fixed as Hence, the enhancement of the SOA yield with increasing NOx concentrations can be attributed to the increased partition ratio of semi-volatile photooxidation products between aerosol and gas phase when more photooxidation products were formed." in the revised manuscript in Line 319-322.

11.

Line283-286. What do the 'volatile oxidation products' refer to? Oxidation products in semi volatility or in all volatility groups? Do the proportions refer to the amount of total semi-volatile oxidation product in the sum of all gas- and particle-phase oxidation products? These confuse me. Also, I would suggest authors to give citations and explain why the assumption given here is correct.

Author reply:

We are very grateful to the reviewer for this comment.

In the study of Chen et al. (2022), the photooxidation products are grouped into five classes based on their saturation vapor pressure (C*), i.e., volatile organic compounds (VOC), intermediate volatility organic compounds (IVOC), semivolatile organic compounds (SVOC), low volatility organic compounds (LVOC), and extremely low volatility organic compounds (ELVOC). And the "different volatile oxidation products" in our manuscript is means the "VOC, IVOC, SVOC, LVOC, and ELVOC" in all volatility groups.

To clarify the statement, we changed the sentence in line 280-286 of the revised manuscript as "Chen et al. (2022) categorized the photooxidation products into five classes based on their saturated vapor pressure (C*), and relative content of different classes of volatile products in both gas and particulate phase were compared. The contributions of semi-volatile oxidized products in the particulate phase were larger, but the proportion of semi-volatile oxidized products in gas-phase intermediate products was lower when experiments had higher VOC consumption and SOA yields. This result indicated that the proportion of semi-volatile organic products condensed into the particulate phase relative to the total formation of semi-volatile organic products was larger when more VOCs were consumed." in the revised manuscript in Line 323-331.

12.

Line367-373. The calculation belongs to the section of Experimental Methods.

Author reply:

We are very grateful to the reviewer for this comment. And the calculation of NOCs has moved to the section of Experimental Methods.

Technical comments:

1.

line60. Abbreviations should be identified when they show up for the first time.

Author reply:

The Abbreviations of VOCs is identified in Line 51. The identification of OH was added in Line 60.

2.

Figure6. In the legend, 'complately' is incorrect.

Author reply:

The "complately" is fixed as "almost".

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