Dear ACP Editor:

As requested by the editor Prof. John Liggio, here we revised our manuscript for a possible publication in ACP. We greatly appreciate the time and effort that the editor and the two reviewers spent in reviewing our manuscript. Their comments are really thoughtful and very helpful for us to improve the quality of our work. After reading the comments from the reviewers, we have carefully revised our manuscript. To address the reviewer concerns, in the revised version we have added five new figures with one into the text and the other four into the SI. All the changes in the manuscript and the supporting information are marked in blue color. Our responses to the comments are itemized below.

Anything for our paper, please feel free to contact me via ghwang@geo.ecnu.edu.cn.

All the best

Gehui Wang

Jan 21., 2025

Response to Reviewer #1

General Comments:

In this work, the authors examine the effects of NO_x on isoprene SOA yields. The authors varied NO_x from 10 ppb up to 2 ppm. The starting concentration of isoprene was about 1 ppm for all experiments. The authors then discuss the effects of oxidant identity and RO_2 fate on the observed SOA yields. The main RO_2 fates in these experiments were RO_2+NO and RO_2+HO_2 and the maximum SOA yield is observed when the ratio between these two is 1:1.

Response: We thank the above comments and have carefully revised our manuscript. Following is our response to the comments.

Comments:

1. It is unclear to me what the goal of these experiments is based on the current presentation of the data. For example, lines 34-37 "We found that NO_x could influence the formation of the ultralow volatility organic compounds(ULVOCs, log10 C* < −8.5), low volatility organic compounds (LVOCs, −4.5 < log10 C* < −0.5) and extremely low volatility organic compounds (ELVOCs, −8.5 < log10 C* < −4.5) by changing the RO_2 fate" is something that is already known so the expectation would be that there is a more quantitative analysis of the NO_x dependence for these species. However, the article only shows that more of these species form at 712 ppb than at 2 ppm (Figure 3) with no other context or information. How was the yield of these species affected by NO_x and how did that in turn affect the overall SOA yields? Does the updated model predict these products? No questions were answered.

Response: Thank you for your important comments and have taken your suggestion.

(1) In the revised version, we supplemented additional experiments and added more discussions about the yield dependence of these species on NO_x with five new figures (Figure 5, Figures S4 -S7) into the revised manuscript. We quantitatively analyzed the the NO_x dependence for LVOCs, ELVOCs and ULVOCs.

We have supplemented two experiments under 488 and 970 NO_x ppb using HR-TOF-CIMS to investigate the NO_x dependence on LVOCs, ELVOCs and ULVOCs in the gas phase. As shown in Table S1, in this study LVOCs are $C_5H_8N_2O_8$, $C_5H_{10}N_2O_8$, $C_5H_8N_2O_9$, $C_5H_{10}N_2O_9$, $C_5H_9N_3O_{10}$, $C_5H_9N_3O_{11}$ and $C_5H_{11}N_3O_{11}$, ELVOCs are $C_6H_{10}N_2O_{14}$ and $C_{10}H_{17}N_3O_{14}$, while ULVOCs are $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$, respectively. By measuring the gas-phase signals of these molecules, we observed a significant NO_x dependence for LVOCs, ELVOCs and ULVOCs (Figure R1). As seen in Figure R1, the normalized signals of LVOCs, ELVOCs and ULVOCs increased along with an increasing NO_x level, maximized at 712 ppb NO_x, and then quickly decreased. Such a NO_x dependence is similar to the SOA yield dependence on NO_x. From Figures 3 and 4, we can see that in addition to the oxygen atoms from nitrate groups and peroxy nitrate groups, the numbers of remaining oxygen atoms in ULVOCs molecules, such as $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$, are greater than 6, suggesting that ULVOCs in the chamber are HOMs. As shown by Figures 4, S5 and S6, LVOCs, ELVOCs and ULVOCs are most abundant at 712 ppb NO_x, resulting in the highest number and the largest diameter of particles in the chamber. HOMs almost disappeared at 2060 ppb NO_x, which means that nucleation hardly happened under the very high NO_x condition.(Figure 5, Table 1).

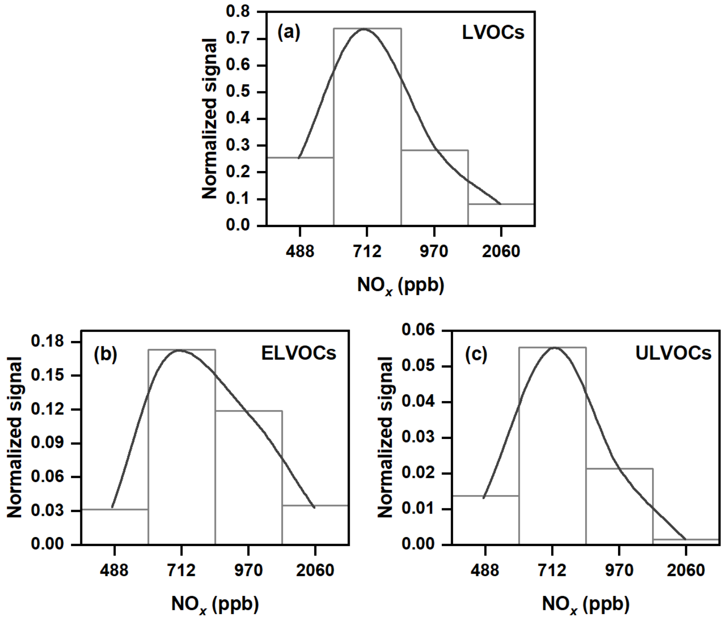

Figure R1. NO_x dependence of three typeso of VOCs (LVOCs, ELVOCs, ULVOCs, according to the calculated values of $\log_{10} C^*$, Table S1). (Figure R1 presents in the revised manuscript as Figure 5)

Please see the discussions in page 11, lines 301-308, 311-321, page12, 326-329, and Figure 5, Figure S5 and Figure S6.

(2) The discussion of modeling applications has been removed from this study. Our original intention is that β can be used to evaluate all RO_2. But we agree with comment (3) by Reviewer 2# that there are differences in volatility between isoprene-derived SOA and other SOA. So, it cannot be said that β can be used as a reference based on the results of this study alone. In order to avoid any possible misleading, we deleted the last sentence of the abstract.

<u>Comments:</u>

2. If the goal is to study the effect of NO_x on SOA yields from isoprene, then why use such atmospherically irrelevant starting concentrations? In fact, there is so much NO_x in this system that there is a significant amount of NO_3 oxidation occurring. Considering the NO_3 concentrations reported in figure S3, it is likely that many of the species that contribute to SOA in this experiment are organic nitrates from multiple generations of NO_3 oxidation. Was the goal to study nighttime isoprene SOA yields? Was the goal to study multi-generation oxidation in the isoprene system? (2) In Figure 1 SOA does not peak until much after the isoprene is consumed.

<u>Response</u>: We agree with you that there is a significant amount of NO_3 oxidation occurring in this study. Here we reply to your above two comments individually:

(1) Because of the low SOA yield of isoprene (Kroll et al., 2006; Kleindienst et al., 2009), if the relationship between NO_x and the SOA yield was investigated under atmospherically relevant conditions by using a chamber simulation techqnique, it can result in significant errors in measuring the concentrations of products in the chamber due to very low level of products, making the kinetic results not reliable enough. In chamber studies, high concentration of VOC, which is much higher than that in real atmosphere, has been used by many studies such as Galloway et al. (2011), and Qi et al.(2020), and so on (Galloway et al., 2011; Qi et al., 2020).

In the past two decades, a few studies on the effect of NO_x on SOA formation from isoprene and found that the yield of SOA from isoprene could be decreased under high NO_x

conditions. However, no study has syetematically investigated the NO_x dependence, resulting in the mechanism still unclear. The goal of this study was to elucidate the mechanism by simultaneously investigating both gas and aerosol species in order to improve our understanding on the SOA formation process in the urban troposphere, where both isoprene and NO_x are abundant and OH radical, NO_3 radical and O_3 all contribute to the generation of isoprene SOA. Since only black light (~365 nm) was used in this study, photodegradation of NO_3 (<400 nm) hardly occurs (Reed et al., 2016). Previous studies have demonstrated that NO_3 radical could be an important oxidant during the daytime. The NO_3 pathway has been recognized as a potentially important chemical transformation pathway in field campaigns especially on haze episodes, because low sunlight intensity, which hardly photolyzes NO_3(Geyer et al., 2003; Brown et al., 2005; Osthoff et al., 2006; Xue et al., 2016; Foulds et al., 2021; Wu et al., 2021a). For example, observation in La Porte near Houston, USA showed that NO_3 was up to 2-5 ppt during daytime haze period in 2003 (Geyer et al., 2003; Brown et al., 2005; Osthoff et al., 2006; Xue et al., 2016; Foulds et al., 2021; Wu et al., 2021a).Thus, the role of NO_3 radical in isoprene SOA formation process in daytime atmosphere cannot be ignored. Thus, in this study we also discussed the effect of NO_3 on SOA yield from isoprene.

We have taken you suggestion and made addition explanation on the importanece of NO_3 radical. Please see page 8, lines 207-225.

(2) When isoprene begins to be oxidized, it will produce gas-phase products with higher m/z , in which volatile organic compounds with low volatility start to nucleate and form particles. And then the number of particles concentration and particle size continue to grow. Therefore, the peak time of SOA is longer than the consumption time of isoprene and SOA does not peak until much after the isoprene is consumed (Figure 1), which is reasonable and consistent with the results of Figure 2b reported by Xu et al.(2014), who also investigated the photooxidation of isoprene (which is cited here as Figure R2).

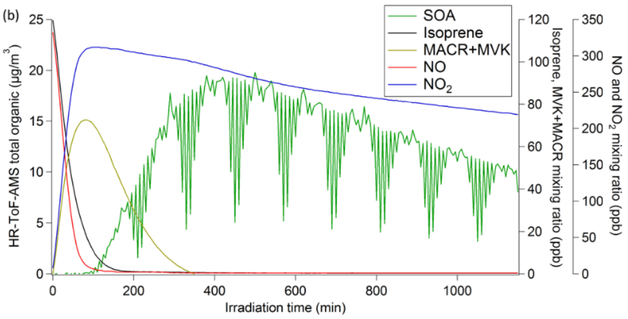

Figure R2. Time profiles for a typical mixed experiment (expt. 6) (cited from Xu et al., 2014).

Comments:

3. Even the β obtained in this work is hard to interpret. In the real atmosphere, RO_2 from isoprene have NO, HO_2, RO_2 and isomerization as reaction pathways, the latter two which are not represented here at all but would be major pathways during nighttime oxidation. Also, considering the oxidant identity is likely a mixture of OH and NO_3 there is no guarantee that the β would work when applied to daytime oxidation where the bulk of the isoprene is consumed. It would not apply to nighttime oxidation either.

Response: (1) We agree with you that there are four reaction pathways for isoprene in the actual atmosphere, which are NO, HO_2, RO_2 and the isomerization reaction pathways. Among them, the isomerization reaction pathway is not the main reaction pathway. Because the fraction of isoprene peroxy radicals reacting by 1,6-H-shift isomerization is estimated to be 8-11% globally(Crounse et al., 2011). Also, we calculated the loss rates of RO_2+NO, RO_2+HO_2, and RO_2+RO_2 pathways using the OBM-MCM model and found that the loss rate of the RO_2+RO_2 pathway was negligible compared to that of the RO_2+NO and RO_2+HO2 pathways (Figure R3a). Previous studies (Kroll et al., 2006; Xu et al., 2014) have also reported that RO_2+NO and RO_2+HO_2 pathways are the main pathways and have a significant impact on the yield. Therefore it is reasonable that we investigated the SOA yield dependence on NO_x by calculating β, which is only based on both RO_2+NO and RO_2+HO_2 pathways without consideration of RO_2 and the isomerization reaction pathways.

We agree with you that oxidant in this study is likely a mixture of OH and NO_3. However, we belive that the β valus we obtained is applicable for both daytime and night chemistry, because recent field observations suggest that NO_3 radical is also important wihle OH radical is non-negligilbe at nighttime. Many studies have pointed out that NO_3 radical in daytime is abundant especially in haze periods, because low sunlight intensity hardly photolyzes NO_3. For example, field observation by Geyer et al.(2003) showed that NO_3 in La Porte near Houston, USA was up to 2-5 ppt during daytime haze period in 2003, and Wu et al (2021a) reported that NO_3 radical at the late afternnon in Xi'an, China is abundant. These field measurments suggest that NO_3 radical in daytime is also important. On the other hand, Zang et al (2023) recently reported that at night decomposition of ozonolysis-derived Criegee intermediates can form OH radicals abundantly during the synergistic oxidation process of O_3 + NO_3 . Those field observation results clearly suggest that for VOC oxidation NO_3 radical is also important in daytime wihle OH radical is non-negligilbe at night. Therefore, we believe that the β values given by ths study is applicable for both day- and night- VOC chemistry.

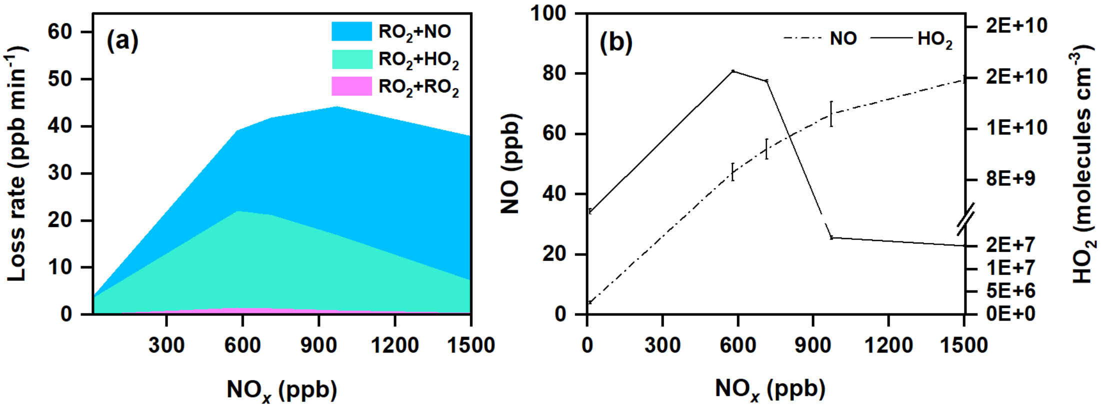

Figure R3. (a) Loss rates of main RO_2 from different oxidation pathways as a function of NO_x concentration calculated by MCMv3.3.1, and (b) variations of NO and HO_2 concentrations. (a) Loss rates of main RO_2 from different oxidation pathways as a function of NO_x concentration calculated by MCMv3.3.1, and (b) variations of NO and HO_2 concentrations. (NO_X in Figures 6a and 6b represent the initial concentrations, in Figure 6a the loss rate is the maximum values of RO_2+NO, RO_2+HO_2, and RO_2+RO_2 during the whole reaction process, while in Figure 6b HO_2 is the maximum value during the whole reaction process) (Figure R3 presents in the revised manuscript as Figure 6)

Comments:

4. I do not believe the current article should be accepted. If the authors wish to use the data from these experiments then they should focus on the observed products as a function of NO_x and accurately identify the oxidant identities per experiment along with the RO_2 lifetimes and fates.

Response:. We have taken you suggestion. We investiagted the observed products as a function of NO_x and accurately identified the oxidant identities in the different experiment along with the RO_2 lifetimes and fates. (See the Figure S3, new figures: Figure 5, , Figure S5 and Figure S6, and updated Figure 4 and 7).

(1) As we responsed to comment (1), we have supplemented two groups of experiments under 488 and 970 NO_x ppb using High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-TOF-CIMS) to investigate the NO_x dependence on LVOCs, ELVOCs and ULVOCs in the gas phase. LVOCs includes $C_5H_{8-11}N_{2,3}O_{8-11}$; ELVOCs includes $C_6H_{10}N_2O_{14}$ and $C_{10}H_{17}N_3O_{14}$; ULVOCs inludes $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$. We found a significant NO_x dependence for LVOCs, ELVOCs and ULVOCs, which is similar to the NO_x dependence on SOA yield (Figure R1).

The relevant discussions are shown in the revised manuscript, page 11-12, lines 311-329.

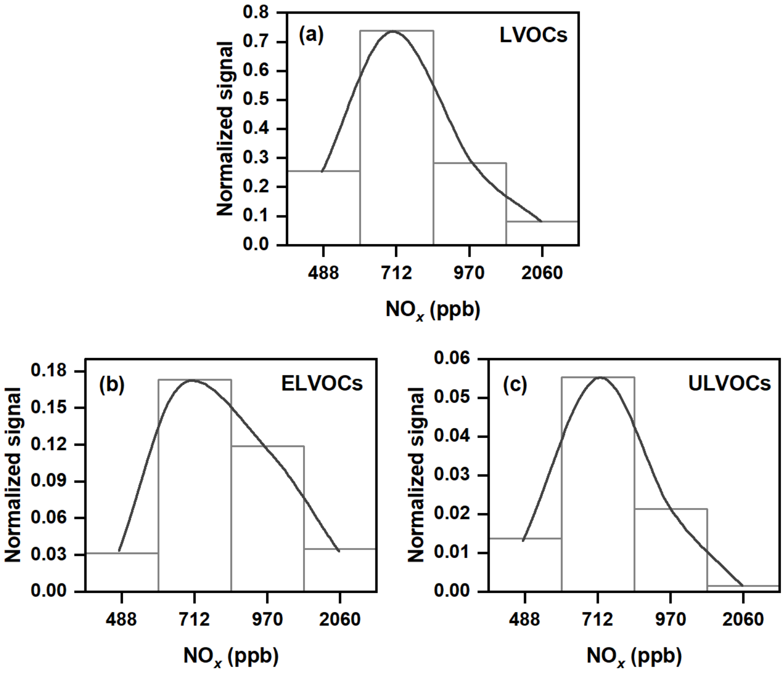

Figure R1. NO$_x$ dependence of three types VOCs (LVOCs, ELVOCs, ULVOCs, according to the calculated value of log$_{10}$ C*, Table S1). (Figure R1 presents in the revised manuscript as Figure 5)

(2) In all the experiments of this study, the range of NO$_x$ is 10-2060 ppb. According to the calculated β (Figure R4), when the reaction was stable, we determined the main oxidation pathway for each experiment. When NO$_x$ is at 10-577 ppb NO$_x$, the main oxidation pathway is RO_2+HO_2; when NO$_x$ is at 712 and 811 ppb, the proportion of the NO and HO_2 oxidation pathways is basically equal; when NO$_x$ is between 970-2060 ppb, the main oxidation pathway is RO_2+NO.

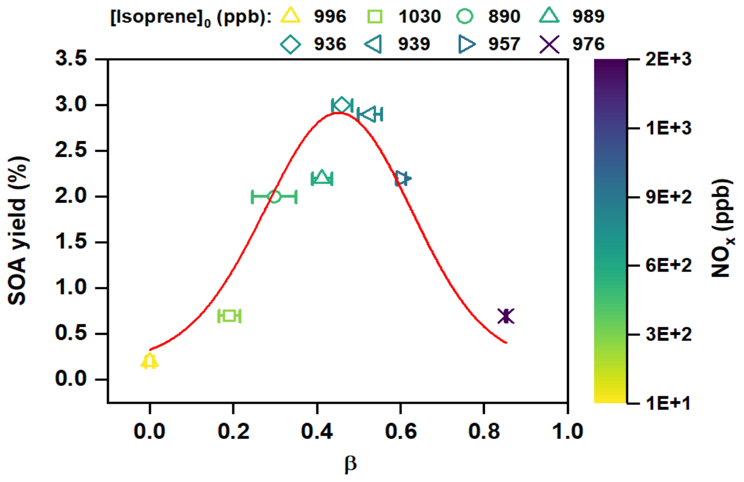

Figure R4. The relationship between β and SOA yield (The different shapes and colors of the data points represent the different concentrations of isoprene and NO_x injected into the chamber). (Figure R4 presents in the revised manuscript as Figure 6).

(3) In this study, we focused on the impact of the changes in RO_2 fate under different NO_x levels on the SOA yield. First, we have illustrated the evolution of the three types VOCs in Figure R5, showing the variations in normalized signals of these VOCs during the reaction process. Then the role of these VOCs in SOA generation process is discussed. Finally, the effect of RO_2 fate on SOA yield under different NO_x conditions is discussed in Section 3.3.

Please see the revised manuscript,page 10-11, lines 285-329, and page 12-13, lines 330-377.

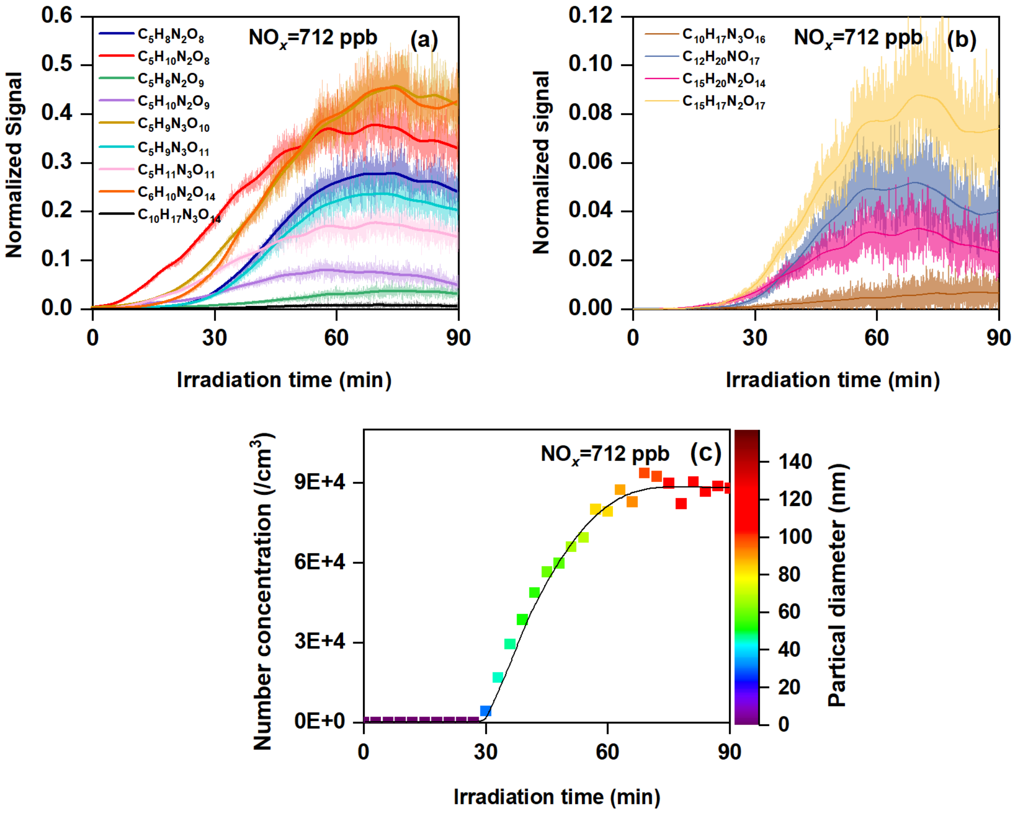

Figure R5. Isoprene SOA formation process under 712 ppb NO$_x$ condition. (a) Evolution of gas phase LVOCs and ELVOCs, (b) evolution of gas phase HOMs-ACCs, and (c) particle number and diameter. (Figure R1 presents in the revised manuscript as Figure 4).

Comments:

5. Line 28: “oxidezene”

Response: Thank you for your comment. We have fixed that mistake in the revised manuscript. Please see page 2, lines 23-28.

Comments:

6. Line 152: The use of HOM in the context of this paper is inadequate. HOMs refer to molecules that incorporate a significant number of O$_2$ through unimolecular isomerization which does not happen in this work according to the presented RO$_2$ fates. The large number of oxygens are from nitrate and peroxynitrate functional groups and peroxides is from RO$_2$+HO$_2$.

Response: We identify HOMs based on Bianchi et al. (2019), which is defined as highly oxygenated organic molecules, referring to gas-phase molecules with 6 or more oxygen atom numbers, formed through the autoxidation of peroxy radicals. Among the gas-phase products identified in this study, we only consider ULVOCs as HOMs. ULVOCs inludes $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$. After subtracting the corresponding oxygen atoms from the nitrate and peroxynitrate functional groups in these compounds, we can see that the number of oxygen atoms in ULVOCs is still greater than 6. Thus, we believe the ULVOCs are HOMs, which originated from unimolecular autoxidation.

<u>Comments:</u>

7. Line 192: "Figure S1 illustrates the simplified formation mechanism of four monomers in this system. $C_5H_8N_2O_8$ is formed form the H shift and unimolecular autoxidation of the $C_5H_8NO_5$-RO_2." This is an incomplete description of the reactions required for this product to form although it is correctly depicted in the SI.

Response: Thank you for your comment. Isoprene first reacts with nitrate radicals, then through autoxidation with addtion of oxygen to form $C_5H_7NO_7$ radical, and finally reacts with NO to regenerate $C_5H_8N_2O_8$. The above modifications have been added to the revised manuscript. Please see page 10, lines 266-267.

Comments:

8. Figure S3: The color scale for the data points in panel b is likely incorrect.

Response: We made a correction by adding a color bar to Figure S2 (also see Figure R6 below). Please see the revised manuscript, page S5, line 111.

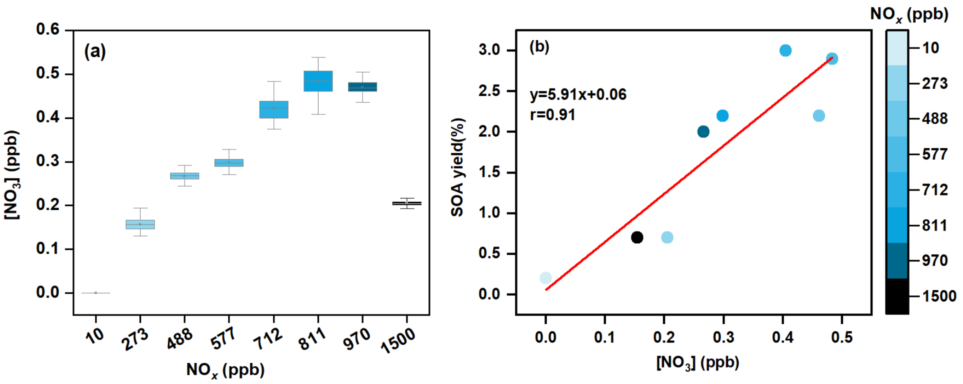

Figure R6. (a) calculated concentrations of NO_3 radicals in the varying NO/NO_2 experiments; (b) correlation between NO_3 and SOA yield. (Figure R6 presents in the revised manuscript as Figure S2).

Response to Reviewer #2

General Comments:

The authors report on their research results on the mechanism of secondary aerosol formation from the photochemical oxidation of isoprene as a function of initial NO_x concentration. The results of the chemical ionization mass spectrometer and secondary aerosol yield measurements examined as a function of initial NO_x concentration presented in this paper are similar to the results of previous papers (D'Ambro et al., 2017; Kroll et al., 2005; 2006). The new experimental results of this study are the systematic investigation of online measurements of secondary products as a function of NO_x, but the NO_x dependence is not discussed in detail in Figs. 3-4 of this paper, and it is difficult to say that the results are sufficiently presented. There is concern about the generality of the conclusions, as the initial VOC concentration is a single point. There is a lack of specific comparison with previous studies. There are related papers that are not cited. The order of explanation of the results is not appropriate in some places. The explanation of the calculation method for Figures 5a and 5b, which are related to the conclusions, is insufficient. Based on the above, I think that this paper needs significant revision. The detailed points are listed below.

Response: We thank the comments and carefully revised our manuscript. Since these comments are individually given by the reviewer in details in the follow section, our responses to the comments are itemized as follows.

Comments:

1. I think that the experimental results of the chemical analysis of SOA composition using CIMS with systematically varied NO_x are new primary information obtained in this study. However, with regard to the CIMS analysis results, only the similarity to previous reports is discussed in the first paragraph of section 3.2, and two points with different NO_x concentrations are shown in Fig. 3. I think that the value of this research as an original paper would be enhanced if detailed experimental results on the initial NO_x concentration dependence of the chemical composition were presented and compared with the results of

the SOA yield. I have written specific comments in Comment (17), so please refer to that as well.

<u>Response</u>: Suggestion taken. We have supplemented two experiments under 488 and 970 NO_x ppb conditions and analyzed the initial NO_x concentration dependence of the chemical composition and the SOA yiled in the chamber. As shown in Figyre R1, along with the inceasing NO_x the normalized signals of LVOCs, ELVOCs and ULVOCs increased and peaked at 712 ppb NOx, then quickly decreased, which is consistent to the NO_x dependence of the SOA yield. For more specific discussion on Figure 5, please refer to our reply for the following Comment (17).

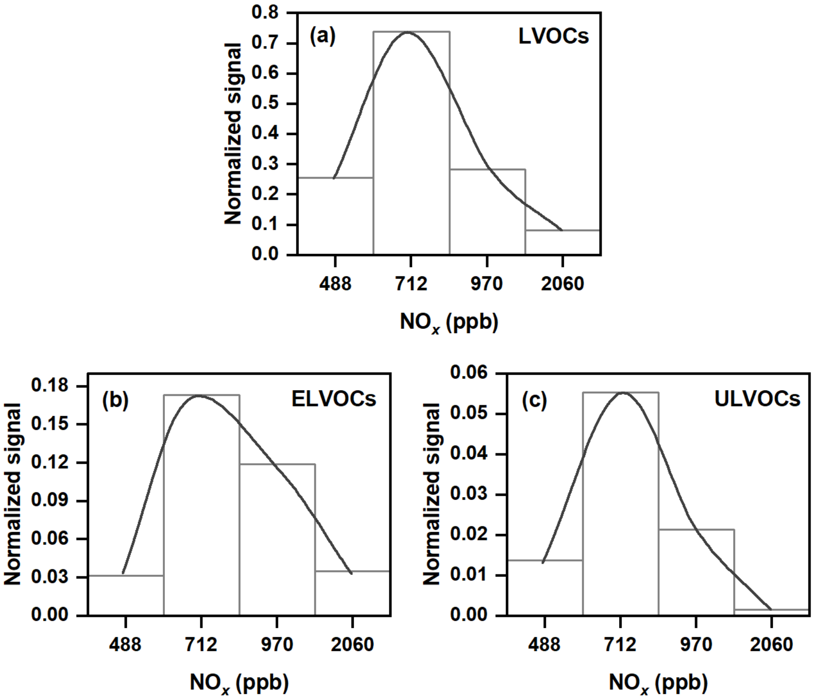

Figure R1. NO_x dependence of three types VOCs (LVOCs, ELVOCs, ULVOCs, according to the calculated value of $\log_{10} C^*$, Table S1). (Figure R1 presents in the revised manuscript as Figure 5)

<u>Comments:</u>

2. Page 12, lines 315-326. This study discusses the results of experiments conducted under conditions where the initial isoprene concentration is kept constant. If the initial isoprene concentration decreases, the concentration of SOA produced also decreases, and the gas particle partitioning shifts to the gas phase side. If the gas particle partitioning shifts to the

gas phase side, there is a possibility that the β value, which is the maximum SOA yield, will be affected. In this study, it was concluded that the SOA yield is maximized when β = 0.5, but it is unclear how universal this conclusion is based on the experimental evidence presented in this study alone. The conclusion should be toned down, or the discussion should be based on additional experiments or additional MCM calculations to confirm the universality of the conclusion under conditions with different isoprene concentrations.

Response: We full understand your concern on the universality of our conclusion about the SOA yield maximum at β = 0.5 and we believ your suggestion is important.

We agree with you that if the initial isoprene concentration decreases, the concentration of SOA produced also decrease. However, the decrease in initial isoprene concentration does not necessariy make the gas particle partitioning shifts to the gas phase side, because the isoprene decrease also reduce the concentrations of gas phase compounds. To confirm this assumption, we supplemented the calculated β values under 273, 488 and 811 NO_x ppb and updated Figure R4. Although we initially tried to keep the concentration of injected isoprene constant, the initial concentration of isoprent was actually not constant due to the variation in the volume each time we injected into the chamber. As seen in the following figure (Figure R4), the initial concentration of isoprene spanned from 890 ppb to 1030 ppb with a difference up to 140 ppb. By adding the addional three data points into the figure (273, 488 and 811 NO_x ppb, Figure R4), we recalculated the SOA yiled dependence, and found tht the β values still conformed to the original dependence (Figure R4), suggesting that variations in the intial concentation of isoprene did not change the β values..Thus, we believe that our conclusion that the SOA yield is maximized when β = 0.5 is universal for different level of isoprenes.

We have updated Figure 7 and revised the discussions according to the above discussions and your comments. Please see the revised discussion in page 13, line 367-777, and page 26, Figure 7.

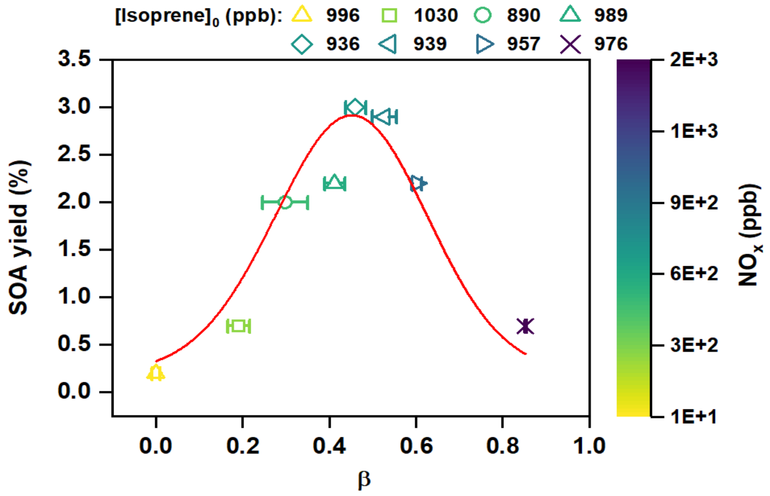

Figure R4. The relationship between β and SOA yield (The different shapes and colors of the data points represent the different concentrations of isoprene and NO$_x$ injected into the chamber). (Figure R4 presents in the revised manuscript as Figure 7).

Comments:

3. Abstract, lines 46-47. As far as I can tell, this is a sentence that is not discussed in the main text. What does it mean that β can be used as a reference? What is the significance of discussing only the yield of isoprene-derived SOA in outdoor observations and atmospheric 3D model calculations, and is it even possible to do so? Or are you saying that future research should focus on the fact that β, which is evaluated for all RO_2, not just isoprene-derived RO_2, can be used as an indicator to evaluate the generation rate of all SOA? There must be differences in volatility between isoprene-derived SOA and other SOA, so it cannot be said that β can be used as a reference based on the results of this study alone. The above points should be discussed in the main text and clarified in terms of their meaning before this sentence is added to the abstract.

Response: Suggestion taken. Our original intention is that β can be used to evaluate all RO_2. But we agree with you that there are differences in volatility between isoprene-derived SOA and other SOA. So, it cannot be said that β can be used as a reference based on the results of this study alone. In order to avoid any possible misleading, we deleted the last sentence of the abstract.

Comments:

4. Lines 39-40 of the abstract. It is difficult to understand why the “fraction” of RO_2+HO_2 and RO_2+NO increases at the same time, when there is a competitive relationship between RO_2+HO_2 and RO_2+NO. Are you referring to the total loss rate caused by RO_2+HO_2 and RO_2+NO?

Response: Yes, in this manuscript we refer to the total loss rate caused by RO_2+HO_2 and RO_2+NO. We have rephrased the sentences, please see page 2, lines 42 and 46, page 4, line 104, page 12, lines 339, page 13, lines 359 and 361.

Comments:

5. Page 3, line 62. In this paragraph, the effect of NO_x on the oxidation reaction of isoprene is discussed from the perspective of physical chemistry. However, I feel that the discussion would be enhanced if the significance of the reaction between biogenic isoprene and anthropogenic NO_x in the atmospheric environment were discussed first. For example, the importance of BVOCs is increasing in countries that have taken measures to combat air pollution due to the reduction of emissions of anthropogenic VOCs and the increase in emissions of plant-derived VOCs caused by global warming (Pfannerstill et al., 2024). We need a more sophisticated understanding of the interaction between biogenic VOCs and anthropogenic NO_x in order to control air pollution.

Ref.: Pfannerstill et al., Temperature-dependent emissions dominate aerosol and ozone formation in Los Angeles, Science, 384, 1324-1329, 2024.

Response: Suggestion taken. We have modified the manuscript according to your comments, please see page 3, lines 58-63.

Comments:

6. Page 6, line 141. The concentration of OH radicals suddenly appears as an experimental result. How was the concentration of OH radicals determined? You need to include an explanation somewhere before here or here.

Response: Suggestin taken. We used an observation-based model (OBM) incorporated with the Master Chemical Mechanism (MCM) to further investigate the changes in the levels of

OH, HO_2 and loss rates of main RO_2 radicals in isoprene photo-oxidation under different NO_x conditions. The relevant explanations are described in section 2.3, page 5, lines 140-142.

<u>Comments:</u>

7. Page 6, lines 145-147. The oxygen atoms that react with H_2O are produced by the photolysis of O_3, not by the photolysis of NO_2. Although this is how it is written in the reaction equation, it seems to me that the text says that the O atoms produced by the photolysis of NO_2 react with H_2O. Please fix this.

<u>Response</u>: We are sorry for the inaccurate description. We corrected the description of the formation of O_3 and OH in the manuscript. Please see page 6, lines 153-155.

<u>Comments:</u>

8. Page 6, lines 150-154. This paragraph discusses the results of Fig. 1. However, the description of the product in the previous paper (Jiang et al., 2017) is not directly related to the results of Fig. 1. If this description is necessary here, the relationship with Fig. 1 should be clarified. Alternatively, the discussion of the product should be made in the section on the results of chemical composition analysis.

<u>Response</u>: Suggestion taken. We agree with you that the descriptions of the product in the paper (Jiang et al., 2017) are not directly related to the research in this paper. We replaced it by other relevant references. Please see page 6, lines 163-164.

<u>Comments:</u>

9. Page 6. The chemical reaction formula in Eq. 1-5 is easy to read immediately after the explanation in the main text (pp. 144-147).

<u>Response</u>: Thank you for your comment. According to your comment (7), the corresponding explanation of the formula(Eq. 1-5) has been modified in the manuscript. Please see page 6, lines 153-155.

Comments:

10. Page 6, lines 158-163. Regarding the NO_x dependence of the chemical mechanism, the RO_2 chemistry described by the authors is important, but consideration of HO_x chemistry, which is involved in the formation of OH, is also important. Kroll et al. supply high concentrations of OH radicals by photolysis of H_2O_2. In this study, on the other hand, RO_2+HO_2 acts as a reaction that stops the HO_x cycle during the reaction time after NO_x is consumed under low NO_x conditions. The yield of SOA may decrease due to the decrease in the generation rate of ELVOC and ULVOC and the increase in their wall loss. In fact, the results of Kroll et al. did not show such a decrease in the SOA yield on the low-NO_x side as in the present study. In order to explain the difference with the results of Kroll et al., it is also necessary to discuss the effect of HO_x chemistry.

Response: We thank you for your very important comments above and have taken your suggestion. We have added additional discussion about HO_x chemistry into the revised version.

(1) The NO_x dependence of HO_x radical concentrations contributes to a certain extent to the NO_x dependence of the isoprene chemistry (Barket et al., 2004). H_2O_2 was added in the experiments conducted by Kroll et al and Xu et al (Kroll et al., 2006; Xu et al., 2014), which would affect the HO_x chemistry. Therefore, the SOA yield on the relatively low NO_x side in this study (Figure 2a) shows a more significant decrease compared to the results of Kroll et al. (2006). This difference can be explained as follows. First, the starting point for SOA yield in Kroll et al. (2006) is higher than that in this study. The formation of SOA is obvious without adding NO_x in Kroll et al. (2006). Because the UV photolysis of added H_2O_2 produces abundant OH radicals, which react with isoprene and produce HO_2 radicals, thus generating SOA. In contrast, under the low NO_x conditions in our study, the more NO_x added, the more O_3 is generated, which in turn generates more OH and HO_2 through HO_x chemistry, and ultimately the more SOA is generated. Therefore, the starting point for SOA yield in Kroll et al. (2006) is higher than that in this study. Second, $[\text{Isoprene}]_0/[NO_x]_0$ ratio at the SOA yield tuning point in this study being higher than that of Kroll et al.(2006). We compared the differences in the SOA yield turning point by using a $[\text{Isoprene}]_0/[NO_x]_0$ ratio,

and found that the SOA yield turning point for the study by Kroll et al (2006) with the addition of H_2O_2 was at $[Isoprene]_0/[NO_x]_0 = 0.33$, while $[Isoprene]_0/[NO_x]_0$ turning point in this study was 1.31(Table 2). Such a difference is reasonable, because in Kroll et al (2006) experiments the addition of H_2O_2 produced higher level of HO_2 radicals, which required more NO to participate in the reaction in order to reach the SOA yield maximum, resulting in the $[Isoprene]_0/[NO_x]_0$ ratio at the SOA yield tuning point in this study being higher than that of Kroll et al.(2006).

We added the above discussions on the HO_x chemistry effect and the differences in results of Kroll et al (2006) into the revised manuscript Page 7, lines 172-194.

(2) We calculated the wall loss coefficients for LVOC, ELVOC, and ULVOC in this study, which are approximately 0.008 s^{-1} (the calculation method is given as Text S1 in the supporting information). The wall loss coefficient for the gas-phase VOCs in this paper is very low, so the influence of gas-phase wall loss on SOA yield and other conclusion is negligible in this study.

Comments:

11. Page 7, line 174. Is OSc the average carbon oxidation state? Explain, as this is the first time it has been mentioned.

Response: Suggestion taken. OSc is the average carbon oxidation state, which is the elemental ratio of SOA (2O/C-H/C) and refers to the average carbon oxidation state after SOA concentration kept constant for approximately 60 min. The related description on the OSc calculation was added into the manuscript. See page 9, line 236-238.

Comments:

12. Figure 3. Change the abbreviations LVOC, ELVOC, and ULVOC in the figure to the same notation as in the abstract.

Response: Suggestion taken.The abbreviation of the Figure 3 has been modified. Please see page 22, Figure 3.

Comments:

13. Page 7, lines 187-191. Zhao et al. and Chen et al. focused on the dark reaction of NO_3+isoprene. If you are going to explain the products detected in this study by citing Zhao et al. and Chen et al., you should explain why there are similarities between the NO_3 reaction and the photo-oxidation in this study, either here or before. In addition, the results of D'Ambro et al. (2017), who detected the products of photo-oxidation using CIMS in the same way as this study, should be compared with the results of this study, and the similarities and differences should be discussed.

Response: Suggestions taken.

(1) Since NO_2 and O_3 are abuandnt in this study and react into N_2O_5, which subsequently pyrolyzes and produces NO_3 radicals. Since only black light (~365 nm) was used in this study, photodegradation of NO_3 (<400 nm) hardly occurs (Reed et al., 2016). Thus, being similar to Zhao et al.(2021) and Chen et al.(2022), NO_3+isoprene chemistry is also important in this study. In our chamber experiments NO_2 photolyzes to produce NO throughout the reaction time, the reaction rate of NO with RO_2 (8.8×10^{-12} cm^3 $molec^{-1}$ s^{-1}) is similar to that of NO with HO_2 (8.1×10^{-12} cm^3 $molec^{-1}$ s-^{1}). Therefore, the high signal intensity of gas-phase products with higher m/z are mostly organic nitrates.We identified the high signal intensity gas-phase products,which are also reported by(Zhao et al., 2021) and (Chen et al., 2022) during their experiments on the nocturnal oxidation of NO_3+isoprene.

The relevent discussion has been added to the revised manuscript. Please see page 8, lines 210-212, page 9-10, lines 254-264.

(2) D'Ambro et al. (2017) used iodide-adduct ion time of flight chemical ionization mass spectrometer coupled to a Filter Inlet For Gases and Aerosols (FIGAERO) to measure products in the gas and particle phases, respectively. In this study we used CIMS of nitrate ion source to determine the gas-phase compounds, which is suitable for the determination of gas-phase low volatility oxidized organic products with a m/z higher than those measured by the FIGAERO (D'Ambro et al. 2017). In this study, we examined the gas-phase products $C_5H_{12}O_{5-6}$ and $C_5H_{11}NO_7$, which were also reported by (D'ambro et al., 2017). These three products are semivolatile organic compounds (SVOC) and intermediate volatility organic

compounds (IVOC), with m/z values of 214, 230, and 259, respectively(Table S1). We compared the differences in their normalized signals under 712 ppb and 2060 ppb NO_x levels. As seen in Figure R7, compared to those under 721 ppb NO_x conditions a significant reduction in normalized signal of the three compounds under 2060 ppb NO_x is consistent with the compounds shown in Figure 3. The signal of the three compounds was quite low event at 712 ppb NO_x, and most entirely disappeared at 2060 ppb NO_x (Figure R8), indicating that they are likely not important in this study.

The above discussion has been added to the manuscript. Please see page 10, lines 275-284. The calculation results of $\log_{10}C^*$ for $C_5H_{12}O_{5\text{-}6}$ and $C_5H_{11}NO_7$ are added to revised SI, page S9, line 141.

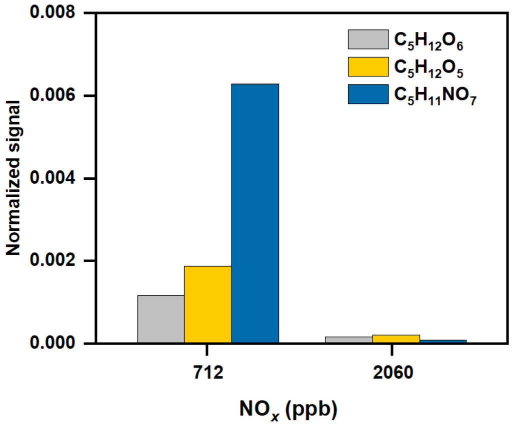

Figure R7. The normalized signal comparison of $C_5H_{12}O_{5\text{-}6}$ and $C_5H_{11}NO_7$ under 712 and 2060 ppb NO_x using HR-TOF-CIMS. (Figure R7 presents in the revised manuscript as Figure S4).

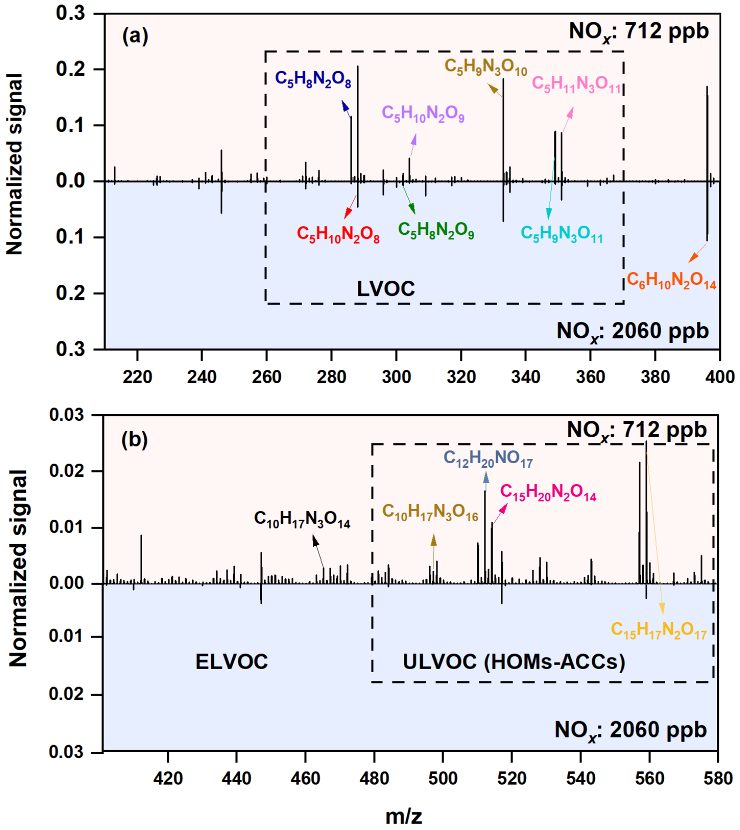

Figure R8. An example of NO_3^- chemical ionization mass spectra illustrating the suppression of highly oxygenated organic molecules formation by NO$_x$. The upper panel shows spectrum measured at 712 ppb NO$_x$ (the highest yield level) and the lower panel shows the spectrum measured at 2060 ppb NO$_x$ (excess NO$_x$, no SOA was produced). Both experiments were measured throughout using ToF-CIMS only. Gas phase molecule identities are based on the literatures (Chen et al., 2022); (Zhao et al., 2021); (Rissanen, 2018); (Wu et al., 2021b). (Figure R8 presents in the revised manuscript as Figure 3).

Comments:

14. Page 7, lines 192-193. Regarding the conditions of this study, it is necessary to discuss the possibility that the addition reaction of the reagent ion NO_3^- affects the measured signal. If it has been confirmed in other studies, please show that as well.

Response: Suggestion taken. Using HNO_3 as the region ion sources to detect HOS hae ben widely used recently and addition reaction of the reagent ion NO_3^- affects the measured signal is very minor, which is negligible. Liu et al (2024) has made a comprehensive evaluation on the accuracy by analyzing nitrophenl and perfluoalkyl acids, and found that the addition reaction of the reagent ion NO_3^- accounted for 1% to 7% of the total measured target compounds. They pointed out that the uncertainty using the HR-TOF-CIMS method is below 8%.$^-$Thuerefoee, we believe the results reported in this study is accurate enough.

<u>Comments:</u>

15. Page 8, lines 201-204. It says "rate coefficient of OH oxidation", but based on the context, isn't it actually the rate (k[OH]) rather than the rate coefficient (k)?

<u>Response</u>: We are sorry for the inaccurate statement. We have replaced "rate coefficient of OH-oxidation were higher than NO_3^-oxidation" with "reaction rate of isoprene-OH were higher than isoprene-NO_3". Please see the revised manuscript, page 10, lines 286-288.

<u>Comments:</u>

16. Page 8, lines 217-222. The explanation that new particle formation occurs due to the ULVOC of the nitrate oligomers detected in this study does not necessarily match the argument based on the MCM calculation results that the decrease in NO causes auto-oxidation and the formation of HOM, which triggers SOA formation. According to Figure 4, the concentration of oligomers increases between 15 and 30 minutes, but the concentration of SOA increases at 30 minutes. It is also possible that new particle formation is triggered by the formation of nitrate-free HOMs, which occur when NO concentrations are low at 30 minutes. The discussion of the mechanism of new particle formation in this paragraph needs to be carefully considered.

<u>Response</u>: Thank you for your important comments above. We agree with you that it is possible that new particle formation is triggered by the formation of nitrate-free HOMs, which occur when NO concentrations are low at 30 minutes. As shown in Figure R9, in our study nitrate-free HOMs did exist after SOA was detected by SMPS. According to the calculated value of $\log_{10} C^*$, $C_{10}H_{14}O_{18}$ is ULVOC (Table S1). Thus, we revised the related discussions. See page 11, lines 301-308.

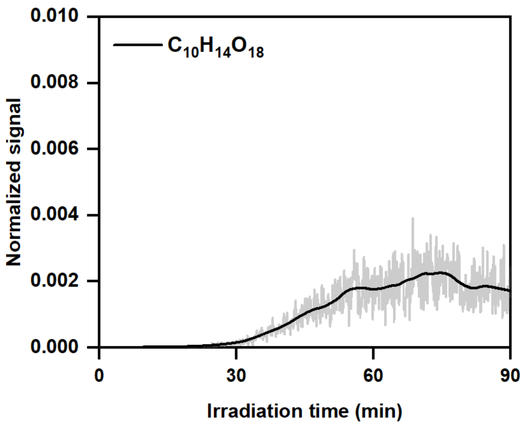

Figure R9. Evolution of nitrate-free HOMs detected by HR-TOF-CIMS under 712 ppb NO_x condition. (Figure R9 presents in the revised manusciprt as Figure S7)

Comments:

17. Page 8-9, lines 223-232. I understand that the NO_x dependence of the concentration of nitrate oligomers is consistent with previous research by Rissanen et al. However, I wonder if there is something new that the authors could investigate by systematically varying the NO_x level. For example, the authors state in the results of Fig. 4 that nitrate oligomers are related to new particle formation. If this is the case, when the NO_x concentration is systematically changed, is there always a consistency between the time when the concentration of nitrate oligomers increases and the time when the concentration of SOA increases? The presentation of such results enhances the value of this research as an original paper and leads to a discussion evaluating the relationship between nitrate oligomers and new particle formation.

Response: We agree with your comments totally and have taken your suggestion. We have supplemented two experiments under 488 and 970 NO_x ppb using HR-TOF-CIMS to investigate the NO_x dependence on LVOCs, ELVOCs and ULVOCs in the gas phase. As shown in Table S1, in this study LVOCs are $C_5H_8N_2O_8$, $C_5H_{10}N_2O_8$, $C_5H_8N_2O_9$, $C_5H_{10}N_2O_9$, $C_5H_9N_3O_{10}$, $C_5H_9N_3O_{11}$ and $C_5H_{11}N_3O_{11}$, ELVOCs are $C_6H_{10}N_2O_{14}$ and $C_{10}H_{17}N_3O_{14}$, while ULVOCs are $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$, respectively. By measuring the gas-phase signals of these molecules , we observed a significant NO_x dependence for LVOCs, ELVOCs and ULVOCs (Figure R1). As seen in Figure R1, the normalized signals of LVOCs, ELVOCs and ULVOCs increased along with an increasing NO_x level, maximized at 712 ppb NO_x, and then quickly decreased. Such a NO_x dependence is similar to the SOA yield dependence on NO_x. From Figures 3 and 4, we can see that in addition to the oxygen atoms from nitrate groups and peroxy nitrate groups, the numbers of remaining oxygen atoms in ULVOCs molecules, such as $C_{10}H_{17}N_3O_{16}$, $C_{12}H_{20}NO_{17}$, $C_{15}H_{20}N_2O_{14}$ and $C_{15}H_{17}N_2O_{17}$, are greater than 6, suggesting that ULVOCs in the chamber are HOMs. As shown by Figures 4, S5 and S6, LVOCs, ELVOCs and ULVOCs are most abundant at 712 ppb NO_x, resulting in the highest number and the largest diameter of particles in the chamber. HOMs almost disappeared at 2060 ppb NO_x, which means that nucleation hardly happened under the very high NO_x condition.(Figure 5, Table 1).

The relevant discussions are showed in the revised manuscript, page 11, lines 311-321.

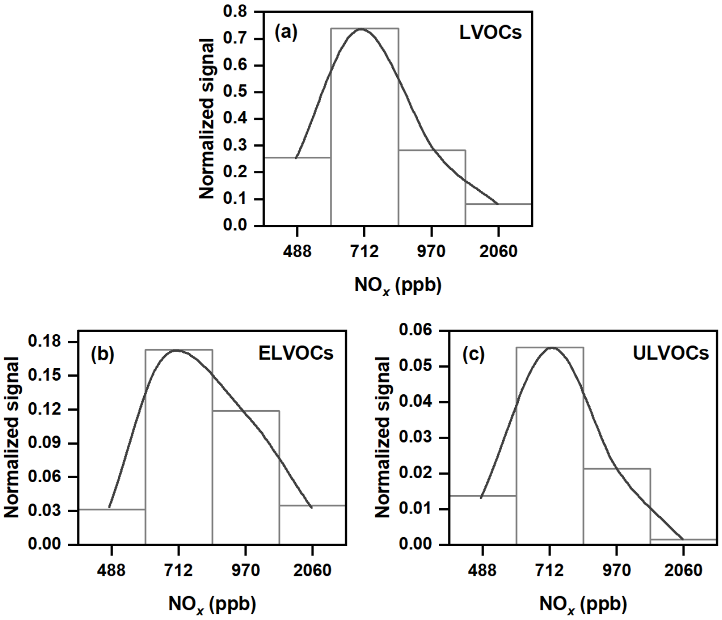

Figure R1. NO_x dependence of three types VOCs (LVOCs, ELVOCs, ULVOCs, according to the calculated value of $\log_{10} C^*$, Table S1). (Figure R1 presents in the revised manuscript as Figure 5)

<u>Comments:</u>

18. Page 9, lines 235-245. I think it would be better to have this discussion after the author presents the experimental results on the NO_x dependence of SOA yield (Fig. 2). I don't think it is necessary to present the CIMS results between Fig. 2 and this discussion.

Response: Suggestion taken. We have reloacted this discussion after presenting the experimental results on the NO_x dependence of SOA yield (Fig. 2). Please see page 7-8, lines 195-206.

Comments:

19. Pages 9-10, lines 246-258. The authors cited a previous NO_3^+ isoprene paper in the section explaining the results of the CIMS. The importance of NO_3 in this paragraph should be discussed before that section. Also, since black light (~365 nm) is used in this study, photodegradation of NO_3 (>400 nm) hardly occurs, and this point should be discussed as being different from the reaction of sunlight in the atmosphere (see, for example, Fig. 6 of Reed et al., 2016).

Ref. Reed et al., Interferences in photolytic NO_2 measurements: explanation for an apparent missing oxidant? Atmos. Chem. Phys., 16, 4707-4724, 2016.

Response: Suggestion taken. We have moved the discussion of NO_3 in this study to page 8, and added additional discussion on the importance of NO_3 in this study. Please see the revised manuscript, pages 8, lines 207-225.

Comments:

20. Page 10, lines 261-265. Does the NO_x concentration in Fig. 5 represent the initial concentration? Also, what point in the reaction does the loss rate, NO concentration, and HO_2 concentration represent? Or are they the average values for the entire calculation interval? A detailed explanation of what the authors calculated is needed.

Response: Suggestion taken.

(1)Yes, the NO_x concentration in Figure 6 (i.e., Figure 5 in the ACPD version) represents the initial concentration. (2) The loss rate in Figure 6a refers to the maximum values of RO_2+NO, RO_2+HO_2, and RO_2+RO_2 during the whole reaction under different initial concentrations of NO_x conditions, which reached their maxima at 50 min of the reaction and were calculated by using OBM-MCM model. (3) NO concentration in Figure 6b refers to the peak value after turning on the black light under different NO_x levels, as measured by NO-

NO_2-NO_x analyzer (Figure R3). (4) HO_2 concentration in Figure 5b refers to the peak value of HO_2 during the reaction calculated by OBM-MCM model under different NO_x conditions. We added these information into the figure caption (see Figure R3 below).

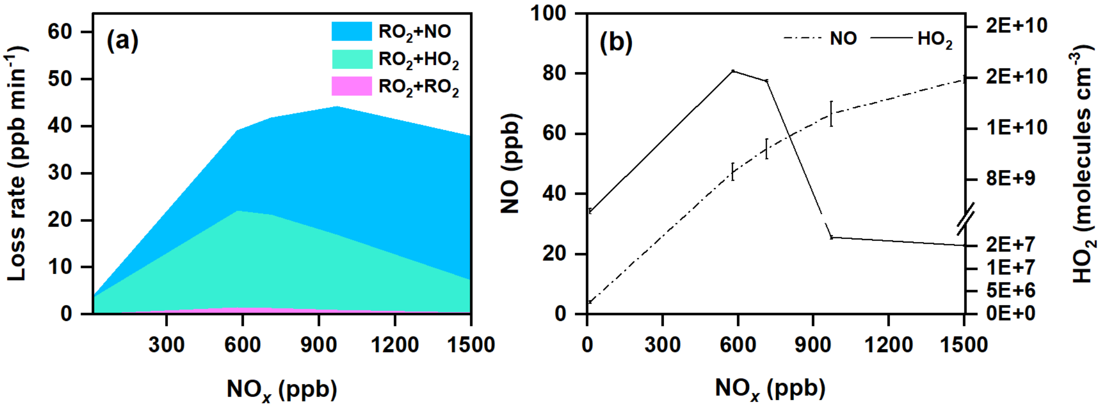

Figure R3. (a) Loss rates of main RO_2 from different oxidation pathways as a function of NO_x concentration calculated by MCMv3.3.1, and (b) variations of NO and HO_2 concentrations._(a) Loss rates of main RO_2 from different oxidation pathways as a function of NO_x concentration calculated by MCMv3.3.1, and (b) variations of NO and HO_2 concentrations. (NO_x in Figures 6a and 6b represent the initial concentrations, in Figure 6a the loss rate is the maximum values of RO_2+NO, RO_2+HO_2, and RO_2+RO_2 during the whole reaction process, while in Figure 6b HO_2 is the maximum value during the whole reaction process) (Figure R3 presents in the revised manuscript as Figure 6).

Comments:

21. Page 10, lines 267-268. The same as the abstract. Are you referring to the total loss rate of RO_2+HO_2 and RO_2+NO, rather than the "proportion" of RO_2+HO_2 and RO_2+NO?

Response: Yes, We have replaced "proportion" with "total loss rate" in the revised manuscript. Please see page 12, line 339.

Comments:

22. Page 10, lines 271-274. The text is difficult to understand. Explain it in plain English. Also, explain the meaning of "no" in "p-HOMs-RO_2 (no<7)".

Response: Suggestion taken. We rewrote these parapgraph and aadded more explanation on the the meaning of "no" in "p-HOMs-RO_2 (no<7)". Please see page 12, lines 343-347.

Comments:

23. Page 12, lines 315-326. The same as comment 20. How were the concentrations of [NO] and [HO_2] determined here? It would be meaningless to conclude that the SOA yield is maximized when β is 0.5 without clearly defining the concentrations.

Response: We agree with your comments. In the discussion of the second paragraph of the conclusion section, we discussed the relative proportions of RO_2+HO_2 and RO_2+NO under different conditions. And here [HO_2] and [NO] are the values after the SOA concentrations became constant. In the revised manuscript, we explained that β is the calculated average value based on the [HO_2] and [NO] concentrations per minute after the SOA has stabilized. Please see page 13, lines 367-368.

Comments:

24. In this study, do the wall adsorption losses of LVOC, ELVOC, and ULVOC, etc. have any effect on the conclusions? Some discussion of this is needed somewhere in the main text.

Response: Suggestion taken. We calculated the wall loss coefficients for LVOC, ELVOC, and ULVOC in this study to be approximately 0.008 s^{-1} (the calculation method is given by Table S1). The wall loss rate for the gas-phase VOCs in this paper is very low, so the influence of gas-phase wall loss was ignored in this study. The description on the gas phase VOC wall loss was added into the revised manuscript, page 5, lines131-132.

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