

Response to Reviewer #2

We are grateful to the reviewer for the thoughtful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer's comments are in black font and our responses are in blue font).

General Comments

Zang and coworkers investigated synergistic effects on the reduction of low-volatile organic compounds during nighttime oxidation of α -pinene. Through laboratory flow tube experiments, the authors found that $\text{NO}_3\text{-RO}_2$ reacts with $\text{CI-RO}_2/\text{OH-RO}_2$ and impedes the formation of low-volatile HOMs that would form a secondary organic aerosol. The results robustly show the synergistic effect on low-volatile organic compound reduction via well-designed experiments under conditions with and without NO_3 radicals. The findings in this study would improve our understanding of complex and more realistic environments where different atmospheric radicals present and affect the oxidation chemistry of biogenic volatile organic compounds.

However, there are drawbacks in this study that need to be improved. My main concern is that the experimental conditions would not successfully represent the ambient atmosphere conditions. In Section 3.4., the authors commented on the input conditions of the model they ran, which were similar to the ambient atmosphere conditions of boreal forests reported in previous studies. While the authors ran the model under humid conditions, lab experiments in this study were performed only under dry conditions. The humidity condition would affect RO_2 /ozonolysis reaction chemistry as well as the fate of Criegee intermediates and the other oxidation products. I suggest conducting additional experiments and validating if the authors would get the same experimental results between dry and humid conditions, and then applying such results to the model to understand if the findings in this study can be applied to the actual ambient environment.

Response: Thanks for the reviewer's comment. We agree that under humid conditions, water vapor may affect the fate of Criegee intermediates (CIs) and RO_2 radicals and thereby product formation during the oxidation of organics. However, the importance of such effects is highly dependent on the molecular size and structure of the precursor organics. Overall, in the α -pinene oxidation system, the influences of RH on the chemistry of CIs and RO_2 , as well as the formation of HOMs are small (see details below).

Kinetics studies have found that the stabilized Criegee intermediates (SCIs) arising from α -pinene ozonolysis can undergo fast unimolecular decay at a rate constant of $60 - 250 \text{ s}^{-1}$ (Vereecken et al., 2017; Newland et al., 2018), which is rapid compared to their reaction with water vapor, in particular for syn-SCIs, under atmospheric conditions (Vereecken et al., 2017; Newland et al., 2018). In addition, the yield of OH radicals from CI decomposition is independent of RH (Atkinson et al., 1992; Aschmann et al., 2002). Consistent with the fast unimolecular reaction kinetics revealed by these studies, recent laboratory measurements have shown that the contribution of SCIs to the formation of gas-phase and particle-phase dimers are small (<20%) during α -pinene ozonolysis (Zhao et al., 2018; Zhao et al., 2022). Furthermore, the molecular composition and abundance of HOM monomers and dimers (Li et al., 2019) and the formation of particle-phase dimers (Zhang et al., 2015; Kenseth et al., 2018) do not change significantly with RH ranging from 3% to 92%. These studies suggest that the humidity condition does not strongly affect the HOM formation chemistry in the α -pinene ozonolysis system. In the present study, using a kinetic model updated with the latest advances in the RO_2 and CI chemistry, we also find a large decrease in $\text{C}_x\text{H}_y\text{O}_z$ -HOMs due to the synergistic $\text{O}_3 + \text{NO}_3$ oxidation under typical nocturnal atmospheric

conditions (RH = 50%), demonstrating that the conclusions obtained from the flow tube experiments are also valid under typical atmospheric conditions. In addition, model simulations show that the variation in RH has negligible influence on the relative changes in $C_xH_yO_z$ -HOMs under typical nocturnal atmospheric conditions (Figure S11).

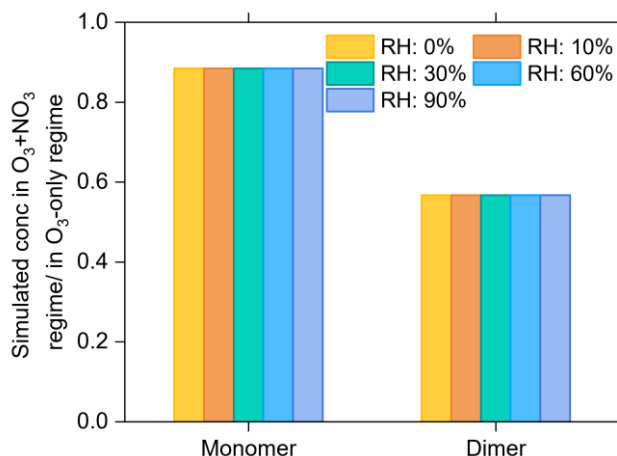


Figure S11 Influence of relative humidity on the relative changes of $C_xH_yO_z$ -HOMs in the $O_3 + NO_3$ regime compared to those in the O_3 -only regime under typical nocturnal atmospheric conditions.

We have added the above discussion to Section 3.4 of the revised manuscript.

Specific Comments

Line 180 - 183: What was the RO_2 fate like at each experiment? Might be helpful if providing figures in the SI

Response: Thanks for the reviewer's comment. We have added a figure showing the RO_2 fate in both O_3 -only and $O_3 + NO_3$ regimes in the SI. We have also added the following statement in Section 3.1.

“Also, NO_3 radicals almost entirely (over 98.5%) react with α -pinene and their reaction with RO_2 has negligible influence on the fate of RO_2 (Figure S2).

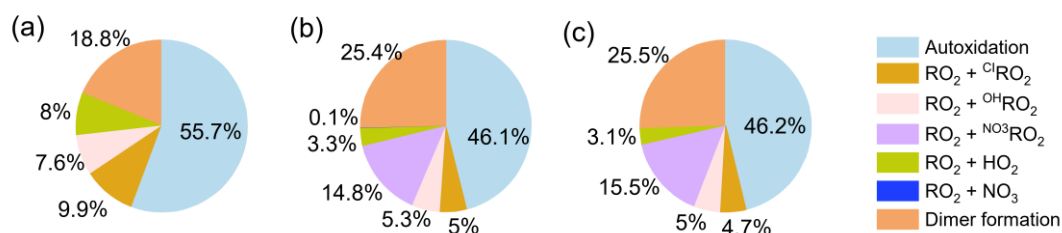


Figure S2 RO_2 fates in the (a) O_3 -only and (b, c) $O_3 + NO_3$ regimes, taking $C_{10}H_{15}O_6$ - ClRO_2 in Exps 3 and 8 as an example. The reactions of $NO_3 + RO_2$ are considered in (b) but not in (c).”

Line 192: Why did you normalize by $\Delta[a\text{-pinene}]_{O_3}$? Please add a more detailed explanation.

Response: There are two major reasons for the strong reduction in HOM formation in the synergistic oxidation regime compared to the O_3 -only regime: (i) the fast competitive consumption of α -pinene by NO_3 radicals, which leads to a reduction in the reacted α -pinene by O_3 ($\Delta[a\text{-pinene}]_{O_3}$) and thereby $C_xH_yO_z$ -HOM signals, and (ii) the cross reactions of ${}^{NO_3}RO_2$ with ClRO_2 or OHRO_2 , which suppress the

autoxidation and self/cross reactions of $^{\text{Cl}}\text{RO}_2$ and $^{\text{OH}}\text{RO}_2$ to form $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$. To quantify the contribution of synergistic cross reactions of $^{\text{NO}_3}\text{RO}_2$ with $^{\text{Cl}}\text{RO}_2/^{\text{OH}}\text{RO}_2$ to the suppressed formation of $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$ in the synergistic oxidation regime, $\text{C}_x\text{H}_y\text{O}_z\text{-HOM}$ signals are first normalized to $\Delta[\alpha\text{-pinene}]_{\text{O}_3}$ in each oxidation regime and then compared between different oxidation regimes.

We have added the following explanations in the revised manuscript.

“The strong reduction in HOM formation in the synergistic oxidation regime compared to the O_3 -only regime is likely due to (i) the fast competitive consumption of α -pinene by NO_3 radicals, which leads to a reduction in the reacted α -pinene by O_3 ($\Delta[\alpha\text{-pinene}]_{\text{O}_3}$, Figure S3) and thereby $\text{C}_x\text{H}_y\text{O}_z\text{-HOM}$ signals, and (ii) the cross reactions of $^{\text{Cl}}\text{RO}_2$ or $^{\text{OH}}\text{RO}_2$ with $^{\text{NO}_3}\text{RO}_2$, which suppress the autoxidation and self/cross reactions of $^{\text{Cl}}\text{RO}_2$ and $^{\text{OH}}\text{RO}_2$ to form $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$. To quantify the contribution of synergistic cross reactions of $^{\text{NO}_3}\text{RO}_2$ with $^{\text{Cl}}\text{RO}_2/^{\text{OH}}\text{RO}_2$ to the suppressed formation of $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$ in the synergistic oxidation regime, $\text{C}_x\text{H}_y\text{O}_z\text{-HOM}$ signals shown in Figure 1a are first normalized to $\Delta[\alpha\text{-pinene}]_{\text{O}_3}$ in each oxidation regime and then compared between different oxidation regimes (see Figure 1b).”

Line 209 - 213: Would the low signal of $\text{NO}_3\text{-RO}_2$ ($\text{C}_{10}\text{H}_{16}\text{NO}_x$) be indeed because of less autoxidation? Or could it be due to $\text{NO}_3\text{-CIMS}$'s limitation on sensitivity over such compounds? Were there possibilities that unidentified compounds were being lost to the wall or particles?

Response: We appreciate the reviewer's point. The low signals of $^{\text{NO}_3}\text{RO}_2$ are partly due to the relatively low sensitivity of nitrate-CIMS to such compounds. In addition, the instrument's mass resolution is not high enough to differentiate the mass closure between some of $^{\text{NO}_3}\text{RO}_2$ and $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$, limiting the detection of $^{\text{NO}_3}\text{RO}_2$ species. During the HOM formation experiments, there was extremely low SOA formation observed by SMPS (see details in our responses to the reviewer #1, comments #2), which would have negligible effects on the production and signals of $^{\text{NO}_3}\text{RO}_2$ species. In addition, the model simulation shows that wall losses only account for 7 – 8% of the total production of $^{\text{NO}_3}\text{RO}_2$ under various experimental conditions.

We have revised the explanations for low $^{\text{NO}_3}\text{RO}_2$ signals in the revised manuscript.

“It should be noted that no obvious signals of highly oxygenated $^{\text{NO}_3}\text{RO}_2$ ($\text{C}_{10}\text{H}_{16}\text{NO}_x$, $x \geq 6$) were observed by nitrate-CIMS in the synergistic $\text{O}_3 + \text{NO}_3$ oxidation system. One possible reason is that nitrate-CIMS exhibits relatively low sensitivity to the organic nitrates. Secondly, the instrument's mass resolution is not high enough to differentiate the mass closure between some of $^{\text{NO}_3}\text{RO}_2$ and $\text{C}_x\text{H}_y\text{O}_z\text{-HOMs}$ with strong peaks (Table S3), limiting the detection of $^{\text{NO}_3}\text{RO}_2$ species. In addition, previous studies revealed that the primary $^{\text{NO}_3}\text{RO}_2$ radicals (i.e., $\text{C}_{10}\text{H}_{16}\text{NO}_5\text{-RO}_2$) in the α -pinene + NO_3 system mainly react to form pinonaldehyde (Kurtén et al., 2017; Perraud et al., 2010).....”

Line 225: What are the "other reactions" in Figure S3? Please specify in the legend or embed those reactions in the figure. Also, would H-abstraction by NO_3 be small?

Response: “Other reactions” are α -pinene ozonolysis and OH oxidation by addition, we have clarified it in the legend.

We have added a discussion about H-abstraction by NO_3 in Section 3.2 of the revised manuscript.

“However, during the NO_3 oxidation of monoterpene, the rate constant for H-abstraction by NO_3 radicals

is $(4 - 10) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is $10^3 - 10^4$ lower than the rate constant for the NO_3 addition channel (Martinez et al., 1998). Besides, the subsequent reactions of RO_2 species formed from H-abstraction by NO_3 radicals should be very similar to those derived from H-abstraction by OH radicals, which was found not important for $\text{C}_x\text{H}_y\text{O}_z$ -HOM formation in the absence of NO (Figure S5). Therefore, the H-abstraction of α -pinene by NO_3 radicals would have negligible influence on $\text{C}_{10}\text{H}_{15}\text{O}_x$ formation.”

Line 233: Do you expect the predominant type of RO_2 would be different among CI- RO_2 , NO_3 - RO_2 , and OH- RO_2 (i.e. if they are primary, secondary, tertiary, or acyl- RO_2)? Could you add more discussion on the NO_3 - RO_2 's termination effect?

Response: Thanks for the reviewer’s comment. The second-generation oxidation processes are strongly inhibited due to an excess of α -pinene in this study. As a result, the predominant type of RO_2 observed is primary RO_2 . Our previous study found that in the absence of NO, acyl RO_2 contributes to a significant fraction of $\text{C}_7 - \text{C}_9 \text{RO}_2$, but a very small fraction of $\text{C}_{10} \text{RO}_2$ (Zang et al., 2023). In the present study, the model simulations show that the consumption of acyl RO_2 by NO_2 lead to reductions of 4 – 5 % and 7 – 12 % in the total $\text{C}_x\text{H}_y\text{O}_z$ -HOM monomer and dimers, respectively. Therefore, the significant reduction in $\text{C}_x\text{H}_y\text{O}_z$ -HOMs in the synergistic oxidation regime is primarily due to the cross reactions of NO_3RO_2 with CIRO_2 or OHRO_2 . In addition, because of the very small contribution of acyl RO_2 to the total $\text{C}_{10} \text{RO}_2$, their consumption by NO_2 leads to less than 2% reduction in the CIRO_2 signals, and the larger decrease in CIRO_2 and related HOMs as compared to the OH-derived ones is mainly due to the more efficient cross reactions of NO_3RO_2 with CIRO_2 than with OHRO_2 .

We have added the discussion of the type of RO_2 in Section 3.2.

“It should be noted that the second-generation oxidation processes are strongly inhibited by the excess of α -pinene in this study, thus the predominant type of RO_2 observed is primary RO_2 .”

In addition, we have added additional discussion regarding the effect of acyl RO_2 consumption by NO_2 and the NO_3RO_2 's termination effect in Sections 3.1 and 3.2.

Section 3.1: “Meanwhile, the depletion of acyl RO_2 by NO_2 only leads to a small reduction (4 – 5% and 7 – 12%, respectively) in total $\text{C}_x\text{H}_y\text{O}_z$ -HOM monomers and dimers in the synergistic regime compared to the O_3 -only regime.”

Section 3.2: “Because of the very small contribution of acyl RO_2 to the total $\text{C}_{10} \text{RO}_2$ (0.4%) (Zang et al., 2023), their consumption by NO_2 leads to less than 2% reduction in the $\text{C}_{10} \text{CIRO}_2$ signals. Therefore, the more significant decrease in signals of CIRO_2 and related HOMs as compared to the OH-derived ones in the synergistic $\text{O}_3 + \text{NO}_3$ regime is primarily due to the more efficient cross reactions of NO_3RO_2 with CIRO_2 than with OHRO_2 .”

Cyclohexane experiment: Why haven't you run any SOA experiments for this condition? If this experiment was just for a sanity check, I suggest moving it to SI. Also, is there a reason why some of OH- RO_2 and HOMs monomer species in Figure 2 are not shown in Figure 4 (i.e., $\text{C}_{10}\text{H}_{17}\text{O}_{10}$, $\text{C}_{10}\text{H}_{18}\text{O}_{11}$)? Additionally, if you labeled specific ON-HOM compounds in Figure 1c, you should have shown how they changed in Figure 4c as well.

Response: The presence of cyclohexane could also affect the SOA formation and composition. But in the present study, we mainly focused on the gas-phase chemistry and did not run SOA experiments with the addition of cyclohexane.

We have added all RO₂, HOMs, and HOM-ONs shown in Figures 1c and 2 to Figure 4.

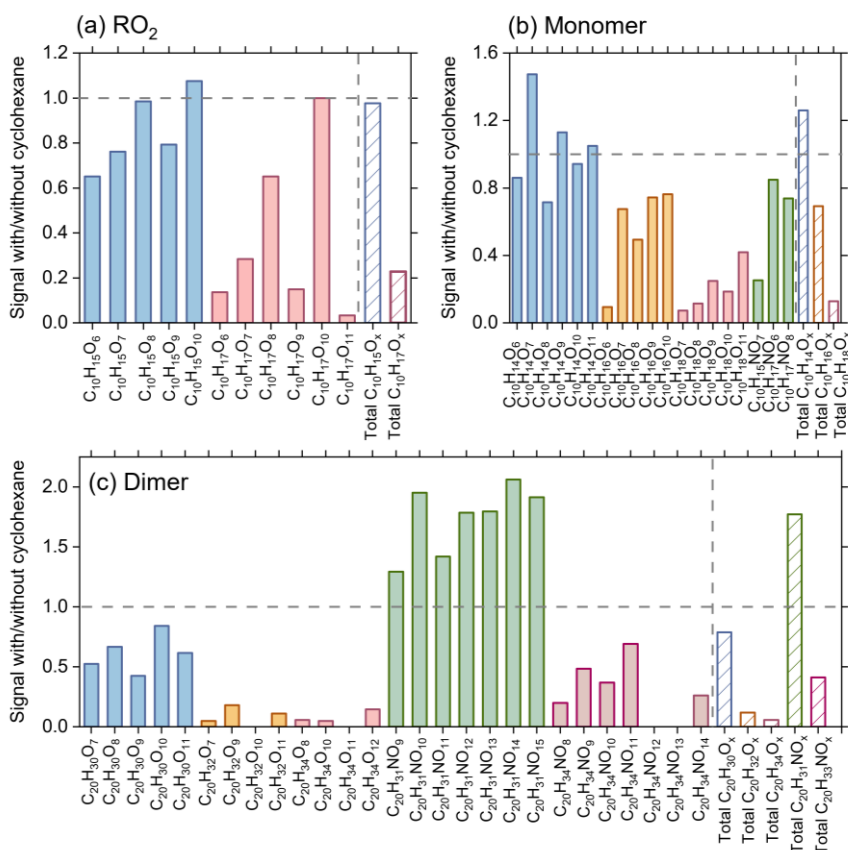


Figure 4. Relative changes in signals of (a) C₁₀ RO₂, (b) C₁₀ HOMs, and (c) C₂₀ dimers due to the addition of 100 ppm cyclohexane as an OH scavenger in the synergistic O₃ + NO₃ regime (Exps 7 and 12).”

Line 301: Weren't the results up to this line showing that CHO-HOMs were terminated via NO₃-RO₂ and CI-RO₂ reactions? Little via OH-RO₂?

Response: Thanks, we have rewritten this sentence in the revised manuscript.

“Compared to the O₃-only regime, there are a remarkable reduction in C_xH_yO₂-HOMs and a strong formation of HOM-ONs, which is mainly due to the efficient cross reactions between ^{NO3}RO₂ and ^{CI}RO₂ in the synergistic oxidation regime.”

Line 328: I suggest the authors shall add more discussion on particle formation and growth. What is the main factor that drives larger mass SOA concentration? Did you identify more numbers of compounds showing higher signals over certain thresholds? Was the entire sum of CPS different by reaction conditions?

Response: Thanks for the reviewer’s comment.

1. We have added more discussion regarding the particle formation and growth and compared the results with the latest studies in Section 3.3 of the main text.

“Figure 6a shows the particle number and mass concentrations formed in the two oxidation regimes in the SOA formation experiments (Table S1, Exps 13 and 14). The particle number concentration decreases by more than 50% whereas the particle mass concentration increases by a factor of 2 in the synergistic

O₃ + NO₃ regime, compared to that in the O₃-only regime. The presence of NO₃ radicals during α -pinene ozonolysis significantly reduces the abundance of ULVOCs and ELVOCs, which are the key species driving particle nucleation (Simon et al., 2020; Schervish and Donahue, 2020), thereby leading to a large reduction in the particle number concentration in the synergistic O₃ + NO₃ regime.

On the other hand, substantial formation of HOM-ONs is expected from the cross reactions of ^{NO3}RO₂ with ^{Cl}RO₂ and ^{OH}RO₂ in the synergistic oxidation regime (Li et al., 2024; Bates et al., 2022), although their signals are relatively low due to the low sensitivity of nitrate-CIMS to ONs in this study. The newly formed HOM-ONs have relatively higher volatilities and are inefficient in initiating particle nucleation, but they are able to partition into the formed particles and contribute to the particle mass growth. Meanwhile, as the particle number concentration decreases drastically in the synergistic oxidation regime, more condensable vapors are available for each particle to grow to larger sizes (Figure 6b), which would in turn favor the condensation of more volatile organic species including ONs due to the reduced curvature effect of the larger particles, ultimately resulting in an increase in SOA mass concentrations. Recently, Bates et al. (2022) also found that in chamber experiments with seed particles, the SOA mass yields were significantly higher during α -pinene oxidation by O₃ + NO₃ than during ozonolysis, mainly due to the substantial formation and condensation of ON dimers.”

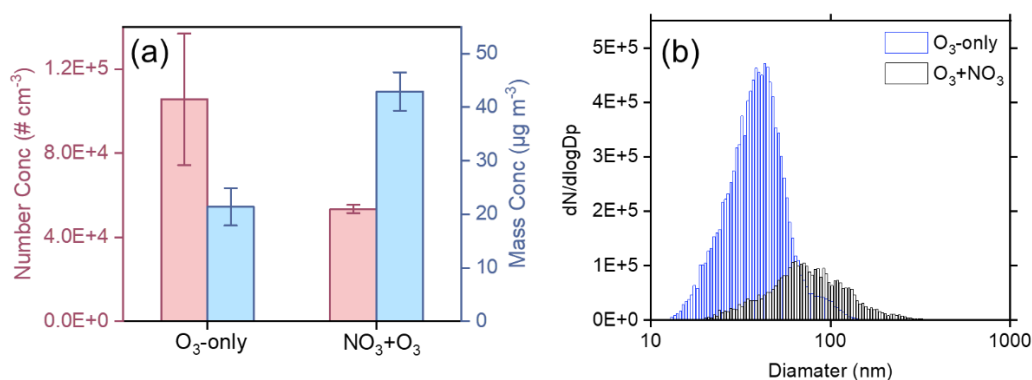


Figure 6. Number and mass concentrations (a), as well as the size distribution (b) of particles formed from the ozonolysis and synergistic O₃ + NO₃ oxidation of α -pinene (Exps 13-14).

2. The sum of CPS is very similar under different reaction conditions, i.e., $(5.9 - 6.2) \times 10^4$ in both oxidation regimes. We have added this information in section 2.1.

“The total ion counts (TIC) with values of $(5.9 - 6.2) \times 10^4$ cps are similar under different reaction conditions.”

Figure 6: At least in SI, I would like to see how size distribution is different between the experimental conditions, and how they vary. That comparison may give some insights into the observation in Figure 6.

Response: Thanks for the reviewer’s comment. As described in our responses to last comment, we have added a figure showing the particle size distributions in different oxidation regimes as well as the relevant discussions to the revised manuscript.

Line 338: How well do the experiments reflect the given ambient condition? How were NO and NO₂ concentrations in the experiments? How would RH variation affect NO₃/N₂O₅? How would the aqueous-phase reaction affect RO₂ formation and fate? Also, high RH would have hydrolysis of ON-HOMs and

the reaction mechanism/products would not be the same as what you explored in your experiments. I think you should validate from additional humid condition experiments if your experimental results can be applied to the atmospheric models regardless of the humidity conditions.

Response: Thanks for the reviewer's comment. In the present study, we aim to elucidate the role of synergistic O₃ and NO₃ oxidation of α -pinene in the formation of low-volatility organic compounds, in particular HOMs, under nighttime conditions. Therefore, we mainly focused on the characterization of the molecular composition and formation chemistry of gas-phase HOMs during the ozonolysis and synergistic O₃ + NO₃ oxidation of α -pinene using a combination of flow tube experiments (primarily with a short residence time to avoid significant production of particles) and detailed kinetic modelling (with the mechanism updated for the latest advances in RO₂ and CI chemistry). The initial NO₂ concentration in the flow tube was 4.5 ppb. To prevent the titration of NO₃ radicals by NO, all the experiments were performed without the addition of NO. To evaluate the atmospheric relevance of the experimental results, we have performed model simulations under typical nocturnal conditions in the boreal forest in Finland and in the southeastern US, for which representative concentrations of NO were considered. As discussed in our responses to the comment #1, the fates of RO₂ and CIs, as well as the formation of HOMs during α -pinene ozonolysis are not strongly affected by the RH. The main findings obtained from the flow tube experiments are corroborated by the model simulations under typical atmospheric conditions.

In this study, we have also performed a few SOA formation experiments to examine the effect of synergistic NO₃ + O₃ oxidation on the formation of SOA. We agree that under humid conditions, aerosol liquid water could affect the aging and composition of SOA, for example, by favoring the hydrolysis of particulate HOM-ONs. However, such processes would not change the main conclusions in the present study (e.g., the nocturnal synergistic NO₃ + O₃ oxidation significantly reduces the formation of ULVOCs from monoterpenes). Given the high abundance and lability of HOMs and HOM-ONs in SOA, the detailed composition and aging chemistry of SOA as well as the influence of RH warrant future investigations.

We have added the following experimental information to Section 2.1 of the revised manuscript.

“The initial NO₂ concentration in the flow tube was ~4.5 ppb. To prevent the titration of NO₃ radicals by NO, all the experiments were performed without the addition of NO.”

We have added the following discussion to Section 3.4.

“In the present study, the flow tube experiments were conducted under dry conditions. Although water vapor may affect the fate of Criegee intermediates (CIs) and RO₂ radicals and thereby HOM formation during the oxidation of organics under humid conditions, there is growing evidence that such effects in the α -pinene oxidation system are small. Kinetics studies have found that the stabilized Criegee intermediates (SCIs) arising from α -pinene ozonolysis can undergo fast unimolecular decay at a rate constant of 60 – 250 s⁻¹ (Vereecken et al., 2017; Newland et al., 2018), which is rapid compared to their reaction with water vapor, in particular for syn-SCIs, under atmospheric conditions (Vereecken et al., 2017; Newland et al., 2018). In addition, the yield of OH radicals from CI decomposition is independent of RH (Atkinson et al., 1992; Aschmann et al., 2002). Consistent with the fast unimolecular reaction kinetics revealed by these studies, recent laboratory measurements have shown that the contribution of SCIs to the formation of gas-phase and particle-phase dimers are small (<20%) during α -pinene

ozonolysis (Zhao et al., 2018; Zhao et al., 2022). Furthermore, the molecular composition and abundance of HOM monomers and dimers (Li et al., 2019) and the formation of particle-phase dimers (Zhang et al., 2015; Kenseth et al., 2018) do not change significantly with RH ranging from 3% to 92%. These studies suggest that the humidity condition does not strongly affect the HOM formation chemistry in the α -pinene ozonolysis system.”

Line 374: Do these HOM monomers and dimers have high numbers of oxygen as what you observed from the lab experiments?

Response: The HOM dimers in the model have high numbers of oxygen (up to 15) as we observed in the flow tube experiments. But for the simulated HOM monomers, their oxygen numbers are no more than 11. This is because the formation of RO₂ with oxygen numbers higher than 11 was not considered in the model, due to the large uncertainty in the autoxidation rate constants of the highly oxygenated RO₂. In fact, the autoxidation rate of the highly oxygenated RO₂ is expected to be small given the significant decrease in the number of active sites for intramolecular H-abstraction in the molecule. As a result, the contribution of the most oxygenated HOMs to the total HOM monomers could be relatively small (Zhao et al., 2018; Claffin et al., 2018).

We have added a relevant discussion to Section 3.4 of the revised manuscript.

“The formation of RO₂ with oxygen numbers higher than 11 was not considered in the model, due to the large uncertainty in the autoxidation rate constants of the highly oxygenated RO₂. In fact, the autoxidation rate of the highly oxygenated RO₂ is expected to be small given the significant decrease in the number of active sites for intramolecular H-abstraction in the molecule. As a result, the contribution of the most oxygenated HOMs to the total HOM monomers could be relatively small (Zhao et al., 2018; Claffin et al., 2018).”

Line 388: How about under very low NO₂, NO₃, and N₂O₅ environments? Would NO₃ still suppress CHO-HOMs during nighttime?

Response: Thanks for the reviewer’s comment. We have considered a relatively low NO₃ concentration of 0.2 ppt in this study. Under this condition, ozonolysis is the primary loss pathway of α -pinene (68%), and NO₃ oxidation contributes to 30% of α -pinene oxidation. The synergistic O₃ + NO₃ oxidation of α -pinene leads to a reduction of 3% and 13% in the formation of C_xH_yO_z-HOM monomers and dimers, respectively. To get a picture for the very low NO₂ and NO₃ conditions, we also performed model simulations with NO₂ and NO₃ concentrations of 0.7 ppb and 0.08 ppt (Zhang et al., 2018), respectively. The simulated result shows that under this condition, the vast majority of α -pinene is oxidized by O₃ (87%), and NO₃ only contributes for 9.6%. As a result, the influence of synergistic oxidation of NO₃ and O₃ on the HOM formation is minor, with a reduction of 1.4% and 6% in the formation of C_xH_yO_z-HOM monomers and dimers, respectively. However, it should be noted that in many forested atmospheres, NO₃ radicals play an important role in the nocturnal oxidation of monoterpenes (Bianchi et al., 2017; Yan et al., 2016; Lee et al., 2018) and significant effects of synergistic O₃ + NO₃ oxidation on low-volatility organics formation are expected.

I think you should add a discussion on the role of CI-RO₂ on dimer & ULVOC formation as well. Additional discussion on this based on the comparison with previous studies would help readers learn about nighttime oxidation chemistry and would help emphasize why your findings are important.

Response: We appreciate the reviewer's point. We have added a discussion on the role of $^{\text{Cl}}\text{RO}_2$ on dimer and ULVOC formation.

“The above model simulations suggest that under nocturnal atmospheric conditions with a very low NO_3 concentration, the RO_2 radical pool is dominated by $^{\text{Cl}}\text{RO}_2$ and their self/cross reactions are a major contributor to ULVOCs such as the highly oxygenated C_{20} dimers as observed in boreal forest (Bianchi et al., 2017). When the NO_3 concentration is high, the production of $^{\text{NO}_3}\text{RO}_2$ becomes significant and their cross reactions with $^{\text{Cl}}\text{RO}_2$ would suppress the formation of ULVOCs.”

Technical comments:

Line 178: Please add a more detailed explanation on the y-axis of Figure 1.

Response: We have redrawn Figure 1, and added more detailed explanations for the y-axis in the figure caption.

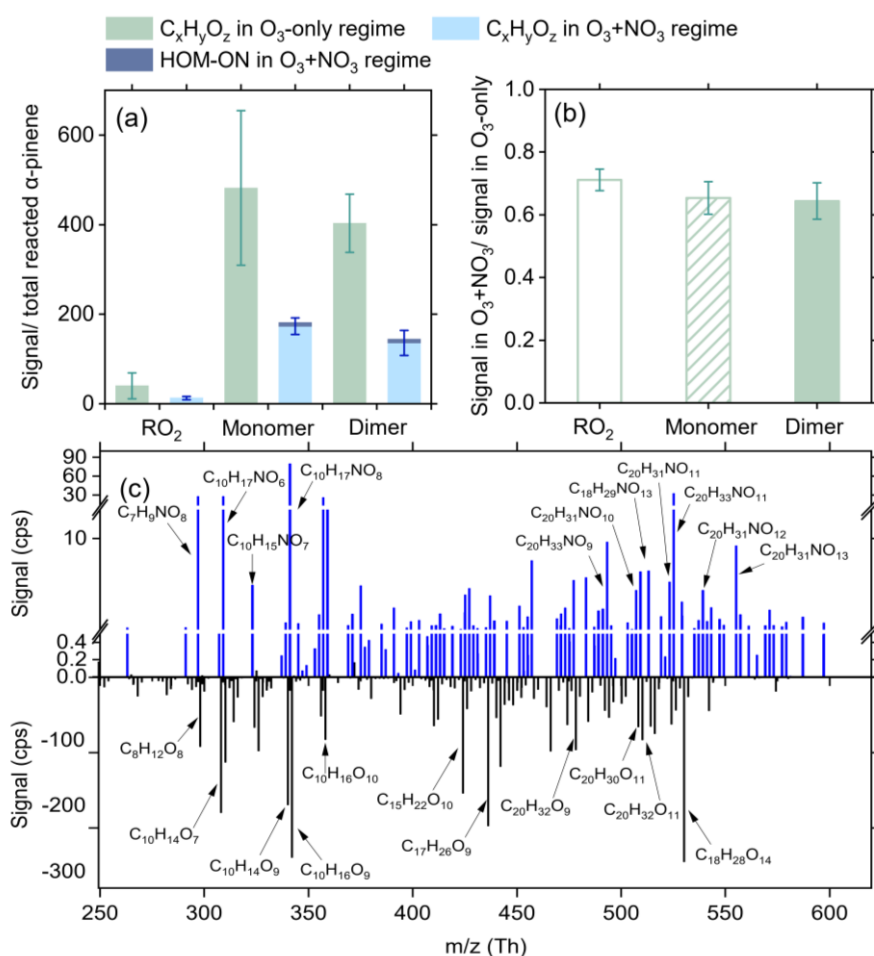


Figure 1 Distributions of RO_2 and HOMs in the O_3 -only and $\text{O}_3 + \text{NO}_3$ regimes. (a) Signals of total RO_2 , as well as HOM monomers and dimers normalized by the reacted α -pinene in each oxidation regime (Exps 1-5, 7-11). (b) Relative changes in the normalized signals of $\text{C}_x\text{H}_y\text{O}_z$ -HOMs in the $\text{O}_3 + \text{NO}_3$ regime versus the O_3 -only regime. Ion signals are normalized to $\Delta[\alpha\text{-pinene}]_{\text{O}_3}$ in each oxidation regime to highlight the suppression effect of the synergistic chemistry between $^{\text{NO}_3}\text{RO}_2$ and $^{\text{Cl}}\text{RO}_2$ or $^{\text{OH}}\text{RO}_2$ on $\text{C}_x\text{H}_y\text{O}_z$ -HOM formation. (c) Difference mass spectrum between the two oxidation regimes. The positive and negative peaks indicate the species with enhanced and decreased formation in the $\text{O}_3 + \text{NO}_3$ regime compared to the O_3 -only regime, respectively.

Line 180 & Table S1: How about adding a footnote of experimental conditions that are compared to each other?

Response: We have added a footnote as follows.

“Exps 1-6 and 7-12 are HOM formation experiments in the O₃-only and NO₃+O₃ regimes, respectively, and Exps 13 and 14 are SOA formation experiments in the two oxidation regimes.”

Line 198: Could you also specify that these monomers & dimers are CHO-HOMs? Because the next figure focuses on ON-HOMs, it would be better to make it clear to avoid confusion.

Response: We have redrawn Figure 1 and specified C_xH_yO_z-RO₂, HOM monomers and dimers in the figure caption.

Line 200: Add "among experiments with same initial a-pinene concentration" before "(Exps 1-10)"

Response: Thanks, we have added it.

Line 215: Were you trying to say that the instrument's resolution is not good enough to separate these? If so, I would say "the instrument's resolution is not enough to differentiate the mass closure between NO₃-RO₂ and CHO-HOMs (Table S3), limiting the detection of NO₃-RO₂ species."

Response: We have revised this sentence as “In addition, the instrument's resolution is not high enough to differentiate the mass closure between some of ^{NO₃}RO₂ and C_xH_yO_z-HOMs (Table S3), limiting the detection of ^{NO₃}RO₂ species.”

Line 257: Please add a statement in general words and specify what this reaction efficiency means to the observations in Figure 1 and/or 2 results.

Response: We have added a statement as follows: “Therefore, we conclude that the cross-reaction rate constants of ^{NO₃}RO₂ + ^{Cl}RO₂ are on average 10 – 100 times larger than those for ^{NO₃}RO₂ + ^{OH}RO₂. This different RO₂ cross-reaction efficiency is the main reason for the significantly larger decrease in the abundance of ^{Cl}RO₂ and related HOMs as compared to the OH-derived ones (see Figure 2).”

Figure 4: What is "CA" on the right axis?

Response: We have replaced “CA” with “cyclohexane” in the revised manuscript.

Line 307 & 311: Figure 5 only has one figure, not any subfigures

Response: We have revised this.

Line 349: I think it would be better to have a pie chart showing RO₂ fate in SI (both from your experiments and model application)

Response: The RO₂ fates in the HOM-formation experiments are added in Figure S2 (see our responses above), and the RO₂ fates under typical atmospheric conditions are added in Figure S10.

We have added a description of the RO₂ fates under typical atmospheric conditions in the revised manuscript.

“When a relatively low NO₃ concentration (0.2 ppt) is considered, the reactions of RO₂ + HO₂, RO₂ + NO, and RO₂ + RO₂ account for ~49%, ~27%, and ~24% of the total RO₂ fate, respectively

(Figure S10a). When the NO₃ concentration is as high as 1 ppt as reported in field studies the RO₂ + RO₂ reactions account for ~34% of the total RO₂ fate (Figure S10b)”

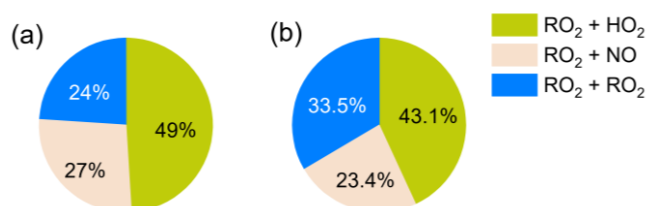


Figure S10 RO₂ fates under typical nighttime atmospheric conditions in the boreal forest in Finland. Conditions with both low (0.2 ppt, a) and high (1 ppt, b) NO₃ concentrations are considered.

Line 369 - 371: Please check the grammar in this sentence.

Response: We have rewritten this sentence as follows.

“As a result, a model simulation was conducted using a 10 times higher OH concentration (5×10^5 molecules cm⁻³). The concentration of NO₃ radicals was 1 ppt and the concentrations of other species were the same as the values mentioned above.”

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