

Response to Reviewer #3

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

This manuscript presents measurements of gas-phase organic peroxy radicals (RO₂), highly oxygenated organic molecules (HOMs), and dimeric compounds formed from oxidation of α -pinene by either O₃ or NO₃ + O₃ in a flow tube reactor made using a nitrate chemical ionization mass spectrometer (NO₃-CIMS), together with kinetic model simulations. The authors find that the formation of ultra-low and extremely low volatility organic compounds (ULVOC and ELVOC) measurable by NO₃-CIMS is significantly reduced in the NO₃ + O₃ system and further conclude that “the formation of new particles in the synergistic oxidation regime is substantially inhibited compared to the O₃-only regime.” However, aerosol mass concentrations in the NO₃ + O₃ system were observed to be a factor-of-two higher than in the O₃-only system, directly contradicting this conclusion. Although the manuscript is well written, in many respects it replicates the work of Li et al. 2024 and Bates et al. 2022. For these reasons, I recommend that publication be considered only after the comments detailed below are addressed.

1. Table S1. Please specify how the initial α -pinene, cyclohexane, and O₃ concentrations were determined (i.e., measured, modeled, or estimated). Please add columns that report the modeled fractions of α -pinene that reacted with each oxidant (i.e., O₃, OH, and NO₃) as well as the modeled initial NO₂ concentrations.

Response: Thanks for the reviewer's comment. We have specified the determination methods of α -pinene, cyclohexane, and O₃ concentrations in the footnote of Table S1.

“The initial concentration of α -pinene was estimated according to its gas concentration in the canister and the dilution ratio in the flow tube, the concentration of cyclohexane was derived assuming that the cyclohexane in the gentle flow of ultra-high-purity N₂ bubbled through its liquid was saturated, and the O₃ concentration was measured with an ozone analyzer (T400, API).”

We have also added the modeled initial NO₂ concentration and the fractions of α -pinene that reacted with each oxidant in Table S1.

2. Figure 1. Figures 1a and 1b are redundant. Please replace Figure 1a with one that shows the signals of total RO₂, total monomer, and total dimer normalized by the total α -pinene reacted for both the O₃ + NO₃ and O₃-only systems, with the bars subdivided to indicate the fractions of CHO and CHON species. Please include a discussion of this figure (e.g., were normalized signals of total monomers and dimers higher in the O₃ + NO₃ or O₃-only system?) and revise L176–196 accordingly. Please also include a CIMS spectrum of an O₃-only experiment for comparison to Figure 1c.

Response: We have replaced Figure 1a with a new figure according to the reviewer's suggestion. In addition, we have provided a difference mass spectrum (i.e., mass spectrum in O₃ + NO₃ regime minus that in O₃-only regime) in Figure 1c, which highlights the changes in the species distribution in the synergistic oxidation regime compared to the O₃-only regime.

We have rewritten the discussion of this figure in Section 3.1 of the revised manuscript.

“The abundance of gas-phase RO₂ species and HOMs in different oxidation regimes is shown in Figure

1a. The species signals are normalized by the total reacted α -pinene in each regime. Compared to the O_3 -only regime, the normalized signals of total RO_2 and HOMs decrease by 62 – 68% in the synergistic $O_3 + NO_3$ regime. Although NO_3 oxidation accounts for a considerable fraction of reacted α -pinene in the synergetic oxidation regime, the signal contributions of HOM-ONs are not significant. This might be due to the low sensitivity of nitrate-CIMS to the ONs formed involving NO_3 oxidation (Section 2.1).Figure 1c shows a difference mass spectrum highlighting the changes in species distribution between the two oxidation regimes. Almost all $C_xH_yO_z$ -HOM species decrease significantly in the $O_3 + NO_3$ regime compared to the O_3 -only regime. Besides, a large set of HOM-ON species are formed, despite their relatively low signals.....”

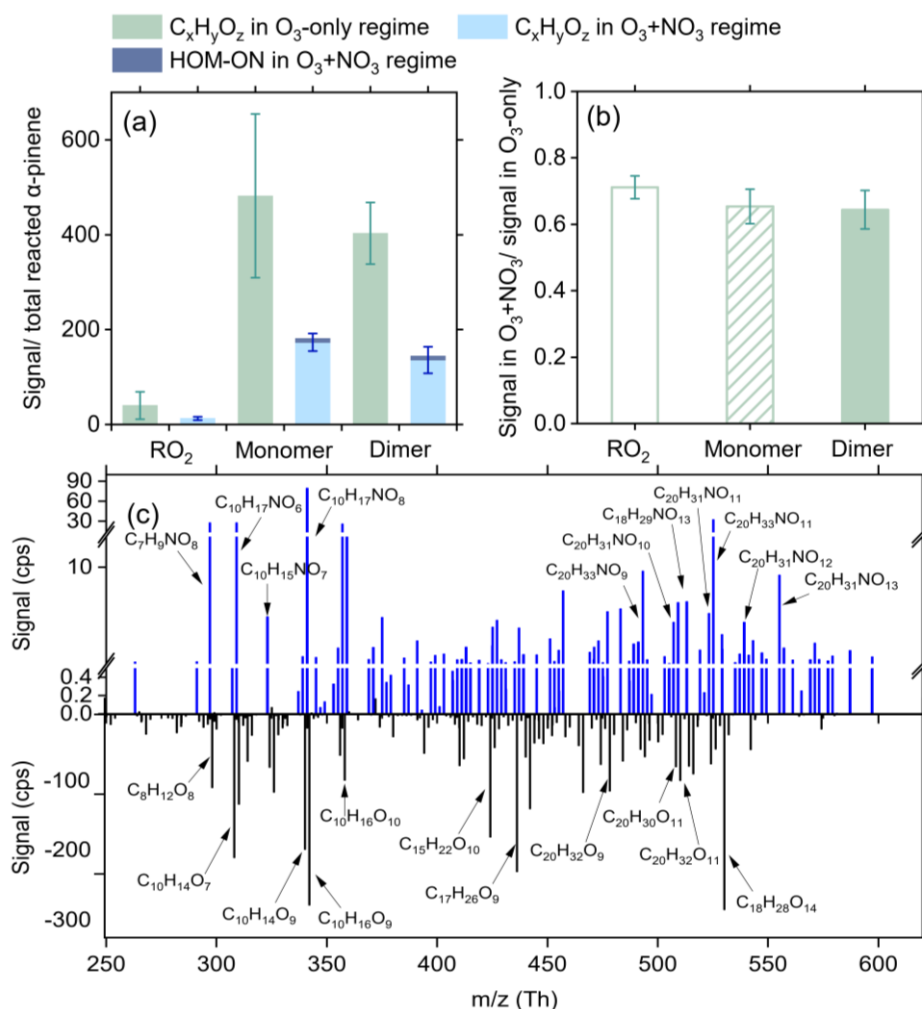


Figure 1 Distributions of RO_2 and HOMs in the O_3 -only and $O_3 + NO_3$ regimes. (a) Signals of total RO_2 , as well as HOM monomers and dimers normalized by the reacted α -pinene in each oxidation regime (Exps 1-5, 7-11). (b) Relative changes in the normalized signals of $C_xH_yO_z$ -HOMs in the $O_3 + NO_3$ regime versus the O_3 -only regime. Ion signals are normalized to $\Delta[\alpha\text{-pinene}]_{O_3}$ in each oxidation regime to highlight the suppression effect of the synergistic chemistry between NO_3RO_2 and $ClRO_2$ or $OHRO_2$ on $C_xH_yO_z$ -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 $O_3 + NO_3$ regime compared to the O_3 -only regime, respectively.

3. CHON Dimers. Both Bates et al. 2022 and Li et al. 2024 observe significant (and often dominant)

contributions of CHON₂ dimers to total (CHO + CHON) dimer signals, yet in this work “HOM-ONs mainly consist of...C₂₀ dimers that only contain one nitrogen atom.” Please include a discussion of potential explanations for these differences.

Response: In this study, some CHON₂ dimers were also observed in the O₃ + NO₃ regime, despite their much lower signals than CHON dimers. A potential explanation for the differences in the contribution of CHON₂ dimers to total dimer signals observed in different studies is the difference in the instrument sensitivity. In general, the nitrate-CIMS has lower sensitivities to ONs than to the C_xH_yO_z-HOM counterparts (Shen et al., 2022; Hyttinen et al., 2015). Bates et al. (2022) used CF₃O⁻ as the reagent ion of CIMS. Its sensitivity to ONs might be significantly higher than the nitrate ion. Li et al. (2024) used CI-Orbitrap with ammonium or nitrate reagent ions to detect oxygenated organic molecules in the synergistic oxidation regime and found that both the signal intensity of ONs and their signal contribution to the total dimers were much larger when using ammonium as reagent ions. Particularly, the signal contribution of CHON₂ is significantly lower than CHON dimers. Despite both using nitrate reagent ions, the nitrate CI-Orbitrap in Li et al. (2024) possibly exhibits higher sensitivities to ONs than the nitrate-CIMS in our study.

We have added a discussion regarding the instrument’s sensitivity in Section 2.1.

“However, the highly oxygenated organic nitrates may have a significantly lower sensitivity compared to the C_xH_yO_z-HOM counterparts, given that the substitution of -OOH or -OH groups by -ONO₂ group in the molecule would reduce the number of H-bond donors, which is a key factor determining the sensitivity of the nitrate CIMS (Shen et al., 2022; Hyttinen et al., 2015). In addition, Li et al. (2024) used CI-Orbitrap with ammonium or nitrate reagent ions to detect oxygenated organic molecules in the synergistic O₃ + NO₃ regime, and found that both the signal intensity of ONs and their signal contribution to the total dimers were much larger when using ammonium as reagent ions.”

We have also added a discussion about the reason why CHON₂ dimers were not significantly observed in this study in Section 3.1.

“The CHON₂ dimers were also observed in the O₃ + NO₃ regime, despite their much lower signals than CHON dimers, which is different from recent studies by Bates et al. (2022) and Li et al. (2024), who found CHON₂ dimers account for an important fraction of the total dimer signals in the synergistic oxidation regime. A potential explanation for this discrepancy is the difference in the instrument sensitivity in these studies (see Section 2.1). In general, the nitrate-CIMS has lower sensitivities to ONs than to the C_xH_yO_z-HOM counterparts (Shen et al., 2022; Hyttinen et al., 2015). Bates et al. (2022) used CF₃O⁻ as the reagent ion of CIMS. Its sensitivity to ONs might be significantly higher than the nitrate reagent ion. In addition, Li et al. (2024) observed a significantly lower signal contribution of CHON₂ dimers using CI-Orbitrap with nitrate reagent ions than with ammonium ions. Despite both using nitrate reagent ions, the nitrate CI-Orbitrap in Li et al. (2024) possibly exhibits higher sensitivities to ONs than the nitrate-CIMS in our study.”

4. Trends in O₃- and OH-Derived RO₂. L226–229 report a larger decrease in the normalized signals of C₁₀H₁₅O_x-RO₂ than C₁₀H₁₇O_x-RO₂ in the O₃ + NO₃ vs. O₃-only system. Conversely, Li et al. 2024 report that “the measured C₁₀H₁₅O_x rose with NO₃ radicals” while “C₁₀H₁₇O_{5,7} radicals from OH chemistry decreased by a factor of 9.” Please include a discussion of these discrepancies and potential explanations.

Response: Li et al. (2024) reported a slight increase in C₁₀H₁₅O_x-RO₂ with increasing NO₃ concentrations,

and indicated that this phenomenon was likely due to the additional $C_{10}H_{15}O_x$ production from the H-abstraction pathway of NO_3 oxidation in their experiments. However, during the NO_3 oxidation of monoterpenes, 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 $10^3 - 10^4$ times 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 $C_xH_yO_z$ -HOM formation in the absence of NO (Zang et al., 2023). Therefore, the H-abstraction of α -pinene by NO_3 radicals would have negligible influence on $C_{10}H_{15}O_x$ formation.

As Li et al. (2024) used a low α -pinene concentration and relatively high O_3 and NO_3 concentrations in their experiments, the secondary oxidation of aldehydes, such as the substantially formed pinonaldehyde, by NO_3 radicals might be important, which could contribute to the additional formation of $C_{10}H_{15}O_x$ - RO_2 . However, in the present study, the second-generation oxidation processes are strongly inhibited due to the excess of α -pinene, therefore the formation of secondary $C_{10}H_{15}O_x$ - RO_2 is not important.

In addition, Li et al. (2024) reported that the fraction of α -pinene oxidized by OH radicals decreased from 44% in the O_3 oxidation system to 6% in the $O_3 + NO_3$ system mainly due to the depletion of OH radicals by NO_2 and the competitive consumption of α -pinene by NO_3 radicals, which resulted in a significant decrease in $C_{10}H_{17}O_{5,7}$ radicals from OH chemistry as observed in their experiments. However, in the present study, because of the excess of α -pinene, over 97% of OH radicals react with α -pinene and the depletion of OH by NO_2 is minor (0.2 – 1.3%) in the $O_3 + NO_3$ regime. The reduction in the reacted α -pinene by OH radicals is less than 10% compared to the O_3 -only regime. As a result, a smaller decrease in $C_{10}H_{17}O_{5,7}$ radicals was observed in our study.

We have added the above discussions in Section 3.2 of the revised manuscript.

5. Figure 3. How/why were these particular RO_2 and HOM species selected? Why not report simulated ratios for all RO_2 and HOMs in Figure 2 as well as for total CI- RO_2 , OH- RO_2 , CI-HOM, and OH-HOM? Please reformat figure to make radicals open symbols and HOMs closed symbols.

Response: Thanks for the reviewer's comment. We have added more RO_2 and HOMs in Figure 3. However, as detailed oxidation mechanisms of α -pinene are still not well understood (especially for the RO_2 autoxidation), it is difficult to simulate all species well using one set of parameters. In addition, the autoxidation rate constants for the highly oxygenated RO_2 (with oxygen numbers larger than 11) are even more uncertain, thus we did not add them to the figure. Overall, the RO_2 and HOMs shown here have relatively high abundance. Although the data points seem more discrete with the addition of more compounds, it is still the case that the best model-measurement agreements are obtained when k_{NO_3+CI}/k_{NO_3+OH} is 10 – 100.

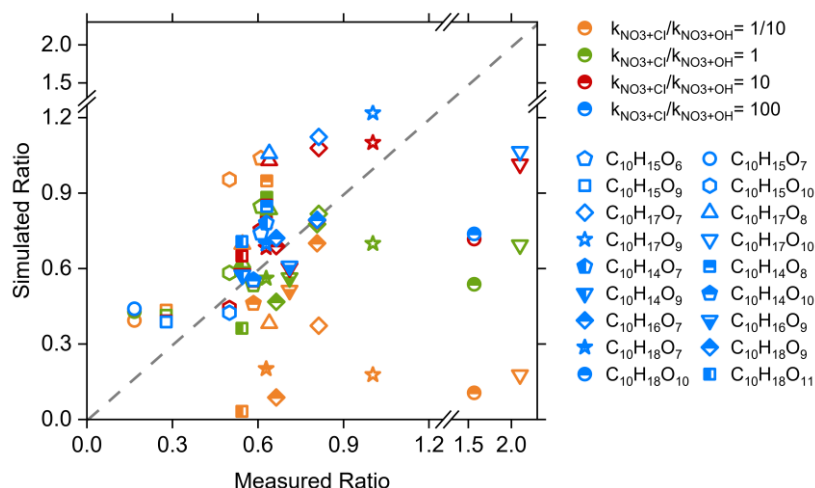


Figure 3. Measurement-model comparisons of the signal ratios of different C₁₀ RO₂ and HOMs in the synergistic O₃ + NO₃ regime vs. the O₃-only regime. The cross-reaction rate constant of $\text{NO}_3\text{RO}_2 + \text{ClRO}_2$ was set to $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the rate of $\text{NO}_3\text{RO}_2 + \text{OHRO}_2$ was varied from $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the model.

6. RO₂ Rate Constants and Branching Ratios. This work sets the rate constant for $\text{NO}_3\text{RO}_2 + \text{ClRO}_2$ to $1 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ and then constrains the rate constant for $\text{NO}_3\text{RO}_2 + \text{OHRO}_2$ to be $1 \times 10^{-13-14} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$. Bates et al. 2022 constrains the bulk rate constant for NO_3RO_2 self/cross reactions to be $1 \times 10^{-13} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ with an upper limit of $1 \times 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$. Please include a discussion that justifies and compares the chosen rate constants. Additionally, Bates et al. 2022 report a branching fraction to the ROOR for $\text{NO}_3\text{RO}_2 + \text{NO}_3\text{RO}_2$ self/cross reactions of 16% while the ROOR branching fraction for the self-reaction of ethene-derived RO₂ was recently shown by Murphy et al. 2023 (DOI: 10.1039/D3EA00020F) to be over an order of magnitude higher than previously assumed (23% vs. 1%). What branching fraction to the ROOR was assumed for the kinetic modeling? Did it vary depending on the identity of the RO₂ (i.e., NO_3RO_2 vs. OHRO_2 vs. ClRO_2)? Please include a sensitivity analysis that explores the impact of the assumed ROOR branching ratio(s) on the modeling results.

Response: Thanks for the reviewer's comments.

(1) Recently, Zhao et al. (2018) revealed the bulk rate constant for ClRO_2 and OHRO_2 self/cross reactions to be $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and Bates et al. (2022) constrained the rate constant for NO_3RO_2 self/cross reactions to be $1 \times 10^{-13} - 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the present study, a default rate constant of $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was chosen for $\text{NO}_3\text{RO}_2 + \text{ClRO}_2$. Considering that there remains large uncertainty in this rate constant, we have conducted a sensitivity analysis to evaluate its influence on the ratio of $k_{\text{NO}_3+\text{Cl}}/k_{\text{NO}_3+\text{OH}}$. It should be noted that the self/cross-reaction rate constants of ClRO_2 and OHRO_2 are held constant at $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Zhao et al., 2018) in this analysis. As shown in Figure S6, when the $\text{NO}_3\text{RO}_2 + \text{ClRO}_2$ rate constant increase from $2 \times 10^{-13} - 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the best agreements between modelled and measured signal ratios of RO₂ and HOMs are achieved consistently with a $k_{\text{NO}_3+\text{Cl}}/k_{\text{NO}_3+\text{OH}}$ ratio of 10 – 100. These results suggest that the uncertainty in the $\text{NO}_3\text{RO}_2 + \text{RO}_2$ kinetics would not alter the conclusion regarding the relative reaction efficiency of $\text{NO}_3\text{RO}_2 + \text{ClRO}_2$ versus $\text{NO}_3\text{RO}_2 + \text{OHRO}_2$.

We have added the above discussion in Section S2 of the Supplement.

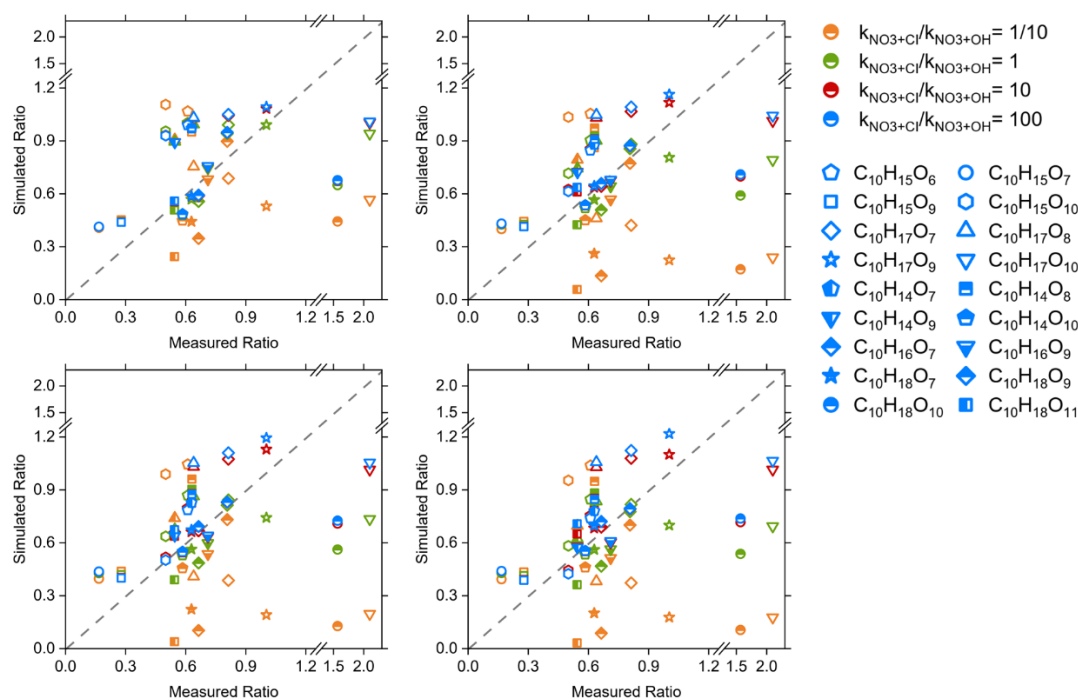


Figure S6 Measurement-model comparisons of the signal ratios of different C_{10} RO₂ and HOMs in the synergistic O₃ + NO₃ regime vs. the O₃-only regime. The cross-reaction rate constant of $^{NO_3}RO_2 + ^ClRO_2$ was set to $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in (a), $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in (b), $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in (c), $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in (d).

(2) Recent studies suggested that the ROOR dimer formation branching ratio from the highly oxygenated RO₂ are fast (Berndt et al., 2018; Molteni et al., 2019), therefore a relatively high dimer formation branching ratio of 50% was used in this study. This branching ratio does not change with different RO₂ cross reactions. To estimate the influence of dimer formation branching ratio on the simulated changes in RO₂ and related HOM concentrations in the synergistic O₃ + NO₃ regime vs. the O₃-only regime, we have conducted a sensitivity analysis of this ratio and added the following discussion to Section S3 of the Supplement.

“Currently, quantitative constraints on the ROOR dimer formation branching ratio are rather limited. Recent studies suggested that the dimer formation rates from the highly oxygenated RO₂ are fast (Berndt et al., 2018; Molteni et al., 2019), therefore a relatively high and consistent dimer formation branching ratio of 50% was used for different RO₂ (e.g., $^{Cl}RO_2$, $^{OH}RO_2$, $^{NO_3}RO_2$) in this study. Considering the large uncertainties in this branching ratio, we conducted a sensitivity analysis to evaluate its influence on the relative changes in RO₂ and related HOM concentrations in the synergistic O₃ + NO₃ regime versus the O₃-only regime. As shown in Figure S8, as the dimer formation branching ratio increases from 9% to 50%, the variation in the abundance $C_xH_yO_z$ -RO₂ and HOMs due to the concurrence of NO₃ oxidation changes slightly (< 9% and < 10%, respectively). These sensitivity analyses indicate that the uncertainties in the RO₂ autoxidation rate and dimer formation branching ratio slightly affect the simulated distribution of RO₂ and HOMs across different oxidation regimes but do not significantly change the k_{NO_3+Cl}/k_{NO_3+OH} ratio obtained in this study.”

In addition, we have added the following statement to Section 3.2 of the main text.

“Further sensitivity analyses on the rate constant and dimer formation branching ratio of RO₂ cross

reactions indicate that the uncertainties in these reaction kinetics do not alter the conclusion regarding the $k_{\text{NO}_3+\text{Cl}}/k_{\text{NO}_3+\text{OH}}$ ratio either (see details in Sections S2 and S3).”

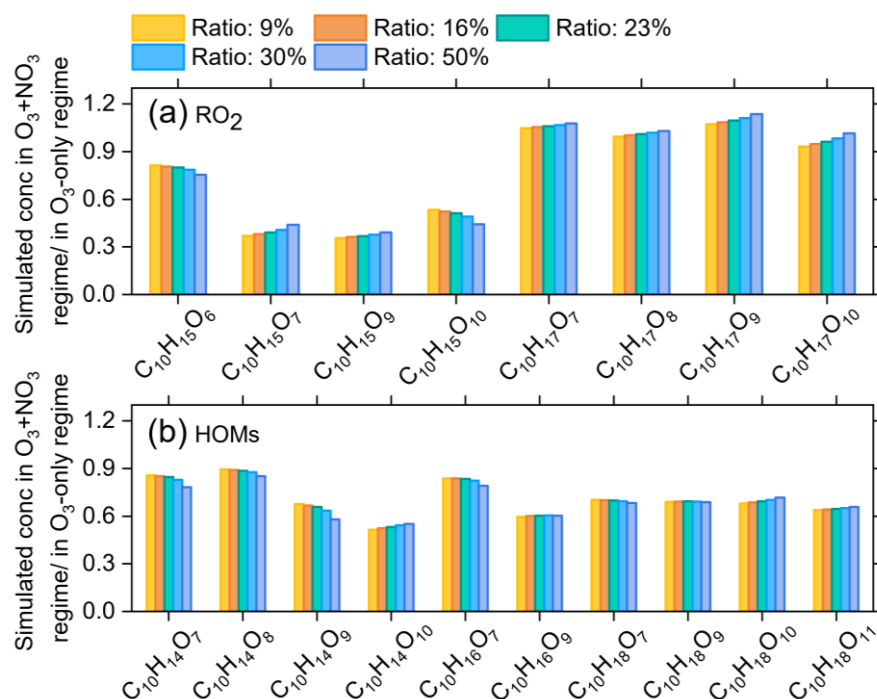


Figure S8 Influences of the dimer formation branching ratio on the relative changes in RO₂ and related HOM concentrations in the synergistic O₃ + NO₃ regime vs. the O₃-only regime.

7. OH Scavenger Experiments. Based on results from the OH scavenger experiments, it is suggested that “the cross-reaction of $^{\text{Cl}}\text{RO}_2 + ^{\text{NO}_3}\text{RO}_2$ is fast compared to that of $^{\text{Cl}}\text{RO}_2 + ^{\text{Cl}}\text{RO}_2$ and $^{\text{Cl}}\text{RO}_2 + ^{\text{OH}}\text{RO}_2$.” However, the observed trends are determined by the relative reactivities (concentrations \times rate constants) of the $^{\text{NO}_3}\text{RO}_2$, $^{\text{Cl}}\text{RO}_2$, and $^{\text{OH}}\text{RO}_2$ toward reaction with $^{\text{Cl}}\text{RO}_2$. As such, without knowledge of the RO₂ concentrations, an assessment of the relative magnitudes of the rate constants cannot be made. That said, in order to observe both C₂₀H₃₀O_x and C₂₀H₃₁NO_x signals, the $^{\text{Cl}}\text{RO}_2 + ^{\text{Cl}}\text{RO}_2$ and $^{\text{Cl}}\text{RO}_2 + ^{\text{NO}_3}\text{RO}_2$ reactions must be competitive. As such, the qualitative statement in L292–294 is valid.

Response: We appreciate the reviewer’s point. In the revised manuscript, we have changed the qualitative statement to “Such an enhanced production of C₂₀H₃₁NO_x as compared to the slightly decreased formation of C₂₀H₃₀O_x indicates that the $^{\text{Cl}}\text{RO}_2 + ^{\text{NO}_3}\text{RO}_2$ reactions are competitive compared to the $^{\text{Cl}}\text{RO}_2 + ^{\text{Cl}}\text{RO}_2$ and $^{\text{Cl}}\text{RO}_2 + ^{\text{OH}}\text{RO}_2$ reactions.”

8. Figure 4. Please report ratios for all RO₂, HOMs, and dimers in Figure 2. The vertical line in panel b is misplaced. The x-axis labels in the total column of panel c are mislabeled. The y-axis labels should be signals not concentrations. Please use the same color/labeling schemes in Figures 2 and 4.

Response: Thanks for the reviewer’s suggestion. We have added all RO₂, HOMs, and HOM-ONs shown in Figures 1c and 2 to Figure 4. We have also corrected all the labelling and format issues pointed out by the reviewer.

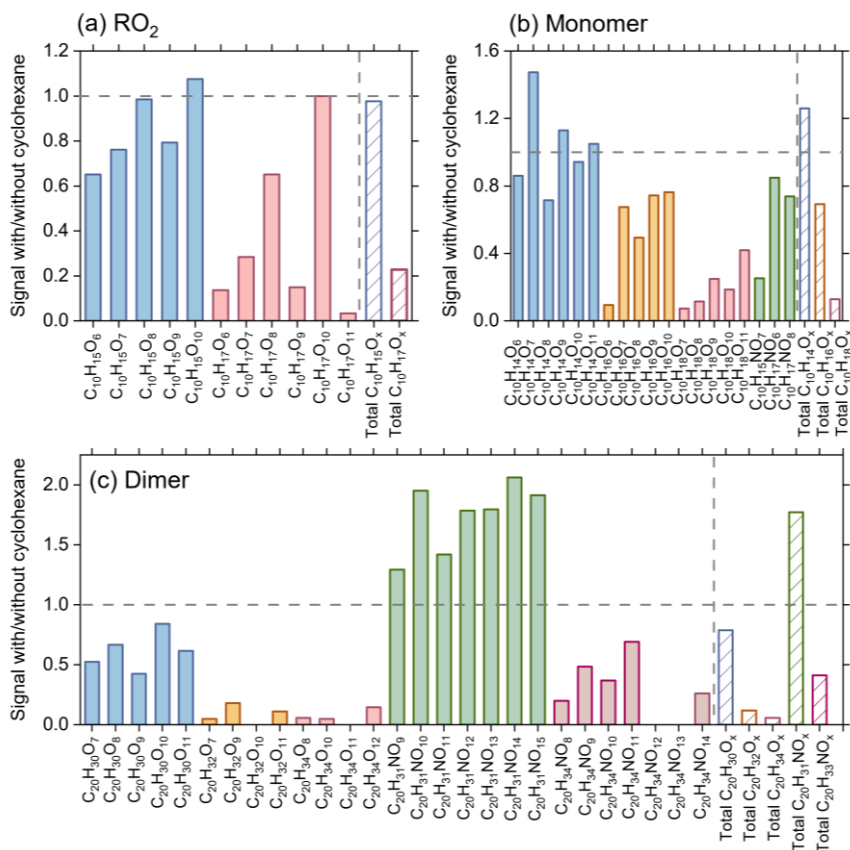
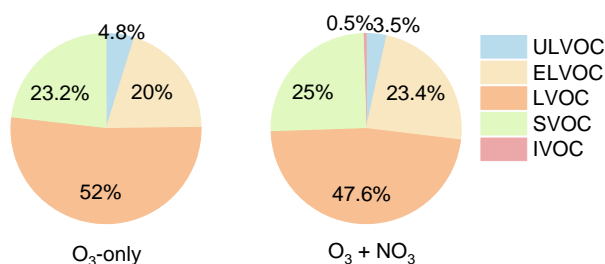


Figure 4. Relative changes in signals of (a) C₁₀ RO₂, (b) C₁₀ HOMs, and (c) C₂₀ dimers due to the addition of 100 ppm cyclohexane as an OH scavenger in the synergistic O₃ + NO₃ regime (Exps 7 and 12).

9. Figure 5. Analogous to Figures 3b and 3c in Li et al. 2024, please include pie charts showing the fractional contributions of total (CHO + CHON) IVOC, SVOC, LVOC, ELVOC, and ULVOC to the total normalized signals measured in the O₃ + NO₃ and O₃-only systems. Please use the same color/labeling schemes in Figures 5 and 7.

Response: Thanks for the reviewer's comments. Because the nitrate-CIMS exhibits a relatively low sensitivity to the ONs in this study, the pie charts showing the fractional contributions of different species groups are not a very accurate representation of the volatility changes across the two oxidation regimes. As shown in figures below, although the contribution of ULVOCs decreases in the O₃ + NO₃ regime compared to the O₃-only regime, the contribution of ELVOCs increases in the O₃ + NO₃ regime. This phenomenon is due to the significant decrease in the highly abundant C₁₀ HOMs, resulting in a large reduction in LVOCs and SVOCs. Meanwhile, ONs contribute less to the LVOCs and SVOCs due to their low signals. As a result, the contribution of LVOCs decreases significantly, leading to a slightly increased contribution of ELVOCs in the O₃ + NO₃ regime. We noticed that in Li et al. (2024), the two pie charts showing the contributions of volatility classes reflected the pure O₃ and NO₃ chemistry, respectively, rather than the O₃-only and O₃ + NO₃ chemistry. Even so, the contributions of LVOCs, SVOCs, and IVOCs did not change significantly between the two systems in their study.



In the revised manuscript, we have used the same color and labelling schemes in Figures 5 and 7.

10. Compound Abundances. It is important to note that “abundances” (e.g., L311–313) are measured CIMS signals and that different compounds could potentially have different CIMS sensitivities.

Response: Thanks for the reviewer’s comment.

In this study, we assume that the C_xH_yO_z-HOMs derived from ozonolysis and OH oxidation of α-pinene exhibit the same sensitivity in nitrate-CIMS. However, the highly oxygenated organic nitrates may have a significantly lower sensitivity compared to the C_xH_yO_z-HOM counterparts, given that the substitution of -OOH or -OH groups by -ONO₂ group in the molecule would reduce the number of H-bond donors, which is a key factor determining the sensitivity of the nitrate CIMS (Shen et al., 2022; Hyttinen et al., 2015).

Considering that different compounds could potentially have different CIMS sensitivities, we have conducted a sensitivity analysis by using different instrument sensitivities for different compounds to clarify their influences on the relative changes in RO₂ and HOMs in the O₃ + NO₃ regime versus the O₃-only regime. Taking a 10 times higher sensitivity to the compounds with an O/C ratio less than 0.7, the total signals are elevated in both oxidation regimes, but there remain significant decreases in total RO₂ and HOM signals in the synergistic oxidation regime compared to the O₃-only regime (Figure S4a). In addition, given that the sensitivity of nitrate-CIMS to ONs are relatively low, a 10 times higher sensitivity was also considered for the ONs. Under this condition, although ONs make a larger contribution to the total HOM monomers and dimers in the O₃ + NO₃ regime (Figure S4b), the signals of both total and C_xH_yO_z RO₂ and HOMs still decrease significantly due to the presence of NO₃ oxidation. Therefore, different instrument sensitivities to RO₂ and HOMs with different oxygenation levels would not significantly influence the results (e.g., Figure 1) in this study.

We have added the above first paragraph to Section 3.1 of the main text and the second paragraph to Section S1 of the supplement.

We have also added the following statement to Section 3.1.

“Although there remain considerable uncertainties in instrument sensitivities to different compounds, sensitivity analyses suggest that varying the CIMS sensitivities to RO₂ and HOMs by a factor of 10 would not significantly influence their relative distribution across different oxidation regimes (see Section S1 for details).”

In addition, considering the high uncertainty in the instrument sensitivities to ONs, we have deleted the discussion regarding the abundance of ONs in L311-313.

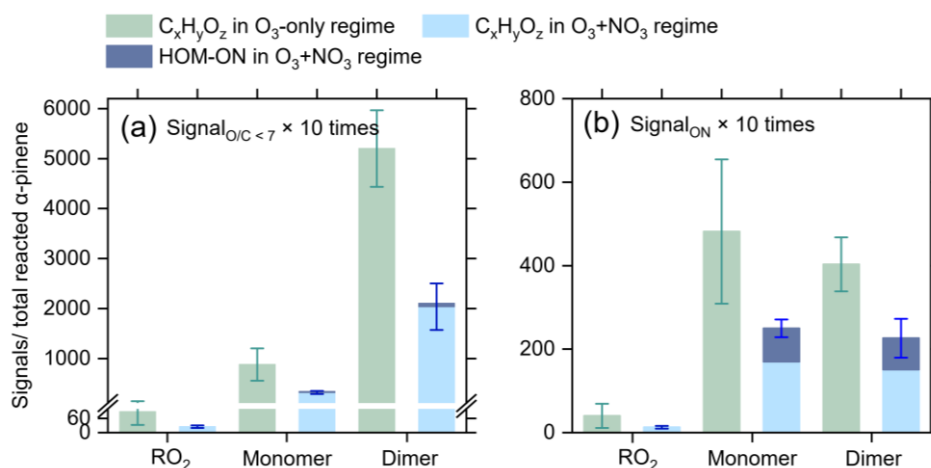


Figure S4 Influences of different instrument sensitivities on the relative changes in RO₂ and HOMs in the synergistic oxidation regime versus the O₃-only regime. A 10 times higher instrument sensitivity to (a) compounds with O/C < 0.7 and (b) ONs was considered.

11. Figure 6. Please include measured particle-size distributions for the O₃ + NO₃ and O₃-only systems.

Response: We have added a figure showing the particle size distributions in different oxidation regimes as well as the relevant discussions to the revised manuscript.

“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.”

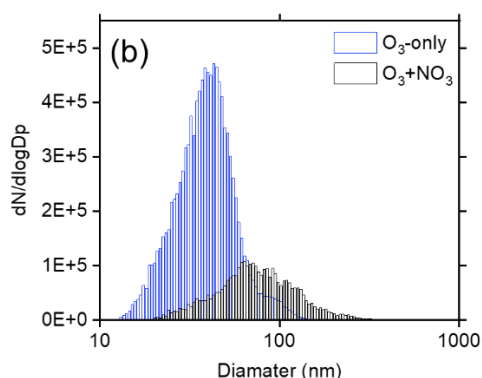


Figure 6b. Size distributions of particles formed from the ozonolysis and synergistic O₃ + NO₃ oxidation of α -pinene (Exps 13-14).

12. New Particle Formation. Consistent with Li et al. 2024, this work finds that the presence of NO₃ radicals during α -pinene ozonolysis reduces the abundance of ELVOC and ULVOC measured in the gas

phase. However, in contrast to Li et al. 2024, this work observes a factor-of-two increase in aerosol mass concentrations in the O₃ + NO₃ vs. O₃-only system. Given that these experiments were conducted in the absence of seed aerosol, the higher aerosol mass loadings in the O₃ + NO₃ system indicate more efficient particle nucleation and growth, despite the reduced signals of gas-phase ELVOC and ULVOC measurable by NO₃-CIMS. The reduced particle number concentrations in the O₃ + NO₃ system are “ascribed to the suppressed formation of ULVOCs,” however, enhanced coagulation seems more likely given the differences in mass loading. These results are also in contrast to Bates et al. 2022, which found that O₃ + NO₃ oxidation of α -pinene does not nucleate. However, they align with the seeded chamber experiments in Bates et al. 2022, which demonstrate that “high ^{NO₃}RO₂ + RO₂ contributions without any ozonolysis exhibited some of the highest measured SOA yields, suggesting perhaps that the ^{NO₃}RO₂ + ^{NO₃}RO₂ pathway on its own results in even higher SOA yields while ^{NO₃}RO₂ + other RO₂ pathways have lower yields.” Please include a discussion of these discrepancies and potential explanations (e.g., efficient formation of ELVOCs and ULVOCs in O₃ + NO₃ system that are not measurable by NO₃-CIMS).

Response: Thanks for the reviewer’s comment. This comment is partly addressed in our responses to last comment.

The presence of NO₃ radicals during α -pinene ozonolysis reduces the abundance of ULVOCs, which are the key species driving particle nucleation, thereby leading to a reduction in the particle number concentration in the O₃ + NO₃ regime. On the other hand, as discussed in our responses to last comment, 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. However, in the absence of seed particles, synergistic O₃ + NO₃ oxidation of α -pinene does not nucleate in their study. This phenomenon might be due to the high concentrations of NO₂ (72 ppb) and O₃ (102 ppb) as well as the relatively low concentration of α -pinene (27 ppb) in their experiments. As indicated by Bates et al. (2022), under this conditions NO₃ radicals were substantially formed and contributed to a dominant fraction (75%) of α -pinene oxidation, which strongly inhibited the production of low-volatility species and particle nucleation.

We have added the above discussions to the revised manuscript.

13. Termination Reactions. The term “termination reaction” is used throughout the manuscript to refer to RO₂ self/cross-reactions. In addition to radical termination to either alcohols and carbonyls or ROOR accretion products, however, alkoxy radical propagation is also possible. As such, please replace instances of “termination reaction” with RO₂ self/cross-reaction.

Response: Thanks for the reviewer’s comment. We have replaced “termination reaction” with “self/cross-

reaction” or “cross-reaction” in the revised manuscript.

14. Atmospherically Relevant Simulations. Are the stated reductions in L351 compared to simulations with the same initial conditions but with NO₃ concentrations and formation rates set to zero? Is the same amount of α -pinene consumed in the simulations with and without NO₃? Please clarify. Please also compare with the atmospherically relevant modeling results in Bates et al. 2022.

Response: Thanks for the reviewer’s comment. The reductions in C_xH_yO_z-HOMs in the O₃ + NO₃ regime are compared to the simulations with the same initial concentrations but with NO₃ concentrations and formation rates set to zero. The amount of α -pinene consumed by O₃ is the same with and without NO₃ oxidation, but the total consumption of α -pinene in the synergistic O₃ + NO₃ regime is larger than that in the O₃-only regime as a result of NO₃ oxidation.

We have added the following clarifications in the revised manuscript.

“In the absence of NO₃ radicals (with NO₃ concentrations and formation rates set to zero), the amount of α -pinene consumed during 4 hours of simulation is 1.04 ppb. When a relatively low NO₃ concentration (0.2 ppt) is considered, the amount of α -pinene consumed is 1.48 ppb.....When the NO₃ concentration is as high as 1 ppt as reported in field studies (Liebmann et al., 2018), the consumption of α -pinene reaches 3.24 ppb.....”

“Given that the concentrations of α -pinene and oxidants were held constant during the simulation, the consumptions of α -pinene by O₃ and OH radicals are the same across different oxidation regimes.”

We have also added a discussion of the simulation results in Bates et al. (2022) relevant to the present study.

“..... these HOM-ONs can be an important contributor to the particle mass growth. As suggested by the model simulations in Bates et al. (2022), the NO₃ oxidation of α -pinene led to a particulate nitrate yield of 7% under nocturnal atmospheric conditions in rural Alabama during the SOAS campaign.”

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