

## Response to Reviewer #1

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 work studied nocturnal oxidation of alpha-pinene synergistically by O<sub>3</sub>, NO<sub>3</sub>, and OH. The manuscript reports that in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime, CHO-HOM production is substantially suppressed compared to O<sub>3</sub>-only regime, due to rapid termination reactions between RO<sub>2</sub> formed from alpha-pinene + NO<sub>3</sub> and those formed from ozonolysis and OH oxidation, which is 10-100 times faster. This effect also leads to a reduction in ultralow and extremely low-volatility organic compounds. The work is solid and well written. However, there are a few issues and unclear details that need to be addressed before published at ACP.

### Specific Comments

1. Line 23 in Abstract. Stating that termination reactions are “10-100 times more efficient” is vague. In the kinetic model later, does it assume that the difference is only about RO<sub>2</sub> + RO<sub>2</sub> reaction rate constant, but not about dimer yields from these reactions?

Response: Thanks for the reviewer's comment. In the kinetic model, the difference is only about the cross-reaction rate constant of RO<sub>2</sub> + RO<sub>2</sub> and not the dimer formation yields.

We have modified the description as “Measurement-model comparisons further reveal that the cross-reaction rate constants of NO<sub>3</sub>-derived RO<sub>2</sub> with O<sub>3</sub>-derived RO<sub>2</sub> are on average 10 – 100 times larger than those of NO<sub>3</sub>-derived RO<sub>2</sub> with OH-derived RO<sub>2</sub>.”

2. Line 117. A reaction time of 25 seconds is long enough to form particles in precursors' concentrations are high. Was particle measurement performed for this?

Response: We used a scanning mobility particle sizer (SMPS, TSI) employing both long and nano differential mobility analyzers (model 3081 and 3085), with a measurable size range of 4.61 – 156.8 nm and 14.6 – 661.2 nm, respectively, to monitor particle formation in the flow tube. Even under conditions with the highest initial  $\alpha$ -pinene concentration (500 ppb), only a tiny amount of particles was formed, with mass concentrations of  $(6.4 \pm 1.6) \times 10^{-3}$  and  $(1.0 \pm 0.3) \times 10^{-2} \mu\text{g m}^{-3}$  and number concentrations of  $574 \pm 138$  and  $256 \pm 68 \text{ cm}^{-3}$  in the O<sub>3</sub>-only regime (Exp 5) and O<sub>3</sub> + NO<sub>3</sub> regime (Exp 11), respectively. These results suggest that the formation of SOA particles in the HOM formation experiments is negligible and would have no significant influence on the fate of RO<sub>2</sub> and closed-shell products.

We have added the results of the particle size measurements to Section 2.1 of the revised manuscript.

“A scanning mobility particle sizer (SMPS, TSI), consisting of an electrostatic classifier (model 3082), a condensation particle counter (model 3756), and a long or nano differential mobility analyzer (model 3081 and 3085) with a measurable size range of 4.61 – 156.8 nm and 14.6 – 661.2 nm respectively, was employed to monitor the formation of particles in the flow tube. During the HOM formation experiments, even under conditions with the highest initial  $\alpha$ -pinene concentration (500 ppb), only a tiny amount of particles was formed, with mass concentrations of  $(6.4 \pm 1.6) \times 10^{-3}$  and  $(1.0 \pm 0.3) \times 10^{-2} \mu\text{g m}^{-3}$  and number concentrations of  $574 \pm 138$  and  $256 \pm 68 \text{ cm}^{-3}$  in the O<sub>3</sub>-only regime (Exp 5) and O<sub>3</sub> + NO<sub>3</sub>

regime (Exp 11), respectively. These results suggest that the formation of SOA particles in the HOM formation experiments is negligible and would have no significant influence on the fate of RO<sub>2</sub> and closed-shell products.”

3. Section 2.1. A few important details should be provided in this section: (1) under the mixed O<sub>3</sub>/NO<sub>3</sub> condition, how much of alpha-pinene was oxidized by either oxidant? (2) Was NO<sub>2</sub> also present when alpha-pinene was oxidized? (3) What were the typically reacted alpha-pinene concentrations? (4) A model-based estimation of RO<sub>2</sub> bimolecular lifetime under these conditions should be provided. And (5) Did the authors assume that in NO<sub>3</sub>-CIMS, all HOM species have the same sensitivity?

Response: Thanks for the reviewer’s comments.

(1) We have added the concentration of  $\alpha$ -pinene oxidized by each oxidant in Table S1 in the Supplement.

(2) NO<sub>2</sub> was present in the experiments, and we have added a description of its concentration in Section 2.1.

“The initial NO<sub>2</sub> concentration in the flow tube was ~4.5 ppb.”

(3) The total reacted  $\alpha$ -pinene under different experimental conditions is also provided in Table S1.

(4) We have added the model-predicted RO<sub>2</sub> bimolecular lifetimes under different experimental conditions in Section 2.3.

“With these default kinetic parameters, the RO<sub>2</sub> bimolecular lifetimes were predicted to be 10.9 – 25.9 s in the O<sub>3</sub>-only regime and 8.4 – 11.8 s in the O<sub>3</sub> + NO<sub>3</sub> regime in the HOM formation experiments.”

(5) In this study, we assume that the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-HOMs derived from ozonolysis and OH oxidation of  $\alpha$ -pinene exhibit the same sensitivity in nitrate-CIMS. However, the highly oxygenated organic nitrates may have a significantly lower sensitivity compared to the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-HOM counterparts, given that the substitution of -OOH or -OH groups by -ONO<sub>2</sub> group in the molecule would reduce the number of H-bond donors, which is a key factor determining the sensitivity of nitrate-CIMS (Shen et al., 2022; Hyttinen et al., 2015). Recently, Li et al. (2024) used CI-Orbitrap with ammonium or nitrate reagent ions to detect oxygenated organic molecules in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime and found that both the ion intensity of ONs and their signal contribution to the total dimers were much lower when using nitrate as reagent ions.

We have added the above paragraph to Section 2.1 of the revised manuscript.

4. Line 185-189. Besides these two reasons, it is also possible that the presence of NO<sub>2</sub> scavenged all acyl RO<sub>2</sub>, which may be key to forming dimers. Earlier in the text, the authors stated that RO<sub>2</sub> + NO<sub>2</sub> reactions are considered. How about acylRO<sub>2</sub> + NO<sub>2</sub> specifically to remove acylRO<sub>2</sub>s out of the system? <sup>Cl</sup>RO<sub>2</sub> contain more aldehydes and thus its product RO<sub>2</sub>s are more likely acylRO<sub>2</sub> than the <sup>OH</sup>RO<sub>2</sub>. This could make sense if NO<sub>2</sub> has a major impact on the termination reactions for the <sup>Cl</sup>RO<sub>2</sub> pathways.

Response: We appreciate the reviewer’s point. The model simulations show that the concentrations of acyl RO<sub>2</sub> decrease by 60 – 79 % due to the consumption by NO<sub>2</sub>. However, our previous study found that in the absence of NO, acyl RO<sub>2</sub> accounts for a significant fraction (32 – 94%) of C<sub>7</sub> – C<sub>9</sub> RO<sub>2</sub> but a very small fraction (0.4%) of C<sub>10</sub> RO<sub>2</sub> (Zang et al., 2023). As the  $\alpha$ -pinene HOMs are dominated by C<sub>10</sub> species, the consumption of acyl RO<sub>2</sub> by NO<sub>2</sub> only leads to reductions of 4 – 5 % and 7 – 12 % in total

C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-HOM monomers and dimers, respectively. Therefore, the significant reduction in C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-HOMs in the synergistic oxidation regime is primarily due to the cross reactions of <sup>C</sup>RO<sub>2</sub> and <sup>OH</sup>RO<sub>2</sub> with <sup>NO3</sup>RO<sub>2</sub>. In addition, because of the very small contribution of acyl RO<sub>2</sub> to total C<sub>10</sub> RO<sub>2</sub>, their consumption by NO<sub>2</sub> leads to less than 2% reduction in the C<sub>10</sub> <sup>C</sup>RO<sub>2</sub> signals, and the larger decrease in <sup>C</sup>RO<sub>2</sub> and related HOMs as compared to the OH-derived ones is mainly due to the more efficient cross reactions of <sup>NO3</sup>RO<sub>2</sub> with <sup>C</sup>RO<sub>2</sub> than with <sup>OH</sup>RO<sub>2</sub>.

We have added a discussion of the effect of NO<sub>2</sub> in Section 3.1.

“Meanwhile, the depletion of acyl RO<sub>2</sub> by NO<sub>2</sub> only leads to a small reduction (4 – 5% and 7 – 12%, respectively) in total C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-HOM monomers and dimers in the synergistic regime compared to the O<sub>3</sub>-only regime.”

We have also added a discussion of the effect of NO<sub>2</sub> on the relative changes in <sup>C</sup>RO<sub>2</sub> in Section 3.2.

“Because of the very small contribution of acyl RO<sub>2</sub> to the total C<sub>10</sub> RO<sub>2</sub> (0.4%) (Zang et al., 2023), their consumption by NO<sub>2</sub> leads to less than 2% reduction in the C<sub>10</sub> <sup>C</sup>RO<sub>2</sub> signals. Therefore, the more significant decrease in signals of <sup>C</sup>RO<sub>2</sub> and related HOMs as compared to the OH-derived ones in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime is primarily due to the more efficient cross reactions of <sup>NO3</sup>RO<sub>2</sub> with <sup>C</sup>RO<sub>2</sub> than with <sup>OH</sup>RO<sub>2</sub>.”

5. Figure 1. For (a) and (b), I suggest further clarifying what fractions of the RO<sub>2</sub>, monomers, and dimers are made of compounds containing nitrogen. For (c), I suggest including CHO compounds as well, but using a different color. It might be also nice to show a mass spectrum with O<sub>3</sub> only, so that the comparison can be more clarified. In Line 207, the authors claimed “substantial formation of these dimeric ONs”; having a direct comparison can support this. In (c), C<sub>10</sub>H<sub>17</sub>NO<sub>8</sub> is the largest peak. Its formation should be briefly discussed. How does it form if C<sub>10</sub>H<sub>16</sub>NO<sub>5</sub> does not autoxidize rapidly, and the RO from RO<sub>2</sub>+RO<sub>2</sub> reactions mainly release NO<sub>2</sub> and produce pinonaldehyde? Besides these suggestions, I wonder if the relative changes can be affected if the sensitivities are different from different species. This is such a major assumption, but it was not discussed in the manuscript.

Response: Thanks for the reviewer’s comment.

(1) We have replaced Figure 1a with a new figure that shows the signals of total RO<sub>2</sub>, total monomers, and total dimers normalized by the total reacted α-pinene, with the bars subdivided to indicate the fractions of CHO and CHON species, in both O<sub>3</sub>-only and O<sub>3</sub> + NO<sub>3</sub> systems. In addition, we have provided a difference mass spectrum (i.e., mass spectrum in O<sub>3</sub> + NO<sub>3</sub> regime minus that in O<sub>3</sub>-only regime) in Figure 1c, which highlights the changes in the species distribution in the synergistic oxidation regime compared to the O<sub>3</sub>-only regime.

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

“The abundance of gas-phase RO<sub>2</sub> 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<sub>3</sub>-only regime, the normalized signals of total RO<sub>2</sub> and HOMs decrease by 62 – 68% in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime. Although NO<sub>3</sub> 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<sub>3</sub> 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.....”

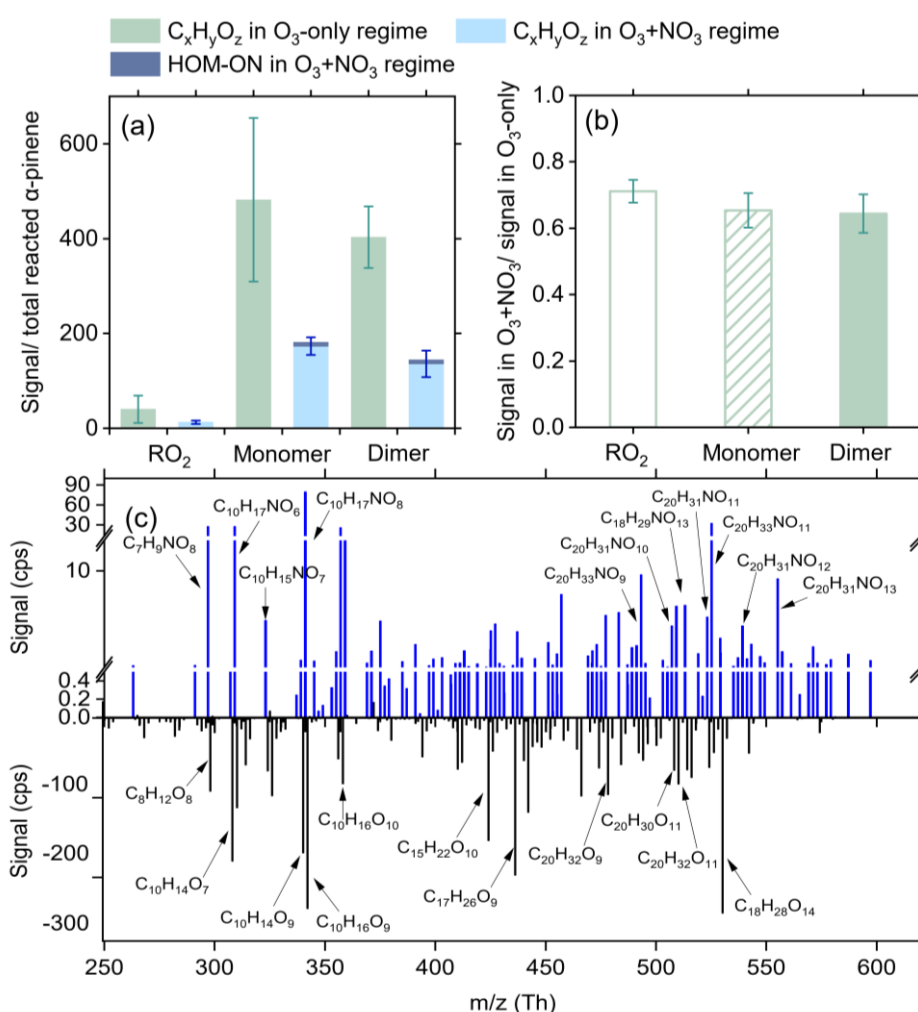


Figure 1 Distributions of RO<sub>2</sub> and HOMs in the  $O_3$ -only and  $O_3 + NO_3$  regimes. (a) Signals of total RO<sub>2</sub>, as well as HOM monomers and dimers normalized by the reacted  $\alpha$ -pinene in each oxidation regime (Exps 1-5, 7-11). (b) Relative changes in the normalized signals 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  $^{NO_3}RO_2$  and  $^{Cl}RO_2$  or  $^{OH}RO_2$  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.

(2) There are two possible explanations for the relatively high signal intensity of  $C_{10}H_{17}NO_8$ : (i) Although the RO radicals from cross reactions of  $C_{10}H_{16}NO_5$ -RO<sub>2</sub> are prone to release  $NO_2$  and form pinonaldehyde, a small fraction of them possibly undergo intramolecular H-shift/ $O_2$  addition to form  $C_{10}H_{16}NO_6$ -RO<sub>2</sub>, followed by further autoxidation to form  $C_{10}H_{17}NO_8$ ; (ii) Although CI is a soft ionization method, the fragmentation of chemically labile species still occurs during the ionization in nitrate-CIMS. It is possible that some of dimeric HOM-ONs are fragmented to  $C_{10}H_{17}NO_8$  during nitrate-CIMS measurements. We noticed that in a recent study by Li et al. (2014),  $C_{10}H_{17}NO_8$  was also identified

during the synergistic oxidation of  $\alpha$ -pinene by  $O_3$  and  $NO_3$ . However, the exact origin of this species remains to be clarified.

We have rewritten this part of discussion in the revised manuscript.

“As shown in Figure 1c, although several closed-shell monomeric HOM-ONs have been observed in the synergistic oxidation regime, only a few of them exhibit relatively high signals. Among them,  $C_{10}H_{17}NO_8$  may be formed by the autoxidation of  $C_{10}H_{16}NO_6-RO_2$  derived from the intramolecular H-shift of primary  $NO_3RO$  radicals ( $C_{10}H_{16}NO_4-RO$ ). In addition, although CI is a soft ionization method, the fragmentation of chemically labile species still occurs during the ionization in nitrate-CIMS. It is possible that some of dimeric HOM-ONs are fragmented to  $C_{10}H_{17}NO_8$  during nitrate-CIMS measurements. In a recent study by Li et al. (2024),  $C_{10}H_{17}NO_8$  was also identified during the synergistic oxidation of  $\alpha$ -pinene by  $O_3$  and  $NO_3$ . However, the exact origin of this species remains to be clarified.”

(3) 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  $RO_2$  and HOMs in the  $O_3 + NO_3$  regime versus the  $O_3$ -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  $RO_2$  and HOM signals in the synergistic oxidation regime compared to the  $O_3$ -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  $O_3 + NO_3$  regime (Figure S4b), the signals of both total and  $C_xH_yO_z$   $RO_2$  and HOMs still decrease significantly due to the presence of  $NO_3$  oxidation. Therefore, different instrument sensitivities to  $RO_2$  and HOMs with different oxygenation levels would not significantly influence the results (e.g., Figure 1) in this study.

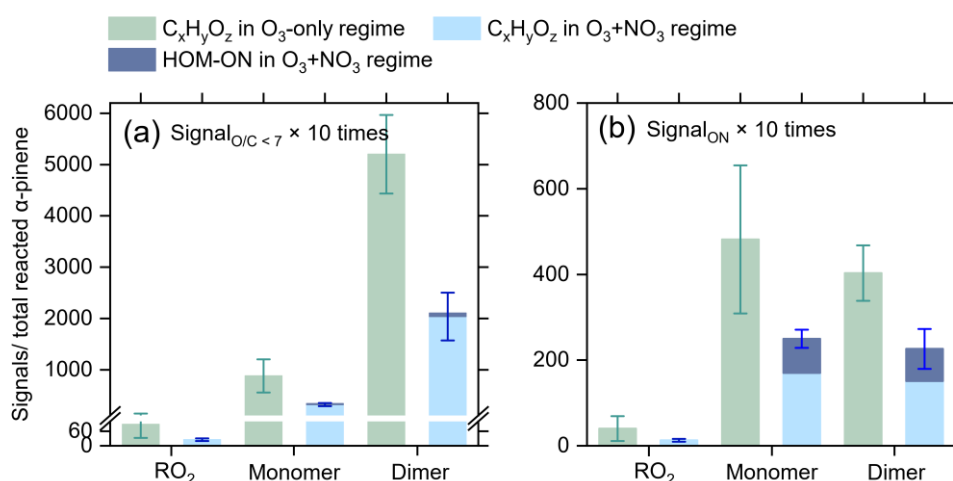


Figure S4 Influences of different instrument sensitivities on the relative changes in  $RO_2$  and HOMs in the synergistic oxidation regime versus the  $O_3$ -only regime. A 10 times higher instrument sensitivity to (a) compounds with  $O/C < 0.7$  and (b) ONs was considered.

We have added the above discussion in Section S1 of the supplement and the following statement in Section 3.1 of the main text.

“Although there remain considerable uncertainties in instrument sensitivities to different compounds,

sensitivity analyses suggest that varying the CIMS sensitivities to RO<sub>2</sub> and HOMs by a factor of 10 would not significantly influence their relative distribution across different oxidation regimes (see Section S1 for details).”

6. Line 249. This is related to comment #1. It is not true if the different RO<sub>2</sub> cross reactions could also change branching ratios of ROOR. This possibility needs to be discussed.

Response: Thanks for the reviewer’s comment. Recent studies suggested that the rate constants of the ROOR dimer formation for the highly oxygenated RO<sub>2</sub> appear to be 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 RO<sub>2</sub> cross reactions. To estimate the influence of dimer formation branching ratio on the relative changes in RO<sub>2</sub> and related HOM concentrations in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime versus the O<sub>3</sub>-only regime, we have conducted a sensitivity analysis of this ratio and added the following discussion to Section S3 in the Supplement.

“Currently, quantitative constraints on the ROOR dimer formation rate constant are rather limited. Recent studies suggested that the dimer formation rates from the highly oxygenated RO<sub>2</sub> 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 RO<sub>2</sub> (e.g., <sup>C</sup>RO<sub>2</sub>, <sup>OH</sup>RO<sub>2</sub>, <sup>NO<sub>3</sub></sup>RO<sub>2</sub>) 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 RO<sub>2</sub> and related HOM concentrations in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime versus the O<sub>3</sub>-only regime. As shown in Figure S8, as the dimer formation branching ratio increases from 9% to 50%, the variation in the abundance C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>-RO<sub>2</sub> and HOMs due to the concurrence of NO<sub>3</sub> oxidation changes slightly (<9% and <10%, respectively). These results suggest that the uncertainties in the dimer formation branching ratio of RO<sub>2</sub> cross-reactions do not significantly affect the distribution of RO<sub>2</sub> and HOMs across different oxidation regimes.”

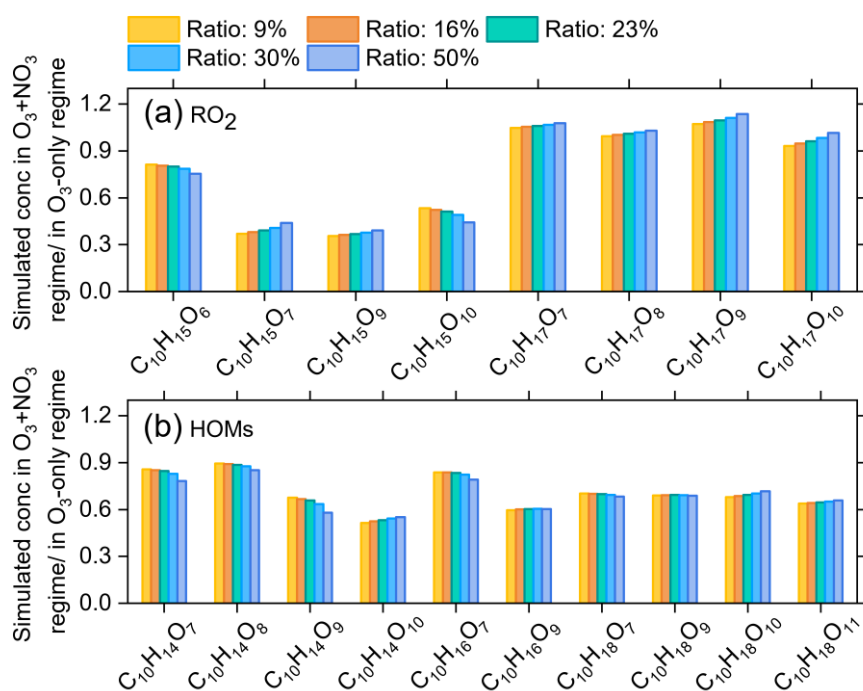


Figure S8 Influences of the dimer formation branching ratio on the relative changes in RO<sub>2</sub> and related HOM concentrations in the synergistic O<sub>3</sub> + NO<sub>3</sub> regime vs. the O<sub>3</sub>-only regime.

7. Line 290-294. Can these findings be explained by the kinetic model?

Response: The model simulations show that the concentrations of  $C_{20}H_{31}NO_x$  in the  $O_3 + NO_3$  regime increase with the addition of cyclohexane as an OH scavenger (Figure S9). However, the simulated enhancement is slightly lower than the measurements, which might be due to the uncertainties in the  $RO_2$  cross-reaction kinetics in the model.

We have added the above discussion to Section 3.2 of the main text and Figure S9 to the Supplement.

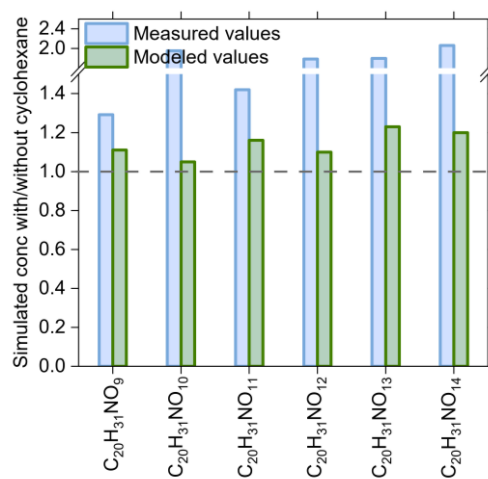


Figure S9 Simulated and measured relative changes in concentrations of  $C_{20}H_{31}NO_x$  due to the addition of 100 ppm cyclohexane as an OH scavenger in the synergistic  $O_3 + NO_3$  regime (Exps 6 and 12).

8. Line 326-328. However, the  $C^*$  distribution in Figure 5 does not show higher abundance for the SVOC & IVOC range under  $NO_3/O_3$  mixed oxidation conditions. How come the SOA mass loading is higher?

Response: The higher SOA mass loading in the synergistic oxidation regime is mainly due to the formation and condensation of HOM-ONs. However, as discussed in our response to comment #3, nitrate-CIMS may exhibit a significantly lower sensitivity to ONs than to  $C_xH_yO_z$ -HOMs, thus the measured signals of HOM-ONs are relatively low and have a small contribution to SVOC signals in the  $O_3 + NO_3$  regime.

We have added a more detailed discussion regarding the growth of particles in Section 3.3.

“On the other hand, substantial formation of HOM-ONs is expected from the cross reactions of  $^{NO_3}RO_2$  with  $^{Cl}RO_2$  and  $^{OH}RO_2$  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.”

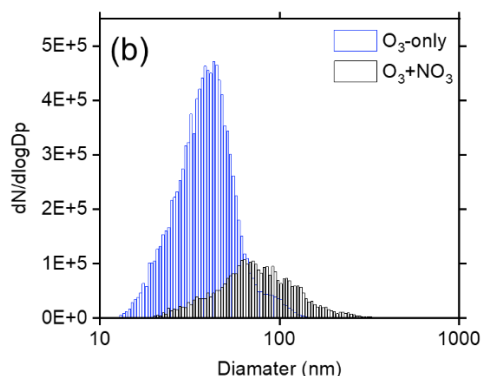


Figure 6b. Size distributions of particles formed from the ozonolysis and synergistic  $O_3 + NO_3$  oxidation of  $\alpha$ -pinene (Exps 13-14).

9. Section 3.4. It is nice to expand the chemistry into real-world conditions. The authors considered boreal forest conditions where monoterpenes are high. But they also mentioned southeast US conditions, where isoprene is high. Can the southeast US scenario be modeled? I think this is doable as the same authors published a paper on mixed isoprene/monoterpene oxidation.

Response: We appreciate the review's point. We have conducted a model simulation to evaluate the influence of the synergistic  $O_3 + NO_3$  oxidation on HOM formation under typical nocturnal conditions in the southeastern US. We find that in the mixed isoprene/monoterpene oxidation regime, the synergistic  $O_3 + NO_3$  oxidation can still suppress the formation of  $C_xH_yO_z$ -HOM monomers and dimers, and the presence of isoprene can strengthen this inhibition effect to some extent.

We have added the following detailed discussion to Section S4 of the Supplement.

“A model simulation was also conducted to evaluate the influences of synergistic oxidation on HOM formation under typical nocturnal conditions of the southeastern United States. The constant concentrations of  $\alpha$ -pinene (1.5 ppb), isoprene (4.5 ppb),  $O_3$  (30 ppb), NO (20 ppt),  $NO_2$  (2 ppb),  $NO_3$  radicals (1.4 ppt), OH radicals ( $2.5 \times 10^5$  molecules  $cm^{-3}$ ), and  $HO_2$  radicals (4 ppt) were used according to field observations in this region (Ayres et al., 2015; Lee et al., 2016). The rate constant of self/cross reactions involving isoprene-derived  $RO_2$  radicals (termed  $RO_2(isop)$ ) was set to  $2 \times 10^{-12}$   $cm^3$  molecule $^{-1}$  s $^{-1}$ , with a dimer formation branching ratio of 50% for  $RO_2(isop)$  with  $RO_2$  arising from  $\alpha$ -pinene (termed  $RO_2(\alpha p)$ ) and 30% for  $RO_2(isop) +$  for  $RO_2(isop)$  (Berndt et al., 2018; Wang et al., 2021).”

We have also added the following paragraph to Section 3.4 of the main text.

“Furthermore, model simulations for conditions typical of the southeastern United States (see details in Section S4) suggest that the coexistence of isoprene appears to exacerbate the suppression effect of synergistic oxidation on HOM formation from monoterpenes. As shown in Figure S14, in the absence of isoprene, the synergistic  $O_3 + NO_3$  oxidation of  $\alpha$ -pinene leads to a reduction of 13% and 24% in the formation of  $C_xH_yO_z$ -HOM monomers and dimers, respectively. When isoprene is present, as the isoprene +  $NO_3$  oxidation produces a significant amount of nitrooxy  $RO_2$  that can also scavenge  $\alpha$ -pinene-derived  $^ClRO_2$  and  $^OHRO_2$  via cross reactions, the synergistic oxidation leads to a slightly larger reduction in  $C_xH_yO_z$ -HOM monomers and dimers (15% and 31%, respectively).”



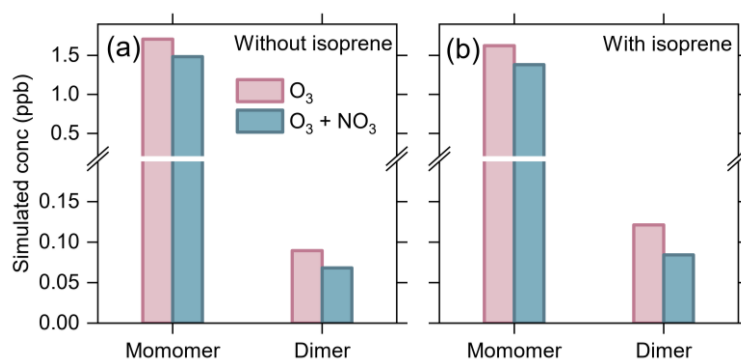


Figure S14 Simulated concentrations of  $C_xH_yO_z$ -HOMs from the ozonolysis and synergistic  $O_3 + NO_3$  oxidation of  $\alpha$ -pinene in the (a) absence and (b) presence of isoprene under typical nocturnal conditions in the southeastern United States.

Technical comments:

1. Line 109. Change “their” to “its”.

Response: We have revised this.

2. Line 164. Does  $^{NO_3}RO_2$  represent only the primary  $RO_2$  from  $NO_3 + \alpha$ -pinene (i.e.,  $C_{10}H_{16}O_5-RO_2$ ) throughout the manuscript? It should be clarified if that is the case.

Response:  $^{NO_3}RO_2$  represents the  $RO_2$  radicals from  $NO_3 + \alpha$ -pinene, and here we want to highlight the primary  $^{NO_3}RO_2$ , i.e.,  $C_{10}H_{16}NO_5-RO_2$ , the cross reactions of which were added to the model.

We have clarified this statement in the revised manuscript.

“We added the cross reactions of the primary nitrooxy- $RO_2$  derived from  $NO_3$  oxidation ( $^{NO_3}RO_2$ ), i.e.,  $C_{10}H_{16}NO_5-RO_2$ , with  $RO_2$  derived from ozonolysis ( $^CRO_2$ ) and OH oxidation ( $^{OH}RO_2$ ).”

3. Line 233. Change “strong” to “stronger”.

Response: We have revised this.

4. Figure 4. On the y-axis, “conc” is not accurate. Should be intensity or signal. Also, does “CA” mean cyclohexane? It should be clarified.

Response: We have changed “conc” to “signal” and “CA” to “cyclohexane”.

## References

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