Nocturnal Atmospheric Synergistic Oxidation Reduces the Formation of Low-volatility Organic Compounds from Biogenic Emissions

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Abstract

Volatile organic compounds (VOCs) are often subject to synergistic oxidation by different oxidants in the atmosphere. However, the exact synergistic oxidation mechanism of atmospheric VOCs and its role in particle formation remain poorly understood. In particular, the reaction kinetics of the key reactive intermediates, organic peroxy radicals (RO_2), during synergistic oxidation is rarely studied. Here, we conducted a combined experimental and kinetic modelling study of the nocturnal synergistic oxidation of α-pinene (the most abundant monoterpene) by O_3 and NO_3 radicals as well as its influences on the formation of highly oxygenated organic molecules (HOMs) and particles. We find that in the synergistic O_3 + NO_3 regime, where OH radicals are abundantly formed via decomposition of ozonolysis-derived Criegee intermediates, the production of $C_xH_yO_z$-HOMs is substantially suppressed compared to that in the O_3-only regime, mainly because of the ~~termination~~ depletion of α-pinene RO_2 derived from ozonolysis and OH oxidation by those arising from NO_3 oxidation via cross reactions. Measurement-model comparisons further reveal that the cross-reaction rate constants of NO_3-derived RO_2 with O_3-derived RO_2 ~~is~~are on average 10 – 100 times larger than th~~at~~ose of NO_3-derived RO_2 with OH-derived RO_2~~termination reactions between ozonolysis- and NO_3-derived RO_2 are on average 10 – 100 times more efficient than those of OH- and NO_3-derived RO_2~~. Despite a strong production of organic nitrates in the synergistic oxidation regime, the substantial decrease of $C_xH_yO_z$-HOM formation leads to a significant reduction in ultralow- and extremely low-volatility organic compounds, which significantly inhibits the formation of new particles. This work provides valuable mechanistic and quantitative insights into the nocturnal synergistic oxidation chemistry of biogenic emissions and will help to better understand the formation of low-volatility organic compounds and particles in the atmosphere.

1. Introduction

The Earth's atmosphere is a complex oxidizing environment in which multiple oxidants coexist. During the nighttime, NO_3 radicals (generated by the reaction of NO_2 and O_3) and O_3 contribute significantly to the oxidation of volatile organic compounds (VOCs) (Huang et al., 2019), while during the daytime, the fast photolysis of NO_3 radicals and rapid photochemical formation of OH radicals and O_3 make the latter two the major oxidants for VOCs (Zhang et al., 2018). Therefore, the degradation of ambient VOCs is subject to concurrent oxidation by different oxidants. Gas-phase oxidation of VOCs from biogenic emissions (BVOCs) by these major atmospheric oxidants produces a key type of reactive intermediates, organic peroxy radicals (RO_2), a portion of which can undergo fast autoxidation forming a class of highly oxygenated organic molecules (HOMs) with low volatilities (Jokinen et al., 2014; Mentel et al., 2015; Berndt et al., 2016; Zhao et al., 2018; Iyer et al., 2021; Shen et al., 2022; Ehn et al., 2014). HOMs typically contain six or more oxygen atoms, and plays a key role in the formation of atmospheric new particles and secondary organic aerosol (SOA) (Kirkby et al., 2016; Berndt et al., 2018a; Zhao et al., 2018; Ehn et al., 2014; Bianchi et al., 2019), which have important influences on air quality (Huang et al., 2014), public health (Pye et al., 2021), and Earth's radiative forcing (Shrivastava et al., 2017).

Due to the complexity of oxidation mechanisms of BVOCs, previous laboratory studies typically featured only one oxidant and a single SOA precursor (Berndt et al., 2016; Berndt, 2021; Claflin et al., 2018; Iyer et al., 2021; Boyd et al., 2015). However, the synergistic oxidation by different oxidants may significantly alter the fate of RO_2 intermediates, therefore influencing the formation of HOMs and SOA (Bates et al., 2022). Recently, a field study at a boreal forest site in Finland observed a series of nitrate-containing HOM-dimers from the coupled O_3 and NO_3 oxidation of monoterpenes (Zhang et al., 2020). At the same site, Lee et al. (2020) found that the synergistic oxidation of BVOCs by OH radicals and O_3 contributed to the largest fraction of SOA. These studies suggest that the synergistic oxidation of BVOCs by different oxidants plays an important role in the formation of HOMs and SOA in the atmosphere and highlight the needs to investigate the synergistic oxidation mechanisms of BVOCs for a better representation of atmospheric particle formation.

Several laboratory studies have attempted to address the role of synergistic oxidation of BVOCs in the formation of new particles and SOA (Kenseth et al., 2018; Inomata, 2021; Liu et al., 2022; Li et

al., 2024). Kenseth et al. (2018) identified a suite of dimer esters in flow tube experiments that can be only formed from the OH and O_3 synergistic oxidation of β-pinene. These dimers exhibit extremely low volatility and contributed 5.9 – 25.4% to the total β-pinene SOA. Similarly, Inomata (2021) found that the presence of OH radicals during α-pinene ozonolysis is a key factor for the production of low-volatility organic species and significantly promotes new particle formation (NPF). On the other hand, the addition of O_3 in the monoterpene photooxidation system also significantly increases the SOA mass yield (Liu et al., 2022). In addition, a recent chamber study by Bates et al. (2022) showed that the synergistic oxidation of α-pinene by NO_3 radicals and O_3 can significantly enhance the SOA yield compared to the NO_3 + α-pinene regime, which has nearly 0% SOA yield (Fry et al., 2014; Hallquist et al., 1999; Mutzel et al., 2021), and they revealed that the SOA yield in the NO_3 + O_3 oxidation system largely depends on the RO_2 fates. Most recently, Li et al. (2024) found that during α-pinene ozonolysis, the presence of nitrooxy-RO_2 radicals formed from NO_3 oxidation can significantly suppress the production of ultralow-volatility organic compounds (ULVOCs) and thereby NPF. These laboratory studies together provide growing evidence that synergistic oxidation of BVOCs by different oxidants have profound impacts on atmospheric particle formation. However, the specific synergistic mechanisms of different oxidants and oxidation pathways remain obscure. Although a few studies underscored the importance of the RO_2 fates (Bates et al., 2022; Li et al., 2024), the exact interactions between RO_2 species derived from different oxidants are still unclear, and quantitative constraints on the reaction rate of different RO_2 species are quite limited.

Here we conducted an investigation of the synergistic O_3 + NO_3 oxidation of α-pinene, one of the most abundant monoterpenes in the atmosphere, using a combination of laboratory experiments and detailed kinetic modelling, and focusing on the fate of RO_2 intermediates arising from different oxidation pathways. The α-pinene oxidation experiments were conducted in a custom-built flow reactor. The molecular composition of RO_2 species and HOMs in different oxidation regimes was characterized using a chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-APi-ToF) employing a nitrate ion source. The measured distributions of specific RO_2 and HOMs across different oxidation regimes were fitted with a kinetic model using Master Chemical Mechanisms (MCM v3.3.1) updated with recent advances of α-pinene RO_2 chemistry

(Wang et al., 2021; Iyer et al., 2021; Shen et al., 2022; Zang et al., 2023), which allows for quantitative constraints on RO_2 kinetics and synergistic oxidation mechanisms. Atmospheric relevance of the experimental results was evaluated by modelling the investigated oxidation chemistry under typical nocturnal atmospheric conditions.

2. Materials and Methods

2.1 Flow tube experiments

Experiments of α-pinene oxidation in different regimes (i.e., synergistic O_3 + NO_3 oxidation vs. O_3-only) were carried out under room temperature (298 K) and dry (relative humidity < 5%) conditions in a custom-built flow tube reactor (FTR, Figure S1). O_3 and NO_2 were added into a glass tube (Figure S1) to form NO_3 radical and its precursor N_2O_5:

$NO_2 + O_3 \rightarrow NO_3 + O_2$ （R1）

$NO_3 + NO_2 \leftrightarrow N_2O_5$ （R2）

O_3 was generated by passing a flow of ultra-high-purity (UHP) O_2 (Shanghai Maytor Special Gas Co., Ltd.) through a quartz tube housing a pen-ray mercury lamp (UV-S2, UVP Inc.) and its concentration was measured by an ozone analyzer (T400, API). NO_2 was obtained from a gas cylinder (15.6 ppm, Shanghai Weichuang Standard Gas Co., Ltd.). The initial NO_2 concentration in the flow tube was ~4.5 ppb. To prevent the titration of NO_3 radicals by NO, all the experiments were performed without the addition of NO. The total air flow in the NO_3 generation glass tube was 0.6 L min^{-1} and 0.4 L min^{-1} for the gas-phase HOM and SOA formation experiments, respectively. The produced N_2O_5 and NO_3 radicals, as well as the excessive O_3 were added into the FTR to initiate α-pinene oxidation. For the O_3-only experiments, only O_3 was added into FTR.

The α-pinene gas was generated by evaporating a defined volume of ~~their~~ its liquid (99%, Sigma-Aldrich) into a cleaned and evacuated canister (SilcoCan, RESTEK), and then added into FTR through a movable injector at a flow rate of 22 – 108 mL min^{-1}. The initial concentration of α-pinene in the flow reactor ranged from 100 – 500 ppb. In some experiments, the gas of cyclohexane (~ 100 ppm), which was generated by bubbling a gentle flow of UHP N_2 through its liquid (LC-MS grade, CNW), was added into the flow reactor as a scavenger of OH radicals formed from α-pinene ozonolysis.

For experiments characterizing the formation of HOMs, the total air flow in the FTR was 10.8 L min^{-1} and the residence time was 25 seconds. The short reaction time and the small amount of reacted α-pinene (see Table S1) in these experiments prevented the formation of particles. For the experiments characterizing the formation of SOA particles, a larger FTR was used, with a total air flow of 5 L min^{-1} and a residence time of 180 seconds. A summary of the conditions including the simulated concentrations of NO_2, N_2O_5 and NO_3 radicals~~-~~, as well as the concentration of α-pinene oxidized by each oxidant in different experiments are shown in Table S1.

The gas-phase RO_2 radicals and closed-shell products were measured using a nitrate-based CI-APi-ToF (abbreviated as nitrate-CIMS; Aerodyne Research, Inc.), which has been described in detail previously (Zang et al., 2023). A long ToF-MS with a mass resolution of ~10000 Th/Th was used here. The mass spectra within the m/z range of 50-700 were analyzed using the tofTools package developed by Junninen et al. (2010) based on Matlab. The total ion counts (TIC)~~, i.e.,~~ with values of (5.9 – 6.2) × 10^4 cps~~,~~ are similar under different reaction conditions. 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 $–ONO_2$ 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_3 + NO_3 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.

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~~or 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 α-pinene concentration (500 ppb), only a tiny amount of particles was formed, with mass concentrations of (6.4 ± 1.6) × 10^{-3} and (1.0 ± 0.3) × 10^{-2} μg m^{-3} and number concentrations of 574 ± 138 and 256 ±

68 cm^{-3} in the O_3-only ~~regime~~ (Exp 5) and O_3 + NO_3 regimes (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_2 and closed-shell products~~a differential mobility analyzer (model 3081), and a condensation particle counter (model 3756), was employed to monitor the formation of particles in different oxidation experiments~~.

2.2 Estimation of HOM volatility

A modified composition-activity method was used to estimate the saturation mass concentration (C^*) of HOMs in this study according to the approach developed by Li et al. (2016):

$$\log_{10}C^* = (n_C^0 - n_C)b_C - n_O b_O - 2\frac{n_C n_O}{n_C + n_O}b_{CO} - n_N b_N - n_S b_S$$

where n_C^0 is the reference carbon number; n_C, n_O, n_N, and n_S are the atom numbers of carbon, oxygen, nitrogen, and sulfur, respectively; b_C, b_O, b_N, and b_S are the contribution of each atom to $\log_{10}C^*$, respectively; b_{CO} is the carbon–oxygen nonideality (Donahue et al., 2011). These *b*-values were provided by Li et al. (2016).

It should be noted that the CHON compounds used in the data set by Li et al. (2016) are mostly amines, amides, and amino acids, and only contain a limited number of organic nitrates (0.07%). Since different types of CHON compounds have very different vapor pressures (Isaacman-Vanwertz and Aumont, 2021), this formula-based approach can be biased to estimate the C^* of organic nitrates. Considering that the $-ONO_2$ and –OH groups have similar impacts on vapor pressure and that the CHON species are predominantly organic nitrates in our study, all $-ONO_2$ groups are treated as OH groups during the estimation of vapor pressure (Daumit et al., 2013; Isaacman-Vanwertz and Aumont, 2021).

Gas-phase HOMs are grouped into five classes based on their $\log_{10}C^*$ (Donahue et al., 2012; Bianchi et al., 2019; Schervish and Donahue, 2020), that is, ULVOCs ($\log_{10}C^* < -8.5$), extremely low-volatility organic compounds (ELVOCs, $-8.5 < \log_{10}C^* < -4.5$), low-volatility organic compounds (LVOCs, $-4.5 < \log_{10}C^* < -0.5$), semi-volatile organic compounds (SVOCs, $-0.5 < \log_{10}C^* < 2.5$), and intermediate-volatility organic compounds (IVOCs, $2.5 < \log_{10}C^* < 6.5$).

2.3 Kinetic model simulations

Model simulations of specific RO_2 radicals and closed-shell HOMs formed in different oxidation regimes were performed to constrain the reaction kinetics and mechanisms using the Framework for 0-D Atmospheric Modeling (F0AM v4.1) (Wolfe et al., 2016), which employs MCM v3.3.1 (Jenkin et al., 2015). The α-pinene oxidation mechanism was updated with the state-of-the-art knowledge on the chemistry of RO_2 autoxidation and cross- reactions forming HOM monomers and dimers, respectively (Zhao et al., 2018; Wang et al., 2021; Iyer et al., 2021; Shen et al., 2022). The detailed updates have been described in our previous study (Zang et al., 2023). In particular, the formation and subsequent reactions of the ring-opened primary $C_{10}H_{15}O_4$-RO_2, the highly oxygenated acyl RO_2, as well as the $C_{10}H_{15}O_2$-RO_2 arising from H-abstraction by OH radicals during α-pinene ozonolysis are included in the model according to recent studies (Iyer et al., 2021; Zhao et al., 2022; Zang et al., 2023; Shen et al., 2022).

To investigate the synergistic reactions of RO_2 derived from the oxidation of α-pinene by different oxidants, we added the cross- reactions of the primary nitrooxy-RO_2 derived from NO_3 oxidation ($^{NO3}RO_2$), i.e., $C_{10}H_{16}NO_5$-RO_2, with RO_2 derived from ozonolysis ($^{CI}RO_2$) and OH oxidation ($^{OH}RO_2$). Recently, Zhao et al. (2018) revealed the bulk rate constant for $^{CI}RO_2$ and $^{OH}RO_2$ self/cross reactions to be 2×10^{-12} cm^3 molecule^{-1} s^{-1}, and Bates et al. (2022) constrained the rate constant for $^{NO3}RO_2$ self/cross reactions to be $1 \times 10^{-13} - 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. In the present study, the default rate constant for $^{NO3}RO_2 + {}^{CI}RO_2$ was set to 2×10^{-12} cm^3 molecule^{-1} s^{-1}, the same to that for self/cross reactions of $^{CI}RO_2$ and $^{OH}RO_2$. The ratio of the cross-reaction rate constant of $^{NO3}RO_2 + {}^{CI}RO_2$ to that of $^{NO3}RO_2 + {}^{OH}RO_2$ was tuned to achieve a good measurement-model agreement for the distribution of specific RO_2 and HOMs across different oxidation regimes. Recent studies suggested that the ROOR' dimer formation rates from the highly oxygenated RO_2 are fast (Berndt et al., 2018b; Molteni et al., 2019). As a result, a relatively high dimer formation branching ratio of 50% was used for different RO_2 (e.g., $^{CI}RO_2$, $^{OH}RO_2$, $^{NO3}RO_2$) in this study. With these default kinetic parameters, the RO_2 bimolecular lifetimes were predicted to be 10.9 – 25.9 s in the O_3-only regime and 8.4 – 11.8 s in the O_3 + NO_3 regime in the HOM formation experiments. Considering that the RO_2 cross-reaction kinetics remain highly uncertain, sensitivity analyses were performed to evaluate their influences on the results in this study (see Section 3.2). Previous studies indicated that

the primary $^{NO3}RO_2$ radicals arising from α-pinene are prone to lose the nitrate group and form pinonaldehyde with high volatility (Kurtén et al., 2017; Fry et al., 2014). Therefore, we did not consider the autoxidation of primary $^{NO3}RO_2$ in the model. Considering the presence of NO_2 in the experiments, the reactions of $RO_2 + NO_2 \leftrightharpoons ROONO_2$ were also included in the model (Zang et al., 2023).

3. Results and Discussion

3.1 Molecular distribution of RO_2 and HOMs in the synergistic oxidation regime

The ~~relative changes in the~~ abundance of gas-phase RO_2 species and ~~$C_xH_yO_z$-~~HOMs in ~~the synergistic O_3 + NO_3 oxidation of α-pinene vs.~~versus ~~the O_3-only regime are shown~~different oxidation regimes is shown in Figure 1a. The species signals are normalized by the total reacted α-pinene in each ~~oxidation~~ 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 (~~see~~ Section 2.1). ~~The signals of $C_xH_yO_z$-HOMs significantly decrease by 29 – 36% in the synergistic O_3 + NO_3 regime compared to those in the O_3-only regime (Figure 1a).~~ Although there remain considerable uncertainties in instrument sensitivities to different compounds, sensitivity analyses suggest that varying the ~~instrument~~CIMS sensitivities to RO_2 and HOMs by a factor of 10 ~~with different oxygenation levels~~ would not significantly influence their relative distribution across different oxidation regimes (see Section S1 for details).

Note that the initial concentrations of α-pinene and O_3 in the two oxidation regimes were the same. In addition, model simulations show that in the synergistic O_3 + NO_3~~oxidation~~ regime, over 97% of OH radicals react with α-pinene and the depletion of OH by NO_2 is minor (0.2 – 1.3%). 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). Meanwhile, the depletion of acyl RO_2 by NO_2 only leads to a small reduction (4 – 5% and 7 – 12%, respectively) in total $C_xH_yO_z$-HOM monomers and dimers in the synergistic regime compared to the O_3-only regime. As a result, the strong reduction in HOM formation due to the presence of NO_3 oxidation is likely mainly 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 ($\Delta[\alpha\text{-pinene}]_{O3}$, Figure S3) and thereby $C_xH_yO_z$-HOM signals, and (ii) the cross reactions of $^{CI}RO_2$ or $^{OH}RO_2$ with $^{NO3}RO_2$, which suppress the autoxidation and self/cross reactions of $^{CI}RO_2$ and $^{OH}RO_2$ to form $C_xH_yO_z$-HOMs.

To quantify the contribution of cross reactions of $^{NO3}RO_2$ with $^{CI}RO_2$/$^{OH}RO_2$ to the suppressed formation of $C_xH_yO_z$-HOMs in the synergistic oxidation regime, $C_xH_yO_z$-HOM signals shown in Figure 1a are first~~ly~~ normalized to $\Delta[\alpha\text{-pinene}]_{O3}$ in each oxidation regime and then compared between different oxidation regimes (see Figure 1b).~~Therefore, the strong reduction in HOM formation in the synergistic oxidation regime vs. the O_3-only regime is likely due to the following two reasons. The first one is the fast competitive consumption of α-pinene by NO_3 radicals, which results in a reduction in the reacted α-pinene by O_3 ($\Delta[\alpha\text{-pinene}]_{O3}$, Figure S2) and thereby the formation of $C_xH_yO_z$-HOMs. The second reason is associated with the reactions of $^{NO3}RO_2$ with $^{CI}RO_2$ or $^{OH}RO_2$ from α-pinene, which suppresses the autoxidation and self/cross-reactions of $^{CI}RO_2$ and $^{OH}RO_2$ to form $C_xH_yO_z$-HOMs.~~

~~To quantify the contribution of the synergistic RO_2 chemistry to the suppression of $C_xH_yO_z$-HOM formation in the O_3 + NO_3 oxidation regime, the $C_xH_yO_z$-HOM signal ratios in Figure 1a are further normalized to the ratio of $\Delta[\alpha\text{-pinene}]_{O3}$ in the synergistic oxidation regime vs. the O_3-only regime (see Figure 1b).~~ Notably, after excluding the influence of reduced $\Delta[\alpha\text{-pinene}]_{O3}$, the $C_xH_yO_z$-HOMs signals still drop by 24 – 32% in the O_3 + NO_3 regime compared to those in the O_3-only regime, indicating a significant contribution of the coupled reactions between $^{NO3}RO_2$ and $^{CI}RO_2$ or $^{OH}RO_2$ to suppressed $C_xH_yO_z$-HOM formation.

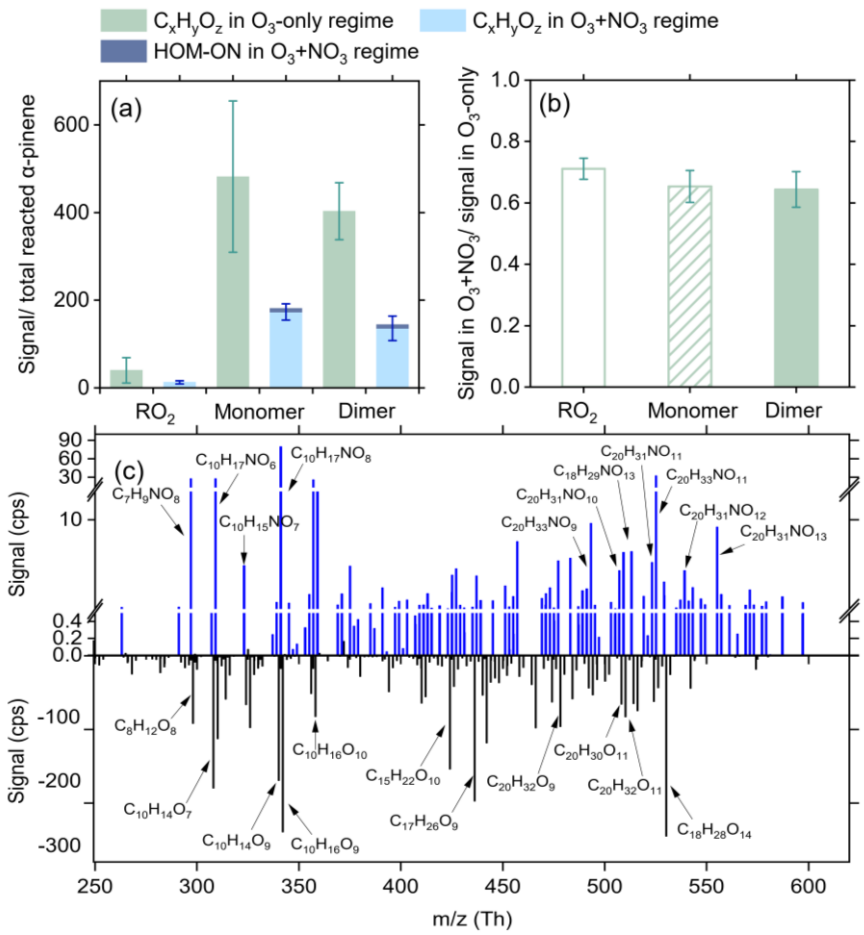
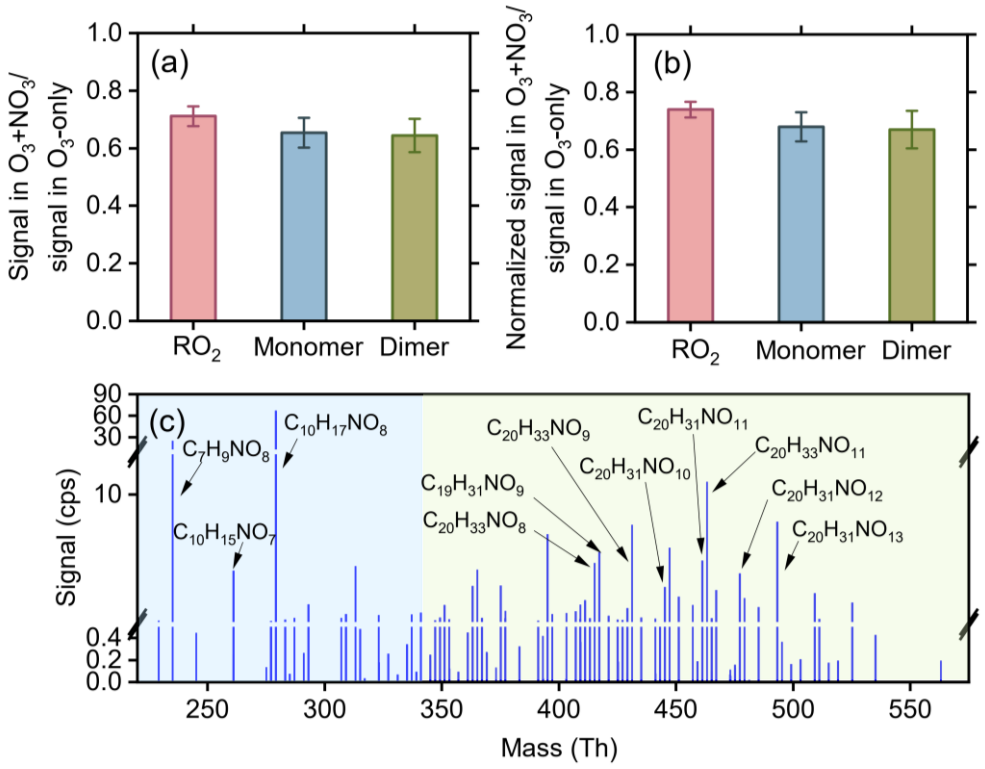


Figure 1 Distributions of RO_2 and HOMs in the O_3-only and O_3 + NO_3 regimes. (a) Signals of total RO_2, as well as HOM monomers and dimers normalized by the reacted α-pinene in each oxidation regime (Exps 1-5, 7-11). (b) Relative changes in the normalized signals of $C_xH_yO_z$-HOMs in the O_3 + NO_3 regime versus the O_3-only regime. Ion signals are normalized to $\Delta[\alpha\text{-pinene}]_{O3}$ in each oxidation regime to highlight the suppression effect of the synergistic chemistry between $^{NO3}RO_2$ 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.



~~Figure 1. Distributions of RO_2 and HOMs in the synergistic O_3 + NO_3 regime. (a) Relative changes in the signals of $C_xH_yO_z$-RO_2 radicals, HOM monomers, and HOM dimers in the O_3 + NO_3 regime compared to those in the O_3-only regime (Exps 1-10). (b) Similar to (a), but with ion signals normalized to $\Delta[\alpha\text{-pinene}]_{O3}$ in each oxidation regime. (c) HOM nitrates measured in the O_3 + NO_3 regime.~~

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. It should be noted that no obvious signals of highly oxygenated $^{NO3}RO_2$ ($C_{10}H_{16}NO_x$, $x \geq 6$) were observed by nitrate-CIMS in the O_3 + 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 $^{NO3}RO_2$ and $C_xH_yO_z$-HOMs with strong peaks (Table S3), limiting the detection of $^{NO3}RO_2$ species. Furthermore, previous studies revealed that the primary $^{NO3}RO_2$ radicals (i.e., $C_{10}H_{16}NO_5$-RO_2) in the α-pinene + NO_3 system mainly react to form pinonaldehyde (Kurtén et al., 2017; Perraud et al., 2010). It is likely that only a very small amount of $^{NO3}RO_2$ can undergo intramolecular H-shift/O_2 addition to form highly oxygenated $^{NO3}RO_2$. It should be pointed out that although the primary $C_{10}H_{16}NO_5$-RO_2 species arising from NO_3 oxidation may not undergo

fast autoxidation, they tend to efficiently terminate $^{Cl}RO_2$ and/or $^{OH}RO_2$ and suppress the formation of $C_xH_yO_z$-HOMs.

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 ^{NO3}RO 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 α-pinene by O_3 and NO_3. However, the exact origin of this species remains to be clarified.

The C_{20} dimers with only one nitrogen atom are very likely to be formed from the cross reactions of $^{Cl}RO_2$ or $^{OH}RO_2$ with $^{NO3}RO_2$, which~~Figure 1c shows the signals of closed-shell monomeric and dimeric HOM nitrates (HOM-ONs) that were only observed in the synergistic O_3 + NO_3 regime. Their specific formulas are listed in Table S2. These HOM-ONs mainly consist of C_{10} monomers and C_{20} dimers that only contain one nitrogen atom. The C_{20} HOM-ONs are believed to be formed from the cross-reactions of $^{Cl}RO_2$ and $^{OH}RO_2$ with $^{NO3}RO_2$. The substantial formation of these dimeric ONs~~ provides direct evidence for the synergistic RO_2 chemistry in the O_3 + NO_3 regime. The $CHON_2$ dimers were also observed in the O_3 + NO_3 regime, despite their much lower signals than CHON dimers, which is different from the recent studies by Bates et al. (2022) and Li et al. (2024), which found $CHON_2$ dimer account for an important fraction of the total dimer signals in the synergistic oxidation regime~~make important contribution to the total dimer signals~~. A potential explanation for this discrepancy is the difference in the instrument sensitivity in these studies (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 CF_3O^- as the reagent ion of CIMS. Its sensitivity to ONs might be significantly higher than the nitrate ion. In addition, Li et al. (2024) observed a significantly lower signal contribution of $CHON_2$ dimers using CI-Orbitrap with nitrate reagent ions than with ammonium ions. Despite both using nitrate regent ions, the nitrate CI-Orbitrap in Li et al. (2024) possibly exhibits higher sensitivities to ONs than the nitrate-CIMS

in our study.

3.2 Synergistic reaction efficiencies of different RO_2 species

In the $O_3 + NO_3$ regime, synergistic reactions are likely to occur between $^{CI}RO_2$, $^{OH}RO_2$ and $^{NO3}RO_2$. Figure 2 shows the $\Delta[\alpha\text{-pinene}]_{O3}$-normalized signal ratios of specific C_{10} RO_2 as well as their related $C_xH_yO_z$-HOM monomers and dimers in the synergistic $O_3 + NO_3$ regime vs. the O_3-only regime. It should be noted that the second-generation oxidation processes are strongly inhibited by ~~an~~the excess of α-pinene in this study, th~~erefore~~us the predominant type of RO_2 observed here is primary RO_2. Model simulations show that the H-abstraction of α-pinene by OH radicals contributes less than 2% to the formation of $C_{10}H_{15}O_x$-RO_2 and related HOMs under different experimental conditions (Figure ~~S3~~S5). Therefore, $C_{10}H_{15}O_x$-RO_2 observed in this study are primarily $^{CI}RO_2$. Notably, the $^{CI}RO_2$ ($C_{10}H_{15}O_x$) and related $C_{10}H_{14}O_x$-HOMs decrease by ~30 – 60% in the $O_3 + NO_3$ regime (Figures 2 a, b), while the decreasing extent of $^{OH}RO_2$ ($C_{10}H_{17}O_x$) and related $C_{10}H_{18}O_x$-HOMs are significantly smaller (0 – 40%). In particular, some of the most oxygenated $C_{10}H_{17}O_x$-RO_2 and $C_{10}H_{18}O_x$-HOMs ($x \geq 9$) even increase unexpectedly in the synergistic oxidation regime. For the $C_{10}H_{16}O_x$-HOMs that can be derived from the ~~termination~~ self/cross reactions of both $^{CI}RO_2$ and $^{OH}RO_2$, their reductions are at a medium level. Because of the very small contribution of acyl RO_2 to the total C_{10} RO_2 (0.4%) (Zang et al., 2023), their consumption by NO_2 leads to less than 2% reduction in the C_{10} $^{CI}RO_2$ signals. Therefore, t~~T~~he more significant~~ly larger~~ decrease in signals of $^{CI}RO_2$ and related HOMs as compared to the OH-derived ones in the synergistic $O_3 + NO_3$ regime is primarily due to~~indicates that in the synergistic $O_3 + NO_3$ regime,~~ the more efficient cross reactions of $^{NO3}RO_2$ with $^{CI}RO_2$ than with $^{OH}RO_2$~~the $^{NO3}RO_2$ species have a strong termination effect on $^{CI}RO_2$ than on $^{OH}RO_2$ (especially for the most oxygenated $^{OH}RO_2$)~~. Because a large amount of $^{CI}RO_2$ is terminated by $^{NO3}RO_2$, fewer $^{CI}RO_2$ are available to terminate $^{OH}RO_2$. As a result, more $^{OH}RO_2$ can undergo autoxidation to form highly oxygenated $C_{10}H_{17}O_x$-RO_2 and $C_{10}H_{18}O_x$-HOMs ($x \geq 9$), leading to an increase in signals of these species. Consistently, the signals of C_{20} HOM dimers decrease by 20 – 40% in the $O_3 + NO_3$ regime compared to that in O_3-only regime, and the signal reduction of dimers ($C_{20}H_{30}O_x$) formed by $^{CI}RO_2$ is slightly larger than that of the dimers ($C_{20}H_{34}O_x$) arising from $^{OH}RO_2$ (Figure 2c). Note that the highly oxygenated $C_{20}H_{34}O_x$ dimers ($x \geq 13$) that can be formed from self/cross- reactions of $C_{10}H_{17}O_x$-RO_2 ($x \geq 9$) are not observed in this study, likely

due to their low abundance and the limitation of instrument sensitivity.

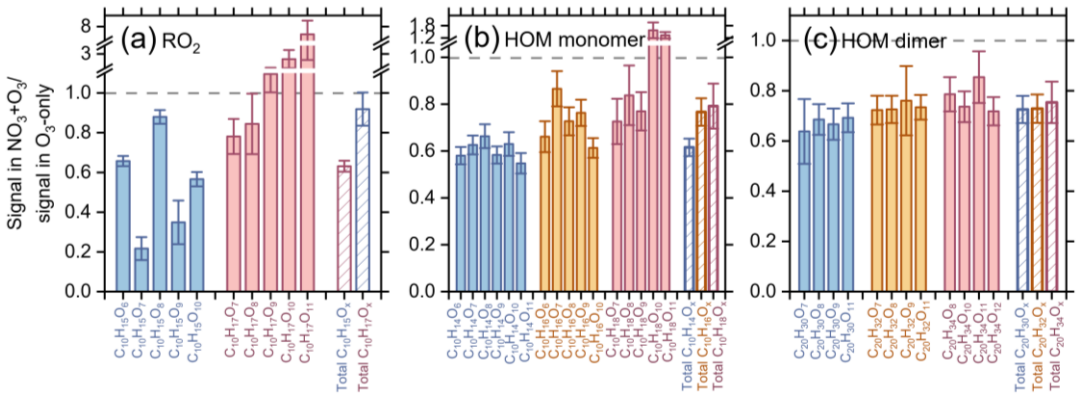


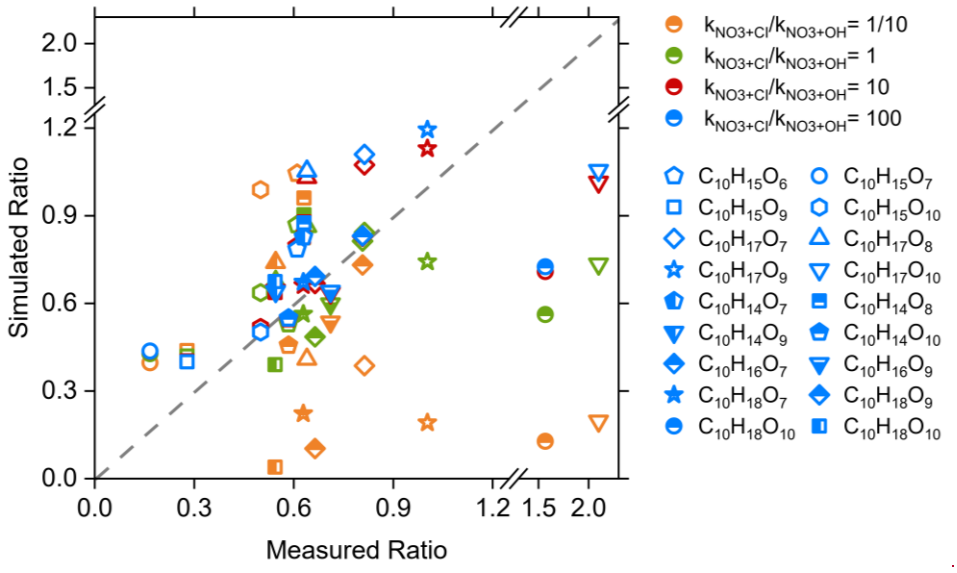
Figure 2. Normalized signal ratios of (a) specific and total $C_{10}H_{15,17}O_x$-RO_2 radicals, as well as their related (b) C_{10} HOM monomers and (c) C_{20} HOM dimers in the O_3 + NO_3 regime vs. the O_3-only regime (Exps 1-10). Ion signals observed in each oxidation regime are normalized to $\Delta[\alpha\text{-pinene}]_{O3}$.

These above results are somewhat different from the most recent study by Li et al. (2024), which found that the measured $C_{10}H_{15}O_x$-RO_2 increased slightly with NO_3 radicals while $C_{10}H_{17}O_{5,7}$-RO_2 from OH chemistry decreased by a factor of 9. Li et al. (2024) indicated that additional $C_{10}H_{15}O_x$ could be produced from the H-abstraction pathway of NO_3 oxidation of α-pinene. However, in the monoterpene oxidation system, the rate constant for H-abstraction by NO_3 radicals is $(4 – 10) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, which is $10^3 – 10^4$ times lower than that 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~~as noted above, the second-generation oxidation processes are strongly inhibited due to the excess of α-pinene in this study, 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.

To gain quantitative constraints on the relative reaction efficiency of $^{NO3}RO_2$ + $^{CI}RO_2$ vs. $^{NO3}RO_2$ + $^{OH}RO_2$ (i.e., k_{NO3+CI}/k_{NO3+OH}), the signal ratios of C_{10}-$^{CI}RO_2$ and $^{OH}RO_2$ as well as their related C_{10} HOMs in the synergistic oxidation regime vs. the O_3-only regime were predicted using a kinetic model (see Section 2.3) with different k_{NO3+CI}/k_{NO3+OH} ratios. Figure 3 shows a measurement-model comparison of those signal ratios. When the ratio of k_{NO3+CI}/k_{NO3+OH} is smaller than or equal to 1, the simulated signal ratios of many RO_2 and HOMs differ significantly from the measured ratios, especially for some $C_{10}H_{17}O_x$-RO_2 and $C_{10}H_{18}O_x$-HOMs. When the ratio of k_{NO3+CI}/ k_{NO3+OH} is 10 – 100, there is a good measurement-model agreement for most of RO_2 and HOMs. Therefore, we conclude that the cross-reaction rate constants of $^{NO3}RO_2$ + $^{CI}RO_2$ are on average 10 – 100 times larger than those for $^{NO3}RO_2$ + $^{OH}RO_2$. This different RO_2 cross-reaction efficiency is the main reason for the significantly larger decrease in the abundance of $^{CI}RO_2$ and related HOMs as compared to the OH-derived ones (see Figure 2).



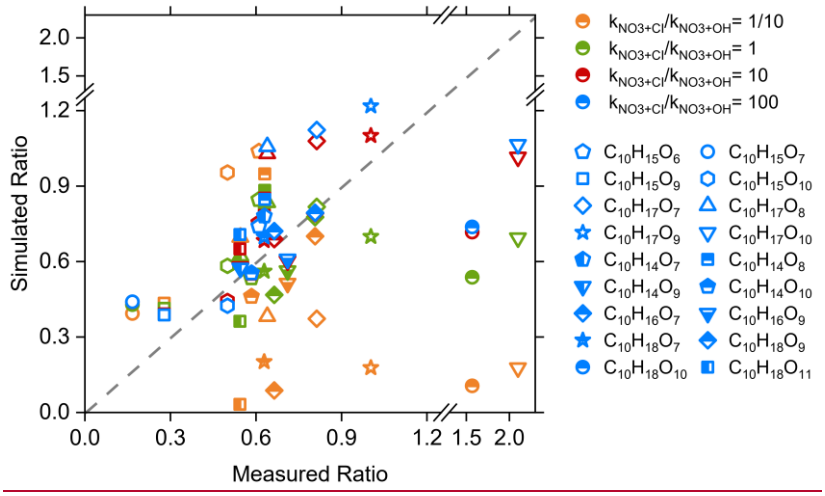
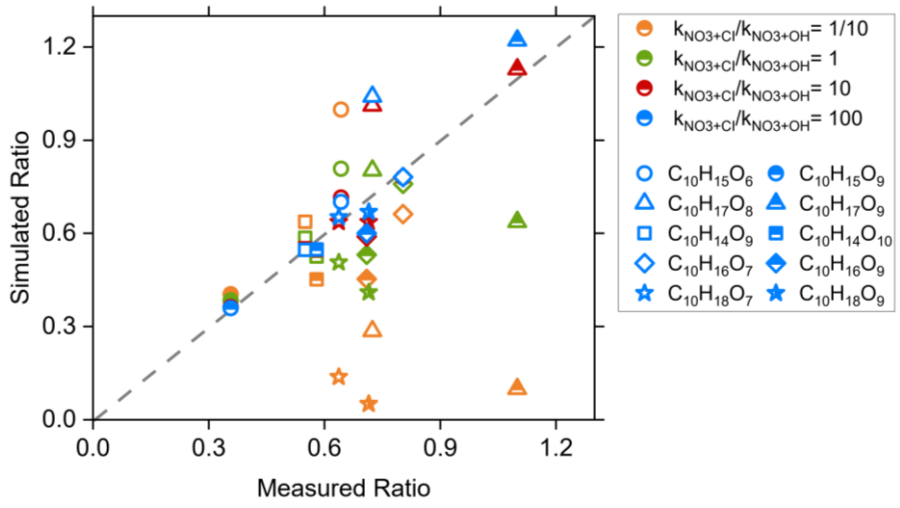


Figure 3. Measurement-model comparisons of the signal ratios of different C_{10} RO_2 and HOMs in the synergistic O_3 + NO_3 regime vs. the O_3-only regime. The cross reaction rate constant of $^{NO3}RO_2$ + $^{Cl}RO_2$ was set to 2 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and the rate of $^{NO3}RO_2$ + $^{OH}RO_2$ was varied from 2 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} to 2 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} in the model.

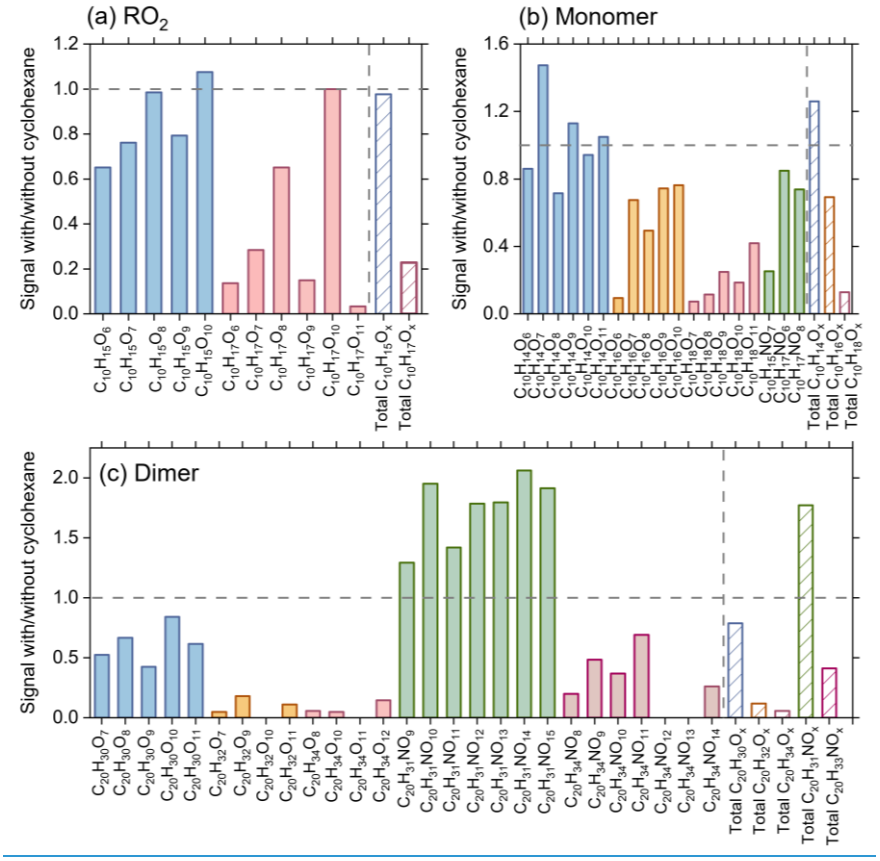
As a competitive reaction pathway, the autoxidation rates of RO_2 can affect the extent to which RO_2 cross- reactions influence the RO_2 fate and HOM formation. Therefore, sensitivity analyses of the autoxidation rate of RO_2 were conducted to evaluate its influence on the changes of RO_2 and related HOM concentrations in the synergistic O_3 + NO_3 regime vs. the O_3-only regime (Figure ~~S4~~S7). In these analyses, a k_{NO3+Cl}/k_{NO3+OH} ratio of 10 was used according to the above discussions. As the autoxidation rate of $^{OH}RO_2$ increases from 0.28 to 10 s^{-1}, corresponding to the rate range reported in previous studies (Berndt et al., 2016; Zhao et al., 2018; Xu et al., 2019), the simulated reduction of highly oxygenated $^{OH}RO_2$ and related $C_{10}H_{18}O_x$-HOMs in the synergistic O_3 + NO_3 regime exhibits a slight decrease (< 9%) but still agrees reasonably well with the measured value (Figures ~~S4~~ S7 a-d). Considering that the autoxidation rates of $^{Cl}RO_2$ used in the model approach their upper limits reported in the literature, i.e., ~1 s^{-1} for the butyl ring-opened $C_{10}H_{15}O_4$-RO_2 (Iyer et al., 2021) and relatively smaller rates for ring-retained $C_{10}H_{15}O_4$-RO_2 (0.02 – 0.29 s^{-1}, see Scheme S1) (Zhao et al., 2021), we also lowered the autoxidation rate constants of $^{Cl}RO_2$ by a factor of 10 to see its influence on RO_2 and HOM distribution in the O_3 + NO_3 regime. The simulated reduction of $^{Cl}RO_2$ and $C_{10}H_{14}O_x$-HOMs in this case decreases by 10 – 16% (Figures ~~S4~~ S7 e-h), while that of $C_{10}H_{16}O_x$-HOMs increases by up to 30% (Figures ~~S4~~ S7 i, j). However, the simulated results are still close to the measured values. These sensitivity analyses suggest that the uncertainty in the autoxidation rates of $^{OH}RO_2$ and $^{Cl}RO_2$ could slightly affect the simulated distribution of RO_2 and HOMs across

different oxidation regimes but not significantly change the k_{NO3+Cl}/k_{NO3+OH} ratio obtained in this study. Further sensitivity analyses on the rate constant and dimer formation branching ratio of RO_2 cross reactions indicate that the uncertainties in these reaction kinetics do not alter the conclusion regarding the k_{NO3+Cl}/k_{NO3+OH} ratio either (see details in Sections S2 and S3).



Cyclohexane was added in some experiments as an OH scavenger to elucidate the role of $^{OH}RO_2$ chemistry in HOM formation in the O_3 + NO_3 regime. In the presence of cyclohexane, $^{OH}RO_2$ ($C_{10}H_{17}O_x$) and related HOM monomers ($C_{10}H_{18}O_x$) and dimers ($C_{20}H_{32}O_x$ and $C_{20}H_{34}O_x$) decrease by more than 80% (Figure 4), while $^{Cl}RO_2$ ($C_{10}H_{15}O_x$) and related HOM monomers ($C_{10}H_{14}O_x$) and dimers ($C_{20}H_{30}O_x$) only decrease slightly (< 30%), in a good agreement with previous measurements (Zhao et al., 2018; Zang et al., 2023). The $C_{10}H_{16}O_x$ species, which can arise from both $^{Cl}RO_2$ and $^{OH}RO_2$, exhibit a medium reduction (Figure 4b). It is interesting to note that with the addition of cyclohexane, there is a significant increase in $C_{20}H_{31}NO_x$, which are formed from the cross-reactions of $^{Cl}RO_2$ with $^{NO3}RO_2$. Such an enhanced production of $C_{20}H_{31}NO_x$ as compared to the slightly deceased formation of $C_{20}H_{30}O_x$ indicates that the $^{Cl}RO_2 + {}^{NO3}RO_2$ reactions are competitive compared to the $^{Cl}RO_2 + {}^{Cl}RO_2$ and $^{Cl}RO_2 + {}^{OH}RO_2$ reactions~~the cross-reaction of $^{Cl}RO_2 + {}^{NO3}RO_2$ is fast compared to that of $^{Cl}RO_2 + {}^{Cl}RO_2$ and $^{Cl}RO_2 + {}^{OH}RO_2$~~. As a result, when the $^{OH}RO_2$ are depleted, the $^{Cl}RO_2$ that are supposed to react with $^{OH}RO_2$, efficiently react with $^{NO3}RO_2$ to form $C_{20}H_{31}NO_x$, leading to the increase in $C_{20}H_{31}NO_x$ signals. Consistent with the experimental measurements, 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.



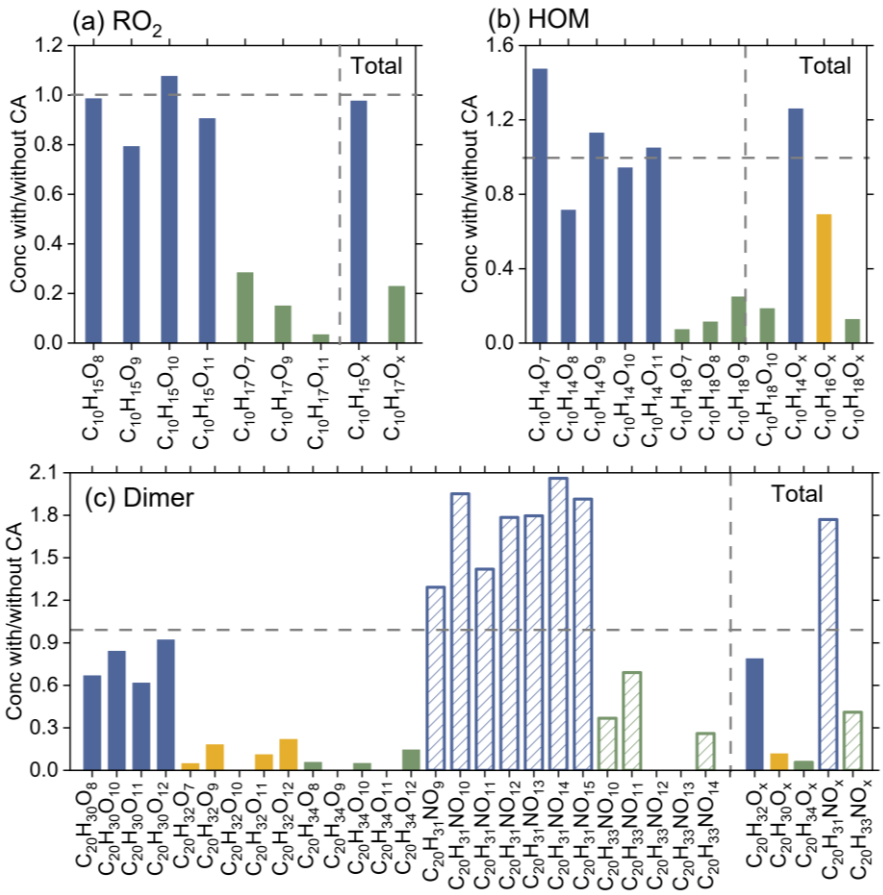


Figure 4. Relative changes in signals of (a) C_{10} RO_2, (b) C_{10} HOMs, and (c) C_{20} dimers due to the addition of 100 ppm cyclohexane as an OH scavenger derived in the synergistic O_3 + NO_3 regime (Exps ~~6~~ 7 and 12).

3.3 Influence of synergistic oxidation on low-volatility organics and particle formation

Compared to the O_3-only regime, there ~~is~~ are a remarkable reduction in $C_xH_yO_z$-HOMs and a strong formation of HOM-ONs due to the ~~termination reactions~~efficient cross reactions between $^{NO3}RO_2$ and $^{Cl}RO_2$ ~~or $^{OH}RO_2$~~ in the synergistic oxidation regime. This significant change in HOM composition and abundance would alter the volatility distribution of HOMs and influence the formation of particles. The volatilities of HOMs formed in the two oxidation regimes are estimated using a modified composition-activity method (see Section 2.2) and shown in Figure 5. The abundance of $C_xH_yO_z$-HOMs characterized as ULVOCs and ELVOCs decreases considerably in the synergistic O_3 + NO_3 regime compared to the O_3-only regime (Figure 5a), in agreement with the very recent observations by Li et al. (2024) who found that the presence of NO_3 radicals during α-pinene ozonolysis significantly reduced the abundance of ULVOCs. Although substantial amounts of HOM-ONs are formed in the O_3 + NO_3 regime, they generally have higher volatilities (i.e.,

characterized as ELVOCs to IVOCs) (Figure 5b). ~~In addition, the total abundance of newly formed HOM-ONs characterized as ELVOCs in the synergistic O_3 + NO_3 regime is significantly lower than the reduced formation of ultra- and extremely low-volatility $C_xH_yO_z$ HOMs.~~ Therefore, the synergistic O_3 + NO_3 oxidation of α-pinene significantly reduces the formation of ULVOCs and increases the overall volatility of total HOMs.

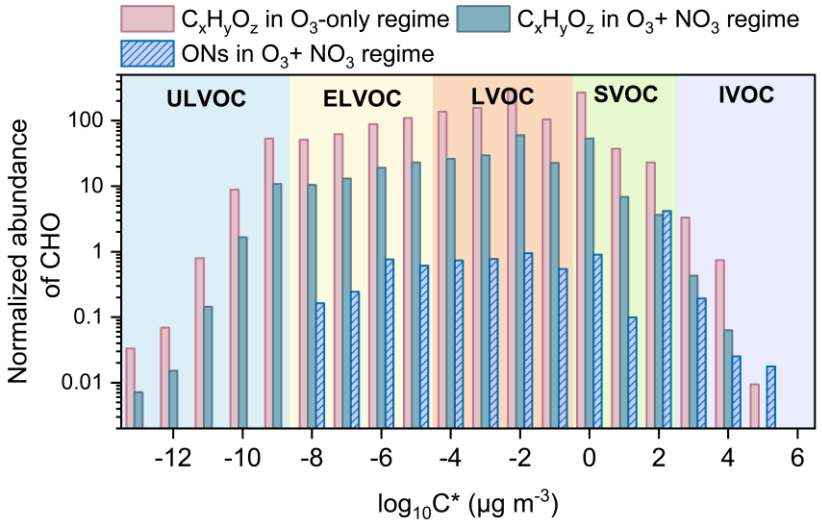


Figure 5. Volatility distribution of $C_xH_yO_z$-HOMs and HOM-ONs formed in the O_3 + NO_3 regime and O_3-only regime (Exps 1, 6). Ion signals in each oxidation regime are normalized to the corresponding total reacted α-pinene.

Figure 6a shows the particle number and mass concentrations formed in the two oxidation regimes in SOA formation experiments (Table S1, Exps 13, 14). The particle number concentration decreases by more than 50% whereas the particle mass concentration increases by a factor of 2 in the synergistic O_3 + NO_3 regime, compared to that in the O_3-only regime. The presence of NO_3 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 O_3 + NO_3 regime. On the other hand, substantial formation of HOM-ONs is expected from the cross reactions of $^{NO3}RO_2$ 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.

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 O_3 + NO_3 than during ozonolysis, mainly due to the substantial formation and condensation of ON dimers. However, in the absence of seed particles, synergistic O_3 + NO_3 oxidation of α-pinene does not nucleate in their study. This phenomenon might be due to the high concentrations of NO_2 (72 ppb) and O_3 (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 NO_3 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. ~~The reduced particle number concentration in the O_3 + NO_3 regime is ascribed to the suppressed formation of ULVOCs, which are the key species driving the particle nucleation (Simon et al., 2020; Schervish and Donahue, 2020). However, although the newly formed HOM-ONs with relatively higher volatilities are inefficient in initiating particle nucleation, they are able to partition into the formed particles and contribute significantly to the particle mass growth. This result is consistent with a recent chamber study which found that the SOA mass concentration is much higher during α-pinene oxidation by O_3 + NO_3 than during ozonolysis .~~

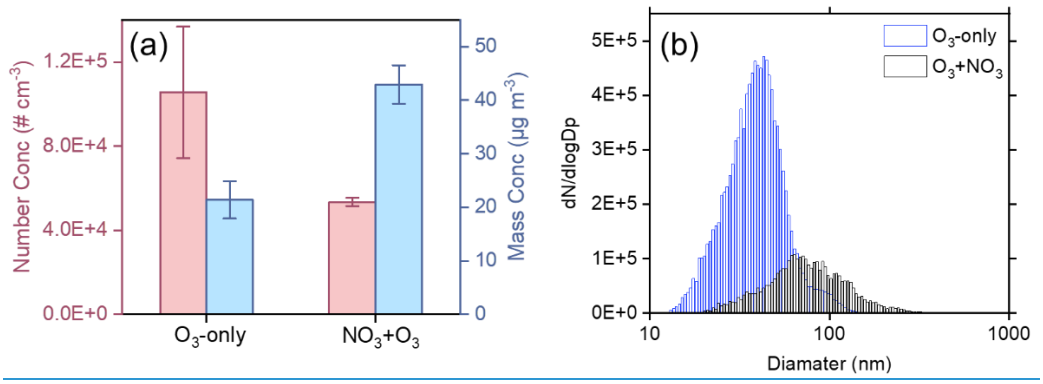
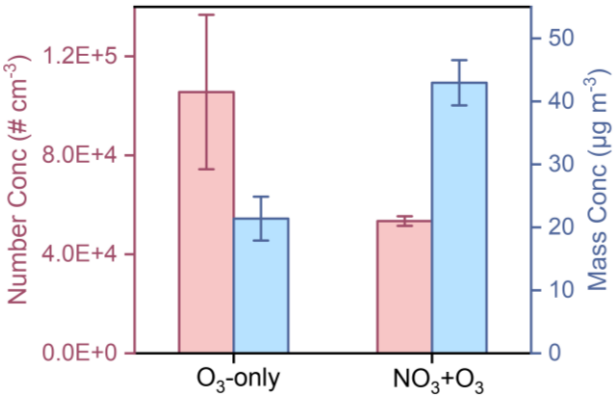


Figure 6. Number and mass concentrations (a), as well as the size distribution (b) of particles formed from the ozonolysis and synergistic O_3 + NO_3 oxidation of α-pinene (Exps 13-14).



~~**Figure 6. Number and mass concentrations of particles formed from the ozonolysis and synergistic O_3 + NO_3 oxidation of α-pinene (Exps 13-14).**~~

3.4 Atmospheric relevance of experimental results

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 RO_2 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.

To evaluate the relevance of our experimental findings to the real atmosphere, we performed

chemical model simulations of HOM formation from nocturnal synergistic O_3 + NO_3 oxidation of α-pinene under typical atmospheric conditions. In these simulations, constant concentrations of α-pinene (1 ppb), O_3 (30 ppb), NO (5 ppt), NO_2 (1.8 ppb), NO_3 radicals (0.2 or 1 ppt), OH radicals (5 – 50 $\times 10^4$ molecules cm^{-3}), HO_2 radicals (4 ppt), as well as a constant RH of 50% and temperature of 298 K were used as typical nocturnal conditions in the boreal forest according to the field studies (Stone et al., 2012; Lee et al., 2016a; Brown and Stutz, 2012; Geyer et al., 2003b; Kristensen et al., 2016; Hakola et al., 2012; Liebmann et al., 2018). Considering the rapid deposition of oxidized biogenic compounds (Nguyen et al., 2015), a typical dilution lifetime of 5 h (i.e., k_{dil} = 1/5 h^{-1}) was assumed in the model. According to the above analysis, the cross-reaction rate constants for $^{NO3}RO_2$ + $^{Cl}RO_2$ and $^{NO3}RO_2$ + $^{OH}RO_2$ were set to 1 $\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and 1 $\times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} in the model, respectively. The formation of RO_2 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 RO_2. In fact, the autoxidation rate of the highly oxygenated RO_2 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; Claflin et al., 2018).

In the absence of NO_3 radicals (with NO_3 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 NO_3 concentration (0.2 ppt) is considered (Figure 7a), the amount of α-pinene consumed is 1.48 ppb, and the ozonolysis is the primary loss pathway of α-pinene (68%), followed by NO_3 (30%) and OH oxidation (2%). The reactions of RO_2 + HO_2, RO_2 + NO, and RO_2 + RO_2 account for ~49%, ~27%, and ~24% of the total RO_2 fate, respectively (Figure S10a). Compared to the ozonolysis of α-pinene, the synergistic O_3 + NO_3 oxidation leads to a reduction of 3% and 13% in the formation of $C_xH_yO_z$-HOM monomers and dimers, respectively (Figure 7b). Given that the concentrations of α-pinene and oxidants were held constant during the simulation, the consumptions of α-pinene by O_3 and OH radicals are the same across different oxidation regimes. Therefore, the decreases in the concentrations of $C_xH_yO_z$-HOM monomers and dimers in the presence of NO_3 oxidation are mainly due to the cross reactions of $^{NO3}RO_2$ with other RO_2. When the NO_3 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, of which 68% is contributed by NO_3 oxidation (Figure 7c). Under this condition, the RO_2 + RO_2 reactions account for ~34% of the total RO_2 fate (Figure S10b). As a result, the cross reactions of $^{NO3}RO_2$ with other RO_2 play a more important role in the HOM formation. The production of $C_xH_yO_z$-HOM monomers and dimers decreases by 13% and 43%, respectively, due to the presence of NO_3 oxidation (Figure 7d). We note that the variation in RH from 0-90% in the model has negligible influence on the relative changes in $C_xH_yO_z$-HOMs under these nocturnal atmospheric conditions (Figure S11). Considering that there are uncertainties in the dilution rate constant, a sensitivity analysis was performed by varying the k_{dil} in the range of 0.04 – 0.2 h^{-1}. It is found that the variation within these rate values does not significantly influence the response of $C_xH_yO_z$-HOM dimer formation to concurrent NO_3 oxidation (Figure S12).

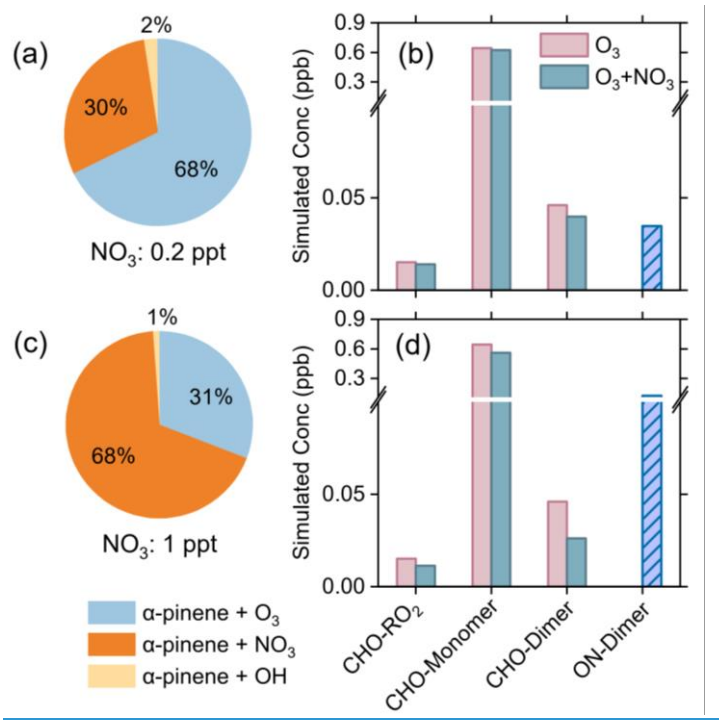
Field observations have shown that NO_3 radicals, O_3, and OH radicals all had important contributions to monoterpene oxidation during the early morning after sunrise and late afternoon before sunset in the southeastern United States (Zhang et al., 2018). In addition, relatively high nighttime OH concentrations of (2 – 10) × 10^5 molecules cm^{-3} were measured in some areas such as Germany and New York City (Faloona et al., 2001; Geyer et al., 2003a). As a result, a model simulation was conducted using a 10 times higher OH concentration (5 × 10^5 molecules cm^{-3}). The concentration of NO_3 radicals is 1 ppt and the concentrations of other species are the same as the values mentioned above. With a higher OH concentration, O_3, NO_3, and OH radicals account for 28%, 62%, and 10% to the total α-pinene consumption, respectively (Figure S13 a). Compared to the results under low OH concentration, the formation of $C_xH_yO_z$-HOM monomers and dimers are all enhanced under high OH concentration (Figure S13 b). This is mainly due to the promoted self/cross reactions of $^{OH}RO_2$, as well as the promoted formation of $C_{10}H_{15}O_x$-RO_2 derived from H-abstraction pathway by OH radicals. Nevertheless, the presence of NO_3 oxidation still reduces the formation of $C_xH_yO_z$-HOM dimers by 26% (Figure S13 b).~~The same species concentration (NO_3 = 1 ppt) as mentioned above but a 10 times higher OH concentration (5 × 10^5 molecules cm^{-3}) were also conducted. With a higher OH concentration, O_3, NO_3, and OH radicals account for 28%, 62%, and 10% to the total α-pinene consumption, respectively (Figure S6 S12 a). Compared to the results under low OH concentration, the formation of $C_xH_yO_z$-HOM monomers and dimers are all enhanced under high OH concentration (Figure S6 S12 b). This is mainly due to the promoted self/cross-~~

~~reactions of $^{OH}RO_2$, as well as the promoted formation of $C_{10}H_{15}O_x$-RO_2 derived from H-abstraction pathway by OH radicals. Nevertheless, the presence of NO_3 oxidation still reduces the formation of $C_xH_yO_z$ HOM dimers by 26% (Figure S6 S12 b).~~

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 α-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 aslo scavenge α-pinene-derived $^{CI}RO_2$ and $^{OH}RO_2$ 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).

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 $^{CI}RO_2$ 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 $^{NO3}RO_2$ becomes significant and their cross reactions with $^{CI}RO_2$ would suppress the formation of ULVOCs. Although HOM-ON dimers are readily produced by cross reactions between $^{NO3}RO_2$ and $^{CI}RO_2$, they generally have higher volatilities than $C_xH_yO_z$-HOM dimers and therefore are less efficient in initiating particle formation. However, 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 NO_3 oxidation of α-pinene led to a particulate nitrate yield of 7% under nocturnal atmospheric conditions in rural Alabama during the SOAS campaign.~~The above model simulations clearly suggest that under typical nocturnal atmospheric conditions, the synergistic oxidation of α-pinene by O_3 and NO_3 radicals can significantly inhibit the formation of $C_xH_yO_z$-HOMs,many of which are characterized as ULVOCs capable of driving particle nucleation and initial growth. Although HOM-ON dimers are readily produced by cross- reactions between $^{NO3}RO_2$ and $^{CI}RO_2$, they generally have higher volatilities than $C_xH_yO_z$ HOM dimers and therefore are less efficient in initiating particle formation.~~ Our results offer mechanistic and quantitative insights on how the synergistic oxidation of α-pinene by O_3 and NO_3 radicals can influence the formation of low-volatility organic compounds and hence particle

formation and growth. They also provide a potential explanation for field observations that NPF events frequently occur in monoterpene-rich regions during daytime but not at nighttime (Mohr et al., 2017; Kulmala et al., 2001; Junninen et al., 2017).



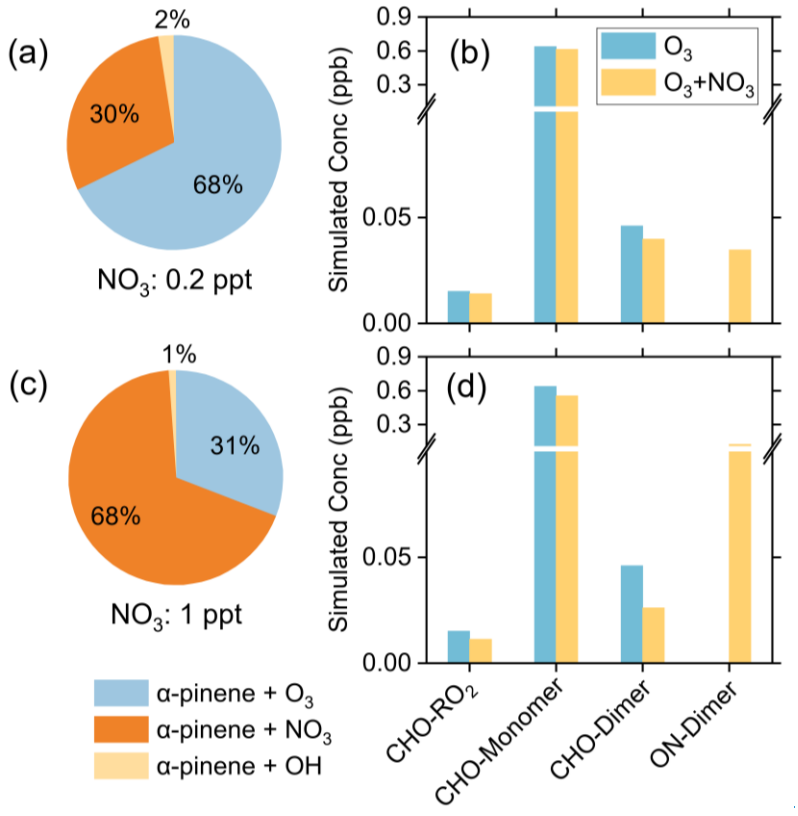


Figure 7. Model simulations of α-pinene oxidation and HOM formation under typical nighttime

conditions in the boreal forest. (a, c) Contributions of different loss pathways of α-pinene by different oxidants at NO_3 concentrations of 0.2 and 1 ppt, respectively; (b, d) Concentrations of $C_xH_yO_z$-HOMs and HOM-ONs formed by synergistic O_3 + NO_3 oxidation and ozonolysis of α-pinene under conditions corresponding to (a) and (c). The simulations were run for 4 h after an 8-h spin-up for intermediates and secondary species.

4. Conclusions

This study provides a comprehensive characterization of the nocturnal synergistic oxidation of α-pinene by O_3 and NO_3 radicals and its influence on the formation of HOMs and low-volatility organic compounds using a combination of flow reactor experiments and detailed kinetic model simulations. It is found that the formation of $C_xH_yO_z$-HOMs in the O_3 + NO_3 regime is significantly suppressed compared to that in the O_3-only regime, mainly due to the ~~termination~~ depletion of ozonolysis-derived RO_2 (i.e., $^{CI}RO_2$ and $^{OH}RO_2$) ~~by~~ by $^{NO3}RO_2$ via cross reactions. In addition, the decreases in the abundance of $^{CI}RO_2$ and related HOMs are significantly larger than those of OH-derived ones, indicating that the $^{NO3}RO_2$ species react more efficiently ~~on~~ with $^{CI}RO_2$ than ~~on~~ with $^{OH}RO_2$. Detailed measurement-model comparisons for the distribution of a suite of $^{CI}RO_2$, $^{OH}RO_2$, and associated HOMs across different oxidation regimes further reveal that the ~~terminations reactions~~cross reactions between $^{CI}RO_2$ and $^{NO3}RO_2$ are averagely 10 – 100 times more efficient than those of $^{OH}RO_2$ and $^{NO3}RO_2$.

The suppressed formation of $C_xH_yO_z$-HOMs in the synergistic O_3 + NO_3 regime results in a significant reduction in ULVOCs. Although substantial amounts of HOM-ONs are formed from the cross- reactions between $^{NO3}RO_2$ and $^{CI}RO_2$ or $^{OH}RO_2$ in the synergistic oxidation regime, they have higher volatilities and are less likely to participate in the formation and initial growth of new particles. As a result, in our experiment the formation of new particles in the synergistic oxidation regime is substantially inhibited compared to the O_3-only regime. Chemical model simulations further confirm that the synergistic oxidation of α-pinene by O_3 and NO_3 radicals can significantly inhibit the formation of $C_xH_yO_z$-HOMs, especially the ultra-low volatility $C_xH_yO_z$-HOM dimers under typical nighttime atmospheric conditions. Our study sheds lights on the synergistic oxidation mechanism of biogenic emissions and underscores the importance of considering this chemistry for a better depiction of the formation of low-volatility organics and particles in the atmosphere.

Data availability. The data presented in this work are available upon request from the corresponding author.

Author contributions. YZ and HZ designed the study, HZ and DH performed the experiments. YZ and HZ analyzed the data, conducted model simulations, and wrote the paper. All other authors contributed to discussion and writing.

Competing interests. The authors declare no conflict of interest.

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