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Gas-phase products from nitrate radical oxidation of five monoterpenes: insights from free-jet flow-tube experiments

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Abstract. Formation of secondary organic aerosol (SOA), which affects climate and health, is largely driven by the gas-particle transfer of highly oxygenated organic molecules (HOMs). These HOMs form via autoxidation following reactions of volatile organic compounds (VOCs) with atmospheric oxidants. While the oxidation of monoterpenes, the most important biogenic VOCs for SOA formation, by ozone (O_3) and hydroxyl radicals (OH) is well-studied, the role of the nitrate radical (NO_3), a crucial nighttime oxidant, remains less understood.

This study investigated NO_3-initated oxidation of five monoterpenes: α-pinene (AP), Δ-3-carene, limonene, β-pinene (BP), and β-myrcene. Using a newly built free-jet flow-tube system (8.8 s reaction time) and chemical ionization mass spectrometry (amine/nitrate ionization), we observed a wide range of peroxy radicals and closed-shell products. Product closure was reasonably achieved for AP, limonene, and myrcene (estimated to 50%–70%), but was lower for carene and BP (20%–40%). AP and limonene predominantly yielded $C_{10}H_{16}O_2$ (molar yields > 50%), while a notably high signal for carene was the peroxy radical $C_{10}H_{16}NO_8$, for myrcene the radical $C_{10}H_{16}NO_7$, and for BP the accretion product $C_{20}H_{32}N_2O_8$. The distinct HOM yields further emphasize highly structure-dependent oxidation pathways: 6.5% (myrcene), 6.1% (carene), 1.8% (BP), 1.1% (limonene), and 0.8% (AP). The HOM yields differ from those of ozonolysis, but overall HOM yields from NO_3 oxidation are comparable in magnitude (0–10%). This study provides comprehensive and quantitative distributions of NO_3 oxidation products for the most common monoterpenes, providing important knowledge of their fast (aut)oxidation pathways.

1 Introduction

Secondary organic aerosol (SOA) is a major component of atmospheric particulate matter (Hallquist et al., 2009; Jimenez et al., 2009), affecting climate through interactions with radiation and cloud formation (Boucher et al., 2013; Spracklen et al., 2011), and impacting human health via inhalation exposure (Kelly and Fussell, 2015). SOA formation is attributed to the gas-to-particle transfer of a wide range of oxidized products with low volatility (Donahue et al., 2012; Hallquist et al., 2009; Kroll and Seinfeld, 2008), which are generated from atmospheric degradation processes of volatile organic compounds (VOCs) (Atkinson and Arey, 2003). Recently, highly oxygenated organic molecules (HOMs) have been discovered to be a new and important group of VOC oxidation products, contributing significantly to SOA through condensation (Bianchi et al., 2019; Ehn et al., 2014) or even nucleation (Huang et al., 2024). Formed in the gas phase under atmospherically relevant conditions and generally containing more than five oxygen atoms (Bianchi et al., 2019), HOMs are produced through rapid peroxy radical (RO_2) autoxidation (i.e., intramolecular H-shift or ring closures followed by O_2 addition), following the initial oxidation of VOCs by atmospheric oxidants (Bianchi et al., 2019; Crounse et al., 2013; Ehn et al., 2014). Among all VOCs, monoterpenes (MTs), $C_{10}H_{16}$, represent one of the largest biogenic emissions, alone outnumbering the total anthropogenic VOC emissions, making them a crucial source of atmospheric condensation vapors (Guenther et al., 2012; McFiggans et al., 2019).

Although considerable progress has been made in understanding HOM formation from ozone (O_3) and hydroxyl radical (OH) initiated oxidation of MTs (Berndt et al., 2016, 2018a; Berndt, 2021, 2022; Bianchi et al., 2019; Ehn et al., 2014; Iyer et al., 2021; Jokinen et al., 2015; Luo et al., 2024; Meder et al., 2025; Molteni et al., 2019; Shen et al., 2022; Zhao et al., 2015, 2024), the role of the nitrate radical (NO_3), a key nighttime oxidant (Brown and Stutz, 2012), remains less well characterized. While NO_3-initated nocturnal oxidation can significantly contribute to total oxidized organic aerosol production in fall and winter (Liu et al., 2024), recent findings by Dewald et al. (2024) suggest that NO_3-initated organic nitrate formation can also be substantial during the daytime, underscoring the need for deeper insight into NO_3-driven autoxidation processes. Moreover, gaseous organic nitrates from NO_3 oxidation are potentially an important NO_x reservoir, due to the possible rapid photolysis (Takeuchi et al., 2025; Wang et al., 2023). This further highlights the importance of an improved understanding of NO_3 oxidation mechanisms.

Most studies over the last decades on NO_3 oxidation used smog chambers to investigate SOA formation (Bates et al., 2022; Bell et al., 2022; Boyd et al., 2015; Claflin and Ziemann, 2018; Fry et al., 2014; Hallquist et al., 1999; Nah et al., 2016; Ng et al., 2017; Perraud et al., 2010; Spittler et al., 2006). Recently, HOMs were identified to play a vital role in SOA from the NO_3 oxidation of MTs (Dam et al., 2022; Day et al., 2022; Draper et al., 2019; Graham et al., 2023; Guo et al., 2022; Harb et al., 2025; Shen et al., 2021). However, these studies either focused on one to two MTs or did not provide distributions covering products from less-oxygenated compounds to HOMs. Offering a controlled environment closely mimicking the atmosphere, smog chambers are good at studying complex multiphase chemistry and long-lived oxidation products, due to their typical residence times ranging from half an hour to several hours. In contrast, flow-tubes operate on timescales of seconds to minutes, providing valuable insights into fast autoxidation and short-lived radicals. The last decade witnessed a series of free-jet flow-tube experiments focusing on early-stage O_3/OH oxidation products, including short-lifetime RO_2 radicals, with multiple chemical ionization reagents applied (Berndt et al., 2015a, 2018a, b; Berndt, 2021, 2022). Specifically, the short reaction time of the flow-tube system (1.1–7.5 s; Berndt et al., 2015b) enables the direct comparison of the competing pathways of RO_2 radicals (Bianchi et al., 2019): unimolecular termination or isomerization leading to autoxidation; and bimolecular reactions leading to the formation of alkoxy radicals (RO), closed-shell monomers (e.g., RC=O, ROH), or dimers (ROOR). The advantage of short-reaction-time flow-tube experiments for studying gas-phase oxidation mechanisms has only sparingly been applied to investigations of NO_3-initiated oxidation processes.

In this study, we investigated NO_3 oxidation mechanisms of five common MTs (α-pinene, Δ-3-carene, limonene, β-pinene, and β-myrcene) by directly comparing their early-stage gas-phase RO_2 radicals and closed-shell products, using a newly built free-jet flow-tube system with short reaction times and a chemical ionization mass spectrometer. Avoiding the high level of NO_3 typically produced by N_2O_5 thermal decomposition (Bates et al., 2022; Fry et al., 2014), we used a pre-reactor to generate the NO_3 radical from the reaction $NO_2 + O_3$. The deployment of diethylamine ($C_4H_{11}N$) and isotopically labeled nitric acid ($H^{15}NO_3$) as reagent sources for the mass spectrometer allowed us to explore wide spectra covering oxidation products with two oxygen atoms onward (Cai et al., 2024; Riva et al., 2019). By varying the concentrations of MTs, NO_2, and O_3, we identified the NO_3 oxidation products, compared their concentrations, and explored their behaviors with increasing NO_3 radicals. We also developed a simple 0-D box model, which describes the flow-tube experiments, to calculate the reacted MT concentrations. Finally, we compared the fractions of all observed NO_3-initiated products over reacted MT by NO_3 radicals, and the HOM yields.

2 Methods

2.1 Flow-tube system

The experiments (temperature: 298 ± 2 K; pressure: 1 atm; dry conditions: relative humidity < 1 %) were carried out in a newly constructed free-jet flow-tube system (Fig. 1), located in the Physicum building at the University of Helsinki. Similar to the design by Berndt et al. (2015b), our flow-tube system consists of a quartz tube (length: 2 m, inner diameter: 15 cm) and a movable stainless-steel injector (length: 1.8 m, inner diameter: 8 mm) with a nozzle (inner diameter: 3 mm). A total flow of 100 L min^{-1} is supplied by a 250 L min^{-1} zero-air generator (ZA-737-250, Tisch Environmental) and regulated by various mass flow controllers (MKS, Inc.). Oxidants such as O_3 or NO_3 are carried by 5 L min^{-1} of zero air to the central injector and then mixed into the 95 L min^{-1} main gas flow, which contains reactants such as various VOCs. The narrow nozzle at the end of the injector enables a high flow velocity, causing turbulent mixing at beginning of the reaction. As the flow slows down, it gradually becomes laminar, as also observed visually using smoke (see Section S1 for details). The open outlet design and the exhaust port placed downstream (Fig. 1) help maintain laminar flow while sampling takes place at the center of the outlet. The experimental design allows investigations under nearly wall-free conditions (Berndt et al., 2015b). To enable the use of a box model for simulating reactions inside the free-jet flow-tube system, effective reaction times were experimentally determined via ozonolysis of 2,3-dimethyl-2-butene (TME, ≥ 99%, Sigma-Aldrich) at varying reaction distances (Fig. S1 and Section S1) (Berndt et al., 2015b): 2.5 s (50 cm), 4.6 s (70 cm), 6.4 s (90 cm), and 8.3 s (110 cm).

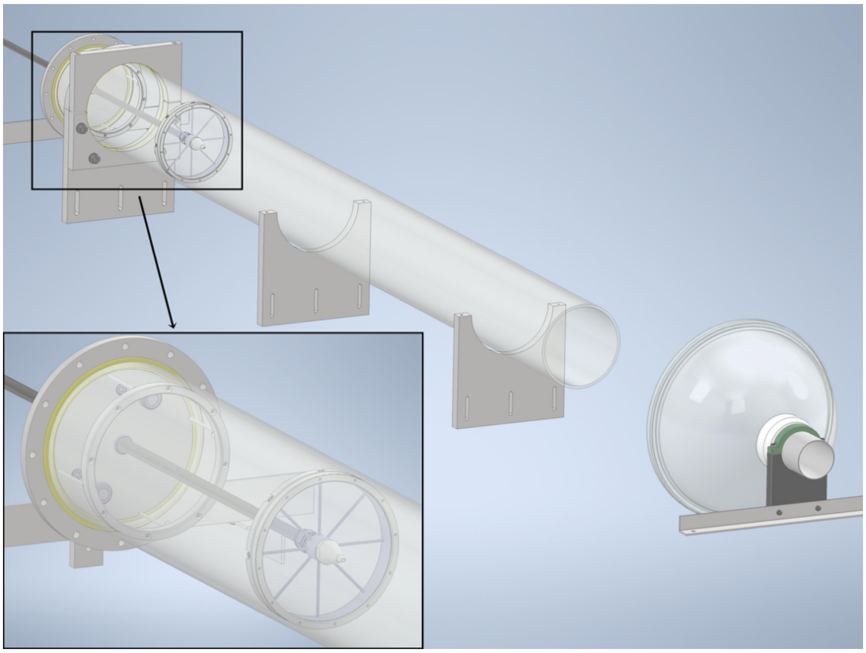

Figure 1. Schematic of the free-jet flow-tube system. The gas injecting side is shown in a zoomed-in view. An exhaust port with a film hood is placed downstream the flow-tube outlet. The reaction distance is defined as the distance from the nozzle to the sampling port, which is located at the center of the outlet.

2.2 Experiment design

Using the free-jet flow-tube system at an effective reaction time of 8.3 s, we investigated the formation of RO_2 radicals and closed-shell products in the NO_3 oxidation of five MTs, i.e., α-pinene (AP, 99%, Sigma-Aldrich), Δ-3-carene (99%, Sigma-Aldrich), limonene (96%, Sigma-Aldrich), β-pinene (BP, 99%, Sigma-Aldrich), and β-myrcene (90%, Sigma-Aldrich). These precursors were injected into the main gas flow using a 1.5 L min^{-1} zero-air flow and a syringe pump system (Fusion F100T2, Chemyx, Inc.).

O_3 and NO_2, generated from an ozone generator (Dasibi 1008-PC) and a NO_2 cylinder (0.1% NO_2 in N_2, Linde Gas) respectively, were mixed in an external 0.7 L cylindrical glass reactor (Meder et al., 2025) to produce NO_3 and N_2O_5. The total flow through the pre-reactor was fixed at 1 L min^{-1}, resulting in a reaction time of 42 s and concentrations of O_3 and NO_2 ($[O_3]_{0,\text{ pre-reactor}}$ = 1200 – 1800 ppb and $[NO_2]_{0,\text{ pre-reactor}}$ =1450 – 8600 ppb) approximately 100 times higher than those in the free-jet flow-tube after dilution. An additional 4 L min^{-1} of zero air was added to the pre-reactor outflow before it entered the injector. The NO_3 concentration in the reaction region of the flow-tube was sustained at a few ppt (Fig. S2), which is comparable to atmospheric levels (Ayres et al., 2015; Bates et al., 2022).

The experiments were designed to first ramp up MT concentrations in four stages, followed by a ramp-up of NO_2, with background stages included throughout (Fig. 2). This approach allowed us to distinguish products formed via NO_3 oxidation from those formed by O_3/OH oxidation (see Section 3.1). The initial concentrations of each stage shown above each subplot in Fig. 2 refer to the values present in the total flow of 100 L min^{-1}, without any chemical conversion. Since NO_2 and O_3 were reacted in the pre-reactor before entering the flow-tube, their actual concentrations at the start of the oxidation process were slightly lower than the initial values. No particles were present in the input gas, and particle formation did not occur due to low reactant conversion and the short reaction time (Section S1).

2.3 Instrumentation

Gas-phase RO_2 radicals and closed-shell products containing two or more oxygen atoms were measured using a chemical ionization mass spectrometer (CIMS, Tofwerk AG/Aerodyne Research, Inc.), coupled with an Eisele-type inlet (Eisele and Tanner, 1993) and operated with either diethylamine (DEA, $C_4H_{11}N$, ≥ 99.5%, Sigma-Aldrich) or isotopically labeled nitric acid ($H^{15}NO_3$, ~10 N in H_2O, 98 atom % ^{15}N, Sigma-Aldrich) as the reagent ion source (referred to as DEA- or nitrate-CIMS). The DEA mode allows detection of compounds with two or more oxygen atoms, while the nitrate mode is highly selective for HOMs (Cai et al., 2024; Ehn et al., 2014; Riva et al., 2019). The ^{15}N-labeled nitric acid was used in this study to unambiguously identify the organic nitrate products by distinguishing the N originating from unlabeled oxidant NO_3 (formed via NO_2 + O_3) from the labeled reagent ions. The sampling flow rate was 10 L min^{-1}, and additional operational details are provided in Section S2. The CIMS was equipped with a long time-of-flight mass spectrometer (LTOF), achieving a mass resolution of ~7000 at mass-to-charge ratio (m/z) of 149 Th in DEA mode, and ~8500 at m/z 125 Th in nitrate mode. Sampling was conducted through a 90-degree bent ¾-inch stainless-steel inlet tube (total length: 40 cm; 25 cm from the Eisele inlet to the bend, and 15 cm from the bend to the flow-tube outlet), positioned to sample from the center of the open outlet of the flow-tube. The 90-degree bend allows side sampling without disturbing the laminar outflow. The reaction time within the inlet is calculated to be 0.46 s, resulting in a total effective reaction time of roughly 8.8 s (at the reaction distance of 110 cm) for measurements taken by the CIMS. The same inlet tube was used in sulfuric acid calibration experiments for the CIMS (Kürten et al., 2012). Based on a two-dimensional (2-D) flow reactor calibration model (He et al., 2023), a calibration factor of 7.3×10^9 cm^{-3} (± 50%) was determined, and applied for both DEA and nitrate mode for product quantification (see Section S2).

A Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-TOF, Tofwerk AG) was used to monitor VOC concentrations and validate the syringe pump system (see Section S2 for details). Initial concentrations of O_3 and NO_2 were measured using gas monitors: a photometric O_3 analyzer (model 400, Teledyne API) and an NO-NO_2 analyzer (model T200UP, Teledyne API), respectively (see Section S2 for details). The O_3 analyzer was also used to quantify O_3 consumption during the reaction time characterization experiments involving the reaction TME + O_3. Data from both the Vocus PTR-TOF and DEA-/nitrate-CIMS were analyzed using the Igor-based Tofware software (Tofware_v3_3_0).

2.4 Box model

We constructed a simple 0-D box model to describe the chemical reactions occurring in the flow-tube system with a defined effective reaction time. Rather than simulating specific RO_2 or closed-shell products, the model was primarily used to estimate the concentrations of reacted MTs (or equivalently, the total amount of products) resulting from NO_3, O_3, and OH oxidation, based on the dominant reaction pathways (Table S1). Specifically, in the case of the flow-tube system, the model was used in batch mode, meaning no continuous input was applied and only the initial concentrations of precursors were set. The simulation spans the entire experimental setup, from the pre-reactor through the injector to the free-jet flow-tube, as illustrated in Fig. S2. The NO_3 oxidation product molar yields (or fractions) were calculated via dividing the measured product concentrations by the modeled MT concentration ([MT]) reacted by the NO_3 radical (Shen et al., 2021).

3 Results and Discussions

3.1 Experiment overview and the determination of NO_3 oxidation products and HOMs.

A total of ten sets of NO_3 oxidation experiments were conducted, two for each of the five MTs using both DEA- and nitrate-CIMS, with time series presented in Fig. 2 and Figs. S3–S6. The experimental procedure varied the initial concentrations of MT (i.e., $[MT]_0$), NO_2, and O_3 across distinct stages (concentrations for each stage shown directly above the plots in Fig. 2 and Figs. S3–S6). The sequence of these stages included: two initial background stages (with and without MTs); four MT-ramping stages (varying $[MT]_0$ from 10 to 120 ppb); three background stages (ramping $[MT]_0$ down to 20 ppb); three NO_2-ramping stages (varying $[NO_2]_0$ from 32.5 to 86 ppb); a single O_3 perturbation stage (with decreased $[NO_2]_0$ and a 50% increase in $[O_3]_0$); and finally, three different background stages. The experimental stages, excluding background stages, are numbered from 1 to 8 (Fig. 2).

During the MT-ramping stages (Stages 1–4 in Fig. 2), products from O_3 or OH (produced from MT + O_3) oxidation are expected to increase substantially, as the chemical conversion ratio of both MT and O_3 is small (Section S1). In contrast, NO_3 oxidation products would show a much slower increase, limited by the NO_3 radical concentration. This differential behavior is clearly illustrated in Fig. S7, where the ratio of reacted [MT] by NO_3 to total reacted [MT] by all oxidants is shown to decrease significantly as $[MT]_0$ is ramped from 10 to 120 ppb. Conversely, during the NO_2-ramping stages (Stages 5–7), NO_3 oxidation products would increase notably due to the rising NO_3 radical concentration, while O_3/OH oxidation products would decrease slightly due to enhanced O_3 consumption by NO_2. In the O_3 perturbation stage (Stage 8), where $[O_3]_0$ was increased by 50%, O_3/OH oxidation products are expected to increase accordingly, while NO_3 oxidation products are expected to stay almost unchanged or even decrease due to the lower $[NO_2]_0$. This systematic design allowed us to attribute product origins. For example, in the AP experiments (Fig. 2), compounds such as $C_{10}H_{15}O_{4,8,10}$ and $C_{10}H_{14}O_7$ were identified as ozonolysis products, while $C_{10}H_{16}NO_{5,7,9}$ and $C_{10}H_{16}O_2$ were identified as NO_3 oxidation products. It should be noted that for the DEA mode (Figs. 2A, and S3A–S6A), the injection of MT without added oxidants increased the signal for certain products (e.g., $C_{10}H_{16}O_2$), possibly due to MT impurity or surface reactions. Consequently, the background stages with MT injection were used for background subtractions.

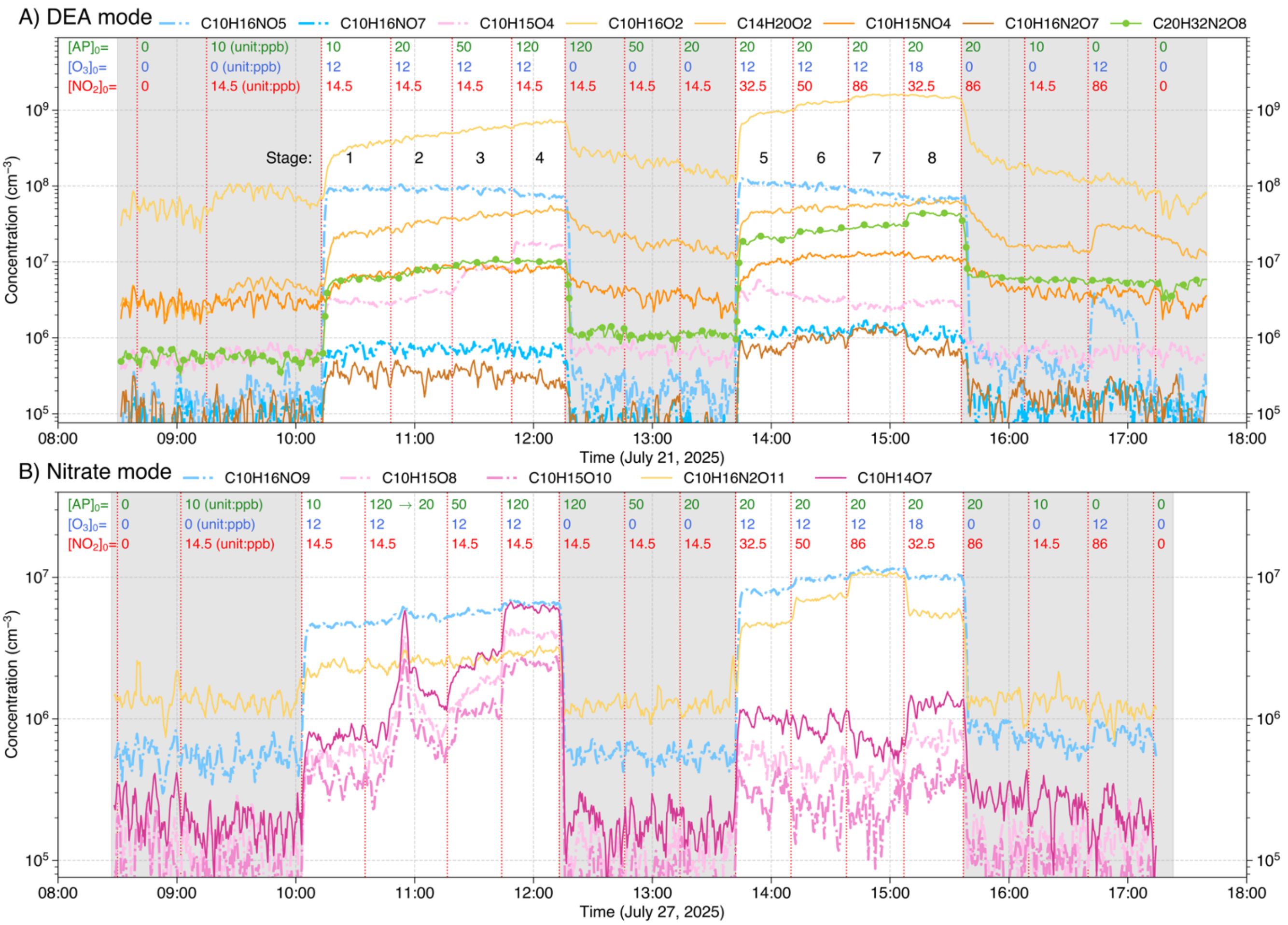

Figure 2. Timeseries of major products from α-pinene (AP) + NO_3 experiments, measured using both DEA (panel A) and nitrate (panel B) modes. Concentrations (in cm^{-3}) of radicals, closed-shell monomers, and closed-shell dimers are shown as dash-dot lines, solid lines, and solid lines with markers, respectively. Products are color-coded by origin: expected NO_3 oxidation products (radicals, closed-shell monomers, and dimers) are shown in blue, yellow-orange, and green colors, respectively, while expected O_3/OH oxidation products are shown in pink. Grey shaded areas represent background stages. Initial precursor concentrations (in ppb) shown above each subplot correspond to values present in the total flow of 100 L min^{-1}, without any chemical conversion. The effective reaction time is 8.8 s.

The volatility of multifunctional organic molecules is a function of their carbon number and the type and quantity of functional groups they contain. While a high oxygen-to-carbon ratio (O:C) typically indicates low volatility, it has been suggested that the nitrate group (–ONO_2) contributes to volatility reduction by an amount comparable to a single hydroxyl group (–OH) (Chuang and Donahue, 2016). Therefore, products with a nitrate group (e.g., those initiated by NO_3 radicals) necessitate a higher total oxygen atom count than the common threshold (≥ 6 oxygen atoms) established for non-nitrate HOMs from O_3/OH oxidation (Bianchi et al., 2019) to reach an equivalent Low Volatility Organic Compound (LVOC) or Extremely LVOC (ELVOC) regime.

O_3, OH or NO_3 can initiate oxidation by directly adding to a double bond, leading to a C-centered radical followed by fast O_2 addition, which yields a primary RO_2 (Atkinson and Arey, 2003) that can then undergo autoxidation (Ehn et al., 2014). The primary peroxy radicals will contain 2–5 O atoms, depending on oxidant and whether the cleavage of the double bond results in fragmentation or not. The recommended definition for HOMs is that they have undergone autoxidation and contain 6 or more O-atoms. We take a slightly more restrictive approach here, since NO_3 oxidation adds more O-atoms to the RO_2 than the more often studied O_3 and OH oxidation. When using the term "HOM", we the following criteria: HOM monomers include RO_2 radicals with 8 or more oxygen atoms ($C_{10}H_{16}NO_x$, $x \geq 8$), closed-shell products with 7 or more oxygen atoms ($C_{10}H_{15,17}NO_x$, $x \geq 7$), and peroxynitrates with 10 or more oxygen atoms ($C_{10}H_{16}N_2O_x$, $x \geq 10$); HOM dimers are defined as species with 9 or more oxygen atoms (starting from $C_{20}H_{32}N_2O_9$, formed by $C_{10}H_{16}NO_5 + C_{10}H_{16}NO_6$). We also include "cross dimers" from NO_3-initiated RO_2 reacting with O_3- or OH-initiated RO_2, i.e. $C_{20}H_{31}NO_x$/$C_{20}H_{33}NO_x$ with $x \geq 8$ or $x \geq 7$, respectively, as the initial RO_2 from O_3/OH oxidation has four or three oxygen atoms.

A comparison of concentrations for major monomer compounds ($O \geq 7$), dimers ($O \geq 11$), and peroxynitrates ($O \geq 10$) between nitrate and DEA modes is presented in Fig. S8. For all MTs except carene, the first-autoxidation RO_2 ($C_{10}H_{16}NO_7$) was detected much more efficiently by the DEA mode. Conversely, the nitrate mode exhibited greater selectivity for products resulting from two or more autoxidation steps (i.e., RO_2 with $O \geq 9$, or $O \geq 8$ if one RO_2 to RO conversion occurred) for all MTs except myrcene. Closed-shell monomers corresponding to these two-autoxidation-step RO_2 species (with $O \geq 8$ or 7) showed comparable concentrations between the two modes, with differences being less than one order of magnitude only for BP and myrcene. Therefore, the monomer results are consistent with the fact that nitrate-CIMS is usually utilized for investigating HOMs due to its high selectivity (Bianchi et al., 2019; Riva et al., 2019). It is notable that some defined HOM dimers exhibited higher signals in the DEA mode (Fig. S8). Furthermore, the HOM dimers $C_{20}H_{32}N_2O_{9,10}$ were absent from nitrate spectra (Fig. 4), despite their non-negligible signals in the DEA spectrum of MTs such as BP (Fig. 3D).

3.2 Peroxy radicals and closed-shell products from DEA- and nitrate-CIMS

As the DEA and nitrate modes collectively cover a wide range of oxidation products ($O \geq 2$), their representative spectra (Figs. 3 and 4) provide insightful molecular information on the NO_3 oxidation products of the five MTs. Normalized signals are displayed for the experimental stage 6 ($[MT]_0 = 20$ ppb, $[O_3]_0 = 12$ ppb, and $[NO_2]_0 = 50$ ppb), where the NO_3 radical dominates the oxidation (Fig. S7), making these spectra highly representative of the NO_3-initiated chemistry. It is worth noting that products in the DEA mode were charged by clustering with $C_4H_{12}N^+$, while products in the nitrate mode were charged by clustering with either a primary ion monomer (NO_3^- or $^{15}NO_3^-$) or a dimer ($H^{15}NO_3 \cdot {}^{15}NO_3^-$ or $HNO_3 \cdot {}^{15}NO_3^-$ or $HNO_3 \cdot NO_3^-$) (see Fig. S9 for detailed charging scheme). For further investigation of the molar yields and trends of individual products as a function of reacted [MT] by NO_3 radicals, Figures 5 and S10 utilize data from five experimental stages (2 and 5–8) with $[MT]_0 = 20$ ppb and the NO_3 oxidation was the dominant oxidation process (Fig. S7).

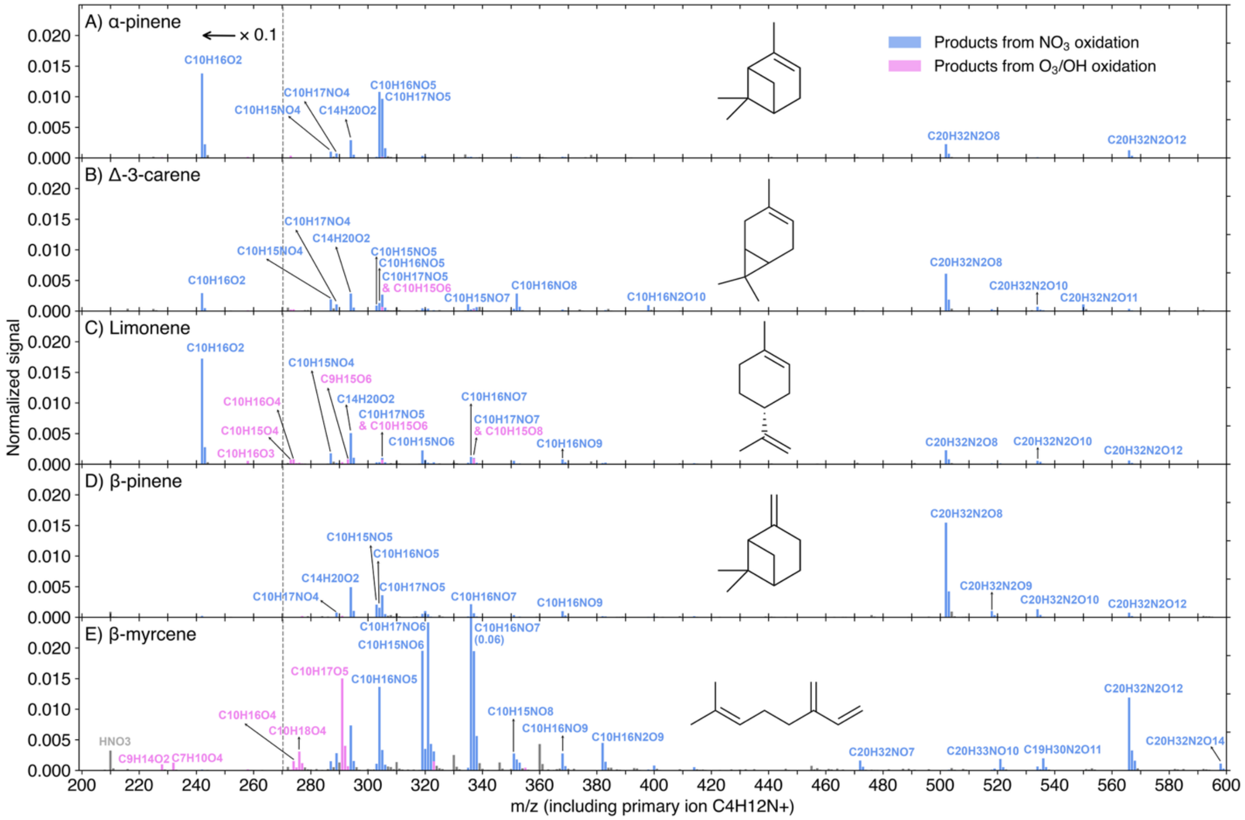

Figure 3. DEA-CIMS spectra (10 min average) of MT + NO_3 reactions at the experimental stage 6. Initial concentrations were $[MT]_0$ = 20 ppb, $[O_3]_0$ = 12 ppb, and $[NO_2]_0$ = 50 ppb, with an effective reaction time of 8.8 s. The spectra display the normalized peak signals (see Equation S4) and were corrected by subtracting background signals. Blue bars represent products (including both radicals and closed-shell species) from NO_3 oxidation, pink bars show products from O_3 or OH oxidation, and grey bars are for peaks not of interest. All compounds of interest were charged by clustering with the $C_4H_{12}N^+$ reagent ion, which is omitted from the displayed molecular formulas for clarity. Peaks smaller than 271 Th are divided by 10.

The DEA-CIMS spectra (Fig. 3) show that the closed-shell species $C_{10}H_{16}O_2$ was the dominant product for limonene, AP, and carene, with yields exceeding 50% for the former two (Fig. 5A and 5C). This finding is consistent with earlier chamber studies which identified pinonaldehyde and endolim as the major NO_3 oxidation products of AP (reported yields of 39–71%) and limonene (reported yields of 25–72%), respectively (Hallquist et al., 1999; Spittler et al., 2006; Wängberg et al., 1997). Although the yield of caronaldehyde from carene + NO_3 was previously estimated to be minor (2–3%; Hallquist et al., 1999), our results suggest that $C_{10}H_{16}O_2$ represents the largest single molar yield for carene at approximately 10% (Fig. 5B). The formation of $C_{10}H_{16}O_2$ can be attributed to bimolecular reactions of the peroxy radical $C_{10}H_{16}NO_5$ forming the nitrooxy alkoxy radical (RO) $C_{10}H_{16}NO_4$. This RO radical then undergoes nitrooxy-side β-scission (i.e., breaking the C–C bond in ·O–C–C–ONO_2), a process followed by NO_2 loss, resulting in the $C_{10}H_{16}O_2$ product (Fig. S11) (Bates et al., 2022; Draper et al., 2019; Kurtén et al., 2017; Novelli et al., 2021). The comparative low $C_{10}H_{16}O_2$ yield observed from carene + NO_3 is consistent with its alkoxy radical $C_{10}H_{16}NO_4$ tending toward alkyl-side β-scission (i.e., breaking of the RC–CO· bond), which favors further autoxidation over $C_{10}H_{16}O_2$ formation (Fig. S11) (Draper et al., 2019; Kurtén et al., 2017).

This favored alkyl-side β-scission for carene would initiate a sequence of RO_2 radicals ($C_{10}H_{16}NO_{6,8,10}$), aligning with the high signals of $C_{10}H_{16}NO_{8,10}$ observed (Figs. 3B–5B). The relative low concentration of $C_{10}H_{16}NO_6$ suggests rapid autoxidation to the more oxygenated $C_{10}H_{16}NO_8$. Conversely, the absence of $C_{10}H_{16}NO_8$ and the low signals of $C_{10}H_{16}NO_6$ for AP and limonene align with their high yields of $C_{10}H_{16}O_2$ (Figs. 3–5), reinforcing that the alkyl-side β-scission is unfavored for these two MTs. For limonene, NO_3 addition could also occur at the exocyclic double bond forming $C_{10}H_{16}NO_5$, then leading to the formation of $C_{10}H_{16}O_2$ via bimolecular reactions or initiation of autoxidation (Mayorga et al., 2022). The dominance of odd-oxygen-number RO_2 ($C_{10}H_{16}NO_{7,9}$) for AP and limonene (Figs. 3–5) indicates “direct” autoxidation steps from $C_{10}H_{16}NO_5$ with minor RO_2 to RO conversion. It is noteworthy that, for limonene, the second NO_3 addition to the double bond of $C_{10}H_{16}O_2$ could directly produce $C_{10}H_{16}NO_7$, followed by autoxidation to $C_{10}H_{16}NO_{9,11}$ (Guo et al., 2022). But this second NO_3 addition was unfavored due to the short effective reaction time at 8.8 s. Overall, the comparative low signals and yields of each HOM for AP and limonene (panels A and C in Figs. 4, 5, and S10), suggest that they do not possess ring-opening processes as effective as carene for fostering subsequent autoxidation, and the second NO_3 addition for limonene is negligible.

In contrast, BP and myrcene, which do not have the same endocyclic double bond as the other three MTs, did not generate $C_{10}H_{16}O_2$ in NO_3 oxidation (Fig. 3). BP has the highest yields of the radical $C_{10}H_{16}NO_6$ and closed-shell species $C_{10}H_{15,17}NO_5$ (formed from bimolecular reactions of $C_{10}H_{16}NO_6$) among the five MTs (Figs. 3 and 5), supporting the mechanism proposed by Claflin and Ziemann (2018), where the RO radical $C_{10}H_{16}NO_4$ from bimolecular reactions of $C_{10}H_{16}NO_5$, experiences a ring-opening process leading to $C_{10}H_{16}NO_6$. Subsequent bimolecular reactions can convert $C_{10}H_{16}NO_6$ to the RO radical $C_{10}H_{16}NO_5$, which can consequently trigger another ring-opening to form $C_{10}H_{16}NO_7$ after O_2 addition. With less constraints by rigid cyclic structures (Kurtén et al., 2015), $C_{10}H_{16}NO_7$ is expected to easily undergo autoxidation steps. The presence of considerable $C_{10}H_{16}NO_{7,9}$ and the absence of $C_{10}H_{16}NO_8$ (Figs. 3D and 4D) suggest the second ring-opening process and subsequent autoxidation. Although abundant $C_{10}H_{16}NO_8$ was observed in an earlier chamber study focusing on BP + NO_3 (Shen et al., 2021), it was not formed fast as $C_{10}H_{16}NO_9$ at the beginning based on their timeseries, suggesting that $C_{10}H_{16}NO_8$ likely resulted from $C_{10}H_{16}NO_7$ undergoing RO-forming bimolecular reactions followed by one autoxidation step. Furthermore, due to the short reaction time of 8.8 s in our flow-tube experiments, we did not detect second-generation peroxy radicals (i.e., those resulting from two NO_3 additions) with two nitrogen atoms, which were reported in Shen et al. (2021).

The acyclic structure, featuring three double bonds, makes the reaction of myrcene with the NO_3 radical mechanistically distinct from the other four cyclic MTs. The dominance of odd-oxygen-number peroxy radicals $C_{10}H_{16}NO_{5,7,9,11}$ suggest the fast autoxidation steps of myrcene comparing to RO-forming bimolecular reactions (Figs. 3E–5E). Moreover, the ring closures between RO_2 and double bonds are normally fast, leading to the formation of C–O–O–C peroxide groups (Vereecken et al., 2021). The proposed ring-closure processes are supported by the relative detection efficiency of myrcene + NO_3 products by DEA and nitrate modes (Fig. S8E): only when RO_2 radicals reached $C_{10}H_{16}NO_{10,11}$ and dimers reached $C_{20}H_{32}N_2O_{18}$, were they detected more efficiently by the nitrate mode. Because after two ring-closure steps (which consume the remaining two double bonds following NO_3 addition), those species would just begin to possess –OH/–OOH groups (via H-shift), which enhance the detection efficiency by the nitrate mode as hydrogen bond donors (Hyttinen et al., 2015). Considering bimolecular reactions RO_2 + R'O_2 forming ROH and R'C=O (Bianchi et al., 2019), the substantial amount of closed-shell species $C_{10}H_{15,17}NO_{6,8,10}$ potentially indicates that these RO_2 bimolecular reactions were fast for myrcene (Figs. 3E, 4E, and S10E).

It's notable that for AP, the concentration of the closed-shell monomer $C_{10}H_{17}NO_5$ is almost 100 times higher than that of the RO_2 radical $C_{10}H_{16}NO_6$, without the presence of the closed-shell $C_{10}H_{15}NO_5$ (Figs. 3A, 5A, and S10A). This suggests that the formation of $C_{10}H_{17}NO_5$ is likely due to the reaction $C_{10}H_{16}NO_5$ + HO_2, which was reported as an important pathway with a high molar yield (Bates et al., 2022). The potential involvement of HO_2 in other MTs could also be indicated by the relative abundance of some closed-shell monomers. For instance, the $C_{10}H_{17}NO_5$ was more abundant than $C_{10}H_{15}NO_5$ for both carene and BP (Fig. 3).

An unexpected observation is the considerable amount of $C_{14}H_{20}O_2$ across all MTs (Fig. 3). Since this species always increased when both MTs and NO_3 were available and followed trends similar to other NO_3 products (Figs. 2, and S3–S6), it is attributed to NO_3 oxidation. Its presence even for BP and myrcene (Figs. S5 and S6), which did not have $C_{10}H_{16}O_2$, rules out the initial speculation that it was formed by $C_{10}H_{16}O_2$ clustering with a C_4H_4 (which is possibly a fragment of the primary ion and had constant high concentration for all MTs; see Fig. S5A for example), and suggests the involvement of some unknown fragmentation processes.

The RO_2 bimolecular reactions also form dimers (ROOR') besides RO radicals and closed-shell monomers (Bianchi et al., 2019). The dimer $C_{20}H_{32}N_2O_8$ (from two $C_{10}H_{16}NO_5$) was the dominant dimer for all MTs except myrcene, where the most abundant dimer was $C_{20}H_{32}N_2O_{12}$, likely formed from two $C_{10}H_{16}NO_7$ (Fig. 3). It's notable that among all MTs, BP has the highest yield of $C_{20}H_{32}N_2O_8$, which is approximately an order of magnitude higher than its $C_{10}H_{16}NO_5$ (Figs. 3 and 5). Claflin and Ziemann (2018) proposed that in BP + NO_3, $C_{20}H_{32}N_2O_8$ was formed in the particle phase by two closed-shell monomers, however, our observation suggests that the $C_{20}H_{32}N_2O_8$ could be formed rapidly in the gas phase. It remains unclear why BP in particular has such a high yield of this dimer.

The dimer patterns overall match the RO_2 radical distributions. AP, limonene, and myrcene, having major RO_2 radicals with odd oxygen number, produced series of even-oxygen-number dimers $C_{20}H_{32}N_2O_x$ (Figs. 3–4). On the contrary, with considerable even-oxygen-number RO_2 radicals present alongside the odd ones, carene and BP also have noticeable amounts of odd-oxygen-number dimers $C_{20}H_{32}N_2O_{11}$ (via $C_{10}H_{16}NO_5$ + $C_{10}H_{16}NO_8$) and $C_{20}H_{32}N_2O_9$ (via $C_{10}H_{16}NO_5$ + $C_{10}H_{16}NO_6$), respectively. In the DEA spectrum of myrcene (Fig. 3E), the formation of dimers $C_{20}H_{32}NO_7$ and $C_{19}H_{30}N_2O_{11}$ was likely due to the fragmentation occurring during bimolecular reactions of two NO_3-initiated RO_2 (namely NO_3-RO_2), while $C_{20}H_{33}NO_{10}$ could be from a NO_3-RO_2 ($C_{10}H_{16}NO_7$) reacting with an OH-RO_2 ($C_{10}H_{17}O_5$).

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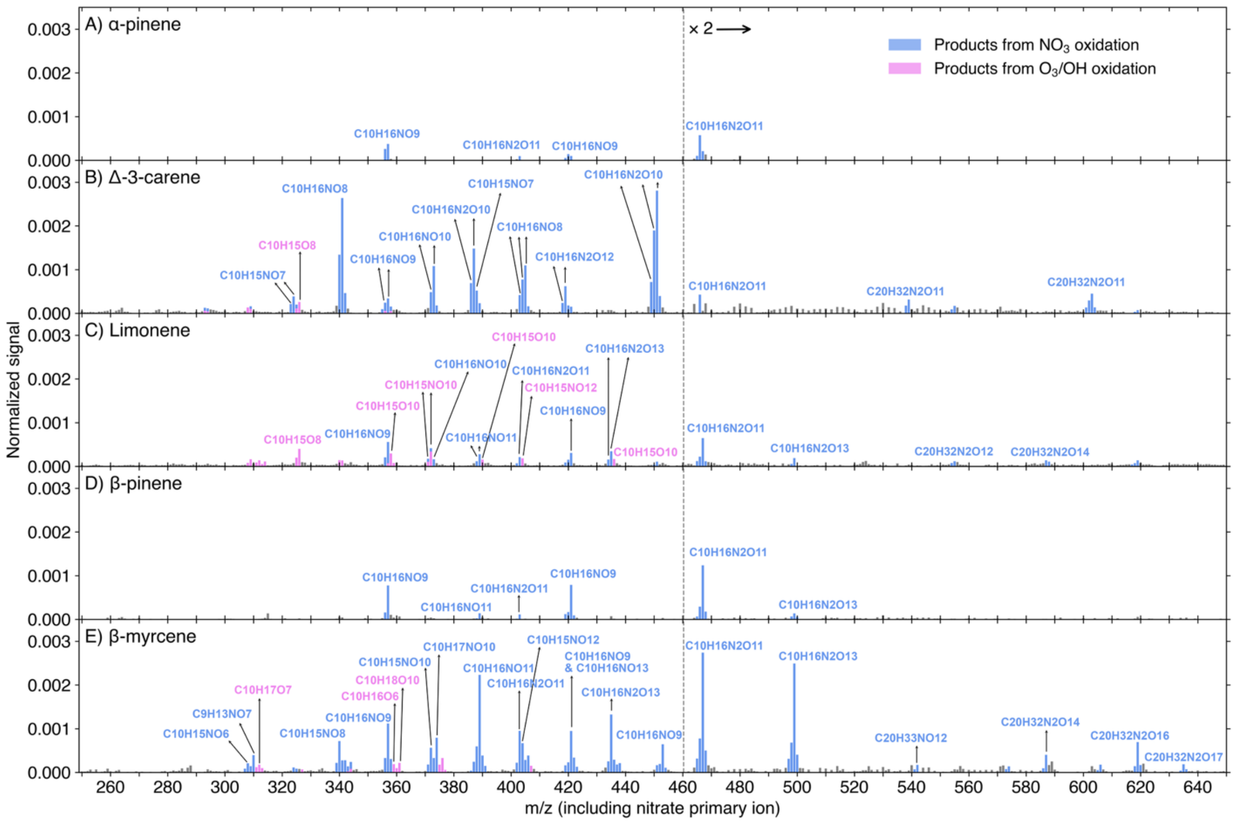

Figure 4. Nitrate-CIMS spectra (10 min average) of MT + NO$_3$ reactions at the experimental stage 6. Initial concentrations were [MT]$_0$ = 20 ppb, [O$_3$]$_0$ = 12 ppb, and [NO$_2$]$_0$ = 50 ppb, with an effective reaction time of 8.8 s. The spectra display the normalized peak signals (see Equation S3) and were corrected by subtracting background signals. Blue bars represent products (including both radicals and closed-shell species) from NO$_3$ oxidation, pink bars show products from O$_3$ or OH oxidation, and grey bars are for peaks not of interest. Compounds of interest were charged by clustering with either a primary ion monomer (e.g., $^{15}NO_3^-$) or a dimer (e.g., $H^{15}NO_3 \cdot {}^{15}NO_3^-$), which is omitted from the displayed molecular formulas for simplicity. The detailed charging schemes are shown in Fig. S9. Peaks larger than 460 Th are multiplied by 2.

From both DEA and nitrate spectra, we observed abundant peroxynitrates (RO_2NO_2) from NO_3-RO_2 + NO_2, such as $C_{10}H_{16}N_2O_{10}$ for carene (Figs. 3B and 4B) and $C_{10}H_{16}N_2O_{9,11,13}$ for myrcene (Figs. 3E and 4E), and the yields of these RO_2NO_2 expectedly increased with higher NO_2 concentrations (Fig. S10). Earlier studies using NO_2 + O_3 as NO_3 source also reported noticeable amounts of RO_2NO_2 (Dam et al., 2022; Draper et al., 2019; Guo et al., 2022; Mayorga et al., 2022). These RO_2NO_2 were especially significant among the HOMs in nitrate spectra (Fig. 4) and tended to be charged by clustering with dimer primary ions (e.g., $H^{15}NO_3 \cdot {}^{15}NO_3^-$) (Fig. S9). Furthermore, we also observed a noticeable amount of $C_{10}H_{15}NO_{10,12}$ in NO_3 + limonene (Figs. 4C and S4B), as previously reported by Guo et al. (2022). However, instead of attributing these species directly to NO_3 oxidation products, we regard them as RO_2NO_2 formed from $C_{10}H_{15}O_{8,10}$ (O_3-RO_2) + NO_2, since their behavior in the time series mirrored that of $C_{10}H_{15}O_{8,10}$ during stages 1–4 (Fig. S4). Generally, more oxygenated RO_2 radicals exhibited higher conversion to RO_2NO_2 (Fig. S12). This is likely due to the formation of more stable RO_2NO_2 structures, such as peroxyacetyl nitrates (PANs), which feature longer atmospheric lifetimes (Atkinson, 2000; Russell et al., 2025).

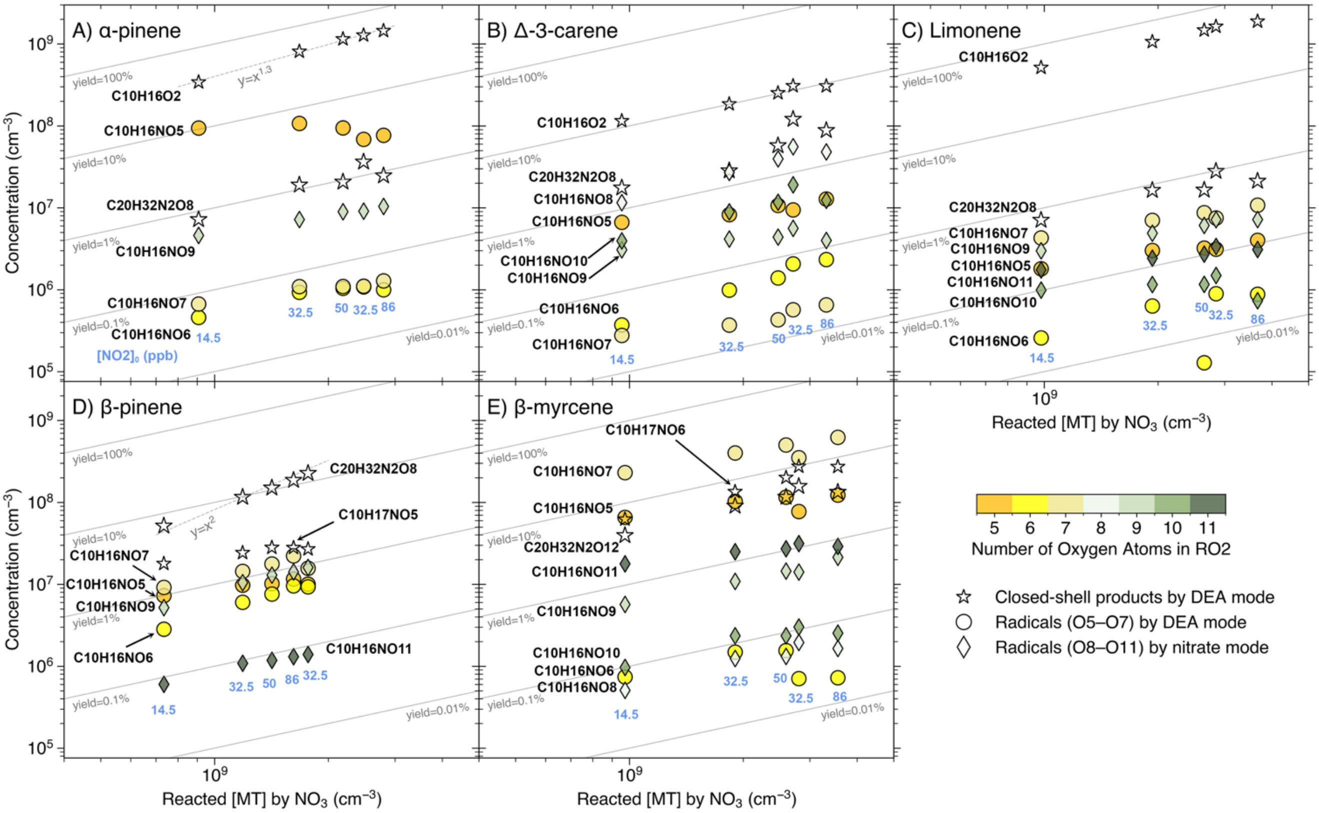

Figure 5. Concentrations (in cm^{-3}) of the dominant closed-shell monomer and dimer, and the RO_2 radicals, from the MT + NO_3 reactions, as a function of reacted [MT] by the NO_3 radical. Data from experimental stages 2 and 5–8 are presented as 10 min averaged measurements taken at an effective reaction time of 8.8 s. The reacted [MT] by NO_3 was varied primarily by increasing $[NO_2]_0$ (values in ppb shown beneath each column). The only exception is the transition from stage 7 to stage 8, where $[O_3]_0$ increased from 12 to 18 ppb and $[NO_2]_0$ decreased from 86 to 34.5 ppb (see Fig. 2). Radicals are grouped and colored by the number of oxygen atoms: circles represent radicals with O = 5 to 7 measured by the DEA mode, and diamonds show radicals with O = 8 to 11 measured by the nitrate mode. The dominant closed-shell monomer and dimer measured by the DEA mode are both shown by hollow stars, with the dimer distinguished by a larger marker size.

Generally, the concentrations of most NO_3 products increased monotonically with the rising reacted [MT] by the NO_3 radicals (Figs. 5 and S10). The most notable exception is that for AP, the peroxy radical $C_{10}H_{16}NO_5$ and its closed-shell monomer $C_{10}H_{17}NO_5$ significantly decreased with increasing reacted [MT], beyond expectation (Figs. 5A and S10A). As all stages in Figures 5 and S10 have the same $[MT]_0$, the reacted [MT] by NO_3 is directly proportional to the amount of NO_3 in the system. The faster-than-linear increase of $C_{10}H_{16}O_2$ (which approximately follows a 1:1.3 line, as shown in Fig. 5A) suggests that with increasing [NO_3], the peroxy radical $C_{10}H_{16}NO_5$ was converted to $C_{10}H_{16}O_2$ more efficiently. Also, AP has the highest yield of the radical $C_{10}H_{16}NO_5$ among all five MTs studied (Fig. 5), proposing that both autoxidation and bimolecular reactions are comparatively slow. The findings appear to be consistent with the previous studies that estimated the SOA yield of AP + NO_3 to be near 0% using N_2O_5 as NO_3 source (Fry et al., 2014), as high [NO_3] could significantly enhance the role of the RO_2 + NO_3 reaction in the experiments, leading to the formation of the comparatively volatile $C_{10}H_{16}O_2$ (Bates et al., 2022). We observed that only the dimer $C_{20}H_{32}N_2O_8$ from BP + NO_3 follows a near-quadratic trend with the reacted [MT] (Fig. 5D). This indicates that the reaction coefficient of the dimer-forming bimolecular reaction is the fastest compared to other competing pathways, which is consistent with $C_{20}H_{32}N_2O_8$ being the main product (Figs. 3D, 5D, and S10D). It is noteworthy that the data points corresponding to the column with $[NO_2]_0$=32.5 ppb but the higher reacted [MT] (stage 8), often deviated from the general trend (Figs. 5 and S10). This deviation occurred because the increased $[O_3]_0$ in stage 8 enhanced the production of O_3/OH oxidation products, such as O_3/OH-RO_2 radicals, which subsequently affected the concentrations of NO_3 oxidation products.

3.3 Product closure and HOM yields

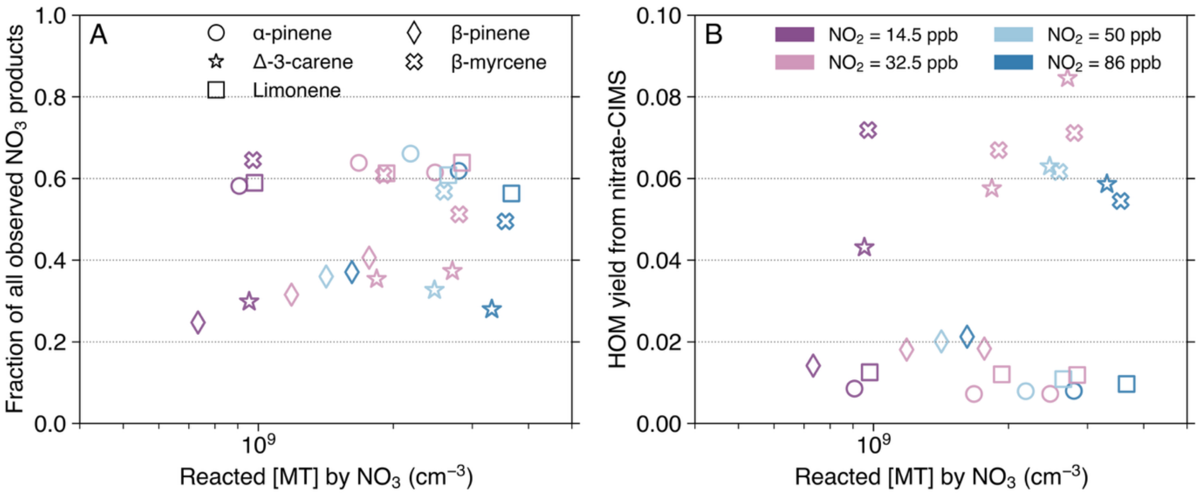

Figure 6. Fraction of all observed NO_3-initiated products over reacted [MT] by the NO_3 radical (panel A) and HOM yield (panel B), as a function of reacted [MT] by the NO_3 radical. Data from experimental stages 2 and 5–8 are presented as 10 min averaged measurements taken at an effective reaction time of 8.8 s. The HOM yield (panel B) is solely based on nitrate-CIMS measurement. The calculation for the fraction of observed NO_3-initiated products (panel A) combines HOM concentrations from the nitrate mode with less oxygenated products from the DEA mode. Exceptions were made for some HOM dimers: $C_{20}H_{32}N_2O_{9,10}$ (for all MTs) and $C_{20}H_{32}N_2O_{12}$ (for myrcene) were taken from the DEA mode due to their absence in the nitrate spectra (Fig. 4E). Different MTs are distinguished by marker shape: circle (AP), star (carene), square (limonene), diamond (BP), and cross (myrcene). Marker colors denote the distinct $[NO_2]_0$ used in the experiments.

Product closure was reasonably reached for AP, limonene, and myrcene, given that the fractions of all observed NO_3-initiated products over reacted [MT] by the NO_3 radical were calculated to be 50–70% (Fig. 6A). Considering the inherent uncertainties stemming mainly from the calibration factor applied to CIMS quantification (Section S2) and the estimated coefficients of NO_3 and N_2O_5 wall losses within the box model (Table S1), it is possible that we were able to observe almost all the products. On the contrary, carene and BP exhibited lower fractions, at 20–40% (Fig. 6A). This reduced closure could be attributed to the unaccounted formation of products containing one O-atom, as these cannot be effectively detected by the DEA mode (Riva et al., 2019). An earlier flow-tube study reported that the yield of nopinone ($C_9H_{14}O$) from BP + NO_3 varied substantially (20–80%) across different experimental pressures and NO concentrations (Berndt et al., 1999). To our knowledge, no previous studies have explicitly identified and quantified any major products containing only one O-atom from carene + NO_3, proposing either a new reaction pathway or a severely underestimated calibration factor for some carene products.

To maintain consistency with previous studies, which exclusively used nitrate-CIMS for HOM investigations (Dam et al., 2022; Day et al., 2022; Draper et al., 2019; Ehn et al., 2014; Guo et al., 2022; Harb et al., 2025; Li et al., 2024; Luo et al., 2022; Shen et al., 2021; Zhang et al., 2024a, b; Zhao et al., 2024), HOM yields were calculated solely using data from the nitrate mode in this study. However, we note that the HOM yields may be underestimated because of the low selectivity of nitrate-CIMS toward some HOM dimers with relatively low oxygen numbers (discussed in Section 3.1). One example is that the proposed formation of C–O–O–C groups inhibited the effective detection by the nitrate mode of some HOMs formed from myrcene + NO_3 (such as $C_{10}H_{16}NO_9$). Despite this underestimation, the acyclic myrcene exhibits the highest average HOM yield (~6.5%; Fig. 6B), as could be expected, since its open structure imposes fewer constraints on autoxidation compared to the cyclic MTs. Among the four cyclic MTs, NO_3 oxidation of carene produced the highest average HOM yield at approximately 6.1%, closely approaching that of myrcene. This is consistent with the finding that carene undergoes a ring-opening process (i.e., the alkyl-side β-scission of the nitrooxy alkoxy radical) that facilitates autoxidation (Section 3.2; Figs. 3–5, and S11) (Draper et al., 2019; Kurtén et al., 2017). The HOM yield of BP + NO_3 (at ~1.8%) exceeds that of AP (~0.8%) and limonene (~1.1%). Directly compared to our results, Guo et al. (2022) reported a similar HOM yield (1.5%) for limonene + NO_3, while Shen et al. (2021) estimated a much higher HOM yield (4.8%) for BP. Due to the difference of experimental setups and conditions (e.g., reaction time and NO_3 source), direct quantitative comparison of HOM yields across various studies is often challenging. Nevertheless, if combining findings from earlier studies that have measured HOM yields from more than one MT using the same sampling system, we can conclude that HOM yields from ozonolysis can be listed in the order (from highest to lowest): limonene > carene > AP > myrcene > BP (Jokinen et al., 2015; Zhao et al., 2024). This order contrasts with the NO_3 oxidation results in this study. The relatively low HOM yield of myrcene + O_3 is likely due to decomposition into smaller fragments following the breaking of the primary ozonide (Atkinson and Arey, 2003). Conversely, Jokinen et al. (2015) reported myrcene having the highest HOM yield in OH oxidation (~1 %), followed by limonene, BP, and AP.

We can compare the HOM yields from NO_3 oxidation (Fig. 6B) to their corresponding SOA formation reported in earlier studies. These studies consistently found that AP has the lowest SOA yield (DeVault et al., 2022; Hallquist et al., 1999), even approaching zero (Fry et al., 2014). This is possibly due to excessive [NO_3] that favors volatile product formation, as discussed in Section 3.2. However, the relative SOA yields for cyclic MTs vary across different studies (DeVault et al., 2022; Fry et al., 2014; Hallquist et al., 1999), thereby making comparisons to our HOM yields inconclusive. The discrepancies may relate to different conditions during the experiments and suggest that simultaneous measurements of HOMs might have shed some light on the relevant reaction pathways taking place in the experiments.

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3.4 Implications, challenges, and limitations

We directly compare the gas-phase products and relevant yields from NO_3 oxidation of five common MTs at a short effective reaction time of 8.8 s, allowing us to capture the early-stage evolution of peroxy radicals involving autoxidation processes. Our findings validate the previous observations that small structural differences among the MTs strongly influence the products, e.g. whether the nitrooxy alkoxy radicals undergo alkyl-side or nitrooxy-side β-scission. We also report new findings, e.g. a high gas-phase yield of the dimer $C_{20}H_{32}N_2O_8$ from BP + NO_3 and suggest potentially unknown pathways leading to the abundant formation of a product with one O-atom from carene + NO_3. The HOM yield of an individual MT from NO_3 oxidation can differ significantly from that by O_3/OH oxidation, yet the overall HOM yields are comparable between oxidants, generally falling in the range 0–10%, although yields from OH oxidation are typically the lowest (Bianchi et al., 2019; Jokinen et al., 2015; Zhao et al., 2024). The discrepancy between the relative magnitudes of HOM and SOA yields of each MT (DeVault et al., 2022; Fry et al., 2014; Hallquist et al., 1999) can partly be explained by the potentially underestimated HOM yields and contribution of non-HOM products to SOA formation, but also by differing reaction conditions between studies. In our flow-tube experiments, we have much shorter residence time compared to traditional chamber SOA yield experiments (seconds vs. hours), during which multigenerational products can form and contribute to SOA formation, for instance, NO_3 addition to the first-generation product $C_{10}H_{16}O_2$ from limonene + NO_3 reactions. Moreover, particle-phase reactions occurring after condensation introduce additional uncertainties when directly comparing our HOM yields with previously reported SOA yield results. Overall, our results revealed that the NO_3 oxidation mechanisms are highly structure-dependent, and their contribution to atmospheric particles varies significantly among different MTs.

A major challenge in studying NO_3 chemistry is replicating atmospherically relevant RO_2 radical fates. Since we used NO_2 + O_3 to supply NO_3, the excessive NO_2 relative to NO_3 (Fig. S2) resulted in the formation of a noticeable amount of RO_2NO_2 (Figs. 3, 4, S9, S10, and S12). This competing pathway (RO_2 + NO_2) may obscure the importance of other reactions involving RO_2 radicals. While using the thermal decomposition of N_2O_5 could avoid the RO_2NO_2-forming issue, it often provides too high [NO_3], causing the bimolecular reaction RO_2 + NO_3 to dominate (Bates et al., 2022). For instance, this excessive [NO_3] pushes AP + NO_3 to form more volatile $C_{10}H_{16}O_2$, underestimating the importance of AP in SOA formation. This highlights the inherent difficulty in studying NO_3 + MTs mechanisms in laboratory settings.

One major limitation of our study is the incomplete product closure observed for carene and BP, possibly due to the DEA mode failing to detect products containing one O-atom. The formation of these unseen products can be investigated by future studies using instruments with better selectivity. Another limitation is the inability to perform dilution experiments without a well-designed dilution unit attached to the CIMS inlet, preventing us from ruling out potential ion-induced clustering taking place in the chemical ionization inlet (Berndt et al., 2016; Peräkylä et al., 2023). The design of the dilution unit is crucial, as our unit caused too much turbulence that decreased all signals far beyond the expected dilution factor, warranting future study. It is worth noting that the reagents which are selective to low-oxygenated compounds (O < 6), such as the DEA used in this study, can be very sensitive to contaminants. For example, nitric acid (HNO_3) from the NO_2 cylinder initially depleted our

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primary ion ($C_4H_{12}N^+$), affecting quantification, but the addition of a HEPA filter (Whatman plc) after the gas cylinder removed most, though not all, of the HNO_3. Moreover, the lack of more specific standard calibration compounds than sulfuric acid (Section S2) limits our CIMS quantification for the larger organic compounds.

4 Conclusions

This study utilized a newly built free-jet flow-tube system with a moveable injector that allows changing the reaction time to measure products from monoterpene (AP, carene, limonene, BP, myrcene) oxidation by NO_3. Switching a CIMS between DEA and nitrate modes enabled us to investigate a wide range of gas-phase radicals and closed-shell products, at an effective reaction time of 8.8 s (8.3 s in the flow-tube at 110 cm reaction distance and 0.46 s in the CIMS sampling inlet). The nearly wall-free experimental conditions, direct comparison of the five MTs, and the wide coverage of oxidation products provide valuable insights into early-stage NO_3 oxidation pathways including autoxidation. The design of our NO_3 experiments allowed us to distinguish NO_3-initiated products from O_3/OH-initiated ones.

Consistent with previous studies (Draper et al., 2019; Hallquist et al., 1999; Kurtén et al., 2017; Spittler et al., 2006), NO_3 oxidation of AP and limonene produced substantial $C_{10}H_{16}O_2$ with yields exceeding 50%, while carene produced much less $C_{10}H_{16}O_2$ and instead underwent more efficient autoxidation. Several surprising features were also observed for the different MTs: i) for AP, with rising [NO_3], the concentration of the primary RO_2 radical $C_{10}H_{16}NO_5$ did not increase as expected, but instead showed an increased yield of $C_{10}H_{16}O_2$, ii) while our results agree with the previously proposed ring-opening process of BP following reaction with NO_3, a dominant dimer $C_{20}H_{32}N_2O_8$ (with a yield of ~10% and a quadratic trend with reacted [BP]) was observed, suggesting very rapid accretion product formation in the gas phase, while an earlier study hypothesised that this dimer forms solely in the particle phase (Claflin and Ziemann, 2018), iii) the considerable amount of RO_2 species $C_{10}H_{16}NO_{5,7,9,11}$ from the acyclic myrcene suggests efficient autoxidation, but instead of H-shifts to form –OOH groups, we speculate that the RO_2 undergo ring-closure processes with double bonds to form C–O–O–C groups, based both on expectations from its structure and on the relative detection efficiency of the products by DEA and nitrate modes.

The fractions of total observed NO_3-initiated products indicate that product closure was reasonably reached for AP, limonene, and myrcene, considering the uncertainties of CIMS quantification and modeled reacted [MT]. In contrast, the incomplete closure of carene and BP is likely due to the low sensitivity of the DEA mode toward products with only one O-atom. While the formation of nopinone, $C_9H_{14}O$, in BP + NO_3 was previously reported, there may be unknown processes for carene to produce large amounts of such products. The average HOM yields from NO_3 oxidation follow the order: myrcene (6.5%), carene (6.1%), BP (1.8%), limonene (1.1%), and AP (0.8%). This result confirms that NO_3 oxidation yields significant amount of HOMs, and the overall range is comparable to O_3 oxidation (0–10%).

Overall, our results highlight that the product formation from MT + NO_3 reactions is highly structure-dependent and behaves differently from O_3 and OH oxidation. Our study provides individual product yields for the most abundant compounds, radical distributions, and HOM yields, which are all essential for correctly implementing MT + NO_3 oxidation mechanisms into models. Future studies using instruments with better selectivity toward low-oxygenated compounds can validate whether our missing closure for carene and BP was indeed due to lack of sensitivity toward such compounds. Moreover, a comprehensive study on SOA yields of these different MTs together with HOM measurements will clarify to what extent HOMs are able to explain SOA formation from NO_3 oxidation of monoterpenes.

Data availability. Data are available upon request by contacting the corresponding authors. Data presented in the paper are archived in Zenodo (https://doi.org/10.5281/zenodo.17250833; Zhang et al., 2025).

Supplement. The supplement related to this article is available online.

Author contributions. ME and JYZ designed the study. JYZ and YZ conducted the experiments. JYZ analyzed the data with the help of ME and JZ. ME, JYZ, JZ, and HK designed the flow-tube system, with HK further developing the concept into a CAD model. JYZ prepared the manuscript with contributions from all co-authors.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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