

Chemical composition and volatility of organic nitrate products from NO₃ radical initiated oxidation of Δ³-carene

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HIGHLIGHTS

- Increasing NO₃ to Δ³-carene ratios promote more oxygenated organic nitrates and enhanced fragmentation.
- NO₃ oxidation of Δ³-carene produces higher detected organic nitrate signals than α-pinene under comparable conditions.
- Low-volatility C₂₀ dimer nitrates dominate the particle phase, likely reflecting efficient condensation and possible particle-phase accretion.
- T_{max}-derived vapor pressures of organic nitrates are consistent with observed gas-to- particle partitioning trends.

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ABSTRACT

Organic nitrates (ONs) formed from nighttime NO₃ initiated oxidation of monoterpenes (C₁₀H₁₆) are an important contributor to secondary organic aerosol. Δ³-carene is among the most abundant monoterpenes, where previous static chamber studies highlighting contrasting ON formation compared to the extensively studied isomeric α-pinene. Here, NO₃-initiated oxidation of Δ³-carene under varying oxidation conditions was studied using an oxidation flow reactor (Go:PAM) combined with an iodide chemical ionization mass spectrometer coupled to a filter inlet for gases and aerosols (FIGAERO-CIMS). The ONs produced by Δ³-carene were approximately four times higher than those produced under similar conditions from the structurally similar α-pinene. Under various ratios of oxidant to Δ³-carene experiments, monomer ONs with 10 carbons (C₁₀-ONs) were dominating (48–63%) in the gas phase where C₁₀H₁₇NO₄, C₁₀H₁₇NO₅, and C₁₀H₁₅NO₇ being the most abundant. Increasing oxidants levels promote the formation of further-generation peroxy radicals, leading to more highly oxygenated C₁₀-ONs and enhanced fragmentation processes. Seeded experiments showed that particle-phase ON products were mainly accretion products with 20 carbons (C₂₀-ONs), along with C₁₀-ONs. Among the accretion products, C₂₀H₃₂N₂O₈ and C₂₀H₃₂N₂O₁₁ were highly abundant in the particle phase likely due to both gas-to-particle condensation and particle-phase accretion reactions of monomers. Vapor pressures derived from both experimental and parameterization methods show good agreement and exhibit a decreasing trend with increasing oxygen number for both monomers and dimers. The vapor pressures of the major ONs are also comparable to those reported for an α-pinene + NO₃ system.

1. Introduction

Secondary organic aerosol (SOA) constitutes a significant fraction of submicron particles in the atmosphere, which influences climate change

and human health (Hallquist et al., 2009; Huang et al., 2014; Jimenez et al., 2009; Shrivastava et al., 2017). The SOA formation involves the oxidation of biogenic and anthropogenic volatile organic compounds (VOCs) that undergo a series of homogeneous and heterogeneous

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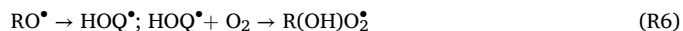
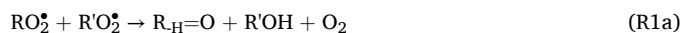
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reactions (Hallquist et al., 2009; Nozière et al., 2015; Shrivastava et al., 2017). An important contributor to SOA both day and night is organic nitrates, which can be formed from photooxidation of VOCs in the presence of nitrogen oxides ($\text{NO}_x = \text{NO}_2 + \text{NO}$) or from nitrate radical (NO_3) initiated oxidation of unsaturated VOCs (Kroll and Seinfeld, 2008; Lee et al., 2016). Organic nitrates are also a significant reservoir of NO_x and play an important role in the deposition of oxidized nitrogen (Lee et al., 2016; Sun et al., 2016). NO_3 radical is the dominant nocturnal oxidant, formed from the reaction of NO_2 with O_3 , accompanied by the formation of N_2O_5 (Brown and Stutz, 2012). NO_3 initiates the formation of organic nitrates via reactions with unsaturated VOCs. The extent and explicit mechanism are still lacking for many reaction systems (Ng et al., 2017).

Monoterpene Δ^3 -carene is one of the most emitted monoterpenes in the boreal forests, (Bäck et al., 2012; Vanhatalo et al., 2018). The NO_3 radical initiated oxidation of Δ^3 -carene gives substantial particle formation and has a higher SOA yield compared to for example the structural similar α -pinene (Hallquist et al., 1999). Kurtén et al. (2017) found that the bond scissions of the primary nitrooxy alkoxy radical ($\text{RO}^\bullet$) from NO_3 initiated oxidation of Δ^3 -carene more likely lead to further-generation reactive radicals that subsequently can give condensable products, like highly oxygenated organic nitrates while bond scissions of primary $\text{RO}^\bullet$ from NO_3 oxidation of α -pinene mainly produce the volatile product pinonaldehyde ($\text{C}_{10}\text{H}_{16}\text{O}_2$) (Fig. S1). These insights have been made possible by utilizing a chemical ionization mass spectrometer (CIMS) to characterize products formed in Δ^3 -carene + NO_3 oxidation (Day et al., 2022; DeVault and Ziemann, 2021; Draper et al., 2019; Jenks et al., 2023). Draper et al. (2019) reported a mechanism for the Δ^3 -carene + NO_3 system detailing the unimolecular pathways including hydrogen shifts and ring closing of peroxy radicals ($\text{RO}_2^\bullet$) and $\text{RO}^\bullet$ as well as $\text{RO}^\bullet$ decomposition that was in agreement with their measurement using CIMS with NO_3^- reagent (NO_3 -CIMS) of gas phase organic nitrate products. Another observation from NO_3 -CIMS shows Δ^3 -carene + NO_3 more readily forms gas-phase highly oxygenated molecules (HOM) compared to α -pinene + NO_3 (Day et al., 2022). Measurements using CIMS with I^- reagent (I-CIMS) concluded the gas-phase organic nitrates distribution, mainly hydroxy nitrate, carbonyl nitrate, and dicarbonyl nitrate from the Δ^3 -carene + NO_3 system (DeVault et al., 2022; DeVault and Ziemann, 2021; Jenks et al., 2023). These studies have advanced our understanding of the Δ^3 -carene + NO_3 gas-phase chemical scheme. However, further experiments are needed to investigate the effects of varying oxidant levels on gas-phase chemistry, as well as studies on particle-phase composition, and the partitioning behavior of organic nitrates.

Generally, the NO_3 radicals react with Δ^3 -carene by addition to the double bond, followed by molecular oxygen addition to form a nitrooxy $\text{RO}_2^\bullet$ (Ng et al., 2017; Wayne et al., 1991). A series of nitrooxy $\text{RO}_2^\bullet$ can be subsequently formed in the NO_3 radical initiated oxidation of Δ^3 -carene (DeVault et al., 2022; DeVault and Ziemann, 2021; Draper et al., 2019; Hallquist et al., 1999; Jenks et al., 2023; Kurtén et al., 2017). The bimolecular reaction of nitrooxy $\text{RO}_2^\bullet$ with another $\text{R}'\text{O}_2^\bullet$ (R1a) or a hydroperoxy radical ($\text{HO}_2^\bullet$) (R2), can form closed-shell organic nitrates preserving the number of carbon of the initial nitrooxy- $\text{RO}_2^\bullet$ (Atkinson and Arey, 2003; Day et al., 2022; Hallquist et al., 2009). However, the reactions of $\text{RO}_2^\bullet$ have also large yields from the radical chain reaction with $\text{R}'\text{O}_2^\bullet$ forming $\text{RO}^\bullet$ (e.g., R1b) or by adding more oxygen via autoxidation (R3) (Bianchi et al., 2019; Crounse et al., 2013). In a similar way the bimolecular reaction with NO_3 radicals also produce nitrooxy $\text{RO}^\bullet$ (R4). The nitrooxy $\text{RO}^\bullet$ can give closed shell molecules when reacting with O_2 (R5) or undergo hydrogen-shift and O_2 addition (R6). Depending on its structure, it may also do bond scission, which can lead to ring-opening and fragmentation, producing products with fewer carbon than the precursor. Products with higher carbon number than the precursor form via accretion reactions, e.g. the $\text{RO}_2^\bullet + \text{R}'\text{O}_2^\bullet$ reaction leading to the formation of ROOR' products (R1c), which may represent an important pathway for the formation of low-volatility products that

contribute to SOA in the monoterpenes + NO_3 system (Berkemeier et al., 2020).



In this study, a series of experiment on NO_3 initiated oxidation of Δ^3 -carene and one comparable α -pinene oxidation were performed using the laminar-flow Gothenburg Potential Aerosol Mass reactor (Go:PAM) with an iodide time-of-flight chemical ionization mass spectrometer combined with a filter inlet for gases and aerosols (FIGAERO-ToF-CIMS). Compared to previous chamber experiments of Δ^3 -carene + NO_3 system, fast-flow reactor experiments minimize wall losses and allow observation of products under a steady state condition over extended period with stepwise change in oxidation conditions. The measurements of organic nitrate by I-CIMS give a direct comparison between the two monoterpene precursors, Δ^3 -carene and α -pinene, illustrating how molecular structure influences product distribution and providing insights into how oxidation levels affect the formation and chemical composition of organic nitrates. The FIGAERO inlet enables the simultaneous characterization of organic nitrates in both the gas and particle phases, and also provides thermal desorption, gas-to-particle partitioning, and vapor pressure characteristics of organic nitrates (Li et al., 2024). By studying the formation, distribution, and physical properties of organic nitrates under varying oxidation conditions, this study contributes to a better understanding of the nighttime oxidation of monoterpenes, the mechanism of organic nitrate formation, and their contribution to SOA.

2. Materials and methods

2.1. Go:PAM reactor set-up

A series of experiments of NO_3 radical initiated oxidation of Δ^3 -carene, and for comparison an experiment with α -pinene, were conducted using Go:PAM. The Go:PAM is described in detail by Watne et al. (2018). The Go:PAM consists of a 100 cm long and 9.6 cm inner diameter quartz cylinder. N_2O_5 , a source of NO_3 radical, was pre-synthesized by reacting NO_2 with O_3 , following the procedure described by Faxon et al. (2018) and entrained using 0.2 L per minute (LPM) pure N_2 from a diffusion vial held at -20°C . The quantification of N_2O_5 were determined by titration with NO (Hallquist et al., 2000) (Fig. S2). The bulk flow of clean air was generated by a zero-air generator (model 737-4, Aadco Instruments, Inc.) and flowing into the Go:PAM from the top center as shown in Fig. 1. After oxidant signals stabilized, Δ^3 -carene or α -pinene was introduced using a small flow of pure N_2 via a temperature-controlled diffusion vial, where the flux of the monoterpene was determined gravimetrically. The total flow into the Go:PAM was adjusted to 5.2 LPM and thus the median residence time was 72 s for all experiments (Watne et al., 2018). The FIGAERO-ToF-CIMS (Aerodyne Research, Inc.) was used to characterize both gas- and particle-phase products. A scanning mobility particle sizer (SMPS, model 3080, TSI, Inc.) was used to measure particle number distribution and particle mass. To prevent the influence of the flow closest to the reactor wall, only the center part of the flow was sampled (CIMS at 2 LPM for gas phase sampling, SMPS at 0.3 LPM) and conveyed via a sampling funnel positioned at the end of the flow reactor. Each oxidation

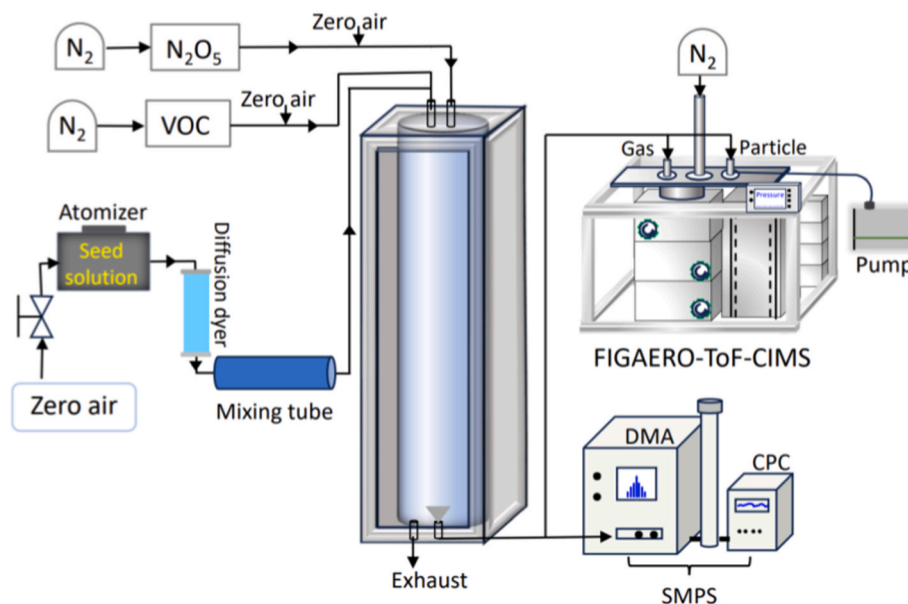


Fig. 1. Schematic of the experimental setup with the Go:PAM during Δ^3 -carene + NO_3 experiments.

condition was set and held for at least 5 h to enable stabilization and characterization.

An overview of all experiments is summarized in Table 1, including 8 unseeded Δ^3 -carene experiments, 2 seeded Δ^3 -carene experiments, and 1 unseeded α -pinene experiment. Experiments 1 to 8 were designed to study gas-phase chemistry of Δ^3 -carene oxidation under varying oxidant levels. In experiments 9 to 10, neutral and acidic seed particles were added to create condensation surfaces to probe occurrence of low volatile compounds and measure volatility and the partitioning of organic nitrates from Δ^3 -carene + NO_3 system. One α -pinene experiment was also conducted as a comparison to the primary focus on Δ^3 -carene + NO_3 system. For the two seeded experiments (Experiments 9 and 10 in Table 1), neutral or acidic seed particles were added to the Go:PAM via an atomizer after an initial 5 h characterization without seed and allowed to stabilize for an additional 1 h. Subsequently, the products in gas phases were measured for 30 min and the particles were simultaneously collected on a Teflon filter at a flow rate of 2.5 LPM for aerosol

phase analysis. The mass concentrations and surface area of the neutral seed (ammonium sulfate: $(\text{NH}_4)_2\text{SO}_4$) were $158 \pm 7 \mu\text{g m}^{-3}$, $6.2 \times 10^9 \pm 1.4 \times 10^8 \text{ nm}^{-2} \text{ cm}^{-3}$ (maximum number concentration at $\sim 80 \text{ nm}$) respectively in the Go:PAM. The mass concentrations and surface area of the acidic seed (ammonium bisulfate: NH_4HSO_4) were $162 \pm 12 \mu\text{g m}^{-3}$, $6.4 \times 10^9 \pm 3.6 \times 10^8 \text{ nm}^{-2} \text{ cm}^{-3}$ respectively in the Go:PAM. For the unseeded experiments no particle formation could be observed and only the gas-phase was analyzed.

2.2. FIGAERO-ToF-CIMS

The ToF-CIMS identified oxidized products and the oxidant related species (N_2O_5 and its decomposition ions) in a negative ionization mode. As reagent ion, iodide (I^-) was used in this study, which was produced by ionizing methyl iodide (CH_3I) with a polonium-210 radioactive source. The ion molecule reactor (IMR) was humidified by 20 standard cubic centimeters per minute (sccm) water-saturated N_2 flow. The ToF-CIMS data were mass calibrated using I^- (126.905 m/z), H_2OI^- (144.915 m/z), HNO_3I^- (189.900 m/z), I_3^- (380.713 m/z), $\text{C}_5\text{HF}_9\text{O}_2\text{I}^-$ (perfluoropentanoic acid, 390.888 m/z), and $\text{C}_7\text{HF}_{13}\text{O}_2\text{I}^-$ (perfluoroheptanoic acid, 490.881 m/z). The acquired data was processed using Tofware v3.3.0 (Aerodyne Research, Inc) and the formulas of products in this study were determined through high-resolution multi-peak fitting of each mass. All extracted ion signals were normalized to the sum of the signals of I^- and H_2OI^- and subtracted by each experiment's background. The detection efficiency of the I-CIMS may vary across different compounds due to differences in ionization and clustering behavior. The same voltage setting was applied for all experiments and voltage scanning was also performed during each experiment to characterize instrument response.

For seeded experiments, the particles were collected using the FIGAERO inlet and subsequently evaporated by gradually heating N_2 over the filter from room temperature to 200°C within 40 min. This is followed by a 20-min soak stage, maintaining the temperature constant at 200°C , and finally, a 10-min cooling down to room temperature. The maximum desorption signal temperature (T_{max}) in the thermogram of the oxidation products was extracted using exponentially modified gaussian fitting (Geretti et al., 2025). The fitting results are described in Supporting Information (SI). Subsequent, the T_{max} can be used as a proxy for volatility, thus providing estimates on vapor pressure for a specific measured formula (Bannan et al., 2019; Stark et al., 2017;

Table 1

Experimental conditions, all experiments were done at low RH < 10% and room temperature (25°C).

ID	VOC	VOC (ppb)	N_2O_5 (ppb)	Oxidant: VOC ratio	Seed particles
1	Δ^3 -carene	13 ± 3	2.7 ± 0.2	0.2	none
2	Δ^3 -carene	13 ± 3	11.7 ± 0.9	0.9	none
3	Δ^3 -carene	13 ± 3	21.4 ± 1.8	1.6	none
4	Δ^3 -carene	13 ± 3	37.3 ± 3.1	2.9	none
5	Δ^3 -carene	30 ± 5	1.7 ± 0.1	0.1	none
6	Δ^3 -carene	30 ± 5	9.3 ± 0.7	0.3	none
7	Δ^3 -carene	30 ± 5	15.6 ± 0.9	0.5	none
8	Δ^3 -carene	30 ± 5	38.4 ± 3.1	1.3	none
9	Δ^3 -carene	30 ± 5	37.5 ± 5.3	1.3	$(\text{NH}_4)_2\text{SO}_4$
10	Δ^3 -carene	30 ± 5	34.1 ± 2.4	1.1	NH_4HSO_4
11	α -pinene	30 ± 8	15.5 ± 1.4	0.5	none

Ylisirniö et al., 2021). Geretti et al. (2025) presented a new method to derive vapor pressures, i.e. saturation concentration (C^*), from $T_{\max}$ measured with the FIGAERO inlet. It took advantage of a general linear relationship between $T_{\max}$ and parametrized vapor pressures using molecular formulas, where the scatter around the linear fit could represent the variability in evaporation properties of isomers with the same molecular formulas (Geretti et al., 2025). The measured $T_{\max}$ could then by this general relationship be converted into an absolute value for C^* . For Δ^3 -carene + NO_3 oxidation products, the relationship between $T_{\max}$ and the parameterized $\log_{10}C^*$ using Equation (1) was determined using linear regression ($R^2 = 0.72$; Fig. S3).

There exist several formula-based parameterization methods providing a larger range in estimated C^* (Donahue et al., 2011; Li et al., 2016; Mohr et al., 2019; Stolzenburg et al., 2018). In this study, we selected the modified Li et al. (2016) parameterization method because it was trained on a large dataset and includes an improvement to account for organic nitrate functional groups, as shown in Equation (1) (Graham et al., 2023; Isaacman-VanWertz and Aumont, 2021; Li et al., 2016):

$$\log_{10}C^*(298\text{K}) = (n_C^0 - n_C)b_C - (n_O - 3n_N)b_O - 2 \frac{n_C n_O}{n_C + n_O} b_{CO} - n_N b_N \quad (1)$$

Where n_C , n_O , and n_N are the number of carbon, oxygen, and nitrogen atoms in the organic compound. n_C^0 represents the reference carbon number, while b_C , b_O , and b_N denote the contribution of each atom to $\log_{10}C^*$. Additionally, b_{CO} refers to the carbon-oxygen nonideality (Donahue et al., 2011). For organic compounds containing C, H, and O atoms, the values used are: $n_C^0 = 22.66$, $b_C = 0.4481$, $b_O = 1.656$, and $b_{CO} = -0.07790$. For organic compounds containing C, H, O, and N atoms, the values used are, $n_C^0 = 24.13$, $b_C = 0.3667$, $b_O = 0.7732$, $b_{CO} = -0.07790$, and $b_N = 0.7732$ (Isaacman-VanWertz and Aumont, 2021; Li et al., 2016).

The derived C^* was used to calculate saturation vapor pressure (p_{sat}) of each product according to Equation (2) (Donahue et al., 2006; Pan-kow, 1994).

$$C^* = \frac{p_{\text{sat}} \times \text{MW} \times \gamma}{RT} \quad (2)$$

Where MW is the molecular weight of a given species; γ is the activity

coefficient assumed to be 1; R is the universal gas constant, and T is 298 K.

3. Results and discussion

3.1. General overview of organic nitrates from monoterpenes + NO_3 radicals

A series of experiments were conducted in the Go:PAM, including NO_3 radical limited, Δ^3 -carene limited, and similar levels of Δ^3 -carene and NO_3 , as well as one experiment involving α -pinene (Table 1). Approximately 350 organic species were identified in the Δ^3 -carene experiments using FIGAERO-CIMS, while fewer compounds observed during α -pinene + NO_3 oxidation, i.e. 248 species. The detected products primarily consist of organic nitrates, alongside with some products containing only carbon, hydrogen, and oxygen atoms.

Fig. 2 compares the gas-phase mass spectra of the NO_3 radical reacting with Δ^3 -carene and, under similar conditions, with α -pinene. For the Δ^3 -carene + NO_3 system, the high signal intensities were observed for the monomers e.g., $\text{C}_{10}\text{H}_{17}\text{NO}_4$, $\text{C}_{10}\text{H}_{17}\text{NO}_5$, and $\text{C}_{10}\text{H}_{15}\text{NO}_7$, fragments, e.g., $\text{C}_5\text{H}_7\text{NO}_5$, $\text{C}_9\text{H}_{15}\text{NO}_6$, as well as for the dimers $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_8$ and $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{11}$ (Fig. 2). The resulting mass spectrum agrees with previously reported gas-phase products from similar carene systems (DeVault et al., 2022; Draper et al., 2019; Jenks et al., 2023). The experiment done with α -pinene under a similar condition shows a different product distribution. For α -pinene system, the highest intensities were observed for monomer products, e.g., $\text{C}_{10}\text{H}_{16}\text{O}_3$, $\text{C}_{10}\text{H}_{15}\text{NO}_5$, $\text{C}_{10}\text{H}_{17}\text{NO}_5$, and $\text{C}_{10}\text{H}_{15}\text{NO}_6$ (Fig. 2). The monomer product distribution is consistent with other α -pinene + NO_3 experiments (Takeuchi et al., 2022; Takeuchi and Ng, 2019; Wu et al., 2021). A higher signal of $\text{C}_{10}\text{H}_{16}\text{O}_3$ from α -pinene + NO_3 compared to Δ^3 -carene + NO_3 was observed. This is attributed to differences in RO radical bond scission, which promote the formation of pinonaldehyde in α -pinene system, subsequently oxidized by NO_3 radicals to pinonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_3$) (Kurtén et al., 2017; Saunders et al., 2003). The total signal intensity of organic nitrate products from the Δ^3 -carene + NO_3 experiment is around four times higher than that of the α -pinene + NO_3 experiment (Fig. 2). Voltage scanning was performed in both experiments, i.e. the voltage at half signal maximum (dV_{50}) (Lopez-Hilfiker et al., 2016), as a measure of relative binding enthalpy and thus reflecting detection sensitivity. There are differences in dV_{50} among the

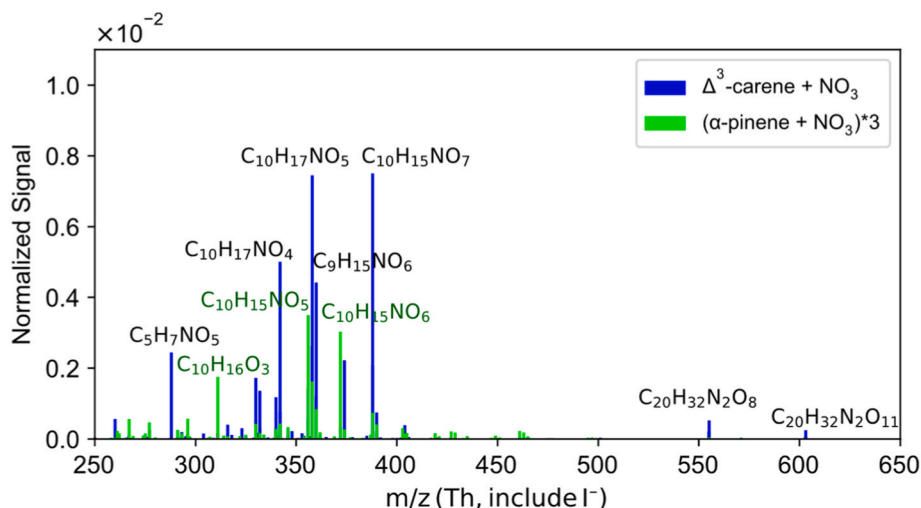


Fig. 2. Mass spectra of the gas phase oxidation products from (a) Δ^3 -carene + NO_3 experiment (Experiment 7 in Table 1) and (b) α -pinene + NO_3 experiment (Experiment 11 in Table 1). The extracted ion signals were normalized to the sum of the signals of $\text{I}^- + \text{H}_2\text{OI}^-$. Representative high peaks in Δ^3 -carene + NO_3 experiment are labeled with molecular formula ions in black color. Representative high peaks in α -pinene + NO_3 experiment are labeled with molecular formula ions in green color. The signal intensity of products from α -pinene + NO_3 experiment is multiplied by a factor of 3. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

products but no clear trends were observed and without authentic standards a unified sensitivity was used. One may note that the dV_{50} values (Table S1) indicate comparable sensitivity factors for most organic nitrates between the two systems, Δ^3 -carene + NO_3 system and α -pinene + NO_3 system which makes sensitivity unlikely to fully explain the differences in formed organic nitrates. These experiments confirm the reported differences in the formation of nitrated products. In agreement with the early study of Hallquist et al. (1999) and many subsequent studies (Day et al., 2022; DeVault et al., 2022; Draper et al., 2019; Kurtén et al., 2017), higher amounts of nitrated products were observed for Δ^3 -carene compared to α -pinene. The yield of organic nitrates is also in line with the mechanistic insight outlined in previous studies assigned to differences in the $\text{RO}^\bullet$ bond scissions (Draper et al., 2019; Kurtén et al., 2017). As pointed out, the bond scission of $\text{RO}^\bullet$ from α -pinene mainly leads to the formation of the relatively volatile product pinonaldehyde (that the I-CIMS cannot detect with high sensitivity) while the bond scission of $\text{RO}^\bullet$ from Δ^3 -carene mainly gives the reactive keto-nitrooxy-alkyl radicals that subsequently gives multiple nitrated closed shell products, that can be observed using the I-CIMS (Fig. S1).

3.2. Gas-phase product distribution and formation of organic nitrates

For the Δ^3 -carene + NO_3 experiment (Experiments 1 to 8 in Table 1), the distribution of products in gas phase under different oxidant: VOC ratios are presented in Fig. 3. The identified products are classified into $\text{C}_x\text{H}_y\text{O}_z$ (organic species without nitrogen), monomeric organic nitrates with 10 carbons (C_{10} -ONs), organic nitrates fragments with fewer than 10 carbon atoms ($\text{C} <_{10}$ -ONs), and accretion organic nitrates containing more than 10 carbon atoms ($\text{C} >_{10}$ -ONs). Generally, the total signals of

products increase with the oxidant level for the same level of Δ^3 -carene (Fig. S4). The signals of the organic nitrate products account for 83% to 94% of the total signals of all measured compounds, making them a primary focus of this study. C_{10} -ONs dominate the nitrated products, accounting for 48–63% of the identified species. Two C_{10} -ON families, same backbone but with different number of oxygens, $\text{C}_{10}\text{H}_{15}\text{NO}_{4-8}$ and $\text{C}_{10}\text{H}_{17}\text{NO}_{4-8}$, represent the majority of the gas-phase products (Fig. 3). $\text{C}_{10}\text{H}_{17}\text{NO}_4$, $\text{C}_{10}\text{H}_{17}\text{NO}_5$, and $\text{C}_{10}\text{H}_{15}\text{NO}_7$ are the most abundant products among the measured products. In the experiments conducted with same initial VOC concentrations but varying oxidant concentrations, the fractions of $\text{C}_{10}\text{H}_{15}\text{NO}_4$, $\text{C}_{10}\text{H}_{15}\text{NO}_5$, $\text{C}_{10}\text{H}_{17}\text{NO}_4$, and $\text{C}_{10}\text{H}_{17}\text{NO}_5$ from the two families decrease while the fractions of $\text{C}_{10}\text{H}_{15}\text{NO}_7$ and $\text{C}_{10}\text{H}_{17}\text{NO}_{6-8}$ increase as the N_2O_5 : VOC ratios increase (Fig. 3). This shows that the formation of more oxygenated C_{10} -ONs is favored under increasing oxidation conditions. For the fraction of other C_{10} -ONs, there is a small increase as the N_2O_5 : VOC ratios increase (Fig. 3).

The observed $\text{C}_{10}\text{H}_{15}\text{NO}_{4-8}$ and $\text{C}_{10}\text{H}_{17}\text{NO}_{4-8}$ families are consistent with the major organic nitrates proposed by the gas-phase oxidation chemical mechanism of Δ^3 -carene + NO_3 (DeVault et al., 2022; DeVault and Ziemann, 2021; Draper et al., 2019; Jenks et al., 2023; Kurtén et al., 2017). The formation mechanism of dominant nitrooxy RO_2 with 10 carbon atoms is summarized in Scheme 1. In the NO_3 radical-initiated oxidation of Δ^3 -carene, the NO_3 radical adds to the double bond, forming first-generation nitrooxy RO_2 radicals ($\text{C}_{10}\text{H}_{16}\text{NO}_5^\bullet$). The alkoxy radicals derived from first-generation RO_2 radicals undergo six-membered ring-breaking bond scission, followed by direct O_2 addition or a second three-membered ring-breaking reaction and O_2 addition, leading to the formation of second-generation nitrooxy RO_2 ($\text{C}_{10}\text{H}_{16}\text{NO}_6^\bullet$) (Dibble, 2001; Draper et al., 2019; Kurtén et al., 2017;

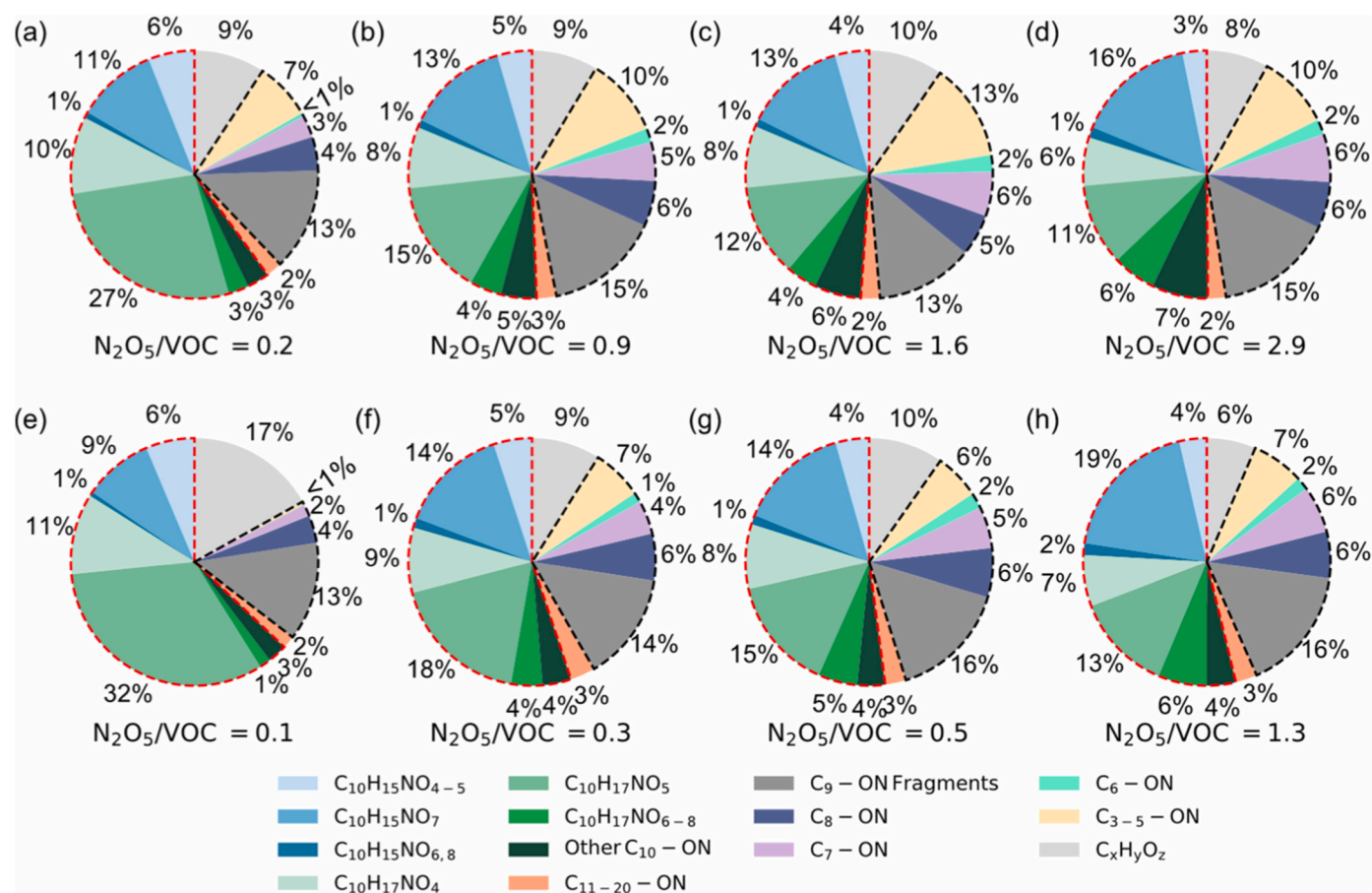
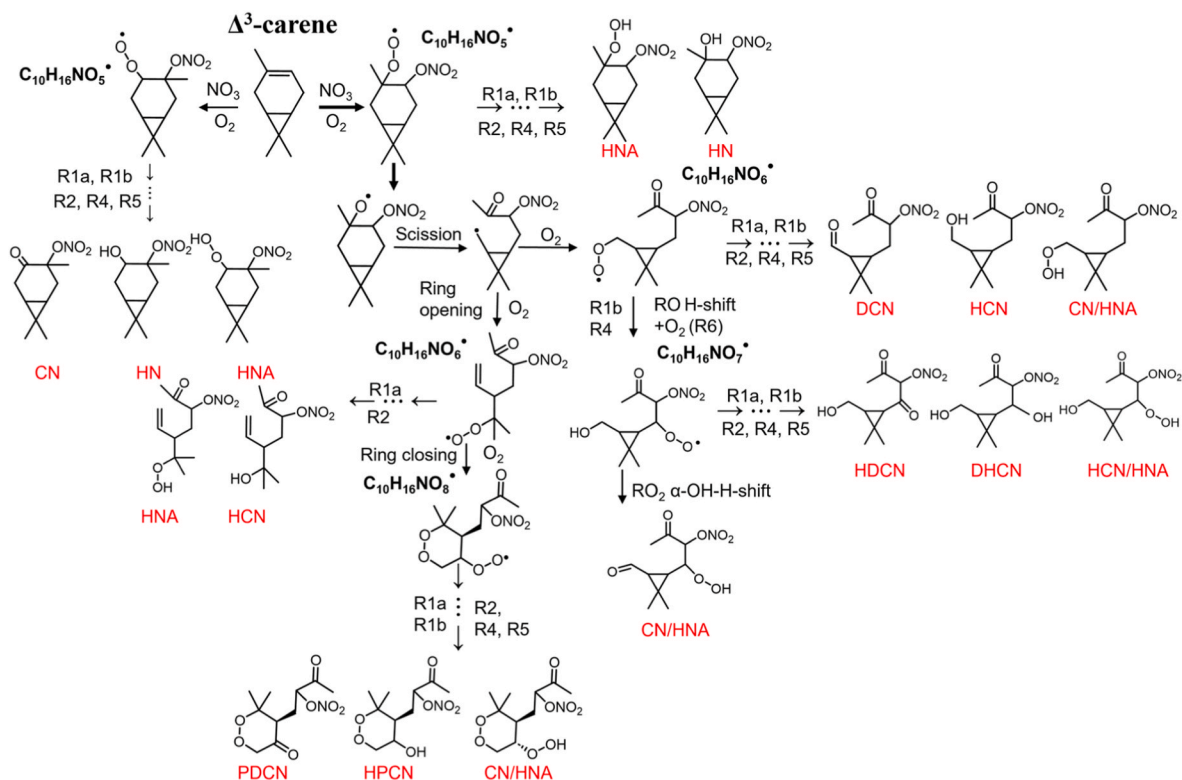


Fig. 3. Distribution of identified products in the gas phase from Δ^3 -carene + NO_3 experiments. (a) Experiment 1, (b) Experiment 2, (c) Experiment 3, (d) Experiment 4, (e) Experiment 5, (f) Experiment 6, (g) Experiment 7, and (h) Experiment 8. The red dashed-line frame and black dashed-line frame represent organic nitrates monomers and fragments, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



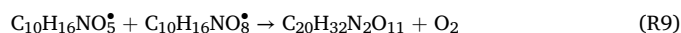
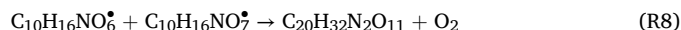
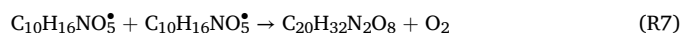
Scheme 1. Simplified dominant RO_2 chemical mechanisms and formation pathway of major C_{10} -ONs in Δ^3 -carene + NO_3 oxidation. The red marked compounds are closed shell organic nitrates matching the formulas measured in our experiments.

Vereecken and Peeters, 2009). The alkoxy radical derived from $\text{C}_{10}\text{H}_{16}\text{NO}_6^\bullet$ radicals can undergo intramolecular H-shifts followed by further O_2 addition, resulting in the formation of more oxygenated nitrooxy $\text{RO}_2^\bullet$ radicals ($\text{C}_{10}\text{H}_{16}\text{NO}_7^\bullet$) (DeVault and Ziemann, 2021; Draper et al., 2019; Vereecken and Peeters, 2010). The $\text{C}_{10}\text{H}_{16}\text{NO}_6^\bullet$ radicals, formed by two ring-breaking pathways, can undergo isomerization via ring closure followed by O_2 addition, leading to the formation of nitrooxy $\text{RO}_2^\bullet$ radicals with more oxygen atoms ($\text{C}_{10}\text{H}_{16}\text{NO}_8^\bullet$) (Crounse et al., 2013; DeVault and Ziemann, 2021; Draper et al., 2019). The aforementioned $\text{RO}_2^\bullet$ radicals subsequently lead to the formation of closed-shell compounds via R1a, R2, and R5 reaction pathways. In general, a variety of products formed contains two to more functional groups and are categorized as hydroxynitrate (HN), carbonylnitrate (CN), hydroxynitrate acid (HNA), hydroxycarbonyl nitrate (HCN), dicarbonyl nitrate (DCN), hydroxydicarbonyl nitrate (HDCN), dihydroxycarbonyl nitrate (DHCN), peroxydicarbonyl nitrate (PDCN), and hydroperoxydicarbonyl nitrate (HPCN) in Scheme 1. Some HNA products also contain additional functional groups and are referred to using combined names such as CN/HNA or HCN/HNA. The first-generation $\text{C}_{10}\text{H}_{16}\text{NO}_5^\bullet$ explains the high intensity of $\text{C}_{10}\text{H}_{17}\text{NO}_4$, and $\text{C}_{10}\text{H}_{17}\text{NO}_5$. A competitive pathway of α -OH H-shift of $\text{C}_{10}\text{H}_{16}\text{NO}_7^\bullet$ to form $\text{C}_{10}\text{H}_{15}\text{NO}_7$ may contribute to the high intensity of $\text{C}_{10}\text{H}_{15}\text{NO}_7$ (Draper et al., 2019; Otkjær et al., 2018).

Organic nitrate fragments with 1 to 9 carbon atoms were also observed in the gas phase. The fraction of the sum of fragments increases distinctly with rising N_2O_5 : VOC ratios, from 28% at 0.2 to 39% at 2.9 (Fig. 3). C_9 -ONs (e.g., $\text{C}_9\text{H}_{13}\text{NO}_5$, $\text{C}_9\text{H}_{11}\text{NO}_6$, $\text{C}_9\text{H}_{13}\text{NO}_6$, $\text{C}_9\text{H}_{15}\text{NO}_6$), C_8 -ONs (e.g., $\text{C}_8\text{H}_{13}\text{NO}_5$, $\text{C}_8\text{H}_{13}\text{NO}_6$, $\text{C}_8\text{H}_{11}\text{NO}_7$), and C_7 -ONs (e.g., $\text{C}_7\text{H}_9\text{NO}_6$, $\text{C}_7\text{H}_{11}\text{NO}_6$, $\text{C}_7\text{H}_{11}\text{NO}_7$) make important contributions to measured compounds. The abundance and contributions to the overall products across different conditions from Δ^3 -carene + NO_3 oxidation has not been reported before but can be understood from previous studies on NO_3 chemistry (Hallquist et al., 1997; Nah et al., 2016). One possible formation pathway of C_9 formation involves alkoxy radical

decomposition from ring openings of Δ^3 -carene, followed by rapid loss of a methyl group due to a terminal site nitrooxy group at the α position (Dam et al., 2022). Another pathway of C_9 -ONs is from the oxidation of caronaldehyde, which is produced from the scission of primary alkoxy radicals during Δ^3 -carene + NO_3 oxidation (Fig. S1). C_8 -ONs have been reported in the NO_3 initiated oxidation of monoterpenes (Δ^3 -carene, α -pinene, β -pinene, and limonene), which is also formed via C-C bond scissions of alkoxy radicals (DeVault et al., 2022; Nah et al., 2016). The plausible formation pathway of the C_7 -ONs involves the decomposition of alkoxy radical, which can originate from $\text{C}_{10}\text{H}_{16}\text{NO}_6^\bullet$ radicals with two ring opening in Scheme 1, producing acetone and the C_7 - $\text{RO}_2^\bullet$ radicals that then react to form C_7 -ONs (Draper et al., 2019; Kurtén et al., 2017). A single abundant $\text{C}_5\text{H}_7\text{NO}_5$ compound increased at high oxidant levels and has been reported in the NO_3 radical oxidation of Δ^3 -carene (DeVault et al., 2022). For C_3 -ONs, C_4 -ONs, C_5 -ONs excluding $\text{C}_5\text{H}_7\text{NO}_5$, and C_6 -ONs account for very small fractions (<3%) and their fragmentation mechanisms are more unclear and not discussed in this study.

Accretion products with more than 10 carbon atoms (C_{11-20} -ONs) account for a small portion, about 2%, of the total detected gas-phase signals (Fig. 3) but might have an important role for SOA formation due to their low volatility. The fraction of C_{11-20} -ONs remains relatively constant despite changes in the N_2O_5 : VOC ratios. The contribution of $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{8-12}$ family is higher than other accretion products but still contributes to only around 1% of total product ions in the gas phase. This agrees with DeVault et al. (2022) reporting that the gas-phase formation of ROOR' dimers was negligible. In the $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{8-12}$ family $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_8$ and $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{11}$ were most prominent. They are likely formed via self- and cross-reactions of dominant monomer peroxy radicals in the gas phase (R7, R8, and R9).



However, the signal intensities of $C_{20}H_{32}N_2O_9$ and $C_{20}H_{32}N_2O_{10}$ are relatively low, likely due to their low formation rates. Thus, the monomer radicals, e.g. $C_{10}H_{16}NO_6^\bullet$ and $C_{10}H_{16}NO_7^\bullet$, needed to produce these dimers primarily produce closed-shell monomers rather than undergo dimerization. Other accretion products (C_{11-19} -ONs) were lower than C_{20} -ONs, which could be caused by fragmentation occurring later than the initial formation of the C_{10} - monomer peroxy radicals.

3.3. Particle-phase organic nitrates

In Experiments 9 and 10, neutral $(NH_4)_2SO_4$ and acidic NH_4HSO_4 seeds were introduced, respectively, to provide condensation surfaces for studying particle-phase organic nitrates. The mass spectra of the particle-phase products from the two types of seed aerosols exhibit similar product distributions (Fig. 4 and S5). High signal intensities of organic nitrates including $C_9H_{15}NO_6$, $C_{10}H_{15}NO_7$, $C_{10}H_{17}NO_6$, $C_{10}H_{17}NO_7$, $C_{20}H_{32}N_2O_8$, and $C_{20}H_{32}N_2O_{11}$ were observed for both $(NH_4)_2SO_4$ and NH_4HSO_4 seeds.

In these experiments, the dimeric organic nitrates (e.g., $C_{20}H_{32}N_2O_{8-12}$) dominated in the particle phase, contributing to 48% and 39% of the total organic nitrate signal in seeded $(NH_4)_2SO_4$ and NH_4HSO_4 experiments, respectively (Fig. 5). The possible dimerization mechanism for the gas-phase $C_{20}H_{32}N_2O_{8-12}$ is two nitrated monomer peroxy radicals combined to form a dimer (R1c). Then the dimeric organic nitrates efficiently condensed on the seeds due to their high MW and low volatility. However, gas-phase dimers were observed in a rather low fraction of total gas-phase ON (about 1%) both before and after seed introduction (Fig. S6) and do not match the enhancement in the particle phase. The gas-phase dimerization is therefore unlikely to explain all the dimer signal identified from the particle phase measurements. Although the Go:PAM has a sheet-flow design limiting wall losses, very low-volatility compounds may still be underestimated due to wall losses, e.g., in the transfer line between the Go:PAM and the FIGAERO-CIMS; adding accumulation-mode seed particles provides an efficient condensable sink with much less brownian diffusional losses than gas molecules. This might partly explain the high condensed-phase C_{20} dimers signal but also particle-phase accretion reactions of monomers can contribute to the formation of dimers, providing another plausible explanation for the dimers observed in particle phase. DeVault and Ziemann (2021) reported that acetal and hemiacetal dimers are the dominant dimers in the

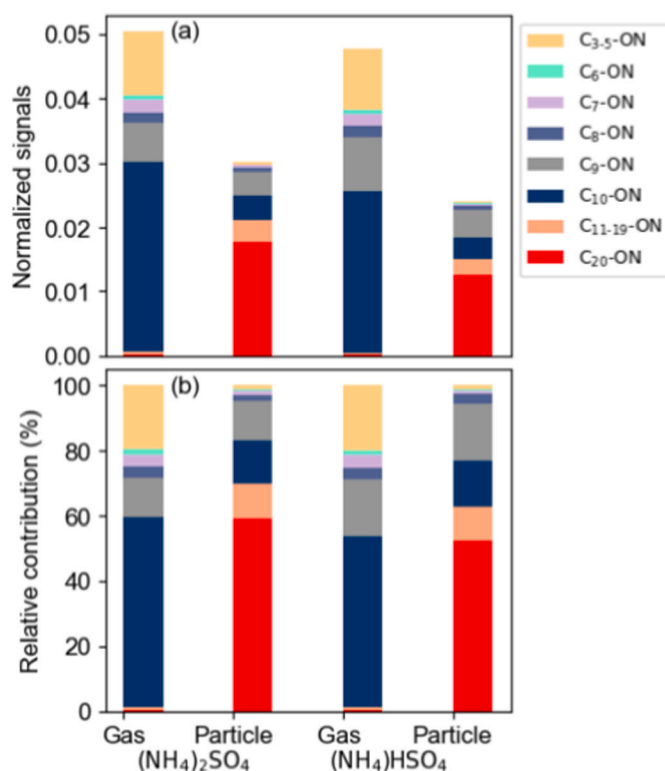


Fig. 5. Distribution of all measured organic nitrates with 3 to 20 carbon atoms in the gas and particle phases from seeded $(NH_4)_2SO_4$ and NH_4HSO_4 experiments (a) signals of products and (b) relative distribution. The organic nitrate signals in the gas and particle phases were normalized to the sum of the signals of I^- and H_2OI^- .

particle phase from Δ^3 -carene + NO_3 radical oxidation. In the particle phase, reactions R10 and R12 between aldehydes and alcohols form hemiacetal dimers ($C_{20}H_{32}N_2O_8$ and $C_{20}H_{32}N_2O_{11}$) (Claflin and Ziemann, 2018; DeVault and Ziemann, 2021; Ziemann and Atkinson, 2012). In addition, hydroxycarbonyl products can undergo intramolecular cyclization to form hemiacetals, which can subsequently react

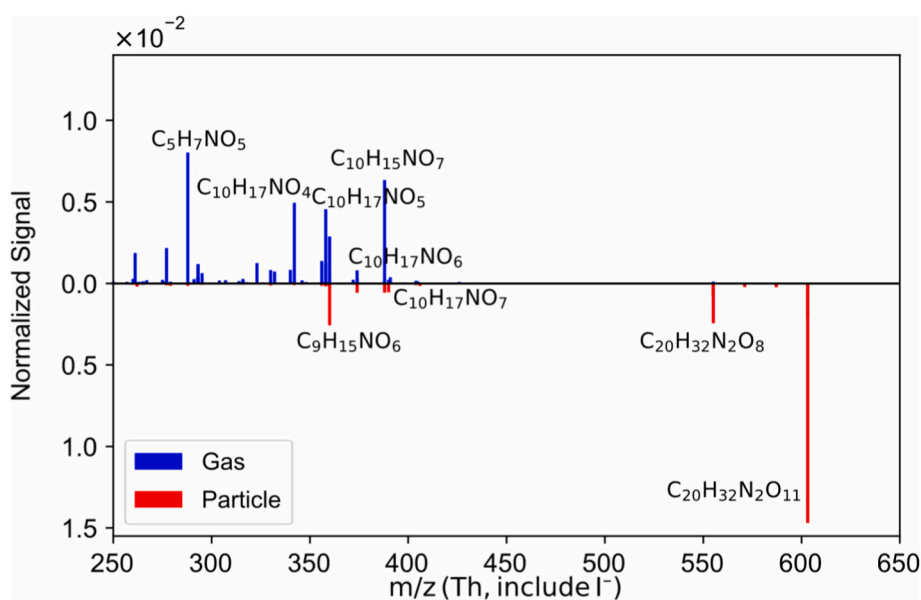
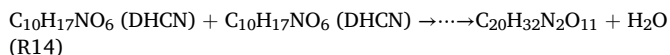
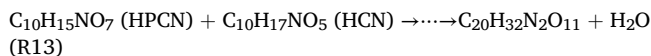
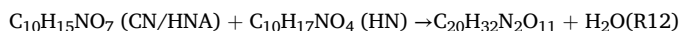
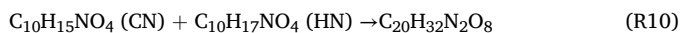


Fig. 4. Mass spectra of the gas- and particle-phase products from Δ^3 -carene + NO_3 with $(NH_4)_2SO_4$ (Exp.9). The gas-phase mass spectrum is plotted in an upward direction, while the particle-phase spectrum is plotted downward with the same magnitude. The extracted ion signals were normalized to the sum of the signals of I^- and H_2OI^- . The processing of particle-phase signals is described in the SI.

with alcohols via reactions R11, R13, and R14 to yield acetal dimers ($C_{20}H_{32}N_2O_8$ and $C_{20}H_{32}N_2O_{11}$) in the particle phase (Claflin and Ziemann, 2018; DeVault and Ziemann, 2021). Given the high gas-phase intensities of $C_{10}H_{17}NO_4$, $C_{10}H_{17}NO_5$, and $C_{10}H_{15}NO_7$, the particle-phase accretion reactions R11, R12, and R13 are plausible formation pathways occurring in the presence of seed particles.



In addition to dimers, the monomers and fragments make a contribution to particle-phase organic nitrates. However, monomer nitrates were less abundant in the particle phase than in the gas phase, as shown in Experiments 9 and 10 where the signal intensity and fractions of C_{10} -ON decreased in the particle phase (Figs. 4 and 5). The total fragments signals also decreased, where the fractions of the small ONs with 3 to 8 carbon atoms, become negligible in the particle phase (Fig. 5). But certain C_9 organic nitrates (i.e. $C_9H_{15}NO_6$ and in the acidic case $C_9H_{13}NO_5$) show increased abundance in the particle phase (Fig. 4 and Fig. S5). The particle-phase organic nitrates categorized by carbon number show similar patterns in Experiment 9 with $(NH_4)_2SO_4$ seed and Experiment 10 with NH_4HSO_4 seed (Fig. 5). It has been reported from chamber studies that aerosol acidity can affect acid-catalyzed heterogeneous reactions, and increase further oxidation, dimerization, uptake of oxygenated species, and SOA mass (Czochke et al., 2003; Czochke and Jang, 2006; Riva et al., 2016, 2019). However, the total signals of particle-phase organic nitrates with acidified seeds did not show an increase (Fig. 5a). The relative fractions and particle-to-gas concentration ratios of top ONs from seeded experiments using $(NH_4)_2SO_4$ and NH_4HSO_4 are very similar (Figs. S7 and S8). The effect of acidity is not clearly evident from the results of these two experiments, likely because the seed particles remain crystalline under the dry conditions, in contrast to prior studies using deliquesced seeds (Riva et al., 2016).

3.4. Vapor pressures of organic nitrates

The derived T_{max} for the detected produce as measured using the FIGAERO are related to the vapor pressure of the species (Bannan et al., 2019; Thornton et al., 2020; Ylisirniö et al., 2021, 2025). For the dominant products in the particle phase, i.e. the dimers, the thermograms are shown in Fig. 6 and Fig. S9. They all desorb with a clear profile where the T_{max} could directly be used as a proxy for volatility. Here the T_{max} increases with the number of oxygens in the dimeric organic nitrates for both $(NH_4)_2SO_4$ and NH_4HSO_4 seeded experiments. This is expected since more oxygen gives higher molecular weight, more functional groups and likely also more polar compounds. For some monomer and fragments families, the thermogram did not show monomodal distribution. For example, the thermograms of $C_9H_{15}NO_6$ and $C_{10}H_{15}NO_7$ exhibit multiple peaks that were separated by gaussian fitting (Fig. S10). The first peak corresponds to the desorption of the respective species, while the additional peaks were likely influenced by surface interactions or decomposition of larger molecules. The multiple peak profiles were more prominent in fragments and monomers rather than accretion products, and for some products they show different patterns for the $(NH_4)_2SO_4$ and NH_4HSO_4 seeded experiments (Figs. S10 and S11), respectively. For $C_{10}H_{15}NO_{4-8}$, $C_{10}H_{17}NO_{4-8}$, and $C_{20}H_{32}N_2O_{8-12}$ families, T_{max} values derived from the first fitted peaks are in the range of $\sim 40^\circ C - 100^\circ C$ (Table 2). The T_{max} values of these families are very similar between $(NH_4)_2SO_4$ and NH_4HSO_4 seeded

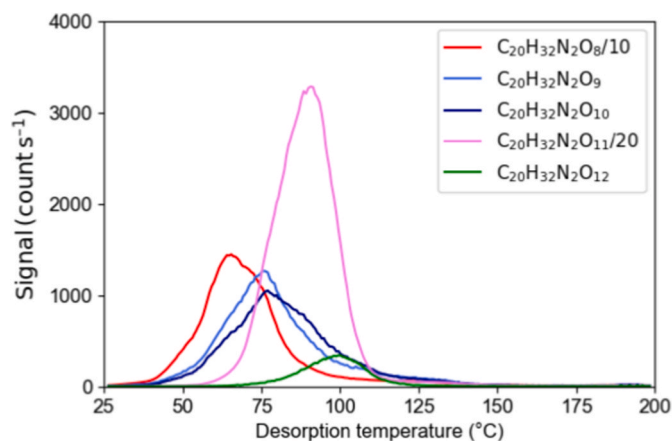


Fig. 6. Thermogram of dimers from Experiment 9: $(NH_4)_2SO_4$ seeded experiment. The signals of $C_{20}H_{32}N_2O_8$ and $C_{20}H_{32}N_2O_{11}$ are scaled by factors of 10 and 20, respectively.

experiments. For monomers, T_{max} values show an increasing trend with oxygen number, but the trend is less pronounced than that observed for $C_{20}H_{32}N_2O_{8-12}$ family (Table 2). These also follow the trend in particle-to-gas concentration (P/G) ratios; another way to describe volatility from FIGAERO measurement (Li et al., 2024). For example, there is a clear trend in P/G ratio going from $C_{10}H_{17}NO_4$ to $C_{10}H_{17}NO_8$ matching the expectation that more oxygenated compounds will have a tendency for a higher portion in the particle phase (Table 2).

The volatility of the main C_{10} and C_{20} organic nitrates from monoterpene oxidation was in addition calculated from their molecular formula using a modified Li et al. (2016) parameterization adding a nitrogen coefficient for organic nitrates (Isaacman-VanWertz and Aumont, 2021). To better constrain the trends and compare the similarities in volatility of the organic nitrates from different terpenes, the data set was compared with the published data from NO_3 radical initiated oxidation experiments using α -pinene (Wu et al., 2021). Fig. 7 shows the $\log_{10}C^*$, as calculated from the same parameterization method (Isaacman-VanWertz and Aumont, 2021; Li et al., 2016) for C_{10} and C_{20} organic nitrates for α -pinene + NO_3 and Δ^3 -carene + NO_3 experiments compared to their T_{max} values. Generally, T_{max} increases as $\log_{10}C^*$ decreases and show a consistent trends for both monoterpene + NO_3 systems (α -pinene and Δ^3 -carene).

The C^* from the formula-based parameterization was converted into saturation vapor pressure, p_{sat} , and presented in Table 2 for the molecular families $C_{10}H_{15}NO_{4-8}$, $C_{10}H_{17}NO_{4-8}$, and $C_{20}H_{32}N_2O_{8-12}$. To improve the estimations the measured T_{max} values were used in combination with the parameterization as presented in a recent study (Geretti et al., 2025). This formula-based parameterization provides an expected volatility based on elemental composition, while measured T_{max} captures experimental evaporation behavior of the detected ion signal, including the influence of isomer distribution and matrix interactions. In analogue to a recent study (Geretti et al., 2025), the linear relationship between measured T_{max} and parameterized $\log_{10}C^*$ (Fig. 7) was therefore used to convert measured T_{max} into vapor pressures. The derived values were in general directly related to measured P/G ratios where the use of measured T_{max} in combination to the parameterization shows a slightly stronger correlation (Fig. S12). It should be noted that for two highly oxygenated species, i.e. $C_{20}H_{32}N_2O_{12}$ and $C_{10}H_{17}NO_8$, the fit to the general relationship was very poor and they were considered as outliers.

In our previous study we estimated vapor pressures product from ozonolysis of Δ^3 -carene using a quantum chemistry based statistical thermodynamics program COSMOtherm (BIOVIA COSMOtherm, 2021; Hyttinen et al., 2024). Here we applied the same methodology on the two dominant dimers $C_{20}H_{32}N_2O_8$ and $C_{20}H_{32}N_2O_{11}$. The calculated

Table 2

$T_{\max}$, particle-to-gas concentration ratio (P/G), and vapor pressure (p_{sat}) of monomers and dimers. p_{sat} values derived from $T_{\max}$ were calculated using the linear fitting in Fig. S3.

Class	Family	$T_{\max}$ (°C)		P/G		p_{sat} from $T_{\max}$ (Pa) ^a		Parameterized p_{sat} (Pa) ^b
		(NH ₄) ₂ SO ₄	NH ₄ HSO ₄	(NH ₄) ₂ SO ₄	NH ₄ HSO ₄	(NH ₄) ₂ SO ₄	NH ₄ HSO ₄	
Monomers	C ₁₀ H ₁₅ NO ₄	52.5	54.2	0.01	0.02	4.7×10^{-1}	2.1×10^{-1}	1.4×10^{-1}
	C ₁₀ H ₁₅ NO ₅	51.8	51.3	0.03	0.03	6.2×10^{-1}	7.8×10^{-1}	2.6×10^{-2}
	C ₁₀ H ₁₅ NO ₆	61.6	62.4	0.22	0.25	5.4×10^{-3}	3.7×10^{-3}	4.8×10^{-3}
	C ₁₀ H ₁₅ NO ₇	51.1	51.3	0.07	0.06	7.8×10^{-1}	6.8×10^{-1}	8.6×10^{-4}
	C ₁₀ H ₁₅ NO ₈	63.3	60.9	0.42	0.22	4.8×10^{-3}	6.7×10^{-3}	1.5×10^{-4}
	C ₁₀ H ₁₇ NO ₄	51.3	42.0	0.01	0.01	8.4×10^{-1}	7.0×10^1	1.4×10^{-1}
	C ₁₀ H ₁₇ NO ₅	51.1	52.2	0.03	0.03	8.8×10^{-1}	5.1×10^{-1}	2.6×10^{-2}
	C ₁₀ H ₁₇ NO ₆	65.4	63.3	1.37	0.76	8.8×10^{-4}	2.4×10^{-3}	4.7×10^{-3}
	C ₁₀ H ₁₇ NO ₇	58.5	59.4	1.77	1.25	2.2×10^{-2}	1.4×10^{-2}	8.5×10^{-4}
	C ₁₀ H ₁₇ NO ₈	71.1	80.4 ^c	5.66	2.27 ^c	5.3×10^{-5}	6.1×10^{-7c}	1.5×10^{-4}
Dimers	C ₂₀ H ₃₂ N ₂ O ₈	68.1	66.4	16.2	9.7	1.4×10^{-4}	3.1×10^{-4}	1.2×10^{-6}
	C ₂₀ H ₃₂ N ₂ O ₉	76.2	72.2	50.7	24.4	2.9×10^{-6}	1.4×10^{-5}	2.3×10^{-7}
	C ₂₀ H ₃₂ N ₂ O ₁₀	79.8	76.1	65.7	29.9	5.0×10^{-7}	4.0×10^{-6}	4.4×10^{-8}
	C ₂₀ H ₃₂ N ₂ O ₁₁	89.9	84.8	1110	757	3.9×10^{-9}	4.3×10^{-8}	8.4×10^{-9}
	C ₂₀ H ₃₂ N ₂ O ₁₂	96.6	93.5	134.4 ^c	41.1 ^c	1.5×10^{-10c}	6.7×10^{-10c}	1.6×10^{-9}

^a $T_{\max}$ (for both seeds) converted into p_{sat} using the modified Li et al. (2016) parameterization.

^b p_{sat} calculated from molecular formula using modified Li et al. (2016) parameterization.

^c These value were regarded as outliers when comparing P/G vs p_{sat} from $T_{\max}$, see Fig. S12.

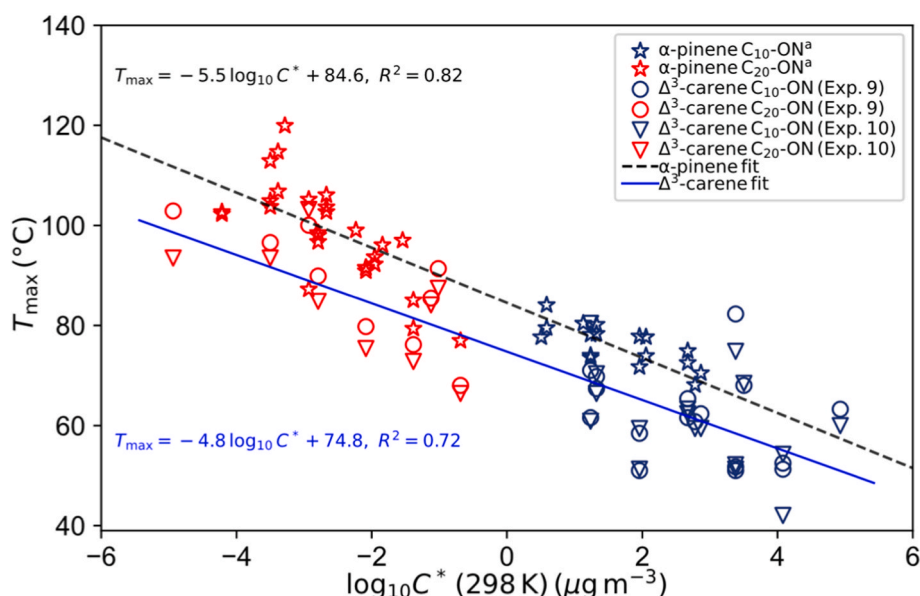


Fig. 7. $T_{\max}$ of C₁₀ and C₂₀ organic nitrates versus their saturation concentrations in $\log_{10}(\log_{10}C^*)$ at 298K derived from modified Li et al. (2016) parameterization.

^aThe α -pinene dataset originates from α -pinene + NO₃ experiment reported by Wu et al. (2021). The blue line is the linear regression between average $T_{\max}$ values from Exp.9 and Exp.10 versus the parametrized $\log_{10}C^*$, same as the fitting in Fig. S3. The black dash line is the linear regression between $T_{\max}$ values from α -pinene + NO₃ experiment reported by Wu et al. (2021) versus the parametrized $\log_{10}C^*$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

vapor pressures of these (Fig. S13) by COSMOtherm are 5.6×10^{-4} Pa and 3.5×10^{-9} Pa at 298K, respectively. For C₂₀H₃₂N₂O₈, COSMOtherm value is in agreement with the vapor pressure derived from $T_{\max}$ method (1.4×10^{-4} Pa and 3.1×10^{-4} Pa for (NH₄)₂SO₄ and NH₄HSO₄ seeded experiments, respectively). In contrast, the parameterization method underestimate the vapor pressure by approximately two orders of magnitude (1.2×10^{-6} Pa). For C₂₀H₃₂N₂O₁₁, COSMOtherm value agrees with both $T_{\max}$ derived vapor pressures (3.9×10^{-9} Pa and 4.3×10^{-8} Pa for (NH₄)₂SO₄ and NH₄HSO₄ seeded experiments, respectively) and the parameterization method derived vapor pressure (8.4×10^{-9} Pa).

4. Conclusion and atmospheric implication

A series of Δ^3 -carene + NO₃ experiments and an α -pinene + NO₃ experiment were conducted in the flow reactor Go:PAM. The oxidation products were measured using iodide-FIGAERO-CIMS, revealing that the organic nitrate products are the major contributors to the total oxidation products. The higher signal of nitrate products from Δ^3 -carene oxidation compared to α -pinene aligns with the mechanisms involving different RO bond scission pathways. Additionally, in the Δ^3 -carene + NO₃ experiment, high signal intensities were observed for monomers C₁₀H₁₇NO₄, C₁₀H₁₇NO₅, and C₁₀H₁₅NO₇ in the gas phase, while in the α -pinene + NO₃ experiment, monomers C₁₀H₁₅NO₅, C₁₀H₁₇NO₅, and C₁₀H₁₅NO₆ showed high signal intensities in the gas phase. The different

monomer distributions can be used to differentiate the nocturnal oxidation of Δ^3 -carene and α -pinene in ambient measurements. This study emphasizes the potentially important SOA formation from the nighttime oxidation of Δ^3 -carene and provides molecular-level insight into the underlying chemistry using FIGAERO-CIMS, especially in boreal forest environments dominated by monoterpene emissions.

The effect of the varying concentration of the NO_3 radicals on products distribution was evident. The total signal of gas-phase organic nitrate products increases with the oxidant concentration under the constant concentration of Δ^3 -carene. Under oxidant-limited conditions, $\text{C}_{10}\text{H}_{17}\text{NO}_4$ and $\text{C}_{10}\text{H}_{17}\text{NO}_5$ are more prominent, while $\text{C}_{10}\text{H}_{15}\text{NO}_7$, along with higher signals of fragments such as $\text{C}_5\text{H}_7\text{NO}_5$ and $\text{C}_9\text{H}_{15}\text{NO}_6$, are more abundant under VOC-limited conditions, indicating the oxidant levels play a crucial role in the fragmentation pathway.

With the addition of seeds particles, the measured particle-phase composition is distinct from that of the gas phase. These seeded experiments provide insight into the condensation and partitioning of organic nitrates under low RH conditions. At high RH water will influence the gas to particle partitioning but also promote hydrolysis of organic nitrates in the particle phase (Bean and Hildebrandt Ruiz, 2016; Koponen et al., 2007; Rindelaub et al., 2016; Seinfeld et al., 2001; Surdu et al., 2023). Therefore, the particle-phase composition and accretion chemistry observed here should be interpreted as representative of dry conditions, and further experiments are needed to quantify the RH dependence. The particle phase is dominated by C_{10} monomers and C_9 fragments with 6 and 7 oxygen, and dimers ($\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{8-12}$), among which the $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_8$ and $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_{11}$ dimers exhibit the highest signal intensities. The low-volatility dimer nitrates constitute a substantial fraction of SOA and could indicate that particle-phase accretion reactions of monomers maybe be an important formation pathway, in addition to dimers formed from gas-phase RO_2 self- and cross-reactions followed by condensation. The effect of non-acidified and acidified ammonium sulfate seed did not show an obvious difference. T_{max} values of C_{10} -ONs and C_{20} -ONs from NO_3 oxidation of Δ^3 -carene and α -pinene showed comparable linear relationships with the logarithm of the C^* derived from a parametrization using molecular formulas. The data thus illustrate that NO_3 oxidation of Δ^3 -carene has to be considered separately in atmospheric chemical transport models regarding the yield of SOA products while the volatility properties likely could be merged with other similar systems, like nighttime α -pinene oxidation.

CRediT authorship contribution statement

Linjie Li: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Cheng Wu:** Data curation, Investigation, Supervision, Writing – review & editing. **Veronica Geretti:** Data curation. **Christian Mark Salvador:** Data curation, Methodology. **Epameinondas Tsiliannis:** Data curation, Methodology. **Michael Priestley:** Data curation, Methodology. **Noora Hyttinen:** Data curation. **Mattias Hallquist:** Conceptualization, Funding acquisition, Investigation, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2026.122084>.

Data availability

Data will be made available on request.

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