



Investigation of organic nitrate product formation during hydroxyl radical initiated photo-oxidation of β -pinene

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ABSTRACT

A series of experiments have been carried out in the York University smog chamber designed to study the products and pathways of the HO radical oxidation of β -pinene. Experiments on the oxidation of β -pinene and its most prominent oxidation product, pinaketone, by HO radicals with initial NO ranging from 0 to 2.5 ppm have been undertaken. An atmospheric pressure chemical ionization (API) mass spectrometer was operated for online, real-time identification and time profiling of the gas phase oxidation products. The formation of six organic nitrate products has been distinguished of which two have been assigned identifications, C₁₀ dihydroxy nitrate (C₁₀H₁₇NO₅) and nitrooxy-pinaketone (C₉H₁₃NO₄). The real-time profiling and sensitivity to initial NO mixing ratio of each product has provided new insight into the β -pinene + HO radical oxidation mechanism. The distinguished products exhibited either no sensitivity or enhanced formations upon increasing the initial NO mixing ratio. The results also provide evidence supporting the formation of higher order organic nitrate products with formation pathways independent of pinaketone oxidation.

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1. Introduction

Hydrocarbons are continuously emitted into the earth's atmosphere at estimated global rates upwards of 1000 TgC year⁻¹ from both anthropogenic (incomplete combustion) and biogenic (vegetation emissions) sources (Koppmann, 2007). Once in the atmosphere the oxidation of hydrocarbons leads to the formation of a diverse range of products from large organic molecules to ozone, therefore hydrocarbons contribute to the formation of smog. The organic products can also contribute to poor air quality through the formation of secondary organic aerosol. Although, originating from natural sources the organic products that arise due to oxidation of biogenic hydrocarbons can contribute to the formation of polluted air masses. Monoterpenes are a class of biogenic hydrocarbons composed of two isoprene units with a linear or cyclic structure and a molecular formula of C₁₀H₁₆. Global monoterpene emission estimates of 128–450 TgC year⁻¹ suggest these compounds are entering the atmosphere with comparable flux rates to anthropogenic hydrocarbons (Schnitzler et al., 2002). The unsaturated nature of monoterpenes makes them highly reactive to oxidation in the atmosphere by species including ozone and hydroxyl (HO) radicals.

One of the most abundant monoterpenes is β -pinene (Owen, 1997; Geron, 2000), which has a bicyclic structure with an exocyclic double bond (Fig. 1a) that is highly reactive to the atmospheric oxidants ozone ($k_{O_3} = 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), NO₃ ($k_{NO_3} = 2.51 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and HO radicals ($k_{HO} = 7.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson and Arey, 2003). Thus β -pinene is a major contributor to hydrocarbon control of the oxidation state of the atmosphere and to secondary organic particulate production.

Identification of products from individual precursor hydrocarbons provides atmospheric markers allowing insight into the impact of specific hydrocarbons on the dominant oxidation chemistry in the atmosphere. While major contributions have been made regarding the identification of individual products formed from β -pinene oxidation in both the gas and particulate phase there remains a significant portion of unidentified products (Aschmann et al., 1998; Calogirou et al., 1999b; Yu et al., 1999; Winterhalter et al., 2000; Larsen et al., 2001; Jaoui and Kamens, 2003). Identifications have primarily focused on oxygenated products containing carbonyl, hydroxyl, peroxy and acid functionalities with very limited identification of organic nitrate products, which are radical chain terminators and potential contributors to SOA. Organic nitrate oxidation products are expected to have sufficiently low vapour pressures to partition into SOA, the presence of a nitrate functional group has been estimated to impact the vapour pressure by a factor of 6.8×10^{-3} (Pankow and Asher, 2008). Organic nitrate

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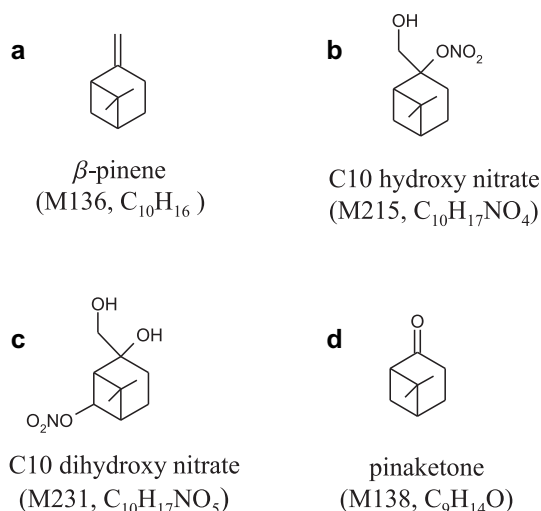


Fig. 1. The chemical structures of a) β -pinene b) C10 hydroxy nitrate c) C10 dihydroxy nitrate and d) pinaketone. Only a single isomer of the C10 hydroxy nitrate and C10 dihydroxy nitrate structure are presented.

products have been previously identified in both laboratory generated and ambient SOA (Palen and Allen, 1993; Presto et al., 2005; Reemtsma et al., 2006; Matsunaga et al., 2009). With respect to β -pinene oxidation only two nitrate product identifications are available to date including a C10 hydroxy and a C10 dihydroxy nitrate product by Aschmann et al., (1998) (Fig. 1b and c).

Additionally, oxidation mechanisms of many large hydrocarbons including β -pinene are currently not well characterized using direct experimental results instead they are extrapolated based on the observed oxidation of smaller systems. While many general oxidation reactions of radical intermediates are well understood, oxidation of large hydrocarbons, such as β -pinene, provides many potential branches in their oxidation mechanisms including isomerization and cyclization, which complicate the straightforward application of simple mechanisms. Pinaketone (Fig. 1d) is currently identified as the major product of β -pinene oxidation as well as the intermediate to the majority of higher oxidation products. However, limited experimental studies have been used to show these pathways. Only one study has been found which identified three oxidation products formed during the oxidation of pinaketone with hydroxyl radicals, oxo-pinaketone, hydroxy-pinaketone and dihydroxy-pinaketone (Calogirou et al., 1999a).

Here we report on a series of experiments designed to study the products and pathways of the HO radical oxidation of β -pinene. Given the importance of pinaketone in current oxidation mechanisms, experiments on the oxidation of β -pinene and pinaketone by HO radicals over a range of initial NO mixing ratios have been undertaken. All experiments were conducted in the York University smog chamber using an atmospheric pressure chemical ionization (API) mass spectrometer for online, real-time identification and time profiling of the gas phase oxidation products. The formation of six organic nitrate products has been distinguished during the oxidation of β -pinene + HO radicals in this study. The real-time profiling and sensitivity to the initial NO mixing ratio of each product has provided new insight into the β -pinene + HO radical oxidation mechanism.

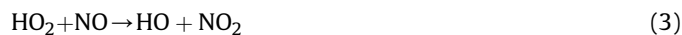
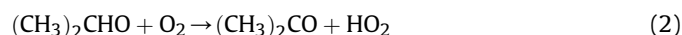
2. Experimental section

2.1. Smog chamber

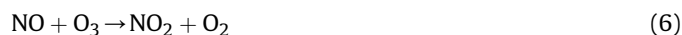
The York University smog chamber is cylindrical in shape with Teflon coated aluminium endplates and transparent Teflon walls. It

is $\sim 8 \text{ m}^3$ in volume, can be irradiated by up to 24 ultraviolet lights (Philips F40BL, 40 Watt) and has an internal fan to enhance mixing. Prior to each experiment, the chamber was flushed with clean air for at least 24 h. Although this study only focuses on gas phase products, it is part of a multiphase investigation, so to stabilize the gas to particle conversion, ammonium sulphate ((NH₄)₂SO₄) seed particles of mean diameter 80 nm were added in all experiments to provide a surface for gas particle partitioning of the reaction products. The seed particles were generated from a $\sim 0.5 \text{ g l}^{-1}$ (NH₄)₂SO₄ solution using a Collison Nebulizer (BGI Inc., Waltham, MA, USA), introduced into the clean chamber and allowed to stabilize for approximately 1 h prior to the injection of the reagents. The reagents β -pinene (Sigma Aldridge), the HO radical source isopropyl nitrite (IPN synthesized in house based on Noyes (1936)) and NO (Air Liquid diluted 1:100 with nitrogen) were admitted to the seeded chamber and allowed to mix for 1 h with the lights off. Typical initial reagent mixing ratios were: 0.5 ppm β -pinene or pinaketone, 0.4 ppm IPN and 0–2.5 ppm NO. Quantitative measurements of gas phase β -pinene and NO as well as particle size distributions were then taken every 5 min. Qualitative mass spectral data was acquired with the same time resolution. Quantitative measurements of pinaketone were not acquired however it was monitored qualitatively using the mass spectral data. The experiments were allowed to proceed for between 1 and 3 h although the primary reaction had ceased after about 100 min.

Turning on the lights initiated the chemistry in the chamber, primarily through IPN photolysis resulting in HO radical production:



The acetone ((CH₃)₂CO) produced is less reactive than the expected products of the β -pinene oxidation and so should have limited impact on the reaction system; however it is in high concentrations and was observed to produce clusters with some of the target ions in the mass spectral data analysis. Nitric oxide is added to ensure rapid conversion of HO₂ to HO (reaction (3)), and to limit the accumulation of ozone from the photolysis of NO₂ (reaction (6)):



2.2. Instrumentation

2.2.1. API triple quadrupole mass spectrometer

The mass spectrometer used in this work was a Sciex TAGA 6000E API triple quadrupole mass spectrometer (MDS Sciex, Concord, ON, CA) (Dawson et al., 1982). The instrumentation and methodology is only briefly outlined here, further details can be found in a previous publication (Auld and Hastie, 2009). The reaction mixture is sampled in real time from the smog chamber into the API source at a flow rate of $\sim 2 \text{ l min}^{-1}$. A 25 mm diameter quartz fibre filter (PALLflex* Tissuquartz*, PALL Ltd., Toronto, ON, CA) was placed in line prior to the source to isolate the gas phase by removing the particulate in the sample. Air from an Aadco pure air generator (Advanced Analytical Device Company, Cleves, OH, USA) is

introduced through a perpendicular inlet in the glass tube to dilute the sample and obtain an optimal flow for the ion source, 5 l min^{-1} .

The ionization takes place in air using a corona discharge. Under positive conditions, the corona discharge produces N_2^+ and O_2^+ which subsequently react with water vapour to produce intermediate ions $[\text{H}_3\text{O} + [\text{H}_2\text{O}]_n \text{ n} = 0,1,2,\dots]^+$. For most hydrocarbons the proton affinity is greater than that of the hydrated hydronium ion so proton transfer is energetically favoured to produce an ion of nominal mass plus 1 u $[\text{M} + \text{H}]^+$. For hydrocarbons with much lower proton affinities charge transfer to produce a true molecular ion M^+ is possible. Thus the API source produces M^+ or $[\text{M} + \text{H}]^+$ ions in high numbers with limited fragmentation. The ions are drawn from the source region into the analyzer region through a nitrogen curtain gas by a potential drop of 610 V between the interface plate and orifice ring.

The high pressure of the API source allows a number of ion molecule reactions to produce higher m/z ions of the form $[\text{M} + \text{H} + [\text{H}_2\text{O}]_n]^+$ (Good et al., 1970a, b) and $[\text{M}_1 + \text{H} + \text{M}_2]^+$ where M_1 and M_2 may be the same or different species. The most prominent form of the latter cluster in these experiments involves the highly abundant acetone with other products.

This instrument was used in three modes full scan MS mode, MS/MS mode and SRM mode. In the MS mode the mass spectrum of all the ions is generated. This spectrum is used for the preliminary identification of molecular and cluster species. In the MS/MS mode a single target ion is selected in the first quadrupole and subjected to collision induced dissociation with argon gas present in the second quadrupole. The resulting fragment ions are subsequently analyzed by the third quadrupole. Examination of these fragment ions gives structural information on the target ion and so allows more definitive assignment of the peaks in the MS spectrum.

Finally Selected Reaction Monitoring (SRM) scan mode was used to obtain time profiles of individual products. During SRM mode the signal profile of a specific fragment ion (F) from specific target ion (T) is acquired by setting the first quadrupole to only pass a single ion T and the third quadrupole to only pass a single ion F. The selection of T \rightarrow F ion pairs is based on observations from MS/MS mode and the results of SRM can provide a highly specific and possibly unique molecular identification. Using a T \rightarrow F ion pair for a reaction product under study reduces the scanning time associated with each reaction product increasing the efficiency of the method allowing a larger number of products to be monitored as the reaction proceeds. SRM evolution profiles can also provide separation of isobaric products, which form through different oxidation pathways and therefore different rates. Further coupling of these data, for many products, with an understanding of possible reaction pathways can improve our understanding of the reaction system as a whole.

2.2.2. Ancillary monitors

The concentration of the β -pinene was followed using a HP 5890 Gas Chromatography Flame Ionization Detection system (GC/FID) calibrated against standards generated by diluting the emission from a temperature controlled permeation tube (VICI Valco Instruments Co. Inc.) calibrated by weight loss. A chemiluminescence NO_x analyzer (TE Inc. Model 42S) calibrated against a certified standard mixture of NO in N_2 (Air Liquide) was used to measure the NO mixing ratio. Particle size distributions were acquired using a differential mobility analyzer (DMA, TSI 3071) and condensation particle counter (CPC, TSI 3010) in tandem.

2.3. Data analysis

2.3.1. Experiment characterization

In order to compare the qualitative mass spectral results within each set of β -pinene and pinaketone experiments, the experiments

have been quantitatively characterized with respect to the initial reagent quantity, reagent time profiles (if available), as well as the temperature and relative humidity profiles.

Within each set of experiments, β -pinene and pinaketone, the quantitative results indicated excellent reproducibility with respect to the time profiles of the hydrocarbon consumption, particle size distribution, as well as the temperature and relative humidity time profiles. These results are consistent with the design of each set of experiments for which the goal was to only vary the initial level of NO. The β -pinene and pinaketone experiments are separated into two groups based on the measured initial NO, which have been labelled high and low NO to simplify future discussion. The initial NO mixing ratios for the β -pinene experiments grouped as high NO ranged between 1.0 and 2.5 ppm and as low NO between 0 and 0.6 ppm. For the pinaketone experiments high NO ranged between 0.4 and 1.0 ppm and low NO ranged between 0 and 0.3 ppm. The impact of the NO categories on the formation of the observed nitrate products is examined in later sections when discussing the proposed oxidation mechanisms.

The chemiluminescence NO_x analyzer also reports a measurement of NO_x , which in principle can be used to determine the concentration of NO_2 based on the difference calculation $\text{NO}_x - \text{NO}$. However, it was observed that the NO_x channel was inconsistently sensitive to IPN, the HO radical source in our experiments. As a result accurate NO_2 concentrations could not be determined but are estimated to be at least an order of magnitude lower than the NO.

As stated in Section 2.1, a high NO mixing ratio was used to reduce the build up of ozone in our system allowing for isolation of HO initiated photo-oxidation. This is only important for the β -pinene experiments since pinaketone is not known to react with ozone. The loss of β -pinene due to reaction with ozone has been estimated using a steady state model, and reaction with ozone is delayed sufficiently that the primary decay of β -pinene is by the desired reaction with HO radicals.

2.3.2. Product identification

The mass of a molecular ion of interest is the starting point for determining chemical composition. The dominant ions observed in this system are $[\text{M} + \text{H}]^+$, so the nominal mass is $m/z + 1$. There are many molecular formulas possible for a given mass however only a limited number will be reasonable as potential products of β -pinene and pinaketone oxidation. Products of β -pinene are expected to have a maximum carbon content of C10 while a product observed during both the β -pinene and pinaketone experiments constrains expected molecular formulas to $\leq \text{C9}$.

Nitrate products will have an even nominal mass with minimum nitrogen to oxygen ratio of 1:3 in the molecular formula. Organic nitrates are also expected to fragment under MS/MS mode to lose NO_2 (46 u), HNO_3 (63 u). Overall, organic nitrate products were identified based on the observation of target ions of odd m/z and observed characteristic losses of NO_2 , HNO_3 .

In some cases additional ions can be used to gain information regarding the identity of a product. Although API is a soft ionization technique, some fragmentation can occur in the source region resulting in the observation of source fragment ions in the full scan mode. The abundant cluster ion $[\text{M} + \text{H} + 58]^+$ of products can also provide useful information for identification.

Each proposed product has been assigned a product label in order to simplify discussion. The label has at most three components a capital "P" to designate a product, the numerical nominal mass and in the case of multiple products proposed with the same nominal mass a small case letter is associated (starting with a). For example, products with a nominal mass of 138 u would be labelled P138a, P138b, etc.

2.3.3. Product time profile comparison

Comparison of the observed signal magnitude, sensitivity to changes in NO levels and relative signal onsets of the SRM time profiles within each set of experiments was used to provide information on the product formation pathways. Pinaketone is considered as a key intermediate species in all current mechanisms of β -pinene oxidation. Thus separate oxidation experiments were performed using β -pinene or pinaketone. Comparison of the data from these experiments is useful to identify products that are produced from β -pinene through pinaketone as an intermediate, and those that do not. Such comparisons are only valid if similar amounts of pinaketone are reacted in both sets of experiments.

For the β -pinene experiments, the GC–FID β -pinene decay profiles and the known rate constant were used to estimate the HO concentration profiles. In a time interval, the estimated HO concentration, measured β -pinene concentration and known rate constant were used to determine the amount of pinaketone produced and reacted.

$$-d[\text{Pk}]/dt = k_{(\text{Pk},\text{HO})}[\text{Pk}][\text{HO}] \quad (7)$$

$$\% \text{Pk}_{(\text{rxtd},t)} = k_{(\text{Pk},\text{HO})}[\text{HO}]_t \Delta t * 100 \quad (8)$$

where the rate constant for the reaction of pinaketone with hydroxyl radicals, $k_{(\text{Pk},\text{HO})}$, is $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calogirou et al., 1999a; Atkinson and Arey, 2003), $[\text{HO}]_t$ is the estimated hydroxyl radical concentration at time, t and Δt is the time interval between points. The percent consumed over the experiment is simply the sum of all time steps, which after averaging overall experiments yields a result in this study of 31% reacted pinaketone after 60 min of reaction. The consistency of the β -pinene decay and therefore HO estimation results translates to a relatively low 7% standard deviation for this estimation.

Gas phase molar yields for pinaketone from β -pinene oxidation by hydroxyl radicals have been reported to range from 22 to 79% (Calogirou et al., 1999b). Taking an upper limit estimate of 80% yield it is estimated that after 60 min of reaction the average upper limit consumption of pinaketone is approximately $530 \mu\text{g m}^{-3}$.

During the pinaketone experiments the SRM ion pairs identified as representing the decay of pinaketone, m/z 157 \rightarrow 139 and m/z 157 \rightarrow 121 were used to estimate the percent reaction for the pinaketone experiments. The standard deviation for the percent reaction determined using the m/z 157 \rightarrow 139 and m/z 157 \rightarrow 121 ion pairs indicates the correlation of the two ion pair profiles within an experiment is very good. These results for the experiments Pk-4 and Pk-11 suggested that pinaketone did not react, which was unexpected given the observation of organic particulate mass formation and oxidation product formation via SRM monitoring. These experiments have not been included in the estimation of pinaketone consumption and the observations have been considered during the analysis and interpretation of related results.

The average reacted pinaketone after 60 min reaction was 46% with a standard deviation of 12%. The injected mass concentration of pinaketone was approximately $2500 \mu\text{g m}^{-3}$ during each experiment. Using this value it is estimated that after 60 min of reaction approximately $1150 \mu\text{g m}^{-3}$ of pinaketone has reacted.

The methods outlined here for estimating the average reacted pinaketone during each set of experiments are crude. However, the results indicate that there is a significantly larger consumption of pinaketone during the experiments when it was the primary reagent even when compared to the upper estimation from the β -pinene experiments. In the context of comparisons between the two sets of experiments these estimations indicate that the level of pinaketone consumption is comparable.

This allows us to use the measurements reported here to distinguish two classes of mechanism. The first arises when a product has lower signal in the pinaketone data set than the β -pinene, which indicates the product has a formation pathway independent of pinaketone. Whereas in the second, a product that has equivalent or higher signal in the pinaketone data set compared to the β -pinene indicates the product results from a formation pathway that proceeds through pinaketone.

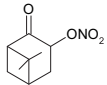
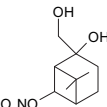
3. Results and discussion

3.1. Identified organic nitrate products

As stated in the introduction, the identification of only two organic nitrate products from the HO radical initiated photo-oxidation of β -pinene (Fig. 1b and c) has been reported (Aschmann et al., 1998). In this work a total of six organic nitrate products have been distinguished, five of which have not previously been identified (Table 1). Two of these have been assigned specific molecular structures (Table 1), C10 dihydroxy nitrate ($\text{C}_{10}\text{H}_{17}\text{NO}_5$, P231a) and nitrooxy-pinaketone ($\text{C}_9\text{H}_{13}\text{NO}_4$, P199). The remaining four organic nitrates have been distinguished (P231b, 215a, 231c and 215b) but no specific molecular formulas have been isolated.

Table 1

A summary of organic nitrate products distinguished in this study including, when applicable, the molecular mass (M), molecular formula (MF), identified functional group(s) (FG) and present identification (ID) are provided.

Label	Ion Pair(s)	Formation	Identification
P199	$[\text{M} + \text{H}]^+$ 200154	1. Pinaketone oxidation 2. NO insensitive	M - 199 MF - $\text{C}_9\text{H}_{13}\text{NO}_4$ FG - nitrate, carbonyl Present ID - nitrooxy-pinaketone  (multiple isomers)
P215a	$[\text{M} + \text{H}]^+$ 216152	1. Independent of pinaketone 2. NO insensitive	M - 215 MF - undefined FG - nitrate
P215b	$[\text{M} + \text{H}]^+$ 216152 216158	1. Pinaketone oxidation 2. NO insensitive	M - 215 MF - C9 max FG - nitrate
P231a	$[\text{M} + \text{H}]^+$ 232151 $[\text{M} - \text{H}_2\text{O}]^+$ 214168	1. Independent of pinaketone 2. NO insensitive	M - 231 MF - $\text{C}_{10}\text{H}_{17}\text{NO}_5$ FG - nitrate, hydroxy Present ID - C10 dihydroxy nitrate  (multiple isomers)
P231b	$[\text{M} + \text{H}]^+$ 232151	1. Independent of pinaketone 2. Enhanced formation under high NO conditions	M - 231 MF - C9 max FG - nitrate
P231c	$[\text{M} + \text{H}]^+$ 232151	1. Pinaketone oxidation 2. NO insensitive	M - 231 MF - C9 max FG - nitrate

Peroxynitrates are also potential nitrogen containing oxidation products formed via an analogous reaction pathway to organic nitrates involving NO_2 rather than NO . The formation of peroxynitrate products can therefore compete with the formation of the organic nitrates however, these products were not observed in this system.

3.1.1. Products P231a, P231b and P231c

Three distinct organic nitrate products were identified to contribute to the ion signal at m/z 232. The even target ion (m/z 232) indicates an odd nominal mass of 231 u and the MS/MS spectra for m/z 232 (Fig. 2) shows losses of 18 u (H_2O), 46 u (NO_2), 64 u ($\text{H}_2\text{O} + \text{NO}_2$) and 81 u ($\text{H}_2\text{O} + \text{HNO}_3$) consistent with a multi-functional organic nitrate. In addition to the m/z 232 $[\text{M} + \text{H}]^+$ ion, the associated cluster ions m/z 250 $[\text{M} + \text{H} + \text{H}_2\text{O}]^+$ and m/z 290 $[\text{M} + \text{H} + 58]^+$ and source fragment ion m/z 214 $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$ also support a multi-functional organic nitrate.

The T→F time profiles acquired for these ions have provided further insight, indicating contributions of three unique organic nitrate products at the target ion m/z 232. All three products contribute to the m/z 232→151 time profiles during the β -pinene experiments. The first product, labelled P231a, was isolated using the source fragment ion pair m/z 214→168. Comparing the m/z 214→168 and m/z 232→151 β -pinene experiment time profiles under high and low initial NO conditions (Fig. 4), it can be seen that there is good initial correlation of the time profiles with respect to onset and shape. However, under high initial NO a deviation between the profiles becomes apparent at longer reaction times due to the formation of additional organic nitrate products.

In the pinaketone experiments the signal intensities of the m/z 232→151 and m/z 214→168 time profiles were more than an order of magnitude lower than during the β -pinene experiments. Additionally, the m/z 232→151 pinaketone experiment time profiles indicate no sensitivity to variation of the initial NO. These observations lead to the distinction of at least three organic nitrates that we label P231a, P231b, and P231c. The observation of a product at m/z 232→151 characterized by a very low signal intensity during the pinaketone experiments indicates the formation of a unique organic nitrate whose signal is swamped by the signals from other organic nitrates coming from the β -pinene reaction. We label this P231c. The β -pinene experiments point towards at least two products, which we label P231a for that present at the early stages of the reaction and P231b for the product that becomes apparent under high initial NO conditions and at longer reaction times.

The identification of P231a as C10 dihydroxy nitrate is consistent with the results of Aschmann et al. (1998). The m/z 214→168 ion pair indicates a unique fragmentation path for this product of m/z 232→214→168 consistent with the loss of $\text{H}_2\text{O} + \text{NO}_2$, which are

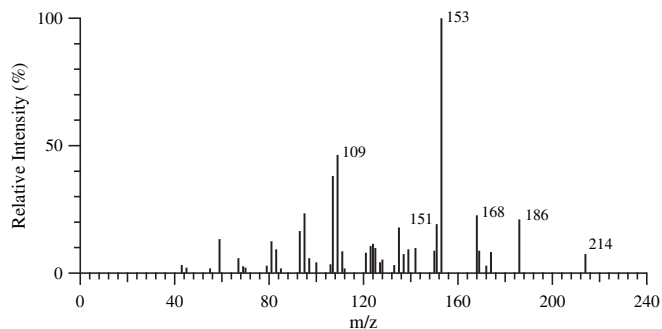


Fig. 2. Representative (+)MS/MS of target ion m/z 232 during the β -pinene experiments. The even target ion (m/z 232) indicates an odd molecular mass of 231 and the losses of 18 u (H_2O), 46 u (NO_2), 64 u ($\text{H}_2\text{O} + \text{NO}_2$) and 81 u ($\text{H}_2\text{O} + \text{HNO}_3$) are consistent with the identification of a multi-functional organic nitrate. The spectrum was acquired with collision energy of 5 eV.

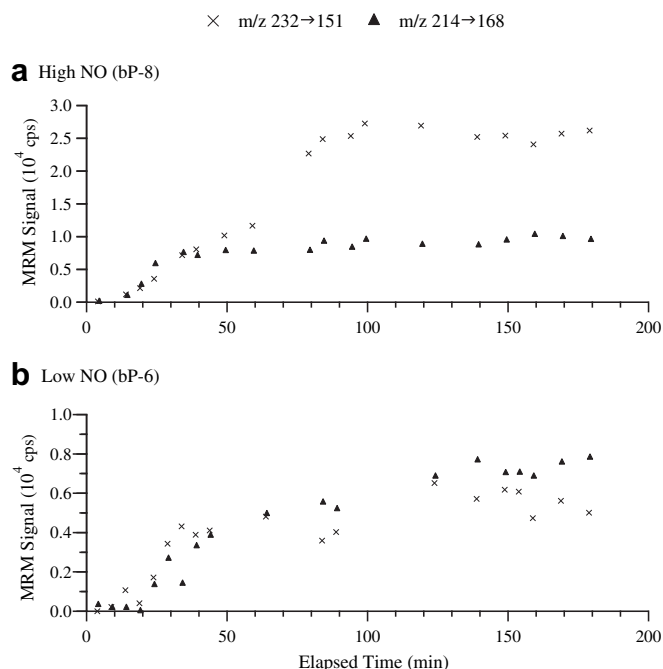


Fig. 3. Example individual β -pinene experiment SRM time profile comparisons of m/z 232→151 and m/z 214→168 under a) high NO and b) low NO conditions. The formation of the identified organic nitrate product P231a is proposed to be isolated using the ion pair m/z 214→168. The m/z 214→168 profile shows good correlation with the m/z 232→151 overall at low NO and only the early section of m/z 232→151 at high NO as expected as a result of additional products contributing to m/z 232→151 at high NO.

expected losses for a molecule containing hydroxyl and nitrate functionality. The identity of P231b has not been isolated to a unique molecular formula or structure however the signal deviation from P231a in the SRM profiles in Fig. 3 occurs after 50 min of reaction time, suggesting a higher oxidation product. Although no further information is known at this time regarding the structure of P231b the formation to P231b has been determined to be by pass pinaketone, with enhanced formation at high NO. Finally, the identity of P231c has been narrowed to a multi-functional organic nitrate with a maximum C9 backbone forming from pinaketone oxidation with no observed sensitivity to the variation of initial NO studied.

3.1.2. Products P215a and P215b

Two organic nitrate products have been identified at the target m/z 216, labelled P215a and P215b. Product P215a has been

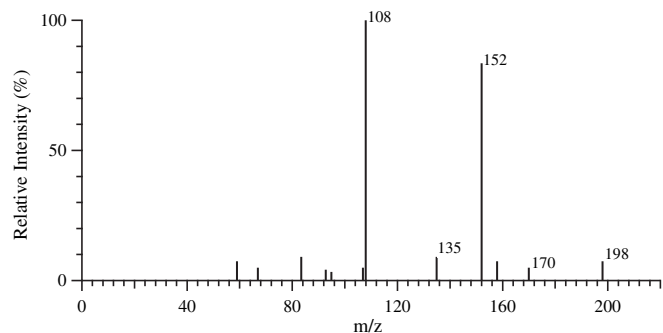


Fig. 4. A representative (+)MS/MS spectrum of m/z 216 during the β -pinene experiments. The product P215a, an organic nitrate formed independent of pinaketone, is proposed to form an $[\text{M} + \text{H}]^+$ ion at m/z 216. The spectrum was acquired at collision energy of 5 eV.

identified using the SRM ion pair m/z 216 \rightarrow 152. P215a is produced independent of pinaketone as indicated by the more than an order of magnitude signal decrease for the m/z 216 \rightarrow 152 ion pair when comparing the profiles from the β -pinene and pinaketone experiments. The (+)MS/MS of the target ion m/z 216 during the β -pinene experiments (Fig. 4) shows fragment ions attributed to the presence of a nitrate and other oxygenated functionalities at m/z 198 (-18 u, H_2O), m/z 170 (-46 u, NO_2), m/z 152 (-64 u, $H_2O + NO_2$), m/z 135 (-81 u, $H_2O + HNO_3$). For the same reaction system, Aschmann et al. (1998) proposed identification for the m/z 216 ion of a C10 hydroxy nitrate (Fig. 1b). The observed (+)MS/MS of m/z 216 published by Aschmann et al. (1998) has a consistent fragmentation pattern to that acquired in this work. However, based on the delayed onset of the m/z 216 \rightarrow 152 SRM time profiles relative to that of pinaketone (m/z 157 \rightarrow 121) (Fig. 7) this identification is not supported for this study. Thus it is likely that P215a results from additional oxidation of the carbon backbone suggesting a molecular formula containing a maximum of C9.

The MS/MS of the m/z 216 ion signal in the pinaketone experiments, namely the loss of 46 u (NO_2) and 64 u ($H_2O + NO_2$), supports the identification of a second organic nitrate, P215b. The formation pathway from pinaketone indicates a molecular formula containing a maximum of C9 similar to that proposed for P215a. However, the structures of P215a and P215b are believed to be different based on the differences in observed fragmentation in the (+)MS/MS spectra of m/z 216 during the β -pinene and pinaketone experiments (Fig. 6). Most notable is the reduced significance of the

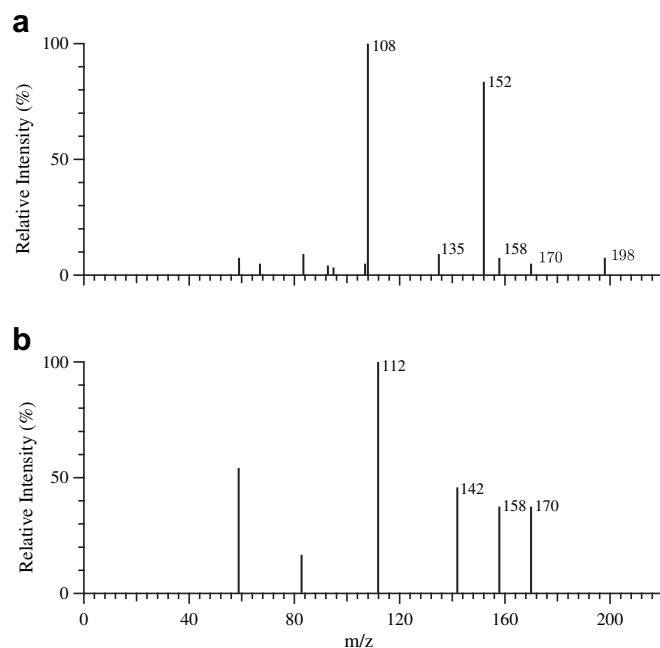


Fig. 6. The (+)MS/MS for m/z 216 during the a) β -pinene and b) pinaketone experiments. The spectra were acquired at collision energy of 5 eV.

m/z 152 fragment and presence of the m/z 112 fragment observed in the m/z 216 ion signal in the pinaketone experiment.

At this time identifications of P215a and P215b are limited to potential molecular formulas. Given both have been identified to contain a maximum of C9 the remaining discussion of identifications is applicable to both. The most reasonable molecular formula for a C9 organic nitrate of mass m/z 215 is $C_9H_{13}NO_5$. A nitrate product retaining the β -pinene bicyclic backbone would require a hydroxyl and ketone functionality, while one with a C9 monocyclic backbone would require two carbonyl functionalities. Products containing less than a C9 backbone will be at most monocyclic, containing multiple carbonyl groups in addition to the nitrate

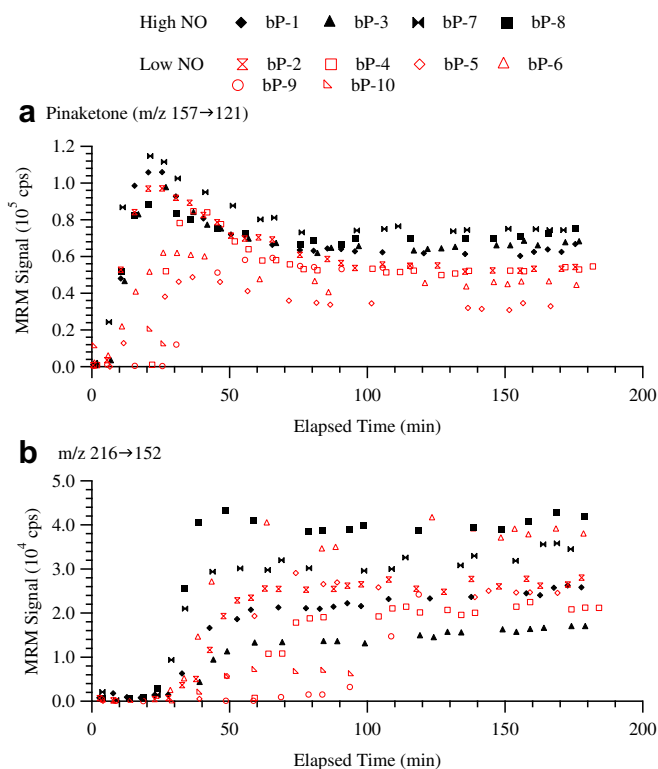


Fig. 5. The β -pinene experiment SRM time profiles for a) pinaketone (m/z 157 \rightarrow 121) and b) m/z 216 \rightarrow 152 are presented. The high and low NO experiment categories are distinguished using black filled and red open symbols respectively. The β -pinene experiment m/z 216 \rightarrow 152 time profiles are proposed to dominantly represent the product P215a and the delayed onset relative to pinaketone (m/z 157 \rightarrow 121) indicates a more highly oxidized product than a C10 hydroxy nitrate. Colour requested for this figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

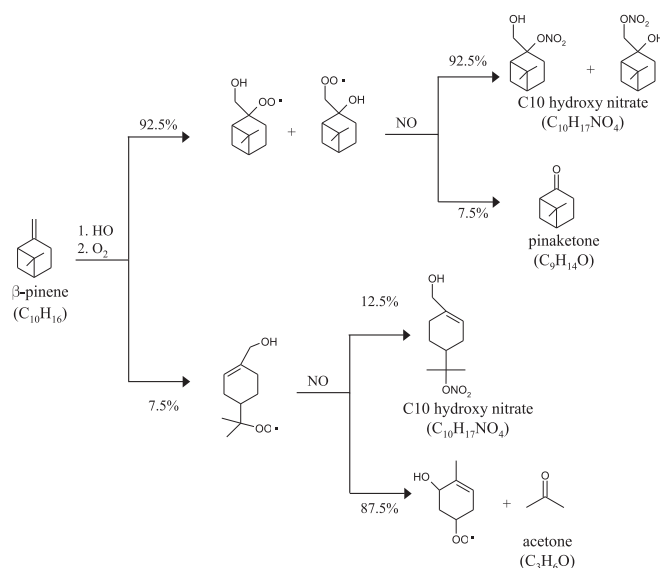


Fig. 7. The primary reactions included in the MCM for HO radical oxidation of β -pinene, which result in the formation of organic nitrates, are summarized in the schematic presented.

group. Currently there are no literature identifications of organic nitrate products with this level of oxidation. At this time P215a and P215b are identified as multi-functional organic nitrates with a maximum carbon backbone of C9.

3.1.3. Product P199

The organic nitrate product labelled P199 has been identified at $[M + H]^+$ target ion m/z 200 with a formation pathway via pinaketone based on the similarity of the product ion spectrum and the m/z 200 \rightarrow 154 SRM profile signal, onset and shape during both sets of experiments. The even $[M + H]^+$ m/z together with the observed fragmentation (-46 u, NO_2 and -63 u, HNO_3) indicate the presence of the nitrate functionality. In addition, identification of the formation pathway through pinaketone indicates a molecular formula containing a maximum C9 hydrocarbon backbone corresponding to the molecular formula $\text{C}_9\text{H}_{13}\text{NO}_4$. Considering this formula and the pinaketone precursor the most reasonable structure is that of pinaketone with a nitrate substituent, nitroxy-pinaketone. This product has not been identified previously however three isomers are proposed in the Master Chemical Mechanism (MCM, University of Leeds) (Jenkin et al., 1997). While the possibility of P199 having a molecular formula containing less than C9 such as $\text{C}_8\text{H}_9\text{NO}_5$ or $\text{C}_7\text{H}_5\text{NO}_6$ has not been directly disproved, inspection of the potential structures show they would require an unreasonable level of unsaturation. Therefore P199 is assigned the identity of nitroxy-pinaketone.

3.2. Formation pathways to organic nitrate products

One of the objectives of product identification in laboratory studies is to shed light on the dominant reaction mechanisms operating in the atmosphere. The best available mechanism in which to analyse the results obtained here is the MCM. The primary reactions included in the MCM for HO radical oxidation of β -pinene, which result in the formation of organic nitrates are compiled in Fig. 7. It shows that the initial HO attack is on the exocyclic double bond followed by reaction with oxygen to give a β -hydroxy alkylperoxy radical with ring retention in 92.5% yield with the remaining 7.5% resulting in breaking of the 4-membered ring to give essentially an isolated peroxy radical. The formation of organic nitrate products occurs through the reaction of such peroxy radicals with NO. In the MCM subsequent reaction of the β -hydroxy alkylperoxy radical with NO gives 24% β -hydroxy nitrate and 76% pinaketone. The radical from the ring breaking pathway reacts with NO giving 12.5% C10 hydroxy nitrate and 87.5% acetone and a C7 peroxy radical. Within this mechanism most higher oxidation products come from further reaction of pinaketone. Such secondary products would be expected to exhibit some delay in formation as shown in the formulation of Hurley et al. (2001). The SRM profiles, while not quantitative, allow us to examine the onset of products to separate primary and higher order products.

The identification of product P231a, as a C10 dihydroxy nitrate, is consistent with the structure suggested by Aschmann et al. (1998) but not the proposed mechanism (Fig. 8). They propose that the C10 dihydroxy nitrate forms from isomerization of the β -hydroxy alkoxy radical to form several isomers of a dihydroxy alkyl radical each of which could react with O_2 and NO to form this product. This mechanism has no stable intermediates and so the product would be produced with no delay and should mirror pinaketone production. However the SRM time profiles for P231a (m/z 214 \rightarrow 168, early portion) are presented in Fig. 9 as a function of reacted β -pinene and they show a consistently delayed onset. This delayed onset does not support a primary formation mechanism such as the isomerization pathway proposed by Aschmann et al. (1998). Other pathways may occur (Fig. 8) via opening of the 4-

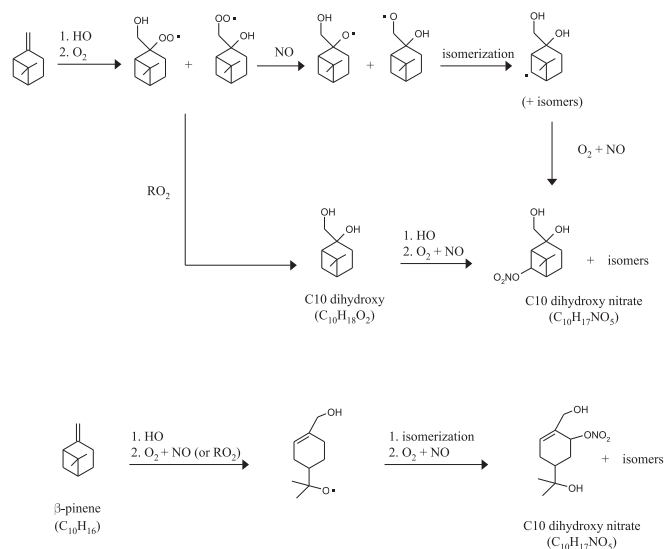


Fig. 8. Proposed oxidation formation pathways to the proposed C10 dihydroxy nitrate product P231a. The isomerization pathways via opening of the 4-membered ring and that maintaining the 4-membered ring Aschmann et al., (1998) are primary formation pathways while the pathway through the C10 dihydroxy product is a secondary pathway.

membered ring upon hydroxyl radical addition to β -pinene and via the C10 dihydroxy product, which can undergo hydrogen abstraction by a hydroxyl radical. The mechanism involving the opening of the 4-membered ring would also be expected to give a product without delay and so does not fit the observations. The pathway through a stable intermediate such as the C10 dihydroxy product must be operational, although this particular product was not observed in this study. Formation pathways to C10 dihydroxy nitrate products are not currently included in the MCM. Further investigations with improved temporal and species resolution focused on the initial oxidation steps of β -pinene may provide the necessary evidence to fully characterize the formation pathways to this product.

The organic nitrate products P231b and P215a differ by one oxygen atom and have been identified as multi-functional organic nitrates with a maximum C9 backbone and formation pathways

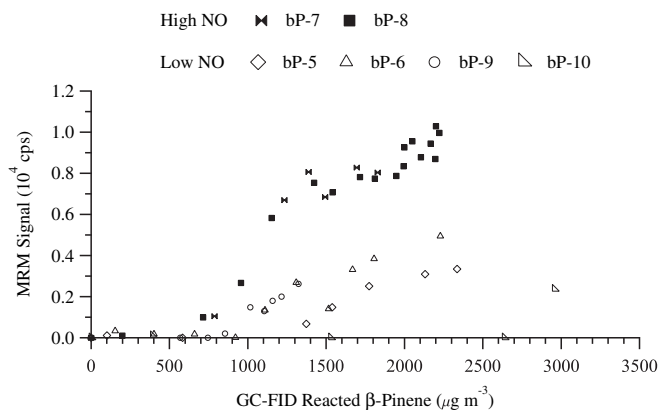


Fig. 9. The SRM profiles for m/z 214 \rightarrow 168 identified as P231a, a C10 dihydroxy nitrate product, as a function of reacted β -pinene are presented. The high and low NO experiment categories are distinguished using filled and open symbols respectively. The observed delayed onset is inconsistent with currently proposed primary formation pathways to C10 dihydroxy nitrate products.

that do not pass through pinaketone. This implies they could share a similar production mechanism, but the difference in response to NO variation distinguishes these products as having unique formation pathways. P231b only appears in the m/z 232 \rightarrow 151 SRM profiles following the onset of P231a formation during the high NO experiments (Fig. 3a). In contrast the SRM profiles for P215a (m/z 216 \rightarrow 152) shown in Fig. 5b indicate a delayed onset but no observed sensitivity to changes in NO levels. Thus they cannot have a common reaction sequence, however additional evidence on the structural formulas of each of these products is necessary for further isolation of the formation pathways. What is gained from these observations is evidence of higher order oxidation product formation pathways that do not pass through pinaketone. Such pathways are lacking from many oxidation mechanisms used in modelling this system including the MCM.

The proposed organic nitrates, labelled P231c and P215b, have also been identified as multi-functional organic nitrates with a maximum C9 backbone, but with formation mechanisms that pass through pinaketone. The pinaketone experiment SRM time profiles for these products suggest a similar time onset and indicate no sensitivity to NO within the range studied. There is little supporting data to assist in further identifications.

Finally, the product P199, identified as nitrooxy-pinaketone (Section 3.1.3), is monitored at the target ion m/z 200 $[M + H]^+$ using the ion pair m/z 200 \rightarrow 154 and has been identified to have a formation pathway through pinaketone. The m/z 200 \rightarrow 154 SRM time profiles for this product points to a delayed onset relative to pinaketone and intercomparison of the P199 profiles indicates the formation pathway is not sensitive to NO within the range investigated. The MCM mechanism includes primary formation pathways from pinaketone to three isomers of nitrooxy-pinaketone. For a primary formation mechanism the delayed onset observed in the SRM profiles of P199 identified, as nitrooxy-pinaketone is not expected. The observation of a delayed onset points to a formation mechanism that includes a stable intermediate and therefore a more highly oxidized product. However, as examined in Section 3.1.3 the formation of structures of this nature from pinaketone oxidation are not reasonable for an organic nitrate of this nominal mass. The incompatibility of the observed formation profiles with the proposed formation mechanism is not understood at this time. Suggestion of an alternate pathway is inconceivable as that currently proposed is composed based on well-established oxidation chemistry. Alternatively, suggestion of an alternate identity of the product P199 is also unlikely. Overall, these results indicate the need for further examination of the initial pinaketone oxidation steps and the potential for indirect influences within the reaction system on observed product formation profiles.

3.3. Conclusions

Multi-functional organic nitrate products from the oxidation of β -pinene by HO radicals have been identified. Pinaketone is thought to be the dominant first product in this oxidation sequence through which the majority of higher oxidation products have been proposed to form. In this study the formation of higher oxidation multi-functional organic nitrate products through pinaketone has been shown. However, also shown is the formation of such products independent of pinaketone thus highlighting a need to examine the contributions of oxidation channels bypassing pinaketone in current β -pinene oxidation mechanisms.

Additional mechanistic insight is gained by varying the initial NO level. Investigation of formation sensitivity to changes in the initial NO levels (0–2 ppm), indicates the presence of organic nitrate product oxidation pathways that are insensitive to initial NO and enhanced at high initial NO levels. The observation of variable

responses to changes of the initial NO level suggests it is not the common nitrate functionality formation step that controls the influence of NO. Observed sensitivities to initial NO levels indicate that the formation of nitrates is competitive with the reduction of peroxy radicals to alkoxy radicals for many of the identified products and that there is potentially a branching ratio dependence on the structure of the peroxy radicals. Overall, these results indicate that the use of generalized mechanisms for understanding the role of a class of products within a given environment, such as organic nitrates, has the potential to be misleading. Continued investigation of individual product formation from atmospherically relevant hydrocarbons is essential to fully understanding and mapping these complex oxidation mechanisms. The ability to jointly acquire highly resolved speciation information and time resolved results during oxidation experiments is necessary in achieving this information. Real time, online acquisition of individual product formation is an asset for both identification of products and investigation of oxidation mechanisms.

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