

A smog chamber study of secondary organic aerosol (SOA) formation from the photo-oxidation of β -pinene

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INTRODUCTION

Hydrocarbons are emitted into the atmosphere from anthropogenic and biogenic sources. On a global scale, the emission of biogenic volatile organic compounds (BVOC) exceeds those of anthropogenic compounds by a factor of 10. One of the important constituents of BVOC are monoterpenes ($C_{10}H_{16}$) which are emitted mainly by forest vegetation. β -pinene as one of the abundant monoterpene compounds is highly reactive in the atmosphere, primarily reacts with HO radicals during daylight hours and produces a diverse range of organic products. A large fraction of these products are semi-volatile which partitions between gas and particle phase based on their volatility. The low volatility products in the gas phase partition into the condensed phase to form secondary organic aerosol (SOA). SOA accounts for a majority of ambient tropospheric aerosols and these aerosols have been linked with adverse effects on human health (e.g. respiratory and cardiovascular diseases) and a wide range of direct and indirect climate effects (e.g. scattering and absorption of solar radiation, cloud formation). However, lack of knowledge on atmospheric particle sources, composition and mechanism of formation lead to the uncertainties in the true impact of them on climate and health¹.

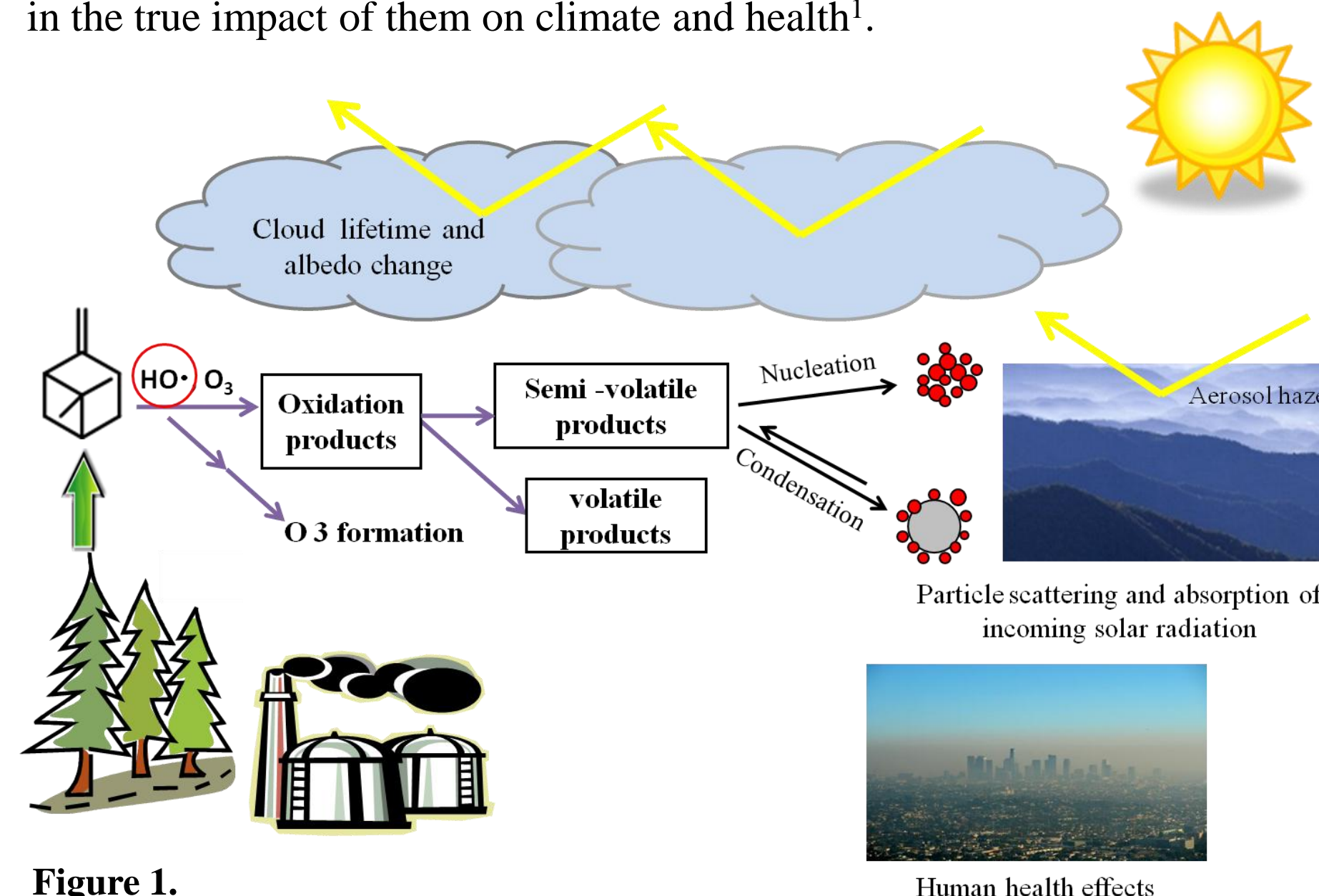


Figure 1.

EXPERIMENTAL SYSTEM

The photo-oxidation reaction of β -pinene was carried out in the York University smog chamber which is composed of an inner 8 m³ Teflon bag surrounded by 24 UV lights. $(NH_4)_2SO_4$ seed particles were first introduced into the chamber using a Collision nebulizer to provide a surface for partitioning of gas and particle phase products. Following stabilization of seed particles, β -pinene and isopropyl nitrite (IPN), as the HO radical source, were injected into the chamber. All reagents were allowed to mix in dark for one hour followed by the initiation of the reaction by turning on the lights. The photo-oxidation reaction of β -pinene with HO radicals lasted for 3-4 hours. Gas phase hydrocarbon concentration is monitored using a gas chromatograph with a flame ionization detector (GC-FID), produced organic particulate mass and particle size distribution are determined by a Differential Mobility Analyzer (DMA) coupled with a Condensation Particle Counter (CPC) and a Chemiluminescence NO/NO_x analyzer is used to monitor NO and NO_x. The Atmospheric Pressure Chemical Ionization (APCI) triple quadrupole mass spectrometer-API 365 is used for identification of oxidation products. Counter Flow Membrane Denuder (CFMD) followed by an inline heater has been used for particle phase analysis.

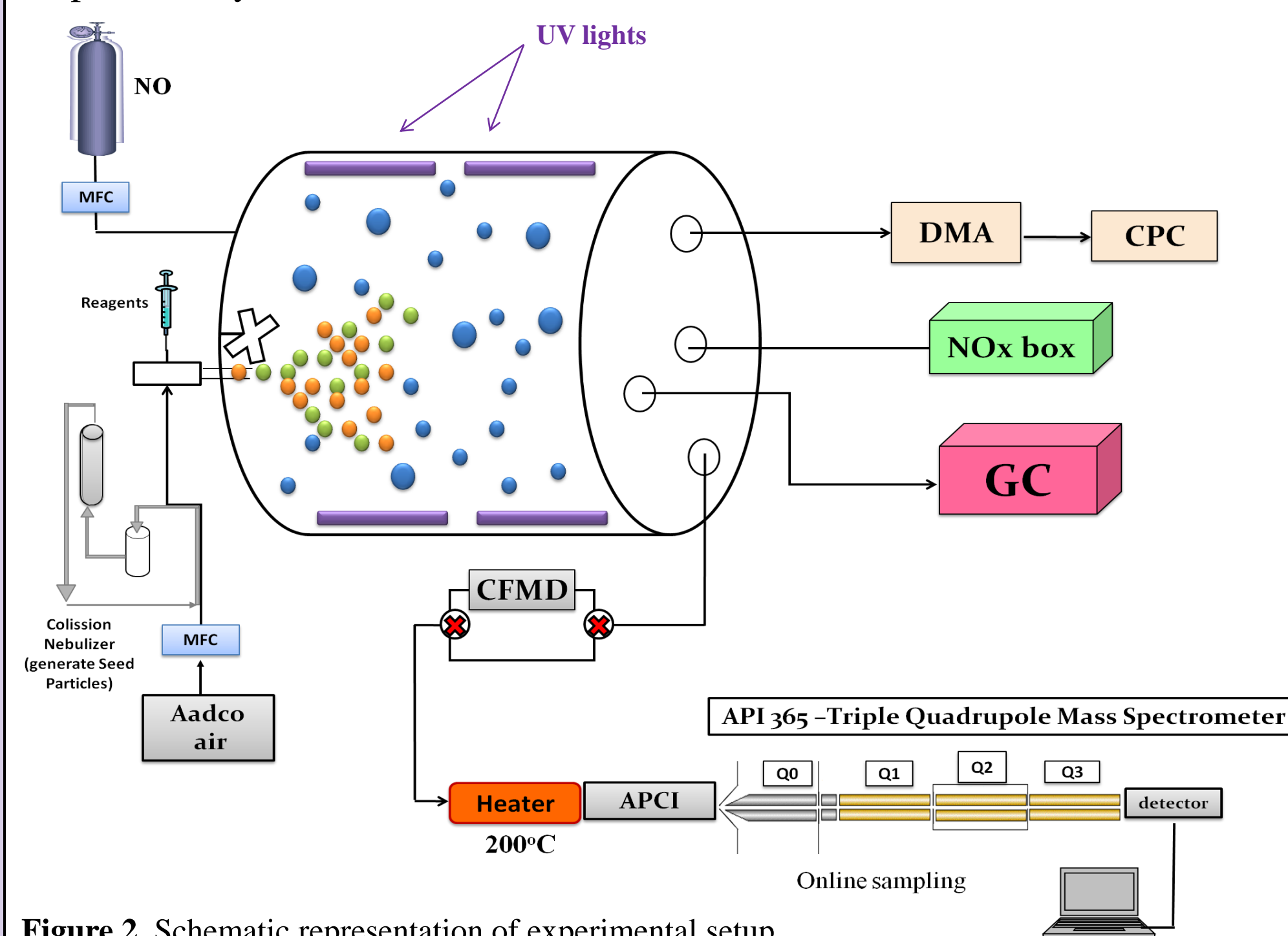


Figure 2. Schematic representation of experimental setup.

RESULTS

i) Quantitative Results: Organic Particulate Matter Formation

One example of quantitative measurements are illustrated in Figure 3. The data from DMA-CPC, organic particulate mass concentration, is combined with β -pinene decay profile from the GC and plotted over time. The vertical red line is the time of the initiation of the reaction. As reaction proceeds, β -pinene decays and more products are produced which contribute in the formation of organic particulate matter.

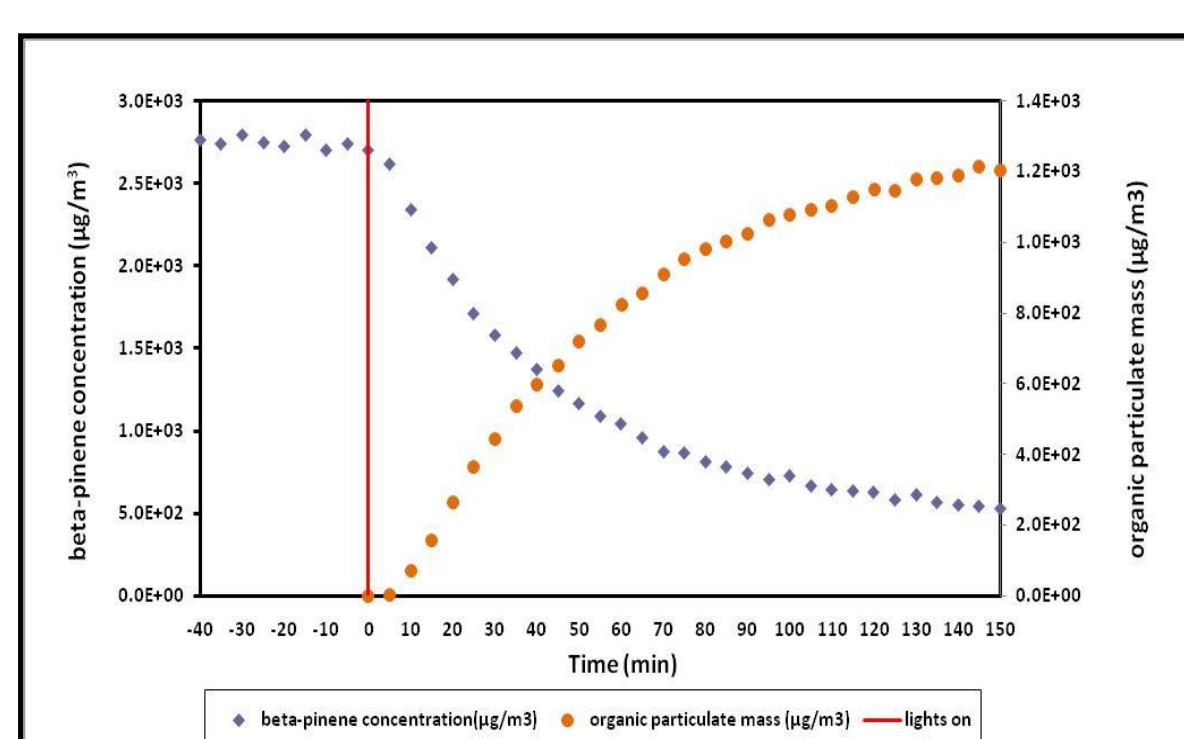


Figure 3. Concentration profiles of gas-phase β -pinene and organic particulate mass concentration versus time during β -pinene experiment.

ii) Qualitative Results: Product Identification by Mass Spectrometry

Multiple scan modes are used to identify and profile oxidation products including: Mass Spectrum (MS) mode, MS/MS mode and Selected Reaction Monitoring (SRM) mode. Analysis of the reaction products is started with the MS mode which provides a full mass spectrum of all ions within the mass range of 10-300 amu (figure 4).

Products that appeared at m/z 139 and m/z 187 have been identified as the dominant products in the gas and particle phase respectively. Structural and functional groups information are obtained using MS/MS scan mode. The unique MS/MS spectrum of products can be used for identification confirmation only when standards are available by comparison of their fragmentation patterns. The product at m/z = 139 and m/z = 187 was attributed to nopinone and pinic acid respectively (Figure 6 & 7).

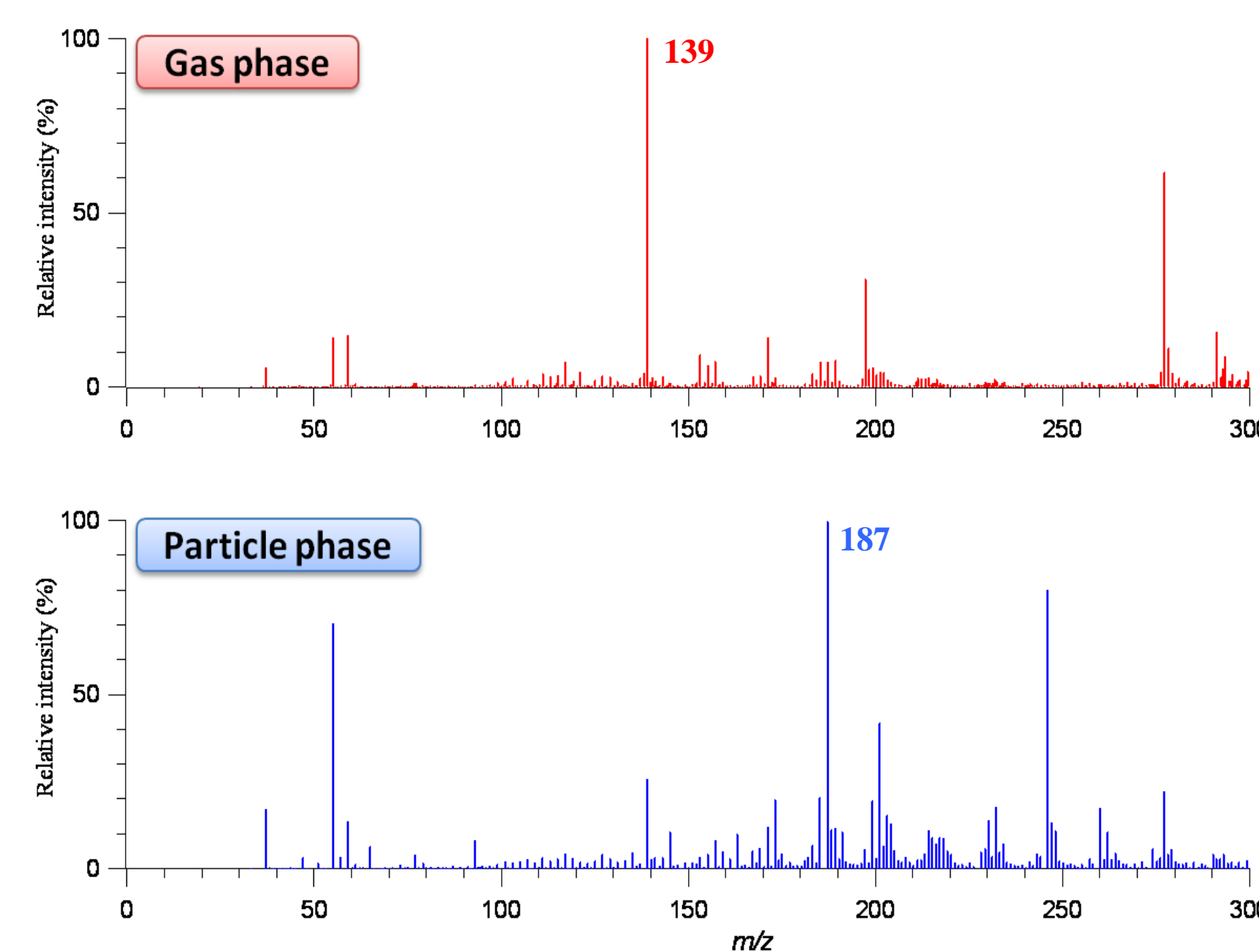


Figure 4. Comparison of MS scans of oxidation products formed from β -pinene/HO reaction in the gas and particle phase.

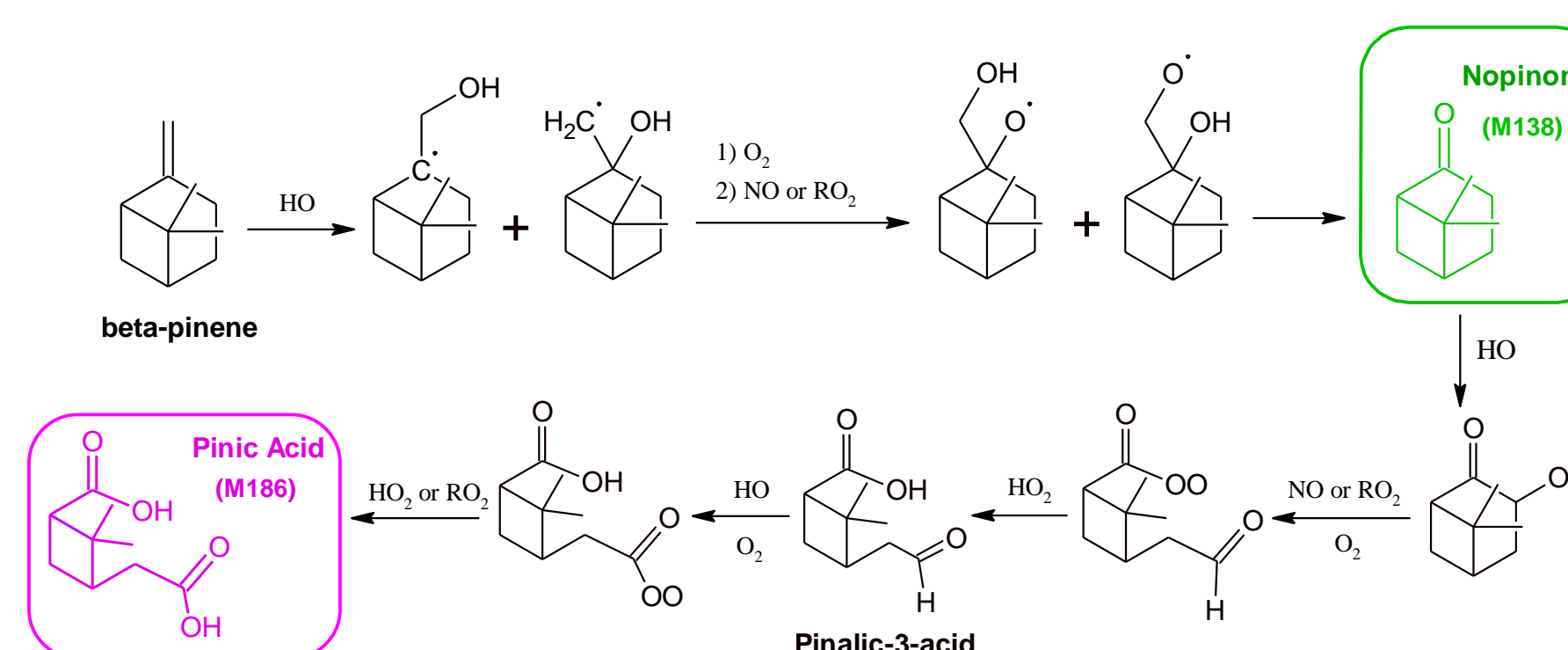


Figure 5. Mechanism of formation of nopinone and pinic acid.

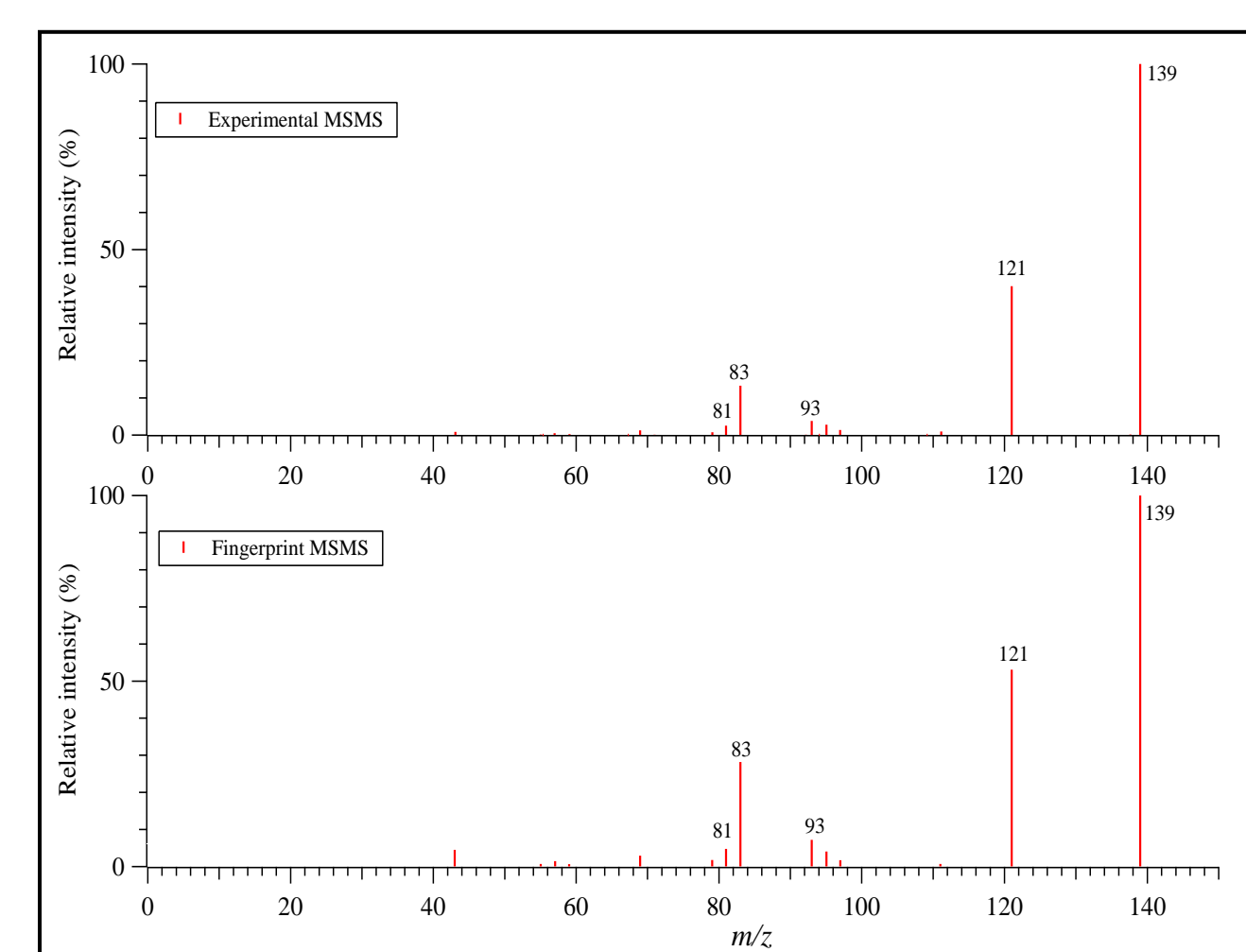


Figure 6. Comparison of (+)MS/MS spectrum of 139 m/z during the β -pinene experiment and from the nopinone fingerprint.

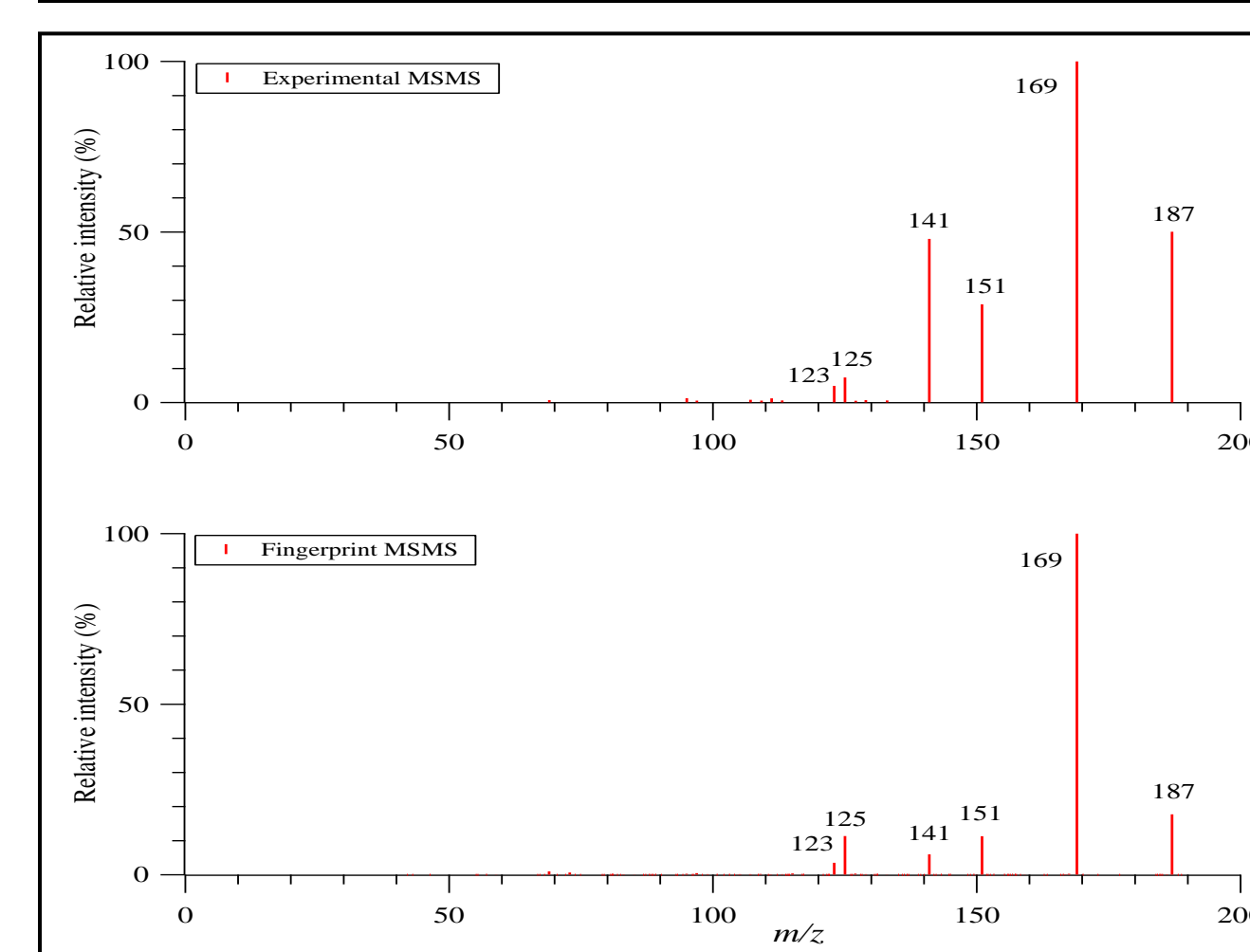


Figure 7. Comparison of (+)MS/MS spectrum of 187 m/z during the β -pinene experiment and from the pinic acid fingerprint. Discrepancy in the ratio of fragments shows contribution from other species into this mass.

iii) Effect of NO_x Level on SOA Formation

Probing the effect of nitrogen oxides (NO_x) on products formation has been done by performing β -pinene/HO experiments under varying NO_x condition. Understanding the NO_x sensitivity of products is important on a large scale since the NO_x level is variable between rural and urban areas and SOA yields can vary substantially depending on NO_x level. For investigating the dependence of SOA yield (mass of SOA formed per mass of hydrocarbon reacted) on the NO_x level, the organic particulate yield was obtained for 5 experiments with varied level of NO_x (0.2, 0.4, 1, 1.5 and 2 ppm).

$$\text{Particulate Yield (\%)} = \frac{\text{Organic particulate mass}}{\text{Reacted } \beta\text{-pinene}} \times 100$$

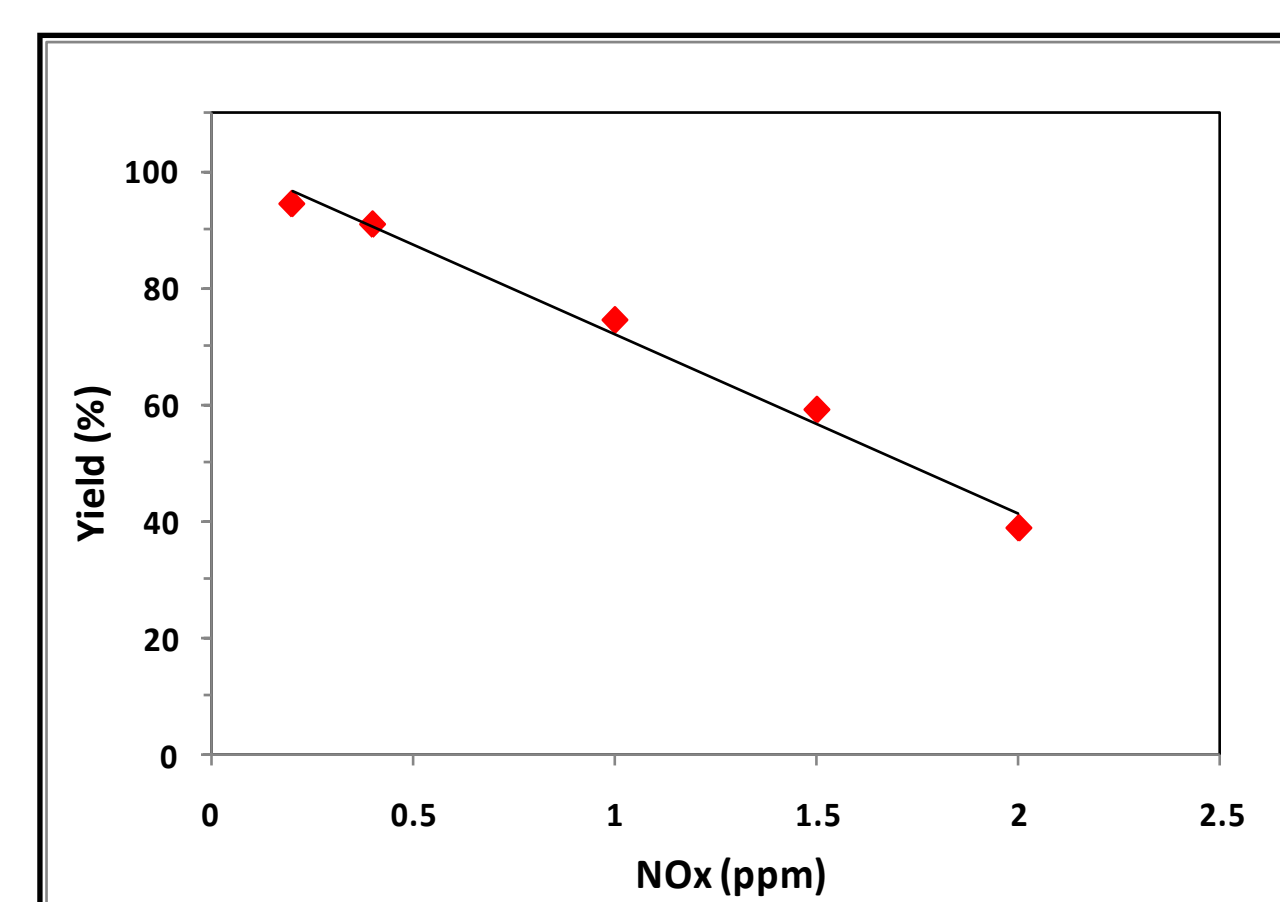


Figure 8. The organic particulate yield profile shows an inverse dependence to NO_x level.

The organic particulate yield showed an inverse dependence to NO_x level.

Table 1: Selected Identified Products and their NO_x Sensitivity

Table 1 presents a selection of current identified products from β -pinene photo-oxidation. m/z of products which are identified only in the particle phase are shown in red. The investigation of the NO_x sensitivity of products leads to insights into the dependence of their formation mechanism on NO_x level. The effect of the initial NO_x level on the formation of products were investigated and shown here.

m/z	Possible Molecular Formula(s)	Chemical Composition	Structure	Evidence	NO _x Sensitivity
139	$C_9H_{14}O$	nopinone		MSMS Fingerprint confirmation	NO _x insensitive
153	$C_9H_{12}O_2$	oxo-nopinone (multiple isomers)		MSMS fragmentation	Enhanced under low NO _x
155	$C_9H_{14}O_2$	3-hydroxy nopinone (multiple isomers)		MSMS fragmentation pattern	Enhanced under low NO _x
173	$C_9H_{14}O_3$	norpinic acid		MSMS fragmentation pattern	Enhanced under low NO _x
187	$C_9H_{14}O_4$	pinic acid ²		MSMS Fingerprint Confirmation (+) and (-) MSMS	Enhanced under low NO _x
201	$C_{10}H_{16}O_4$	10-hydroxy pinonic acid ²		MSMS fragmentation pattern	Enhanced under low NO _x
203	$C_9H_{14}O_5$	C9-peroxy acid ³		MSMS fragmentation pattern (+) and (-) MSMS	undetermined
214	$C_9H_{11}NO_5$ or $C_{10}H_{15}NO_4$	dioxo nitrate or aldehyde nitrate		MSMS fragmentation pattern	Enhanced under low NO _x
216	$C_{10}H_{17}NO_4$ or $C_9H_{13}NO_5$	C10-hydroxy nitrate or C9-hydroxy oxo nitrate (multiple isomers)		MSMS fragmentation pattern	NO _x insensitive
232	$C_{10}H_{17}NO_4$	C10-Dihydroxy nitrate (multiple isomers)		MSMS fragmentation pattern	NO _x insensitive

CONCLUSION

The results of this study showed that there are a significant number of products that are formed in gas and particle phase from β -pinene photo-oxidation. Many of these products have been tentatively identified online by applying MS and MS/MS scan mode. However, due to some challenges not all the observed products were identified. These challenges include: overlapping of different species at the same m/z ratio, similar fragmentation pattern for products with similar functional groups, and limited availability of standards. Further improvements to the current identification method need to be done. In addition, the investigation of the dependence of SOA yield on NO_x showed that SOA yields are larger under low-NO_x condition. NO_x sensitivity results in the current study have been shown to have impacts on the oxidation products which was varied on different products. The next goal is to determine whether or not the products formation mechanisms are consistent with their NO_x sensitivity.

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