



Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes

N. L. Ng, P. S. Chhabra, A. W. H. Chan, J. D. Surratt, J. H. Kroll, A. J. Kwan, D. C. McCabe, P. O. Wennberg, A. Sorooshian, S. M. Murphy, et al.

► To cite this version:

N. L. Ng, P. S. Chhabra, A. W. H. Chan, J. D. Surratt, J. H. Kroll, et al.. Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes. *Atmospheric Chemistry and Physics Discussions*, 2007, 7 (4), pp.10131-10177. hal-00302965

HAL Id: hal-00302965

<https://hal.science/hal-00302965>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes

N. L. Ng¹, P. S. Chhabra¹, A. W. H. Chan¹, J. D. Surratt², J. H. Kroll³, A. J. Kwan⁴, D. C. McCabe⁴, P. O. Wennberg⁴, A. Sorooshian¹, S. M. Murphy¹, N. F. Dalleska⁴, R. C. Flagan^{1,4}, and J. H. Seinfeld^{1,4}

¹Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

²Department of Chemistry, California Institute of Technology, Pasadena, CA 91125, USA

³Aerodyne Research, Inc., Billerica, MA 01821, USA

⁴Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, CA 91125, USA

Received: 7 June 2007 – Accepted: 3 July 2007 – Published: 12 July 2007

Correspondence to: J. H. Seinfeld (seinfeld@caltech.edu)

NO_x dependence of
SOA formation from
terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

EGU

Abstract

ACPD

7, 10131–10177, 2007

Secondary organic aerosol (SOA) formation from the photooxidation of one monoterpene (α -pinene) and two sesquiterpenes (longifolene and aromadendrene) is investigated in the Caltech environmental chambers. The effect of NO_x on SOA formation for these biogenic hydrocarbons is evaluated by performing photooxidation experiments under varying NO_x conditions. The NO_x dependence of α -pinene SOA formation follows the same trend as that observed previously for a number of SOA precursors, including isoprene, in which SOA yield (defined as the ratio of the mass of organic aerosol formed to the mass of parent hydrocarbon reacted) decreases as NO_x level increases. The NO_x dependence of SOA yield for the sesquiterpenes, longifolene and aromadendrene, however, differs from that determined for isoprene and α -pinene; the aerosol yield under high- NO_x conditions substantially exceeds that under low- NO_x conditions. The reversal of the NO_x dependence of SOA formation for the sesquiterpenes is consistent with formation of relatively low-volatility organic nitrates, and/or the isomerization of large alkoxy radicals leading to less volatile products. Analysis of the aerosol chemical composition for longifolene confirms the presence of organic nitrates under high- NO_x conditions. Consequently the formation of SOA from certain biogenic hydrocarbons such as sesquiterpenes (and possibly large anthropogenic hydrocarbons as well) may be more efficient in polluted air.

20 1 Introduction

Atmospheric oxidation of certain volatile organic compounds (VOCs) leads to the formation of low volatility species that partition into the condensed phase and form secondary organic aerosol (SOA). Biogenic hydrocarbons, such as isoprene (C_5H_8), monoterpenes ($\text{C}_{10}\text{H}_{16}$), and sesquiterpenes ($\text{C}_{15}\text{H}_{24}$), are important contributors to the total atmospheric burden of SOA owing to their large global emissions and high reactivity with hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3) (Guenther

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

EGU

et al., 1995; Griffin et al., 1999a; Geron et al., 2000; Owen et al., 2001; Atkinson and Arey, 2003; Seinfeld and Pankow, 2003; Kanakidou et al., 2005).

Over the last two decades, numerous laboratory chamber experiments have been conducted to study aerosol formation from biogenic hydrocarbons. Level of odd nitrogen (NO_x) has been found to be highly influential in SOA production for a variety of compounds. Recent studies on isoprene photooxidation, α -pinene ozonolysis, and benzene, toluene, and *m*-xylene photooxidation have demonstrated that aerosol yields are generally highest at low levels of NO_x (Hatakeyama et al., 1991; Kroll et al., 2006; Presto et al., 2005; Song et al., 2005; Ng et al., 2007). These observations are consistent with competitive chemistry of peroxy radicals between NO and HO_2 , with the $\text{RO}_2 + \text{HO}_2$ reaction producing products of lower volatility than the $\text{RO}_2 + \text{NO}$ reaction (Hatakeyama et al., 1991; Johnson et al., 2004, 2005; Kroll et al., 2005, 2006; Presto et al., 2005; Ng et al., 2007). For example, in α -pinene ozonolysis, Presto et al. (2005) observed relatively volatile organic nitrates under high- NO_x conditions, while less volatile products, such as 10-hydroxy pinonic acid, were more abundant under low- NO_x conditions. Although a decreasing SOA yield with increasing NO_x level has been established for relatively small hydrocarbons (10 carbons or fewer), it is unknown whether larger molecules, such as sesquiterpenes, exhibit a similar NO_x dependence of SOA yield.

In the present study, we focus on two sesquiterpenes, longifolene and aromadendrene, and compare the NO_x -dependence of their SOA formation with that of α -pinene. Longifolene reacts very slowly with ozone (Atkinson and Arey, 2003), making it ideal for the study of OH photooxidation. Moreover, both longifolene and aromadendrene have only one double bond, thus one can infer more easily the general mechanisms of SOA formation than when multiple double bonds are present (Ng et al., 2006). Experiments are conducted under limiting NO_x conditions (high- NO_x conditions in which HONO is used as the OH precursor, and low- NO_x conditions in which H_2O_2 is used as the OH precursor), as well as with intermediate levels of NO_x .

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

2 Experimental section

ACPD

7, 10131–10177, 2007

Experiments are performed in Caltech's dual 28 m^3 Teflon environmental chambers. Details of the facilities are given elsewhere (Cocker et al., 2001; Keywood et al., 2004). Before each experiment, the chambers are flushed continuously with dry purified air for $\sim 24\text{ h}$. Each chamber has a dedicated Differential Mobility Analyzer (DMA, TSI model 3081) coupled with a condensation nucleus counter (TSI model 3760) for measuring aerosol size distribution, number concentration, and volume concentration. All aerosol growth data are corrected for wall loss, in which size-dependent coefficients determined from inert particle wall loss experiments are applied to the aerosol volume data (Keywood et al., 2004). Temperature, relative humidity (RH), O_3 , NO , and NO_x are continuously monitored. The initial temperature of the chamber is $\sim 20^\circ\text{C}$. Heating from the lights leads to a temperature increase of approximately 5°C inside the chamber over the course of the experiment. The analytical instruments are located outside the chamber enclosure and are at the temperature of the surrounding room ($\sim 20\text{--}22^\circ\text{C}$). The air may cool slightly as it is sampled from the chamber into the instruments, and the measured aerosol likely corresponds to the gas-particle partitioning at the temperature of the surrounding room rather than the chamber enclosure. Such small temperature differences are unlikely to affect results significantly.

Seed particles are introduced into the chamber to act as substrates onto which the gas-phase semivolatile products may condense. Seed aerosols are generated from a 0.015 M aqueous ammonium sulfate solution with a constant-rate atomizer, producing initial particle number concentrations of $\sim 25\,000\text{ particles cm}^{-3}$, with a geometric mean diameter of $\sim 50\text{ nm}$, and an initial aerosol seed volume of $\sim 10\text{--}15\,\mu\text{m}^3\text{ cm}^{-3}$. After introduction of the seed aerosol, a known volume of the parent hydrocarbon is injected into a glass bulb, and then introduced into the chambers by an air stream. For experiments with α -pinene and longifolene, the concentration (mixing ratio) of the parent hydrocarbon is monitored with a Hewlett Packard gas chromatograph (model 5890) with flame ionization detection (GC-FID). The concentration of longifolene in several

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

EGU

experiments is also measured with a Proton Transfer Reaction Mass Spectrometer (PTR-MS), a custom-modified Varian 1200 system (see Appendix A). Owing to the difficulties in measuring aromadendrene with GC-FID, its concentration is measured solely with the PTR-MS. The PTR-MS is calibrated only for aromadendrene.

In the high- NO_x experiments nitrous acid (HONO) serves as the OH precursor. HONO is prepared by dropwise addition of 15 mL of 1% NaNO_2 into 30 mL of 10% H_2SO_4 in a glass bulb. After injection of the seed aerosol and parent hydrocarbon, the bulb is then attached to the chamber and a stream of dry air is passed through the bulb, sending HONO into the chamber. NO and NO_2 , formed as side products in the preparation of HONO, are also introduced into the chamber, and are measured by a commercial NO_x monitor (Horiba APNA-360, Irvine, CA). Additional NO from a 500 ppm gas cylinder (Scott Marrin, Inc.) is introduced into the chamber after the addition of HONO to achieve a target NO_x level in the chamber of about 1 ppm (upper limit of the NO_x monitor).

For low- NO_x experiments, H_2O_2 serves as the OH precursor. The background NO_x level in the chamber during such experiments is ≤ 2 ppb. About 3 ppm H_2O_2 is introduced into the chamber (prior to introduction of seed particles and parent hydrocarbon) by bubbling air through a 50% H_2O_2 solution for 2.5 h at 5 L/min. The air stream then passes through a particle filter to remove any droplets. Variable NO experiments are also carried out, in which a known concentration of NO is introduced into the chamber after the addition of H_2O_2 . This allows for the study of SOA formation under intermediate NO_x conditions. It is noted that for these intermediate NO_x experiments, NO goes to zero during the experiment and so there is a switch from high- to low- NO_x conditions over the course of the experiment.

Once the seed, parent hydrocarbon, and NO_x concentrations stabilize, reaction is initiated by irradiating the chamber with blacklights. Output from the lights is between 300 and 400 nm, with a maximum at 354 nm. Half of the available black lights are used in the experiments. At these wavelengths HONO efficiently photolyzes to OH and NO. By contrast, H_2O_2 absorbs only weakly in this wavelength range, requiring the use of

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ppm mixing ratios of H₂O₂ to achieve target levels of OH.

A comprehensive range of measurements are employed to study the chemical composition of the SOA formed. Real-time particle mass spectra are obtained with an Aerodyne quadrupole Aerosol Mass Spectrometer (Q-AMS) (Jayne et al., 2000). A particle-into-liquid sampler (PILS, Brechtel Manufacturing, Inc.) coupled with ion chromatography is employed for quantitative measurements of water-soluble ions in the aerosol phase (Sorooshian et al., 2006). For offline chemical analysis, aerosol samples are collected on Teflon filters (PALL Life Sciences, 47-mm diameter, 1.0- μm pore size, Teflo membrane) starting at the point when aerosol volume reaches its maximum value. Depending on the total chamber volume concentration of aerosol, the filter sampling time is 2–4 h, which results in \sim 1.5–6 m³ of total chamber air sampled. Teflon filter extraction protocols in HPLC-grade methanol have been described previously (Surratt et al., 2006). The resultant filter extracts are then analyzed by high performance liquid chromatography/electrospray ionization-quadrupole mass spectrometry (HPLC/ESI-MS) and electrospray ionization-ion trap mass spectrometry (ESI-ITMS); details of the protocols are described elsewhere (Surratt et al., 2006). Filter extracts are also analyzed by a Waters ACQUITY ultra performance liquid chromatography (UPLC) system, coupled with a Waters LCT Premier time-of-flight (TOF) mass spectrometer (MS) equipped with an electrospray ionization (ESI) source (see Appendix B), allowing for exact mass and tandem MS measurements.

The parent hydrocarbons studied and their stated purities are as follows: α -pinene (Aldrich, 99+%), longifolene (Aldrich, >99%), and aromadendrene (Aldrich, >97%). Table 1 lists the structures of the parent hydrocarbons and the rate constants of the compounds for reaction with OH radicals (k_{OH}). Experimental conditions and results for each of the parent hydrocarbons studied are given in Tables 2, 3, and 4. In calculating SOA yield, knowledge of the SOA density is required. By comparing volume distributions from the DMA and mass distributions from the Q-AMS, effective densities for the SOA formed can be estimated (Bahreini et al., 2005; Alfarra et al., 2006). The estimated densities of the SOA formed from different parent hydrocarbons are given in

3 Aerosol yields

3.1 α -pinene photooxidation

Under high- NO_x conditions, the efficient photolysis of HONO generates relatively high concentrations of OH ($\sim 2 \times 10^7$ molecules cm^{-3} initially), leading to rapid α -pinene decay. Aerosol growth occurs essentially immediately, even when [NO] is high (100's of ppb). With the high NO concentration throughout the entire experiment, formation of ozone and NO_3 is suppressed.

Under low- NO_x conditions, aerosol growth is also observed immediately after initiation of irradiation. The α -pinene decays at a slower rate than under high- NO_x conditions, owing to the relatively slow production of OH radicals by H_2O_2 photolysis. Ozone formation is observed at an increasing concentration over time (~ 30 ppb at the peak of aerosol growth), possibly from residual material released from the chamber walls. Based on the reaction rate constants of α -pinene+ O_3 ($k_{\text{ozone}} = 8.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson et al., 2003) and α -pinene+OH ($k_{\text{OH}} = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson et al., 2003), and an inferred OH concentration of 3×10^6 molecules cm^{-3} (estimated from longifolene low- NO_x experiments, see Sect. 3.2), it is estimated that an ozone source of ~ 0.1 ppb/min would be required to produce the observed α -pinene decay. It is estimated that only about 35% of the α -pinene reacts by ozonolysis at the point of maximum growth. Therefore, while α -pinene ozonolysis accounts for some of the SOA yield under low- NO_x conditions, it is unlikely that the observed yield differences between high- and low- NO_x conditions (described below) arise solely from the presence of ozone.

Figure 1 shows the time-dependent growth curves (organic aerosol generated, denoted as ΔM_o , as a function of hydrocarbon reacted, ΔHC) for α -pinene under different NO_x conditions. As hydrocarbon measurements are made with a lower frequency than

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

those of particle volume, the α -pinene concentrations shown are obtained by fitting the GC measurements to an exponential decay. In all cases, the initial mixing ratio of α -pinene is about 15 ppb, all of which is consumed by the end of the experiment. It is clear that the aerosol growth under low- NO_x (H_2O_2) conditions substantially exceeds that under high- NO_x (HONO) conditions, while the intermediate NO_x ("H₂O₂+NO") experiment exhibits an aerosol yield between those of the two extremes. The time-dependent growth curve of the intermediate NO_x experiment exhibits a vertical section at the end, indicating that further reactions are contributing to aerosol growth after α -pinene is consumed. We return to this observation in Sect. 5.2.2.

10 3.2 Longifolene photooxidation

For longifolene, a series of high- NO_x (HONO) experiments and low- NO_x (H_2O_2) experiments with varying initial hydrocarbon concentrations are carried out. The time-dependent growth curves for 3 high- NO_x and 3 low- NO_x experiments, with initial longifolene mixing ratios ranging from \sim 10 to 30 ppb, are shown in Fig. 2. In contrast to α -pinene photooxidation, longifolene aerosol yields under high- NO_x conditions exceed those under low- NO_x conditions. Under high- NO_x conditions, the maximum SOA yield is about \sim 100–130% and is reached in \sim 10 min after initiation of the experiments, with the yield decreasing after that point. It is noted that SOA yield is defined on a mass basis so oxidation (addition of O or N atoms) can lead to yields larger than 100%. Under low- NO_x conditions, SOA yield continues to increase over the course of the experiment, reaching a maximum when all the longifolene is consumed. The final SOA yields of each longifolene low- NO_x experiment lie on a straight line that passes through the origin, indicating that under low- NO_x conditions SOA yield is constant (\sim 75%) under the range of ΔM_o studied. It is possible that under lower SOA loadings the yields may decrease as some of the products partition back into the gas phase. Based on the observed longifolene decay and k_{OH} for longifolene, the chamber OH concentration under low- NO_x conditions is estimated to be \sim 3 \times 10⁶ molecules cm⁻³.

The effect of NO_x on longifolene aerosol formation is further illustrated by the time-

N. L. Ng et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

dependent growth curves in Fig. 3. In both experiments H_2O_2 is used as the OH precursor and the initial longifolene mixing ratio is 4–5 ppb; in one experiment no extra NO is added, while in the other experiment about 300 ppb of NO is introduced into the chamber after the addition of H_2O_2 . Aerosol growth in the presence of ~300 ppb NO is substantially higher. A series of experiments with the same initial longifolene concentration but different initial NO concentrations (~100–600 ppb) are also carried out. Figure 4 shows the final aerosol yield as a function of the initial NO_x concentration. The amount of aerosol formed is highly dependent on the level of NO_x present initially; with ~600 ppb NO, the ultimate aerosol yield is twice that at low- NO_x conditions.

10 3.3 Aromadendrene photooxidation

Figure 5 shows the final aerosol yield as a function of initial NO_x concentration for aromadendrene photooxidation. The OH precursor used in these experiments is H_2O_2 and the initial aromadendrene mixing ratio is ~5 ppb. It is clear that aromadendrene aerosol yield also increases with NO_x concentration; as with longifolene, with ~500 ppb NO, the aerosol yield is approximately double that at low- NO_x conditions.

4 Chemical composition of SOA

In this section, the measurements of the chemical composition of α -pinene and longifolene SOA are presented. The aromadendrene experiments are performed mainly to verify the observed NO_x dependence for longifolene, in which SOA yield is higher under high- NO_x conditions, and so detailed analysis of the chemical composition of aromadendrene SOA is not pursued.

20 4.1 Aerosol Mass Spectrometer (Q-AMS) measurements

Figures 6 and 7 show the AMS high- NO_x versus low- NO_x spectrum signal for α -pinene and longifolene photooxidation, respectively. Each mass fragment is normalized by

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

the total signal. For both hydrocarbons, SOA at high NO_x conditions exhibit relatively strong signals at *m/z* 30 and 46, and to a much smaller extent *m/z* 14. The signals at these mass to charge ratios likely correspond to NO₂⁺(46), NO⁺(30), and N⁺(14) fragments from nitrates in the aerosol. The significance of these fragments will be further discussed in Sect. 5.1.

Changes in AMS spectra over the course of the experiment for longifolene under high- and low-NO_x conditions are shown in Figs. 8 and 9, respectively. The corresponding growth curves for these experiments are shown in Fig. 2 (the pair of experiments with ~30 ppb of longifolene injected). The top panel shows the fractional contribution of each mass fragment to the total organic and nitrate signal during the growth phase of the experiment (the first ~100 µgm⁻³ α -pinene reacted); the middle panel shows the fractional contributions at the point when all of the hydrocarbon is consumed (Δ H_C~200 µgm⁻³); the bottom panel shows the percentage change of each mass fragment between these two phases. Under high-NO_x conditions, changes in mass fractions of different fragments during aerosol growth are minimal, indicating that the aerosol composition is not changing significantly over time. Under low-NO_x conditions, however, the mass fraction of *m/z* 44 (corresponding to the CO₂⁺ ion, indicative of highly oxidized organics) increases by 93% during the reaction, while those for higher mass to charge ratios are observed to decrease. The mass fractions of *m/z* 44 and higher mass to charge ratios continue to change even after the aerosol growth levels off, suggesting the presence of further chemistry (either gas-phase or particle-phase) even after all the initial hydrocarbon is consumed.

4.2 Offline chemical analysis

All ions detected by the UPLC/ESI-TOFMS instrument from α -pinene and longifolene photooxidation are listed in Tables 6 and 7, respectively. The tables list the exact masses and their likely molecular formulas corresponding to each of the [M-H]⁻ ions detected (in which M is the molecular weight of the compound). The error between the measured mass and theoretical mass is reported in two different ways, ppm and mDa.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

For most of the ions observed, the error between the measured and theoretical masses is less than ± 2 mDa and ± 5 ppm, allowing for generally unambiguous identification of molecular formulae. Solvent blanks and control filters are also run on the UPLC/ESI-TOFMS instrument; none of the listed ions is observed in these control samples. The ions listed in Tables 6 and 7 are also detected by HPLC/ESI-MS and ESI-ITMS, confirming that these compounds are not the result of artifact formation in a specific mass spectrometer.

Acidic compounds, such as carboxylic acids and sulfate esters, readily ionize under ($-$)ESI-MS techniques (Gao et al., 2004; Surratt et al., 2006; Surratt et al., 2007). Hydroxylated compounds, as well as ketones and aldehydes, however, are generally not ionizable unless carboxylic acid and/or sulfate ester moieties are also present within the same molecule. Therefore, it is expected that all ions listed in Tables 6 and 7 are acidic compounds. For the SOA formed in the presence of NO_x (HONO and “ $\text{H}_2\text{O}_2 + \text{NO}$ ” experiments), even-mass $[\text{M} - \text{H}]^-$ ions are observed in ESI mass spectra, indicating the compound has an odd number of nitrogen atoms, likely within organic nitrate functional groups. Nitrated organics were previously observed in isoprene SOA formed under high- NO_x conditions (both HONO and $\text{H}_2\text{O}_2/\text{NO}$) (Surratt et al., 2006), and are further confirmed by the tandem MS data, which reveals a loss of 63 Da (HNO_3). For α -pinene, only one acidic organic nitrate (m/z 322) is detected in the HONO experiment and none are detected in H_2O_2 and intermediate NO_x experiments. Masses of many ions detected in the α -pinene experiments have been observed in previous laboratory work (Glasius et al., 1999, 2000; Larsen et al., 2001) and field studies (Gao et al., 2006). For longifolene, a much wider array of acidic organic nitrates is detected by the UPLC/ESI-TOFMS instrument in both HONO and intermediate NO_x experiments.

Figure 10 shows the extracted ion chromatograms (EICs) of m/z 346, 374, and 390 from longifolene oxidation under different NO_x conditions. These m/z values correspond to acidic organic nitrates, as confirmed by the exact mass data (Table 7) as well as the loss of 63 Da in the tandem MS data. The chromatographic peaks are much larger in the highest NO_x experiment than those in the intermediate NO_x experiment

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

(except m/z 372, not shown); no chromatographic peaks are observed under low- NO_x (H_2O_2) conditions. In addition, for several $[\text{M}-\text{H}]^-$ ions (e.g. m/z 374 and 390) there are several structural isomers present. Additionally, the intensity of non-nitrogen-containing ions (e.g. m/z 223, 239, 253, 255, 267, 269, and 283), are generally larger under low- NO_x conditions.

5 Discussion

5.1 Effect of hydrocarbon size on NO_x dependence

It has been established that NO_x levels exert a major influence on SOA formation (Hatakeyama et al., 1991; Pandis et al., 1991; Zhang et al., 1992, 2006; Hurley et al., 2001; Johnson et al., 2004, 2005; Song et al., 2005; Presto et al., 2005; Kroll et al., 2005, 2006; Ng et al., 2007). For photooxidation of isoprene, SOA yields increase as the NO_x level decreases (Kroll et al., 2006). The proposed mechanism for this observed NO_x dependence is the competitive chemistry of organic peroxy radicals between NO and HO_2 , in which the semivolatile products formed via the RO_2+HO_2 path are less volatile than those formed via the RO_2+NO route (Hatakeyama et al., 1991; Johnson et al., 2004, 2005; Presto et al., 2005; Kroll et al., 2006; Zhang et al., 2006; Ng et al., 2007). A similar yield dependence on NO_x is observed here for photooxidation of α -pinene (Fig. 1). For an initial α -pinene concentration of ~ 15 ppb, the SOA yield under low- NO_x conditions is about a factor of 3 higher than that under high- NO_x conditions. The observed NO_x dependence is consistent with that of previous studies on α -pinene photooxidation (Hatakeyama et al., 1991) and α -pinene ozonolysis (Presto et al., 2005).

The observed NO_x dependence of SOA yield for the sesquiterpenes, however, is different from that of isoprene and α -pinene (as well as other hydrocarbons with 10 or fewer carbons, such as aromatic species). For longifolene and aromadendrene, aerosol yield increases with increasing NO_x concentration (Figs. 2–5). This reversal of

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

the NO_x dependence of SOA formation could be the result of a number of factors. Figure 11 shows a simplified reaction mechanism involving peroxy radical chemistry. At the two limiting NO_x conditions of this study, the peroxy radical chemistry is relatively well-defined; under high- NO_x conditions, peroxy radicals react virtually entirely with NO , while under low- NO_x conditions, RO_2 reacts predominantly with HO_2 . One of the possible explanations for the higher SOA yield under high- NO_x conditions is the formation of large alkoxy radicals that isomerize rather than fragment. Isomerization is plausible if the alkoxy radical has four or more carbon atoms and can form a 6-membered transition state (Baldwin et al., 1977; Carter and Atkinson, 1985). The isomerization pathway leads to the formation of large hydroxycarbonyls, multifunctional products that are likely low in volatility. The relative importance of isomerization increases with the size of alkoxy radicals (Atkinson, 1994, 1997a, b; Atkinson et al., 1995, 1999), and larger compounds could exhibit increasing SOA yields under high- NO_x conditions as a consequence of this mechanism. For example, Lim and Ziemann (2005) measured SOA yields up to ~50% for C_{15} alkanes in the presence of ppm levels of NO_x . They proposed multiple isomerization steps leading to the formation of multifunctional compounds including nitrooxy, hydroxyl, and carbonyl groups, and it is suggested that the hydroxycarbonyls formed may isomerize to form furan species that can undergo further reactions (Lim and Ziemann, 2005). Gas-phase products that are consistent with the isomerization mechanism have been observed in α -pinene photooxidation but this pathway does not appear to dominate SOA formation under high- NO_x conditions (Aschmann et al., 1998, 2002), possibly due to the higher volatility of these species.

Higher SOA yields observed under high- NO_x conditions for sesquiterpenes may, secondly, be a result of the formation of relatively nonvolatile organic nitrates, evidence for which appears in both Q-AMS data and filter sample data. In AMS data, m/z 30 (NO^+) and m/z 46 (NO_2^+) signals are commonly associated with nitrate species (organic and inorganic nitrates). For both α -pinene and longifolene, the ratio of the sum of the intensities of ions at m/z 30 and m/z 46 to the total ion intensity is higher under high- NO_x conditions: under low- NO_x conditions, the ratio is very small (2%), under

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

high- NO_x conditions, the ratio is about 15–25%. The ratio of m/z 30 to total mass and the ratio of m/z 46 to total mass show the same trend, indicating m/z 30 and m/z 46 are correlated. It is possible that the signal at m/z 30 could be the result of a non-nitrogen containing organic fragment ion; however, given the observed correlation between m/z 30 and m/z 46 and their small signals under low- NO_x conditions, it appears that there is little interference from organics at these signals. Under high- NO_x conditions, $\sim 10 \mu\text{gm}^{-3}$ of inorganic nitrates, as measured by the PILS/IC, are present in the aerosol. Such nitrates may arise from the partitioning or reactive uptake of gas-phase HNO_3 into the aerosol phase. Assuming no non-nitrate contribution to m/z 30 and m/z 46, the total nitrate content of the SOA is estimated as the sum of the signals at each fragment. It is found that the calculated nitrate content ($\sim 20 \mu\text{gm}^{-3}$) exceeds that measured by PILS/IC, suggesting the presence of organic nitrates.

The filter sample data provide a more direct comparison on the amount of organic nitrates formed in α -pinene and longifolene photooxidation under different NO_x conditions. For both α -pinene and longifolene, no acidic nitrates are observed under low- NO_x conditions, consistent with the lack of NO_x and the prevailing $\text{RO}_2 + \text{HO}_2$ reaction in this case. Organic nitrate yield from the $\text{RO}_2 + \text{NO}$ reaction increases with increasing carbon number (Atkinson et al., 1987; Carter and Atkinson, 1989; O'Brien et al., 1998; Arey et al., 2001; Aschmann et al., 2001; Zhang et al., 2004), and with the larger carbon skeleton the organic nitrates formed will be less volatile, this is consistent with the much wider array and larger quantities of acidic nitrates detected in longifolene photooxidation under high- NO_x conditions compared to the α -pinene experiments. Hence for photooxidation of larger compounds such as sesquiterpenes, the nitrate formation channel may play an important role in SOA formation under high- NO_x conditions. With the formation of large molecular weight compounds with nitrate groups, mass-based SOA yields from longifolene photooxidation under high- NO_x conditions actually exceed 100%.

Lacking appropriate analytical techniques for the detection of non-acidic nitrates, the contribution of these species under high- NO_x conditions cannot be assessed. In α -

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

pinene photooxidation, hydroxynitrates have been identified in the gas phase using mass spectrometry (Aschmann et al., 1998, 2002). In SOA formation from alkanes under high- NO_x conditions, Lim and Ziemann (2005) found that, while SOA from oxidation of C_{10} alkane contains no δ -hydroxynitrates, nitrates contribute ~40% of the SOA mass for reactions of the C_{15} alkane. It seems likely that higher levels of hydroxynitrates are present in longifolene SOA than in α -pinene SOA.

5.2 General mechanisms of aerosol growth

5.2.1 Loss of semivolatiles

Substantial insight into the general mechanism of SOA formation and growth kinetics can be gained by examining “growth curves”, showing the amount of SOA formed per hydrocarbon reacted (Ng et al., 2006, 2007). Figure 2 shows the time-dependent growth curves from longifolene photooxidation under high- and low- NO_x conditions. The high- NO_x growth curves have a “convex” shape, indicating that aerosol growth slows down as longifolene approaches complete reaction. Similar behavior for longifolene growth was observed previously in our laboratory (Ng et al., 2006); the authors suggested that this atypical growth behavior may have been spurious, as a result of inaccuracies in PTR-MS measurements, owing to interference from product ions, or changes in the aerosol density over the course of the experiment. In this study, in those experiments in which the longifolene concentration is monitored by both GC-FID and PTR-MS, the shape of PTR-MS hydrocarbon decay agrees with that measured by GC-FID. The density of the aerosol is estimated during oxidation by comparing Q-AMS and DMA data. It is found that the SOA density decreases slightly (<5%) over the course of the experiment, however, such a small decrease in density is within experimental uncertainty and cannot account for the observed atypical growth behavior.

Deceleration in SOA growth can arise from the loss of semivolatiles by photolysis, further reaction with OH to form volatile products, or irreversible loss to chamber walls. Such processes reduce the amount of gas-phase semivolatiles species that partition

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

into the aerosol phase. The effect on SOA growth of gas-phase reaction forming more volatile species has been examined in a recent modeling study (Chan et al., 2007). Figure 12 shows a kinetic scheme depicting the competition between gas-particle partitioning and irreversible loss of the gas-phase semivolatiles. X represents the product of generic loss of semivolatile species A_g ; k'_{OH} is the pseudo-first-order rate constant ($k'_{OH} = k_{OH}[OH]$) for reaction of the parent hydrocarbon; and k_g is the first-order rate constant of loss of semivolatiles. When fitting the observed aerosol growth with this simple kinetic model, it is estimated that k_g is about 5 times larger than k'_{OH} . At the estimated OH concentration of $\sim 2 \times 10^7$ molecules cm^{-3} under high- NO_x conditions, k'_{OH} for longifolene is $\sim 9.6 \times 10^{-4} \text{ s}^{-1}$. A major difference in SOA composition under high- and low- NO_x conditions is the presence of organic nitrates under high- NO_x conditions. Thus the loss of organic nitrates (among other gas-phase species) may play a role in the observed deceleration in aerosol growth. The reaction rate constants of small alkyl nitrates with OH are generally of the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (hence pseudo-first-order reaction rate of $\sim 10^{-6} \text{ s}^{-1}$) and their photolysis rates have been measured to be $\sim 1 \times 10^{-6} \text{ s}^{-1}$ (Talukdar et al., 1997; Finlayson-Pitts and Pitts, 2000). Although the OH reaction rate and photolysis rate of organic nitrates are much slower than the oxidation rate of longifolene, both rates are expected to increase with carbon number (Talukdar et al., 1997; Finlayson-Pitts and Pitts, 2000; Treves and Rudich, 2003). Hence, it is possible that gas-phase reaction of C_{15} organic nitrates may be occurring at an appreciable rate. Further study on the OH reaction rate constant and photolysis rate of larger nitrates would be useful in evaluating the importance of gas-phase nitrate chemistry in aerosol formation.

Such a deceleration in SOA growth is not observed in longifolene low- NO_x experiments. This is in contrast to the rapid decrease in aerosol volume observed in isoprene photooxidation under low- NO_x conditions, in which photolysis and/or further reactions of organic hydroperoxides may be occurring (Kroll et al., 2006). There is evidence for further reactions with longifolene low- NO_x SOA as well: the AMS m/z 44 (CO_2^+) mass fraction increases over the course of the experiment (Fig. 9), indicating the SOA is

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

being further oxidized. Unlike with isoprene photooxidation, however, the compounds formed from the further oxidation of longifolene products are likely sufficiently non-volatile to remain in the particle phase. The photochemistry of larger and more complex hydroperoxides merits further investigation.

5 5.2.2 SOA formation from higher generation products

In Figs. 1 and 3, the growth curves of α -pinene and longifolene photooxidation exhibit a “hook” at the end of the intermediate NO_x experiments, indicating that aerosol growth continues after the complete consumption of the parent hydrocarbon. Organic mass measured by the Q-AMS increases even after all the hydrocarbon is consumed, indicating that this additional aerosol growth is not a result of condensation of inorganic nitrate. Continued aerosol growth can arise from further gas-phase reactions of reactive oxidation products, such as aldehydes and furans, etc, or from further particle-phase reactions. In the intermediate NO_x experiments, the NO concentration goes to zero about 30 min after the commencement of photooxidation, owing to the rapid reaction of NO and peroxy radicals (HO_2 and other peroxy radicals). As a result, a transition from high- NO_x to low- NO_x conditions occurs over the course of the experiment, and the final aerosol formed is potentially a mixture of the products formed under both conditions. It is possible that particle-phase reactions, such as the formation of peroxyhemiacetals from hydroperoxides and aldehyde species, may be contributing to the further aerosol growth observed in the intermediate NO_x experiments (Johnson et al., 2004, 2005).

6 Implications

A series of chamber experiments investigating the NO_x dependence of SOA formation from the photooxidation of one monoterpene and two sesquiterpenes is reported here. SOA formation from monoterpenes such as α -pinene is found to have a similar NO_x dependence as isoprene (as well as other hydrocarbons with 10 or fewer carbons, such

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

as aromatic species), in which the aerosol yields are substantially higher under low- NO_x conditions. The NO_x dependence of SOA formation from the two sesquiterpenes is, however, markedly different; for longifolene and aromadendrene, aerosol yields are at their maximum under high- NO_x conditions. The reason for this reversal of the NO_x dependence, while not unequivocally established here, may be the result of production of highly nonvolatile organic nitrates, the existence of which is suggested by both Q-AMS and filter sample data, and/or isomerization of alkoxy radicals to form low-volatility multifunctional organics.

The increase in SOA yield from photooxidation of the larger biogenic hydrocarbons under high- NO_x conditions could have implications in terms of the effect of anthropogenically influenced air masses on biogenic SOA formation. In the recent study of de Gouw et al. (2005), it is suggested that over the western Atlantic the majority of the measured organic aerosol is from secondary anthropogenic sources, a conclusion that is somewhat at odds with the radiocarbon measurements that indicate high fractions of “modern” (presumably biogenic) carbon (e.g. Klinedinst and Currie, 1999; Weber et al., 2007). If the production of SOA from biogenic hydrocarbons is enhanced in the presence of NO_x , observations of enhanced SOA correlated with anthropogenic sources can occur, even for organic carbon of biogenic origin. Large anthropogenic hydrocarbons may exhibit a similar NO_x behavior as that of the sesquiterpenes studied, as suggested by the substantial SOA yields from the OH-initiated reaction of large alkanes in the presence of ppm levels of NO_x (Lim and Ziemann, 2005). If the NO_x behavior observed for longifolene and aromadendrene extends to other sesquiterpenes as well as larger alkanes, the contribution to the total SOA from these compounds in polluted air may actually be higher than previously estimated (Griffin et al., 1999a, b; Carreras-Sospedra et al., 2005; de Gouw et al., 2005).

In this study, we have investigated the NO_x dependence of SOA formation from photooxidation of only the monoterpene α -pinene and two sesquiterpenes, each containing one double bond. SOA formation from compounds with two or more double bonds can exhibit characteristics that suggest significant contributions from multiple generation

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

products (Ng et al., 2006) and this may have impacts on the NO_x dependence. It is clear that the effect of NO_x on SOA yields from the complete suite of atmospherically relevant aerosol-forming hydrocarbons should be evaluated thoroughly.

Appendix A

5

Description of PTR-MS technique

For PTR-MS sampling, a constant flow of ~2.5 standard liters per minute (slm) is drawn from the chamber through PFA tubing. The residence time in the inlet tubing is roughly 1 s. A small portion of the flow, 93 standard cubic centimeters per minute (sccm), is

10 pulled through a glass critical orifice into a 2.54-cm diameter glass flow tube, in which this sample flow is diluted with dry N₂ (1.6 slm) to maintain the flow tube pressure at 35 mbar. This dilution minimizes confounding effects owing to large concentrations 15 of hydrogen peroxide and other compounds typically used or produced in chamber experiments.

In the flow tube, analyte ionization occurs in a manner similar to that described by Crounse et al. (2006) for negative ionization. N₂ (400 sccm) flows through an ion source cup composed of a cylindrical silver foil lined with ²¹⁰Po and sealed with gold. α bombardment from the ²¹⁰Po, coupled with trace water present in the N₂, leads to the formation of positively charged clusters, e.g. (H₂O)_nH⁺. The electric potentials of the 20 ion source components are set such that these positively charged clusters then pass through a 6.35 mm aperture into the 35 mbar flow tube, flowing perpendicular to the sample flow. The clusters then react via proton transfer with the analyte (e.g. aromadendrene) in the sample flow to form aromadendrene-H⁺ and higher order water clusters.

25 Across the flow tube from the ion source, a pinhole aperture (diameter 0.34 mm) allows a portion of the ions and neutral gas (~30 sccm) to flow into the mass spectrometer, a Varian 1200 tandem mass spectrometer. The spectrometer was modified by

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

removing the electron impact source and extending the hexapole ion guide that leads to the quadrupole mass analyzer to the pinhole aperture. For these measurements, the mass spectrometer was operated exclusively in one-dimensional mass spectrometry mode.

- 5 In order to simplify the mass spectra, a DC potential of -10 V (relative to the pinhole aperture) is applied to the hexapole. This offset pulls ions into the hexapole, where the pressure is relatively high owing to the neutral gas flow (chiefly N_2) through the pinhole. The ions therefore undergo high energy collisions with the neutral gas molecules which dissociate water clusters of analyte A:



Thus, species are predominantly observed at $m/z = M+1$, where M is the molecular mass of the species. Hydrates, $A \cdot (\text{H}_2\text{O})_m \cdot \text{H}^+$, particularly $m=1$, are also observed for some species, though not for aromadendrene or longifolene.

- 15 Each day, the PTR-MS sensitivity towards aromadendrene was determined by sampling standard mixtures of aromandendrene in teflon bags filled with 50 L zero air. The sensitivity was determined to be linear from 0 ppb to at least 5 ppb. Also, because of the large amounts of H_2O_2 utilized in the experiments, the sensitivity as a function of H_2O_2 was determined, with $[\text{H}_2\text{O}_2]$ measured by operating the Varian 1200 in negative ionization mode, exploiting the reaction of CF_3O^- with H_2O_2 (Crounse et al., 2006).
20 Thus, the sensitivity determined from H_2O_2 -free standards was corrected for sampling from the chamber when H_2O_2 was present.

The uncertainty of aromadendrene measurements using PTR-MS is estimated to be $\sim \pm 22\%$, based on the scatter of replicate data and background measurements and uncertainties in the H_2O_2 correction.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Description of UPLC/ESI-TOFMS technique

7, 10131–10177, 2007

Filter extracts (in 1:1 (v/v) solvent mixture of methanol and 0.1% aqueous acetic acid solution) are analyzed by a Waters ACQUITY ultra performance liquid chromatography (UPLC) system, coupled with a Waters LCT Premier time-of-flight (TOF) mass spectrometer (MS) equipped with an electrospray ionization (ESI) source. The ESI source on this instrument contains two individual sprays; one spray is for the eluent and the other is for the lock-mass correction. Optimum ESI conditions are found using a 2.5 kV capillary voltage, 40 V sample cone voltage, 350°C desolvation temperature, 130°C source temperature, 20 L h⁻¹ cone gas flow rate, and a 650 L h⁻¹ desolvation gas flow rate. Data are collected from *m/z* 50–1000 in the negative (–) ionization mode using the TOFMS operated in the W geometry reflectron mode. The W reflectron mode offers the highest mass resolution, which is approximately 12 000, and allows for exact mass measurements to be conducted on detected SOA components. The chromatographic separations are carried out on a Waters ACQUITY HPLC HSS (high strength silica) column (2.1 × 100 mm, 1.8 µm particle size) at 45°C using a gradient elution scheme. The eluent composition is (A) 0.1% acetic acid in water and (B) 0.1% acetic acid in methanol; both eluents are high purity solvents (LC-MS ChromaSolv Grade, Sigma-Aldrich). In the 12-min gradient elution program used, the concentration of eluent B is 0% for the first 2 min, increased to 90% from 2 to 10 min, held at 90% from 10 to 10.2 min; and then decreased back to 0% from 10.2 to 12 min. The flow rate of the eluent is 0.3 mL min⁻¹ and the sample injection volume is 2 µL. At the beginning of each analysis period, the TOFMS is calibrated using a 1:1 (v/v) solvent mixture of acetonitrile and 0.1% phosphoric acid aqueous solution. During each chromatographic run, 2 ng/µL of leucine enkphalin (MW=555) is used for the lock-mass spray for lock-mass correction to obtain accurate masses for each SOA component eluting from the column. The lock-mass syringe pump is operated at 20 uL min⁻¹. In addition to the

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

lock-mass spray, the dynamic range enhancement feature of this mass spectrometer is applied to prevent dead time, which affects mass accuracy, from occurring. As confirmation of the UPLC/ESI-TOFMS technique, a standard sample containing known isoprene and α -pinene sulfate esters previously characterized by Surratt et al. (2007) are analyzed. The known elemental compositions (i.e. molecular formulas) of the previously characterized sulfate esters (Surratt et al., 2007) are in excellent agreement with their measured exact masses (i.e. within ± 2 mDa or ± 2 ppm). In addition to exact mass measurements, further insights into the structures of the SOA components are obtained by generating tandem MS data, which are generated by increasing the first aperature voltage on the TOFMS from 10 V to 25 V.

Acknowledgements. This research was funded by U.S. Department of Energy Biological and Environmental Research Program grant DE-FG02-05ER63983. This material is based in part on work supported by the National Science Foundation (NSF) under grant ATM-0432377. The Waters LCT Premier XT time-of-flight mass spectrometer interfaced to a Waters UPLC system was purchased in 2006 with a grant from the National Science Foundation, Chemistry Research Instrumentation and Facilities Program (CHE-0541745). The LCQ Ion Trap mass spectrometer was purchased in 1997 with funds from the National Science Foundation through the CRIF program (CHE-9709233). J. D. Surratt is supported in part by the U.S. EPA under the STAR Graduate Fellowship Program. A. J. Kwan acknowledges the support of a NSF graduate research fellowship. The authors would like to thank M. Shahgholi of the Chemistry Department at Caltech for her useful communications regarding high-resolution mass spectrometry.

References

- Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prevot, A. S. H., Worsnop, D. R., Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the photooxidation of anthropogenic and biogenic precursors in a reaction chamber, *Atmos. Chem. Phys.*, 6, 5279–5293, 2006,
<http://www.atmos-chem-phys.net/6/5279/2006/>.

Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrates, hydroxyalkyl nitrates

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

- and hydroxycarbonyl formation from the NO_x – air photooxidation of C₅-C₈ n-alkanes, J. Phys. Chem. A, 105, 1020–1027, 2001.
- Aschmann, S. M., Arey, J., and Atkinson, R.: Atmospheric chemistry of three C₁₀ alkanes, J. Phys. Chem. A, 105, 7598–7606, 2001.
- 5 Aschmann, S. M., Atkinson, R., and Arey, J.: Products of reaction of OH radicals with α -pinene, J. Geophys. Res., 107(D14), 4191, doi:10.1029/2001JD001098, 2002.
- Aschmann, S. M., Reissell, A., Atkinson, R., and Arey, J.: Products of the gas phase reactions of the OH radical with α - and β -pinene in the presence of NO, J. Geophys. Res., 103(D19), 4191, 25 553–25 561, 1998.
- 10 Aschmann, S. M., Reissell, A., Atkinson, R., and Arey, J.: Products of the gas phase reactions of the OH radical with a- and b-pinene in the presence of NO, J. Geophys. Res., 103(D19), 25 553–25 561, 1998.
- Atkinson, R., Kwok, E. S. C., Arey, J., and Aschmann, S. M.: Reactions of alkoxy radicals in the atmosphere, Faraday Discuss., 100, 23–37, 1995.
- 15 Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, S197-S219, 2003.
- Atkinson, R., Aschmann, S. M., and Winer, A. M.: Alkyl nitrate formation from the reaction of a series of branched RO₂ radicals with NO as a function of temperature and pressure, J. Phys. Chem., 5, 91–102, 1987.
- 20 Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry, organic species, supplement VII, J. Phys. Chem. Ref. Data., 28, 2, 1999.
- Atkinson, R.: Atmospheric reactions of alkoxy and β -hydroxyalkoxy radicals, Int. J. Chem. Kinet., 29, 99–111, 1997a.
- 25 Atkinson, R.: Gas phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monogr., 2, 11–216, 1994.
- Atkinson, R.: Gas phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and Alkenes, J. Phys. Chem. Ref. Data., 215–290, 1997b.
- Baldwin, A. C., Barker, J. R., Golden, D. M., and Hendry, D. G.: Photochemical smog – rate 30 parameter estimates and computer simulations, J. Phys. Chem., 81, 2483–2492, 1977.
- Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., and Seinfeld, J. H.: Measurements of secondary organic aerosol (SOA) from oxidation of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer, Environ. Sci. Tech-

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

- nol., 39, 5674–5688, 2005.
- Carreras-Sospedra, M., Griffin, R. J., and Dabdub, D.: Calculations of incremental secondary organic aerosol reactivity, *Environ. Sci. Technol.*, 39, 1724–1730, 2005.
- Carter, W. P. L. and Atkinson, R.: Alkyl nitrate formation from the atmospheric photooxidation of alkanes; a revised estimation, *J. Phys. Chem.*, 8, 165–173, 1989.
- Carter, W. P. L. and Atkinson, R.: Atmospheric chemistry of alkanes, *J. Atmos. Chem.* 3, 377–405, 1985.
- Chan, A. W. H., Kroll, J. H., Ng, N. L., and Seinfeld, J. H.: Kinetic modeling of secondary organic aerosol formation: effect of particle- and gas-phase reactions of semivolatile products, *Atmos. Chem. Phys. Discuss.*, 7, 7051–7085, 2007,
<http://www.atmos-chem-phys-discuss.net/7/7051/2007/>.
- Cocker III, D. R., Flagan, R. C., and Seinfeld, J. H.: State-of-the-art chamber facility for studying atmospheric aerosol chemistry, *Environ. Sci. Technol.*, 35, 2594–2601, 2001.
- Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurements of gas-phase hydroperoxides by chemical ionization mass spectrometry, *Anal. Chem.*, 78, 6726–6732, 2006.
- de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.*, 110, D16305, doi:10.1029/2004JD005623, 2005.
- Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower atmosphere: theory, experiments and applications, Academic Press, San Diego, 220–221, 2000.
- Gao, S., Keywood, M. D., Ng, N. L., Surratt, J. D., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Low-molecular weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α -pinene, *J. Phys. Chem. A*, 108, 10 147–10 164, 2004.
- Gao, S., Surratt, J. D., Knipping, E. M., Edgerton, E. S., Shahgholi, M., and Seinfeld, J. H.: Characterization of polar organic components in fine aerosols in the southeastern United States: Identity, origin, and evolution, *J. Geophys. Res.*, 111, D14314, doi:10.1029/2005JD006601, 2006.
- Geron, C., Rasmussen, R., Arnts, R. R., and Guenther, A.: A review and synthesis of monoterpene speciation from forests in the United States, *Atmos. Environ.*, 34, 1761–1781, 2000.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀◀	▶▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Glasius, M., Duane, M., and Larsen, B. R.: Determination of polar terpene oxidation products in aerosols by liquid chromatography-ion trap mass spectrometry, *J. Chrom. A.*, 833, 121–135, 1999.

5 Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., and Larsen, B. R.: Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, *Environ. Sci. Technol.*, 34, 1001–1010, 2000.

Griffin, R. J., Cocker, D. R., Flagan, R. C., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol formation from the oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 17, 2721–2724, 1999a.

10 Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104(D3), 3555–3567, 1999b.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, T., and Zimmerman, P.: A global model of natural volatile organic compound emission, *J. Geophys. Res.*, 100,(D5), 8873–8892, 1995.

Hatakeyama, S., Izumi, K., Fukuyama, T., Akimoto, H., and Washida, N.: Reactions of OH with α -pinene and β -pinene in air: Estimates of global CO production from the atmospheric oxidation of terpenes, *J. Geophys. Res.*, 96(D1), 947–958, 1991.

20 Hurley, M. D., Sokolov, O., Wallington, T. J., Takekawa, H., Karasawa, M., Klotz, B., Barnes, I., and Becker, K. H.: Organic aerosol formation during the atmospheric degradation of toluene, *Environ. Sci. Technol.*, 35, 1358–1366, 2001.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. W.: Development of an Aerosol Mass Spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Technol.*, 33, 49–70, 2000.

25 Johnson, D., Jenkin, M. E., Wirtz, K., and Martín-Reviejo, M.: Simulating the formation of secondary organic aerosol from the photooxidation of aromatic hydrocarbons, *Environ. Chem.*, 2, 35–48, 2005.

Johnson, D., Jenkin, M. E., Wirtz, K., and Martín-Reviejo, M.: Simulating the formation of secondary organic aerosol from the photooxidation of toluene, *Environ. Chem.*, 1, 150–165, 2004.

30 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Everns, B., Nenes, A., Swietlicki, E., Pautaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E.,

Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modeling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005,
<http://www.atmos-chem-phys.net/5/1053/2005/>.

Keywood, M. D., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds, *Environ. Sci. Technol.*, 38, 4157–4164, 2004.

Klinedinst, D. B. and Currie, L. A.: Direct quantification of PM_{2.5} fossil and biomass carbon within the northern front range air quality study's domain, *Environ. Sci. Technol.*, 33, 4146–4154, 1999.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, *J. Geophys. Res.*, 110, L18808, doi:10.1029/2005GL023637, 2005.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.

Larsen, B. R., Di Bellla, D., Glasius, M., Winterhalter, R., Jensen, N. R., and Hjorth, J.: Gas-phase OH oxidation of monoterpenes: Gaseous and particulate products, *J. Atmos. Chem.*, 38, 231–276, 2001.

Lim, Y. B. and Ziemann, P. J.: Products and mechanism of secondary organic aerosol formation from reactions of *n*-alkanes with OH radicals in the presence of NO_x, *Environ. Sci. Technol.*, 39, 9229–9236, 2005.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, *Environ. Sci. Technol.*, 40, 2283–2297, 2006.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, *Atmos. Chem. Phys. Discuss.*, 7, 4085–4126, 2007,
<http://www.atmos-chem-phys-discuss.net/7/4085/2007/>.

O'Brien, J. M., Czuba, E., Hastie, D. R., Francisco, J. S., and Shepson, P. B.: Determination of the hydroxy nitrate yields from the reaction of C₂–C₆ alkenes with OH in the presence of NO, *J. Phys. Chem.*, 102, 8903–8908, 1998.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.:

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Gas/particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol., 30, 2580–2585, 1996.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Aromatics, reformulated gasoline and atmospheric organic aerosol formation, Environ. Sci. Technol., 31, 1890–1897, 1997.

Owen, S. M., Boissard, C., and Hewitt, C. N.: Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale, Atmos. Environ., 35, 5393–5409, 2001.

Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C.: Aerosol formation in the photooxidation of isoprene and β -pinene, Atmos. Environ., 25A, 997–1008, 1991.

Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary organic aerosol production from ozonolysis: 2. Effect of NO_x concentration, Environ. Sci. Technol., 39, 7046–7054, 2005.

Seinfeld, J. and Pankow, J. F.: Organic atmospheric particulate material, Annu. Rev. Phys. Chem., 54, 121–140, 2003.

Song, C., Na, K., and Cocker III, D. R.: Impact of the hydrocarbon to NO_x ratio on secondary organic aerosol formation, Environ. Sci. Technol., 39, 3143–3149, 2005.

Sorooshian, A., Brechtel F. J., Ma, Y. L., Weber R. J., Corless, A., Flagan, R. C., and Seinfeld, J. H.: Modeling and characterization of a particle-into-liquid sampler (PILS), Aerosol Sci. Technol., 40, 396–409, 2006.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517–527, 2007.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmiigelski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Atmos. Chem., 31, 9665–9690, 2006.

Szmiigelski, R., Surratt, J. D., Vermeylen, R., Szmiigelska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry, J. Mass Spectrom., 42, 101–116, 2007.

Talukdar, R. K., Herndon, S. C., Burkholder, J. B., Roberts, J. M., and Ravishankara, A. R.:

- Atmospheric fate of several alkyl nitrates, J. Chem. Soc., Faraday Trans., 93, 2787–2796, 1997.
- Treves, K. and Rudich, Y.: The atmospheric fate of C₃-C₆hydroxyalkyl nitrates, J. Phys. Chem. A, 107, 7809–7817, 2003.
- 5 Weber, R. J., Sullivan, A., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern USA, J. Geophys. Res., 112, D13302, doi:10.1029/2007JD008408, 2007.
- Zhang, J., Dransfield, T., and Donahue, N. M.: On the mechanism for nitrate formation via the peroxy radical + NO reaction, J. Phys. Chem. A, 108, 9082–9095, 2004.
- 10 Zhang, J., Hartz, K. E. H., Pandis, S. N., and Dohmane, N. M.: Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NO_x, J. Phys. Chem., A, 110, 11 053–11 063, 2006.
- Zhang, S. H., Shaw, M., Seinfeld, J. H., and Flagan, R. C.: Photochemical aerosol formation 15 from α -pinene and β -pinene, J. Geophys. Res., 97(D18), 20 717–20 729, 1992.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

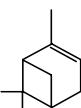
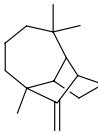
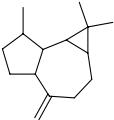
[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Table 1. Parent hydrocarbons used in this study.

Parent Hydrocarbon	Structure	Formula (MW)	k_{OH} (cm ³ molec ⁻¹ s ⁻¹)
α -pinene		C ₁₀ H ₁₆ (136)	5.3 × 10 ⁻¹¹ ^a
longifolene		C ₁₅ H ₂₄ (204)	4.8 × 10 ⁻¹¹ ^a
aromadendrene		C ₁₅ H ₂₄ (204)	1.5 × 10 ⁻¹⁰ ^b

^a Rate constants were obtained from Atkinson et al. (2003).

^b Rate constant was estimated from the rate of aromadendrene decay (experiment 1 in Table 4), assuming an OH concentration of 3×10⁶ molecule cm⁻³ and that aromadendrene reacts with OH only.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

Table 2. Initial conditions and results for α -pinene experiments.

Expt. No.	NO _x Condition	NO (ppb)	NO ₂ (ppb)	T (K)	RH (%)	ΔHC (ppb) ^a	ΔM_o ($\mu\text{g}/\text{m}^3$) ^b	SOA Yield (%) ^c
1	H ₂ O ₂	0	0	298	5.3	13.8±0.2	29.3±2.4	37.9±3.2
2	H ₂ O ₂	0	1	298	6.2	47.5±0.8	121.3±9.4	45.8±3.6
3	H ₂ O ₂ +NO	198	0	296	6.4	13.1±0.2	15.6±1.4	21.2±2.0
4	HONO	475	463	299	3.3	12.6±0.2	4.5±0.9	6.6±1.4
5	HONO	390	578	298	3.7	46.6±0.8	40.8±3.8	15.8±1.5

^a Stated uncertainties (1σ) include scatter in GC measurements and GC calibration errors.

^b Stated uncertainties (1σ) are from scatter in particle volume measurements.

^c Stated uncertainties are propagated from errors in ΔHC and ΔM_o .

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

Table 3. Initial conditions and results for longifolene experiments.

Expt. No.	NO _x Condition	NO (ppb)	NO ₂ (ppb)	T (K)	RH (%)	ΔHC (ppb) ^b	ΔM _o ($\mu\text{g}/\text{m}^3$) ^c	SOA Yield (%) ^d
1	H ₂ O ₂	0	0	298	5.8	4.5±0.2	28.5±2.4	75.7±7.0
2	H ₂ O ₂	0	2	297	6.0	8.4±0.4	52.5±4.2	74.4±6.7
3	H ₂ O ₂	0	2	297	6.3	19.4±0.8	117.1±9.3	72.1±6.5
4	H ₂ O ₂	0	2	299	5.7	24.8±1.1	148.4±11.6	71.8±6.4
5	H ₂ O ₂ +NO	70	31 ^a	297	6.2	3.8±0.2	35.8±2.9	111.7±10.2
6	H ₂ O ₂ +NO	209	26 ^a	297	8.0	4.7±0.2	43.4±3.5	110.2±10.0
7	H ₂ O ₂ +NO	316	0	298	6.4	4.1±0.2	43.4±3.5	127.2±1.5
8	H ₂ O ₂ +NO	394	0	297	6.1	4.8±0.2	50.0±4.1	124.9±11.5
9	H ₂ O ₂ +NO	564	0	297	6.2	3.9±0.2	51.6±4.1	157.0±14.1
10	HONO	428	550	298	3.7	9.7±0.4	68.3±5.1	84.0±7.1
11	HONO	469	502	298	3.7	19.6±0.9	141.9±10.3	86.8±7.3
12	HONO	394	577	299	3.2	26.6±1.2	213.6±15.3	96.3±8.0

^a NO₂ formed due to NO reacting with residual ozone in the chamber.

^b Stated uncertainties (1σ) include scatter in GC measurements and GC calibration errors.

^c Stated uncertainties (1σ) are from scatter in particle volume measurements.

^d Stated uncertainties are propagated from errors in ΔHC and ΔM_o.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

Table 4. Initial conditions and results for aromadendrene experiments.

Expt. No.	NO _x Condition	NO (ppb)	NO ₂ (ppb)	T (K)	RH (%)	ΔHC (ppb) ^a	ΔM _o (μg/m ³) ^b	SOA Yield (%)
1	H ₂ O ₂	0	0	299	5.5	5.7±1.2	19.7±2.0	41.7±10
2	H ₂ O ₂ +NO	120	0	298	9.3	5.3±1.2	23.1±2.2	52.0±12.4
3	H ₂ O ₂ +NO	195	0	298	7.7	6.0±1.4	29.3±2.6	58.8±14.4
4	H ₂ O ₂ +NO	517	0	299	7.4	3.2±0.7	22.6±2.2	84.7±20.0

^a Stated uncertainties (1σ) include scatter in PTR-MS measurements and PTR-MS calibration errors.

^b Stated uncertainties are derived from scatter in particle volume measurements.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

Table 5. Estimated effective SOA densities.

Parent Hydrocarbon	NO _x Condition	Effective Density (g cm ⁻³) ^a
α -pinene	Low-NO _x	1.32±0.10
α -pinene	Intermediate NO _x	1.32±0.10
α -pinene	High-NO _x	1.33±0.10
longifolene	Low-NO _x	1.29±0.10
longifolene	Intermediate NO _x	1.30±0.10
longifolene	High-NO _x	1.40±0.10
aromadendrene	Low-NO _x	1.20±0.10
aromadendrene	Intermediate NO _x	1.35±0.10

^a Stated uncertainties (1σ) are from repeated measurement of ammonium sulfate seed densities.



Table 6. α -Pinene acidic SOA components detected by UPLC/ESI-TOFMS.

Experiment	Measured [M - H] ⁻ ion (m/z)	TOFMS suggested molecular formula	Error (mDa)	Error (ppm)	Retention Time (min)
H ₂ O ₂	157.0497	C ₇ H ₉ O ₄ ⁻	-0.4	-2.5	5.09
	169.0873	C ₉ H ₁₁ O ₃ ⁻	0.8	4.7	6.89
	171.0654	C ₈ H ₁₁ O ₄ ⁻	-0.3	-1.8	5.61
	183.1027	C ₁₀ H ₁₃ O ₃ ⁻	0.6	3.3	7.50
	185.0821	C ₉ H ₁₃ O ₄ ⁻	0.7	3.8	6.85
	199.0983	C ₁₀ H ₁₃ O ₄ ⁻	1.3	6.5	6.17
	199.0982	C ₁₀ H ₁₃ O ₄ ⁻	1.2	6.0	6.29
	199.0976	C ₁₀ H ₁₃ O ₄ ⁻	0.6	3.0	6.34
	215.0923	C ₁₀ H ₁₃ O ₅ ⁻	0.4	1.9	5.99
	215.0930	C ₁₀ H ₁₃ O ₅ ⁻	1.1	5.1	7.18
H ₂ O ₂ + NO	231.0885	C ₁₀ H ₁₃ O ₆ ⁻	1.6	6.9	6.80
	157.0499	C ₇ H ₉ O ₄ ⁻	-0.2	-1.3	5.08
	171.0655	C ₈ H ₁₁ O ₄ ⁻	-0.2	-1.2	5.60
	183.1025	C ₁₀ H ₁₃ O ₃ ⁻	0.4	2.2	7.49
	185.0812	C ₉ H ₁₃ O ₄ ⁻	-0.2	-1.1	6.86
	197.0814	C ₁₀ H ₁₃ O ₄ ⁻	0.0	0.0	8.09
	199.0971	C ₁₀ H ₁₃ O ₄ ⁻	0.1	0.5	6.36
	203.0557	C ₈ H ₁₁ O ₆ ⁻	0.1	0.5	5.50
	215.0925	C ₁₀ H ₁₃ O ₅ ⁻	0.6	2.8	6.23
	229.0718	C ₁₀ H ₁₃ O ₆ ⁻	0.6	2.6	6.17
HONO	231.0856	C ₁₀ H ₁₃ O ₆ ⁻	-1.3	-5.6	6.79
	171.0649	C ₈ H ₁₁ O ₄ ⁻	-0.8	-4.7	5.60
	183.1022	C ₁₀ H ₁₃ O ₃ ⁻	0.1	0.5	7.49
	185.0457	C ₈ H ₉ O ₅ ⁻	0.7	3.8	6.63
	187.0606	C ₈ H ₁₁ O ₅ ⁻	0.0	0.0	5.65
	197.0819	C ₁₀ H ₁₃ O ₄ ⁻	0.5	2.5	8.09
	203.0546	C ₈ H ₁₁ O ₆ ⁻	-1.0	-4.9	5.50
	213.0781	C ₁₀ H ₁₃ O ₅ ⁻	1.8	8.4	5.26
	231.0883	C ₁₀ H ₁₃ O ₆ ⁻	1.4	6.1	6.80
	259.1182	C ₁₂ H ₁₉ O ₆ ⁻	0.0	0.0	5.85
10164	322.1148	C ₁₂ H ₂₀ NO ₉ ⁻	1.0	3.1	7.62

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 7. Longifolene SOA components detected by UPLC/ESI-TOFMS.

Experiment	Measured [M – H] ⁻ ion (m/z)	TOFMS suggested molecular formula	Error (mDa)	Error (ppm)	Retention Time (min)
H ₂ O ₂	223.1344	C ₁₃ H ₁₉ O ₃ ⁻	1.0	4.5	8.92
	237.1500	C ₁₄ H ₂₁ O ₃ ⁻	0.9	3.8	9.06
	239.1651	C ₁₄ H ₂₃ O ₃ ⁻	0.4	1.7	10.50
	253.1445	C ₁₄ H ₂₁ O ₄ ⁻	0.5	2.0	9.36
	249.1499	C ₁₅ H ₂₁ O ₄ ⁻	0.8	3.2	9.25
	249.1501	C ₁₅ H ₂₁ O ₄ ⁻	1.0	4.0	10.14
	255.1611	C ₁₄ H ₂₃ O ₄ ⁻	1.5	5.9	9.88
	255.1622	C ₁₄ H ₂₃ O ₄ ⁻	2.6	10.2	8.99
	267.1602	C ₁₅ H ₂₃ O ₄ ⁻	0.6	2.2	8.88
	267.1606	C ₁₅ H ₂₃ O ₄ ⁻	1.0	3.7	9.01
	267.1611	C ₁₅ H ₂₃ O ₄ ⁻	1.5	5.6	9.28
	267.1601	C ₁₅ H ₂₃ O ₄ ⁻	0.5	1.9	9.70
	269.1392	C ₁₄ H ₂₁ O ₅ ⁻	0.3	1.1	7.71
H ₂ O ₂ + NO	283.1561	C ₁₅ H ₂₃ O ₅ ⁻	1.6	5.7	7.35
	313.2018	C ₁₇ H ₂₉ O ₅ ⁻	0.3	1.0	9.20
	223.1337	C ₁₃ H ₁₉ O ₃ ⁻	0.3	1.3	8.92
	239.1649	C ₁₄ H ₂₃ O ₃ ⁻	0.2	0.8	10.49
	265.1442	C ₁₅ H ₂₁ O ₄ ⁻	0.2	0.8	8.93
HONO	269.1401	C ₁₄ H ₂₁ O ₅ ⁻	1.2	4.5	7.72
	316.1396	C ₁₄ H ₂₂ NO ₇ ⁻	0.0	0.0	9.88
	329.1972	C ₁₅ H ₂₉ O ₆ ⁻	0.8	2.4	9.35
	372.1664	C ₁₇ H ₂₆ NO ₈ ⁻	0.6	1.6	10.58
	374.1829	C ₁₇ H ₂₅ NO ₈ ⁻	1.4	3.7	9.14
	374.1829	C ₁₇ H ₂₆ NO ₈ ⁻	1.4	3.7	9.35
	390.1775	C ₁₇ H ₂₈ NO ₉ ⁻	1.1	2.8	9.46
	223.1334	C ₁₃ H ₁₉ O ₃ ⁻	-0.1	-0.4	8.92
	241.1453	C ₁₃ H ₂₁ O ₄ ⁻	1.3	5.4	7.55
	253.1431	C ₁₄ H ₂₁ O ₄ ⁻	-0.9	-3.6	8.02
HONO	269.1394	C ₁₄ H ₂₁ O ₅ ⁻	0.5	1.9	7.18
	269.1408	C ₁₄ H ₂₁ O ₅ ⁻	1.9	7.1	7.71
	342.1930	C ₁₇ H ₂₅ NO ₆ ⁻	1.3	3.8	9.65
	344.1348	C ₁₅ H ₂₂ NO ₈ ⁻	0.3	0.9	8.25
	346.1502	C ₁₅ H ₂₃ NO ₈ ⁻	0.2	0.6	8.34
	360.1674	C ₁₆ H ₂₆ NO ₈ ⁻	1.6	4.4	8.89
	372.1667	C ₁₇ H ₂₅ NO ₈ ⁻	-0.6	-1.6	10.61
	374.1809	C ₁₇ H ₂₆ NO ₈ ⁻	-0.6	-1.6	8.89
	374.1816	C ₁₇ H ₂₆ NO ₈ ⁻	0.1	0.3	9.13
	374.1808	C ₁₇ H ₂₅ NO ₈ ⁻	-0.7	-1.9	9.35
	390.1773	C ₁₇ H ₂₆ NO ₉ ⁻	0.9	2.3	8.49
	390.1778	C ₁₇ H ₂₅ NO ₉ ⁻	1.4	3.6	9.21
	435.1619	C ₁₇ H ₂₇ N ₂ O ₁₁ ⁻	0.4	0.9	9.56

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

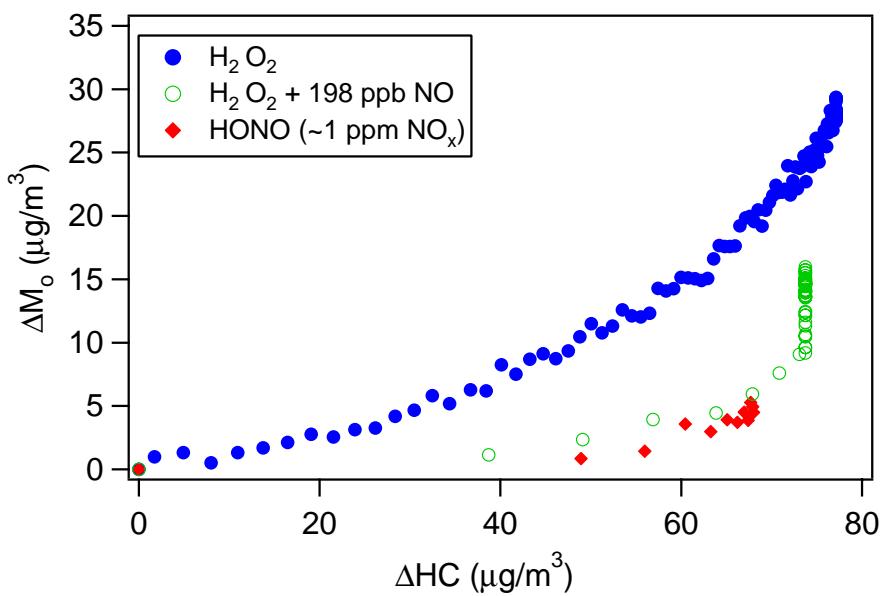


Fig. 1. Time-dependent growth curves for α -pinene photooxidation under different NO_x conditions (Experiments 1, 3 and 4 in Table 2).

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

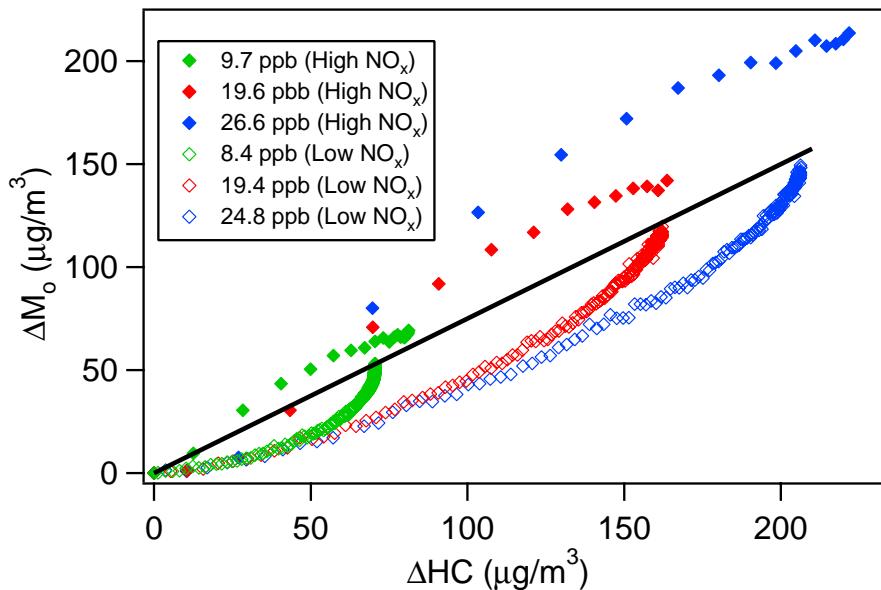


Fig. 2. Time-dependent growth curves for longifolene photooxidation under high- and low- NO_x conditions (Experiments 2, 3, 4, 10, 11, and 12 in Table 3). The mixing ratios in the legend refer to the amount of longifolene reacted in each experiment. The final SOA yields of each low- NO_x experiment lie on a straight line that passes through the origin, indicating that under low- NO_x conditions SOA yield is constant, at ~75%.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

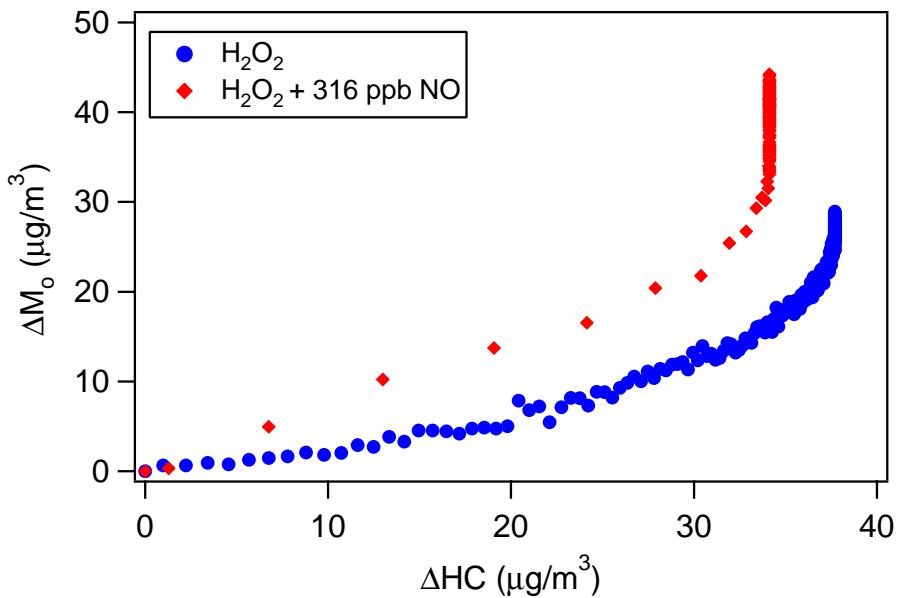


Fig. 3. Time-dependent growth curves for longifolene photooxidation with H_2O_2 as the OH precursor. Aerosol growth in the presence of $\sim 300 \text{ ppb NO}$ (Experiment 7 in Table 3) significantly exceeds that without NO (Experiment 1 in Table 3).

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

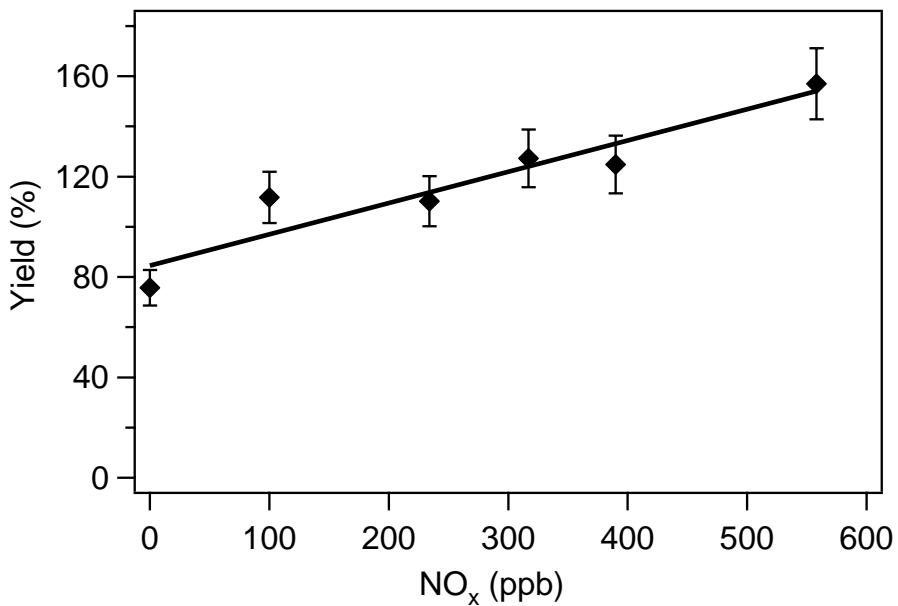


Fig. 4. SOA growth as a function of initial NO_x concentration, for a fixed longifolene concentration (~ 4.3 ppb). Results shown are from Table 3.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

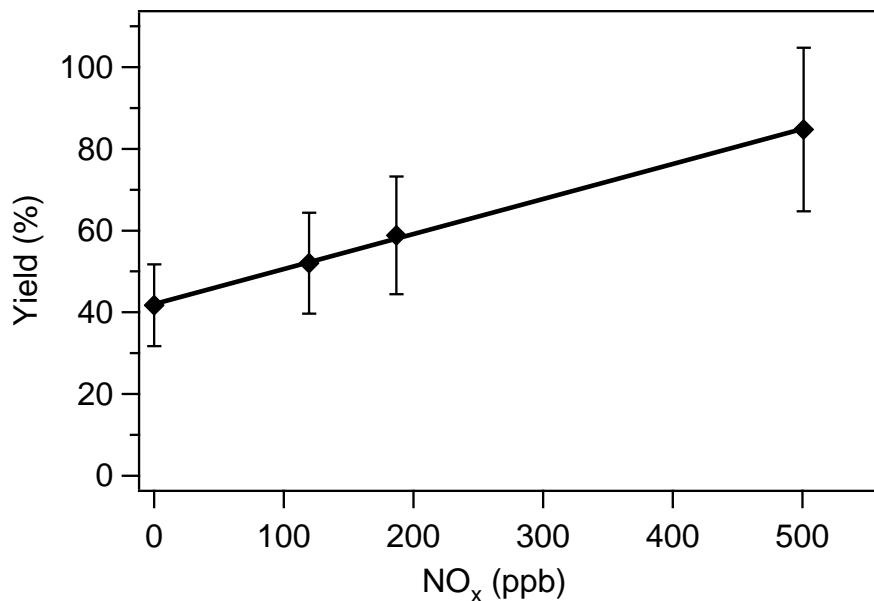


Fig. 5. SOA growth as a function of initial NO_x concentration, at a fixed initial aromadendrene concentration (~5 ppb). Results shown are given in Table 4.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

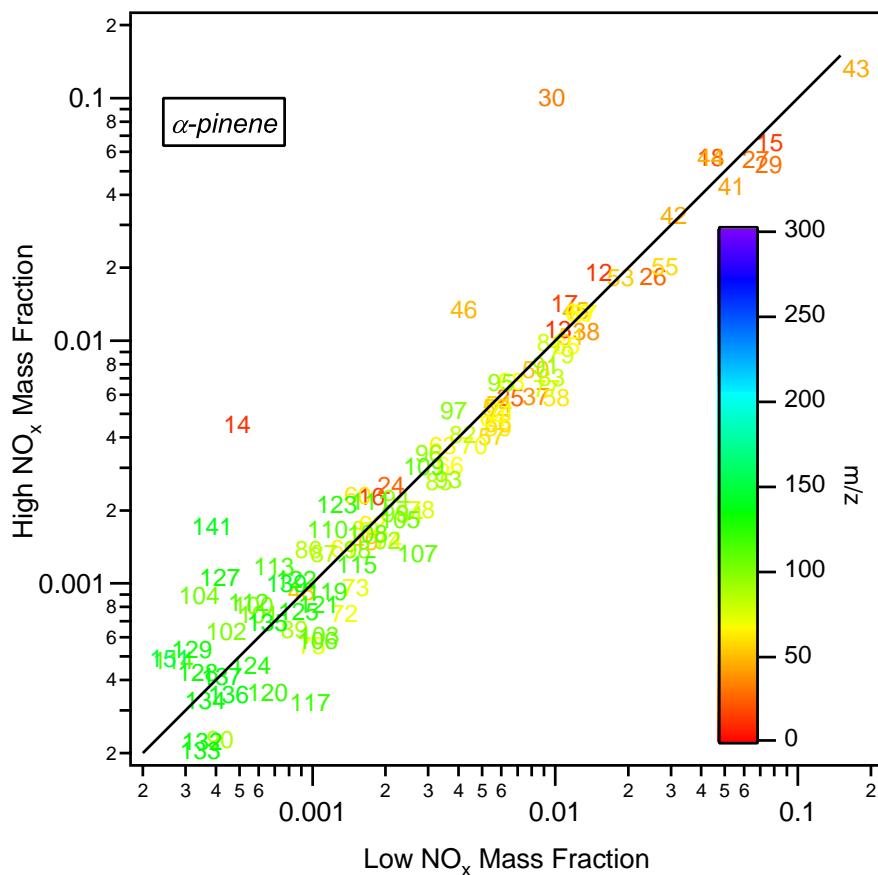


Fig. 6. AMS high-NO_x spectra signal versus low-NO_x spectra signal for α -pinene photooxidation. Each mass fragment is normalized by the total signal. The solid black line is the 1:1 line. The spectra are taken when all hydrocarbon has been consumed.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

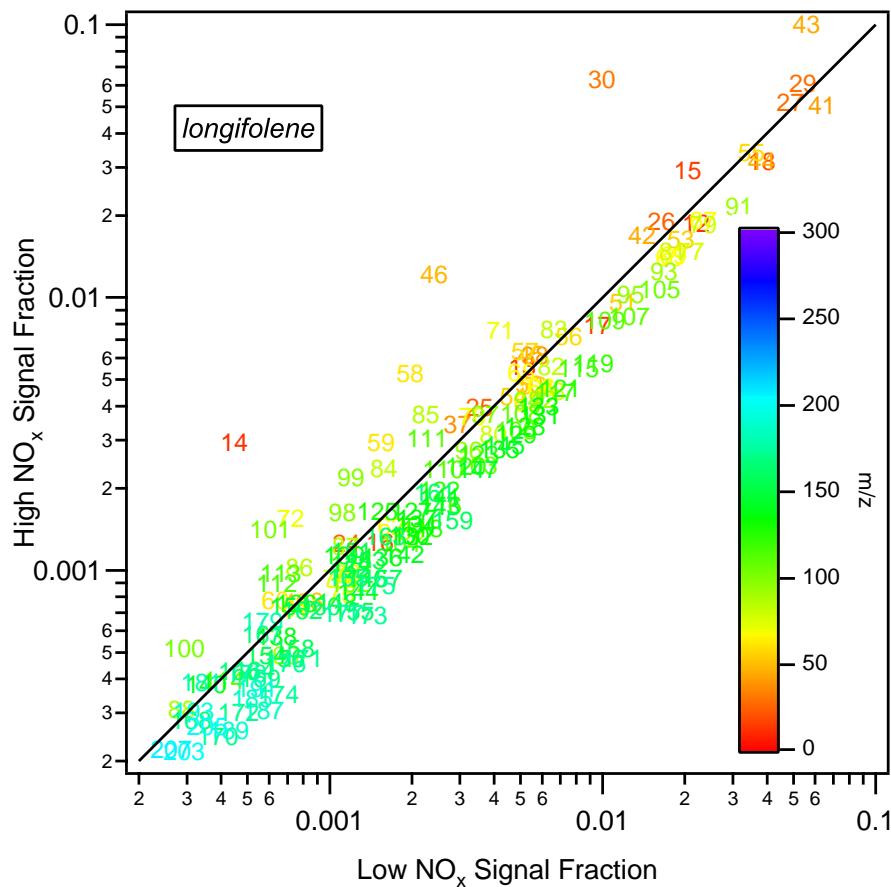


Fig. 7. AMS high- NO_x spectra signal versus low- NO_x spectra signal for longifolene photooxidation. Each mass fragment is normalized by the total signal. The solid black line is the 1:1 line. The spectra are taken when all hydrocarbon has been consumed.

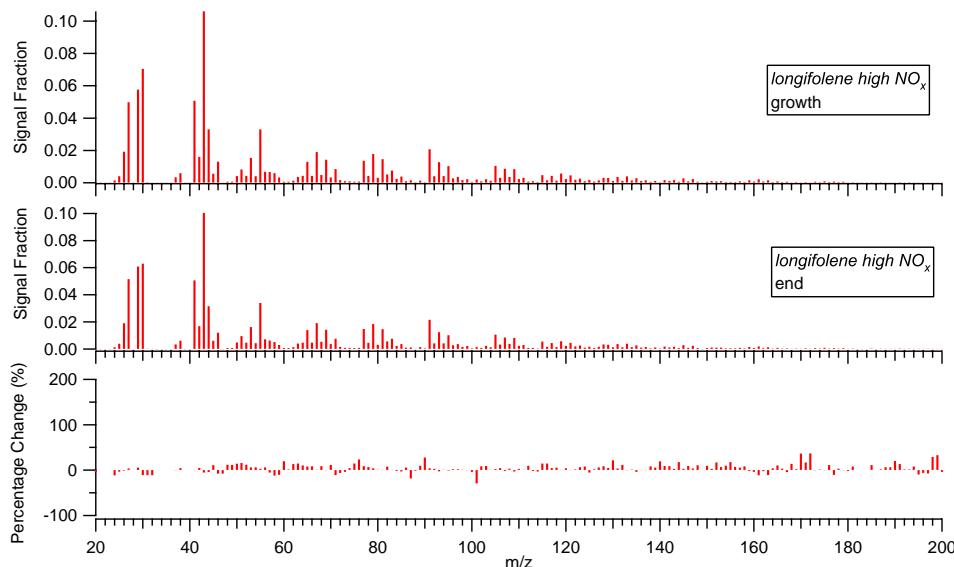


Fig. 8. Change in AMS spectrum over the course of longifolene photooxidation under high-NO_x conditions. Top panel: Fractional contribution of each mass fragment to the total organic and nitrate signal during the growth phase of the experiment. Middle panel: fractional contribution of each mass fragment to the total organic and nitrate signal when all hydrocarbon is consumed. Bottom panel: Percentage change of each mass fragment between the growth phase and the end of the experiment.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

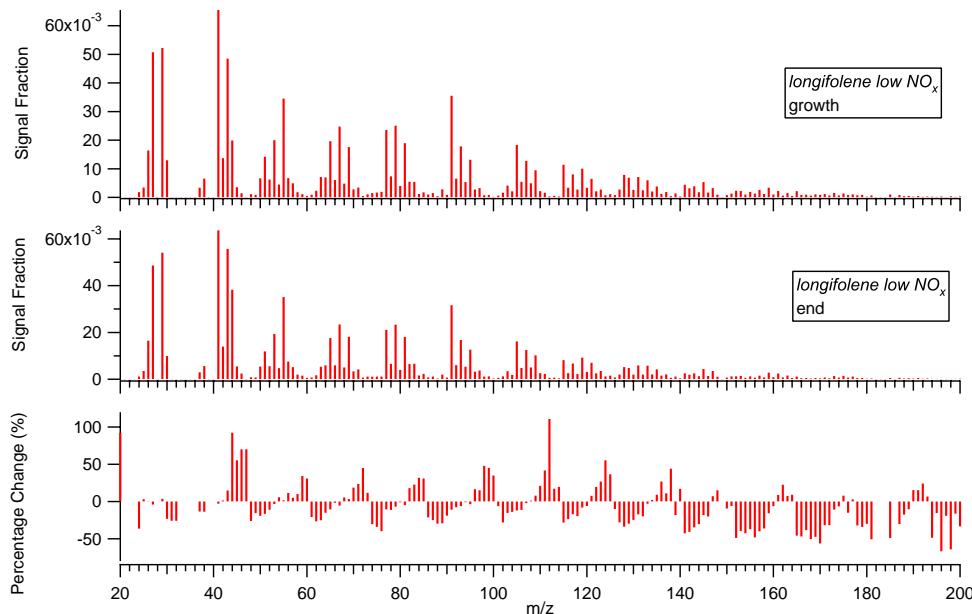


Fig. 9. Change in AMS spectrum over the course of longifolene photooxidation under low- NO_x conditions. Top panel: Fractional contribution of each mass fragment to the total organic and nitrate signal during the growth phase of the experiment. Middle panel: fractional contribution of each mass fragment to the total organic and nitrate signal when all hydrocarbon is consumed. Bottom panel: Percentage change of each mass fragment between the growth phase and the end of the experiment.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

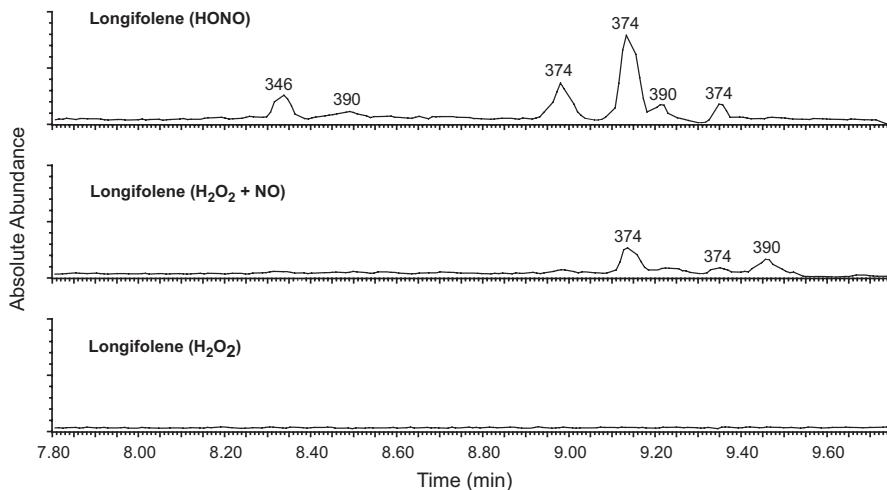


Fig. 10. UPLC/ESI-TOFMS extracted ion chromatograms (EICs) ($=m/z$ 346+374+390) for longifolene photooxidation. The even $[M-H]^-$ ions listed above the chromatographic peaks correspond to organic nitrates detected in longifolene SOA. No organic nitrates are detected in the H_2O_2 experiment (low- NO_x condition). The HONO experiment (high- NO_x condition) has the widest array of organic nitrates detected (as shown in Table 7), as well as the largest chromatographic peaks; m/z 372 is the only exception, and is most abundant in the intermediate NO_x experiment. These EICs are directly comparable as the volume of chamber air sampled is approximately the same (2 m^3).

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

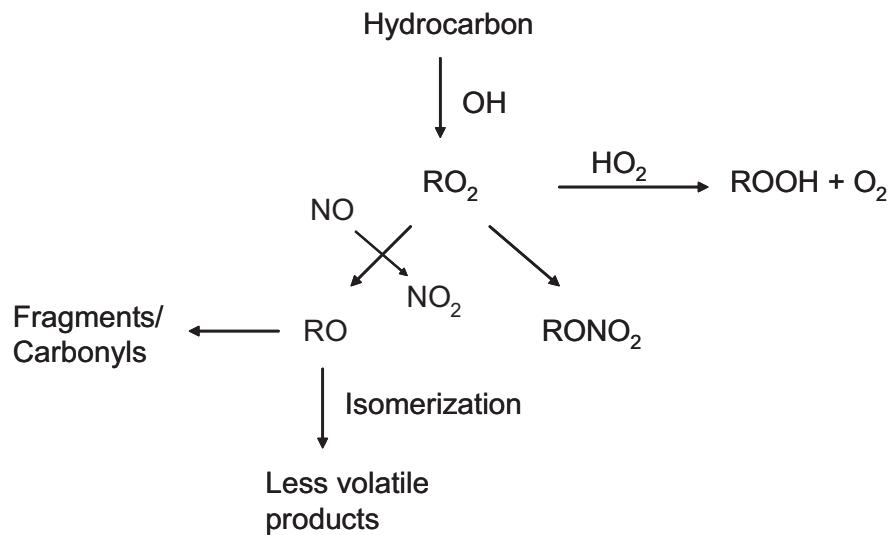


Fig. 11. General schematic of gas-phase peroxy radical chemistry in SOA formation.

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

NO_x dependence of SOA formation from terpenes

N. L. Ng et al.

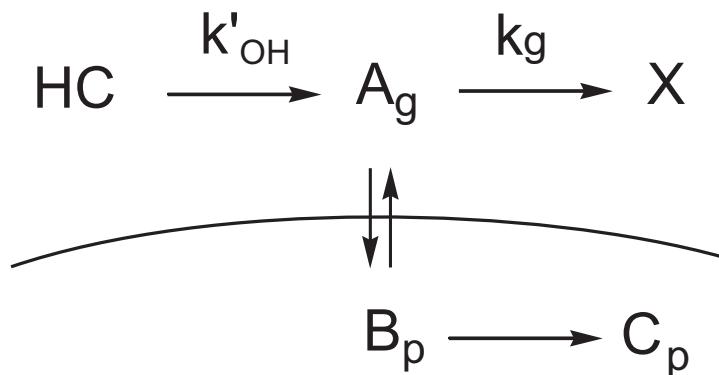


Fig. 12. A kinetic scheme depicting the competition between gas-particle partitioning and irreversible loss of the gas-phase semivolatiles. X represents the product of generic loss of semivolatile species A_g by chemical reaction, and/or loss to chamber walls. k'_{OH} is the pseudo-first-order rate constant ($k'_{\text{OH}} = k_{\text{OH}}[\text{OH}]$) for photooxidation of the parent hydrocarbon; k_g is the first-order rate constant of loss of semivolatiles.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)