

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO₂

D. C. Draper^{1,*}, D. K. Farmer², Y. Desyaterik³, and J. L. Fry¹

¹Department of Chemistry, Reed College, Portland, OR, USA

²Department of Chemistry, Colorado State University, Fort Collins, CO, USA
 ³Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA
 ^{*} now at: Department of Chemistry, University of California Irvine, Irvine, CA, USA

Received: 25 April 2015 - Accepted: 6 May 2015 - Published: 28 May 2015

Correspondence to: J. L. Fry (fry@reed.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

14923

Abstract

The effect of NO₂ on secondary organic aerosol (SOA) formation from ozonolysis of α -pinene, β -pinene, Δ^3 -carene, and limonene was investigated using a dark flow-through reaction chamber. SOA mass yields were calculated for each monoterpene from ozonolysis with varying NO₂ concentrations. Kinetics modeling of the first generation gas-phase chemistry suggests that differences in observed aerosol yields for differences in observed aerosol yie

ent NO₂ concentrations are consistent with NO₃ formation and subsequent competition between O₃ and NO₃ to oxidize each monoterpene. α -pinene was the only monoterpene studied that showed a systematic decrease in both aerosol number concentration and mass concentration with increasing [NO₂]. β -pinene and Δ^3 -carene produced

fewer particles at higher [NO₂], but both retained moderate mass yields. Limonene exhibited both higher number concentrations and greater mass concentrations at higher [NO₂]. SOA from each experiment was collected and analyzed by HPLC-ESI-MS, enabling comparisons between product distributions for each system. In general, the

- ¹⁵ systems influenced by NO₃ oxidation contained more high molecular weight products (MW > 400 amu), suggesting the importance of oligomerization mechanisms in NO₃initiated SOA formation. α -pinene, which showed anomalously low aerosol mass yields in the presence of NO₂, showed no increase in these oligomer peaks, suggesting that lack of oligomer formation is a likely cause of α -pinene's near 0% yields with NO₃.
- Through direct comparisons of mixed-oxidant systems, this work suggests that NO₃ is likely to dominate nighttime oxidation pathways in most regions with both biogenic and anthropogenic influences. Therefore, accurately constraining SOA yields from NO₃ oxidation, which vary substantially with the VOC precursor, is essential in predicting nighttime aerosol production.

1 Introduction

Secondary organic aerosol (SOA) forms in the atmosphere from oxidized volatile organic compounds (VOCs) that are of low enough volatility to be able to partition into the condensed phase. Aerosol directly affects Earth's radiative balance and also con-

- tributes to cloud formation, both of which have important climate forcing implications (IPCC, 2013). Aerosol is responsible for regional haze, and has been shown to cause adverse cardiopulmonary health effects (Pope III et al., 1995; Davidson et al., 2005). SOA constitutes a large fraction of the total aerosol budget, but it is still poorly constrained in global chemical transport models, which underpredict ambient aerosol con-
- ¹⁰ centrations by one to two orders of magnitude (Heald et al., 2005, 2011). These models use laboratory-derived parameters, but uncertainty in precursors, detailed mechanisms, and mechanistic differences between chamber simulations and the real atmosphere result in the vast discrepancies between models and observations (Kroll and Seinfeld, 2008; Hallquist et al., 2009).
- Nearly 90% of the non-methane VOCs emitted globally are biogenic in origin, so it should follow that a large fraction of the uncertainty in model predictions of the SOA budget comes from uncertainty in how biogenic VOCs (BVOCs) form aerosol (Guenther et al., 1995; Middleton, 1995). Different plant species emit different types and ratios of BVOCs, so the specific distribution of BVOCs emitted to the atmosphere is dependent
- ²⁰ on unique mixtures of vegetation and thus varies a great deal regionally. Monoterpenes are one such class of BVOC that is both widely emitted and has been shown in the laboratory to efficiently produce SOA (Goldstein and Galbally, 2007; Sakulyanontvittaya et al., 2008; Griffin et al., 1999; Hallquist et al., 1999; Ng et al., 2006; Ehn et al., 2014; Hoyle et al., 2011). On average in the US, α -pinene is the most dominant monoterpene
- ²⁵ emission, but β -pinene, Δ^3 -carene, and limonene (Fig. 1) are also prevalent and are emitted equally or more than α -pinene in some regions (Geron et al., 2000).

While most VOCs are biogenic, the majority of atmospheric oxidants are anthropogenically sourced, and thus human activity is highly influential on SOA production

14925

(Carlton et al., 2010). At night, most VOC oxidation in the troposphere occurs by way of either photolabile nitrate radical (NO_3) or longer-lived ozone (O_3), which is photochemically produced but is not rapidly and completely consumed at sundown as is the hydroxyl radical (OH). The formation of both of these tropospheric oxidants requires

- NO₂, nearly 90% of which in the US (64% globally) is estimated to come from anthropogenic sources (Reis et al., 2009). Organonitrates have been observed in ambient nighttime aerosol during multiple field studies (Fry et al., 2013; Rollins et al., 2012; Xu et al., 2015), consistent with NO₃ oxidation, and NO₃ initiated production of aerosol organonitrates may even be competitive during the day in some regions with high
- ¹⁰ BVOC emissions (Ayres et al., 2015). These observations are consistent with several laboratory studies that have found moderate to high aerosol yields from NO₃ oxidation (Griffin et al., 1999; Hallquist et al., 1999; Fry et al., 2009, 2011, 2014; Spittler et al., 2006; Moldanova and Ljungström, 2000), but this body of literature is comparatively small relative to OH and O₃ oxidation studies.
- ¹⁵ Most chamber studies of NO₃-derived SOA generate NO₃ through the thermal dissociation of N₂O₅ in order to minimize the complexity caused by introducing a second oxidant (Griffin et al., 1999; Hallquist et al., 1999; Fry et al., 2014). Fewer studies have been done using the atmospherically more relevant conditions of introducing both O₃ and NO₂ into the chamber to mimic this full range of nighttime oxidation chemistry
- ²⁰ (Perraud et al., 2012; Presto et al., 2005; Boyd et al., 2015). Perraud et al. (2012) and Presto et al. (2005) both studied the effects of a range of NO₂ concentrations on dark ozonolysis of α -pinene, and both observed that increased [NO₂] suppresses aerosol formation. To our knowledge, NO₂ effects on dark ozonolysis have not been assessed for any other monoterpenes. Ozonolysis of α -pinene has been previously observed to
- have high aerosol yields (Ng et al., 2006) but strikingly low (0–16%) SOA yields with NO₃ (Hallquist et al., 1999; Fry et al., 2014; Spittler et al., 2006). The observed aerosol suppression in the O₃ + NO₂ system is consistent with the increased contribution of NO₃ at higher [NO₂]. However, α -pinene is the only monoterpene that has been observed to have such drastic SOA yield discrepancies between the two oxidants (Ng

14926

Discussion Paper

Discussion Paper

Discussion Paper Discussion Paper

Discussion Paper

Discussion Paper | Discussion Paper | Discussion Paper

et al., 2006; Yu et al., 1999; Hallquist et al., 1999; Fry et al., 2014), so it may not be reasonable to assume NO_2 has the same effect on other monoterpenes.

Here we focus on the four most prevalently emitted monoterpenes in the US: α -pinene, β -pinene, Δ^3 -carene, and limonene. Table 1 shows rate constants for NO₃

- formation from $NO_2 + O_3$ as well as each of the nighttime oxidants with the monoterpenes used in this study. It is evident that the rates of O_3 loss to NO_3 production and BVOC oxidation are comparable when [NO_2] and [BVOC] are similar. Even considering its smaller ambient concentrations, NO_3 oxidation is often much faster than O_3 oxidation, so it follows that NO_3 oxidation should provide an important contribution to night-
- time aerosol formation in regions that are both biogenically- and anthropogenicallyinfluenced. This work seeks to characterize the role of each competing nighttime oxidant over this broader range of monoterpenes and the influence of each on SOA formation.

2 Methods

- SOA formation experiments were performed in a darkened 400 L PFA film chamber, shown in Fig. 2, run in flow-through mode with precursors added continuously. Each experiment, as described in Table 2, measured the aerosol production from a single monoterpene oxidized by O₃ with varying concentrations of NO₂ added. In order to make comparisons across both the range of monoterpenes and the range of [NO₂], the
- monoterpene source and O₃ source concentrations were kept as constant as possible throughout the full study, allowing only the identity of the BVOC and the concentration of NO₂ to vary.

 $\rm O_3$ (and $\rm NO_2,$ when applicable) were introduced into the chamber first and allowed to reach steady state prior to initiation of each experiment by BVOC injection. O₃ was gen-

erated by flowing zero air (Sabio Model 1001 compressed zero air generator) through a flask containing a Pen-Ray Hg lamp (primary energy at 254 nm) and was continually measured from the outlet of the chamber using a Dasibi Model 1003-AH O₃ monitor.

14927

NO₂ was introduced from a calibrated cylinder (Air Liquide, 0.3 % by volume in N₂), and monitored using a Thermo Model 17i chemiluminescence NO_x/NH₃ analyzer. Chemiluminescence NO_x analyzers are sensitive to any species that is converted to NO in the 350 °C Mb converter responsible for converting NO₂ to NO (Winer et al., 1974;

- ⁵ Grosjean and Harrison, 1985). Some of these additional species include N_2O_5 , peroxynitrates (PNs), and alkyl-nitrates (ANs). At the high concentrations used in this study, these NO_y contributions were significant. Kinetics modeling of the oxidant stabilization period (described in the Supplement), corroborated by a characterization of oxidant stabilization using chemiluminescence NO_x analyzers and a cavity ringdown spec-
- ¹⁰ trometer sensitive only to NO₂, indicates that we detected N₂O₅ with approximately unit efficiency in the NO₂ channel of the Thermo NO_x analyzer. The sensitivity of this NO_x analyzer to PNs and ANs, which would have formed following BVOC addition, was not calibrated, but is expected to be near unity based on previous studies (Winer et al., 1974; Grosjean and Harrison, 1985). Modeling only the oxidant stabilization pe-¹⁵ riod, where NO₂ and N₂O₅ were likely the only species detected in the NO₂ channel,

provided the initial NO₂ concentrations shown in Table 2.

Once the oxidants stabilized, BVOC was introduced by flowing zero air over a small, cooled liquid sample of the target BVOC ((1R)-(+)-alpha-Pinene, TCI America, > 95.0%; (-)-beta-Pinene, TCI America, > 94%; (+)-3-Carene, TCI America,

- > 90.0%; (R)-(+)-Limonene, Aldrich, > 97%). The chiller temperature was held constant (±0.3°C) during a single experiment, and ranged from -27 to -21°C for the different monoterpenes, based on the temperature-dependent vapor pressure that is calculated to give a mixing ratio of approximately 100 ppm in the source flask (Fig. S.3) (Haynes et al., 2012). Since vapor pressure data was unavailable for Δ^3 -carene, it was
- estimated to reach the temperature-dependent vapor pressure at -25 °C between α -pinene and β -pinene's target temperatures due to structural similarities.

Since experiments were initiated by introducing BVOC into an oxidant-rich chamber, online measurement of the reaction of the BVOC was not possible. Instead, initial VOC concentrations were characterized directly from the source flask before and after each

experiment using a SRI Model 8610C gas chromatograph with flame ionization detector (GC-FID). Source concentrations were somewhat variable over time, so BVOC was also modeled independent of measurements in order to verify initial concentrations listed in Table 2. Methodology and uncertainties are described in the Supplement.

- In addition to measurements of the gas-phase precursors, two methods were employed to measure the resulting aerosol loading and composition. Particle size distributions between 20 and 800 nm were measured at 85 s time resolution with a Scanning Electrical Mobility Sizer (SEMS; BMI Model 2002) consisting of a differential mobility analyzer (BMI Model 2000C) coupled to a Water Condensation Particle Counter (TSI
- Model 3781). Size-dependent aerosol loss rates to the chamber walls were characterized and used to correct size distributions to reflect the total aerosol number and volume concentrations produced in each experiment (McMurry and Grosjean, 1985; VanReken et al., 2006; Fry et al., 2014). This methodology is described in further detail in the Supplement. Aerosol samples from each experiment were collected onto
- 15 filters (47 mm quartz fiber). Each filter was extracted by sonication in 3:1 deionized water: acetonitrile to minimize solvent reactions with analyte compounds (Bateman et al., 2008), and the resulting extract was analyzed offline by High Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (HPLC-ESI-MS).
- Due to its relatively soft ionization source and thus minimal fragmentation of analyte compounds, ESI-MS has been employed in several studies to probe SOA composition (Bateman et al., 2008, 2012; Walser et al., 2008; Doezema et al., 2012). The HPLC-ESI-MS system used here consists of an Agilent 1100 Series liquid chromatograph coupled to an Agilent LC/MCD TOF G1969A time-of-flight mass spectrometer with an electrospray ionization source. The chromatographic separation occurred on a Kinetex
- 25 100 mm × 3 mm C18 column with 2.6 µm particle size and a sample injection volume of 50 µL at a flow rate of 0.5 mL min⁻¹. The electrospray ionization system had a nebulizer gas pressure of 50 psi and an electrospray voltage of 3000 V. High mass resolution $(m/\Delta m$ varies between 5000 at m/z 118 amu to 15000 at m/z 1822 amu) and

14929

chromatographic separation of the analytes allowed for straightforward identification of product molecular formulae (Desyaterik et al., 2013).

Results and discussion 3

3.1 Aerosol formation trends

- Raw number and volume concentration time series are presented in Fig. 3. These comparisons are not directly indicative of relative yields due to differences in initial monoterpene concentrations shown in Table 2 (see Sect. 3.2 for true aerosol mass yields). However, they nicely illustrate the vast diversity of the behavior of each monoterpene with respect to systematically changing oxidant conditions, from O₃-dominated to NO₃-
- ¹⁰ dominated. α -pinene exhibits a decrease in both the total number of particles produced (N_{tot}) and total aerosol volume produced (V_{tot}) with increasing NO₂, consistent with the findings of other studies (Perraud et al., 2012; Presto et al., 2005). β -pinene and Δ^3 carene both exhibit a similar decrease in N_{tot} with addition of NO₂ as α -pinene, but at early times in the reaction, the addition of NO2 appears to enhance volume growth
- relative to the O₃-only experiment. Limonene exhibits enhancement in both N_{tot} and 15 $V_{\rm tot}$. While all three of the monoalkene monoterpenes produce fewer particles at higher $[NO_2]$, α -pinene is the only terpene for which the aerosol production seems to be systematically depleted with the addition of NO2. β -pinene and Δ^3 -carene, in contrast, seem to level off at comparable $N_{\rm tot}$ values for the intermediate range of [NO₂]. All
- 20 four monoterpenes exhibit suppression of aerosol formation at the highest [NO2] studied, which may be the result of RO2 + NO2 chemistry becoming kinetically dominant at such high concentrations and producing metastable, less condensable peroxynitrate products (Barthelmie and Pryor, 1999).

3.2 SOA yields

Unitless aerosol mass yields (*Y*) are defined as the aerosol mass produced per hydrocarbon mass consumed ($Y = \Delta M / \Delta HC$). Since the hydrocarbon was not measured online during experiments, ΔHC values were determined using the gas-phase kinetics

- model described in detail in the Supplement. The modeled cumulative concentration of monoterpene reacted was converted to ΔHC in μ g m⁻³ using the molecular weight of monoterpenes (136.23 g mol⁻¹). Δ*M* was determined by converting the wall losscorrected aerosol total volume data to mass, assuming a SOA density of 1.4 g mL⁻¹ (Hoyle et al., 2011). Thus a time series of mass yields was attainable, shown in Fig. 4 as
- ¹⁰ aerosol mass produced (ΔM) vs. Δ HC consumed, where ΔM and Δ HC are calculated relative to the beginning of the experiment. In the kinetics model, Δ HC is calculated based on how much of each oxidant reacts with the monoterpene. However, NO₃ can also react with subsequent RO₂ radicals, thus depleting the concentration available to react directly with BVOC. The rate constant for RO₂ + NO₃ (2 × 10⁻¹² cm³ molec⁻¹ s⁻¹)
- is reasonably well known and constant over a range of RO_2 structures (Vaughan et al., 2006). The rate constant for $RO_2 + RO_2$, the main competing RO_2 sink, is far more variable over RO_2 structures, though, so the "best estimate" employed in this study spans three orders of magnitude (described further in Supplement). Therefore, $k_{RO_2+RO_2}$ is the largest source of uncertainty in Δ HC, and aerosol yield ranges are calculated span-
- ²⁰ ning the minimum $(10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$ and maximum $(10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$ values used. Because O₃ is not expected to react with RO₂ (whereas NO₃ does), Δ HC from the O₃-only experiments does not vary in response to shifting $k_{\text{RO}_2+\text{RO}_2}$ values. Aerosol yields were not constant over the course of each experiment, as seen by the non-linear yield curves in Fig. 4, where the regions with the greatest slopes (relative
- to $\Delta HC = 0$) have the highest mass yield. The yields reported in Table 3 are the maximum yield observed during the course of the experiment, typically observed during the first two hours, for each of the low and high $k_{RO_2+RO_2}$ limits. In some cases, the aerosol growth rapidly exceeded the size range of the SEMS (20–800 nm). Aerosol

14931

data presented here is truncated as soon as the size distribution exceeds the range of the SEMS instrument and is represented as a lower limit to the maximum aerosol yield because all subsequent data will be an underestimation of mass.

- With the mass yield effectively normalizing these mass yields across varying Δ HC, we still see similar trends as were observed in the V_{tot} panels of Fig. 3. Figure 4 and Table 3 illustrate that increasing [NO₂] substantially depletes aerosol formation from α pinene, whereas β -pinene and Δ^3 -carene have comparable yields over the full range of oxidant conditions, and limonene exhibits enhancement of aerosol formation at higher [NO₂]. It should be noted that yield calculations were only performed on the O₃-only and lowest two [NO₂] studied for each monoterpene due to difficulties in reliably reproducing
- Δ HC in the kinetics model for the highest [NO₂] experiments.

3.3 Individual oxidant contributions

Gas-phase kinetics modeling of the steady state conditions in the chamber yielded the time series of relative O_3 and NO_3 (and OH) contributions to BVOC oxidation. Since

- each experiment starts with O₃, NO₂, NO₃, and N₂O₅ at their equilibrium concentrations, initial BVOC oxidation will be dominated by NO₃, which reacts orders of magnitude faster than O₃ (Table 1). Eventually, as concentrations of precursors change over time, rates to each oxidant change and O₃ starts to contribute. We also assume OH is produced from stabilized Criegee intermediates from ozonolysis according to
- the monoterpene-dependent yields found in Atkinson et al. (1992) and described in the Supplement. The timing and relative contribution of O₃ depends on the relative rate constants of O₃ and NO₃ with each monoterpene, and thus the influence of each oxidant varies for all conditions tested.
- For α -pinene, the window where NO₃ is responsible for all oxidation is relatively short (< 30 min for either NO₂ experiment). In general, it can be assumed that any aerosol formed in a period dominated by a single oxidant is the aerosol yield of that BVOC/oxidant combination. Therefore, this period where NO₃ is responsible for all oxidation should give the NO₃ + α -pinene aerosol yield. It is especially notable in all of

Discussion Paper | Discussion Paper

Discussion Paper

Discussion Paper

(1)

(2)

the α -pinene experiments that no aerosol forms until O₃ starts contributing, as seen in Fig. 5. This observation is consistent with several studies that have seen low or even 0% aerosol yields for α -pinene + NO₃ (Hallquist et al., 1999; Spittler et al., 2006; Fry et al., 2014). Because NO₃ gives approximately 0% aerosol yield, any aerosol

⁵ produced from *α*-pinene can be assumed to come from O₃ (and OH) oxidation. We can calculate the O₃ (with OH) aerosol yield in the NO₂-influenced experiments using $\Delta M/\Delta HC_{O_3+OH}$, where any of the BVOC reacted by NO₃ is excluded from the yield calculation. In the O₃-only experiment, *α*-pinene has a 28% mass yield. The lowest NO₂ condition has a 16–28% yield from O₃ (+ OH), which is consistent with the 28% yield

from the O_3 -only experiment. At the next highest [NO₂], the O_3 yield drops to 2–4%, which may simply be explained by having the lowest background aerosol mass and thus smaller absorptive partitioning contributions (Pankow, 1994).

 β -pinene in general produced the least aerosol mass and lowest number concentrations. Due to the very small number concentrations but modest aerosol yields (and

- thus abundant condensable vapors to grow the small number of particles), β -pinene size distributions grew above the size range of the SEMS quite rapidly during the NO₂ experiments. The relatively short span of aerosol data, combined with faster loss of O₃ to reaction with NO₂ than to β -pinene oxidation (Table 1), resulted in the entire period of observable aerosol formation being dominated by NO₃ oxidation at all concentrations
- ²⁰ of NO₂. The two lowest concentrations of NO₂ both had yields within a range of 8– 14 %, further indicating that both experiments were dominated by NO₃ oxidation rather than varying contributions from NO₃ and O₃. Δ^3 -carene displayed similar behavior to β -pinene. Most, though not all, of the oxidation during aerosol production went by NO₃. In the two lowest NO₂ concentration experiments, the maximum aerosol yield during
- the period only influenced by NO₃ oxidation was approximately 12–21%. Limonene maintained relatively high aerosol yields from each set of oxidation conditions, indicating high aerosol yields from both O₃ and NO₃ oxidation. For the lowest [NO₂], the first 30 min of BVOC oxidation was dominated by NO₃, with a 36–42% yield.

14933

During these periods of exclusively NO₃ oxidation, the relative aerosol yields for each monoterpene follow the same trend observed in Fry et al. (2014), which measured aerosol yields from NO₃ oxidation alone at lower initial concentrations of both BVOC and NO₃ and observed α -pinene $\approx 0 < \beta$ -pinene $< \Delta^3$ -carene < limonene. This consistency further stresses the importance of individual oxidant contributions in this complex system. The percentage of BVOC reacted by each of the three oxidants was modeled and is shown in Table 4. Comparisons were made at two hours into the reaction after the initial buildup of NO₃ and N₂O₅ was depleted and chemical production of NO₃ more realistically competes with O₃ oxidation of BVOCs. Even at this point in

¹⁰ time, NO₃ dominates the initial oxidation pathway for all NO₂ concentrations and all monoterpenes.

3.4 Determination of dominant nighttime oxidant using NO₂ to BVOC ratio

Using literature rate constant data (Table 1), we can approximate the NO₂ / BVOC mixing ratio regime where NO₃ will dominate nighttime oxidation for each monoterpene. Since O₃ contributes to both NO₃ formation and BVOC oxidation, and for all monoterpenes NO₃ oxidation is much faster than O₃ oxidation, we assume that once NO₃ production becomes faster than O₃ oxidation of BVOC (Eq. 1), NO₃ becomes the dominant oxidant. The ratio of NO₂ / BVOC at which this crossover occurs, defined in Eq. (2), is calculated for each monoterpene and reported in Table 5.

 $k_{(O_3+NO_2)}[O_3][NO_2] > k_{(O_3+BVOC)}[O_3][BVOC]$

$$\frac{[\text{NO}_2]}{[\text{BVOC}]} > \frac{k_{(\text{O}_3 + \text{BVOC})}}{k_{(\text{O}_3 + \text{NO}_2)}}$$

This calculation leaves out factors like competing sinks for NO_3 and is thus a very crude approximation. Nevertheless, it is noteworthy how small the magnitude of these ratios are. During the 2011 BEACHON-RoMBAS field campaign, which took place in

²⁵ a relatively remote forested location in the Rocky Mountain front range, [NO₂] typ-

ically peaked at night around 2 ppb, and total monoterpene concentrations (1:1:1 α -pinene: β -pinene: Δ^3 -carene) peaked at night around 0.6 ppb (Fry et al., 2013). Assuming 0.2 ppb from each of the speciated monoterpenes, that gives [NO₂] / [BVOC] ratios of 10 for each – well above the minimum values presented in Table 5. These ratios are expected to be substantially higher in regions with stronger anthropogenic

influences. This analysis suggests that NO_3 is not only a relevant contributor to nighttime oxidation chemistry, it may actually dominate oxidation pathways in many regions.

3.5 Bulk SOA composition

Filter samples from experiments that yielded sufficient aerosol mass (all expts in Ta-

- ¹⁰ ble 2 except 1, 5, 9, 13) were collected and analyzed offline by HPLC-ESI-MS at Colorado State University. Because electrospray ionization is a soft ionization technique, this method has been shown to be especially useful for detecting a wide range of m/z products – including oligomer species that are likely to be significant SOA constituents (Walser et al., 2008; Surratt et al., 2006; Doezema et al., 2012). Although
- quantitative comparisons of products are not possible due to differences in mass loadings and a lack of calibration standards, qualitative differences in product distributions were readily apparent and consistent with observed aerosol yield trends.

Introducing NO₂ into ozonolysis of monoterpenes influences the composition of resulting SOA in two different ways: first, by forming NO₃ that can either oxidize BVOC di-

- ²⁰ rectly or react with NO₃- or O₃-initiated RO₂, or second, by directly reacting with RO₂ or other products and reaction intermediates as NO₂. A visual comparison of the total ion chromatograms from ozonolysis of β -pinene with no NO₂ and the two lowest concentrations of NO₂ (Fig. 6) shows that several new products form once NO₂ is added, and that in general increasing [NO₂] simply increases the intensity of those products rather
- than changing product identities substantially. For ease of interpretation, results from all of the NO_2 -containing experiments were combined into a single product distribution from " NO_3 -influenced oxidation." We can then compare those product distributions to those of the O_3 -only experiments. A complete list of compound formulae detected 14025

14935

(> 1.5 % relative intensity, see Supplement) in the O_3 and NO_3 dominated oxidation of each monoterpene is compiled in Table S.2.

To best highlight qualitative differences in the identity of molecules that make SOA for each set of precursors, every unique compound (distinct either in mass, retention

- time, or both) was accounted for once, not normalized by peak intensity. A variety of average bulk composition parameters were calculated for each experiment, highlighted in Table 6, including average number of C, O, and N atoms per compound, molecular weight, and total number of products. Some artifacts may remain in this dataset, such as impurities not captured by the background subtraction or product fragments that do
- not reflect the original identity of the SOA product. The former should affect all samples uniformly in this analysis and thus will not influence qualitative comparisons, and the latter will either affect multiple samples and thus be irrelevant in comparisons or only affect single samples and thus still provide interesting qualitative differences.

A direct correlation between any of the average parameters (MW_{avg}, *C*_{avg}, *O*_{avg}, *N*_{avg}) in Table 6 and absolute aerosol yields is not obvious. Limonene ozonolysis, for example, produced the highest aerosol mass of all the conditions tested, but its average MW and number of C or O atoms are comparable to ozonolysis from all the other monoterpenes, and substantially lower than any of the NO₃ experiments. However, the difference in average values, defined as the difference in each average parameter between

- ²⁰ O₃ and NO₃ dominated oxidation for each monoterpene (Δ_{avg}), are consistent with O₃ vs. NO₃ yield comparisons. β -pinene and Δ^3 -carene have similar Δ_{avg} values for each parameter (as well as similar absolute values for each oxidant condition), suggesting that the addition of NO₃ affects the product distribution of these two monoterpenes similarly. The Δ_{avg} values for limonene are much higher than any other monoterpene
- ²⁵ in this study, consistent with it having the highest NO₃ aerosol yields. Again, perhaps most notably, the Δ_{avg} parameters hover near zero for α -pinene, suggesting that the aerosol composition does not differ much between the two oxidants – consistent with all of α -pinene's aerosol production coming exclusively from O₃-oxidation.

To illustrate some of the finer detail of these product distributions, Fig. 7 shows histograms where each observed product is binned by compound mass, in 50 amu intervals. Every experiment shows some contribution from oligomer products (m/z > 246, according to Perraud et al., 2010, > 300 according to Walser et al., 2008), but this con-

- ⁵ tribution is most pronounced from NO₃ oxidation of β -pinene, Δ^3 -carene, and limonene. In particular, we observe substantially more distinct products > 400 amu from β -pinene, Δ^3 -carene, and limonene with the O₃/NO₂/NO₃ mixture than from O₃ alone. In this region, the mass distributions for α -pinene in both oxidant conditions are identical. Since mass is an important contributing factor to volatility (e.g. Donahue et al., 2011), these
- high mass products are likely important in aerosol formation and growth, and thus may be explanatory of the observed yield differences from NO₃-oxidation. If oligomerization is an important pathway leading to SOA formation and growth from NO₃-initiated chemistry, α -pinene's lack of oligomer products with NO₃ may be responsible for its 0 % aerosol yield. In contrast, comparison of the four O₃-only histograms shows relatively
- 5 small contributions of high MW oligomers for any monoterpene, in spite of quite high aerosol yields in some cases, indicating that aerosol formation by ozonolysis may not require oligomerization.

Recent studies of SOA nucleation and growth from ozonolysis of α -pinene have shown that highly oxidized and/or oligomeric species are likely important in nucleation and early growth, but that growth beginning around 20 nm is dominated by lower MW

- products (140–380 amu) (Zhao et al., 2013; Winkler et al., 2012). This latter MW range is consistent with the ozonolysis products we observe for all four monoterpenes, indicating that high MW products may dominate only early stages of growth and are thus not detectable at the high mass loadings in this study. NO₃ oxidation, on the other hand,
- seems to provide a weaker source of low volatility compounds contributing to nucleation and early growth, as seen in the decrease of N_{tot} with increasing [NO₂] in Fig. 3 (with the exception of limonene), but produces oligomers throughout the full time period of aerosol growth, leading to total aerosol mass concentrations that rival ozonolysis (with the exception of α -pinene), as seen in Fig. 4. Further supporting this observed differ-

14937

ence in products from ozonolysis compared to NO₃ oxidation is the difference in the reaction rate of each process. O₃ + BVOC is much slower than NO₃ + BVOC, which means that RO₂ is produced more slowly from ozonolysis and thus the RO₂ lifetime is much longer with respect to other radical species. Longer RO₂ lifetimes are more ⁵ conducive to isomerization processes like autoxidation (Crounse et al., 2013; Jokinen et al., 2014), which may be responsible for the initial high MW nucleating species ob-

- served in other ozonolysis studies. In contrast, NO₃ oxidation produces RO₂ much more rapidly, therefore increasing the likelihood of RO₂ + RO₂ oligomerization. Mass spectra alone provide limited compositional information since they do not dis-
- tinguish between different functional groups. However, in this system, one functional group that can be easily parsed out of the data is the nitrate group. From the NO₃ initiated oxidation chemistry, we expect that any nitrogen present in a molecule is a part of a nitrate functional group. (Some instances of –NO and –ONO have been found in the compound list, causing relatively high N_{avg} values for α -pinene + O₃, for exam-
- ple, where we expect any nitrogen is due to impurities.) The Δ_{avg} values in Table 6 for N_{avg} provide an approximate estimate of relative aerosol organic nitrate yield. β pinene, Δ^3 -carene, and limonene all exhibit a substantial increase in average number of N per molecule with the addition of NO₂, consistent with the relatively high organic nitrate yields observed from NO₃ oxidation of those species in other studies (Fry
- et al., 2014; Hallquist et al., 1999). α -pinene produces comparatively fewer nitrogencontaining SOA products in the presence of NO₂. While the organic nitrate products from α -pinene may be relatively volatile and thus not partition appreciably into the aerosol phase, it is clear that this is not a universal characteristic of C₁₀ organic nitrates, as many do partition into the aerosol phase for all three other monoterpenes studied – even those with relatively low total aerosol mass loading.
- We note that the products observed here from ozonolysis vs. NO₃ oxidation are consistent with proposed mechanisms in the literature. Table S.3 includes proposed structures for several masses that have been observed in other studies, including several monomeric carboxylic acids and aldehydes from ozonolysis (Glasius et al., 2000; Yu

et al., 1999) as well as multi-functional monomeric nitrates from NO₃-oxidation (Wangberg et al., 1997; Perraud et al., 2010), some of which have been included in Fig. 6 to highlight relative intensities across different NO2 conditions. Several more speculative structures are shown in the Supplement to indicate that observed oligomeric masses can be reasonably achieved from dimers of first generation oxidation products.

Conclusions 4

This work adds to the growing body of monoterpene aerosol yield comparison literature suggesting that monoterpene oxidation has widely varying aerosol yields depending on the specific monoterpene and oxidant combination (Fry et al., 2014; Griffin et al., 1999;

Hallquist et al., 1999; Ng et al., 2006; Glasius et al., 2000; Yu et al., 1999; Lee et al., 2006). We therefore conclude, first and foremost, that there is no single "representative" monoterpene. Furthermore, the monoterpene most often considered representative of BVOC oxidation, α -pinene, presents here as the greatest anomaly with respect to aerosol formation, showing higher ozonolysis aerosol mass yields than even limonene, and showing 0% aerosol yields from reaction with NO₃.

We show that under the influence of NO₃, α -pinene produces comparatively few organic nitrates and oligomers relative to the other three monoterpenes studied. This finding is consistent with α -pinene's negligible aerosol yield with NO₃ and also suggests more generally that oligomers and potentially organic nitrate monomers are important

- products leading to SOA formation from NO₃. Additionally, the difference in product distributions between O_3 and NO_3 oxidation for all monoterpenes studied (except α pinene) indicates that each oxidant broadly employs a different mechanism toward condensable products - where O3 likely nucleates and grows enough aerosol mass early in the reaction that subsequent condensation is governed by comparatively small
- molecular weight species, whereas NO₃ produces less extremely low volatility material 25 early but produces oligomers consistently throughout the period of condensation such that they constitute an observable fraction of the bulk aerosol.

14939

Careful treatment of the first generation kinetics of this atmospherically relevant nighttime oxidant mixture also served to contextualize the relative importance of each observed aerosol precursor in different regions. We propose using NO₂ / BVOC ratios for each monoterpene to predict the dominant nighttime oxidation pathway for each

- (Table 5). For example, for β -pinene at NO₂ / BVOC ratios greater than 0.47, NO₃ oxidation will begin to out-compete O₃ oxidation, suggesting that β -pinene oxidation by O₃ is likely to be minor at night in all but the most pristine environments. β -pinene displays a rather extreme manifestation of this observation, but all four monoterpenes studied have NO₂ / BVOC ratios such that NO₃ oxidation is likely to dominate even in relatively remote regions. 10
 - The complexity shown by just these four BVOCs reacting with two different oxidants suggests that bulk parameters in global and regional models need to be very carefully considered if they are going to accurately match observed ambient organic aerosol loadings. These models use one or two, typically daytime, aerosol yield parameters for
- bulk monoterpenes often considering α -pinene or β -pinene yields to be representative (e.g. Lane et al., 2008). To the knowledge of the authors, the modeling approach of Pye et al. (2010) is the only global-scale model that parameterizes NO₃ chemistry. Future challenges in constraining the global aerosol budget will likely require creating more nuanced approaches to modeling different regions with ostensibly similar chem-
- istry that has been shown to have diverse effects on aerosol formation.

The Supplement related to this article is available online at doi:10.5194/acpd-15-14923-2015-supplement.

Acknowledgements. J. L. Fry and D. C. Draper gratefully acknowledge funding from the National Center for Environmental Research (NCER) STAR Program, EPA#RD-83539901 as well as the Reed College Class of '21 Award. In addition, we thank Rhiana Meade for development of the RECv1.0 as well as Dean Atkinson for donation of PFA film to build the RECv2.0 used

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

in this study. D. K. Farmer acknowledges the National Science Foundation (AGS 1240611) for support.

References

15

- Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605–4638, doi:10.1021/cr0206420, 2003. 14948
- Atkinson, R., Aschmann, S. M., Arey, J., and Shorees, B.: Formation of OH radicals in the gas phase reactions of O₃ with a series of terpenes, J. Geophys. Res.-Atmos., 97, 6065–6073, doi:10.1029/92JD00062, 1992. 14932, 14951

Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Jimenez, J. L., Day, D. A., De Gouw, J.,

- Cohen, R. C., Baumann, K., Takahama, S., Thornton, J. A., Goldstein, A. H., and Fry, J. L.: NO_y fate at SOAS 2013: organic nitrate aerosol formation via NO₃ + BVOC and comparison to inorganic nitrate aerosol, submitted, 2015. 14926
- Barthelmie, R. J. and Pryor, S. C.: A model mechanism to describe oxidation of monoterpenes leading to secondary organic aerosol: 1. α -pinene and β -pinene, J. Geophys. Res.-Atmos., 104, 23657–23699, doi:10.1029/1999JD900382, 1999. 14930
- Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: The effect of solvent on the analysis of secondary organic aerosol using electrospray ionization mass spectrometry, Environ. Sci. Technol., 42, 7341–7346, doi:10.1021/es801226w, 2008. 14929
- Bateman, A. P., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Applications of highresolution electrospray ionization mass spectrometry to measurements of average oxygen to carbon ratios in secondary organic aerosols, Environ. Sci. Technol., 46, 8315–8324, doi:10.1021/es3017254, 2012. 14929
- Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and
 Ng, N. L.: Secondary Organic Aerosol (SOA) formation from the β-pinene + NO₃ system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys. Discuss., 15, 2679–2744, doi:10.5194/acpd-15-2679-2015, 2015. 14926
 - Carlton, A. G., Pinder, R. W., Bhave, P. V., and Pouliot, G. A.: To what extent can biogenic SOA be controlled?, Environ. Sci. Technol., 44, 3376–3380, doi:10.1021/es903506b, 2010. 14926

14941

- Crounse, J. D., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., and Wennberg, P. O.: Autoxidation of organic compounds in the atmosphere, J. Phys. Chem. Lett., 4, 3513–3520, doi:10.1021/jz4019207, 2013. 14938
- Davidson, C. I., Phalen, R. F., and Solomon, P. A.: Airborne particulate matter and human health: a review, Aerosol Sci. Tech., 39, 737–749, doi:10.1080/02786820500191348, 2005. 14925
- Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T., and Collett, J. L.: Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, J. Geophys. Res.-Atmos., 118, 7389–7399, doi:10.1002/jgrd.50561, 2013. 14930
- Doezema, L. A., Longin, T., Cody, W., Perraud, V., Dawson, M. L., Ezell, M. J., Greaves, J., Johnson, K. R., and Finlayson-Pitts, B. J.: Analysis of secondary organic aerosols in air using extractive electrospray ionization mass spectrometry (EESI-MS), RSC Adv., 2, 2930–2938, doi:10.1039/C2RA00961G, 2012. 14929, 14935
- Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility
 basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303–3318, doi:10.5194/acp-11-3303-2011, 2011. 14937
- Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T.,
- Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476– 479, doi:10.1038/nature13032, 2014. 14925
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dubé, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.-P., Brauers, T., and Cohen, R. C.:
- Dubé, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.-P., Brauers, T., and Cohen, R. C.: Organic nitrate and secondary organic aerosol yield from NO₃ oxidation of β-pinene evaluated using a gas-phase kinetics/aerosol partitioning model, Atmos. Chem. Phys., 9, 1431– 1449, doi:10.5194/acp-9-1431-2009, 2009. 14926
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P.,
 ³⁰ Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO₃ in its generation and degradation, Atmos. Chem.
 Phys., 11, 3879–3894, doi:10.5194/acp-11-3879-2011, 2011. 14926

Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Brown, S. S., Cohen, R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B. L., and Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011, Atmos. Chem. Phys., 13, 8585–8605, doi:10.5194/acp-13-8585-2013, 2013. 14926, 14935 Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

- Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkler, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary organic aerosol formation and organic nitrate yield from NO₃ oxidation of biogenic hydrocarbons, Environ. Sci. Technol., 48, 11944–11953, doi:10.1021/es502204x, 2014. 14926, 14927, 14929, 14933, 14934, 14938, 14939
- 14934, 14938, 14939 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, doi:10.1016/S1352-2310(99)00364-7, 2000. 14925
- 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, doi:10.1021/es990445r, 2000. 14938, 14939
 - Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the Earth's atmosphere, Environ. Sci. Technol., 41, 1514–1521, doi:10.1021/es072476p, 2007. 14925
- ²⁰ 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.-Atmos., 104, 3555–3567, doi:10.1029/1998JD100049, 1999. 14925, 14926, 14939
 - Grosjean, D. and Harrison, J.: Response of chemiluminescence NO_x analyzers and ultraviolet ozone analyzers to organic air pollutants, Environ. Sci. Technol., 19, 862–865, doi:10.1021/es00139a016, 1985. 14928
- 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, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res.-Atmos., 100, 8873–8892, doi:10.1029/94JD02950, 1995. 14925
- Hallquist, M., Wängberg, I., Ljungström, E., Barnes, I., and Becker, K.-H.: Aerosol and product yields from NO₃ radical-initiated oxidation of selected monoterpenes, Environ. Sci. Technol., 33, 553–559, doi:10.1021/es980292s, 1999. 14925, 14926, 14927, 14933, 14938, 14939

14943

- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Sur-
- ratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009. 14925

Haynes, W., Bruno, T. J., and Lide, D. R. (Eds.): CRC Handbook of Chemistry and Physics, 93rd edn. (internet version), CRC Press/Taylor and Francis, Boca Raton, FL, USA, 2012. 14928

- Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, 4, doi:10.1029/2005GL023831, 2005. 14925
- Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell, L. M., Jolleys, M., Fu, T.-M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Mor-
- gan, W. T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.: Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model, Atmos. Chem. Phys., 11, 12673–12696, doi:10.5194/acp-11-12673-2011, 2011. 14925
- Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G.,
 Huff Hartz, K., Petters, M. D., Petäjä, T., Rosenoern, T., and Sullivan, A. P.: A review of the anthropogenic influence on biogenic secondary organic aerosol, Atmos. Chem. Phys., 11, 321–343, doi:10.5194/acp-11-321-2011, 2011. 14925, 14931
- IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Cli mate Change, Cambridge University Press, Cambridge, UK and New York, NY, USA,
- doi:10.1017/CBO9781107415324, 2013. 14925
 Jokinen, T., Sipilä, M., Richters, S., Kerminen, V.-M., Paasonen, P., Stratmann, F., Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H., and Berndt, T.: Rapid autoxidation forms highly oxidized RO₂ radicals in the atmosphere, Angew. Chem. Int. Edit., 53, 14596–14600, doi:10.1002/anie.201408566, 2014. 14938
 - Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593–3624, doi:10.1016/j.atmosenv.2008.01.003, 2008. 14925

Discussion Paper

Discussion Paper

Discussion Paper

Discussion

Paper

- Lane, T. E., Donahue, N. M., and Pandis, S. N.: Effect of NO_x on secondary organic aerosol concentrations, Environ. Sci. Technol., 42, 6022–6027, doi:10.1021/es703225a, 2008. 14940
- Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res.-Atmos., 111, D17305, doi:10.1029/2006JD007050,
- 2006. 14939 McMurry, P. H. and Grosjean, D.: Gas and aerosol wall losses in Teflon film smog chambers, Environ. Sci. Technol., 19, 1176–1182, doi:10.1021/es00142a006, 1985. 14929
- Middleton, P.: Sources of air pollutants, in: Composition, Chemistry, and Climate of the Atmosphere, edited by: Singh, H. B., Van Nostrand Reinhold, New York, 1995. 14925
- Moldanova, J. and Ljungström, E.: Modelling of particle formation from NO₃ oxidation of selected monoterpenes, J. Aerosol Sci., 21, 1317–1333, doi:10.1016/S0021-8502(00)00041-0, 2000. 14926

10

30

10

- 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, doi:10.1021/es052269u, 2006. 14925, 14926, 14939
 Pankow, J.: An absorption-model of gas-particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28, 185–188, 1994. 14933
- Perraud, V., Bruns, E. A., Ezell, M. J., Johnson, S. N., Greaves, J., and Finlayson-Pitts, B. J.: Identification of organic nitrates in the NO₃ radical initiated oxidation of *α*-pinene by atmospheric pressure chemical ionization mass spectrometry, Environ. Sci. Technol., 44, 5887– 5893, doi:10.1021/es1005658, 2010. 14937, 14939
- Perraud, V., Bruns, E. A., Ezell, M. J., Johnson, S. N., Yu, Y., Alexander, M. L., Zelenyuk, A.,
 Imre, D., Chang, W. L., Dabdub, D., Pankow, J. F., and Finlayson-Pitts, B. J.: Nonequilibrium atmospheric secondary organic aerosol formation and growth, P. Natl. Acad. Sci. USA, 109,
 - 2836–2841, doi:10.1073/pnas.1119909109, 2012. 14926, 14930 Pope III, C. A., Bates, D. V., and Raizenne, M. E.: Health effects of particulate air pollution: time for reassessment?, Environ. Health Persp., 103, 472–480, doi:10.2307/3432586, 1995. 14925
- Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NO_x concentration, Environ. Sci. Technol., 39, 7046–7054, 2005. 14926, 14930

14945

- Pye, H. O. T., Chan, A. W. H., Barkley, M. P., and Seinfeld, J. H.: Global modeling of organic aerosol: the importance of reactive nitrogen (NO_x and NO₃), Atmos. Chem. Phys., 10, 11261–11276, doi:10.5194/acp-10-11261-2010, 2010. 14940
- Reis, S., Pinder, R. W., Zhang, M., Lijie, G., and Sutton, M. A.: Reactive nitrogen in atmospheric emission inventories, Atmos. Chem. Phys., 9, 7657–7677, doi:10.5194/acp-9-7657-2009, 2009. 14926
- Rollins, A. W., Browne, E. C., Min, K.-E., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell, L. M., and Cohen, R. C.: Evidence for NO_χ control over nighttime SOA formation, Science, 337, 1210–1212, doi:10.1126/science.1221520, 2012. 14926
- Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J., and Guenther, A.: Monoterpene and sesquiterpene emission estimates for the United States, Environ. Sci. Technol., 42, 1623–1629, doi:10.1021/es702274e, 2008. 14925
- Sander, S., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E.,
 Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and
 Photochemical Data for Use in Atmospheric Studies, Evaluation Number 17, JPL Publication,
 Jet Propulsion Laboratory, Pasadena, CA, USA, 10, 2011. 14948
 - Spittler, M., Barnes, I., Bejan, I., Brockmann, K., Benter, T., and Wirtz, K.: Reactions of NO₃ radicals with limonene and *a*-pinene: product and SOA formation, Atmos. Environ., 40, 116–127, doi:10.1016/j.atmosenv.2005.09.093, 2006. 14926, 14933
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, 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. Phys. Chem. A, 110, 9665–9690, doi:10.1021/jp061734m, 2006. 14935
- ²⁵ VanReken, T. M., Greenberg, J. P., Harley, P. C., Guenther, A. B., and Smith, J. N.: Direct measurement of particle formation and growth from the oxidation of biogenic emissions, Atmos. Chem. Phys., 6, 4403–4413, doi:10.5194/acp-6-4403-2006, 2006. 14929
- Vaughan, S., Canosa-Mas, C. E., Pfrang, C., Shallcross, D. E., Watson, L., and Wayne, R. P.: Kinetic studies of reactions of the nitrate radical (NO₃) with peroxy radicals (RO₂): an indirect source of OH at night?, Phys. Chem. Chem. Phys., 8, 3749–3760, doi:10.1039/B605569A,
 - 2006. 14931 Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene,

14946

Phys. Chem. Chem. Phys., 10, 1009–1022, doi:10.1039/B712620D, 2008. 14929, 14935, 14937

Wangberg, I., Barnes, I., and Becker, K. H.: Product and mechanistic study of the reaction of NO₃ radicals with *α*-pinene, Environ. Sci. Technol., 31, 2130–2135, doi:10.1021/es960958n, 1997. 14939

Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N.: Response of commercial chemiluminescent nitric oxide-nitrogen dioxide analyzers to other nitrogen-containing compounds, Environ. Sci. Technol., 8, 1118–1121, doi:10.1021/es60098a004, 1974. 14928

Winkler, P. M., Ortega, J., Karl, T., Cappellin, L., Friedli, H. R., Barsanti, K., McMurry, P. H.,
 and Smith, J. N.: Identification of the biogenic compounds responsible for size-dependent nanoparticle growth, Geophys. Res. Lett., 39, L20815, doi:10.1029/2012GL053253, 2012.
 14937

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V.,

- de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, P. Natl. Acad. Sci., 112, 37–42, doi:10.1073/pnas.1417609112, 2015. 14926
- Yu, J., Cocker, D., Griffin, R., Flagan, R., and Seinfeld, J.: Gas-phase ozone oxidation of monoterpenes: gaseous and particulate products, J. Atmos. Chem., 34, 207–258, 1999.
 - 14927, 14938, 14939

5

Zhao, J., Ortega, J., Chen, M., McMurry, P. H., and Smith, J. N.: Dependence of particle nucleation and growth on high-molecular-weight gas-phase products during ozonolysis of *α*-pinene, Atmos. Chem. Phys., 13, 7631–7644, doi:10.5194/acp-13-7631-2013, 2013. 14937

14947

	$k \times 10^{17}$ (cm ³ molec ⁻¹ s ⁻¹)	$k_{\rm O_3} \times 10^{17}$ (cm ³ molec ⁻¹ s ⁻¹)	$k_{\rm NO_3} \times 10^{12}$ (cm ³ molec ⁻¹ s ⁻¹)
$NO_2 + O_3$	3.2	-	_
α-pinene	_	8.4	6.2
β -pinene	-	1.5	2.51
∆ ³ -carene	-	3.7	9.1
limonene	-	21	12.2

Table 1. Rate constants at 298 K for $NO_2 + O_3$ (Sander et al., 2011) and for both O_3 and NO_3 with selected monoterpenes (Atkinson and Arey, 2003).

Table 2. Conditions for each chamber experiment.

Expt #	Date	[BVOC] _i ^g	$[O_3]_i$	[NO ₂] ^g	RH	Temp	Notes	
		(ppb)	(ppb)	(ppb)	(%)	(K)		
		u-	pinene				4	
1	19 Dec 2012	780	485	_	33	294	'	
2	5 Jan 2013	680	490	-	20	295	а	
3	16 Jan 2013	590–715	480	510	24	294	a, c	
4	18 Jan 2013	780–960	480	840	22	295	a, d	
5	14 Jan 2013	~400	480	1400	22	294	b, e	
		β-	pinene					
6	7 Jan 2013	370	485	_	40	295	а	
7	23 Jan 2013	470–680	480	530	23	295	a, c	
8	25 Jan 2013	~500	480	910	40	295	a, b, d	
9	21 Jan 2013	~700	480	2000	20	295	b, e	
		Δ-	carene					
10	9 Jan 2013	220	470	_	30	294	а	
11	9 Mar 2013	250–340	470	290	27	295	a, c	
12	13 Mar 2013	400-650	470	590	38	295	a, d	
13	6 Feb 2013	~200	470	900	33	295	b, e	
limonene								
14	11 Jan 2013	470	485	_	20	295	а	
15	23 Mar 2013	340-400	470	360	20	295	a, c	
10	07 Mar 0010	470 500	470	700	20	005	a, d	
10	27 iviar 2013	470-560	470	720	31	295	2 h o	
17	21 Mar 2013	~400	465	1000	26	295	а, ь, е	

^a SOA filter sample collected and analyzed by HPLC-ESI-MS.

^b [BVOC] estimated by scaling available GC-FID data to modeled values, making these estimates more uncertain than others.
 ^c Designated "low NO₂."
 ^d Designated "medium NO₂."
 ^e Designated "high NO₂."

⁹ Values calculated using kinetics model.

14949

Table 3. Maximum aerosol mass yield observed, typically occurring within the first two hours of each experiment. The ranges in the low and medium NO_2 experiments reflect uncertainty in Δ HC due to the RO₂ + RO₂ rate constant.

	Aerosol Mass Yield			
	O ₃ -only	low NO ₂	med NO ₂	
α -pinene β -pinene Δ^3 -carene limonene	28 % 16 % 19 % 22 %	6-7 % ≥ 10-14 % ≥ 15-21 % 39-42 %	0.7–0.8 % ≥ 8–12 % ≥ 12–20 % 36–43 %	

14950

Table 4. Percentage of total BVOC reacted by each oxidant at 2 h into each experiment. In the model, OH is produced from Stabilized Criegee Intermediates from ozonolysis at the following ratios: α -pinene = 0.85; β -pinene = 0.35; Δ^3 -carene = 1.06; limonene = 0.86 (Atkinson et al., 1992). Values from NO₂-containing experiments include two values expressed as *low (high)* where "low" denotes the lower RO₂+RO₂ rate constant limit (10⁻¹⁵ cm³ molec⁻¹ s⁻¹), and "high" denotes the upper limit (10⁻¹² cm³ molec⁻¹ s⁻¹) as described in the Supplement.

	[NO ₂] _i (ppb)	% by NO_3	$\%$ by $\rm O_3$	% by OH
<i>α</i> -pinene	0	0	54	46
·	510	44 (68)	34 (21)	22 (11)
	840	58 (78)	26 (15)	16 (7)
β -pinene	0	0	74	26
	530	77 (94)	18 (5)	5 (1)
	910	81 (95)	15 (4)	4 (1)
∆ ³ -carene	0	0	49	51
	290	62 (92)	21 (5)	17 (3)
	590	63 (95)	20 (4)	17 (1)
limonene	0	0	54	46
	360	45 (74)	34 (18)	21 (8)
	720	59 (85)	26 (11)	15 (4)

14951

Table 5. Minimum $[NO_2]/[BVOC]$ value reported for each monoterpene studied at which NO_3 is expected to dominate nighttime oxidation.

$[NO_2]/[BVOC]$	
2.6	
0.47	
1.2	
6.6	
	[NO ₂]/[BVOC] 2.6 0.47 1.2 6.6

Table 6. Average (± one SD) molecular weight, number of C, O, and N atoms, O / C, and total number of products identified by HPLC-ESI-MS analysis of aerosol collected from O₃ and NO₃ (O₃ + NO₂ + NO₃) oxidation of each monoterpene studied. The difference in average value for each parameter (Δ_{avg}) from each oxidation scheme was also tabulated for each monoterpene.

	<i>a</i> -pinene			β -pinene		
	O ₃	NO ₃	Δ_{avg}	O ₃	NO ₃	Δ_{avg}
MW _{avg}	237.6 ±86.9	233.9 ±81.0	-3.7	212.0 ±88.9	249.3 ±104.3	37.3
$C_{\rm avg}$	13.8 ±5.4	13.2 ±5.0	-0.6	12.0 ±4.5	12.7±4.7	0.7
O _{avg}	2.9 ±1.6	3.1 ±1.7	0.2	2.9 ±2.1	4.2 ±2.6	1.3
Navg	0.29 ±0.53	0.40 ± 0.58	0.11	0.14 ±0.36	0.74 ±0.73	0.60
0/Č	0.22 ±0.11	0.25 ±0.14	0.03	0.23 ±0.12	0.32 ±0.16	0.09
# ID'd	28	43	15	29	66	37
	Δ-carene			limonene		
MW _{avg}	191.7 ±56.9	232.1 ±111.5	40.4	216.9 ±81.2	306.5 ±128.6	89.6
$C_{\rm avg}$	11.0 ±3.1	12.4 ±4.7	1.4	12.3 ±4.2	14.7 ±4.8	2.4
O _{avg}	2.4 ±1.2	3.6 ±3.0	1.2	2.9 ±1.8	5.9 ±4.0	3.0
Navg	0.09 ± 0.30	0.41 ±0.67	0.32	0.18 ±0.46	0.94 ±1.06	0.76
0/°C	0.22 ±0.11	0.27 ±0.14	0.05	0.23 ±0.13	0.39 ±0.23	0.16
# ID'd	32	70	38	34	85	51

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

14953



Figure 1. Structures of monoterpenes used in this study.



Figure 2. Reed Environmental Chamber (REC) schematic for the experiments described here.





Figure 3. Raw total number concentrations (N_{tot}) and total volume concentrations (V_{tot}) at each NO₂ concentration for each monoterpene studied, not corrected for wall losses.



Figure 4. ΔM vs. ΔHC for each experiment. ΔM is corrected for wall losses (described in Supplement). Uncertainty ranges arise from modeled Δ HC values using the range of 10⁻¹⁵ to $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for $k_{\text{RO}_2 + \text{RO}_2}$ for the low and medium NO₂ experiments for each monoterpene. O₃-only experiments do not have an analogous uncertainty range since all O₃ was assumed to react with the monoterpene directly.



Figure 5. Time series of wall loss corrected aerosol mass (right axis) and VOC consumed by each oxidant (left axis) for α -pinene and β -pinene at zero (a, d), low (b, e), and medium (c, f) NO₂ concentrations, highlighting how much aerosol is produced at times dominated by NO₃oxidation (shaded regions). Δ HC values shown are the lower limits calculated using the lowest $RO_2 + RO_2$ rate constant $(10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$, which gives the low limit on how much NO_3 reacts with VOC directly.





Figure 6. Comparison of chromatograms from HPLC-ESI-MS samples of SOA derived from β -pinene ozonolysis with 0 (bottom), 530 (middle), and 910 ppb NO₂ (top). Chromatograms are annotated with speculative structures corresponding to the most intense peaks. Proposed structures are listed in Table S.3 based on products observed in other studies, but may actually be isomers of the structures shown.





