Dear Dr. Laskin,

In this document, we provide our revised manuscript, “Nitrate radical oxidation of γ-terpinene: hydroxy nitrate, total organic nitrate, and secondary organic aerosol yields”, and a point-by-point response to the very careful and thoughtful critiques by the three anonymous referees, in the order the comments were raised. We believe we have satisfactorily responded to all referee comments, which has resulted in a significantly improved manuscript. While no changes were made to our original conclusions, the revised manuscript highlights and expands on relevant gas-phase HO$_2$ chemistry, secondary oxidation reactions, and potentially novel chemistry involving peroxyacyl nitrate epoxidation of olefins in the particle phase, further underscoring the importance of polyolefinic monoterpenes in SOA formation and chemistry. We believe the results presented in this manuscript will make a valuable contribution to the current literature and promote future studies on polyolefinic monoterpene oxidation. We hope you agree that our manuscript is in publishable form.

Our responses to each reviewer comment is provided below showing the reviewer comment in *italics* and reviewer response in normal font. Changes to the manuscript resulting from each reviewer comment are specified in each response to the reviewer by section and line number of the revised manuscript. Additions or modifications to the manuscript are indicated in bold font in the revised manuscript found at the bottom of this document.

We hope you agree that we have completely responded to all reviewer comments and that the paper is now in suitable form for publication. Thank you very much for your consideration.

Sincerely yours,

Jonathan H. Slade Jr., Ph.D.
RESPONSES TO ANONYMOUS REVIEWER #1
The authors greatly appreciate the comments and careful critique by reviewer #1, which have improved the quality of the manuscript. Below we provide a point-by-point response (shown in normal font) to the reviewer’s comments (shown in italic font). Corresponding changes to the manuscript are shown in bold font of the revised version of our manuscript and indicated here based on line number.

Reviewer comment #1: on p. 5 around line 85: Perhaps worth mentioning some other measurements of organic nitrate aerosol in the western US, by TD-LIF at BEACHON 2011 in the Colorado front range (http://www.atmos-chem-phys.net/13/8585/2013/), in various locations by FTIR (http://www.pnas.org/content/108/9/3516.full), and at Blodgett (http://www.atmoschem-phys.net/12/5773/2012/acp-12-5773-2012.pdf). In the first two cases, they are surely likely to be multifunctional, and in the latter case the authors explicitly measure multifunctional nitrates. So I’d avoid the statement that these types of molecules have only been measured in the eastern US.

Author response to reviewer comment #1: We thank the reviewer for providing these references. They have been included in the revised version of the manuscript in lines 87-94.

Reviewer comment #2: General comment: your chamber experiment likely has RO2 + NO3 (or RO2+RO2 where VOC » N2O5) as the dominant fate of the RO2 radical, which may bias to a particular product set. Given that ambient nighttime chemistry may have substantially more RO2 + HO2 reactions, maybe it’s worth speculating on how that would affect your conclusions about partitioning implications.

Author response to reviewer comment #2: We appreciate the reviewer’s suggestion here as our chamber conditions may not represent conditions of all nighttime ambient forest environments. Given that ambient nighttime chemistry may have significantly more RO2+HO2 reactions, it is likely that the organic nitrate product distribution in ambient nighttime air is weighted more towards nitrooxy hydroperoxides. We have included a discussion of the impact of relative amounts of HO2 between our chamber experiments and the ambient environment in sec. 3.3, lines 345-354 in the revised manuscript. We have also updated Fig. 9 (new Fig. 10) to show the evolution in the modeled ratio of NO3/HO2 and comparison to with ratios measured in the field.


Author response to reviewer comment #3: Thank you. We have instead referenced Ng et al., [2017].

Reviewer comment #4: p. 11, line 217: “and likely g-terpinene, lose the nitrate moiety and hence are sufficiently volatile. . .”

Author response to reviewer comment #4: This sentence has been modified accordingly in sec. 3.1, line 237 of the revised manuscript.
Reviewer comment #5: p. 12: why would oxidation of 2nd double bond remove observed ON? Wouldn’t this just double the amount of ON detected since you see each functional group and now there are 2 nitrate final groups? The discussion of the secondary oxidation here is a bit confusing.

Author response to reviewer comment #5: We thank the reviewer for highlighting this point. The expected first-generation oxidation products of γ-terpinene oxidation by NO$_3$ have a remaining double bond intact. Thus second-generation oxidation would likely occur at the position of the remaining double bond, potentially producing a second nitrate functionality, and therefore increase our FTIR-derived ON concentrations instead of decreasing them.

We have clarified in the methods section, lines 164-172, the potential effects of dinitrates on our derived ON concentrations, and sec. 3.2.1, lines 272-273 of the revised manuscript.

Reviewer comment #6: p. 14 VERY high Caero. So this makes your conclusions even more striking! Even at very high loading the yield was quite small.

Author response to reviewer comment #6: The authors agree with the reviewer’s comment. Under these extremely high particle mass loadings, the SOA yields are quite low, e.g., compared to β-pinene+NO$_3$ as shown in Fig. 2 and discussed in the revised manuscript, sec. 3.1, lines 227-229.

Reviewer comment #7: p. 15 line 318 – could also be from RO$_2$ + NO$_3$.

Author response to reviewer comment #7: Since this section refers specifically to hydroxy nitrates, the RO$_2$+NO$_3$ pathway would lead to alkoxy radical formation and NO$_2$. It is unclear how this pathway would lead to hydroxy nitrate formation, therefore we have not made any changes to this particular line.

Reviewer comment #7.5: p. 15 line 365: I think there have recently been some hydroxynitrate quantifications during the FIXCIT chamber studies at Caltech, but to my knowledge none are published yet.

Author response to reviewer comment #7.5: To our knowledge, FIXCIT was designed around measurements of isoprene oxidation products and SOA. While we have included a reference to the FIXCIT campaign in the introduction, lines 92-93 of the revised manuscript, we feel the reference is not suited for this particular section of the manuscript.

Reviewer comment #8: p. 18 line 392: pinonaldehyde yield of 71% is not reported in Fry et al. 2014. . . maybe wrong ref?

Author response to reviewer comment #8: The yield of 71% comes from the supplementary information of Fry et al., [2014]. However, since the pinonaldehyde yield was not discussed in the main text of Fry et al., [2014], we have removed the reference. In addition to the pinonaldehyde yield reported in Wangberg et al., [1997], we now include the Berndt and Böge [1997] reference in sec. 3.5, lines 473-474 of the revised manuscript, which reports a pinonaldehyde yield of 75±6%.

Reviewer comment #9: line 394: elaborate on “similar double bond character” – because each is adjacent to a branch point?
Author response to reviewer comment #9: The reviewer is correct that when we refer to γ-terpinene as having similar double bond character as α-pinene, we mean that both are adjacent to a branch point.

Clarification has been provided in sec. 3.5, lines 474-475 of the revised manuscript.

Reviewer comment #10: p. 19 around lines 404-407: does the MCM produce HO2 in your simulations of the α-pinene chemistry, via the mechanism you suggest, or any other?

Author response to reviewer comment #10: The reaction mechanism scheme, which is based on the MCM reaction scheme for α-pinene+NO3 as described in the supplementary material, does include HO2 as one of the byproducts of keto-nitrate formation. The mechanism also includes consumption of HO2 and formation of the hydroperoxy nitrates by the two α- and β-nitrooxy peroxy radical isomers.

We have updated Fig. 9 (new Fig. 10), as requested in the reviewer’s comment #18, to show the evolution of HO2 based on the mechanism applied in the box model and added a discussion in sec. 3.5, lines 502-511 of the revised manuscript.

Reviewer comment #11: p. 19, lines 415-417: Also assumes that only 1 double bond is reacted, right? Or do you include rates for each in your simple box model?

Author response to reviewer comment #11: The mechanism assumes only one double bond is reacted, but the rate constant for NO3 reaction is for that with γ-terpinene. This assumption does not affect the absolute concentration of the products. No changes have been made to the manuscript.

Reviewer comment #12: p. 20 lines 422-425: could split out as a stacked plot to highlight the sources of NO2, whether N2O5 dissociation or decomposition?

Author response to reviewer comment #12: We appreciate the suggestion here by the reviewer to clarify the contributions of N2O5 decomposition and recycling to the measured concentration of NO2. However, since NO2 is present in thermal equilibrium with N2O5 and only a small fraction is recycled following reaction (1-2%), we feel including a stacked plot doesn’t add much value to Fig. 9 (new Fig. 10) or the manuscript. Besides removing the statement that the agreement between modeled and measured NO2 concentrations in the chamber indicates reaction recycling, no other changes have been made.

Reviewer comment #13: p. 23: is figure 1 wall-loss corrected?

Author response to reviewer comment #13: Figure 1 was not corrected for wall loss. However, we have updated the figure to show wall loss-corrected SOA growth, consistent with our wall loss-corrected SOA yields.

Reviewer comment #14: Fig. 2: comment on uncertainty at low Mo – looks like SOA yield is not very well constrained that low.

Author response to reviewer comment #14: The authors agree with the reviewer. The modeled SOA yield is not very well constrained below an aerosol mass loading of ~30 μg m⁻³. From the
95% confidence intervals, we now define the relative uncertainty in the yield at a mass loading of 10 μg m\(^{-3}\) as +100/-50%.

We have modified the text in sec. 3.1, lines 221-224 of the revised manuscript.

**Reviewer comment #15:** line 491: “the right panel shows the same data on a log scale”

**Author response to reviewer comment #15:** Thank you for the suggested change, we have updated the Fig. 2 description as suggested by the reviewer.

**Reviewer comment #16:** Fig. 4: could be clearer if same exponent on both scales – so the number scale could be different, but as it is now, both the scale and exponent are difference which makes it hard to see the slope. Same for Fig. 5

**Author response to reviewer comment #16:** Thank you for the suggested changes. Figures 4 and 5 (new Fig. 6) have been updated as suggested by the reviewer.

**Reviewer comment #17:** Fig. 6: The O16 superscript in the label is a bit odd looking – necessary?

**Author response to reviewer comment #17:** Thank you. It has been removed (please refer to new Fig. 8).

**Reviewer comment #18:** Fig. 9: related to 2 previous comments, could show modeled HO2 here, if it produces any. And could split out NO2 into recycled vs. N2O5 dissociation sources

**Author response to reviewer comment #18:** Please refer to our response to reviewer comments #10 and #12.
RESPONSES TO ANONYMOUS REVIEWER #2

The authors greatly appreciate the thoughtful critique by reviewer #2, which has greatly improved the quality of the manuscript. Below we provide a point-by-point response (shown in normal font) to the reviewer’s comments (shown in italic font). The resulting additions or alterations to the manuscript are indicated in bold font and provided in an updated version of the manuscript.

Reviewer comment #1: More discussion is needed on why no difference in yields was observed between seed and no seed experiments, particularly for the particle-phase ON yields. Current discussion (lines 253-264) is rather confusing. It is stated that under dry conditions, yields should be same with and without seed. Why? The results appear as if the yields are indistinguishable with and without seed, yet the authors state, "However,..." (line 260). Why would hydrolysis result in different yields with and without seed? What is the particle surface area available in each experiment? What is the surface area of the wall? My concern is that much of the multifunctional ON that would readily partition to the particle-phase is getting lost on chamber walls much faster than it is adsorbing to the particle surface, and that this is the reason why no significant difference in yields are observed. Gas-phase ON loss rate due to walls was determined using the signal for C10H17NO4, which presumably would not partition to the particle-phase (or the walls) as fast as the multifunctional ON species. What is the gas-phase ON wall loss rate if C10H17NO5 was used? Perhaps it may be useful to make a figure that shows the calculated wall loss rate versus O:C or oxygen atom number or whatever for each of the major ON species shown in figure 6. The entire discussion on ON_p yields is also muddied by the statement, "...signals close to the measured background noise..." (line 258). Please clarify.

Author response to reviewer comment #1: We greatly appreciate the reviewer’s insightful comments. The insignificant difference in the particle phase ON yields between the seeded and unseeded experiments may be due to the large fraction of organic material in the particles in both cases, and for the seeded experiments, relative to sulfate. During both the seeded and unseeded experiments, particle mass increased by orders of magnitude following uptake of the oxidation products. Thus, in terms of solubility, for example, the particles are essentially the same. Without sufficient liquid water and insignificant mass fractions of hygroscopic ammonium sulfate in the particles, reactions that remove ON, such as hydrolysis, likely play an insignificant role. To clarify, sec. 3.2.2, lines 282-288 have been modified accordingly.

Wall loss of the multifunctional ON products can be a concern in the derivation of both the gas and particle phase ON yields, particularly over long experimental timescales and when the particle surface area is low relative to the surface area of the chamber walls. The effects of semi-volatile wall loss on the reported gas phase ON yields are now included in the revised manuscript, sec. 3.2.1, lines 267-272. An extended discussion of the variability in particle-phase ON yields, including the effects of wall loss, has been included in sec. 3.2.2, lines 289-298 of the revised manuscript.

Reviewer comment #2: Rindelaub et al. (2015) found hydrolysis of ON in the particle-phase can occur at low RH. Any evidence of hydrolysis during these experiments? Possible that with seed addition, some fraction of ON was lost due to hydrolysis that would not occur without seed?
Author response to reviewer comment #2: Thank you. Please refer to the author response given to the reviewer’s initial comment. It is possible that even at the low relative humidity in our experiments, some hydrolysis, catalyzed by the presence of the hygroscopic (NH₄)₂SO₄ seed and particle-phase HNO₃ could aid in the removal of the nitrate functionality (Rindelaub et al., 2015b). Given the virtually indistinguishable yields between the seeded and unseeded experiments, however, we believe that hydrolysis plays a very minor role in our experiments. We have added a brief discussion of the basis of this in sec. 3.2.2, lines 298-306, from two experiments conducted with added humidity. Regardless, we have accounted for these possible effects in the uncertainty of the particle-phase ON yield as described in the text.

Reviewer comment #3: Clarifications are needed for figure 6. What is the source of the signal between ~150 and ~320 m/z before NO₃ addition? These signals do not vary with and without NO₃ radical. Why? Why is there so much nitric acid in the no NO₃ experiment? What is the large red signal left of the "O4" labeled peak? It is clearly enhanced by NO₃. Why? Are all red signal > 320 m/z even mass? Was there no non-nitrate organic material detected with NO₃ + gamma terpinene? Where is di-nitrate on this spectrum? The sum of all signal appear quite high relative to the reagent ion signal. What is iodide signal with nothing in the bag? Is the CIMS still linear with this much signal, that is, is it approaching reagent ion signal titration? Signals attributed to ON with 10 and 11 oxygen atoms highly questionable

Author response to reviewer comment #3: The source of the peaks in Fig. 6 (new Fig. 8) between m/z ~150 and ~320 are associated with the background. Titration was not a concern as the reagent ion signal remained steady throughout the experiment, decreasing by ≤4% at the highest analyte concentrations. For clarity, we have updated Fig. 8 to show the relative enhancement over the background of several peaks in the presence of NO₃ and provide potential peak assignments for many of the unidentified peaks. While it is possible that the O₉-₁₁ compounds are present in our system, we could not unambiguously make molecular assignments for them based on the mass spectra, and therefore, have removed them from Fig. 8.

Figure 6 (new Fig. 8) has been updated to reflect these changes and the discussion of this figure has been modified in sec. 3.4 lines 399-410.

Reviewer comment #4: The discussion in the "atmospheric implication" section is inconsistent with the rest of the manuscript. These experiments were conducted near dry conditions. Discussion on mechanism focused solely on the higher volatility hydroxynitrates, not the multifunctional stuff (species with O=6, 7, 8 atoms in figure 6) that likely make up much of the ON mass in the particle-phase. Low yields all around were found. But the implication section still discusses what this may mean for SOA formation at high RH.

Author response to reviewer comment #4: Thank you. We have added a section to the atmospheric implications regarding likely chemistry under atmospheric conditions, lines 521-523 and lines 530-536. A new figure (new Fig. 7) has been included, which reflects this chemistry.

Reviewer comment #5: What was the relevance of ESI MS/MS to this work? Is the hydroxynitrate distinguishable from hydroperoxynitrate?
**Author response to reviewer comment #5:** We appreciate the reviewer’s comment as we felt we have not sufficiently highlighted the importance of our offline analysis of aerosol filter samples. While not used quantitatively, ESI MS/MS was applied to test for the presence of specific organic nitrate compounds and other oxidation products that we hypothesized were in the particle phase. This served, in part, as a means for support of the proposed mechanism shown in Fig. 8 (new Fig. 5). The hydroperoxy nitrate was distinguishable from the hydroxy nitrate based on its m/z. While we did not have a standard of the hydroperoxy nitrate to ensure the retention times matched that which was observed, we could, based on mass spectra and tandem mass spectra rankings, identify the chemical formula for each m/z.

We have provided clarification in the supplementary section.

**Reviewer comment #6:** The detection of large signal that may be from a hydroperoxy nitrate is intriguing. Schwantes et al. [2015 JPAa] also discussed this RO2+HO2 nighttime pathway (for isoprene). If the signal consistent with C10H17NO5 are in fact epoxides and not hydroperoxides, how would uptake differ with and without seed? What was pH of the seed particles?

**Author response to reviewer comment #6:** The reviewer raises an interesting point regarding uptake of epoxides versus hydroperoxides as a function of seed and seed particle acidity. It is not entirely clear from a mechanistic standpoint how an epoxide would be produced in the gas phase from γ-terpinene oxidation by NO$_3$. Epoxides could, however, be produced in the condensed phase, for example, through a peroxyacyl nitrate (e.g. the corresponding PAN compound that might be produced from NO$_3$ reaction with terpinaldehyde), which could selectively epoxidize the remaining double bond on the hydroxy nitrate, as shown to be a very efficient epoxidation process by Darnall and Pitts (1970). Such a thermal reaction would be necessary for the dark chemistry studies here, as the isoprene epoxidation reported by Surratt et al (2010) requires OH oxidation of the precursor. Applying the Extended Aerosol Inorganics Model (E-AIM) (http://www.aim.env.uea.ac.uk/aim/aim.php), we estimate a pH ~5.5 for the (NH$_4$)$_2$SO$_4$ seed particles under saturated conditions becoming slightly more acidic as the relative humidity is decreased.

We have added a discussion in sec. 3.3, lines 354-368 of the revised manuscript regarding the pH of the particles, and the potential for condensed phase epoxidation and hydrolysis to produce species like a C10H17NO5 poly-ol, as shown in the new Fig.7.

**Reviewer comment #7:** To which alpha-pinene isomers of hydroxynitrate was the iodide CIMS calibrated? Include numbers for each isomer in table. Would you expect much variability from isomer to isomer? Would you expect much variability in the sensitivity to alpha-pine derived versus gamma-terpinene derived ON?

**Author response to reviewer comment #7:** We addressed this limitation in the original manuscript lines 354-363 and included the structure of the isomer in supplementary Fig. S4. The detailed synthesis and characterization of this isomer has been detailed in Rindelaub et al. (2016) and the supplementary information for that text. We have updated the text where applicable to clarify that we calibrate for only one isomer of α-pinene hydroxy nitrate.
Reviewer comment #8: Seed particles introduced into the chamber were \(\sim 100\) nm. But the particle filter had pore size 1 micron.

Author response to reviewer comment #8: The filters were 1 μm pore size polytetrafluoroethylene (PTFE), which boasts a collection efficiency for particles between 0.01 μm and 1 μm of \(\sim 100\%\) (Burton et al., 2007). We have updated the methods section in lines 178-176 of the revised manuscript.

Reviewer comment #9: What was the contribution of di-nitrates to total ON? How do you account for di-nitrates with FTIR? Can FTIR distinguish mono- from di-nitrates? How does this affect the way in which ON yield is calculated?

Author response to reviewer comment #9: This is a good question. We did not differentiate mono- from di-nitrates using FTIR as the asymmetric -NO₂ stretch is not specific to any particular organic nitrate but all organic nitrates (Roberts, 1990). This could result in an overestimation in the reported ON yields as di-nitrates are expected to absorb more than the mono-nitrates in the wavelength region of interest. However, given the relative rate constants of alkoxy radical reaction with NO₂ (\(\sim 10^{-11}\) cm³ s⁻¹) and O₂ (\(\sim 10^{-14}\) cm³ s⁻¹) (Atkinson et al., 1982) and the relative concentrations of NO₂ (\(\sim 8\times10^{12}\) cm⁻³ maximum) and O₂ (\(\sim 5\times10^{18}\) cm⁻³) in the chamber, we expect an insignificant contribution from first-generation di-nitrates (<0.2%). Some contribution of secondary oxidation to di-nitrates (~10%) is possible, based on the relative rates of first-generation to second-generation monoterpene oxidation.

We have updated the Methods section in lines 164-172 of the revised manuscript to address the potential influence of di-nitrates on the reported ON yields.

Reviewer comment #10: "Teflon" (line 158) is trademark product that is similar to PTFE. So unless the filter is from Chemours that manufactures "Teflon", the appropriate description is PFA or PTFE or whatever

Author response to reviewer comment #10: Where applicable, we have removed “Teflon” and replaced with PTFE or PFA.
RESPONSES TO ANONYMOUS REVIEWER #3
The authors greatly appreciate the careful review by reviewer #3. Below we provide a point-by-point response (shown in normal font) to the reviewer’s comments (shown in italic font). The resulting additions or alterations to the manuscript are indicated in bold font in an updated version of the manuscript.

Reviewer comment #1: The introduction is lacking sufficient references to past work and in some instances misrepresents past work. For instance, the recent review by Ng et al. (2017) should be included. Additionally, multifunctional nitrates have been identified in locations other than the Eastern US (line 84). A few (non-comprehensive) examples include Beaver et al. (2012), Rollins et al. (2013), and Yan et al. (2016).

Author response to reviewer comment #1: Thank you. See our response to the first comment from reviewer #1. We have updated the introduction to include several other locations where multifunctional organic nitrates have been measured.

Reviewer comment #2: Some discussion on the fate of the peroxy radical and differences/similarities in between the chamber and the atmosphere is needed. In particular, it is likely that the RO2+HO2 is under-represented in the chamber experiments. How would this influence yields and the discussion in the “atmospheric implications” section? The model based on the master chemical mechanism could help inform this question.

Author response to reviewer comment #2: This is a good question and similar to the second comment raised by reviewer #1. For more details, please refer to the author response given to reviewer #1 and updated Fig. 9 (new Fig. 10). In short, we have updated the section on aerosol partitioning to address how differences in HO2 between our experiments and the ambient environment affects interpretation of the SOA yield and formation of organic hydroperoxides. Moreover, Fig. 10 has been updated to show modeled HO2 and NO3/HO2 ratios in the reaction chamber.

Reviewer comment #3: The in-line reference formatting is inconsistent and do not follow the journal standards. In particular, first initials are included in the in-line references for several authors.

Author response to reviewer comment #3: We have fixed this typo in the revised manuscript.

Reviewer comment #4: Table 1: What is difference between the experiments on 11/12/15 and 11/18/15? They have similar deltaBVOC and ON yields but very different SOA yields. It would be useful to include the experiment length and the NO2 concentration for each experiment as well. This could help explain some of the variability seen in Figures 3-5.

Author response to reviewer comment #4: We have updated table 1 to include the experimental time and concentration of NO2 when it was measured. Considering the significant difference in NO2 concentrations for these two periods, under high NOx conditions (11/12/15 experiment), new particle formation or aerosol growth may be suppressed (lower SOA yield) due to competitive chemistry of peroxy radicals between NO3 and HO2, with the RO2+NO3 pathway leading to more
volatile reaction products. Similar observations have been made, for example, during the ozonolysis of α-pinene under high NOx conditions (Presto et al., 2005).

We have modified the sec. 3.3 heading and provided discussion of the influence of high NO3 concentrations and the fate of RO2 in sec. 3.3, lines 368-375 of the revised manuscript.

Reviewer comment #5: Figure 1: color scale missing

Author response to reviewer comment #5: Figure 1 has been updated to include color scale.

Reviewer comment #6: Figure 2: caption should say log scale (omit x-axis).

Author response to reviewer comment #6: We have removed “x axis” in the caption.

Reviewer comment #7: Figure 3/associated discussion lines 236-250: The data at deltaBVOC less than 300 ppb appears to be more scattered than the confidence interval might suggest. How much is this fit being influenced by the data points at high deltaBVOC? Or is some of the data at lower deltaBVOC influenced by more secondary oxidation? Some information on if the NO3 concentrations were similar/very different would be very helpful here.

Author response to reviewer comment #7: Thank you for the suggestion. The reviewer is correct that the 95% confidence intervals of the fit do not capture the variability, e.g., at ΔBVOC ~ 200 ppb, and the data points above ΔBVOC ~ 300 ppb do lead to an enhancement in the yield. The exact cause of the data variability below ΔBVOC ~ 300 ppb is not entirely clear, but may be a combination of larger relative uncertainties in ΔON and ΔBVOC at lower ΔBVOC and different NO3 concentrations and experimental timescales.

We have included a discussion of the potential causes of the variability in Fig. 3 in sec. 3.2.1, lines 264-273 of the revised manuscript.

Reviewer comment #8: Figure 4: Please include the +2% slope as well that is stated on line 263.

Author response to reviewer comment #8: We have modified the slopes presented in Figs. 4, 5 (new Fig. 6) and 7 (new Fig. 9), to reflect those presented in the main text.

Reviewer comment #9: Figure 6: Please label the hydroxynitrate peak used for the yield calculation. What is the source of the peaks from m/z 200-330 that appear in both experiments? Is the large peak at m/z 190 nitric acid? If so, what is the source in the absence of NO3? Are the O9, O10, and O11 signals real? This seem difficult to identify and are difficult to interpret in the figure in the current form. This figure may benefit from a zoomed in panel of the region of interest and specific identification of the ions discussed in the manuscript.

Author response to reviewer comment #9: Similar comments were made by reviewer #2. Please see our response to their comment #3 for more details. Briefly, the signals between m/z 200 and 330 are attributed to the background. We include a new trace in Fig. 6 (shown in black in new Fig. 8) that shows the enhancement over the background following addition of NO3 to the chamber. We have removed the O9-11 assignments as they could not be unambiguously verified. The hydroxy nitrate peak used for the yield calculation is now stated in the Fig. 8 description.
Reviewer comment #10: Lines 75-80: I find this explanation confusing and more elaboration is needed. The NO3 oxidation of both a-pinene and b-pinene lead to tertiary peroxy radicals.

Author response to reviewer comment #10: The authors agree with the reviewer here that this statement is too general and does not fully explain the differences in yields observed for monoterpenes that also lead to tertiary peroxy radical formation (Fry et al., 2014).

We have provided clarification in the Introduction section, lines 78-84 of the revised manuscript.

Reviewer comment #11: Line 95: “. . .potential for ON and SOA formation are better understood.” Better understood compared to what?

Author response to reviewer comment #11: This should instead read “…better studied compared to other monoterpenes…” Lines 105-106 of the revised manuscript reflect this change.

Reviewer comment #12: Line 133: Why not use the density of ammonium sulfate?

Author response to reviewer comment #12: The reviewer is correct that for the seeded experiments, initial particle density should be that of (NH₄)₂SO₄ of ~1.7 g cm⁻³. We have recalculated the initial seed particle mass concentration based on a density of 1.7 g cm⁻³. Leaving the density of the SOA as 1.2 g cm⁻³ has resulted in a slight but insignificant decrease in ΔM and SOA yields for the (NH₄)₂SO₄ seeded experiments as presented in Table 1 and Fig. 2.

Reviewer comment #13: Line 245-246: Wouldn’t some fraction of this yield dinitrates? How is that accounted for in this calculation?

Author response to reviewer comment #13: We have clarified this limitation in the revised manuscript as detailed in our response to comment #9 by reviewer #2.

Reviewer comment #14: Lines 256-258: This discussion should be elaborated on and clarified. The largest amount of particulate ON measured also corresponds to some of the largest scatter which seems somewhat inconsistent with the given explanation.

Author response to reviewer comment #14: For more details, please see comments #1 and #2 by reviewer #2 and our response to comment #7 here. In short, we have updated the discussion to include the potential influence of hydrolysis, secondary oxidation, and different RO₂ loss pathways at variable NO₃ concentrations in the chamber.

Reviewer comment #15: Line 317: should be “nitrooxyperoxy”

Author response to reviewer comment #15: Thank you, we have fixed this typo.

Reviewer comment #16: Line 408-409: Since a-pinene is being used as a surrogate for γ-terpinene, I assume that the assumption is that only one of the double bonds is reacting. Is this correct or is further oxidation considered?

Author response to reviewer comment #15: The reviewer is correct, we assume that only one of the double bonds of γ-terpinene reacts with NO₃. Please refer to comment #11 by reviewer #1 for more detail.
Nitrate radical oxidation of γ-terpinene: hydroxy nitrate, total organic nitrate, and secondary organic aerosol yields

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Abstract

Polyolefinic monoterpenes represent a potentially important but understudied source of organic nitrates (ON) and secondary organic aerosol (SOA) following oxidation due to their high reactivity and propensity for multi-stage chemistry. Recent modeling work suggests that the oxidation of polyolefinic γ-terpinene can be the dominant source of nighttime ON in a mixed forest environment. However, the ON yields, aerosol partitioning behavior, and SOA yields from γ-terpinene oxidation by the nitrate radical (NO$_3^-$), an important nighttime oxidant, have not been determined experimentally. In this work, we present a comprehensive experimental investigation of the total (gas + particle) ON, hydroxy nitrate, and SOA yields following γ-terpinene oxidation by NO$_3^-$ under dry conditions. The hydroxy nitrate yield = 4(+1/-3)%, total ON yield = 14(+3/-2)%, and SOA yield ≤ 10% under atmospherically-relevant particle mass loadings, similar to those for α-pinene + NO$_3^-$ chemistry. Using a chemical box model, we show that the measured concentrations of NO$_2$ and γ-terpinene hydroxy nitrates can be reliably simulated from α-pinene + NO$_3^-$ chemistry. This suggests that NO$_3^-$ addition to either of the two internal double bonds of γ-terpinene primarily decomposes forming a relatively volatile keto–aldehyde, reconciling the small SOA yield observed here and for other internal olefinic terpenes. Based on aerosol partitioning analysis and identification of speciated particle-phase ON applying high-resolution liquid chromatography–mass spectrometry, we estimate that a significant fraction of the particle-phase ON has the hydroxy nitrate moiety. This work greatly contributes to our understanding of ON and SOA formation from polyolefin monoterpenic oxidation, which could be important in the northern continental U.S. and Midwest, where polyolefinic monoterpenic emissions are greatest.

1. Introduction
The oxidation of volatile organic compounds (VOCs) is a major pathway in the production of secondary organic aerosol (SOA), which can represent up to ~60% of the total submicron aerosol mass, depending on location (Hallquist et al., 2009; Riipinen et al., 2012; Glasius and Goldstein, 2016). Aerosols impact climate by scattering and absorbing radiation as well as modifying cloud optical properties, and can adversely affect human health (Stocker et al., 2013). A large fraction of the total OA budget derives from the oxidation of biogenic VOCs (BVOCs), including isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) (Hallquist et al., 2009; Spracklen et al., 2011). Together, these naturally emitted compounds account for ~60% of the global BVOC budget (Goldstein and Galbally, 2007; Guenther et al., 1995). In particular, monoterpenes, comprising ~11% of the total global BVOC emissions (Guenther, 2002), represent a viable source of SOA following oxidation (Griffin et al., 1999; Lee et al., 2006). However, atmospheric models routinely underestimate the global SOA burden (Kokkola et al., 2014), causing a potential order of magnitude error when predicting global aerosol forcing (Goldstein and Galbally, 2007), and thus the sources and mechanisms responsible for SOA formation require further study.

VOC oxidation produces an array of semi-volatile or organic aerosol precursors, including organic nitrates (RONO₂), herein referred to as “ON”, in the presence of NOₓ (i.e., NO+NO₂) (Kroll and Seinfeld, 2008; Rollins et al., 2010b; Rollins et al., 2012; Darnall et al., 1976). By sequestering NOₓ, ON can perturb ozone concentrations globally (Squire et al., 2015). Moreover, as NOₓ concentrations are expected to decrease in the future (von Schneidemesser et al., 2015), ambient concentrations of NOₓ and thus O₃ will become increasingly sensitive to ON formation (Tsigeridis and Kanakidou, 2007). Monoterpenes contribute significantly to the formation of ON and SOA, especially during nighttime in the presence of nitrate radicals (NO₃), when isoprene concentrations are negligible and the photolytic and NO reaction sinks of NO₃ are cut off (see Ng...
et al. (2017) and references therein). It is estimated that monoterpene oxidation by NO$_3$ may account for more than half of the monoterpene-derived SOA in the U.S., suggesting that ON is a dominant SOA precursor (Pye et al., 2015). However, their formation mechanisms and yields following oxidation by NO$_3$ are not as well constrained as those from OH and O$_3$ oxidation (Hoyle et al., 2011), and previous studies have focused on the NO$_3$ oxidation of only a few monoterpenes (Fry et al., 2014), but almost exclusively on mono-olefinic terpenes such as α- and β-pinene (Boyd et al., 2015; Spittler et al., 2006; Wangberg et al., 1997; Fry et al., 2009; Berkemeier et al., 2016).

An important detail is the relative amount of hydroxy nitrates produced, as the -OH group contributes greatly to water solubility (Shepson et al., 1996), and uptake into aqueous aerosol followed by continuing chemistry in the aqueous phase, which can be an important mechanism for SOA production (Carlton and Turpin, 2013).

A major challenge regarding our understanding of SOA formation from monoterpene oxidation is that there are several isomers of monoterpenes with very different structural characteristics that can exhibit very different yields of SOA following oxidation (Fry et al., 2014; Ziemann and Atkinson, 2012). For example, the SOA mass yield from the NO$_3$ oxidation of α-pinene, which contains one endocyclic double bond, is ~0% under atmospherically relevant particle mass loadings, whereas that from β-pinene, which contains one terminal double bond, is 33% under the same experimental conditions (Fry et al., 2014). Limonene, with one tertiary endo- and one terminal exocyclic double bond, also exhibits relatively larger SOA mass yields following oxidation by NO$_3$ (Fry et al., 2014; Spittler et al., 2006). Because NO$_3$ oxidation of α-pinene primarily leads to tertiary peroxy radical formation (Wangberg et al., 1997), the initially formed alkoxy radical rearranges to a ketone and decomposes the nitrooxy group, releasing NO$_2$ and forming a keto–aldehyde, which has higher saturation vapor pressure compared to its ON analogue.
However, decomposition of the nitrate is not exclusive for all tertiary alkoxy radicals following NO$_3$ oxidation as it may also depend on the structure of the adjacent bond. Based on structure–activity relationships, a β-alkyl substitution is expected to destabilize the adjacent bond more than a β-nitrate substitution (Vereecken and Peeters, 2009). In the case of β-pinene or sabinene, for example, the expected decomposition pathway of the alkoxy radical leaves the nitrooxy group intact to form a keto–nitrate (Fry et al., 2014). SOA yields have also been shown to be strongly dependent on the total (gas + particle) yield of ON. Owing to their low saturation vapor pressures, multifunctional ON such as the hydroxy nitrates are thought to contribute significantly to SOA formation (Rollins et al., 2010a;Rollins et al., 2010b;Lee et al., 2016), and have been the focus of several laboratory and field research campaigns including the BEACHON 2011 field study in the Colorado front range (Fry et al., 2013), the BEARPEX 2009 study at the Blodgett forest site in the Western foothills of the Sierra Nevada (Beaver et al., 2012), the PROPHET and SOAS field studies in the upper Midwest and southeastern US (Xiong et al., 2015;Lee et al., 2016;Grossenbacher et al., 2004), and the Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT) (Nguyen et al., 2014). These ON can rapidly undergo aqueous-phase processing, especially under acid-catalyzed conditions, to form diols and organosulfates (Jacobs et al., 2014;Rindelaub et al., 2015a;Rindelaub et al., 2016;Surratt et al., 2008), which not only complicates quantification of organic nitrates in the aerosol phase (Russell et al., 2011), but affects product saturation vapor pressure and thus aerosol formation, represents a sink for NO$_3$, and may affect the hygroscopic properties of organic aerosol (Suda et al., 2014). However, considering there are only a limited number of studies that have specifically investigated the yield of hydroxy nitrates, namely following OH and NO$_3$ oxidation of isoprene (Chen et al.,
1998; Lockwood et al., 2010; Xiong et al., 2015) and α-pinene (Rindelaub et al., 2015a; Wangberg et al., 1997), further measurements of their yields and role in aerosol formation from the oxidation of other terpenoids is critical.

In the southeastern U.S., α- and β-pinene tend to dominate monoterpene emissions (Geron et al., 2000), and their potential for ON and SOA formation are better-studied compared to other monoterpenes (Ayres et al., 2015; Lee et al., 2016). However, in other regions of the U.S., polyolefinic monoterpenes such as terpinene, ocimene, and limonene can be present in much greater proportions than in the southeastern US, which may be in part due to the relatively smaller abundance of the α- and β-pinene emitter southern pine, but also more polyolefinic monoterpene emitters, including Juniperus scopulorum, a common cedar and γ-terpinene emitter in the Midwestern US (Geron et al., 2000). In particular, model simulations suggest that the oxidation of γ-terpinene, comprising two substituted endocyclic double bonds, can contribute as much as α- and β-pinene to nighttime organic nitrate production in a mixed northern hardwood forest (Pratt et al., 2012). Those authors also showed that NO$_3$ reaction with BVOCs is important in the daytime. However, the ON and SOA yields following NO$_3$ oxidation of γ-terpinene have not been determined in laboratory studies.

Here we present a comprehensive laboratory investigation of the hydroxy nitrate, total gas and particle-phase ON, and SOA yields from the NO$_3$ oxidation of γ-terpinene. For the hydroxy nitrate yield experiments, a surrogate standard compound was synthesized as presented in the supplemental information of Rindelaub et al. (2016), enabling quantitative determination of its yield using a chemical ionization mass spectrometer (CIMS). This work contributes to a broader understanding of SOA formation from the oxidation of polyolefinic monoterpenes, and the role of NO$_3$ oxidation chemistry in the sequestration of NO$_x$. 

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2. Methods

Yield experiments were conducted in a 5500 L photochemical reaction chamber with Teflon walls and perfluoroalkoxy (PFA)-coated endplates, in the dark (Chen et al., 1998). Briefly, the chamber was cleaned by flushing several times with ultra-zero (UZ) air in the presence of ultra-violet light. Experiments were conducted in a dry atmosphere (relative humidity < 1%) and at ambient temperature (~295 K). A total of 13 independent yield experiments were conducted over a range of initial γ-terpinene concentrations in the presence of N₂O₅ with and without (NH₄)₂SO₄ seed particles. N₂O₅ was produced in a dried glass vessel and crystallized at 195 K in a custom-made glass trap following thermal equilibrium with NO₂ and O₃, as indicated in reactions (1) and (2) below.

\[
\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \quad (1)
\]

\[
\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5 \quad (2)
\]

First, the BVOC was transferred to the chamber with UZ air via injection through a heated glass inlet and polytetrafluoroethylene (PTFE) line. For the seeded experiments, (NH₄)₂SO₄ particles were generated by passing an aqueous solution through a commercial atomizer (Model 3076, TSI, Inc.) and subsequently dried through a diffusion dryer prior to entering the reaction chamber. The seed particles were polydisperse with a range in the geometric mean diameter, \(D_{p,g}\), of 57 nm to 94 nm and geometric standard deviation, \(\sigma_g\), of 1.39 to 1.91. Total seed number and mass concentrations were in the range 0.61-5.15\times10^4 \text{ cm}^{-3} \text{ and 8-48 \mu g m}^{-3}, \text{ respectively, assuming a seed particle density of 1.7 g cm}^{-3}. \text{ Yield experiments were initiated (time = 0) by injecting N}_2\text{O}_5 \text{ into the chamber with a flow of UZ air over the crystalline N}_2\text{O}_5 \text{. The reactants were allowed to mix continuously in the chamber with a fan, and the reaction was terminated when no less than}
10% of the γ-terpinene remained to limit secondary particle-phase or heterogeneous NO₃ chemistry.

Real-time measurements were made using several instruments: γ-terpinene concentrations were measured with a gas chromatograph-flame ionization detector (GC-FID; HP-5890 Series II), which was calibrated using a commercial γ-terpinene standard dissolved in cyclohexane. NO₂ concentrations were measured with a custom-built chemiluminescence NOₓ analyzer (Lockwood et al., 2010), and a scanning mobility particle sizer (SMPS; Model 3062, TSI, Inc.) was used to determine size-resolved particle mass concentrations. No direct concentration measurements of NO₃ were made. The hydroxy nitrates were measured online continuously using an iodide-adduct chemical ionization mass spectrometer (CIMS) (Xiong et al., 2015; Xiong et al., 2016). To quantify the production of monoterpene hydroxy nitrates, the CIMS was calibrated with a purified standard of an α-pinene-derived hydroxy nitrate synthesized in-house via nitrification of α-pinene oxide (Sigma–Aldrich, 97%) using Bi(NO₃)₃·5H₂O (Rindelaub et al., 2016). The concentration of the purified hydroxy nitrate was verified via two complementary methods: ¹H-NMR and FTIR, and the structure was verified using ¹³C-NMR, as presented in the supplementary information of Rindelaub et al. (2016). The total ON yields and concentration of the standard were determined via FTIR measurement of the asymmetric –NO₂ stretch located at ~1640 cm⁻¹ using tetrachloroethylene (Sigma–Aldrich, HPLC grade, ≥99.9%) as the solvent (Rindelaub et al., 2015a). We note that the FTIR approach cannot distinguish mono- from poly-nitrated organics. However, given the relatively low concentrations of NO₂ compared to O₂ in the chamber and their rate constants with alkoxy radicals (Atkinson et al., 1982), first-generation di-nitrates constitute an insignificant fraction of ON (<0.2%). Second-generation di-nitrates from NO₃ reaction at the remaining double bond on γ-terpinene, however, may account for a maximum of ~10% of
the total ON based on the relative rates of primary to secondary monoterpane oxidation reactions. Thus the uncertainties for our reported yields include a component from this uncertainty (10%) in the fraction of the nitrates that are dinitrates. The total gas-phase ON yields were determined with FTIR following the sampling of chamber air through an annular denuder (URG-200) coated with XAD-4 resin and extraction from the denuder walls with tetrachloroethylene as in a previous study (Rindelaub et al., 2015a). Aerosol particles were collected on 47 mm PTFE filters (1 μm pore size; ~100% collection efficiency) housed in a cartridge connected to the denuder exit. The collection efficiency of the denuder walls for gas-phase organic nitrates was determined to be >98% based on measurements of the concentration of 2-ethyl-hexyl-nitrate (Sigma–Aldrich, 97%) before and after the denuder with the GC-FID. The particle transmission efficiency was determined to be >98% by measuring the number concentration of particles before and after the denuder with the SMPS.

Wall loss and dilution corrections were applied to both the SOA and ON yields accounting for the time required to sample through the denuder. Following several of the experiments, the SOA concentration was measured as a function of reaction time with the wall with an average wall loss rate constant, $k_{\text{wall,SOA}} = 9 \times 10^{-5} \, \text{s}^{-1}$. The gas-phase ON wall loss rate was determined based on the evolution of the CIMS-derived monoterpane hydroxy nitrate (M=C_{10}H_{17}NO_{4}) signal ([M+I]^+; $m/z = 342$) following an experiment, in which we obtained $k_{\text{ONg}} = 2 \times 10^{-5} \, \text{s}^{-1}$, as shown in Fig. S1.

Selected filter extracts from two separate chamber experiments were analyzed for their chemical composition via ultra-performance liquid chromatography electrospray ionization time-of-flight tandem mass spectrometry (UPLC-ESI-ToF-MS/MS, Sciex 5600+ TripleToF with Shimadzu 30 series pumps and autosampler) to identify potential ON species in the particle phase from γ-terpinene oxidation by NO3. The samples were first dried with ultra-high purity nitrogen
and then extracted with a 1:1 v:v solvent mixture of HPLC-grade methanol and 0.1% acetic acid in nanopure H₂O, which has been used successfully as a solvent system for identifying multifunctional organonitrate and organosulfate species (Surratt et al., 2008).

### 3. Results and Discussion

#### 3.1. SOA yields

Mass-dependent SOA yields ($Y_{SOA}$) were derived from both seeded and unseeded experiments and defined here as the change in aerosol mass concentration ($ΔM$ in µg m⁻³) relative to the concentration of BVOC consumed ($Δ$BVOC in µg m⁻³), i.e., $Y_{SOA} = ΔM/Δ$BVOC. $ΔM$ was derived from individual SOA growth curves as shown in Fig. 1. Here the initial mass is defined as the average SMPS-derived particle mass in the chamber prior to N₂O₅ injection, and the final mass is derived from the maximum of the SOA growth curve when $Δ$BVOC stabilizes, as shown in Fig. S2. Note that under these experimental conditions, SOA formation occurs rapidly, limited on the short end by the thermal decomposition e-folding lifetime of N₂O₅ (~30 s at 295 K) and the e-folding lifetime of NO₃ reaction with γ-terpinene (few milliseconds assuming a rate constant of $2.9\times10^{11}$ cm³ molecule⁻¹ s⁻¹), and on the long end by the time scale for heterogeneous uptake of N₂O₅ of several hours assuming an uptake coefficient at low relative humidity of $10^{-4}$ (Abbatt et al., 2012).

$Y_{SOA}$ with and without seed particles as a function of particle mass loading are depicted in Fig. 2. The curve shows that under low mass loadings, the yields are less than under high mass loadings, indicative of absorptive partitioning (Hao et al., 2011; Odum et al., 1996). To model the measured $Y_{SOA}$ as a function of particle mass loading, we apply an absorptive partitioning model following the method of Odum et al. (1996), as shown in Eq. (1).
\[ Y_{\text{SOA}} = M_0 \sum_i \left( \frac{\alpha_i K_{\text{om},i}}{1 + K_{\text{om},i} M_0} \right) \]

Here, \( \alpha_i \) is a proportionality constant describing the fraction of product \( i \) in the aerosol phase, \( M_0 \) is the aerosol mass concentration, and \( K_{\text{om},i} \) is the absorptive partitioning coefficient of the absorbing material. Assuming a two-product model, the best fit values are \( \alpha_1 = 0.94 \), \( K_{\text{om},1} = 7.9 \times 10^{-4} \), \( \alpha_2 = 0.33 \), and \( K_{\text{om},1} = 2.6 \times 10^{-2} \). Extending this model to a conservative ambient mass loading of 10 \( \mu g \) m\(^{-3}\), characteristic of biogenic SOA-impacted environments (Fry et al., 2014), the SOA yield is \(~10\%\). We caution that the model is not very well constrained at low mass loadings due to the limited number of data points below 30 \( \mu g \) m\(^{-3}\). From the 95\% confidence intervals, a conservative estimate of the relative uncertainty in the yield at 10 \( \mu g \) m\(^{-3}\) is +100/-50\%. In contrast, at mass loadings >500 \( \mu g \) m\(^{-3}\), which is more relevant in highly polluted urban areas such as those along the coast of India (Bindu et al., 2016), \( Y_{\text{SOA}} \) can be as large as \(~50\%\). For comparison, \( Y_{\text{SOA}} \) of other reaction systems applying the absorptive partitioning values derived from those experiments are plotted along with our experimental data in Fig. 2. The \( \gamma \)-terpinene + NO\(_3\) \( Y_{\text{SOA}} \) are significantly less than those involving \( \beta \)-pinene, an important contributor to SOA formation predominately in the southeastern U.S (Boyd et al., 2015). However, at relatively low particle mass loadings, \( Y_{\text{SOA}} \) for NO\(_3\) + \( \gamma \)-terpinene is comparable to those derived from the OH oxidation of \( \gamma \)-terpinene and \( \alpha \)-pinene (Griffin et al., 1999;Lee et al., 2006). Interestingly, our measured \( Y_{\text{SOA}} \) at comparable mass loadings are also within the reported range of \( Y_{\text{SOA}} \) from the NO\(_3\) oxidation of \( \alpha \)-pinene of 0-16\% (see Fry et al. (2014) and references therein), which are relatively small compared to other monoterpene + NO\(_3\) reaction systems, which range from 13\% to 65\% for \( \beta \)-pinene, limonene, and \( \Delta \)-3-carene (Ng et al., 2017). The studies reporting low \( Y_{\text{SOA}} \) also report relatively low ON yields and high ketone yields, suggesting that the NO\(_3\) oxidation...
products of α-pinene, and likely γ-terpinene, lose the nitrate moiety and hence are sufficiently volatile and do not contribute significantly to SOA formation under atmospherically-relevant aerosol mass loadings. In contrast, the experiments reporting higher $Y_{SOA}$ report relatively greater ON/ketone yield ratios, with the exception of sesquiterpenes such as β-caryophyllene, suggesting ON are important aerosol precursors.

3.2. Organic nitrate yields

ON can partition to the particle phase and contribute to SOA formation and mass growth. However, measurements of their yields are limited and highly variable depending on the composition of the reactive organic species and the type of oxidant (Ziemann and Atkinson, 2012). Here we report the measured gas- and aerosol-phase ON yields, and the total (sum of gas and aerosol ON) yield following γ-terpinene oxidation by NO$_3$. The ON yields ($Y_{ON}$) are defined as the concentration of ON produced (ΔON) either in the gas or particle phases, relative to the concentration of BVOC consumed, ΔBVOC, i.e., $Y_{ON} = \Delta ON/\Delta BVOC$. In these experiments, ΔBVOC was varied systematically by altering the concentration of N$_2$O$_5$ added to the chamber and monitoring the change in BVOC concentration with the GC-FID. These experiments were conducted both in the presence and absence of (NH$_4$)$_2$SO$_4$ seed aerosol particles and under dry conditions, and corrected for wall losses and dilution.

3.2.1. Total gas-phase organic nitrate yield

As indicated in Fig. 3, the concentration of total gas-phase ON (ON$_g$; determined via FT-IR) increases linearly as a function of ΔBVOC, independent of the presence or absence of the seed aerosol. By fitting both the unseeded and seeded data using linear regression, we derive a gas-
phase molar ON yield ($Y_{ONg}$) of 11(±1)%, where the relative uncertainty in the yield of ~9% is
derived from the 95% confidence intervals (shown in dashed lines in Fig. 3) of the linear fit to the
data, and accounting for the measurement uncertainties, shown as error bars. The similar yields
with or without seed particles implies that after some uptake, the two cases might appear identical
to the adsorbing molecules. Some of the variability in the yield presented in Fig. 3, particularly
below ΔBVOC ~ 300 ppb, may be attributed to greater relative uncertainty in ΔON and
ΔBVOC for low extents of BVOC reaction, different concentrations of NO$_2$ in the chamber,
and differences in the time frame of the experiment, as indicated in Table 1. While some wall
loss of the lower volatility multifunctional oxidation products could bias the reported yields
low (Zhang et al., 2014), the effects of wall loss on the yield of ON are accounted for in these
experiments and minimal (< 5% correction to the yield), given our relatively short
experimental timescales (~40 min on average) and measured wall loss rate of the hydroxy
nitrate of ~10^{-5} s$^{-1}$. As noted in the methods section, secondary oxidation of the remaining
double bond of γ-terpinene may account for ~10% of the uncertainty in $Y_{ONg}$. Regardless,
$Y_{ONg}$ observed here for γ-terpinene is considerably smaller than those measured from the NO$_3$
oxidation of limonene and β-pinene, but very similar to the yield from NO$_3$ oxidation of α-pinene
(Fry et al., 2014).

3.2.2. Total particle-phase organic nitrate yield

In general, particle-phase ON concentrations ($ON_p$) increase with increasing ΔBVOC as
shown in Fig. 4, with a particle-phase ON yield ($Y_{ONp}$) from the slope of 3(±1)%. Since there were
no significant differences in $ON_p$ between experiments conducted with and without seed
aerosol, the slope (i.e., yield) is derived from a fit to both datasets. The insignificant difference
in the particle phase ON yields between the seeded and unseeded experiments may be due to the large fraction of organic material in the particles in both cases, and for the seeded experiments, relative to sulfate. During both the seeded and unseeded experiments, on average particle mass increased by orders of magnitude following uptake of the oxidation products. Thus, in terms of uptake from the gas phase, and component solubility, for example, the particles in the two cases are effectively identical. \(Y_{ONp}\) can be affected by wall loss of both semi-volatile ON products and particles. Given our relatively short experimental timescales and relatively large particle/wall surface area ratios (upwards of 0.05) compared to other studies (Nah et al., 2016; Zhang et al., 2014), wall loss corrections amount to an increase in the relative uncertainty of the yield of 8% to 39%. The greater spread in ON\(_p\) compared to ON\(_g\) (see Fig. 3) as a function of \(\Delta BVOC\) may be due to variable chemistry occurring in the particle phase and the greater relative uncertainty in the case of the lower particle phase yields. It is possible that the presence of some aerosol liquid water and particle acidity, aided by the presence of hygroscopic \((NH_4)_2SO_4\) and uptake of product HNO\(_3\) by the particles, could result in relatively lower ON\(_p\) yields, even at low relative humidity (Rindelaub et al., 2015a). However, while we did not systematically investigate the dependence of yields on hydrolysis, we did two experiments that reveal that the ONs produced here are less prone to hydrolysis. Specifically, we found that the gas (10%), particle (1%-6%), and total ON yields (11%-16%) at a relative humidity of 50% were within the uncertainty of the yields determined under dry conditions. The expected major ON product shown in the right-hand side of Fig. 5 has a secondary nitrooxy functional group, which has been shown to be less prone to hydrolysis than tertiary nitrooxy groups (Darer et al., 2011).
To account for the effects mentioned above, we estimate a more conservative aerosol organic nitrate yield of 3 (+2/-1)%, based on the upper limit of the data variability.

### 3.3. Organic nitrate aerosol partitioning and effect on SOA yield

The sum of $\text{ON}_g + \text{ON}_p$ (ON$_t$) is plotted as a function of ABVOC in Fig. 6. Together, they result in a total molar ON yield, $Y_{\text{ON}_t} = 14(+3/-2)$%, accounting for the potential loss of aerosol phase ON as described previously, comparable to previously measured ON yields from the NO$_3$ oxidation of α-pinene of 10% (Fry et al., 2014) and 14% (Wangberg et al., 1997). From the ratio $Y_{\text{ON}_p}/Y_{\text{ON}_t}$, ~20% of the total ON produced from γ-terpinene + NO$_3$ partitioned to the particle phase, for these relatively high aerosol mass loading conditions. Assuming an average ON molar mass of 215 g mol$^{-1}$, representing a C$_{10}$-derived hydroxy nitrate (Rindelaub et al., 2015a), roughly 14% of the total aerosol mass is comprised of ON. Gas-to-particle partitioning depends strongly on the molecule’s equilibrium saturation vapor pressure and mass transfer kinetics (Shiraiwa and Seinfeld, 2012). The addition of nitrooxy and hydroxy groups, for example, can reduce the equilibrium saturation vapor pressure by several orders of magnitude (Capouet et al., 2008).

Molecules with saturation vapor pressures $>10^{-5}$ atm are almost exclusively in the gas phase, whereas those below $10^{-13}$ atm are almost exclusively in the condensed phase (Compernolle et al., 2011). We can estimate the saturation vapor pressure of the ON ($p_i^0$) based on the estimated ON aerosol mass fraction ($\varepsilon_i^{\text{aero}}=0.14$) as given in Eq. (2) (Valorso et al., 2011).

$$
\varepsilon_i^{\text{aero}} = \frac{1}{1 + \frac{M_{\text{aero}}Y_i p_i^0}{c_{\text{aero}}RT}}
$$
Here, $M_{aero}$ is the average particle molar mass, $\gamma_i$ is the activity coefficient of molecule “i”, and $C_{aero}$ is the aerosol mass concentration, $R$ is the gas constant, and $T$ is temperature. Assuming ideality, i.e., $\gamma_i=1$, $C_{aero}=835 \, \mu g \, m^{-3}$ (average of $\Delta M$ values from experiments listed in table 1), and $M_{aero}=215 \, g \, mol^{-1}$, we derive a $p_i^0$ for ON of $\sim 6 \times 10^{-7}$ atm or $\log_{10}$ saturation concentration of $\sim 4 \, \mu g \, m^{-3}$, which for a semivolatile C$_{10}$-derived hydrocarbon is expected to have between two and four oxygen atoms (Donahue et al., 2011). This estimated $p_i^0$ for ON is about an order of magnitude greater than that calculated for the expected tertiary hydroxy and hydroperoxy nitrates of $\gamma$-terpinene shown in Fig. 5 of $6.9 \times 10^{-8}$ atm and $3.9 \times 10^{-8}$ atm, respectively, using SIMPOL.1 (Pankow and Asher, 2008), suggesting that the ON$_p$ products of $\gamma$-terpinene likely comprise a mixture of hydroperoxy and hydroxy nitrates, and other more volatile ON species, likely keto–nitrates, e.g. as shown in Fig. 5 for the case of NO$_3$ addition to the more-substituted carbon. For the keto–nitrate shown in Fig. 5, we calculate a $p_i^0$ value of $1.4 \times 10^{-6}$ atm, using SIMPOL, roughly a factor of two greater than our estimate for the average for our aerosol. For comparison, the keto–aldehyde presented in Fig. 5 ($\gamma$-terpinaldehyde) has a $p_i^0$ value of 0.092 atm, using SIMPOL. As presented in the supplementary information, analysis of liquid extracts from filter samples using UPLC-ESI-ToF-MS/MS operated in negative ion mode indicate the presence of masses consistent with the first-generation hydroperoxy nitrate and second-generation di-hydroxy di-nitrates in the aerosol phase, the latter of which may result from both gas- and heterogeneous reactions that proceed at the unsubstituted olefinic C of a $\gamma$-terpinene hydroxy nitrate. In the absence of substantial HO$_2$ in our experiments, the dominant pathway for RO$_2$ is likely to follow either RO$_2$+NO$_3$ or RO$_2$+RO$_2$ (when [VOC] $\gg$ N$_2$O$_5$). However, in ambient nighttime air there may be substantially more RO$_2$+HO$_2$ reactions than in our chamber experiments. Isoprene nitrooxy hydroperoxide, for example, has been identified as the major product from isoprene
oxidation by the nitrate radical in the presence of HO₂ (Schwantes et al., 2015), and organic hydroperoxides have been identified as major SOA products from monoterpane and sesquiterpene ozonolysis (Reinnig et al., 2009; Docherty et al., 2005). Thus our chamber experiments may underestimate the concentration of hydroperoxides formed from γ-terpinene oxidation by NO₃ in the ambient environment. While we did not confirm the presence of epoxides in our experiments, and it is hard to see how an epoxide could form in the dark gas phase in these experiments, the remaining double bond of the first-generation hydroxy nitrate may be susceptible to epoxidation in the particle phase. For example, it is known that peroxyacetyl nitrate (PAN) very efficiently epoxidizes olefins in solution (Darnall and Pitts, 1970). While there would not be PAN as a product in our experiment, there could be very significant yields of the corresponding peroxy acyl nitrate from NO₃ reaction with terpinaldehyde, followed by uptake of that compound into the aerosol phase. As shown in Fig. 7 (A), that PAN compound could then react with, and produce the corresponding epoxide of any particle-phase compound with a double bond, e.g. the hydroxy nitrate, to produce a C₁₀H₁₇O₅ product. That epoxide would then do a pH-dependent hydrolysis in solution to produce the corresponding diol (C₁₀H₁₈O₆) (Jacobs et al., 2014). Applying the Extended Aerosol Inorganics Model (E-AIM) (http://www.aim.env.uea.ac.uk/aim/aim.php), we estimate a pH~5.5 for the (NH₄)₂SO₄ seed particles under saturated conditions, but becoming more acidic as the particles uptake HNO₃. It is important to note that the reaction products and their concentrations and thus degree of aerosol partitioning and SOA yields may also be affected by the concentration of NO₃ in the chamber. Under very high NOₓ conditions as in some of the experiments here, reactions between RO₂ and NO₃ out-compete those with HO₂, which may lead to formation of relatively more volatile carbonyl reaction.
products, as indicated in Fig. 5, and relative suppression of particle mass. This effect is consistent with other studies that report lower SOA yields in the presence of high NOx concentrations (Ng et al., 2007; Presto et al., 2005; Song et al., 2005). Regardless, an aerosol mass fraction of ON of 14% is considerably less than that obtained for other monoterpenes reacting with NO3, with the exception of α-pinene (Fry et al., 2014). This could be a result of both production of mostly volatile ON species, in particular keto–nitrates, and further reaction of the olefinic hydroxy nitrate in the aerosol phase. To verify the potential role of hydroxy nitrates in SOA production from NO3 + γ-terpinene as well as the presence of other ON, the following section focuses on product identification of gas phase ON species using CIMS and determination of gas phase hydroxy nitrate yields.

3.4. CIMS product identification and hydroxy nitrate yields

NO3 reactions with VOCs lead to either abstraction of a hydrogen atom or addition to a double bond. Since γ-terpinene has two double bonds with similar character, NO3 likely has equal probability of adding to either internal double bond. However, addition of NO3 to either one of the olefins is likely to form the more stable tertiary nitrooxy alkyl radical. Subsequent addition of O2 forms the β-nitrooxyperoxy radical that can lead to an array of products, including hydroxy nitrates, most likely from self or cross RO2 + RO2 reactions or isomerization (Yeh and Ziemann, 2014; Ziemann and Atkinson, 2012). C10-derived hydroxy nitrates and other multifunctional ON have been identified in field-sampled SOA particles, and for nighttime ONp, C10-derived ON could account for approximately 10% of the organic aerosol mass during the Southern Oxidant and Aerosol Study (SOAS) campaign in the U.S. southeast (Xu et al., 2015; Lee et al., 2016). However, our current understanding of C10-derived hydroxy nitrate yields is limited to production via
oxidation of α-pinene (Wangberg et al., 1997). Here we expand on this by determining the hydroxy nitrate yield from γ-terpinene oxidation by NO$_3$ and identify other potentially important ON species using CIMS.

Figure 8 shows example CIMS mass spectra (red and blue traces) and the enhancements over the background in the presence of NO$_3$ (black trace) following a chamber experiment, where the enhancement is calculated from the signal for $\frac{\text{NO}_3^- \cdot \text{no}_{\text{NO}_3}}{\text{no}_{\text{NO}_3}}$. Several molecules were detected at masses below the iodide reagent ion signal ($m/z = 127$) following N$_2$O$_5$ addition to the chamber and correspond to NO$_3^-$ ($m/z = 62$), NO$_3^-(\text{H}_2\text{O})_{1,2}$ ($m/z = 80, 98$), N$_2$O$_5^-$ ($m/z = 108$), and what appears to be a nitrate–nitric acid cluster anion, HN$_2$O$_6^-$ ($m/z = 125$) (Dubowsky et al., 2015; Huey, 2007). The water cluster ions and nitric acid (also at $m/z = 190$, corresponding to I$^-\cdot\text{HNO}_3$) result from ion–molecule reactions in the humidified drift tube of our CIMS and residual HNO$_3$ from the N$_2$O$_5$ cold trap. Several larger molecular weight species were detected in the range of $300 \leq m/z \leq 450$, consistent with products from monoterpene oxidation, with enhancements over the background as large as a factor of 50 to 100. Specifically, the first-generation hydroxy nitrates are observed at $m/z = 342$ (C$_{10}$H$_{17}$NO$_4^-\cdot\Gamma$).

Several masses follow, separated by 16 mass units, or addition of a single oxygen atom, whereby each new ON has 15, 17, or 19 H atoms. Similar observations were made in the field during the SOAS campaign for both ON$_g$ and ON$_p$ (Lee et al., 2016), indicating the presence of highly-functionalized ONs. It is important to note that the products observed here are derived from a single monoterpene, whereas the field ON measurements consist of products derived from all ambient monoterpene oxidation. Other major peaks included those at $m/z = 340$, potentially representing an iodide-adduct with either an aldehyde or keto–nitrate (C$_{10}$H$_{15}$NO$_4^-\cdot\Gamma$), and $m/z = 358$, which may be indicative of an iodide-adduct with a hydroperoxy nitrate (C$_{10}$H$_{17}$NO$_5^-\cdot\Gamma$).
cluster of ions was detected above \( m/z = 400 \), potentially representing **molecules with higher degrees of oxygenation and secondary oxidation products such as a** di-hydroxy–di-nitrate at \( m/z = 421 \) (\( \text{C}_{10}\text{H}_{18}\text{N}_{2}\text{O}_{8}–\text{I} \)), which could be formed through second-generation oxidation at the remaining unsubstituted carbon of the double bond on the first-generation hydroxy nitrate. It is important to note that the CIMS sensitivity for each of these species is likely different and depends on the polarity and acidity of the individual compound, which is affected by the type and positions of the different functional groups (Lee et al., 2016). For example, iodide-adduct CIMS is not particularly sensitive to aldehyde and carbonyl nitrates, whereas more acidic and polar molecules such as hydroxy nitrates and carboxylic acids can exhibit much greater sensitivity (Lee et al., 2016). Moreover, in general as the molecular size and number of oxygenated groups increase (particularly –OH groups), the sensitivity also increases. Hence, without commercial or custom synthetic standards, no quantitative analysis of the array of ON products could be reliably performed using this technique.

Here we determine the yield of \( \gamma \)-terpinene-derived hydroxy nitrates. Since there is no commercially-available standard for the expected first-generation \( \gamma \)-terpinene hydroxy nitrate, we use a synthetic olefinic hydroxy nitrate derived from \( \alpha \)-pinene (structure shown in Fig. S4) for quantitative analysis (Rindelaub et al., 2016). It is possible that the CIMS is less sensitive to this nitrate compared to the more sensitive \( \alpha,\beta \)-hydroxy nitrate structure expected of the first-generation \( \gamma \)-terpinene hydroxy nitrates, similar to the differences in the CIMS sensitivity for 4,3-isoprene hydroxy nitrate (4,3-IN) and 1,4-IN (Xiong et al., 2015). However, the use of an olefinic hydroxy nitrate is consistent with that expected from \( \gamma \)-terpinene oxidation because of its diolefinic character. As shown in Fig. 9, \( \gamma \)-terpinene-derived hydroxy nitrate concentrations increase linearly over the range of \( \Delta \text{BVOC} \) with a hydroxy nitrate yield defined from the slope as 4(±1)%. 


Assuming the CIMS sensitivity for the γ-terpinene hydroxy nitrates may be a factor of three greater than for our synthetic α-pinene-derived hydroxy nitrates, a more conservative estimate of the γ-terpinene-derived hydroxy nitrates yield is 4(±1/-3)%. To our knowledge, the only monoterpene hydroxy nitrates yield to have been quantified following NO₃ oxidation is 2-hydroxyperinan-3-nitrate, derived from α-pinene (Wangberg et al., 1997). In that study, the hydroxy nitrates yield was determined using a combination of FT-IR and GC-ECD to be 5(±0.4)%, on the same order as the yield presented in this study for γ-terpinene using CIMS. 3-oxopinan-2-nitrate (C₁₀H₁₅NO₄; 213 g mol⁻¹) and a short-lived, thermally unstable peroxy nitrate (C₁₀H₁₆N₂O₇; 276 g mol⁻¹) were also identified in that study. It is possible that similar products are made following NO₃ oxidation of γ-terpinene, and potentially make up the signals detected at m/z = 340 and m/z = 403, respectively, as shown in Fig. 8. However, the CIMS sensitivity toward these products is expected to be relatively small compared to that for the hydroxy nitrates, due to their relatively lower polarity and acidity. Moreover, peroxy nitrates are thermally unstable and their concentrations are likely greatly reduced during transfer through the heated sampling line.

3.5. Proposed reaction mechanism

The similarities between the, at first seemingly low, γ-terpinene + NO₃-derived Y_{ON}, hydroxy nitrates yield, and Y_{SOA} with those for NO₃ + α-pinene are provocative. This suggests the two monoterpenes may undergo very similar degradation pathways following NO₃ oxidation, which is not observed with other monoterpenes with a substituted endocyclic double bond (Fry et al., 2014). As such, our mechanistic interpretation, shown in Fig. 5, is analogous to that for the α-pinene + NO₃ reaction, as described in the Master Chemical Mechanism (MCM) (Jenkin et al., 1997; Saunders et al., 2003). NO₃ will predominately add to the C-3 (unsubstituted) position
forming the more stable tertiary alkyl radical. However, to some extent, NO\textsubscript{3} may also add to the second carbon forming the less stable secondary alkyl radical, approximately 35\% of the time according to the MCM. Oxygen promptly adds to the alkyl radical to form either a tertiary or secondary peroxy radical (\textit{ROO\textsuperscript{-}}). Excess NO\textsubscript{2}, due to thermal decomposition of N\textsubscript{2}O\textsubscript{5}, can add to the peroxy radical forming a thermally unstable peroxy nitrate (-\textit{OONO\textsubscript{2}}) in equilibrium with the peroxy radical. Subsequent RO\textsubscript{2}\textsuperscript{-} self- and cross-reactions as well as reaction with NO\textsubscript{3} form the alkoxy radical (\textit{RO\textsuperscript{-}}). The alkoxy radical can subsequently decompose to form a carbonyl nitrate or \(\gamma\)-terpinaldehyde (Fig. 5) and release NO\textsubscript{2}. Analogously, pinonaldehyde is the major NO\textsubscript{3} oxidation product of \(\alpha\)-pinene with reported yields of 62(\pm 4)\% (Wangberg et al., 1997) and 75\pm 6\% (Berndt and Böge, 1997). Given the very similar tertiary alkoxy radicals produced from NO\textsubscript{3} oxidation of \(\alpha\)-pinene and \(\gamma\)-terpinene, and the similar SOA, ON\textsubscript{t}, and hydroxy nitrate yields, conceivably \(\gamma\)-terpinaldehyde is produced and with similarly high but undetermined yields as pinonaldehyde from \(\alpha\)-pinene oxidation by NO\textsubscript{3}. Similar results have been reported for the ozonolysis of \(\gamma\)-terpinene, which primarily leads to decomposition and formation of \(\gamma\)-terpinaldehyde with a yield of 58\% (Ng et al., 2006). Alternatively, disproportionation, involving a secondary peroxy radical, produces a hydroxy nitrate and a carbonyl compound from the partnering RO\textsubscript{2} (Yeh and Ziemann, 2014; Ziemann and Atkinson, 2012; Wangberg et al., 1997). As we have shown, the experimentally-derived yield for these products is 4\%, or roughly 25\% of ON\textsubscript{t}. The remaining organic nitrate species likely contains both carbonyl and hydroperoxy (-OOH) functionalities, and perhaps peroxy nitrates, following NO\textsubscript{2} addition to the peroxy radical. A major species detected by our CIMS has an \textit{m/z} = 358, which may represent an I\textsuperscript{-} adduct with a hydroperoxy nitrate. This product is only produced due to reactions between hydroperoxy radicals.
HO\(_2\)· and RO\(_2\)· (Ziemann and Atkinson, 2012). Conceivably, HO\(_2\)· is produced in our system from hydrogen abstraction from alkoxy radicals by oxygen (Wangberg et al., 1997).

To test the hypothesis that γ-terpinene behaves similarly to α-pinene following reaction with NO\(_3\), we ran a simple box model based on the mechanisms for NO\(_3\) oxidation of α-pinene as presented in the MCM, and compared the model output with the measured concentrations of γ-terpinene, NO\(_2\), and hydroxy nitrates. The model is constrained by the initial and final GC-FID-derived concentrations of γ-terpinene. Since the nitrate radical concentration was not determined experimentally, the concentration of NO\(_3\) in the model was determined by adjusting the N\(_2\)O\(_5\) concentration until the fitted concentration change of γ-terpinene matched that which was measured. This approach implicitly assumes γ-terpinene is consumed only from reaction with NO\(_3\), which is expected given the orders of magnitude greater reactivity of NO\(_3\) compared to the other reactants in our system, which includes N\(_2\)O\(_5\) and NO\(_2\). The results of the model are presented in Fig. 10. For comparison, modeled concentrations are plotted along with the measured concentrations of γ-terpinene, NO\(_2\), and hydroxy nitrates derived from one of the experiments. At a first approximation, the modeled concentrations appear to be in agreement with those measured, given the semi-quantitative nature of the product, particularly the hydroperoxides. As shown in the top panel of Fig. 10, NO\(_3\)/HO\(_2\) ratios are ~3 at peak [HO\(_2\)], then decrease to ~1 as the products reach steady state. In comparison, ambient nighttime NO\(_3\)/HO\(_2\) ratios of ~1 have been measured during the PROPHET 1998 field intensive in northern Michigan (Hurst et al., 2001; Tan et al., 2001), and ~0.25 at the BEARPEX field site in north central California (Bouvier-Brown et al., 2009; Mao et al., 2012). The relatively larger ratios in our chamber, initially, suggest hydroperoxy nitrates may be underrepresented compared to the atmosphere. Notably, the agreement between modeled and measured [NO\(_2\)] implies that
model-derived \([N_2O_5]\) is close to that in the reaction chamber as \([NO_2]\) is in equilibrium with \(N_2O_5\). Although not quantified experimentally, qualitative analysis of the CIMS mass spectra indicates the presence of carbonyl and hydroperoxy nitrates, which is consistent with the major ON products expected from the mechanism shown in Fig. 5.

4. Atmospheric Implications

The relatively low SOA and ON yields observed here under dry conditions at ambient mass loadings suggests \(\gamma\)-terpinene may not be an important SOA precursor at night, when NO\(_3\) can be the dominant oxidant. However, the low saturation vapor pressure of the hydroxy nitrates, which constitute a significant portion of the total ON, and the presence of some highly oxygenated products, further suggests that these molecules are potentially important contributors to SOA mass. While our experiments were conducted near dry conditions, in the ambient forest environment, particularly at night and in the early morning when the relative humidity near the surface is high and NO\(_3\) reactions are competitive with \(O_3\) and OH, hydroxy nitrates in the particle phase can enhance SOA formation through acid-catalyzed hydrolysis and oligomerization, and in the presence of sulfates, form organic sulfates (Liu et al., 2012; Paulot et al., 2009; Rindelaub et al., 2016; Suratt et al., 2008; Rindelaub et al., 2015a), ultimately affecting the lifetime of NO\(_x\) (Browne and Cohen, 2012; Xiong et al., 2015). Furthermore, the transformation of the nitrooxy group to a hydroxyl or sulfate group will alter the hygroscopicity of the particle, making them more effective cloud condensation nuclei (Suda et al., 2014).

It is important to note that under relatively clean air conditions, the peroxide radical produced via NO\(_3\) reaction with \(\gamma\)-terpinene will often react with HO\(_2\) to produce nitrooxy hydroperoxides. As shown in the reaction scheme (B) in Fig. 7, these species can then react
with NO$_3$ and then HO$_2$, RO$_2$ or NO$_3$ again, to yield a variety of highly oxidized very low vapor pressure products that will likely partition completely to the aerosol phase. Under humid conditions, the nitrooxy groups may hydrolyze, leaving more polar/water soluble OH groups.

Although the SOA yields are low, these chamber experiments did not represent all possible reactants that can produce particle phase precursors. Recent work indicates keto–aldehydes are potentially an important source of nitrogen-containing low volatility compounds following their reaction with dimethylamine, serving as precursors to SOA and brown carbon (Duporté et al., 2016). As shown in this study, the keto–aldehyde yield is expected to be large, along with other internal olefinic terpenes. It is also important to note that the keto–aldehyde product, γ-terpinaldehyde, is olefinic. Further homogeneous and multiphase oxidation reactions at the remaining reactive double bond can potentially transform these species into oligomeric lower-volatility oxidation products, adding to the overall SOA burden (Liggio and Li, 2008). In regions such as the northern U.S., where there are greater proportions of polyolefinic monoterpenes (Geron et al., 2000), γ-terpinene may be an important reactive VOC, and thus impact aerosol and local-scale NO$_x$.

5. Conclusions

The total molar ON yield from the NO$_3$ oxidation of γ-terpinene was found to be 14(+3/-2)%. Relatively low particle-phase ON and SOA yields are consistent with previous studies that show SOA yields are generally dependent on the yield of ON. Although γ-terpinene is a diolefin, the ON, hydroxy nitrate, and SOA yields are similar to those for α-pinene oxidation by NO$_3$. Considering the position of the two double bonds, the expected major product is γ-terpinaldehyde,
which is considerably more volatile than the ON products. Box model calculations that assume
large keto–aldehyde yields are also in agreement with the measured concentrations of hydroxy
nitrates, suggesting very similar mechanistic behavior to that of α-pinene oxidation. Several gas-
and particle-phase ON products have been inferred from mass spectrometry analysis, indicating
that NO₃ reaction with γ-terpinene may be an important source of ON and dicarbonyl compounds
in forest-impacted environments.

Author Contributions
J. H. S. and P. B. S. designed the research and wrote the manuscript. J. H. S. performed the yield
experiments and analyzed the data. J. H. S. and C. d-P. analyzed the filter samples. L. L. oversaw
the analysis of the filter samples. All authors contributed intellectually to the manuscript.

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CHE-1550398. The authors declare that they have no conflicts of interests.
Table 1. Initial conditions and yields from individual experiments. Time indicates the period between N$_2$O$_5$ addition to the chamber and gas and particle collection by the denuder and filter. “n.m.” indicates “not measured”.

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Figure 1. Example wall loss-corrected SOA growth curve for γ-terpinene + NO$_3$ in the absence of seed aerosol. The color scale represents aerosol number concentration, N (cm$^{-3}$).
Figure 2. Change in aerosol mass concentration (ΔM) and wall-loss corrected SOA yields ($Y_{SOA}$) from the NO$_3$ oxidation of γ-terpinene in unseeded (black circles) and (NH$_4$)$_2$SO$_4$-seeded experiments (blue circles). The data were fitted to a two-product absorptive partitioning model (black curve) and the dashed curves represent the 95% confidence intervals of the fitting function. For comparison, the mass-dependent yield curves of α-pinene and γ-terpinene in the presence of OH are shown in the red and green curves, respectively, and β-pinene + NO$_3$ in purple (Griffin et al., 1999; Lee et al., 2006). For clarity, the right panel shows the left panel data on a log scale.
Figure 3. Total wall loss- and dilution-corrected gas-phase organic nitrate production ($\Delta$ON$_g$) as a function of the amount of BVOC consumed ($\Delta$BVOC) for the unseeded (black circles) and (NH$_4$)$_2$SO$_4$-seeded experiments (blue circles). Horizontal and vertical error bars represent the uncertainty in the GC-FID and FT-IR calibrations, respectively. The black line shows the linear fit of the data through the origin and the dashed lines indicate the 95% confidence intervals of the fit. The slopes of these lines represent the fractional organic nitrate yield and uncertainty presented in the plot, respectively.

Figure 4. Total wall loss- and dilution-corrected particle-phase organic nitrate production ($\Delta$ON$_p$) as a function of the amount of BVOC consumed ($\Delta$BVOC) for the unseeded (black circles) and (NH$_4$)$_2$SO$_4$-seeded experiments (blue circles). The error bars and fits are derived as in Fig. 3.
Figure 5. Proposed initial reaction pathways for the NO$_3$ oxidation of γ-terpinene. For simplicity, only the first-generation oxidation products are shown.
Figure 6. Total wall loss- and dilution-corrected organic nitrate production ($\Delta$ON$_0$) as a function of the amount of BVOC consumed ($\Delta$BVOC) for the unseeded (black circles) and (NH$_4$)$_2$SO$_4$-seeded experiments (blue circles). The error bars and fits are derived as in Fig. 3.

Figure 7. Potential second-generation oxidation reactions and particle-phase chemistry. (A) NO$_3^-$ oxidation of terpinaldehyde and olefin epoxidation by peroxy acyl nitrate, followed by acid-catalyzed hydrolysis of the epoxide to form the diol. (B) RO$_2^-$ and HO$_2^-$ pathways following NO$_3^-$ oxidation of the first-generation nitrooxy hydroperoxide.
Figure 8. CIMS mass spectra before (blue) and after γ-terpinene oxidation by NO₃ (red) correspond to right axis. Signal enhancement by addition of NO₃ is shown in the black trace. The inset figure shows an enhanced region of the mass spectra corresponding to the shaded area, which indicates the presence of multifunctional ON compounds with the number of oxygen atoms consistent with the depicted chemical formula. The “O₄” peak was used to quantify hydroxy nitrate concentrations. Signal enhancement by addition of NO₃ is shown in the black trace.
Figure 9. γ-terpinene hydroxy nitrate production (ΔHORONO$_2$) as a function of the amount of BVOC consumed (ΔBVOC). Colors represent independent experiments performed on different days. All of the experiments were conducted in the absence of seed aerosol. The error bars and fits are derived as in Fig. 3.
Figure 10. Time series of experiment indicating measured (circles) and modeled (lines) concentrations of γ-terpinene (black), N$_2$O$_5$ (dashed violet), NO$_2$ (green), HO$_2$ (gray), keto-aldehyde (red), keto-nitrate (dark blue), hydroperoxy nitrate (dashed pink), and hydroxy nitrate (light blue). **Top panel shows simulated NO$_3$/HO$_2$ ratios (black circles) compared to measured ambient nighttime ratios from the PROPHET and BEARPEX field intensives.** The model is based on the MCM for α-pinene reaction with NO$_3$. 
Supplementary Information

Figure S1. Wall loss rate of m/z 342 as measured by CIMS, corresponding to the monoterpene hydroxy nitrate–I adduct.

Figure S2. Example experimental time series and calculation of SOA yield.

Identification of ON in filter extracts

Figure S3 shows the extracted ion chromatograms (EIC) of the synthetic α-pinene-derived hydroxy nitrate (red), and potential particle-phase organic nitrates, including the first-generation hydroperoxy nitrate (green) and di-hydroxy di-nitrate (blue). For each EIC, there is a
corresponding MSMS (MS²) spectrum, which shows the fragment ions of the parent [M+AcO⁻]
adduct ion species. The synthesized α-pinene-derived hydroxy nitrate adduct with AcO⁻ (m/z =
274.1291) MS² spectrum indicates there are two primary fragment ions that correspond to AcO⁻
and NO₃⁻. These ions were then used as signatures to identify organic nitrate species in the filter
sample extracts. Detected masses and their corresponding mass spectra and tandem mass
spectra were further analyzed and matched according to the chemical formula: C₉H₁₉N₂O₆.
Of the two samples analyzed, the most abundant species with the NO₃⁻ fragment ion have an m/z
= 353.1197, corresponding to a molecule with chemical formula C₁₀H₁₈N₂O₈ + AcO⁻, and m/z =
290.1241 (C₁₀H₁₇NO₅ + AcO⁻).

Figure S3. UPLC-ESI(-)-ToF-MS/MS extracted ion chromatograms (EIC) for the synthetic α-
pinene-derived hydroxy nitrate (red), hydroperoxy nitrates present in the filter extracts (green),
and di-hydroxy–di-nitrates present in the filter extracts (blue). For reference, the background EICs
HPLC-grade methanol) for each mass are also plotted (black). The insets show the MS$^2$ spectra and the listed $m/z$ values in the MS$^2$ spectra correspond to the most intense peak. Potential molecular structures are shown for reference.

Figure S4. Molecular structure of the synthetic α-pinene-derived hydroxy nitrate used for calibration of the CIMS.

**Box model inputs**

The box model applied to simulate the reaction and products from the NO$_3$ oxidation of γ-terpinene was performed in Matlab v7.7.0 using the ordinary differential equations (ODE23s) solver in Matlab. Table S1 lists the various reactions and rate constants applied in the model. The majority of the rate constants were abstracted from those applied in the Master Chemical Mechanism version, with the exception of NO$_3$ + γ-terpinene since the MCM does not explicitly include γ-terpinene. Wall loss rate constants were included in the model for NO$_3$, N$_2$O$_5$, and the hydroxy-, hydroperoxy-, and keto-nitrates as described in the footnotes of Table S1.

**Table S1.** Box model parameters for simulating the NO$_3$+γ-terpinene reaction in the chamber.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O$_5$ ( \rightarrow ) NO$_3$ + NO$_2$</td>
<td>( \frac{1 \times 10^{-12}}{2.13 \times 10^{-27} \ e^{1625 \ T}} ) cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>NO$_3$ + NO$_2$ ( \rightarrow ) N$_2$O$_5$</td>
<td>( 1 \times 10^{-12} ) cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$^a$NO$_3$ + wall ( \rightarrow ) loss</td>
<td>( 6 \times 10^{-4} ) s$^{-1}$</td>
</tr>
<tr>
<td>$^b$N$_2$O$_5$ + wall ( \rightarrow ) loss</td>
<td>( 5 \times 10^{-6} ) s$^{-1}$</td>
</tr>
<tr>
<td>$^c$γ-terpinene + NO$_3$ ( \rightarrow ) α-nitrooxy peroxy radical</td>
<td>( 24 \times 10^{-12} ) cm$^3$ molecule$^{-1}$ s$^{-1}$ *0.35</td>
</tr>
<tr>
<td>Reactions</td>
<td>Rate Constants</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>( \alpha)-nitrooxy peroxy radical + NO(_3) \rightarrow \alpha)-nitrooxy alkoxo radical + NO(_2)</td>
<td>(2.3 \times 10^{-12}) cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>(\alpha)-nitrooxy peroxy radical + HO(_2) \rightarrow \beta)-hydroperoxy nitrate</td>
<td>(2.91 \times 10^{-13} e^{\frac{1300}{T}}) cm(^3) molecule(^{-1}) s(^{-1}) *0.914</td>
</tr>
<tr>
<td>(\alpha)-nitrooxy peroxy radical + RO(_2) \rightarrow \beta)-hydroxy nitrate</td>
<td>(2.5 \times 10^{-13}) cm(^3) molecule(^{-1}) s(^{-1}) *0.1</td>
</tr>
<tr>
<td>(\alpha)-nitrooxy peroxy radical + RO(_2) \rightarrow \alpha)-nitrooxy alkoxy radical</td>
<td>(2.5 \times 10^{-13}) cm(^3) molecule(^{-1}) s(^{-1}) *0.8</td>
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<tr>
<td>(\alpha)-nitrooxy peroxy radical + RO(_2) \rightarrow \beta)-keto nitrate</td>
<td>(2.5 \times 10^{-13}) cm(^3) molecule(^{-1}) s(^{-1}) *0.1</td>
</tr>
<tr>
<td>(\alpha)-nitrooxy alkoxy radical + O(_2) \rightarrow \beta)-keto nitrate + HO(_2)</td>
<td>(2.5 \times 10^{-14} e^{\frac{-360}{T}}) cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>(\alpha)-nitrooxy-(\beta)-alkoxy radical \rightarrow keto-aldehyde + NO(_2)</td>
<td>(4 \times 10^5) s(^{-1})</td>
</tr>
<tr>
<td>(\gamma)-terpinene + NO(_3) \rightarrow \beta)-nitrooxy peroxy radical</td>
<td>(24 \times 10^{-12}) cm(^3) molecule(^{-1}) s(^{-1}) *0.65</td>
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<tr>
<td>(\beta)-nitrooxy peroxy radical + NO(_3) \rightarrow \beta)-nitrooxy alkoxy radical + NO(_2)</td>
<td>(2.3 \times 10^{-12}) cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>(\beta)-nitrooxy peroxy radical + HO(_2) \rightarrow \alpha)-hydroperoxy nitrate</td>
<td>(2.91 \times 10^{-13} e^{\frac{1300}{T}}) cm(^3) molecule(^{-1}) s(^{-1}) *0.914</td>
</tr>
<tr>
<td>(\beta)-nitrooxy peroxy radical + RO(_2) \rightarrow \alpha)-hydroxy nitrate</td>
<td>(6.7 \times 10^{-15}) cm(^3) molecule(^{-1}) s(^{-1}) *0.1</td>
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<tr>
<td>(\beta)-nitrooxy peroxy radical + RO(_2) \rightarrow \beta)-nitrooxy alkoxy radical</td>
<td>(6.7 \times 10^{-15}) cm(^3) molecule(^{-1}) s(^{-1}) *0.9</td>
</tr>
<tr>
<td>(\beta)-nitrooxy alkoxy radical \rightarrow keto-aldehyde + NO(_2)</td>
<td>(1 \times 10^6) s(^{-1})</td>
</tr>
<tr>
<td>(\delta)Wall loss rate of hydroxy nitrate, keto nitrate, and hydroperoxy nitrate</td>
<td>(2 \times 10^{-5}) s(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\)Wall loss rate from Fry et al. (2009). \(^b\)Wall loss rate from Perring et al. (2009). \(^c\)Reaction rate constant from Martinez et al. (1999). \(^d\)Wall loss rates derived from the measurement of hydroxy nitrate wall loss.
References


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mechanistic chamber studies on the oxidation of biogenic compounds, Atmos. Chem. Phys., 14, 13531-13549, 10.5194/acp-14-13531-2014, 2014.


