

Interactive comment on “Nitrate radical oxidation of γ -terpinene: hydroxy nitrate, total organic nitrate, and secondary organic aerosol yields” by Jonathan H. Slade et al.

Anonymous Referee #3

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Overview The manuscript by Slade et al. presents new measurements on the oxidation of γ -terpinene by the nitrate radical with a focus on understanding the organic nitrate yield. Both the gas- and particle-phase yields are reported as well as an SOA yield. A possible reaction mechanism is proposed based on observed products and structural similarities to other monoterpenes. Understanding organic nitrate yields is important for understanding NO_x lifetime. Organic nitrate yields from monoterpene oxidation are currently poorly constrained thus limiting the community's ability to predict and understand NO_x lifetime and reactive oxidized nitrogen partitioning in the atmosphere (particularly in biogenically influenced regions). The measurements presented in this paper are of interest to the community and will fill knowledge gaps. Prior to publication,

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however, several areas need improvement/clarification.

General Comments: 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).

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.

Specific Comments: 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.

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.

Figure 1: color scale missing

Figure 2: caption should say log scale (omit x-axis).

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.

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

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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 NO_3 ? 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.

Lines 75-80: I find this explanation confusing and more elaboration is needed. The NO_3 oxidation of both α -pinene and β -pinene lead to tertiary peroxy radicals.

Line 95: "...potential for ON and SOA formation are better understood." Better understood compared to what?

Line 133: Why not use the density of ammonium sulfate?

Line 245-246: Wouldn't some fraction of this yield dinitrates? How is that accounted for in this calculation?

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.

Line 317: should be "nitrooxyperoxy"

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

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-249, 2017.

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