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Discussions

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

**Anonymous Referee #2**

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Slade et al. present results from atmospheric simulation chamber experiments quantifying the gaseous ON yield, particulate ON yield and total SOA yield from the oxidation of gamma-terpinene (g-terpinene) by the NO3 radical. The work is thorough and contributes useful information for understanding the impact of ON formation on how and to what extent anthropogenic emissions can influence and are influenced by the oxidation of BVOCs. With some clarifications, this work deserves publication in ACP.

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.

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?

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.

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.

What was the relevance of ESI MS/MS to this work? Is the hydroxynitrate distinguishable from hydroperoxynitrate?

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 $C_{10}H_{17}NO_5$ are in fact epoxides and not hydroperoxides, how would uptake differ with and without seed? What was pH of the seed particles?

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?

Minor Seed particles introduced into the chamber were ∼100 nm. But the particle filter had pore size 1 micron.

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 calcualted?

"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.

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