

Interactive comment on “The Production and Hydrolysis of Organic Nitrates from OH Radical Oxidation of β -Ocimene” by Ana Cristina Morales et al.

Anonymous Referee #1

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Summary:

This paper reports novel measurements of alkyl nitrate and SOA yield from OH + ocimene under high NO_x conditions, and assesses hydrolysis rates, which are highly relevant to whether ambient SOA measurements accurately reflect the fraction of aerosol that partitioned to the particle phase via organic nitrates. FTIR functional group analysis enables a total organic nitrate yield measurement, while ESI-MS measurements also enable identification of potential individual nitrate product structures but are not quantitative and thus not possible to determine mechanism branching ratios. These new measurements contribute valuable data to a growing literature on nitrate

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and SOA yields and hydrolysis rates.

Major comments: 1) In the “Atmospheric Implications” section you mention some previous literature on acid catalyzed hydrolysis of nitrates, where tertiary nitrates were found to hydrolyse more rapidly than primary or secondary. This context is useful and I would suggest mentioning it earlier where you report the hydrolysis rate, and using your mechanism figure to call the reader’s attention to this structural dependence of hydrolysis rates by pointing out the tertiary / secondary / primary ocimene nitrates.

2) On p. 5 near bottom: Do you expect similar sensitivity to ocimene hydroxynitrates as apin? What uncertainty?

3) Around line 142: refer to these as “blank and control experiments”? Not all “blanks” as you’ve described. Also, maybe give values for the gas and particle phase wall loss rates used to correct the data (or perhaps show a figure of uncorrected and corrected in a supplemental info, so readers can see how big the effect is.

4) P. 7: How did you “stop” hydrolysis after collecting the 50 μ l aliquots every 2 minutes from your hydrolysis experiments?

5) Around line 314: Include (or add to SI and refer to) information on all of the uncertainties described here as going into the propagated error.

6) Around line 290, where you’re discussing the lower vapor pressure α -pinene products: are the apin products expected to be lower P_{vap} simply because of the rings? Wouldn’t both be C₁₀ hydroxynitrates? Or are you thinking of the aggregated product mix that would include decomposition products?

7) You mention CIMS measurements of hydroxynitrates and report yields, but that time-series data is not in any figure. Would be nice to show other than the averages for each experiment in Fig. 3, if it’s an online measurement. Could maybe add to Fig. 1?

8) Looking at Fig. 2, I would why wouldn’t the non-conjugated double bond be the major radical attack, since it doesn’t disrupt the conjugation of the other 2 double bonds. Also

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in that figure, are the reactants over the top right arrow (OH, NO) correct? Needs a couple more steps maybe. And, the production of the alkoxy radical via rxn with NO in the middle of the second line should come from the peroxy radical (above it and to the right) and not the alkyl radical (directly above it). Finally, one of the structures is labeled "(A)" but no others are labeled. Wouldn't this be the same MW and indistinguishable in ESI-MS from the product on the third line? Some additional brief discussion of the detected structures and connection between this scheme and the chromatograms in Fig 7 would be welcome (maybe labelling more of the structures and putting the correspondence in Fig. 7 caption?)

9) In Figure 6 as in Fig. 2, I believe the NO rxn to produce alkoxy should come from the peroxy radical to the right and not the alkyl radical. But, I wonder if this figure is necessary in a paper focused on the ocimene reaction. Maybe for Fig. 6 you can just mention pinonaldehyde's MW, point out that there aren't obvious other fragmentation pathways, and reference Rindelaub?

Minor / technical suggestions and edits:

1) Line 34 : suggest moving number to read: "atmosphere (<1%) is significantly lower than reported yields..." to be clear that the % is the yield and not the amount lower than other yields.

2) Line 42: suggest change to "daytime monoterpenes not currently included..." to clarify that you are referring to this specific not included MT, and not stating that daytime MTs as a whole are not included in models.

3) Line 49: "which lead to the"

4) Line 57: "upon further oxidation and decomposition"

5) Line 59: "partitioning into the condensed phase"

6) Line 60: "Ambient measurements in forests have indicated"

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7) Line 63: "lifetime of alkyl nitrates in the aerosol Aerosol itself to deposition (~1 week)"

8) Line 75: "Zare et al., 2018), which is sometimes rapid compared to measurements of plume aging." « and here is where you might add more about regiochemistry and hydrolysis rates, and what you expect for this alkene structure.

9) Line 94: replace "chemistry of these species" with "hydrolysis rate" to be more specific?

10) Line 110: sounds like youre also using the evaporation setup for NO and HCHO, but I don't think they require evaporation – maybe reword?

11) Line 224: sub "yield" for "branching ratio"?

12) Lines 258-260: I find this a little confusing, the Henry's law constant of a diol increasing? Consider rewording.

13) Line 303: replace "such production" with "this reaction"? phrasing confused me.

14) Line 313: pH dependence, not RH dependence, right?

15) Line 315-316: list of previous hydrolysis rate constant expts is worded oddly, rework? And omit "Thus"

16) Line 330: suggest: "even though the nitrates have contributed... mass, because they have subsequently transformed to diols."

17) Line 332: looks to me like the similarities are not only at pH4 but across the range! Highlight this? When you call out the similarity at pH 4 it makes me think the agreement must have been worse at other PH's.

18) Line 346-347: suggest "... structure of these oligomers is necessary to develop reliable predictive..."

19) Line 351: suggest to remind the reader " and, for the polyunsaturated terpene

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ocimene, are subject to. . .”

20) Line 356: “should rapidly undergo”

21) General note: the citation “Romer Present” is intermittently listed as 2019 and 2020, unify?

22) Fig 2 image quality is pretty poor, use a higher-res version?

23) Fig 4 : label of “Atmospheric pressure branching ratio” seems odd, maybe “Organic nitrate yield from OH oxidation of ocimene”?

24) Fig 5: “a) Relationship between PM mass. . .”. Also, you determine the 2-product model fits but I don’t think the parameters are reported anywhere in the paper, could add to this figure caption and make reference to in the text?

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