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Interactive comment on "Characterization of organic nitrate constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of limonene using High-Resolution Chemical Ionization Mass Spectrometry" *by* Cameron Faxon et al.

Anonymous Referee #2

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General comments: This paper presents novel flow tube measurements of the chemical composition of SOA produced from NO3 + limonene, with the potential to provide valuable new mechanistic clues and making the (as far as I know) new proposal that dimer formation reactions may be accompanied by HNO3 loss, as a possible explanation for the C20 compounds observed with only a single N. The authors also describe observed thermal desporption profiles that hint at monomers coming from dimer dissociation in the instrument inlet, an important caution to other researchers using this

technique. For these reasons, I think this manuscript will be a valuable contribution to the atmospheric chemistry literature, but it needs substantially more work before it is ready for publication. First, in many places I found the writing confusing and had a difficult time understanding what the authors were saying – I think this draft was at least one round of serious editting away from being ready to submit. I'll flag the sentences I found most confusing below, but after edits, I urge the authors to also find another outside reader to go through the entire manuscript. Second, and more importantly, the analysis of this rich dataset feels incomplete. At present, the paper really just presents FIGAERO MS and thermogram results, cluster analysis, and the HNO3 loss mechanism idea, without much support beyond the chemical formulae observed. I make the following broad suggestions for the authors to further this analysis before resubmitting for publication:

(1) present a better foundation for the idea of HNO3 loss: show a proposed structural mechanism for how this would occur, cite additional literature on the enegetics of such a reaction and of any other experiments that made observations consistent with this proposal, and try to produce an (even coarse) nitrogen budget from your experiments to check if it supports HNO3 loss. How much of the N2O5 you injected didn't show up in gas or aerosol phase CIMS products? is any change in this budget over different experiments consistent with the amount of the products you hypothesize to come from this type of reaction?

(2) The cluster analysis should also be analyzed and discussed in greater detail: thus far, it seems to serve only to highlight the same two "groups" as the MS alone would have – the monomer region (in 3 factors) and the dimer region (in 2 factors). You mention the families in each cluster and have generic chemical formulae for them. Can you propose structures / reasons these would be different? Are they potentially from oxidation at the different double bonds (what would you expect that to look like?) or form RO2 + RO2 reactions vs. RO2 + NO3 reactions? Why is cluster 0 basically spread across the O;C and MW space of clusters 1 and 2 – why is it nevertheless a

separate cluster? Is there any proposed mechanism that would get you this, or could it be that cluster 0 are the fragments of dimers while 1 and 2 are straight monomers? Or, some permutation of this?

(3) It seems you should also be able to do more with the fact that some monomers have double peaks and some don't – can you correlate this to the cluster analysis somehow, or otherwise interpret it mechanistically?

(4) You mention that some observed formulae are in MCM and others are not. Do more with this. Are there any structures predicted to be major products in MCM that you don't observe? I would suggest to show a modeled output of MCM (just a box model) for your expt. conditions. Are the major few predicted products all those that you observe, or are you just observing one product channel / some at random / etc.? You have the data now to truly test the MCM (and you allude to it), and I was disappointed to see that you didn't report a true comparison. For the major formulae that you observed that aren't in MCM, too, I'd like to see more analsysis. You say in your conclusions that these should be included in models, but you haven't told us what they might be. Propose some structures / mechanistic origins / something based on MCM to help guide how your novel observations might be incorporated.

(5) Suggest to read this recent NO3 + limonene paper from the Ng group: http://pubs.acs.org/doi/abs/10.1021/acs.est.7b01460 and include comparisons to these results in your updated draft. Can you make any quantitative estimate of SOA yields to compare to Boyd et al.'s (very high!!) SOA yields from NO3 + limonene, or comment on them based on your mechanism? Are >100% yields consistent with your proposed dimerization mechanism, or inconsistent? Please discuss.

Specific editorial suggestions:

in title: "nitrate-radical-initiated" should be "nitrate radical-initiated", and elsewhere in text

line 11 "reaction of NO3 with limonene"

line 14 "identity and volatility of the most"

Sentence line 17-19 is confusing. How about: "The observed products were compared to those in the Master Chemical Mechanism (MCM) limonene mechanism, and many non-listed species were identified."

line 39-40: "The oxidation of VOCs by"

line 49: find some more recent refs to add to cite list

lines 55-58: seems odd not to have the NO3 + R formation of organonitrates listed here, since this is the one you focus on

line 97 "molecaulr formulae of major nitrate species produced"

line 100 "(based on the Master Chemical. . ."

line 154 "1.4 g cm-3 (Hallquist. . ." { units}

line 167: mention typical [NO3] here too, and comment on whether RO2 + RO2 or RO2 + NO3 reactions should be dominant?

in caption for Table 1, mention hos you know the [N2O5]. Can you use these values to get an approximate SOA yield?

line 210 "silhouette score, s(i) (Rousseuw. . .."

around line 236-240: "regions" is confusing – define as the deignated mass ranges if you'll use for further discussion.

237-238 "These regions corresponded to aerosol samples" : what does this mean? They were always enhanced in aerosol samples relative to gas, or . . .?

line 245: you refer to specific exptal condition of ratio = 2.4. This sounds contradictory to your statement that the regions "always" correspond to aerosol (I interpreted this as

meaning under all ratios of reagents)

line 252: you call C11 a dimer? Also, the carbon number ranges here don't correspond to your shaded regions in Fig. 2, shouldn't they?

line 257: now you're introducing a new designation, the "first" region for what you've called the "monomer" region before (I assume these mean the same thing). I urge you to define a term that refers to these regions at the beginning of this section and stick with it. Even better: label it on Fig. 2.

line 272-273: confused by "at least modestly" ?? wouldn't this just be the remaining 56.5%? I wouldn't call that modestly. Or I don't understand to what you refer here.

line 274-275: confused by "the monomers contain": many? all? on average?

line 276: "Progressively more oxygenated monomers of the general . . ."

line 277: omit the paranthetical after 5âĂŤ9, this is clear.

line 283: how would you know a structure is a PAN? Unless you show a mechanism that would get to those species, I'd just leave this discussion as PNs only, they would all readily dissociate.

line 292: where did the range of formulae you cite for ELVOC come from? Is this your defition, or does it come from Donahue? (similar question for dimer formulae on line 310)

line 299: confused by "using α-pinene." using it as what? Nighttime SOA at SOAS is more likely to be from β-pinene, since its NO3 SOA yields are higher. Not sure what you mean here by invoking α-pinene.

lines 299-303: rework into one sentence; repetitive; confusing. (Maybe because of trying to tie back to the a-pin reference? which you could just remove)

line 304-35: not clear what this sentence means.

C5

line 310-311: parenthetical seems internally contradictory: "only" in aerosol phase, but also "slightly about background" in the gas phase?

line 314 "ion families (defined as groups of molecular formulae with only the number of O atoms varying) to the total . . ." {correct?}

Table 2: the large ranges but with very precise end points for the Tmax reported is weird. If you really think only the range is interesting, truncate sig figs. If as I suspect the actual list of Tmax values for each member of the family (there are always 6 or fewer, so not too crazy) might be interested to aide your interpretation, why not list them instead, on the order of x value to people can see which correspond? then you can discuss more about which Tmax's appear across monomers / dimers and do some analysis / inference about connectedness from those!

line 328 "Additionally, (iii) some. . ."

line 346-348: how is this indicative of monomer contributions? do you mean indicative of LOWER monomere contributions to aerosol?

Fig 3: why are some traces shaded to zero? describe/ discuss or don't have the difference. in caption, "N2O5 ratio" should be "N2O5 to limonene ratio" , right?

lines 362 / 365: do the "few" and the "ten species" refer to the same subset? This para is confusing.

lines 367-369: not sure how / why this suggests favored dimer formation – confusing

line 370: another new designation, "high-MW"! dimer/oligomer? be consistent in how you refer to the different groups

line 373: cite Figure 4

line 374: do you mean "the monomer signal at higher N2O5 to limonene ratio"? If so, say so . If not, clarify what you mean

C6

line 375-376: "The average . . . Fig. 4" : remove this sentence, not clear & not helpful, and can cite Fig. 4 above instead.

line 407: define oxidation state here, where you first mention it, instead of later where you currently define it

Fig. 5: put the labels for mass, desorption temperature, O/C and oxidation state in the same order (1) on the plot, (2) in the caption (and mention all 4!), and put the y axes in the same order, to make life easier on your readers. Also, you show S.D. on the plot (I guess? or, what are the error bars?) – mention this in caption.

line 421 do you mean "and are also represented as members of cluster 0"? i.e., the ions are members of both clusters? Clarify.

lines 424-428: Could an alternative rationale for this difference in oxidation state simply be that monomers, because of their small carbon chain length, need more oxidized functional groups to condense, while dimers are so big they'll condense even with less oxidation? Since you are looking only at the aerosol phase here, this pattern could be skewed by differing volatility.

line 437: oxidation state is defined here, should be at first instance of it earlier in text.

line 438: @ "certain range of masses", state the range

line 440: same comment as lines 424-428.

line 445 "during the process, and"

line 446: as mentioned in general comments above, I think it would be good to include a structural diagram of the HNO3 leaving reaction.

lines 450 & 452: since this relied on having C9 monomers, it would be useful also to explain how these are formed in the mechanism leading up to dimerization.

line 453: at the end of this discussion, I think it would also be good to at least mention

any alternative possible pathway that could make these dimer products – is it really only possible with HNO3 loss, or could you get it some other way? Then, perhaps the nitrogen balance or other evidence can help you bolster your hypothesis that the HNO3 loss is the more likely route.

lines 463-464: "dimer fragmentation . . . monomers." is a confusing sentence

lines 465-469: can't you demonstrate this more conclusively by looking at specific examples of masses with and without double peaks, and possibly matching up the Tmax's, and thus identify the subset of monomers that are also dissociation products and possibly connect them to precursors? Even better – if relative amounts change with different reaction conditions, can you track them rising and falling together? This dataset would seem to have lots of potential to demonstrate these actually linkages, not just make vague statements and what might / could yield what else upon fragmentation.

line 480: "obtained for both gas and condensed-phase" – since you don't discuss gas phase data in this paper, omit, or cite to the companion paper that does study gas phase?

line 484-485: lots of sig figs on these percentages considering the error bars – better to say 63 +/- 7 and 37 +/- 7 %? And perhaps put a few numbers in the abstract?

line 494-496: this has me wondering whether you can learn anything from the relative intensities of the two peaks? would this pattern support that SOA is "largely determined" by low-volatility oligomers?

line 504-505: as mentioned in the general comments, I think you should at least do some discussion of the non-listed products and what they might be.

lines 509-512: are all the hypothesized HNO3-loss dimers in one cluster and others in another? Or, how else can you use the cluster analysis to learn something related to your mechanism speculation?

line 513: "FIGAERO" to be consistent with how you write it above

line 514: "may provide some means of reducing the complexity..." see above general comments. I hope you can work get a bit more out of this.

line 520-521: as mentioned above, hard to include species in modeling studiest if you haven't even suggested what you think they might be.

C9