

We thank the reviewers for the helpful comments! We will now take the benefit from those in improving the manuscript. A point by point response (in black) to the reviewers' comments (in blue) will follow.

## Response to Anonymous Referee #1

This manuscript describes data collected from a FIGAERO-CIMS during laboratory studies using the flow reactor GFROST. Focus is given on the major organic nitrate constituents of secondary organic aerosol from the NO<sub>3</sub> oxidation of limonene. A cluster-analysis method is used in order to distinguish the groups of ions based on their thermodynamic properties and molecular formula information. Mechanisms of dimer formation are suggested based on the grouping performed. The paper is suitable for publication in ACP. My suggestions below are mainly to clarify the presentation

**Reply:** Thanks for the suggestions to clarify the presentations.

Specific comments 1. Recent studies have shown that fragmentation due to thermal dissociation in the FIGAERO-CIMS could strongly affect the chemical formula attribution (Stark et al., 2017). It would be beneficial if a comparison of the different methods of assigning a chemical formula to the major ions could be performed. If not, then the possible uncertainties introduced should be further discussed.

**Reply:** Yes, we should more clearly acknowledge the possibilities for decomposition but would rather be brief and refer to the findings in the Stark et al paper

**Action:** Reference added with discussion on uncertainties.

2. In line 98 it is mentioned that one of the main focuses of this paper is to determine the molecular formula of species that could contribute significantly to SOA formation. Although the uncertainty of calculating the mass concentration using FIGAERO-CIMS would be high it could still indicate whether the compounds measured are indeed a large fraction of the overall mass as has been done from Isaacman-VanWertz et al. (2017).

**Reply:** Assuming common sensitivities for all compounds would enable the reader to find the major contributors to SOA mass in the list of compounds (Table 1 supplemental). The application of various sensitivities for I-CIMS is to date very uncertain and discussed in the literature, e.g. Isaacman-VanWertz et al. (2017).

**Action:** The Isaacman-VanWertz et al. (2017) has been added as reference for current state where they summarising methods to derive concentrations from I-CIMS . In addition, a short notice on the issue brought up by the referee with reference to Table 1 has been added.

3. FIGAERO-CIMS collects both the gas and particle phase compounds on the filter. More information on the gas phase compounds detected would bring light concerning the extent of possible gas phase "interference" during desorption. When the signal of the compounds in the gas phase is high then their contribution to the aerosol during desorption could increase more. Have there been any checks on the contribution of gas phase signal during desorption? How much is it expected to be in the monomer and how much in the dimer range? A figure to illustrate this effect in the supplementary

would be very informative. For example, in lines 346-348 this could also be due to gas phase compounds collected on the filter that undergo evaporation and thus contribute to the aerosol. What is the gas phase concentration of these compounds compared to the aerosol?

**Reply:** The methods and potential artifacts have been described in previous publications. Generally, there are limiting gas-phase contaminations of the condensed phase evaporation. Yes, the gas-phase has also been measured and could be presented to illustrate the ratio between gas and particle phase concentrations.

**Action:** Two figures illustrating partition (ratio between the gas and the particle phase) for ions in monomer and dimer region has been added in supplemental.

4. In Figure 3 for many of the compounds there is a residual signal above zero. How would that affect the signal of the next desorption? When FIGAERO reaches stable conditions what does that exactly mean? It would be fruitful for the reader if background measurements could be provided during these experiments on the Supplementary material. An additional figure to support the stability of the thermograms would be very instructive. For example the average cumulative signal (with error bars indicating the standard deviation of the average) vs temperature, for each compound, with each compound indicated with a different color would be a suggested way.

**Reply:** Usually several cycles are repeated and an average of three desorptions are used for the results

**Action:** Examples of three consecutive desorptions are now presented in supplemental

5. What is the atmospheric relevance with the mixing ratio of N<sub>2</sub>O<sub>5</sub> used? What is the NO<sub>3</sub> expected mixing ratio in the system? A discussion would better inform the reader.

**Reply:** Obviously, the mixing ratio of N<sub>2</sub>O<sub>5</sub> is higher than ambient to provide enough amount of limonene reacting during the time spent in the flow reactor. At a ratio of 1:1 we expect NO<sub>3</sub> to primarily react with the exocyclic double bond, representing the typical case producing primary products, while increasing the ratio will add more possibilities for reactions also to the endocyclic double bond reflecting secondary atmospheric chemistry.

**Action:** Short discussion on our view on this has been added in the manuscript

6. In Figure 4 what is the fit function used? What is the information we gain from this fit choice? Further discussion in the manuscript would clarify these questions. This figure doesn't provide all the data points seen in Table 1. The high N<sub>2</sub>O<sub>5</sub>/limonene ratio of 113.3 is missing. Could that be included or provided in the supplementary? Is this point included in the fit function applied now? Finally, error bars for the y-axis are missing and the fit function should be applied by taking into account this error.

**Reply:** yes, we agree the line is mostly for guidance of the eye and should be removed. The data point at 113.3 was not illustrated as it would extend the x-axes too far.

**Action:** The r<sup>2</sup> has been removed and the missing data point at 113.3 is now noted in the footnote.

7. In section 2.3 was it both gas and particle phase data used as identified species to compare to the MCM? A sentence to make clear that this work is focused on the particulate phase and not the gas phase would better direct the reader at this point.

**Action:** A sentence has been added to direct the reader on this point

8. It would be beneficial for the reader if the discussion in section 3.4 was extended on how the suggested mechanisms can be directly inferred from the grouping technique and the volatility of the compounds.

**Reply:** The lower O/C ratios and loss of one nitrogen compound for some of the dimers while exhibiting a low volatility would support the mechanism suggested. (loss of oxygen(s) and nitrogen in dimerisation)

**Action:** This info has now been clarified.

### Technical comments

Line 47. A broader view of organic nitrates is given by Kiendler-Scharr (2016).

**Action:** Reference added

Line 154. Units are missing.

**Action:** Units of  $\text{g cm}^{-3}$  have been added

Line 167. Delete one dot.

**Action:** Full stop deleted

Line 234. Recent findings suggest that fragmentation due to thermal dissociation occurs in systems like the FIGAERO-CIMS (Stark *et al.*, 2017). See comment 1.

**Action:** The following text has been added to acknowledge the work of Stark *et al.* (2017) and we have considered for possibilities that ions may fragment upon desorption “Stark *et al.* (2017) have recently shown that fragmentation during the desorption can occur within the FIGAERO, although we find no fragmentation here which suggests that the identified ions were products of fragmentation of larger molecules, with exception of one group of compounds in the cluster analysis”

Line 324-337. The authors provide four characteristic desorption patterns and the numbering stops at two.

**Action:** This has now been clarified in the text with the addition of extra numbering in the text

Line 361-362. It would be more informative to add the positive correlation in the supplement as a figure.

**Action:** A Figure on  $\text{Tmax}$  vs  $\text{Mw}$  has been added in supplementary

Line 387. Please define what extremely low signal would be as a value.

**Action:** A definition has now been added.

Line 428. Should be 0-2?

**Action:** Changed to 0-2 in text

Table 1. Sorting of the lists would make the table more readable. Sorting the N2O5 from low to high and within each N2O5 group sorting the limonene from low to high would be one way of performing the sorting. Adding the expected NO3 concentration would be fruitful. Errors for the average SOA mass measured from an SMPS are missing. An additional column of the mass FIGAERO-CIMS could detect (with its much higher uncertainty), as discussed above, would be an indicator of how much of the overall SOA mass is measured in this system.

**Action:** The Table has been ordered as suggested by the reviewer. We did not measure the actual NO<sub>3</sub> concentrations and the total mass from FIGAERO-CIMS is rather uncertain. However, the standard deviation of the mean SOA mass is now included in the Table.

**Table 2. What is the information we gain from the (N/C)x10? Based on all uncertainties the temperature precision could be rounded. Error of the average contribution is missing.**

**Action:** The column displaying N/Cx10 has been removed. The temperatures have been rounded to the nearest degree. Errors of the average contributions are now included.

**Figure 3.** Certain double peak compounds are not highlighted like C10H15NO7, C20H29NO5, C20H24N2O8 etc. The C20H24N2O8 is not written correctly in the annotation. Since there are more compounds that have double peaks plotted it would be clearer to include the double peak compounds with dash lines and avoid highlighting.

**Action:** The highlighting has been removed and the mis-formatted compound name (C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>) has been corrected.

**Figure 5.** It improves the figure if (a) and (b) have the same annotation introduced on the right side outside both figures once. This way you avoid the change in font size that is seen for annotation from Figure (a). For Figure (b) the oxidation state is not mentioned in the axis and the range is not going to minus when it is below zero. It would be beneficial if Figure (c) was separated in two graphs. On the left side a figure of the MW (left-axis) and Tmax (right-axis) and on the right side a figure of the oxidation state (left-axis) and the O/C (right-axis). Box-and-whiskers instead of bars and markers would provide more information on the dataset. This would also show more clearly the temperature increase that is suggested to correlate to the O/C increase. Finally the colors of Figure (c) are similar to the colors of the clusters thus confusing the reader.

**Action:** Changed the plot to a 4-panel plot by separating the bottom graph. The other minor formatting issues were also fixed, like the single legend for the top plots.

References Isaacman-VanWertz, G., P. Massoli, R. E. O'Brien, J. B. Nowak, M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, L. Su, D. A. Knopf, P. K. Misztal, C. Arata, A. H. Goldstein, and J. H. Kroll: Using advanced mass spectrometry techniques to fully characterize atmospheric organic carbon: current capabilities and remaining gaps, Faraday Discussions, doi:10.1039/C7FD00021A, 2017.

Kiendler-Scharr, A.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophys. Res. Lett., 43, 7735–7744, doi:10.1002/, 2016.

Stark, H., R. L. N. Yatavelli, S. L. Thompson, H. Kang, J. E. Krechmer, J. R. Kimmel, B. B. Palm, W. Hu, P. L. Hayes, D. A. Day, P. Campuzano-Jost, M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, and J. L. Jimenez: c, Environ Sci Technol, doi:10.1021/acs.est.7b00160, 2017.

## Response to Anonymous Referee #2

General comments: This paper presents novel flow tube measurements of the chemical composition of SOA produced from  $\text{NO}_3 + \text{limonene}$ , 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  $\text{HNO}_3$  loss, as a possible explanation for the C20 compounds observed with only a single N. The authors also describe observed thermal desorption 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 editing 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  $\text{HNO}_3$  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:

**Reply:** Actually, the manuscript had been sent for English language editing service. However, we might have missed that some of the changes suggested by the English language editing back-fired on the scientific clarity before submission. The paper has now been read again and we have addressed the issues raised by the referee.

(1) present a better foundation for the idea of  $\text{HNO}_3$  loss: show a proposed structural mechanism for how this would occur, cite additional literature on the energetics 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  $\text{HNO}_3$  loss. How much of the  $\text{N}_2\text{O}_5$  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?

**Reply/action:** There are some suggestions in the literature, however, it is not as clear as one hope it should be and we cannot firmly conclude this so we have to leave that open for speculations and following up-studies on simpler systems. The nitrogen budget would be useful but since  $\text{HNO}_3$  is notorious to be “sticky” and we did not measure the other suspected “leaving groups” like  $\text{NO}_2$  and NO we have poor handled on this. However, it is clear that the selected dimers only contain one nitrogen and have lower O/C ratio than the sum of two monomers. Furthermore, the  $T_{\text{max}}$  suggests a high  $M_w$  compound (with low vapor pressure) and not a fragment. We now refer to some recent literature on organic nitrate condensed phase reactions.

(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 RO<sub>2</sub> + RO<sub>2</sub> reactions vs. RO<sub>2</sub> + NO<sub>3</sub> 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?

**Reply:** Maybe, this was the information that was not so clear. However, it is actually stated that cluster 0 is not similar to the monomer cluster 1 and 2 but rather a fragmentation cluster having similar Mw and O/C but different Tmax (much higher). The reason for family m5 and m7 residing exclusively in factor 1 (higher volatility) is not known but clearly interesting results.

**Action:** The language has been polished further and checked.

(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?

**Reply:** Yes, this is already included in the analysis. Some ions have two desorption maximum and then T<sub>max,2</sub> was also added in the analysis. E.g. cluster 0 contains mainly ions with a T<sub>max,2</sub>

(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 analysis. 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.

**Reply:** As stated in the paper 69% of the gas-phase compounds could be referred to MCM compounds (assuming a common sensitivity).

**Action:** The MCM run provided a list of major compounds that is now presented in the supplemental information.

(5) Suggest to read this recent NO<sub>3</sub> + 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 NO<sub>3</sub> + limonene, or comment on them based on your mechanism? Are >100% yields consistent with your proposed dimerization mechanism, or inconsistent? Please discuss.

**Reply:** We realized that this is a recent study that was done in parallel to our work. However, if not necessary we prefer not to explicitly present aerosol yields from a flow reactor study. Furthermore,

with a very different method we abstain also from comments on their high yield .The dimerization mechanism would if anything enhance an aerosol yield since it will increase the observed Tmax.

**Specific editorial suggestions:**

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

**Action:** This has been changed accordingly.

line 11 “reaction of NO<sub>3</sub> with limonene”

**Action:** Text changed to recommended text (replace “and” to “with”)

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.”

**Action:** Text changed to read “Major condensed-phase species were compared to those in the Master Chemical Mechanism (MCM) limonene mechanism, and many non-listed species were identified. The volatility properties of the most prevalent organic nitrates in the produced SOA were determined.”

line 39-40: “The oxidation of VOCs by”

**Action:** Text changed to read “The oxidation of VOCs by”

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

**Action:** reference list updated according to reviewer’s suggestions

lines 55-58: seems odd not to have the NO<sub>3</sub> + R formation of organonitrates listed here, since this is the one you focus on

**Action:** To be added

line 97 “molecular formulae of major nitrate species produced”

**Action:** Text changed to read “molecular formula of major nitrate species produced”

line 100 “(based on the Master Chemical. . .”

**Action:** Text changed to read “(based on the Master Chemical Mechanism)”

line 154 “1.4 g cm<sup>-3</sup> (Hallquist. . .” { units}

**Action:** Units have been added

line 167: mention typical [NO<sub>3</sub>] here too, and comment on whether RO<sub>2</sub> + RO<sub>2</sub> or RO<sub>2</sub> + NO<sub>3</sub> reactions should be dominant? in caption for Table 1, mention how you know the [N<sub>2</sub>O<sub>5</sub>]. Can you use these values to get an approximate SOA yield?

**Reply:** If not necessary we prefer to not explicitly present aerosol yields from this flow reactor study since the experimental design was not aimed at that purpose. The N<sub>2</sub>O<sub>5</sub> was assumed to, under dry conditions, be equal to the amount added into the system. [NO<sub>3</sub>] was not measured.

line 210 “silhouette score, s(i) (Roussew. . .”

**Action:** Text changed to read “silhouette score, s(i) (Roussew

around line 236-240: “regions” is confusing – define as the designated 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 . . .?

**Action:** The regions are now better defined as low and high molecular weight regions and connected to monomer and dimer identification. The statement is basically referring to that elevated ion counts were always present in these region for all the aerosol measurements. This is now rephrased.

line 245: you refer to specific experimental 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)

**Reply:** We selected ratio 2.4 as one example of all the ratios studied and not a specific exceptional condition. We don’t claim it to be exceptional in the text? Rather we follow up showing the Figure 4 where there is a gradual change in monomer/dimer intensities as the  $\text{N}_2\text{O}_5$ /Limonene ratio changes

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?

**Reply:** The definition was based on that C11 compounds must be produced from two carbon containing entities. The definition of monomer/dimers has in atmospheric science been used in a very reluctant way compared to traditional chemistry science, however, we prefer to stick to the more relaxed definition previously used. However, we agree that the carbon numbering does not fit with the figure. Basically, the values are calculated on HR-fit data selected based on carbon number stated while the shading in Figure for simplicity was based on m/z. We agree this is not consistent.

**Action:** This is now revised and clarified in the text.

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.

**Action:** First is changed to monomer

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.

**Action:** Text changed to state significant contribution

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

**Action:** This sentence is confusing and has been removed

line 276: “Progressively more oxygenated monomers of the general . . .”

**Action:** Text now reads “Monomers with Progressively more oxygenated monomers of the general formula  $\text{C}_{10}\text{H}_{15}\text{NO}_x$ ”

line 277: omit the parenthetical

**Action:** Parentheses removed

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.

**Action:** Here we only state that they may be PN or PAN like. The discussion on PAN like compounds are removed as suggested.

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

**Action:** Text amended to read "i.e., ELVOCs, which play a key role in SOA formation (Donahue et al., 2012)."

line 299: confused by "using  $\alpha$ -pinene." using it as what? Nighttime SOA at SOAS is more likely to be from  $\beta$ -pinene, since its NO<sub>3</sub> SOA yields are higher. Not sure what you mean here by invoking  $\alpha$ -pinene.

**Action:** The Lee et al study used lab experiments on  $\alpha$ -pinene to match observations in the field. The sentence has been revised to: "The gaseous parent compounds were identified as monoterpenes, matching ions measured in a laboratory study on  $\alpha$ -pinene."

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

**Action:** removed as suggested by referee

line 304-305: not clear what this sentence means.

**Action:** removed as a consequence of the point above.

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

**Action:** The text has been amended to read "(i.e., they were present only in the aerosol phase and at insignificant levels in the gas samples)."

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

**Action:** The text has been amended to read "The contributions of the 11 most prevalent ion families (defined as groups of molecular compositions with only the number of O atoms varying) to the total desorbed organic signal are summarized in Table 2."

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!

**Action:** The Tmax values have been truncated as suggested by the referee.

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

**Action:** Text changed to read "Additionally, (iii) some"

line 346-348: how is this indicative of monomer contributions? do you mean indicative of LOWER monomeric contributions to aerosol? Fig 3: why are some traces shaded to zero? describe/ discuss or don't have the difference. in caption, "N<sub>2</sub>O<sub>5</sub> ratio" should be "N<sub>2</sub>O<sub>5</sub> to limonene ratio", right?

**Action:** Basically, the compounds with low Tmax were also found in the gas-phase and we then suspect them to not be fragments of larger “dimer compounds” but rather being the same compounds in the condensed phase that evaporates without fragmentation. The sentence has been changed to:

“In general, compounds evaporating at relatively low temperatures were also found in the gas phase, indicative of monomer that partitioning between gas and particle phase.”

line s 362 / 365: do the “few” and the “ten species” refer to the same subset? This para is confusing.

**Action:** These two sentences have been revised and are now reading:

“Monomer, i.e., lower-mass, species ( $C \leq 10$ ) desorbing at high temperatures could be produced as fragments via thermal degradation of higher-MW species. Some of these ions are matching the chemical composition ( $C_{10}H_{16}O_4$ ,  $C_{10}H_{17}NO_5$ ,  $C_{10}H_{17}NO_6$ , and  $C_7H_{10}O_4$ ) of primary products within the MCM, accounting for (on average)  $69.0 \pm 10.8\%$  of the signal detected in the gas phase. Here some possibilities are plausible, one could be that they are produced as monomer but are important building blocks in the dimer formation, thus thermally decompose back to monomers during desorption.”

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

**Action:** See point above

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

**Action:** Changed according to suggestions above.

line 373: cite Figure 4

**Action:** Text now refers to Figure 4

line 374: do you mean “the monomer signal at higher  $N_2O_5$  to limonene ratio”? If so, say so. If not, clarify what you mean

**Action:** The sentence has been modified and now reads: “At high ratios of  $N_2O_5$  to limonene, the fraction of dimer species decreased, whereas the percentage of monomer species (fragments) with high Tmax increased (Figure 4).”

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

**Action:** The sentence has been removed

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.

**Action:** Oxidation state now defined in Line 400. The figure has been changed and the reference to SD is now given in the 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.

**Action:** The text now reads “These results from the fact that 87% and 69% of cluster 1 and 2 ions, respectively, have secondary thermogram peaks and Tmax values, and are represented as members of both clusters 1 and 0.

line s 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.

**Action:** Yes, this could be one reason. This alternative rationale is now included in the discussion.

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

**Action:** Oxidation state now defined in Line 400

line 438: @ “certain range of masses”, state the range

**Action:** The wording has been changed so it is now clear that the dependence are within respectively group and not between the dimer and monomer groups. “A positive correlation between the average O/C ratios and  $T_{max}$  values was obtained within monomer (clusters 1 and 2) and dimer (clusters 3 and 4) groupings, with more highly oxygenated species desorbing at higher temperatures than their less-oxygenated counterparts. This is also reflected in the overall oxidation state of the clusters. It should be noted that these correlations do not hold between the different groups since monomer species had (in general) higher O/C ratios than the dimers.”

line 440: same comment as line s 424-428.

**Action:** ok, see comment on line 424-428

line 445 “during the process, and”

**Action:** Text changed to read “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  $\text{HNO}_3$  leaving reaction.

**Action:** Even if the mechanism on  $\text{HNO}_3$  as the leaving group (in a reverse esterification process) is plausible we now after the review comments would be a little bit more cautious. This cautiousness has now been implemented in the manuscript and in line with that we do not want to be explicit in this formation. However, we include that this could be seen as a reverse esterification but also might be linked to observed hydrolysis of organic nitrates (Rindelaub et al, 2016).

line s 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.

**Reply:** There are several pathways for C9 monomer compounds. E.g. if both double bonds are oxidized and there is a C-C bond breakage for the exocyclic double bond it will create a C9 monomer. Additional oxygens could be produced by internal H abstractions.

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

HNO<sub>3</sub> 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 HNO<sub>3</sub> loss is the more likely route.

**Reply/Action:** Yes, there are some suggestions in the literature, however, it is not as clear as one hope it should be and we cannot firmly conclude this so we have to leave that open for speculations and following up-studies on simpler systems. The nitrogen budget would be useful but since HNO<sub>3</sub> is notorious to be “sticky” and we did not measure the other suspected “leaving groups” like NO<sub>2</sub> and NO we have poor handled on this. However, it is clear that the selected dimers only contain one nitrogen and have lower O/C ratio than the sum of the two monomers. Furthermore, the Tmax suggests a high Mw compound (with low vapor pressure) and not a fragment. We now refer to some recent literature on organic nitrate condensed phase reactions (e.g. Rindelaub et al, 2016)

line s 463-464: “dimer fragmentation . . . monomers.” is a confusing sentence

**Action:** Fragmentation has been replaced and the sentence reworded. The sentence now reads:

“Due to the loss of HNO<sub>3</sub> during dimerization, the potential dimer decomposition during desorption is expected to yield fragments which differ in molecular composition from the precursor (i.e., pre-dimerization) monomers.”

line s 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.

**Reply/Action:** In theory, this could be a way forward. However, the complexity and numbers of free parameters will put constraints on such detailed analysis. Actually, the suggestion is very nice but should be done on simpler systems where more solid conclusions on this mechanism could be done. The suggested mechanism is now brought forward with cautiousness and this is now supported with statements on other possible leaving groups and reference to previous work.

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?

**Action:** Rephrased to state only particle phase “High-resolution mass spectrometric data was analysed for condensed-phase reaction products resulting from NO<sub>3</sub> initiated oxidation of the monoterpane, limonene.”

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?

**Action:** Number of significant figures has been reduced

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?

**Reply:** If the two peaks are two different compounds with two different formation mechanisms and relative contribution to SOA there is little connection between them as for any pair of compounds detected. So we would not draw those conclusions from these observations.

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.

**Action:** The products that were not found in the MCM list are now marked in the full list found in the supplemental. A comment on these and potential sources are now included.

line s 509-512: are all the hypothesized HNO<sub>3</sub>-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?

**Action:** The cluster analysis clearly separated the fragments from the dimers (obviously, since a fragment cannot be formed according to the mechanism) and also classified the dimers in two groups.

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

**Action:** Text changed to read "FIGAERO-CIMS"

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.

**Action:** The text is modified to capture extended use of cluster analysis and how this can be extrapolated and compared to other systems.

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.

**Action:** The compounds are now listed in the supplemental and a short note on potential for extension of the MCM is given.

## Response to Anonymous Referee #3

This work investigated organic nitrate formation from NO<sub>3</sub> oxidation of limonene. Experiments were conducted using different N<sub>2</sub>O<sub>5</sub>/limonene ratios. Speciated gas and particle phase organic nitrates were measured by the FIGAERO-HR-ToF-CIMS. Cluster analysis of the desorption temperatures of organic nitrate species resulted in five clusters; the relationships between O/C, OS, MW, etc of these clusters were discussed. Formation of dimers was observed and reaction mechanisms for dimer formation were proposed.

This is an interesting study and the manuscript is generally well-written and easy to follow. This study will be of interest to the greater atmospheric community. My main comments are 1) while the experiments were conducted over a range of N<sub>2</sub>O<sub>5</sub>/limonene ratios, the authors shall provide more context to this experimental design. Also, the results from experiments with different N<sub>2</sub>O<sub>5</sub>/limonene ratios need to be more extensively and clearly discussed. 2) I have some concerns regarding the discussion of the results shown in Fig. 5, please see details below. 3) There are a number of recent studies on nitrate radical oxidation of biogenic hydrocarbons, it would be appropriate that these studies are referenced in the manuscript to reflect the current state of knowledge. Overall, I recommend publication in ACP once these comments are addressed. Most comments are mainly to improve clarity of the manuscript.

### Main Comments

1. Page 5 line 158. Are potential impurities (e.g., NO<sub>2</sub> and HNO<sub>3</sub>) in the N<sub>2</sub>O<sub>5</sub> synthesized measured and quantified? Please make this clear in the manuscript.

**Action:** This is now clarified in the experimental: “N<sub>2</sub>O<sub>5</sub> was synthesized by reacting ≥20 ppm O<sub>3</sub> with pure NO<sub>2</sub> (98%, AGA Gas) in a glass vessel and then passing the flow through a cold trap maintained at -78.5°C using dry ice. Even if neither HNO<sub>3</sub> nor NO<sub>2</sub> was measured it is known from previous work that this method typically provides a source with impurities less than a few percent. It is well known that the resulting white solid would show signs of yellowing, due to nitric or nitrous acid contamination, if exposed to moisture (e.g., ambient lab air) so handling of the N<sub>2</sub>O<sub>5</sub> was done accordingly.”

2. Page line 168. What is the reason for performing experiments with different N<sub>2</sub>O<sub>5</sub>/limonene ratios? Please provide more context here.

**Reply:** It would reflect a gradual increase in reaction of the exocyclic double bond. At a ratio of 1:1 we expect NO<sub>3</sub> to primarily react with the exocyclic double bond, representing the typical case producing primary products, while increasing the ratio will add more possibilities for reactions also with the endocyclic double bond, reflecting secondary atmospheric chemistry.

**Action:** Short discussion on this has been added in the manuscript

3. Page 6 Table 1. a. With these N<sub>2</sub>O<sub>5</sub>/limonene ratios, are all limonene (and both double bonds?) reacted away? Please clarify and change the “limonene” in the table to either “reacted limonene” or “initial limonene”. b. What is the RO<sub>2</sub> reaction regime in these experiments? RO<sub>2</sub> + NO<sub>3</sub>? RO<sub>2</sub> + RO<sub>2</sub>? c. Can SOA yields be quantitatively calculated from the values in the table? If the “limonene” is

reacted limonene, the SOA yields appear to be very low compared to previous studies by Fry et al. (ACP, 2009), Fry et al. (ACP, 2011), and Boyd et al. (ES&T, 2017). Please discuss the results from this study in the context of these prior studies. Also, do the data shown in Table 1 follow a typical Odum 2- product yield curve?

**Reply:** If not necessary we prefer not to explicitly present aerosol yields from this flow reactor study. The experiments were not designed to derive yields.

4. Page 8 line 238. It was noted that "...the relative signal intensities varied with the amount of limonene and N<sub>2</sub>O<sub>5</sub> present in the system". I think the authors are referring to Fig. 4? Please add the figure number to the sentence to help guide the readers if this is the case.

**Reply:** Yes, the referee is right but we then realize that this figure would then be introduced too early in the manuscript.

**Action:** We have removed the statement "and the relative signal intensities varied with the amount of limonene and N<sub>2</sub>O<sub>5</sub> present in the system."

5. Page 8 line 260. It is not immediately clear what these species are without diving into the entire MCM mechanisms. The authors should at least include the formation mechanisms of these major ions in the SI to help guide the readers. Also, it would be helpful to propose mechanisms for the major species that were observed in this study but are not in MCM. On the related note, Boyd et al. (ES&T, 2017) recently expanded the limonene + NO<sub>3</sub> mechanisms in MCM. It might be worthwhile to evaluate if some species detected in this study are covered in the expanded mechanism in Boyd et al.

**Reply:** The Boyd et al. paper was unfortunately not available when the majority of the analysis in the present study was done. Some of the species in the expanded mechanism have now been considered.

6. Page 9 line 280. What are some of the mechanisms for limonene and its oxidation products to react with NO<sub>2</sub> and HNO<sub>3</sub>?

**Reply:** The possibilities are for example that NO<sub>2</sub> could react with peroxy-radicals and HNO<sub>3</sub> might do condensed phase nitration. We don't think that this of general value and would not add that.

7. Page 10 line 293. Nah et al. (ES&T 2016) also measured a large suite of highly oxygenated organic nitrates from NO<sub>3</sub> oxidation of a-pinene and b-pinene in laboratory experiments, using the FIGAERO-HR-ToF-CIMS. Many of those are also observed in Lee et al. (PNAS, 2016).

**Reply:** We have noted the request for including Nah et al. (ES&T 2016).

**Action:** As the last sentence in this paragraph we added: Recently, Nah et al. (ES&T 2016) also measured a large suite of highly oxygenated organic nitrates from NO<sub>3</sub> oxidation of a-pinene and b-pinene in laboratory experiments.

8. Page 10 line 299. It is noted that "The similarity with ions from the NO<sub>3</sub>-initiated limonene oxidation further emphasizes the importance of monoterpenes as precursors of organic nitrates". It

would be informative if the authors indicate in the Table in SI (the ion list) regarding which ions have also been observed in the ambient (Lee et al.) and other monoterpene experiments (Nah et al).

**Reply:** We would prefer to focus on comparison with limonene studies. It turns out there is now a parallel study by Boyl et al, 2017 (accepted when this manuscript was submitted) that would be better suited for comparisons.

9. Page 10 line 301. Rollins et al. (Science, 2012) discussed the importance of limonene + NO<sub>3</sub> in a field study.

**Action:** This reference has now been added

10. Page 12 line 362. It was noted that there is a positive correlation ( $R^2 = 0.67$ ) between Tmax and molecular mass. Are the authors referring to Fig 5a? If so, it does not look like the overall correlation is that good? Please clarify.

**Reply/action:** There were no figures showing this correlation. However, we have now added one figure in the supplemental showing this correlation.

11. Page 13 line 370-379. (this is also related to comment #2 above). It is not clear to me how the higher N<sub>2</sub>O<sub>5</sub>/limonene experiments lead to formation of more thermally unstable mechanisms. Please explain. More discussions are needed here, to provide context to why experiments are conducted with different N<sub>2</sub>O<sub>5</sub>/limonene in the first place and why/how the resulting compositions are different.

**Reply:** This is discussed in the above #2 comment

12. Page 13 Figure 4. What is the function used for the fit? Is this just to guide the eye or there is a fundamental reason for such a dependence?

**Reply / Action:** This fit has now been removed, as discussed in a previous comment it illustrated a general best fit for the eye of the reader

13. Page 15, discussions of Figure 5. The authors attempted to discuss the relationships between O/C, OS, and MW, etc. However, within uncertainties, there do not seem to be significant differences in the O/C and OS values for all clusters. Hence, this discussion needs to be revised.

a. (related to comments # 2 and 11 above). In Figure 5, will any specific patterns emerge if the authors only look at the data from experiment of a particular N<sub>2</sub>O<sub>5</sub>/limonene ratio?

b. line 418. It was noted that the O/C of cluster 0 is similar to clusters 1 and 2. However, within the uncertainties, the O/C ratios of all clusters are almost the same.

c. line 426, should the high-MW clusters be (3,4)? And the low-MW clusters be (0, 1, 2)?

d. line 427. It was noted that the ions in the high-MW clusters have a lower OS than ions in clusters 0-3. Firstly, should “0-3” be “0-2”? Secondly, it does not look like the high-MW clusters have a lower OS. Within uncertainties, the OS values appear to be the same for all clusters.

e. line 434. It was noted that a positive correlation exists between O/C and Tmax. It is not clear how this is case from the data shown in Fig. 5c. Please provide a figure and show the R<sup>2</sup> value.

**Action:** This section has now been revised considering the points addressed by the referee.

#### Minor Comments

1. Page 2 line 44. Would be appropriate to reference Ng et al. (ACP, 2017).

**Action:** Reference has been added

2. Page 2 line 46. Would be appropriate to also reference Day et al. (AE, 2010); Fry et al. (ACP, 2013); Xu et al. (PNAS, 2015); Xu et al. (ACP, 2015); Boyd et al. (ACP, 2015); Kiendler-Scharr et al. (GRL, 2016); Nah et al. (ES&T, 2016).

**Action:** References have been added

3. Page 2 line 60. Delete “M” in front of Hallquist.

**Action:** The “M.” has been removed

4. Page 3 line 77. Boyd et al. (ES&T, 2017) recently investigated SOA formation from NO<sub>3</sub> oxidation of limonene.

**Action:** Reference has been added

6. Page 14 Figure 5. Missing y-axis label for 5b?

**Action:** This is fixed now.