Atmospheric
Chemistry
and Physics
Discussions

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 #3

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This work investigated organic nitrate formation from NO3 oxidation of limonene. Experiments were conducted using different N2O5/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 N2O5/limonene ratios, the authors shall provide more context to this experimental design. Also, the results from experiments with different N2O5/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., NO2 and HNO3) in the N2O5 synthesized measured and quantified? Please make this clear in the manuscript.

2. Page 5 line 168. What is the reason for performing experiments with different N2O5/limonene ratios? Please provide more context here.

3. Page 6 Table 1.

a. With these N2O5/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 RO2 reaction regime in these experiments? RO2 + NO3? RO2 + RO2?

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?

4. Page 8 line 238. It was noted that "….the relative signal intensities varied with the amount of limonene and N2O5 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.

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 + NO3 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.

6. Page 9 line 280. What are some of the mechanisms for limonene and its oxidation products to react with NO2 and HNO3?

7. Page 10 line 293. Nah et al. (ES&T 2016) also measured a large suite of highly oxygenated organic nitrates from NO3 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).

8. Page 10 line 299. It is noted that "The similarity with ions from the NO3-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).

9. Page 10 line 301. Rollins et al. (Science, 2012) discussed the importance of limonene + NO3 in a field study.

10. Page 12 line 362. It was noted that there is a positive correlation (R2 = 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.

11. Page 13 line 370-379. (this is also related to comment #2 above). It is not clear to me how the higher N2O5/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 N2O5/limonene in the first place and why/how the resulting compositions are different.

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?

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 N2O5/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 R2 value.

Minor Comments

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

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).

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

4. Page 3 line 77. Boyd et al. (ES&T, 2017) recently investigated SOA formation from NO3 oxidation of limonene.

5. Page 3 line 85. Would also be relevant to cite Xu et al. (PNAS, 2015), Xu et al. (ACP, 2015), and Rollins et al. (Science, 2012). Out of all the references listed in the manuscript and these few ones I mentioned here, Rollins et al. will likely be the most relevant to this study due to the relatively higher concentrations of limonene at Bakersfield.

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