

Interactive comment on “Molecular composition and volatility of multi-generation products formed from isoprene oxidation by nitrate radical” by Rongrong Wu et al.

Anonymous Referee #1

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General comments

This study describes chamber studies of the chemistry of secondary organic aerosol (SOA) formation from the reactions of isoprene with nitrate radicals, illustrates the formation mechanisms of the multi-generation organic nitrates, investigates the volatilities of organic nitrates using both parametrization and experimental methods, and evaluates their potential to form SOA. The paper is well written, and the experiments and data analysis are well done. The mechanisms that are proposed are very plausible. Together with the volatility information of the organic nitrates, this study provides valuable information for understanding the isoprene-nitrate radical chemistry. I would

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recommend the publication of the manuscript in Atmospheric Chemistry and Physics. However, there are a few points I would like the authors to clarify or add some more information.

Specific comments

Page 2 line 43-44: Do you mean organic nitrates monomers and organic nitrates dimers? Are CHO compounds also monomer and dimers?

Page 3 line 66-72: It is necessary to mention why isoprene, which is emitted in the daytime, also plays an important role in night-time chemistry.

Page 5 line 145-148: It is a little bit confusing how much you added for each injection “~100, 30 and 10 ppbv of O₃, NO₂, and isoprene, respectively, were added. . . After another ~ 1.5 hours, the chemistry was accelerated again by the third injection, and the concentrations of O₃, NO₂, and isoprene reached ~ 100, 25, and 10 ppbv, respectively, after the injection.” It is better to keep it consistent.

Page 5 line 150: Were there any differences among the different steps?

Page 6 line 174: How many compounds were identified and how many of them were deprotonated ions?

Page 7 line 180: Was PFP used for mass calibration? How did you do the mass calibration for the range between 350 to 500+ Th?

Page 7 line 195: Did it happen only for one experiment or several during the campaign? It is not clear when you say “the influence from isomers and the differences in sensitivity between the two instruments.”

Page 8 line 254: Was the nitrate group (-nN*bN) included in Donahue et al. (2011)?

Page 16 line 499-501: Could the reason also be that the Br- CIMS is not sensitive to those 4N and 5N-dimers, as they have many oxygen atoms?

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Page 17 line 552-556: It would be interesting to compare this value to that of other OH, O₃ initiated systems and/or the ambient aerosols. Could you make it clearer whether the increased OSc is due to the addition of nitrate group(s) only or other functional groups?

Page 26 line 831: The C* values from the three GC methods are higher than those from the experimental method.

Page 27 line 849: Similarly, the GC methods predict higher C* for less-functionalized. . .but lower C* for highly functionalized dimers.

Page 27 line 859-863: This study suggests that the experimental methods might give the most accurate volatility, but why did you use the median value of C* calculated by all parameterization and experimental methods for further evaluation of their potential to form SOA? The latter gave lower values of C* than that from only experimental methods, especially for those dimers with 2 and 3 nitrate groups. The SOA yield (5%) is estimated based on the assumption that all the dimers in the low- or extremely low-volatility range will condense completely. These compounds are exactly those dimers with 2 and 3 nitrate groups. Would the SOA yield become smaller by using values from the experimental methods? Please clarify this point and make it consistent.

Page 28 line 864: Why C₅H₉N₃O₁₂ has much higher C* than C₅H₉N₃O₁₀? If it is because of the same reason as you described for C₅H₉N₃O₆ (vs. C₅H₉N₃O₅), please also mention it.

Page 28 line 885-888: It would be good to clarify the RO₂ fate (reactions with NO₃, HO₂, and RO₂) for the whole experiment, as well as for different steps, and how it compared to the typical branching ratio in the atmosphere. It helps the comparison of the SOA yields to other studies and helps to interpret the multi-generation chemistry observed in this study in the ambient atmosphere.

Page 29 line 889: It is not clear that what are the “minor dimer products”.

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Page 29 line 915: What is the conclusion about the CA methods?

Technical corrections

Page 28 line 864: (1) Please put all markers on the top of the background (2) and change the legend (e.g. red markers for C₅H₈,₁₀N₂O₈-10, and C₅H₆N₂O₈, C₅H₈N₂O₇, C₄H₆N₂O₇), please either use different colours, or change your legend.

Page 29 line 895: Please update the reference of Zhao et al.

SI Table S3: Please clarify which method was used for the volatility.

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