Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-1178-RC2, 2020

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on "Highly oxygenated organic molecules (HOM) formation in the isoprene oxidation by NO$_3$ radical" *by* Defeng Zhao et al.

Anonymous Referee #2

Received and published: 21 December 2020

General:

The authors investigate organic nitrates formed from the oxidation of isoprene with NO3 radicals, illustrate the formation mechanisms of these organic nitrates (including HOM monomer, dimer, and trimers), their yield, and their contribution to SOA yield. The study is well designed and the data are well presented. If the authors can address my points and questions below, I would recommend the publication of the manuscript in Atmospheric Chemistry and Physics.

Specific:

1. Line 46 – It's a bit ambiguous for "both nucleation and growth of SOA". HOM are important in nucleation of gaseous vapours, and they contribute to the growth of aerosol particles. Maybe a bit better to say e.g. HOM play a pivotal role in the atmospheric nucleation and also particle growth on pre-existing particles (secondary organic aerosol, SOA).

2. Line 92 – How about the chemical lifetime of the reaction of isoprene with NO3?

3. Line 94 – How significant is the reaction of isoprene with NO3 contributing to NO3 loss at night? Is it dominating in isoprene-dominated region? How about in monoterpene-dominated region? And during the day, how does it compare to the isoprene oxidation with OH?

4. Line 143 – Please add the RH to describe how dry the condition was, e.g. RH<2% or lower. Also add the temperature inside the SAPHIR chamber somewhere in the Experimental part, e.g. line 125.

5. Line 158 – With a mass resolution of 4000, I am a bit curious is it difficult to distinguish different compounds at the same m/z (especially with one dominating compound), such as CHON1 from CHON3,5 compounds, CHON2 from CHON4 compounds, 1N-radicals from 2N-compounds, etc? It would be nicer to show a few masses of peak-fitting results of some organic nitrates in the supplement.

6. Line 163 – Is the wall loss rate the same at different temperature in the SAPHIR chamber? Did you have the same chamber temperature as in Zhao et al., 2018?

7. Line 195-197 – Why are the 2N-monomers dominating over 1N-monomers? Is it (partly) due to the reaction of NO3 radical with the remaining double bond of 1N-monomer (forming 2N-monomers) being more reactive compared to the reaction of NO3 radical with the first double bond (C1) of isoprene (forming 1N-monomers)?

8. Line 254-255 – If the fast loss of C5H9NO10 after isoprene addition is due to faster wall loss, why did the compound decay slower after ~21:40 PM (which I think is partly due to wall loss) compared to those after isoprene addition? Maybe some other rea-

sons are more important for its fast loss. Maybe it is similar to C5H9N2On radicals, that both its reactions and additionally wall loss contribute.

9. Line 264-265 – If the peak intensity of C5H8NO7 radicals in Fig. S4 is plotted in log scale, maybe it's more obvious that it increased during isoprene addition? As far as in the current figure, I cannot see that clearly and can only see it continuously increasing over time. But it's more clear for C5H8NO8 radicals that is responding to isoprene addition.

10. Line 267-270 – For the RO2 in C5H8NOn radicals series, do you mean the radicals with n>=9 cannot be distinguished from 2N-monomers, but C5H8NO7 radicals and C5H8NO8 radicals (you shown in Fig. S4) can be distinguished because they don't have interference compounds nearby them?

11. Line 303 – Other than SOAS, C5 organic nitrates (C5H7-11NO4-9) were also observed in both gas phase and particle phase with FIGAERO-CIMS in a rural area in Germany (Huang et al., EST, 2019), although their measurement site was not an isoprene-dominating region.

12. Line 349-350 – "C5H9N2On radicals M2b were formed from C5H9NO4 followed by an alkoxy-peroxy step" is from Scheme 3b, not from Scheme 2.

13. Line 356 – It's not the case for C5H10N2On and C5H8N2On with n=7. With increasing oxygen number, they increased and then decreased.

14. Line 506 – For these 1N-dimers, have you checked the monoterpene concentration from PTR in the SAPHIR chamber? Is the monoterpene concentration in the chamber low enough not to produce any C10H16NOn molecules to interference/contaminate the results?

15. Line 523-524 – Why only C5H8NOn radicals with n>8 can react with isoprene? The C5H8NOn radicals detected (in Table 1) has an n range of 7-12, and the n range for C10H16NOn are expected to be between 9 and 14, based on R13. But in Table 2,

the n range for C10H16NOn is between 10 and 16. Could you infer whether the smaller n (n<=8) for C5H8NOn radicals can work or not to form C10H16NOn from R13? If not, could you give a possible explanation why the smaller n cannot work? And also how was C10H16NO16 formed?

16. Line 568-571 – Can you also check the sesquiterpene concentration in the chamber to exclude the contamination of its products?

17. Line 603-604 – From the results, it's suggesting whether they were first-generation products or second-generation products, or a mix/combination of both, if I didn't misunderstand.

Technical:

1. Line 98 – "initials". Do you mean "initial"?

2. Line 116 – Change to "in the isoprene+NO3 system" throughout the manuscript.

3. Line 123 – The first letter "s" in the word "system" is in Italic.

4. Line 148 – Can you plot the Fig. S1 similar to Fig. S2 so that easier to compare with Fig. S2? Or just label those additions directly in Fig. S2? Because there is no x axis in the SAPHIR box in the figure, but it seems the x axis is time.

5. Line 186 – Please specify in the Figure 1 caption that the m/z has included the reagent ion (15NO3-).

6. Line 204 – (a) the labelled species in the figure 2 caption at m/z 351 and 353 should be C5H8N2O8 and C5H10N2O8 with H[15N]2O6-. Also in the figure itself, they are labeled as C5H8N2O14H[15N]2O6- and C5H10N2O14H[15N]2O6-. Please double check them and correct. (b) I suppose the number on the upper left corner of each compound is the m/z including the reagent ion (15NO3-). Please also specify that in the Fig. 2 caption. (c) What's the blue circle in the figure at m/z around 390?

7. Line 211 –In Scheme 1 caption, it says (b) is for n = 8, 10, 12. But in the Scheme 1b

itself, it's showing compounds with n = 4, 6, 8. Complete the Scheme 1b to show the compounds with n = 10 and 12.

8. Line 235 – Remove the first "in".

9. Line 310 – n = 9, 11 are odd number of oxygen atoms, instead of even number.

10. Line 339 – In Scheme 2a, -ONO2 is missed from the 2nd molecule.

11. Line 345 – In Scheme 3b, -ONO2 is missed from the 2nd molecule.

12. Line 372 – Change "VOCs" to "VOC". You have been using "VOC" previously in the manuscript. So make it consistent.

13. Line 385 – Could you separate these 3N-monomers in Fig. S8 into two panels, or use log scale? It's not obvious to see their time profile, especially for compounds with oxygen number bigger than 12, which were overlapping on top of each other.

14. Line 390 – Change "Such an mechanism" to "Such a mechanism".

15. Line 438-439 – Could you visualize the mass defect plots in Fig. 4 in a better way? Compound series were so close to each other to see clearly which compound belongs to which line. And also it's better to label the number of oxygen atoms to guide audience since you are discussing a lot of oxygen numbers. Both for Fig. 4 and Fig. 2. For Fig. S11, compound series were not so many and therefore not so difficult to distinguish.

16. Line 443 – Since you have mentioned the compounds clustered with H[15N]2O6- were labelled in grey in Figure 2 caption. Do the same for Figure 4 caption for the compound in grey (C10H17N3O12-14H[15N]2O6-).

17. Line 551-552 – Most abundant trimers were C15H24N4On (n=17-23), but in Fig. S11, n=16-22. Double check. Also double check all the n ranges for each compound series in the figures, tables, and text throughout the manuscript and supplement.

18. Line 556 – The formation pathways of dimer RO2 C10H16N3On (n=14-20) and C10H17N2On are shown in R10 and R11.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-1178, 2020.