

Responses to Referee # 1

We thank the reviewer for the careful review of our manuscript. The comments and suggestions are greatly appreciated. All the comments have been addressed. In the following, please find our responses to the comments one by one and the corresponding revisions made to the manuscript. The original comments are shown in italics. The revised parts of the manuscript are highlighted.

Anonymous Referee #1

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Isoprene is one of most critical biogenic VOCs precursor world widely towards forming secondary organic aerosols (SOA). This work investigated detailly the HOM formation from NO₃ oxidation of isoprene. Molecules of isoprene-HOM monomer, dimer, and trimer containing 1-5 nitrogen atoms were detected, and their detailed formation pathways were discussed. These HOMs can contribute to SOA significantly globally. I, therefore, recommend this manuscript can be published in ACP after some minor revision.

Specific comments

1. What's the definition of HOM in this work? Does it follow the definition in Bianchi et al., Chemical Reviews 2019, e.g. contains at least 6 oxygens formed from RO₂ auto-oxidation.

Response:

In our study, we used the same definition of HOM as by Bianchi et al. (2019). In the revised manuscript, we have clarified HOM definition explicitly.

“In this study we refer to the definition of HOM by Bianchi et al. (2019), i.e., HOM typically contain six or more oxygen atoms formed via autoxidation and related chemistry of peroxy radicals.”

2. Did the authors find some molecules that can be identified from NO₃ oxidation but not contain any N atom?

Response:

We have identified ~400 peaks in total and most HOM contain nitrogen atoms with few exceptions such as C₅H₁₀O₈ and C₅H₈O₁₁, which were minor peaks (<~1% of the maximum peak). C₅H₈O_{10/11} overlap with the peak of C₅H₁₀NO_{9/10}, and hence cannot be assigned with high confidence. In the revised manuscript, we have added the following information about this question.

“Almost all peaks are assigned HOM containing nitrogen atoms with possibly few exceptions such as C₅H₁₀O₈ and C₅H₈O₁₁ with very minor abundance (<~1% of the maximum peak).”

3. Line 83-84: There was some discussion on NO₃ oxidation of monoterpene to form HOM, e.g. Yan et al., 2016; 2020.

Response:

In the revised manuscript, we have added more references including Yan et al. (2020) and Yan et al. (2016).

4. Line 149-150: I may suggest adding more statements on how to rule out the reaction with O₃ and OH.

Response:

In our study, the reaction of isoprene with O₃ accounted for ~3% of the isoprene consumption for the whole reaction period and <1% in the first isoprene addition period. As OH is mainly formed via Criegee intermediates in isoprene+O₃ (Nguyen et al., 2016), the reaction of isoprene with OH contributes less than that isoprene+O₃. Thus isoprene + OH was negligible because the OH yield is less than one (Malkin et al., 2010). This is consistent with our finding based on OH concentrations measured by LIF that the reaction isoprene with OH only contributed very minor fraction of isoprene consumption. In the revised manuscript, we have further discussed this topic.

“Experiments were designed such that the chemical system was dominated by the reaction of isoprene with NO₃ and the reaction of isoprene with O₃ did not play a major role (<3% of the isoprene consumption).”

“The contribution of the reaction of isoprene with trace amount of OH, mainly produced in the reaction of isoprene+O₃ via Criegee intermediates (Nguyen et al., 2016), is negligible as the OH yield is less than one (Malkin et al., 2010) and thus its contribution is less than that of isoprene+O₃. This is consistent with the contribution determined using measured OH concentration, despite some uncertainty in measured OH concentration due to the interference from NO₃.”

5. Line 158-159: may need to add the reference Jokinen et al., ACP, 2012.

Response:

Accepted.

6. The first panel of Table 1: why molecules with 1 N atom (one nitrate group) can be formed from isoprene+NO₃+NO₃.

Response:

As we discussed in L230-235 and Scheme S1b, the reaction of isoprene with NO₃ can form products containing no N atoms, such as C₅H₈O₂. C₅H₈O₂ can further react with NO₃ forming products containing one N atoms.

7. The 2nd panel of Table 2: what is PN?

Response:

PN denotes peroxyxynitrate. In the revised manuscript, we have changed it to “RO₂NO₂” and added the explanation in the caption of Table 1, as follows.

“RO₂ denotes peroxy radical and ROOH, ROH, R=O, and RO₂NO₂ denote the termination products containing hydroperoxy, hydroxyl, carbonyl group, and peroxy nitrate, respectively.”

8. *Figure 3: how C₅H₁₀N₂O₇ formed? Besides the two nitrate groups, only one oxygen.*

Response:

C₅H₁₀N₂O₇ has a very low signal in the mass spectra and overlaps with the peak of C₅H₈NO₈, which is much higher. Therefore, to be cautious, we omit this compound in the revised manuscript as we are not confident with the assignment of this peak.

9. *Scheme 2: Panel 1: -ONO₂ is missed from the 2nd molecule, RO radical (C₅H₉N₂O₉.) should not be detected. Panel 2: the 3rd reaction stop should not be H-shift.*

Response:

We thank the reviewer for pointing out our mis-labelling. We have corrected them in the revised manuscript. We agree that we did not detect RO radical (C₅H₉N₂O₉). The molecule formula is only to help better track the mechanism. In the revised manuscript, we have marked the formula that we detected in bold. And we explicitly note this in the caption of Scheme 1-3.

10. *Scheme 3: Panel 2: the structure of the final molecule maybe not correct.*

Response:

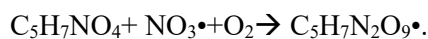
Accepted.

In the revised manuscript, we have corrected this error.

11. *How molecules with 7 H atoms formed? E.g. C₅H₇N₂O₉.*

Response:

C₅H₇N₂O₉• is a peroxy radical, which can be formed from the reaction C₅H₇NO₄ (C5-nitrooxycarbonyl) with NO₃ and O₂ as we discussed in lines 366-367 (original manuscript).



Molecules with seven H atoms and one nitrogen atom (C₅H₇NO_n) can be formed via the reaction peroxy radicals containing eight H atoms, forming a ketone and an alcohol.



12. *Is there any observational evidence on the formation of NO₃-isoprene-HOM dimer and trimer in the real atmosphere?*

Response:

We are not aware of field studies reporting NO_3 +isoprene-HOM dimers and trimers. This might be attributed to the difficulty to distinguish NO_3 +isoprene-HOM trimers from the dimers formed by cross reaction of the RO_2 from monoterpene oxidation ($\text{C}_{10}\text{-RO}_2$) with that from isoprene oxidation ($\text{C}_5\text{-RO}_2$) as their molecular formula can be identical. Similarly, NO_3 +isoprene-HOM dimers can have the identical molecular formula to the HOM monomers from monoterpene oxidation. In one field study, possible contribution of dimer formation in isoprene oxidation to C6-10 HOM is discussed (Chen et al., 2020), although it is attributed to be more likely from monoterpene oxidation. Despite the absence of reporting in field observations, NO_3 +isoprene-HOM dimers have been observed in previous laboratory studies such as Ng et al. (2008) and Kwan et al. (2012) as we discussed in the manuscript.

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