Reviewer #2

Wang et al presents laboratory results where the authors oxidized thrimethylbenzene (TMB) in an oxidation flow reactor (OFR) with OH in the presence and absence of NOx to investigate the role of autoxidation. Using a combination of a Vocus proton transfer reaction mass spectrometer and nitrate chemical ionization mass spectrometer, the authors investigated the products produced from the oxidation of TMB. They argue that the highly oxidized material (HOMs), which has been observed and discussed to be potentially important for new particle formation and particle growth in both clean (e.g., Boreal forests) and polluted environments, is produced upon the second OH oxidation and subsequent reactions of the material instead of the first oxidation. They argue that the NO_x products observed in the NO experiments provides evidence of this.

This paper is of interest to the community and recommend publication after addressing the comments below and potentially restructuring/rephrasing some of the conclusions to address the concerns Matti provided (though disagree with the argument that the OFR is not a tool to be used to understand chemistry and its only role is regulatory).

Response:

We are very grateful for the comments from Reviewer #2 and have now revised our manuscript accordingly.

Major

Q 2.1. *Methods--how long is one condition sampled to ensure things have reached steady state for the calculations (e.g., lifetime of HOMs) to be true? This is also important for the assumption that is used to normalize the signal measured by HOMs divided by the TMB signal with Vocus (which is currently unclear why authors may not have used a signal from the nitrate CIMS instead that was constant).*

Response 2.1:

Once the signals of certain HOM are more than 3 standard deviations of its background signals, we believe that it is positively generated in our system. If the fluctuations in the 1-min-averaged signals of both TMB in the Vocus PTR and typical HOMs (i.e., $C_9H_{14}O_7(NO_3)^-$) in the nitrate CIMS are within 2% during a 10-min period, we assume that a steady state has been reached. We typically sampled for around 20 minutes for each experiment after the adjustment of UV lights. It typically only took around no more than 2 minutes for the signals of HOMs to stabilize after the adjustment of UV lights. This observation is similar to PAM OFR results from other groups (Figure S1 of Cheng et al., 2023).

Our TMB source is a home-made cylinder containing certain concentrations of TMB. The initial concentrations of TMB utilized in the experiments fluctuated slightly as determined with a calibrated Vocus PTR, which resulted from the sample preparation processes, but generally were around 50 ppbv. We tried to minimize potential influences of the differences in the initial TMB concentration on the signals of HOMs by normalizing the HOMs signals with the initial TMB signals..

Meanwhile, the concept of "nominal relative molar yields of HOMs" has been removed in the revised manuscript.

We have revised our manuscript (Line 168 - 174), which reads:

"...$O(^1D) + H_2O \rightarrow 2OH$. After turning on of UV lights, a certain HOM compound is believed to be generated if its signal is more than 3 standard deviations of its background signal. If the

fluctuations in the 1-min-averaged signals of both TMB in the Vocus PTR and typical HOMs (i.e., $C_9H_{14}O_7(NO_3)^-$) in the nitrate CIMS are within 2% during a 10-min period, we assume that a steady state has been reached. It usually took around no more than 2 minutes for the signals of HOMs to stabilize after the adjustment of UV lights. We typically monitored the reaction products for around 20 minutes for each experiment. An ozone …"

and (Line 284 - 288), which reads:

"…of a significant uncertainty. The initial concentrations of TMB utilized in the experiments fluctuated slightly, which resulted from sample preparation processes, but generally were around 50 ppbv. We tried to minimize potential influences of the differences in the initial TMB concentrations on the signals of HOMs by normalizing the HOMs signals with the initial TMB signal. To precisely illustrate …"

Q 2.2 Were any experiments conducted at lower or higher TMB mixing ratios? E.g., this may help address some of the concerns of Matti as lower/higher TMB should change the RO_2/HO_2 ratios and provide insight into the chemistry that is occurring in the OFR.

Response 2.2:

As discussed in our Response 1.1, the RO_2/OH and HO_2/OH, as well as RO_2/HO_2 in our experiments were generally similar to those in the urban Beijing. Theoretically, at a given RH and UV (i.e., a given OH), an increase in the initial TMB would lead to formation of more RO_2, which corresponds to a larger RO_2/OH. However, under our experimental conditions, the $RO_2/OH/HO_2$ channels of RO_2 radicals are always minor, and thus an increase in RO_2/OH would not have a significant impact on the relative distribution of products formed from these channels.

We compared product MS for experiments with a similar OH exposure but different initial concentrations of TMB (e.g., Exp. 3 v.s. Exp. 19, and Exp. 12 v.s. Exp. 22). Clearly, the relative distributions of products in these experiments are quite similar except for abundance differences for a few peaks, indicating a minor difference in the relative distributions of products caused by fluctuations of initial concentrations of TMB.

We have revised our manuscript (Line 396 - 411) , which reads

"Theoretically, at a given RH and UV (i.e., a given OH), an increase in the initial TMB would lead to formation of more RO_2, which corresponds to a larger RO_2/OH. However, under our experimental conditions, the $RO_2/OH/HO_2$ channels of RO_2 radicals are always minor, and thus an increase in RO_2/OH would not have a significant impact on the relative distribution of products formed from these channels We compared product MS for experiments with a similar OH exposure but different initial concentrations of TMB (e.g., Exp. 3 v.s. Exp. 19, and Exp. 12 v.s. Exp. 22). The OH exposures of Exp. 3 and Exp. 19 were estimated by the modified PAM_chem_v8 model to be 5.2×10^9 and 5.3×10^9 molecule cm^{-3} s, respectively, but the initial concentration of TMB of Exp. 3 was 25% more than that in Exp. 19. Meanwhile, the OH exposures of Exp. 12 and Exp. 22 were 4.5×10^{10} and 4.4×10^{10} molecule cm^{-3} s, respectively, but the initial concentration of TMB of Exp. 12 was 48% more than that in Exp. 22. Comparisons between the product MS of Exp. 3 and Exp. 19 (Figure S2), as well as of Exp. 12 and Exp. 22, show that increase in the initial concentration of precursors generally resulted in a minor increment in the absolute signals of HOMs. Clearly, the relative distributions of products in these experiments are quite similar, indicating a minor difference in the relative distributions of products caused by fluctuations of initial concentrations of TMB."
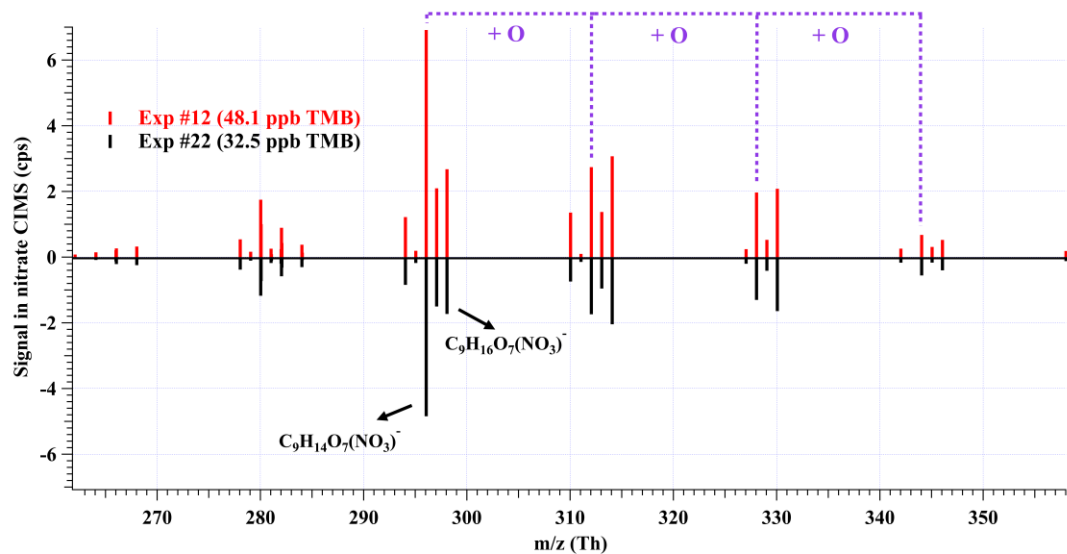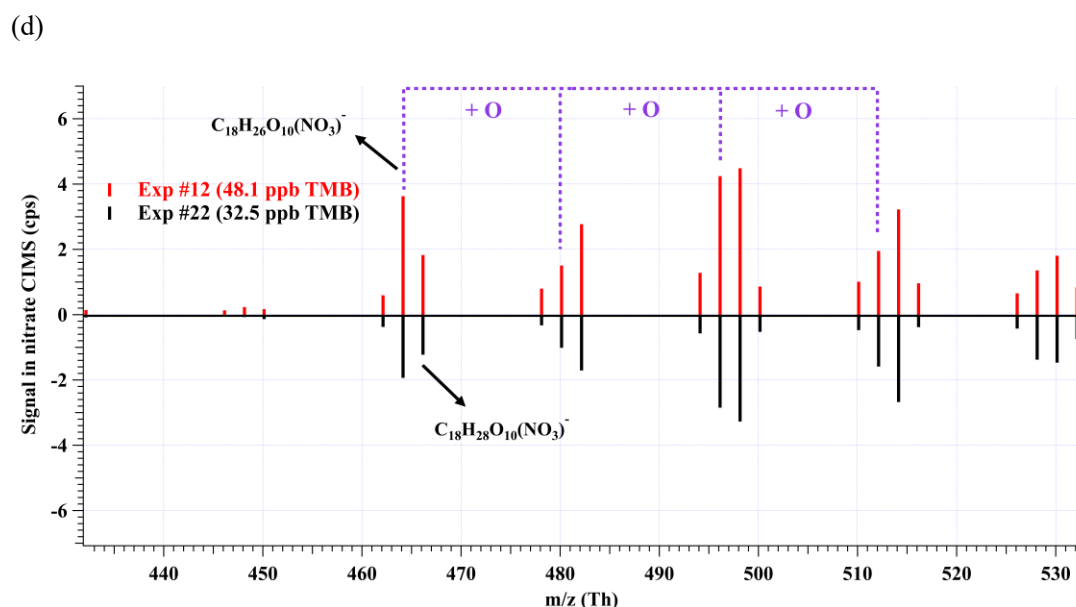
(a)

(b)

(c)

(d)
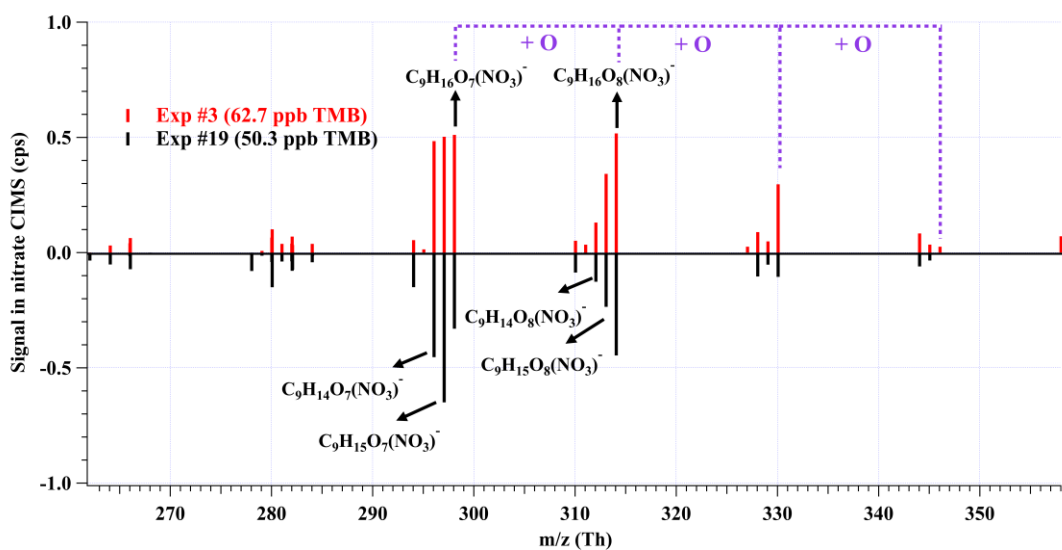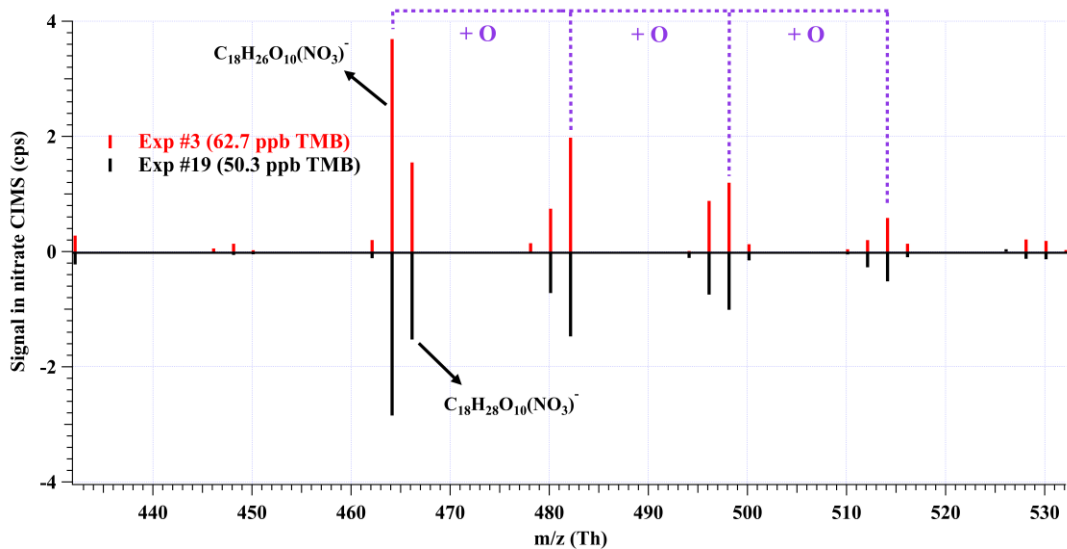
Figure S2. Comparison of the (a) monomer product MS between Exp. 3 and Exp .19, (b) dimer product MS between Exp. 3 and Exp. 19, (c) monomer product MS between Exp .12 and Exp .22, and (d) dimer product MS between Exp .12 and Exp .22. The signals of HOMs were raw ones in the nitrate CIMS.

Q 2.3. Discussion of the mechanism: The purpose of the paper is to elucidate the mechanism of the production of HOMs. However, the authors only present the scheme from MCM without expanding the mechanism/scheme they believe they have observed, which makes the narrative very hard to follow. I strongly recommend expanding the schemes presented in the paper with the chemistry and products observed to improve the narrative and better understand how the second generation HOMs are being formed. To address the concerns of Matti, this can address both the chemistry that may be occurring in the OFR vs the chemistry that may be more prominent in urban atmosphere and the importance/products between the two regimes. Further, I think interspersing the results from the NOx chemistry into the discussion of the production of HOMs and which pathways occur would be beneficial instead of the NOx chemistry being a separate section. Right now, the NOx chemistry seems like a leftover section that is addressed to quickly instead of being used as a tool to verify the hypothesis that it is potentially a second OH attack is necessary to form the HOM.

Response 2.3:

We are very grateful to the helpful suggestions of Reviewer #2. In the evised manuscript, we have proposed formation pathways of HOM monomers with the highest signals observed in our experiments, which are generated with the involvement of multi-generation OH oxidation.

We have revised our manuscript (Line 467 - 469), which reads:

", which can be genreated by an OH attack to $C_9H_{14}O_5$ (Scheme 2), the hydroperoxyl termination product of the BPR $C_9H_{13}O_5\cdot$.
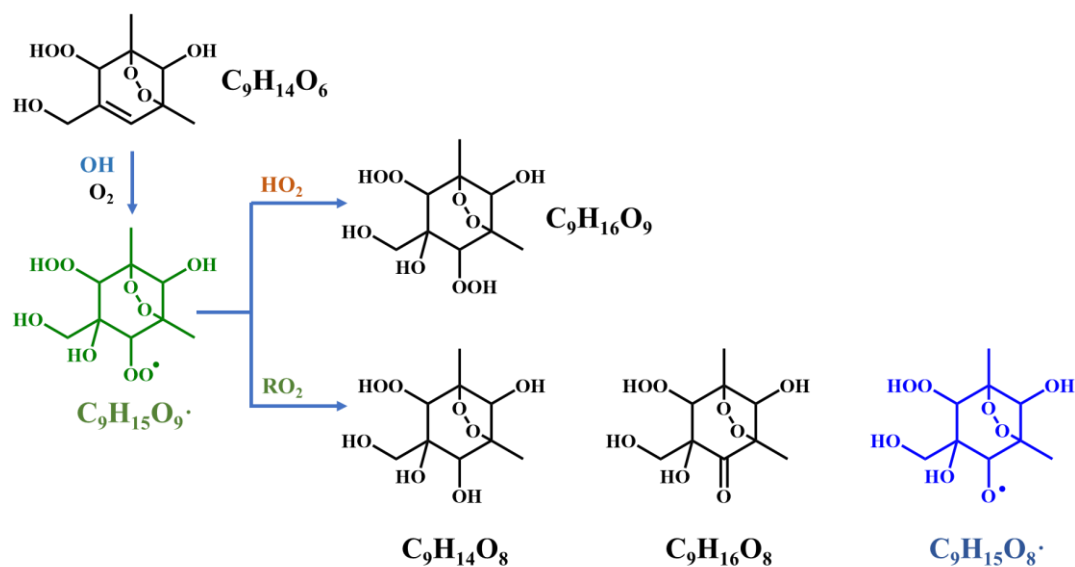
"

and (Line 472), which reads:

"which is highly likely the peroxy radical generated by an OH attack to $C_9H_{14}O_6$ (Scheme 3), i.e., the hydroxyl termination product of $C_9H_{13}O_7\cdot$."

and new schemes in the revised manuscriptt, which reads:

"
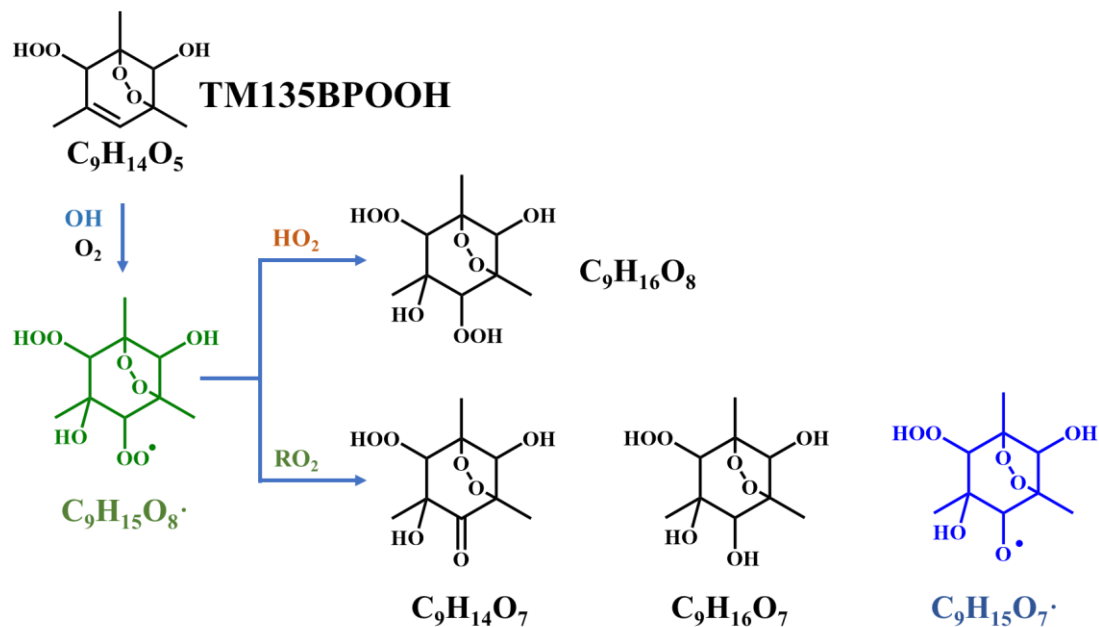
Scheme 2. Proposed formation pathways of $C_9H_{14}O_7$, $C_9H_{16}O_7$, and $C_9H_{16}O_8$ via the secondary OH oxidation of TM135BPOOH.

Scheme 3. Proposed formation pathways of $C_9H_{14}O_8$, $C_9H_{16}O_8$, and $C_9H_{16}O_9$ via the secondary OH oxidation of TM135BPOOH.

"

We also intersperse the NO_x chemistry session into the discussions on HOM monomers and

HOM dimers, respectively.

We have revised our manuscript (Line 516 - 549), which reads:

" … because of their low branching ratio as determined by recent studies (Zaytsev et al., 2019; Xu et al., 2020).

Scheme 4 shows the NO termination pathways of the main BPR $C_9H_{13}O_5 \cdot$ and its autoxidation product, $C_9H_{13}O_7 \cdot$. After introducing N_2O into PAM OFR, quantities of organonitrates were generated, including both C9 and C18 organonitrates. The averaged mass spectrometry of nitrate CIMS in the 1.8 ppb NO experiment and 4.8 ppb NO experiment is shown in Figure S3. Organonitrates were formed via the $NO + RO_2$ reaction, called as NO termination reactions. The distribution of oxidation products under these two NO settings were similar.

As discussed above, most of the first-generation HOMs should contain a C=C bond in the carbon backbone. The ubiquitous existence of organonitrates that contain two nitrogen atoms exactly confirms the extensive secondary OH oxidation in the systems, because the NO termination reaction of RO_2 is the only pathway that can generate organonitrates in our experiments and this pathway can only introduce one nitrogen atom at a time, as indicated in Scheme 2. RO_2 can react with NO_2 to form peroxynitrates ($ROONO_2$) but these species are thermally unstable except at very low temperatures or when the RO_2 is an acylperoxy radical (Orlando and Tyndall, 2012), neither of which were not met in Our experiments The concentrations of NO_3 were estimated to be lower than 1 pptv by our modified PAM_chem_v8 because of the existence of decent concentrations of NO, which would consume NO_3 at a rapid reaction rate, i.e., 2.7×10^{-11} molecule^{-1} cm^3 s^{-1} (IUPAC dataset , https://iupac-aeris.ipsl.fr, last access: 26 October 2023). Therefore, NO_2 and NO_3 were not likely to react with RO_2 to form large amounts of organonitrates in our experiments. Taking the most abundant organonitrate, $C_9H_{14}N_2O_{10}$, as an example, it was exactly the NO termination product of $C_9H_{14}NO_9 \cdot$, which was generated from an OH attack and a subsequent O_2 addition to $C_9H_{13}NO_6$, the NO termination product of $C_9H_{13}O_5 \cdot$. For other organonitrates, $C_9H_{13}NO_8$, the second most abundant organonitrate, could be either a NO termination product of $C_9H_{13}O_7 \cdot$ or, together with other most abundant organonitrates, $C_9H_{15}NO_7$ and $C_9H_{15}NO_8$, classical termination products of $C_9H_{14}NO_9 \cdot$.

and (Line 657 - 669), which reads:

"3.2.2 HOM dimers

…

The OH reaction rate for $C_{18}H_{26}O_8$ should also be fast due to the C=C bonds in its structure, which is activated by the adjacent functionalities. Our calculation result is consistent with this estimation.

The distributions of C18 organonitrates also verified the extensive secondary reactions. The most abundant C18 organonitrate, $C_{18}H_{27}NO_{12}$ was a NO termination product of radical $C_{18}H_{27}O_{11} \cdot$, which, as mentioned above, was the radical generated from the OH reaction with $C_{18}H_{26}O_8$. $C_{18}H_{27}NO_{12}$ can also be formed either by accretion between a $C_9H_{15}O_m \cdot$ radical and a $C_9H_{12}NO_m \cdot$ radical or accretion between a $C_9H_{13}O_m \cdot$ radical and a $C_9H_{14}NO_m \cdot$ radical. Both $C_9H_{15}O_m \cdot$ and $C_9H_{14}NO_m \cdot$ radicals are a typical multi-generation RO_2 and thus prove $C_{18}H_{27}NO_{12}$ is a multi-generation OH oxidation product. Other C18 organonitrates are believed to be formed in a similar pathway. Other C18 organonitrates are believed to be formed in a similar pathway since no evidence supports that a nitrogen-containing monomeric RO_2 can go through accretion reactions. Hence,

plenty of organonitrates have been formed via the multi-generation OH reactions of first-generation stabilized products.

    …
"

Q 2.4. *Units in the normalized relative molar yields: Currently, all figures that show the nominal relative molar yields are not intuitive to interpret and understand. E.g., the values in the y-axis are between 10^-10 to 10^-9, which would suggest that the HOMs are not important fates. It is not clear if it is due to taking the signal from the nitrate CIMS and normalizing to the signal from the Vocus may be the cause of this. Further, it is surprising the yields are apparently higher from the accretion (RO2+RO2) reactions compared to the monomer reactions. Due to the general lack of clarity and the concerns from reviewer number one, it may be better to focus on the fate of RO2 during these experiments instead of the yields, and which fates are more atmospherically relevant vs potentially related to the OFR. I would recommend also, to address the reviewers concerns, to include the estimated fate of the RO2 products due to fragmentation, photolysis, and wall loss in OFR.*

Response 2.4:

We are very grateful to these helpful suggestions. We have revised our manuscript by including "Session 3.1 Validation of experimental settings" that focuses on the estimation of radical concentrations and fates of RO_2. The concept of "nominal molar yield of HOMs" has been removed in the revised manuscript to address both reviewers' concerns. Please also refer to our Response 1.1.

Minor
Q 2.5. *Color scheme. Please avoid using red and green in the same plot, as that will be difficult to interpret for color blind people.*
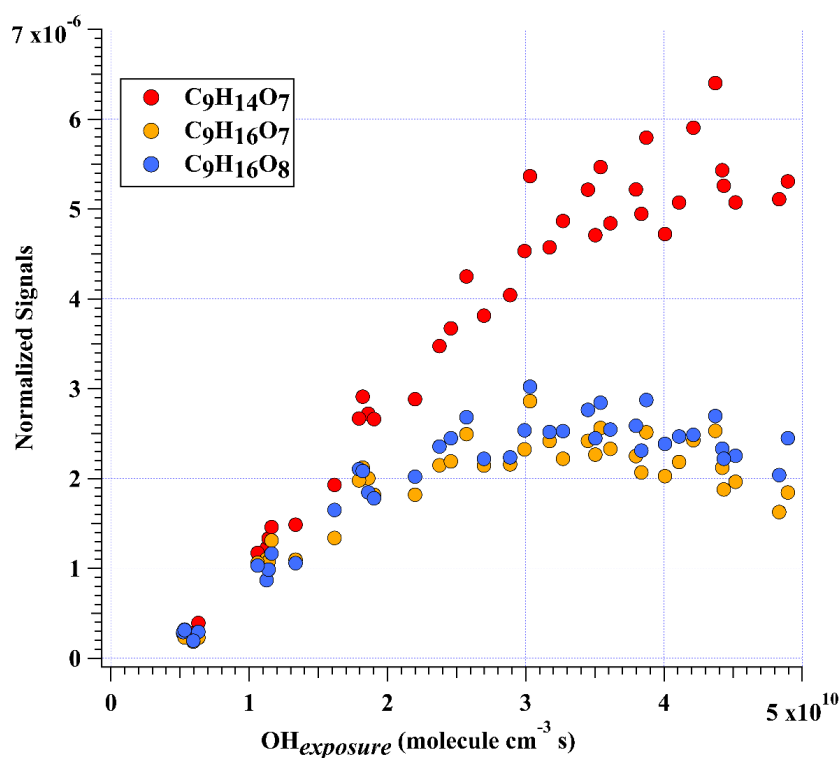
Response 2.5:

We have revised the Figure 1, Figure 2, Figure 3, Scheme 1, and Scheme 2 to address the concerns of Reviewer #1. The revised Figures avoid potential color scheme problems as mentioned. Please also refer to our Response 1.10 for Figure 1, as well as Response 1.9 for Scheme 1 and Scheme 2,.
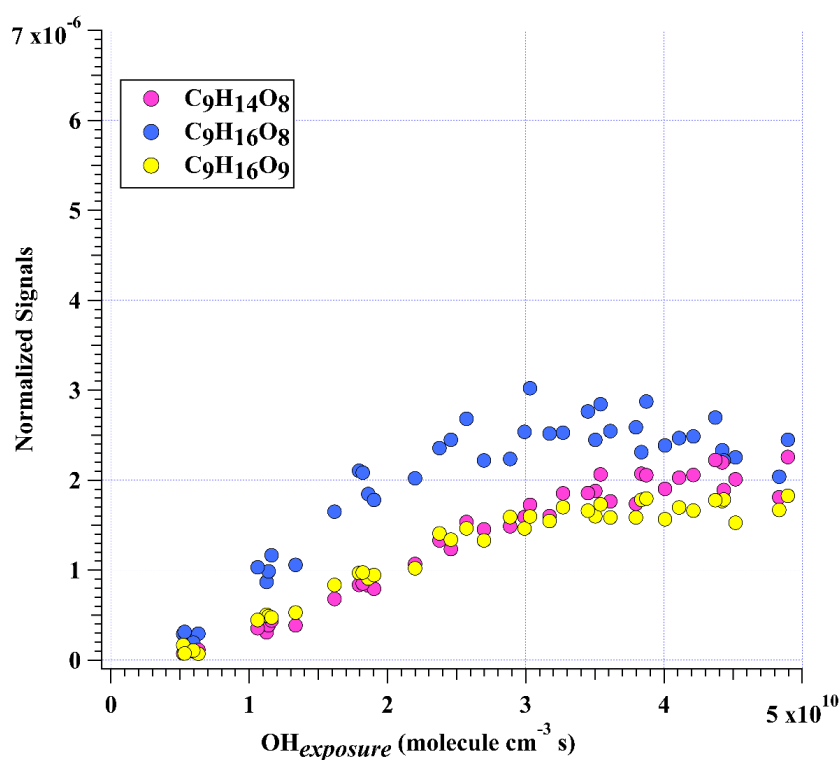
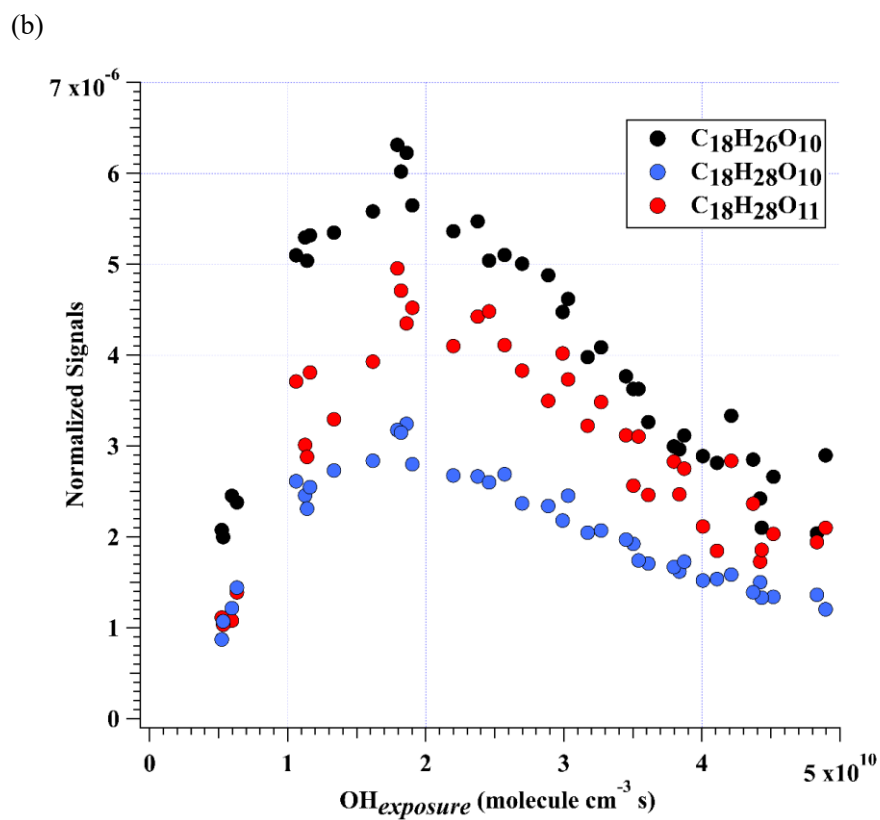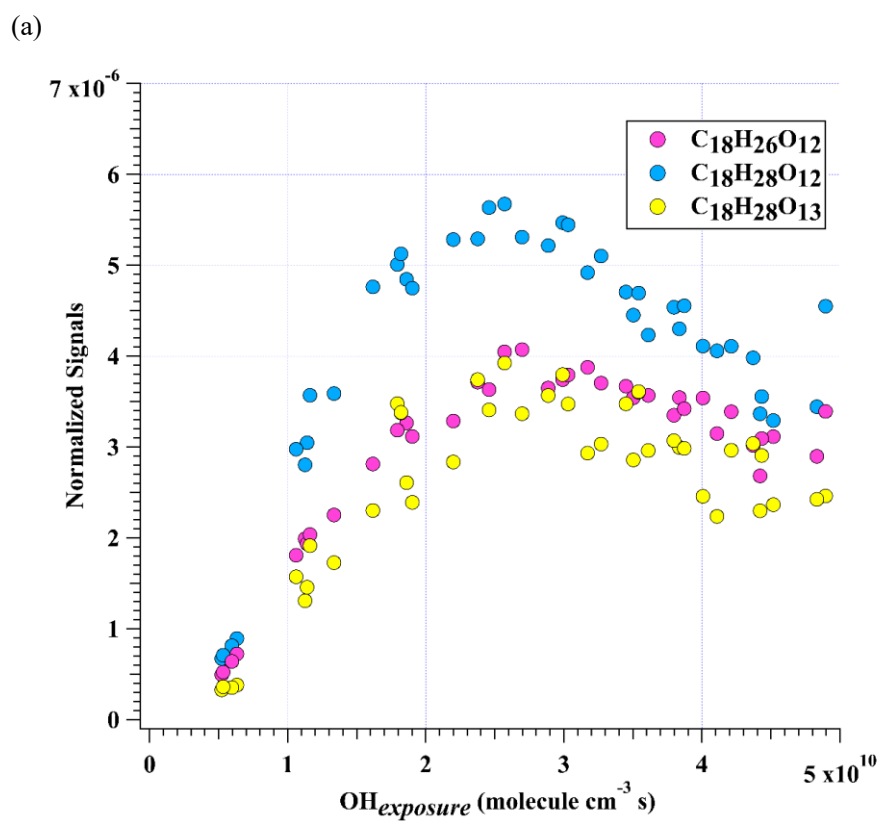We have revised Figure 2 and Figure 3, which reads:

"

(a)

(b)

Figure 2. Normalized signals of (a) $C_9H_{14}O_7$, $C_9H_{16}O_7$, and $C_9H_{16}O_8$ and (b) $C_9H_{14}O_8$, $C_9H_{16}O_8$, and $C_9H_{16}O_9$ measured at the exit of OFR in experiments without NO_x as a function of OH exposure. $C_9H_{16}O_8$ are shown in both plots to better illustrate the chemical profiles of different compound groups.

(a)

(b)

Figure 3. Normalized signals of (a) $C_{18}H_{26}O_{12}$, $C_{18}H_{28}O_{12}$, and $C_{18}H_{28}O_{13}$, and (b) $C_{18}H_{26}O_{10}$, $C_{18}H_{28}O_{10}$, and $C_{18}H_{28}O_{11}$ measured at the exit of OFR in experiments without NO_x as a function of OH exposure.

"

Q 2.6. *Ensure that SI figures are presented in same order discussed in paper (e.g., Fig. S4 is discussed after Fig. S5).*

Response 2.6:

Sorry for this. We have double-checked our manuscript to make sure that figures are presented in the same order as discussed in paper.

Q 2.7. *Line 335: declining instead of declination*

Response 2.7:

Since we have removed the nominal molar yield part in the manuscript. This word has been removed.

Q 2.8. *Line 350 - 363: It is confusing which ratio is being discussed as it is switched from HO2:RO2 to OH:HO2. Please clarify (and may be addressed with the rephrasing of products/RO2 fates).*

Response 2.8:

Thanks for the suggestions. We have revised this. Please refer to our Response 1.22.

We also focus on fates of RO_2 and the detailed branching ratios of their termination reactions in Session 3.1 and Supplementary Text S1 of revised manuscript. Please refer to our Response 1.1.

References

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Orlando, J. J. and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: An overview with emphasis on recent issues of atmospheric significance, Chem. Soc. Rev., 41, 6294–6317, https://doi.org/10.1039/c2cs35166h, 2012.

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