Review of "Effect of NOx on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation" by Hammes et al.

This manuscript investigates the formation of highly oxygenated molecules (HOMs) from the oxidation of TMB under different conditions (i.e., OH exposure and NOx concentrations). The HOMs are measured by a NO_3^- CIMS and the distributions of HOMs species under different reaction conditions are reported. As there are few studies on the HOMs from aromatics oxidation, these results are worthy to be documented. The major finding is that NOx inhibits the formation of HOMs and enhances the formation of organonitrates, by altering the RO_2 chemistry. The experiments are nicely designed and conducted and the manuscript is clearly written. I recommend publication after major revision.

Major Comments

1. In the kinetic model, the oxidized peroxy radicals (HOMRO2) were considered to be formed after 3 autoxidation steps of a general RO_2 with a rate constant of 0.1667 s^{-1}. This rate is inferred from α-pinene + O_3 RO_2. However, the isomerization rate of biogenic RO_2 is generally not applicable to aromatic RO_2, because of the presence of C-C double bonds in aromatics. The isomerization rate of the TMB-OH-OO to bicyclic alkyl radical could be on the order of 1000 s^{-1} [1-2]. For the second isomerization step (i.e., potentially form a tricyclic alkyl radical), the rate is uncertain, but is likely much larger than 0.17 s^{-1} [3]. Even though there are large uncertainties in the RO_2 isomerization rates, more appropriate values should be used. A book chapter by Vereecken et al.[3] has a nice summary on this topic.

   In fact, the tuning of the photon flux to match the measured decay of O_3 may be related to the poor representation of RO_2 chemistry.

2. The authors compare observed HOMs distribution with that in Molteni et al. (2018) and noticed many important discrepancies. The authors must discuss potential causes for the discrepancies.

3. Reaction schematics on the formation mechanism of key HOMs monomer and dimers should be added. This is clearer than describing the mechanism with words.

Minor Comments

1. How is NOx added into the reactor? I can't find the information in the method section nor schematic figure.
2. Page 12 Line 18-20. Figure 7 is not in the manuscript. Also, it is highly unlikely that the ON yield from RO_2+NO is closed to unity.
3. Page 12 Line 32. $C_9H_{13}O_5$ is formed after one isomerization step (i.e., initial OH addition, O_2 addition, RO_2 isomerization, and O_2 addition), not two steps.
4. Page 13 Line 1. What do authors mean by "the formation of RO2 precursor species with lower O numbers"? $C_9H_{15}O_{7-8}$ has many O atoms.
5. Page 13 Line 26. Zhang et al. (2018) is not in the reference list.
6. Figure 5 should be combined with figure 2 somehow to facilitate the comparison.

Reference

1. Wang, S.; Wu, R.; Berndt, T.; Ehn, M.; Wang, L. Formation of Highly Oxidized Radicals and Multifunctional Products from the Atmospheric Oxidation of Alkylbenzenes. *Environ Sci Technol* **2017,** *51*, 8442-8449.
2. Glowacki, D. R.; Wang, L.; Pilling, M. J. Evidence of Formation of Bicyclic Species in the Early Stages of Atmospheric Benzene Oxidation. *The Journal of Physical Chemistry A* **2009,** *113*, 5385-5396.
3. Vereecken, L., Reaction Mechanisms for the Atmospheric Oxidation of Monocyclic Aromatic Compounds. In *Advances in Atmospheric Chemistry*, pp 377-527.