

Authors response on Referee #1-2

Text in blue is original comment from referee followed by a reply and suggested action to improve the manuscript.

Response to Anonymous Referee #1

General comments

This manuscript reports results of laboratory experiments on secondary organic aerosol (SOA) formation from the photooxidation of 1,3,5-trimethylbenzene (TMB). TMB is an SOA precursor emitted from anthropogenic sources. The authors employ an original flow reactor combined with a chemical ionization mass spectrometer to investigate effects of OH exposure and NO_x level on the distribution of oxidation products including particles, highly oxygenated molecules (HOMs), dimeric HOMs, and nitrated HOMs. They concluded that anthropogenic VOCs such as TMB could lead to new particle formation (NPF) but NPF is suppressed under high NO conditions. The research subject of this study is paid central attention in the field of atmospheric chemistry. The authors employ cutting edge instruments and provide new physical insight into the field of atmospheric chemistry. Because flow reactor experiments under high NO_x conditions are very new, the authors should discuss difference between examined reaction conditions and ambient ones. This manuscript suits for the scope of this journal and will be publishable after revisions are made by taking into account reviewer's comments.

Major comments:

(1) Please describe ozone concentration data in the text to discuss the reaction of remaining ozone with NO. If ozone level is higher than 50 ppb, the reaction of ozone with NO (with the rate constant of $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) can significantly occur within a reaction time of 34 s, and NO is converted to NO₂. The authors primarily assume that nitrated HOMs are formed from the reactions of HOM-RO₂ radicals with NO. However, formation of peroxy nitrates from the reactions of HOM-RO₂ with NO₂ or formation of nitrates from the reactions of HOM-RO with NO₂ might be important if NO₂ level is much higher than NO level. In experiments with NO_x under high ozone levels, NPF was observed. These results may suggest that NO becomes very low levels due to the reaction with ozone within the reaction time of 34 s, and the reactions of HOM-RO₂ with NO₂ may become more important than the reactions of HOM-RO with NO.

Reply: Yes, the titration of NO with ozone is a concern. However, as shown in a new Figure (S3) there is still some NO left at the end of the flow reactor. i.e. after 34 s there is still NO available to react with any HOM-RO₂.

In the experiment with NO_x in which NPF was observed, the NO_x concentration was the lowest and the OH exposure was the highest among the experiments with NO_x (Table 1). In addition, the ten compounds with the highest contribution includes only one nitrogen-containing compound, in contrast to the other NO_x experiments where the nitrogen-containing compounds were the majority of the top ten (Table S1). This makes us to conclude that the OH concentration was high enough to lead to the formation of more oxidized products, by allowing a second OH reaction to take place, and the formation of dimers which are more likely to contribute to NPF rather than products from the reaction of HOM-RO₂ with NO or NO₂.

Action: A new Figure (S3) is added to the SI. New text is added to elucidate the effect of titration and the remaining NO.

“As already has been described NO_x were introduced to the Go:PAM as NO. After the addition of ozone, the ozone concentration decreases from 100 ppb to ~80 ppb at the experiment with lower NO_x levels and to ~50 ppb at the experiment with higher NO_x levels, as it reacts with NO producing NO₂. For both high and low NO_x conditions there is NO left after the initial reaction with ozone (See grey areas of Figure S3).”

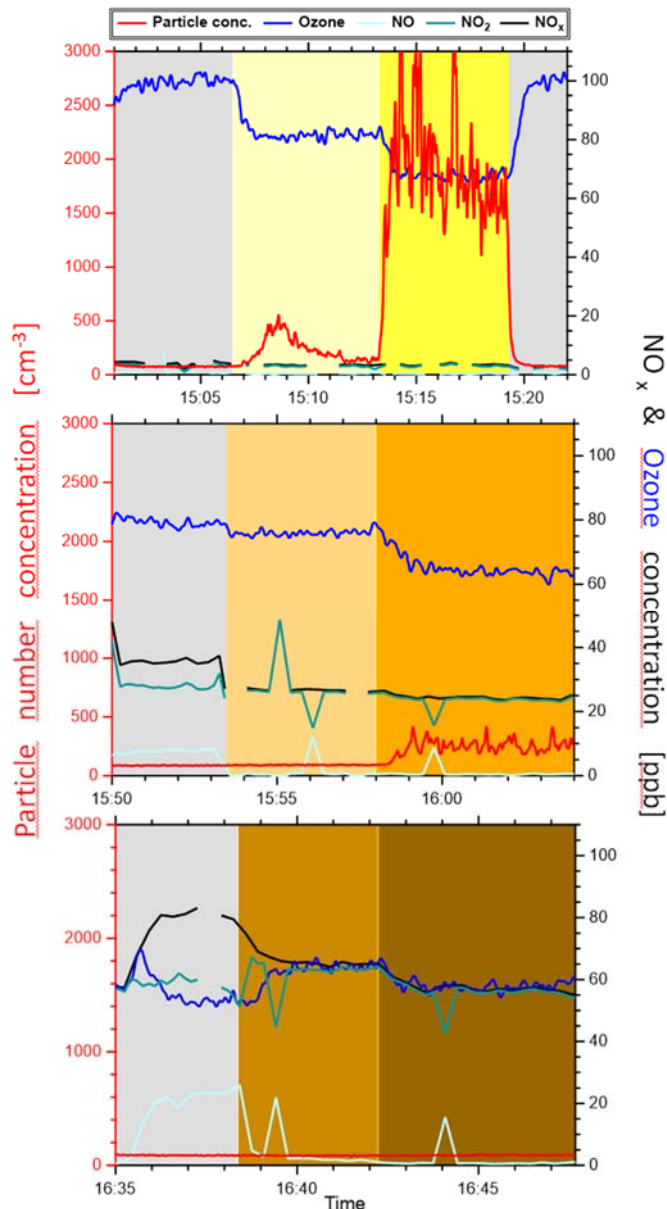


Figure S3: Particle number (red), ozone (blue), NO_x (black), NO (light blue) and NO₂ (cyan) concentrations under NO_x free conditions (top panel), initial NO_x:VOC≈1 (middle panel) and NO_x:VOC≈3 (bottom panel). The grey areas represent dark conditions, the light yellow, orange and brown represent lower OH exposure conditions (only 1 UV lamp is on in the Go:PAM) and the yellow, orange and brown represent higher OH exposure conditions (both UV lamp are on in the Go:PAM).

(2) The authors use NO_x levels of 35-82 ppbv, which are similar to NO_x levels in urban air, whereas they use HO_x (including OH and HO₂) levels much higher than ambient levels to accelerate reactions in the laboratory. These conditions may result in overestimation of HOM-RO₂ + HO₂ reactions and underestimation of HOM-RO₂ + NO, HOM-RO₂ + NO₂, and HOM-RO₂ autoxidation, compared to ambient conditions. The authors should discuss difference in branching of HOM-RO₂ reactions between present laboratory conditions and ambient conditions.

Reply: Yes, there could be an overrepresentation of HO_x chemistry relative to NO_x. However, the idea is to indicate a shift from HO_x to NO_x chemistry so the effect observed might be even more pronounced in polluted environments. The model (even if rather simple) provides some insight into this and can be used to elaborate more on this issue.

Action: We have enhanced our discussion on ambient relevance adding more discussion on the branching ratio for HOM-RO₂.

(3) The authors assume that nitrogen-containing products formed from the oxidation of TMB in the presence of NO_x are nitrates or peroxy nitrates; however this is not evident and further discussion will be necessary in the text. Basically the reviewer agrees with authors' assumption, but in general major nitrogen-containing products, formed from the oxidation of aromatic hydrocarbons, are nitro-aromatic compounds. 1,3,5-Trimethylbenzene is highly methyl-substituted aromatic hydrocarbon and multiple methyl groups inhibit formation of nitro-aromatic compounds (Sato et al., 2012). At this point of view, TMB employed in this study is not a typical aromatic hydrocarbon and a specific molecule, which barely lead to formation of nitro-aromatic compounds.

Reply: We agree with the reviewer that nitro-aromatic compounds are quite unlikely to be formed from TMB (Sato et al., 2012). Aromaticity will get lost before initial products react with NO. That's why we assume that's addition of NO_x leads to organonitrates (RONO₂) or peroxy nitrates (ROONO₂), with higher contribution from the RONO₂. We also agree that a schematic with proposed reaction mechanisms for the formation of organonitrates will be beneficial to illustrate this.

Action: A figure with a proposed formation mechanism of organonitrates is now included (Figure 5).

The following sentences are included:

"These compounds are expected to be nitrates or peroxy nitrates, as it is highly unlikely to form nitro-aromatic compounds from TMB (Sato et al., 2012)."

"A proposed detailed reaction mechanism assuming no kinetic restrictions is depicted in Figure 5."

"A brief description of the mechanism"

Specific comments:

(4) Page 3, line 14 and reference list in page 18. Sato et al., 2018 should be Sato et al., 2012

Action: Done.

(5) Page 3, line 32. In the unit, "L mol⁻¹", "-1" should be superscript.

Action: Done.

(6) Page 4, lines 1-5. Please discuss the phase of products detected by APi-TOFMS. If it detects products in the aerosol phase, how were these particulate products vaporized in the ion source? Brief explanations would be necessary in the text.

Reply: Only the gas phase oxidation products are detected by the APi-TOFMS.

Action: It is now clarified in the text that the detected products are measured in the gas-phase.

(7) Page 9, lines 14-15. The formation process of compounds with 12 H and 16 H should be explained more in detail. For example, the words, “(terminated from C₉H₁₃O_x radicals)”, should be written as “(formed from the C₉H₁₃O_x + RO₂ -> C₉H₁₂O_{x-1} + ROH + O₂ reaction)”.

Reply: ok

Action: Selected reactions have been added to the text. See Reactions 3-10.

(8) Page 9, lines 32-34. C₉H₁₄O_x products include first-generation and second generation products, i.e., these are formed from the C₉H₁₃O_{x+1} + RO₂ -> C₉H₁₄O_x + R'CHO + O₂ reaction as well as C₉H₁₅O_{x+1} + RO₂ -> C₉H₁₄O_x + ROH + O₂ reaction. Please explain why C₉H₁₄O_x products have mainly characteristics of second generation products.

Reply: That's true C₉H₁₄O_x products can be either first or second generation products. They have mainly characteristics of secondary products, as their contribution to the top ten compounds (Table S1) increases for the experiments with higher OH exposures, in which more oxidized products can be formed.

Action: The text now includes the following:

“C₉H₁₄O_x can be either first or second generation products and originate from either C₉H₁₃O_x or C₉H₁₅O_x (reactions 5 and 6).”

“The C₉H₁₄O_x products have mainly characteristics of second generation products, as their contribution is enhanced in the experiments with higher OH exposures (Table S1), in which there is an enhanced possibility for secondary chemistry initiated by reaction of OH with the first generation products.”

(9) Page 9, last sentence. The authors describe “the contribution of C₉H₁₅O_x is reduced at expense of C₉H₁₄O_x and C₉H₁₆O_x – HOM and dimers,” but the meaning of this sentence is unclear. Do the authors mean that the contribution of C₉H₁₅O_x is reduced at the expense of C₉H₁₄O_x and C₉H₁₆O_x?

Reply: Maybe unclear but we were arguing that the formation of secondary products (C₉H₁₄O_x & C₉H₁₆O_x), due to higher OH exposure, is responsible for the reduction of the C₉H₁₅O_x radicals.

Action: We modify the text as following: “At the highest OH exposures in exp 4, the contribution of C₉H₁₅O_x radicals, one of the top ten contributors to the signal (Table S1), is reduced, while the contribution of the second generation products (C₉H₁₄O_x and C₉H₁₆O_x) and dimers increases.”

(10) Page 12, line 20. The reviewer cannot find “Figure 7.”

Reply: Figure 7 was missed out but should have been found in the supplemental as Figure S3.

Action: The missed out Figure 7 is now included in the Supplementary Information as Figure S3.

(11) Page 13, line 4. The description, “hydroxyl”, should be “RO₂”.

Action: ...Via “peroxy”... is included in the text.

(12) Page 13, eq. (6). The chemical formula, R=O, would not be accurate. If the authors use "R=O", please explain that R=O represents carbonyl products.

Action: "R=O" replaced by "Carbonyl Products".

(13) Page 13, line 29. Please correct "reaction 56".

Reply: The "reaction 56" refers to the corresponding reaction in Table S2. The rate coefficient that is used is based on the recommended one from Berndt et. (2018)

Action: The text has been corrected accordingly.

(14) Page 15, line 15. "Wang et al. (2018)" should be "Wang et al. (2017)".

Action: Done.

(15) The caption of FigureS1. In the caption it is explained "Bottom: Modelled product distribution for all 8 experiments", but the reviewer cannot find this bottom figure.

Reply: The caption "Bottom: Modelled...experiments with NOx." is referring to the Figure 5 in the main text.

Action: It is now corrected.

(16) Table S2. The symbol, "=", represents reversible reaction if it is used in reaction equations. The reviewer recommends for the authors to use arrow symbols instead.

Reply: We agree.

Action: Done.

Response to Anonymous Referee #2

General comments

This manuscript investigates the formation of highly oxygenated molecules (HOMs) from the oxidation of TMB under different conditions (i.e., OH exposure and NO_x concentrations). The HOMs are measured by a NO₃- 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 NO_x inhibits the formation of HOMs and enhances the formation of organonitrates, by altering the RO₂ 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 RO₂ with a rate constant of 0.1667 s⁻¹. This rate is inferred from α-pinene + O₃ RO₂. However, the isomerization rate of biogenic RO₂ is generally not applicable to aromatic RO₂, 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 RO₂ 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 O₃ may be related to the poor representation of RO₂ chemistry.

Reply: Yes, this part could be more elaborated. A comment is that even if the first step is very fast the following two steps will be rate limiting steps reducing the rate of the overall three step process and might be approaching our rather slow reaction rate used. However, we have now considered this more thoughtfully and the resulting rate of this reaction used in the simplified model has been increased with a factor of 2.

The considerations were:

According to the oxygen content in the majority of the C₉ products the oxidized peroxy radicals (HOMRO₂) should contain either seven, nine or eleven oxygens which would be formed after two, three and four autoxidation steps, respectively. To simplify the model the produced HOMRO₂ in the model were assumed to be formed after 3 autoxidation steps. As pointed out by the referee it is not as simple as each step has the same rate coefficient. However, there are large uncertainties where our best estimate would be the following assumptions. The 1st step where the O₂ group make a bicyclic radical has a large rate coefficient where Jenkin et al., 2019 suggests a rate coefficient for similar reaction to be larger than 3.6 x 10² s⁻¹ (Jenkin et al., 2019). For the 2nd step we assume an internal hydrogen shift potentially facilitated by a conjugated three carbon system. Here Wang et al., 2017 give a large range in reaction rates for similar reactions where the radical from toluene is slow (2.6 x 10⁻²) while the radical from larger compounds has higher values (e.g. 7.0 s⁻¹). We use a value of 1 s⁻¹ to represent this step. For the final 3rd step that would represent another hydrogen shift we use the value of 0.5 s⁻¹ originally suggested in the paper by Ehn et al., 2014. The combined rate of these three subsequent steps would then be 0.33 s⁻¹. This value is a factor of 2 higher than the original value but does not dramatically change our conclusions from the model experiments.

Action: The rate of this reaction has been increased in the model and new text has been added to describe the motivation of using such rate for this parametrized three step reaction.

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.

Reply: The experimental conditions and set up are the most important reasons. The Molteni et al. study react only a fraction of the TMB and would thus not form so many secondary products as in the current study. Their initial TMB concentration is 3 times higher (100ppb) compared to our study (30ppb) while the residence time is almost half, 20 sec compared to 34 sec. This may explain the formation of more oxidized compounds, especially more oxidized dimers. In addition, in Molteni et al. the OH radicals are produced outside of the flow tube (see Figure 1 at Molteni et al., 2018), then pre-mixed with the sample flow before the flow reactor. This, in conjunction with the higher TMB initial concentration, may lead to an early consumption of the OH radicals in the initial part of the flow reactor (see Figure S1-1, Supplement at Molteni et al., 2018) minimizing further oxidation, while in our study the OH radicals are produced inside the flow reactor, allowing a higher and more evenly distribution of OH radical concentrations in the flow reactor also favoring secondary reactions.

The formation of new particles in the flow reactor can change the HOM distribution, especially the dimers (Mohr et al., 2017), due to condensational sink. In our study one can see this effect in Figure 3. The product distribution depends on the OH concentration levels as well as on the particle number concentration. A direct comparison to Molteni et al. is not possible, as no

values for the particle number concentration are reported. But for the given values of initial TMB (100ppb) and OH (higher than our highest value) concentrations a high particle concentration is expected. This large particle concentration may increase the dimer loss, change the product distribution pattern and make the comparison to our study more difficult. The relative humidity is another parameter which was different during the two studies (75% in Molteni et al., 38% in this study).

Despite these differences the conclusion is the same in both studies, that TMB under NO_x free conditions can rapidly form HOM of very low volatility, as they can initiate NPF.

Action: The following text has been added to explain the potential discrepancies.

“These differences can be the result of different experimental conditions and set up. In our study the residence time is almost the double compared to Molteni et al., leading to the formation of more oxidized compounds, especially more oxidized dimers, which have been reported in this study. In addition, we produce OH radicals in the full length of the flow reactor enhancing the effects of secondary chemistry. Despite these differences there is a general agreement on the conclusions for NO_x free conditions with the Molteni study where one rapidly form HOM of very low volatility, that can initiate NPF.”

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.

Action: Reaction equation have been included (Reactions 3-10), as well as a figure (Figure 5) with a proposed reaction mechanism for the formation of organonitrates.

Minor comments

1. How is NO_x added into the reactor? I can't find the information in the method section nor schematic figure.

Action: “...while NO was introduced via a NO gas cylinder.” is added to the main text.

2. Page 12 Line 18-20. Figure 7 is not in the manuscript. Also, it is highly unlikely that the ON yield from RO₂+NO is closed to unity

Reply: Figure 7 was missed out but should have been found in the supplemental as Figure S3.

Action: A new Figure S3 is now included in the Supplementary Information. New text reads: “The yield of ON from NO+RO₂ might be high based on the measurable increase of ON and the decrease of NO_x in the system (see **Error! Reference source not found.**)”

3. Page 12 Line 32. C₉H₁₃O₅ is formed after one isomerization step (i.e., initial OH addition, O₂ addition, RO₂ isomerization, and O₂ addition), not two steps.

Reply: That's true.

Action: New text reads: “one autoxidation step”

4. Page 13 Line 1. What do authors mean by “the formation of RO₂ precursor species with lower O numbers”? C₉H₁₅O₇₋₈ has many O atoms.

Reply: Yes, this is a relative term referring to comparison with other systems, yielding higher number of oxygen but was not clear from the content.

Action: We have now modified the text.

“The formation of RO₂ precursor species with 7-8 O numbers, i.e. C₉H₁₅O₇₋₈ likely stem from compounds terminated earlier in the radical chain process (C₉H₁₄O₄₋₅), which do not fall in the typical HOM class (O:C ≥ 6:9).”

5. Page 13 Line 26. Zhang et al. (2018) is not in the reference list.

Action: Done. It is actually Zhao et al. (2018).

6. Figure 5 should be combined with figure 2 somehow to facilitate the comparison.

Reply: Ok.

Action: Figure 5 is now merged with Figure 2.

References:

1. Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506, 476-479, 10.1038/nature13032, 2014.
2. Jenkin, M. E.; Valorso, R.; Aumont, B.; Rickard, A. R., Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction. *Atmos. Chem. Phys.* 2019, 19, 7691-7717.
3. Mohr, C., Lopez-Hilfiker, F. D., Yli-Juuti, T., Heitto, A., Lutz, A., Hallquist, M., D'Ambro, E. L., Rissanen, M. P., Hao, L. Q., Schobesberger, S., Kulmala, M., Mauldin, R. L., Makkonen, U., Sipila, M., Petaja, T., and Thornton, J. A.: Ambient observations of dimers from terpene oxidation in the gas phase: Implications for new particle formation and growth, *Geophys Res Lett*, 44, 2958-2966, 10.1002/2017gl072718, 2017.
4. Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M. J., Dommen, J., and Baltensperger, U.: Formation of highly oxygenated organic molecules from aromatic compounds, *Atmospheric Chemistry and Physics*, 18, 1909-1921, 10.5194/acp-18-1909-2018, 2018.
5. Sato, K., Takami, A., Kato, Y., Seta, T., Fujitani, Y., Hikida, T., Shimono, A., and Imamura, T.: AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of NO_x: effects of chemical structure on SOA aging, *Atmos. Chem. Phys.*, 12, 4667-4682, 10.5194/acp-12-4667-2012, 2012.
6. Wang, S., Wu, R., Berndt, T., Ehn, M., and Wang, L.: Formation of Highly Oxidized Radicals and Multifunctional Products from the Atmospheric Oxidation of Alkylbenzenes, *Environ Sci Technol*, 51, 8442-8449, 10.1021/acs.est.7b02374, 2017.