

2nd round review of Wang et al.,

I thank the Authors for considering my comments on the work. While I do feel that several of my concerns were not really answered, I nevertheless appreciate the invested effort.

I am still not convinced that PAM type OFR setups could be used to study atmospheric relevant chemical mechanisms due to their high oxidant load conditions, and the usage of high doses of UV light, especially in connection to studying aromatic compound oxidation reactions. PAM type setups are apparently useful for deriving emission regulations as it is possible to, at least to an extent, estimate the amount of SOA produced during a long atmospheric processing time. These systems, by design, deviate from ambient concentration ranges, and thus are generally unsuited to study ambient relevant reaction mechanisms.

Also, I would advise the authors to be careful what they consider as an "ORF setup". It seems they have considered OFR to be everything where oxidation is studied, notwithstanding that several other setups have been previously meticulously characterized and assigned as well-controlled flow reactors and environmental chambers that aim to investigate the processes under ambient relevant conditions. Especially the setups mentioned in the response letter, the Jülich JPAC chambers and the very carefully controlled free-jet flow reactor of Torsten Berndt in TROPOS, Leipzig. In JPAC (e.g., Garmash et al., 2020) the reaction time is much larger (ca. 50 minutes), surface-to-volume smaller and the oxidation mixture more dilute, leading to more ambient relevant conditions. In TROPOS (e.g., Wang et al., 2017) the reactions have been studied in short reaction times (at 7.9 s) in a practically wall-less setup with careful control over the reagent concentrations. Equating these setups and works with the PAM and the current work appears wrong.

The chosen autoxidation rate of 7 s^{-1} is very high, and not supported by the referenced study. The Authors state they based this on the expected autoxidation rate of ethylbenzene, yet this higher rate in the referenced work is due to a secondary hydrogen on the ethyl substituent, which is absent from methyl groups in the studied TMB molecule. Instead, the autoxidation rate from a methyl group was found 270 times slower ($7 \text{ s}^{-1} / 0.026 \text{ s}^{-1}$). If one takes into account the symmetry with three methyl groups, then one could expect the 1,3,5-TMB rate as around 3 times higher, yet still likely less than 0.1 s^{-1} . Thus, this choice necessarily leads to severely overestimated fraction of autoxidized products. In fact, the Authors even state that "We arbitrarily set the autoxidation reaction rate...", and this seems to be critical for the analysis, leading to conclusion that 81% to 89.7% of the reaction products are due to autoxidation.

Similarly, as the pool of simulated RO₂ consists only of the two prominent RO₂ radicals (i.e., BPR and C₉H₁₃O₇) which both have been assigned with a very high accretion rate, and then the whole pool of ROOR is counted based on these same two radicals. That would also seem to indicate an overestimated importance for the accretion reaction, or do I read it wrong? Furthermore, I still find the decreasing ROOR signal problematic, as under such short timescales it would seem to indicate either particle formation, or secondary reactions of the formed ROOR, neither which would be expected under atmospheric conditions at such short times. It is stated that no particle formation was observed with long SMPS, but I suppose the

SMPS cut-off limit is so high that it would not see the fresh particles in any case. Or what was the smallest measurable particle size with the SMPS system?

The Authors seem to several times make the claim that the OH concentration in the work of Garmash et al., was higher, which is not the case. Even the highest $[OH] = 4.5 \times 10^8 \text{ cm}^{-3}$ was still considerably smaller than reported in the current study (i.e., $1.5 \times 10^9 \text{ cm}^{-3}$). Moreover, in the work of Garmash et al., it was recognized that with such an unrealistically high OH, you can't really derive sound mechanistic conclusions, and thus no mechanisms were proposed. However, the fact that the rate coefficients increase together with the number of OH substituents was recognized during the study, which is why the potential for "multi-generation OH oxidation" in product formation was acknowledged as a complication for data analysis, and no other mechanistic description was provided due to the non-conventional reaction conditions.

This comparison seems in any case problematic, as the Authors talk about 0.7-6.9 hours of atmospheric aging at $2 \times 10^6 \text{ cm}^{-3} [OH]$, yet the residence time in the setup is only 53 seconds. The exact $[OH]$ used seemed to be unknown, yet with the response letter the Authors quote an OH concentration of $1.5 \times 10^9 \text{ cm}^{-3}$. Now, in Garmash et al., the residence time is roughly 60 times longer and the maximum used $[OH]$ is $4.5 \times 10^8 \text{ cm}^{-3}$, naturally leading to longer aging timescale. What the Authors seem to miss here is that what is more important is the absolute concentrations of the reagents, as they push the chemistry to an unrealistic regime, and not the equivalent dose. And repeating from above, Garmash et al., did not derive mechanistic conclusion from the higher $[OH]$ experiments, other than the sequential oxidation behavior.

So, my problem with the current documentation is that PAM, and the OFR approach, is really a methodology for reaching emission regulations, but it's ill-suited for detailing complex chemistry under atmospheric relevant concentration regimes. It would make an interesting comparison to see how the products change between atmospheric 10^6 to 10^7 cm^{-3} to OFR 10^9 cm^{-3} , but unfortunately such an analysis was not provided. (*To put it another way, if you would have written the story like "if HOMs would survive a day – what would happen", and not trying to insist this is strictly atmospherically relevant product distribution, then this would have made much more sense*). Also, the Authors probably slightly misunderstood my comment about the potential influence of light: It would be expected to be a problem for the aromatic oxidation products undergoing photo-oxidation, not that the precursor TMB would be photolyzed. Also, I don't understand the comment that says: "Meanwhile, photolysis of HOMs can lead to decomposition, decreasing detected signals of HOMs, but unlikely to generate new HOMs." If the photolysis yields radical intermediates, as it does, then these new intermediates can continue oxidation to HOM as well. It's quite likely that this was occurring in the experiments.

Thanks for educating me that in PAM a $\frac{1}{4}$ " Teflon tube is used. This is not adequate for measuring very condensable products. This is a problem I had overlooked in the common PAM methodology.

Unfortunately, with these shortcomings I can't support publishing the work.