

Review of Egusphere submission: Secondary reactions of aromatics-derived oxygenated organic molecules lead to plentiful highly oxygenated organic molecules within an intraday OH exposure, *by Wang, Y. et al.*

Significance

Aromatic compound oxidation is responsible for a sizeable fraction of urban air pollution. Aromatics contribute significantly to the condensable product pool, and consequently are an important source, often even the dominant, of anthropogenic secondary organic aerosol (SOA). The autoxidation pathways to highly oxygenated organic compounds (HOM) from aromatics have puzzled the atmospheric community for around a decade and the major achievements on the topic have been published in several previous works (e.g., Wang et al., 2017, Molteni et al., 2018, Garmash et al., 2020 etc.). The current work aims to add to this by studying 1,3,5-trimethylbenzene (mesitylene) in an oxidation flow reactor setup using far above ambient OH concentrations, attempting to simulate long atmospheric oxidation timescales.

While the research performed is certainly timely, it has been performed with methodology that unrealistically biases the oxidation conditions, and thus prevents gaining the sought after mechanistic insight. While the used oxidation flow reactor approach has its merits in developing emission regulations, it is not a platform for studying detailed molecular level oxidation chemistry of atmospheric relevant condensable product formation. As such, I can only recommend rejecting the work with its current analysis and conclusions.

Below I detail why I feel the work is performed with inadequate research methodology, and I'll point out several issues I hope the authors will pay attention in preparing the next draft for submission.

Major comments

Unfortunately, the PAM OFR setup used in the current work with very high [OH] is not suitable for studying mechanistic details of atmospheric oxidation, perhaps even less of aromatic compound oxidation where the sequential OH oxidation and photo-oxidation of intermediates and products is important. The PAM methodology has been constructed to allow estimating the potential aerosol mass from a given emission, and it is really a method aiming for emission regulations, rather than molecular level mechanistic details. The high OH concentrations lead to unrealistically high primary radical concentrations and skew the reaction system towards very rapid RO₂ + OH pathways. The design also necessarily leads into higher RO₂ + RO₂ rates favoring accretion product formation, but also radical propagation channels by RO formation. Additionally, the formation rate of closed-shell species is accelerated allowing for more efficient sequential OH oxidation. According to the presented results, even oxidation of the accretion products is possible that commonly would be expected to contribute to the growing aerosol, and not be lost in chemical degradation by reactions with oxidants. In the atmosphere it really matters what is the correct reaction timescale, and thus the order of the sequential reactions. Hence, it's difficult to see how a PAM type setup could be used to study mechanistic details of atmospheric oxidation chains.

So, once again, PAM was constructed to enable making emission regulations, and not for studying details of atmospheric chemistry, though several groups have seemed to adopt it for

such a purpose recently. PAM is by design non-linear in oxidation chemistry regime and is thus not capable for detailing the molecular mechanisms. As the Authors also confess, the autoxidation pathways are the most important at low loadings, when processes like RO₂ + RO₂, and RO₂ + OH, are suppressed. The timing and order of reactions happening in a sequential oxidation do make a big impact.

Further comments I hope will help in sketching the next draft.

What is the influence of aromatic photochemistry in your PAM setup? Aromatics are known to strongly absorb light at relatively long wavelengths, and the oxygenated aromatics even more (see e.g., <https://www.uv-vis-spectral-atlas-mainz.org/uvvis/>), so I'm wondering how was the relevance of the used light sources tested in this work? This is not irrelevant for aromatic oxidation.

You used a relatively long ¼ inch Teflon sampling tube for the CIMS. This is the smallest tube diameter I've ever come across with nitrate CIMS sampling. One would expect the HOM losses, especially the most oxygenated ones, to be very significant in this tube. Nevertheless, HOM with high O-content seems to be detected with this setup too!

Note that ELVOC would rarely be expected to nucleate by itself, and LVOC basically never.

Jenkin 2003 reference does not have autoxidation.

The autoxidation reaction of BPR by H-abstraction has been found relatively slow by Wang et al 2017, not rapid.

Several of the products detected seem to have worryingly many H-atoms in the structures. Especially the C₉H₁₇O_m radicals.

How well does the relatively low NO with the high RO₂ simulate atmospheric NO_x chemistry?

"On the other hand, the structure of resulting C_xH_{2x-6}O₇ is strongly different from that of BPR," → Do you mean the rings are broken?

"Such a slow autoxidation reaction rate cannot explain the extensive existence of HOM monomers with more than 7 oxygen atoms and HOM dimers with more than 10 oxygen atoms, which are the maximum numbers of oxygen atoms in stabilized monomer and dimer products, respectively, formed from C_xH_{2x-6}O₇ (Mentel et al., 2015; Molteni et al., 2018; Wang et al., 2020)."

→ There's a recent paper from my group that could provide an explanation what is observed here: <https://www.nature.com/articles/s41467-023-40675-2>.

I find it confusing to draw the "double-peroxide-ring" pathways in Schemes 1 and 2, if you even explicitly mention that they are unlikely. I advise to remove them, and the text "Another possibility is the formation of a second oxygen bridge after the hydrogen shift of BPR (Molteni et al., 2018)," altogether.

“with an OH exposure equivalent to 2.4 – 19.4 days of atmospheric photochemical ageing. Certainly, such extremely high OH exposures favor secondary OH chemistry and help to facilitate our understanding on product distributions”

→ I would argue it doesn't, except for PAM conditions. As explained above, it does matter at what order and rate different oxidation steps happen in the atmosphere, and using such a high OH doses seem to necessarily skew up the chemistry. Figure 1 seems to be a good indication of this, as the “dimers” are generated faster than the monomers, and at the higher OH dose even the sum of “dimers” decrease.

“Indeed, laboratory experiments show that RO₂ formed during the second-generation OH oxidation of the first-generation stabilized oxidation products can also undergo autoxidation reactions,”

→ This is extremely natural, as autoxidation is ‘auto-catalytic oxidation’ and mainly enabled by the loosening of the adjacent H-atoms next to the gained functional groups. Autoxidation inherently accelerates in many, if not all, chemical systems.

“High atmospheric concentrations of OH”

→ What is high atmospheric concentration to you? In the atmosphere [OH] is mostly buffered by [CO] and [CH₄].

Figure S4 has a good idea but is difficult to read with such a small scale.

Was the aromatic sample illuminated with the same light source that was used for N₂O photolysis? If so, then the influence of photochemistry is likely important for the results obtained.

You make a point that estimating HOM penetration through the system to the detector is difficult to quantify, yet it seems your calculations assume that 1,3,5-TMB and HOMs have similar losses in the system. This does not seem reasonable. How does this then influence the determined “nominal relative molar yields of HOMs”?

What do you mean by increase being monotonic or non-monotonic?

Almost all the monomeric termination products in Scheme 1 have two strong H-bonding functional groups (i.e., -OH and -OOH), and thus would be expected to be seen with nitrate ion charging (see, e.g., <https://pubs.acs.org/doi/10.1021/acs.jpca.7b10015>). Perhaps the proposed scheme is not correct?

“because products from the secondary reactions cannot share the same structure as that of the one from the first-generation reaction.”

→ Except perhaps in recycling or regeneration reactions. However, the important bit here is that you can make isomeric products, and the mass spectrometric detection utilized here would not separate them.

“C₁₈H₂₆O₈ can only be formed via the accretion reaction of two C₉H₁₃O₅·”

→ Nope. Could be, for example, through O₃ and O₇ radicals as well.

I don't understand what the point of the next sentence is: "There are currently no evidences supporting that $C_9H_{15}O_m$ radicals can participate in the formation of HOM dimers with 28 hydrogens." Why would you expect the H15 radicals behave in a unique way? But also, supposedly none of the previous studies used as high OH dose, which would explain why such products were not observed. The general observation of dimers with H28 dominating seems worrying.

It seems worrying that the dimer products decrease already at such a short reaction times. This seems to amply indicate how skewed the chemical system is and that either further chemical processing, or aerosol formation, reduced the dimer yield.

A OH:HO₂ ratio is given two times although it should presumably be RO₂:HO₂.

Consider the part: "In addition, high concentrations of radicals might also terminate the RO₂ chain earlier, which inhibits the autoxidation reactions in the PAM OFR." This is true. The RO₂ lifetime is critically shortened likely inhibiting normally competitive H-shift isomerization reactions. Then consider: "However, these could only influence the distribution of oxidation products at most, and would not affect the chemical behaviors of HOMs under different OH exposures." This is not true. Both conditions favor oxidation of the aromatic parent molecule, but the same HOMs are unlikely to form under so different oxidation conditions.

"The OH reaction rate for C₁₈H₂₆O₈ should be around twice of these values, as there are two C=C bonds in its structure. Our calculation result is consistent with this estimation."

→ This seems extremely unlikely as the indicated rate is already basically at the collision limit and the big dimer compound is sterically hindered, which would imply a lower reaction rate.

"because the NO termination reaction of RO₂ is the only pathway that can generate organonitrates"

→ Why would NO₃ or NO₂ chemistry not form organonitrates?

A strange comment considering previous literature: "since no evidence supports that a nitrogen-containing monomeric RO₂ can go through accretion reactions."