

My responses to the author's replies are in red text below. – Referee #2

While the APPA OFR appears to be capable of generating sulfuric acid from the aqueous-phase SO₂/O₃ reaction, its ability to initiate aqueous-phase OH oxidation chemistry was not conclusively demonstrated here. The authors did investigate SOA generated from gas-phase OH oxidation of benzene, followed by partitioning of OVOC/SOA into ALW/droplets. While this is a novel application that the APPA OFR seems to be well suited to, this is not a demonstration of aqSOA formation according to even the authors' own definition: "water-soluble products of gas-phase chemistry [that] enter cloud droplets or aerosol liquid water and react in the aqueous phase with the hydroxyl radical (OH) or other oxidants" (L83-L86). In that regard, I think they should have used K₂SO₄ seed particles containing H₂O₂ and/or H₂O₂/FeSO₄ to initiate aqSOA formation (e.g. Nguyen et al., 2013; Daumit et al., 2016), then repeated the same experiments without H₂O₂/FeSO₄, and inferred the difference in aerosol loading and composition as aqSOA. It is not clear to me why this was not done here – this is what I would need to see to be convinced that the APPA OFR can be used to investigate aqSOA formation.

We certainly recognize that it is challenging to isolate the contribution of aqueous phase chemistry in a system in which it is occurring simultaneously with gas phase oxidation. But that is exactly the type of chemical system the APPA was developed to study. It is true that water soluble products of gas phase oxidation will preferentially partition into the aqueous aerosol and droplets, but without further oxidation those species will evaporate with the water as the aerosol/droplets exit the reactor, pass through two Nafion driers, and travel through a few meters of stainless tubing prior to measurement in the SMPS or AMS. Though the precursor studied was different (isoprene), Lamkaddam et al. (2021) reported that the aqSOA formed in their wetted-wall flow reactor could not be explained as simply the result of dissolution of products of gas phase oxidation: "...the dissolution of isoprene oxidized vapors cannot explain the aqSOA production and provides strong evidence that aqSOA results from OH reactions of the dissolved species in the aqueous phase." Adding H₂O₂ and/or H₂O₂/FeSO₄ would be challenging for this system. As is described, the seed particles/droplets are always produced through size classification of an atomized and dried aerosol. H₂O₂ from the atomizer solution would be lost to evaporation unless the aerosol were not dried below the ERH of K₂SO₄ of approximately 65%. Uncertainty in the calculated change in mass concentration of the aerosol following processing in the reactor would be substantially higher if a correction for the water content of the aerosol when initially classified is required. The alternative would be injection of gas-phase H₂O₂ into the reactor, but then estimating how much gets into the droplets and how much is lost to the walls would be difficult. Furthermore, even with H₂O₂/FeSO₄ in the aerosol/droplets, it is likely that the source of OH near their surface where more reactive species would be oxidized would still be that from the gas phase (which is needed to generate the oxidation products) and so interpretation of the with/without H₂O₂/FeSO₄ would be difficult.

My opinion is that conclusive demonstration of the APPA's ability to mimic aqueous phase OH processes was not shown in this manuscript. OH was generated in the gas phase and its reaction with benzene and its oxidation products also occurred in the gas phase. Given diffusional limitations of OH to the surface of the particles, it is not clear to me how significant aqueous phase OH oxidation could have occurred here.

Analogous to the aqueous SO_2/O_3 reaction presented by the authors, H_2O_2 or $\text{H}_2\text{SO}_4/\text{FeSO}_4$ are, to my knowledge, the canonical precursors for initiating controlled aqueous phase OH oxidation in laboratory studies. In my opinion, to demonstrate the APPA OFR for this type of application, the experiments could have, and should have been designed to accommodate their use by working around their limitations. It is a fair point that drying/size selecting the aerosols, and/or interpreting results with/without $\text{H}_2\text{SO}_4/\text{FeSO}_4$, could make it challenging to implement them. However, there are other ways that these aqueous OH precursors could have been used: for example, seed aerosols could have been maintained above the ERH of K_2SO_4 , or polydisperse seeds could have been used, and aerosol compositional changes with the AMS could have been measured with and without illumination of $\text{H}_2\text{O}_2/\text{FeSO}_4/\text{K}_2\text{SO}_4$ particles mixed with SOA surrogates or water-soluble SOA extracts rather than needing to generate the SOA in the gas phase as was done here.

In its current form, in my opinion, the revised paper adequately demonstrates the APPA's ability to study the aqueous phase $\text{S(IV)}/\text{O}_3$ reaction because the gas-phase $\text{SO}_2 + \text{O}_3$ reaction rate is negligible. It is hard for me to come up with any alternative explanation other than that S(VI) formation is occurring via aqueous phase O_3 oxidation processes. I don't think the same can be said for the benzene/OH reaction, so I think it is misleading to claim that the APPA can be used for this type of application.

Similarly, how did the authors conclude that aqueous phase OH oxidation was responsible for the increase in ambient OA oxidation state as RH was increased from 40%-->85%->100% (Fig. 17 and related text)? Hypothetically, couldn't this change have been driven by the higher RH (and LWC) promoting more efficient partitioning of low-volatility gas-phase oxidation products into the aerosol?

For the reasons mentioned in above comment, it is not clear to me that this evolution in OA oxidation state was in fact due to aqueous phase oxidative aging in the APPA OFR. Similar to part of the response to the above comment, without subsequent oxidation in the aqueous phase, water-soluble products of the gas phase oxidation are expected to evaporate when the aerosol/droplets are dried prior to measurement in the SMPS and AMS. It is also unclear why preferential partitioning to the aqueous aerosol/droplets would be more pronounced for more oxidized (and presumably lower volatility) species.

My current interpretation of the results shown here is that the yield of gas-phase benzene/OH oxidation products that partition into aerosol liquid water simply increased as a function of increasing humidity in the APPA, and that this is what is driving the humidity-dependent compositional changes (rather than aqueous-phase OH oxidation).