Xu et al. present the evaluation of their "Accelerated Production and Processing of Aerosols" (APPA) OFR that is designed to enable aqueous-phase OH-initiated oxidative aging processes. The APPA OFR combines the authors' PFA OFR with injected K2SO4 seed particles at the inlet and controlled humidification that enables control of the particle liquid water content (the range of RH discussed in this paper is 40 - 100% RH). The authors perform characterization studies of gas and particle transmission efficiencies, residence time distributions, droplet size distributions, and radiation/oxidant profiles. To demonstrate applications of the APPA OFR, they generated sulfuric acid from SO2/O3 reactions, benzene OH-SOA in the presence of dry/aqueous seeds and "cloud droplets", and aged ambient aerosol.

Comments

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 H_2O_2 and/or $H_2O_2/FeSO_4$ 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. H_2O_2 from the atomizer solution would be lost to evaporation unless the aerosol were not dried below the ERH of K_2SO_4 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 H_2O_2 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 $H_2O_2/FeSO_4$ 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 $H_2O_2/FeSO_4$ would be difficult.

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.

Unless signification dilution flow is added downstream of the APPA OFR, its relatively low 1.5 L min-1 sample flow capacity limits its application outside of measurements that can be made with particle counter(s) and instruments such as an AMS. What design changes would need to be made to increase this flow capacity to something in the range of 5-10 L min-1 that is closer to other commonly used OFR techniques?

We do not intend to redesign the reactor to accommodate higher flow rate instruments. The reactor volume cannot easily be increased by increasing the length because of height restrictions in the lab and any increase achieved through increasing the diameter would likely result in broadening of the RTD. The flow rate could easily be ~doubled to 3 L min^{-1} if, as with reactors such as the PAM, a single outlet flow was used rather than subsampling just the core flow, but again at the expense of the RTD.

L25 and L230 - Quantify "low RH"

The sentence in which it was included on L25 was removed in response to a comment by Reviewer # 1 that the abstract was too long.

We could add (40%) in parentheses after "low RH", but the exact value is unimportant and what matters is that it is low enough that there is no ALW (which is stated in the sentence).

L70 – Clarify which "new pathways" are being referred to here

We were referring to those described in studies such as Liu et al. (2020), but should have made the connection between that sentence and the following one clearer. We added "As just one example," to the second sentence in the paragraph ("Liu et al. (2020 measured sulfate...).

L160 – Rather than "The APPA...is typically operated as a 254 nm-type OFR", I suggest instead saying "the APPA reactor is typically operated in OFR254 mode"

We changed the text to "When used as an OFR, the APPA reactor is operated in OFR254 mode," The suggested replacement could give the impression that it is sometimes operated in OFR185 mode (which it isn't).

L376 – typo ("to a to a")

Thank you. Fixed.

L446-L448 – Please indicate the relative humidity that was established in the APPA OFR when the RTD measurements were conducted, and please clarify if the lamps were on or off. Is there any humidity-dependence to the RTD?

The sentence "For both tests the RH was controlled to 40% and the UV lights were off." was added after the sentence "The particle and CO_2 concentrations in the outlet-center flow were measured with the CPC and CO_2 analyzers identified in the previous section."

Though we did not repeat the experiments at different RH, we do not believe that there should be a significant dependence for either particles or low solubility gases such as CO_2.

L450 – Why are the gas/particle RTD's in the APPA OFR narrower than in the PFA OFR when the two reactors are nominally the same design?

The biggest differences between the two reactors, and those we believe are responsible for the narrower RTD with the APPA are: i) an inlet that was redesigned to minimize development of a jet near the core of the reactor and ii) addition of a water jacket around the reactor that minimizes temperature gradients and the convective mixing they would promote.

L464 – I did not notice any explicit discussion of temperature control in the APPA OFR in this section.

Thank you. The section title has been changed to just "Droplet size distribution"

L492 - The experiments describing sulfuric acid formation from SO2/O3 were not clearly described. I assume sulfuric acid was generated from SO2 + O3 --> SO3 + O2 followed by SO3 + H2O --> H2SO4, but it would be useful to clarify this. How is the concentration of "dissolved" SO2 controlled and measured? Is O3 uptake onto the K2SO4 seed particles required to initiate this reaction?

The original introduction to this section included: "...first evaluated through the well-studied oxidation of dissolved SO$_2$ by O$_3$, leading to formation of sulfuric acid and growth of the particles on which the droplets formed."

Which has now been expanded to "...first evaluated through the well-studied oxidation of dissolved SO$_2$ by O$_3$, leading to growth of the particles on which the droplets formed accompanying the formation of sulfuric acid through the generic reaction:

$$S(IV) + O_3 \rightarrow S(VI) + O_2$$

Where S(IV) represents the +4 oxidation state sulfur species $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} that will not remain in the aerosol phase following evaporation of the droplet and S(VI) represents the +6 oxidation state sulfur species H_2SO_4, HSO_4^-, and SO_4^{2-} that will remain in the aerosol phase."

Regarding the amount of SO$_2$ and O$_3$ in the droplets, these are controlled only by the gas phase concentrations, the Henry's Law constants, and, for SO$_2$, the dissociation equilibrium coefficients. Those parameters and the reaction rate constants were used to calculate the expected increase in diameter shown in original Figure 9 (not Figure 8). Rather than including all of the details of those calculations, we referenced Caffrey et al. (2001), which includes a thorough description of the relevant chemistry and equations.

L583 – Typo (the)

We inserted "the" in front of GC-FID.

L608- Assuming that the authors are referring to the benzene/OH system here, I disagree that the "distribution of [benzene] oxidation products and their OH reaction constant(s) are generally unknown."See, for example, Xu et al. (2020); Priestley et al. (2021).

You are correct. This statement is reasonable for some precursors, but not for benzene. We have removed the sentence.

L721. Please clarify the author contributions of C. Le and D. R. Cocker.

The author contributions has been updated to include C. Le and D. R. Cocker. "D. R. Collins designed the reactor and edited the paper. N. Xu performed the experiments and simulations, processed the data, and wrote the paper. C. Le and D. R. Cocker contributed to some of the experiments and data analysis."

Some of the figures should be moved to the Supplement - in my opinion, Figures 4, 8, 9, 10, 12, 13, and 16 would be a better fit there.

We moved Figures 4, 10, and 16 to the Supplement. We feel that the others are needed for understanding the accompanying text in the manuscript and should be left there so that readers can view them more easily.

The KinSim mechanism and case files that were used here should be uploaded with the Supplement.

These will be included in the Supplement.

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