

review of Xu et al.

Anonymous Referee #2

Referee comment on "An oxidation flow reactor for simulating and accelerating secondary aerosol formation in aerosol liquid water and cloud droplets" by Ningjin Xu et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-285-RC2>, 2022

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 K_2SO_4 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 SO_2/O_3 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 SO_2/O_3 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 K_2SO_4 seed particles containing H_2O_2 and/or $H_2O_2/FeSO_4$ to initiate aqSOA formation (e.g. Nguyen et al., 2013; Daumit et al., 2016), then repeated the same experiments without $H_2O_2/FeSO_4$, 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.
- 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.

- Unless significant 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 $5\text{-}10 \text{ L min}^{-1}$ that is closer to other commonly used OFR techniques?
- **L25 and L230** - Quantify "low RH"
- **L70** - Clarify which "new pathways" are being referred to here
- **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"
- **L376** - typo ("to a to a")
- **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?
- **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?
- **L464** - I did not notice any explicit discussion of temperature control in the APPA OFR in this section.
- **L492** - The experiments describing sulfuric acid formation from SO_2/O_3 were not clearly described. I assume sulfuric acid was generated from $\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$ followed by $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, but it would be useful to clarify this. How is the concentration of "dissolved" SO_2 controlled and measured? Is O_3 uptake onto the K_2SO_4 seed particles required to initiate this reaction?
- **L583** - Typo (the)
- **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).
- **L721**. Please clarify the author contributions of C. Le and D. R. Cocker.
- 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.
- The KinSim mechanism and case files that were used here should be uploaded with the Supplement.

References

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