

Interactive comment on “Secondary organic aerosol formation from OH-initiated oxidation of *m*-xylene: effects of relative humidity on yield and chemical composition” by Qun Zhang et al.

Anonymous Referee #1

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Zhang et al. presented a chamber study that examined the effect of RH on SOA mass yields and composition. This paper is potentially useful to the SOA community. However, there are portions of the manuscripts that need to be addressed before the manuscript can be considered for publication.

1. Page 4 line 3: Clarify how H₂O₂ and *m*-xylene were introduced into the chamber. Via an injection into a glass bulb using a syringe? Using a bubbler? How did the authors determine when the chamber contained 20 ppm of H₂O₂? Was the concentration of gas-phase H₂O₂ in the chamber measured in real-time? If yes, what instrument was used?

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2. Page 4 line 5: Explain the rationale behind not using any seed aerosols in this study. Seed aerosols are typically used in chamber studies to promote the condensation of SOA-forming vapors onto seed aerosol instead of the chamber walls. The mass yields reported by the authors are likely under-estimated since most of the vapors are likely lost to the chamber walls in these experiments (See examples provided in Zhang et al., PNAS 2014, Nah et al., ACP 2016, 2017). Vapor wall loss is also going to affect the types of products formed in these SOA experiments since highly oxygenated and least volatile compounds are lost to the chamber walls at faster rates (See Zhang et al., ACP 2015). The authors should comment on how vapor wall loss affects their results. Can they also provide an estimation on how much their SOA mass yields are under-estimated by?

Nah, T., McVay, R. C., Zhang, X., Boyd, C. M., Seinfeld, J. H., and Ng, N. L.: Influence of seed aerosol surface area and oxidation rate on vapor wall deposition and SOA mass yields: a case study with α -pinene ozonolysis, *Atmos. Chem. Phys.*, 16, 9361-9379, <https://doi.org/10.5194/acp-16-9361-2016>, 2016.

Nah, T., McVay, R. C., Pierce, J. R., Seinfeld, J. H., and Ng, N. L.: Constraining uncertainties in particle-wall deposition correction during SOA formation in chamber experiments, *Atmos. Chem. Phys.*, 17, 2297-2310, <https://doi.org/10.5194/acp-17-2297-2017>, 2017.

Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, *Atmos. Chem. Phys.*, 15, 4197-4214, <https://doi.org/10.5194/acp-15-4197-2015>, 2015.

3. Page 4 line 11: How were the particle wall loss rates determined? In seed aerosols only experiments? Were these particle wall loss rates measured by tracking the decay of the aerosol mass or volume? How often were particle wall loss experiments conducted? Were the reported particle wall loss rates consistent with previously measured rates? Was the particle wall loss rate always faster in high RH experiments or is this

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measurement within experimental uncertainty?

4. Page 4 line 14: It is not clear how the aerosol LWC was calculated. More details should be provided.

5. Page 4 line 20: The PILS only samples water-soluble species in the SOA, not the total SOA composition. Hence, the compositional results reported by the authors in this study are really the water-soluble species, and the authors should specify this in their manuscript. On a related note, why did the authors decided to collect aerosol samples with a PILS instead of on filters. Filter collection and analysis would have allowed them to analyze both the water-soluble and water-insoluble species. Do the authors know what fraction of the SOA formed is composed of water-soluble vs. water-insoluble species?

6. Page 5 line 8: Show the corresponding reaction time profile of m-xylene measured by the GC-MS that accompanied the observed SOA growth for the four experiments. This can be placed in the supplementary information. It is currently unclear how quickly the reactions took place. Perhaps the time profiles can be used to explain the differences in SOA formation in dry vs. humid conditions? For example, did m-xylene react faster in the dry experiments thus resulting in higher SOA mass yields? Ng et al., ACP 2007 previously showed that SOA formation in the m-xylene system will be faster at faster oxidation rates. From Fig. 1, it looks like peak SOA growth was not achieved at the end of the dry experiments (SOA mass looks like it may still increase). Why the authors decide to stop these dry experiments early? Won't that affect their calculated SOA mass yields?

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, 7, 3909-3922, <https://doi.org/10.5194/acp-7-3909-2007>, 2007.

7. Page 5 line 21: Regarding the authors' definition of SOA yield, did they calculate the SOA yield by dividing the SOA mass obtained at the end of the experiment by the total

reacted m-xylene at the end of the experiment? If yes, why did they decide to use this calculation? Previous chamber studies calculated the SOA mass yield by taking the ratio of the SOA mass at peak SOA mass divided by the mass of VOC reacted. Was peak SOA mass only reached at the end of each experiment (reaction time profiles of SOA mass growth with the corresponding reacted m-xylene for the four experiments will be useful; see comment 6)? Related to this point, are the authors confident that peak SOA mass have already occurred before they ended their experiment. Given that the authors are comparing their measured SOA mass yields with previous studies, they should make sure that their calculation of SOA mass yields are consistent with those of previous studies before they compare mass yields.

8. Page 5 line 23: How was LWC subtracted from the SOA measurement? How did the authors determine the amount of LWC in the aerosols? The authors should briefly describe this process even if this was previously mentioned in one of their previous paper. The sentence “It should be pointed out that. . . would evaporate back into the gas phase when aerosol water is removed” is confusing. The experimental section did not mention that authors removed aerosol water prior to SMPS measurement. If aerosol water was not removed prior to SMPS measurement, then this sentence seems out of place. Unless the authors are proposing a hypothetical situation?

9. Page 5 line 27: Table 1 should also state the m-xylene concentration in ug/m³ so that readers can more easily compare this study’s reaction conditions with those of previous studies.

10. Page 5 line 28: Why were the temperatures in the high RH experiments higher than those in the low RH experiments?

11. page 7 line 25: A magnified view of the mass spectra shown in Fig. 3 would be more useful for comparison purposes.

12. Page 7 line 27: The sentence “It should be pointed out that the signal intensities. . .” is confusing. Were the mass spectra for the different experiments obtained using dif-

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ferent MS operation conditions (e.g., ESI spray conditions, MS collision gas)?

13. Page 7 line 25 to page 8 line 11: The mass peaks discussed here do not seem to be the major peaks shown in Fig. 3. Why did the authors choose to focus their discussion only on these selected peaks? The major peaks seem to be $m/z > 200$. How were these products formed? The authors should include a list of all the product ions identified. Do these identified products match their proposed reaction mechanism show in Scheme 1?

14. General comment: What compounds are the -ve MS mode sensitive to? Were these compounds identified in their collected mass spectra?

15. General comment: The authors mentioned in the experimental system that they used a HPLC-MS system in their study. It is not clear from their presented results whether this was the case. Was HPLC not used to separate the products via their volatilities prior to MS analysis?

16. Page 9 line 30: The authors claimed that they used the distribution of relative intensity of SOA products with the same carbon number to investigate the potential RH effect on HOMs. The rationale behind this course of action seems to contradict their previous statement in Page 7 line 27 that signal intensities can be biased by ionization properties.

17. Scheme 1: The authors should indicate explicitly in Scheme 1 which are the products that they have identified.

18. Page 10 line 27: The sentence “Together with the previous study on toluene SOA, it is conceivable that the effect of RH on SOA yield is a common feature of SOA formation from oxidation of all OH-initiated aromatics” is too generalized and needs to be re-phrased. As discussed by the authors in their introduction, an increase RH does not necessarily cause a decrease in SOA mass yields in aromatics SOA systems. Other factors such as NO_x can also alter the effect that RH has on SOA mass yields in these

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systems.

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