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Interactive comment on "Effect of Relative Humidity on the Composition of Secondary Organic Aerosol from Oxidation of Toluene" *by* Mallory L. Hinks et al.

Anonymous Referee #2

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The Hinks et al. manuscript reports on differences in secondary organic aerosol (SOA) mass concentration and composition during high vs. low relative humidity (RH) chamber experiments. Toluene was oxidized under low-NOx and high-NOx and low (<2%) and high RH (up to 90%) conditions. Differences in mass concentration were evaluated using an SMPS; and differences in composition using nano-DESI-HRMS. While chamber experiments and SOA formation studies largely have been conducted under dry conditions, much recent attention has been given to the effects of water on particle formation and composition. Much of that effort has been focused on understanding the effects of RH on particle viscosity. There is much opportunity to advance the mechanistic understanding of SOA formation through compositional studies such as the one

presented in the Hinks et al. manuscript. That said, while the methodology and results are presented clearly, the analysis and discussion could be more robust. There have been a large number of papers published on the photooxidation of toluene (and other aromatics) and subsequent SOA formation. The results of the experiments presented are not adequately placed in the context of what is already known about toluene SOA formation, including recent mechanistic studies looking at the role of aerosol liquid water on SOA formation from toluene. The results presented are new, and with some further analysis and discussion, this work could become a significant contribution to the field. This work is suitable for publication in ACP, following some strengthening of the analysis and discussion.

Technical and Editorial Comments:

The abstract reports that the nano-DESI-HRMS analysis was performed on filters from the low (<2%) and high (75% only) experiments, and particle size analysis on a wider range of high RH (75-90%). This is not as clear in the manuscript itself. Are the nano-DESI-HRMS results from a single experiment? Or averaged over all of the 75% RH experiments? This should be made clearer in the text and in the figures/tables.

p. 4, lines 1-4 (referencing Fig. 1/Table 1): The observation that there seems to be no mechanistic difference between high and low RH and only differences in the formation of oligomers is not completely satisfactory. For the positive ion mode, it is clear that the mass spectra are more similar (samples share the same "compounds"); it is not quite as clear that there is a reduction in peak abundance. For the negative ion mode, it is clearer that there is a reduction in peak abundance, but it is not as clear that there is similarity among the most abundant compounds. For both positive and negative mode there seems to be a reduction in peak diversity, with significant differences in the negative ion mode.

Can these differences be further probed to support the hypothesis or provide alternative hypotheses?

There have been a number of mechanistic/product studies of toluene, and other aromatics, under high- and low-NOx conditions. Do those studies (e.g., observed gas-phase intermediates) combined with what is known about oligomerization pathways (e.g., as discussed on p.6) support the RH dependence under low NOx but not high NOx conditions? Citation of similar results in Cao et al. (2010) is not sufficient.

p. 4, lines 5-10 (referencing Fig. 2): While the formation of higher order oligomers is suppressed, it is interesting that the most abundant peak > C7 in the positive ion mode spectra under high RH appears to be a dimer.

p. 4, lines 31-34: The fraction of compound detected in the particle phase is discussed in terms of ambient organic aerosol (OA) levels, and an explanation is given for gas-phase adsorption artifacts. However, based on table 2 (and discussion in the manuscript) the experimental OA levels vary widely between the low and high RH experiments. The discussion of partitioning and artifacts needs to be expanded to reflect the range of experimentally observed OA levels. One question that arises is whether there are more artifacts with high RH than low RH and if so what may be the reason for that?

There is little to no discussion of the role gas-phase chemistry plays in the observations. There is an underlying assumption that because the initial VOC and oxidant concentrations were the same between experiments that the reacted VOC concentrations were also the same. Are there measurements to support that assumption? While many things can influence SOA yield, were the observed yields (if known) generally consistent with other published studies?

Did the average particle size change between high and low NOx conditions?

p. 5, lines 17-27: The authors mention the hygroscopicity of SOA here, but further discussion may be helpful. Is the amount of aerosol liquid water under high RH (75%) sufficient to prohibit/limit condensation reactions?

p. 7, lines 3-12: The extension of the experimental observations to atmospheric implications is not well supported and unnecessary. There are so many elements of experimental design that may affect the results and the extension to the ambient atmosphere; these include absence of seed aerosol (chemical and physical effects), absolute levels of precursors and particles, and relative levels of radicals. Further in the ambient atmosphere the gas-phase chemistry is controlled by more than a single VOC precursor, and the particle composition will affect the extent of aerosol liquid water.

Figures: It is recommended to specify the NOx and RH conditions in the figure captions just as a reminder since high-NOx and a range of RH are discussed in the manuscript.