

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 #2

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Overview:

This study explore the role of relative humidity (RH) on the *m*-xylene SOA formation under OH initiated no NO_x condition. The results showed that the SOA yield under high RH is significantly lower than that under low RH conditions. This study provides SOA yields and particle-phase SOA products under different RH levels. The LWC was measured by the particles mass deduction in the DAASS. The authors measured the SOA compositions by using a Fourier transform infrared (FTIR) spectra and ultrahigh performance liquid chromatograph electrospray ionization-high-resolution mass spectrometer (UPLC-ESI-HRMS). The authors reported that SOA yield found to be about 7

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times high in dry condition (RH~13%) than that in wet condition (RH~75%). Overall, the experimental data to show the impact of RH on SOA yields and products and the conclusion originating from the chamber are doubtful. The small chamber used in this study will be significantly influenced by the gas-wall processes of organic species increasing the uncertainty in data and interpretation of results. This paper in its current form is not acceptable. Please find the comments below.

Major Comments:

1. The aromatics VOCs are gas pollutants that is found to be high in urban environments where the NO_x is also abundant. It is unclear why the authors chose no NO_x condition to study the humidity effects on the formation of xylene SOA. Clarify this. 2. What is the effect of the wall on the loss gaseous H₂O₂? H₂O₂ is very hydrophilic and sticky to the wall. When RH is high, the water on the chamber wall becomes high forming a water film. This wat film can absorb a large amount of H₂O₂ and modulate the concentration of OH radicals. Please clarify how the authors measured OH radical concentrations under varying RH conditions. Why did the author use 20 ppm of H₂O₂ which was 40 times higher than the m-xylene concentration? What is the photolysis rate constant of H₂O₂ in the chamber ? 3. The size of chamber used in this study was one cubic meter and relatively very small. Thus, the wall of chemical species is very high. Additionally, the loss of chemical species to the chamber is very sensitive to humidity. The impact of RH on SOA yields can be very uncertain and doubtful. The reduction of SOA yields at the high humidity is more likely due to the chemical loss to the wet chamber wall. Thus, the conclusion made by the authors could be incorrect. Hydrophilic products and reactive chemical species can more deposit to the wall at high humidity. 4. In order to analyze the chemical compositions in gas and particles phase using a variety of aerosol, a large amount of air volume should be collected. The size of the chamber used in this study was only one cubic. It is hard to believe how the authors analyzed gas and aerosol with the air volume less than one cubic meter. Additionally, the chamber volume was getting small as the experiment progressed. The

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consumption of the chamber air increased the wall effect. The authors should clarify this problem. 5. Page 5, line 4. The Master Chemical Mechanism can only provide the gas-phase reaction pathways. The yield of the products in particle phase may not directly connected to the yield of products in gas-phase. How does the author compare gas-phase oxygenated m-xylene products predicted using MCM to the measured particle-phase products from HRMS ? 6. Page 5, line 11. The value of the maximum SOA mass in Figure 1 is not consist with the values reported in the text and the Table 1. The value of SOA mass under 73.6% and 79.1% in Figure 1 is about 40 and 10 ug/m³ but the value reported in the text is only 1.9 and 0.8 ug/m³ and the value reported in Table 1 is 15.8 and 7.9 ug/m³. 7 It is not clear how much LWC was present at the end of experiments and how much SOA mass was obtained after subtracting the LWC from total aerosol mass. What is the effects of LWC on the SOA formation in this study? The author mention that LWC can explain the positive effect of RH on SOA formation under high NO_x condition. What is the difference in LWC between SOA with the high NO_x condition and that with the low or no NO_x condition? 8. What is the particle size distribution of m-xylene SOA? Does all of the particle size smaller than 1000 nm and within the SMPS measurement range? 9. Section 3.2. The intensity of the functional groups in FTIR spectrum was correlated to the sample mass. What was the SOA mass that collected on the disk and that measured using FTIR? Or does the author use same sampling duration for both RH conditions? What was the collection efficiency of the impactor on a sampling disk as a function of the particle size? Without knowing the mass of measured SOA, it is unreasonable to compare the peak intensity of the functional group between SOA from different samples. 10. Figure 2 and Table 2. There is also peak at 3000 cm⁻¹ which is missing in Table 2. 11. What is the measured glyoxal fraction in m-xylene SOA? Was oligomerization impacted by the RH in this study? Even though the concentration of highly oxygenated molecule (HOM) is much lower at high RH, the overall trend of the SOA mass, which is much less at high RH compare to low RH, can not be explained by solely through HOMs. As mentioned in the previous comment above, the effect of the wet wall on SOA formation can be very significant

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particularly in small reaction. The time scale of the gas-wall partitioning of organic species can be significantly fast and results in the less SOA yields at higher humidity. 12 The author claimed that the increase of the C-O-C stretching was resulted from the oligomerization of carbonyls under the high RH condition. However, the IR absorption at 1080 cm^{-1} can be also due to the existence of C-OH group. Clarify this. 13. Fig. 2. Authors assigned the peak at 1600 cm^{-1} as carboxylate. The reviewer is doubt this assignment. In general, dry organic aerosol cannot produce carboxylic acid ions. Even if the organic aerosol is produce in the wet condition, the aerosol water content is not enough to product the dissociation of carboxylic acid. In general, the pKa of carboxylic acid ranges from 2 to 6. Even in the dilution in water, less than 1% of carboxylic acid is dissociable. In SOA, most carboxylic acids will be in the un-dissociated form. 14. Fig. 4. Based on Fig. 4, a large mass appeared in negative ion mode suggesting that the aerosol has a large fraction of carboxylic acid. It is contradictable compared to either MCM simulation or the conclusion by the authors in the glyoxal was abundant. In general, a large fraction of gaseous products from MCM prediction are alcohols and carbonyls, and amount of carboxylic acids are small. Please clarify this. 15. Fig. 4. Low carbon number products are generally more volatile than high carbon number products. Fig.4 showed that low carbon number products are high with the SOA with the low RH, possibly suggesting that volatile low carbon number products more likely deposited to the wall due to the gas-wall process. 16. What was the RH of the environment inside the FTIR spectrometer when FTIR spectra were obtained for Fig. 4 ? 17. What is the atmospheric implication of this study? What is the potential impact of RH on p-xylene and o-xylene as well as other aromatics? Will other aromatics also have the similar RH effects with m-xylene? What is the uncertainty of this study? Does the impaction or the PILS sampling has uncertainty? What is the duration of the experiments? 18. There are numerous grammatical problems. The manuscript needs to be approved by a native English speaker. 19. Page 3 Line 13. The author may need to provide the reason why the author set the density of m-xylene SOA is set as 1.4 g/cm^3 . According to the citation Ng et al. 2007 gives the density of m-xylene SOA as 1.33 \pm

0.1 g/cm and Sato et al. 2007 provide the density of Toluene SOA as 1.42 ± 0.8 g/cm. 20. Page 3 Line 17. The author mention about the uncertainty of SMPS. However, the uncertainty of SMPS measurement for the used data in the paper was not reported. 21. Page 4 Line 6. For comparing the SOA yield between cited values and that of this study, it may need to provide the error range of the values. Additionally, numerous data of this paper need errors. 22. Pages 6 and 7 (section 3.2): The description to construct the functional group distribution using FTIR spectra is unclear. How to separate the FTIR peaks for each functional group ? The intensity of each function group varies with vibration force constant and peak broadening changes with compositions.

Minor comments: Page 2, line 21. The sentence is confused that it compares the RH effects between low NO_x condition and with NO_x condition. Figure 3. The y-axis scale is negative for high RH and positive for Low RH. It is better to make them as a same positive scale. Figure 5: RH scale should range from 0 to 100 (negative is incorrect). Page 2 line 15: it is better to use “have been conducted”. Page 2 line 19: after “as an OH radical source,” there supposed to use period instead of comma. Table 3. The form of the table is better to unify with other tables.

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