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Interactive comment on “Aging of secondary organic aerosol from small aromatic VOCs: changes in chemical composition, mass yield, volatility and hygroscopicity” by L. Hildebrandt Ruiz et al.

Anonymous Referee #2

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The manuscript reports SOA formation from toluene under different conditions, with/without seed and different OH exposure. The different SOA is compared for chemical composition, yield, oxidation state, volatility and hygroscopicity. They report an inverse dependence between the oxidation state and the volatility but find no correlation between the hygroscopicity and the oxidation state. To compare the volatilities of the different SOA they use a novel approach based on the VBS. The topic covered by this paper is of interest to readers of ACP. The paper is well written but there are several points not so clear or contradicting. In my view, the authors do also overly interpret

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the data. The statements are based on a small data set and the differences between the experiments are not so clear. Trends within an experiment are contradicting trends between experiments. Even the authors state at the end that the results are puzzling. The paper needs some more clarification before it can be published. There are 9 experiments with somewhat different starting conditions but not very dramatically. Only in three experiments the OH exposure was measured. It is not really obvious from the paper, what leads to the observed changes in the oxidation state. They observe differences between seeded/unseeded experiments, which most likely are due to vapor wall losses as described in Zhang et al. 2014, but this is not discussed. The authors attribute a lot to aging of the SOA, but looking at the few (3) experiments, it is actually not very strongly aged. For the other experiments it is more or less guessing. I feel a bit uncomfortable about some results/statements based on the AMS analysis. a) They attribute all NO/NO₂ observed in AMS to organic nitrate since “no inorganic nitrate is added to or expected to be formed” (Page 31448, line 20). However, they add HONO which is photolyzed to NO, which is oxidized to NO₂ and further to HNO₃. The observed ratio of NO/NO₂ = 8 is not a unique indicator for organic nitrate. This ratio varies from AMS to AMS and depends on the structure of ON. It has to be compared to the one recorded during their calibration using NH₄NO₃. b) The measured O:C are rather high for the rather low OH exposures. The H:C seems to be very high, in some cases higher than 2 (exp 3, 9). The precursor toluene has a H:C of 1.14. Where does all that hydrogen come from? Could it be a problem of the AMS analysis? c) They conclude that “the methyl carbon atom is about three times less likely than the aromatic carbon atoms to form organic acids” (page 31462, line 11). Can they show from seeded blank experiments that there is no background formation of SOA producing CO₂ from 12C? d) Experiment 2 shows extremely high OSc in the beginning. These values (~3) are unbelievable even considering the multiperoxide formation mechanism recently reported. This experiment is reported with the highest OSc and defines basically the correlation between OSc and volatility (Fig. 9). All other points would yield a different dependence. How sure are the authors about the analysis of experiment 2.

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In Table 2 the OSc is given as 0.45. From Figure 2 it seems to be even higher and in Figure 10 it is shown as -0.2. It is also puzzling to see in Table 2 that the H₂O/CO₂ is completely different from all the other experiments. Is this real or an issue of data analysis? Figure 2 indicates a background aerosol. How much does this influence the result? e) Although not being an AMS specialist I wonder why the collection efficiency is so low (0.25), even for organics? They do not find a general correlation between OSC and hygroscopicity as was found by others. Thus they speculate on surfactants playing a role. I assume that kappa was calculated using ZSR for the mixed aerosols. As mentioned above, the aerosol might also contain inorganic nitrate which is not considered here and could explain observations. In the conclusions the authors state “experiments with higher OH exposure showed higher SOA mass yields”. This is shown for exactly 2 experiments. Two experiments were performed with other aromatics as seen in Table 1. No other information is given in the manuscript. Technical comments P31450, line 15: here density is fixed to 1.5 gcm⁻³. In table S1 other densities are reported. P31456, line 20: the ratio would be 1/7 P31457, line 2: Light is reported at 100% in Table 1 for all four experiments. Therefore there is not lower UV intensity. P31459, line 6: Table 1 reports 100% UV lights Table 1: correct units for OH exposure Figure 4: correct numbers for OH exposure

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: PNAS, 111, 5802-5807, 10.1073/pnas.1404727111, 2014.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 31441, 2014.

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