

Atmos. Chem. Phys. Discuss., referee comment RC2  
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## Comment on acp-2021-951

Anonymous Referee #3

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Referee comment on "Functionality-based formation of secondary organic aerosol from *m*-xylene photooxidation" by Yixin Li et al., Atmos. Chem. Phys. Discuss.,  
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Overall comment:

This work examined the functionality-based SOA formation from *m*-xylene photooxidation, combining gas-phase composition measurements, aerosol property measurements, and a kinetic simulation. The main conclusion is that the authors categorized the total SOA products into four major functionality-based groups: dicarbonyls, carboxylic acids, polyhydroxy aromatics/quinones, and nitrophenols. Then the authors argued that the parameterized uptake coefficients of the four groups can simulate the SOA mass concentration and concluded that functionality-based approach could extend to the SOA formation from other VOCs as well. However, this conclusion is in strong contrast to the established volatility-based SOA formation understanding. Unfortunately, the authors did not provide convincing evidence for their conclusion. One obvious problem is that evaporation of these products from SOA back to the gas phase is not considered in their model. There are also other technical issues. Thus, the manuscript needs to be revised before consideration for publication.

Detailed comments:

1. Line 50 – 57. I think a mechanism figure could help explain the chemical reactions here. Figure 1f helps a little, but I feel a more comprehensive mechanism separately shown is better.
2. Line 80 – 84. Although it is true that non-equilibrium processes exist, volatility still dominates the overall gas-particle partitioning process. There have been many, many measurements suggesting that. That the volatility-based approach under-predicts SOA

formation does not mean volatility-based idea is wrong. The non-equilibrium processes and particle-phase reactions only make the gas-particle partitioning estimated based on vapor pressure inaccurate in some cases, but overall, volatility is the driving property.

3. A lot of the details of the experiments and model should be provided in the main text. For example, what is the ion chemistry of the ID-CIMS? What is the mass resolution and if low mass resolution, how were the chemical formulas resolved? How was the thermal desorption carried out? At what temperature for how long? How were the products quantified? What were the uncertainties? How were the product yield quantified? How were the uptake coefficients determined? How was the model developed? These are all very important details to help readers understand the discussion and should move from the supporting information to the main text.

4. The authors claimed that the product identification method does not induce fragmentation. However, it appears that the IT-CIMS is essentially similar to (H<sub>3</sub>O<sup>+</sup>) PTR-MS. It is known that PTR-MS does have some fragmentation for some compounds (see Yuan and de Gouw, *Chem. Rev.* 2017, 117, 13187). How can the authors be certain that the measured ions did not induce fragmentation? Also, thermal desorption was used for SOA composition? Thermal desorption is known to cause fragmentation of species. Could there be fragmentation?

5. The experiments involve many different conditions (RH, seeds, NO<sub>x</sub>, NH<sub>3</sub>). I suggest adding a table listing all performed experiments and number the experiments. Refer to the numbers in the discussion.

6. Line 156. The absence of HOM could be due to instrument limitation. In fact, some other species may not be well detected under H<sub>3</sub>O<sup>+</sup> mode.

7. In the kinetic model, the authors only represent the uptake/condense process and showed some evidence the functionality-based approach could work. However, the desorption/evaporation of the species from SOA to gas-phase unmentioned. As it is well known, the condense process and equation (e.g, eq. S3) is independent of volatility, but volatility determines gas-particle partitioning in controlling the desorption rate. It was not considered in this manuscript.