

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 #3

Received and published: 25 February 2015

General Comments:

This paper describes a set of experiments that investigated the effects of oxidative aging on the formation and chemical and physical properties of secondary organic aerosol formed from the oxidation of toluene by hydroxyl radicals in the presence of NO_x. The experiments were conducted in a large Teflon film chamber and the chemical composition was analyzed using an AMS, the volatility using a thermal denuder, and the hygroscopicity using a CCN counter. The experiments appear to be well done and

C12385

the data analysis, modeling, and interpretation seem appropriate and reasonable. The paper is concise and easy to read, though quite dry and not very inspiring. It is primarily observational: “We saw this, and it is similar to what so-and-so saw,” and if not, then some speculation about why not. A long general introduction is provided, but I don’t see any hypotheses to be tested or strong justification for why these experiments needed to be conducted. And it is not at all clear what if anything new was learned and if so why it is important. It is a nice data set and the paper deserves to be published, but I encourage the authors to put in some additional work to emphasize the high points and dig a bit deeper into the details of the results and explanations so others might find a reason to read it. As currently written, there is not much of a take-home message regarding why these results mattered to the authors or should to the larger atmospheric chemistry community. In my opinion the paper should be published in ACP after the authors address those issues and the following comments.

Specific Comments:

1. Why was toluene (the only aromatic studied in any detail) chosen for these experiments? Is there something about the chemistry that makes it an interesting and important choice?
2. Page 31450, Second paragraph: How does OA density compare with values calculated using the parameterization developed by Kuwata et al. (2012), ES&T, 46, 787? This is a useful way of checking for significant errors.
3. Page 31450, bottom paragraph: The approach for correcting for vapor loss to walls ignores the uptake into the Teflon film walls, which has been shown recently to be significant. Zhang et al. (2014) PNAS, 111, 5802 have shown that vapor wall losses in studies of SOA formation from toluene oxidation lead to underestimates in SOA yields by factors of 2–4. This issue should be discussed here and its potential effects on results, such as SOA mass, O/C ratios (loss of oxidized products to the walls that prevents further aging), etc.

C12386

4. Page 31453, first paragraph: This is the first I have heard of “shifting factors” and imagine this will be the case for many other readers. It would help to give the reader a feeling for what a certain relative reduction in “volatility” (an imprecise term) means in this framework. Is it somehow related to a relative change in average SOA vapor pressure or saturation concentration? Without this insight it is difficult to know if these represent large or small changes in “volatility”.

5. Page 31455, whole page: There is no discussion of the observation that SOA was higher with seed than without. Why? According to the PNAS paper referenced in Comment 3, this is likely due to reduced wall loss of vapors, which will affect the interpretation of SOA results and O/C ratios. I suggest discussing this.

6. Page 31455, bottom line: What compounds are expected to photolyze at significant rates in these experiments?

7. Figures 2 and 3. I suggest adding toluene time profiles to these figures so that one can determine the extent to which early-generation products are still being formed vs. more aged products. These profiles should also be discussed along with the other quantities.

8. Page 31456, lines 20-25: I am not aware of a mechanism for forming organic acids under the high NO_x conditions of these experiments. Please provide a reference of definitive evidence by others that acids are formed.

Might the CO₂⁺ ion instead come from acylperoxynitrates (PAN-type compounds with formula R-C(O)OO-NO₂) formed by oxidation of aldehydes, which are well-established products of toluene oxidation, in the presence of NO₂? See Chan et al. (2010), ACP, 10, 7169. This would be consistent with the large nitrate content of the SOA.

9. Page 31457, lines 14-22: The Chan et al. (2010) reference given in Comment 8 indicates that for systems that form significant aldehydes, such as the one studied

C12387

here, that SOA yields increase with increasing NO₂/NO ratio. This is worth including in this discussion.

10. Page 457, bottom paragraph: With regards to acylperoxynitrates, it might be mentioned that they might still be mostly stable in the TD for the 15 s residence time. Thermal decomposition lifetimes range from about 20 min to 5 s for temperatures 40–100 C [Orlando and Tyndall (2012), Chem. Soc. Rev., 41, 6294].

11. Page 31459, lines 15–20. My recollection is that past TD measurements/modeling by the CMU group has indicated a mass accommodation coefficient for SOA of 0.01. Any idea what is so different here?

12. Page 31460, lines 14–21: Can anything be said about what this 0.5 unit reduction in volatility corresponds to with regards to vapor pressure, and what the change corresponds to in carbon number or functional group composition (e.g., using the SIMPOL method)?

13. Page 31461, bottom paragraph: What about the possibility that carbon chain length affects CCN activity? This is not accounted for in O/C ratio and oligomers eventually reach a solubility limit.

14. Page 31462, line 2: The attempt to generalize these results to “small aromatic VOCs” seems inappropriate, since although a few are listed in Table 1 as being added to toluene in 2 experiments, and there is no discussion of what effects they had, if any. In the absence of such results and discussion I suggest limiting the conclusions to toluene, with perhaps some comments on whether there is reason to believe that other small aromatics might behave similarly or differently and why. I also suggest changing the title from “small aromatic VOCs” to “toluene” for the same reasons.

15. Page 31462, Conclusions: It is stated in the Introduction: “A main objective is to connect the extent of oxidation and the changes in volatility of these experiments with the 2D-VBS framework.” Was that objective met satisfactorily? How do these results

C12388

contribute to broader objectives? Do these results help to explain what anyone else has observed, or are they specific to this study?

16. Table 1: I suggest adding final concentrations of toluene and also the concentrations of other aromatics added.

17. Table 2: How was NO₂ measured? NO_x analyzers measure NO₂ + organic nitrates, which can be significant.

18. Table 2: Some additional description of how NO/NO₂ was determined would be useful. It is not obvious how this was done using linear regressions.

19. Figure 8. It seems like the nice linear relationship here deserves a little more discussion than "Figure 8 shows a comparison of the modeled vs. the measured MFRs." If it is so un-noteworthy perhaps just leave it out.

Technical Comments:

1. Page 31447, bottom line: I suggest using a term other than "molecular ions", since this can be interpreted as non-fragmented ions formed from reaction products, whereas given their low mass these are probably all ion fragments. Perhaps use "ion masses".

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