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Atmospheric Chemistry and Physics Discussions

Interactive comment on "AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of NO_x: effects of chemical structure on SOA aging" *by* K. Sato et al.

Anonymous Referee #2

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General:

This manuscript describes secondary organic aerosol (SOA) formed from benzene and 1,3,5-trimethylbenzene as they undergo oxidative aging under high-NO_x conditions. The chemical composition of the SOA was measured using a high-resolution time-of-flight Aerodyne aerosol mass spectrometer (AMS) and offline filter samples analyzed by liquid chromatography/time-of-flight mass spectrometry (LC/TOF-MS). SOA formed from benzene was further oxidized and contained more ketocarboxylic acids and organonitrates than that formed from 1,3,5-trimethylbenzene. The authors suggest that the oxidative aging occurs as a result of ketocarboxylic acid oxidation. This manuscript presents new and interesting results that are within the scope of ACP. I recommend the manuscript for publication after my comments have been addressed.

Major comments:

The authors are not especially careful in distinguishing between processes occurring during SOA formation and those occurring during oxidative aging. It may not be appropriate to call the processes reported in this manuscript "aging." The OH concentration throughout the experiments is not reported so it is not discernible from the manuscript whether the particles and vapors in the reaction chamber were continuously oxidized. The authors state that the benzene or 1,3,5-trimethylbenzene does not react away completely during irradiation, which means that SOA formation and growth is ongoing throughout the experiments. If OH is generated continuously throughout irradiation, then new SOA will always be condensing onto existing particles, and any aging processes that occur will not easily be distinguishable from SOA growth. If OH generation ceases at some point during the experiment, and oxidant is no longer available, oxidative aging processes cease. More discussion on the OH levels and timescales of particle growth and aging in the present experiments is needed.

The authors discuss carboxylic acid formation from carbonyls multiple times in the manuscript, typically in relation to AMS measurements of ions at m/z 43 and 44. During these discussions, it is unclear whether the carboxylic acid formation takes place in the gas or particle phase. The sentence on p. 291 lines 2-4 implies that this oxidation takes place in the particle phase, whereas the sentences on p 296 lines 15-19 discuss gas-phase oxidation of carbonyls. If carbonyl products of benzene and 1,3,5-trimethylbenzene oxidation must undergo subsequent gas-phase oxidation to carboxylic acids to decrease their vapor pressures and allow them to condense and form SOA, then this oxidation to form carboxylic acids should be classified as a SOA formation mechanism and not a SOA aging mechanism, as is done on p. 296, lines 4-6. The authors need to address the likelihood of carbonyl oxidation in the gas vs particle phases, including expected partitioning of the aldehyde, ketone, and carboxylic acid species produced from benzene and 1,3,5-trimethylbenzene photooxidation and sources of oxidant in the present experiments in both the gas and particle phases.

p. 286, line 24. Was the added NO_x in the form of NO or NO_2? Why was it added?

p. 289, line 7. What order of magnitude are the wall losses in your chamber? How much of an effect are they expected to have on the yield? Did you assess the effects of vapor-phase wall loss on SOA growth?

p. 289, sentence starting on line 13. At the hydrocarbon and NO_x concentrations in the present experiments, do you expect RO_2 + HO_2 to be competitive with RO_2 + NO or RO_2 + RO_2? It seems unlikely that hydroperoxide formation would be significant under high-NO_x conditions.

p. 316 (Fig. 4). To be precise, the benzene reactive intermediates react with NO to form ring-opened products, not NO_x in general. Also, gas-particle partitioning of the first-generation products is depicted in Fig. 4a, but it is not supported by the LC/TOF-MS data (all ring-opened products identified in Tables 2 and 3 have at least one carboxylic acid moiety). Is there any evidence to support the condensation of the first-generation products?

p. 317 (Fig. 5) Why does the $HRNO_3$/HROrg start higher for the experiments with higher initial NO_x? It is more prevalent with benzene (run 2 and 3 vs run 1) but is also observed with 1,3,5-trimethylbenzene. Does a higher initial NO_x concentration

increase the background $HRNO_3$ before the onset of SOA growth?

Additional comments:

p. 284, line 4. It would be appropriate to specify what type of SOA aging is occurring (physical, chemical, etc.).

p 286, line 14: “Newly-developed AMS data analysis methods..." I believe that the AMS data analysis procedure (ToF-AMS analysis toolkits SQUIRREL and PIKA) is not new; however, the presentation of the AMS data using the van Krevelen or triangle plots is new. Consider rewording to clarify.

p. 287, line 1. What is 1ppm RH in %RH (as is commonly reported)?

p. 287, line 6. The SMPS does not directly measure the volume concentration. It measures particle diameter and number concentration. Volume concentration is a calculated quantity.

p. 287, line 9. Were W-mode AMS data available? If so, why were they not used?

p. 287, line 18. At what time(s) were filter samples taken during each experiment?

p. 289, Sect. 3. At what time during the experiments was the yield reported?

p. 289, line 9. Why was a density of 1.4 g cm^{-1} used?

p. 290, sentence starting on line 17. Runs 2 and 3 produced different SOA mass concentrations, but run 3 overlaps run 2 on the triangle plot. The plot contradicts the conclusion made in this sentence. Please explain.

p. 290, sentence starting on line 20. It is not clear why the ions at m/z 44 are formed "efficiently." Is this a comment about the ion efficiency of species at m/z 44 in the AMS?

p. 290, sentence starting on line 23. It may be useful to state specifically what changes have been made to the frag table (perhaps include this in the supplement).

p. 290, line 24. I am not sure what you mean by "data migration."

p. 290, sentence beginning on line 27. This trend is not readily apparent from Fig. 1. Runs 2 and 3 have f_{44} similar to or lower than that of toluene and ethylbenzene. The range of f_{44} for benzene also overlaps that observed for *p*-xylene and *m*-xylene. The f_{44} for *m*-xylene, 1,2,4-trimethylbenzene, and run 4 are all approximately the same.

p. 291, line 15. Were HR-AMS ions NO^+ and NO_2^+ included in O/C and H/C calculations?

p. 295, line 19. "Since the oxidation of ketone groups is slow, formation of carboxylic acids from dicarbonyl products is much slower than from benzene." Carboxylic acids do not form directly from benzene. Both benzene and 1,3,5-trimethylbenzene form dicarbonyl products. This sentence is confusing and should be reworded.

p. 298, lines 4-5. "...laboratory chamber experiments cannot simulate the reactions of organics in the aqueous phase that take place in cloud processing." Chamber experiments can be run under humid conditions with aqueous seed particles, and there are numerous examples of this in the literature. The lack of humid chamber aging experiments does not necessarily mean that this type of experiment cannot be performed. Instead of presenting these experiments as impossible, consider suggesting them as future work to enhance the understanding of aqueous-phase SOA chemistry.

p 298, line 22. "This shows that nitrophenols and organic peroxides decrease as a result of chemical reactions." Do you mean organic nitrates?

p. 298, sentence beginning on line 25. I am confused how gas-phase photolysis acts as a sink of particle-phase compounds.

p. 301 line 5. "On the other hand, only ring-opened carboxylic acids were identified." This sentence does not specify from which samples these carboxylic acids were identified. Please clarify.

p. 310 (Table 1). It would be beneficial to include ΔHC in this table. Also, what is the uncertainty of the SOA yields?

Supplement Fig. S3 and S6. The legends on these figures are confusing if one is not familiar with the AMS Igor data analysis software. Consider remaking the legends to make them understandable to those outside of the AMS community.

Technical correction: p. 292 line 13. Change "higher" to "lower."

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