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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.

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Dear Sir or Madam:

Thank you for your careful reading and useful comments. I reply to your comments as follows:

"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 appro-

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priate 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 OH concentrations during each experiment were estimated assuming that benzene or 1,3,5-TMB decreased by the reaction with OH radicals. In the calculations, the literature values of the rate constants (Atkinson, 1984; Aschmann et al., 2006) were used. In each experiment, the concentration reached the maximum immediately after the start of irradiation and then decreased with time, but the OH concentration maintained >5 x 10ˆ5 molecules cm-3 during irradiation. This indicates that particles and vapors in the reaction chamber were continuously oxidized during irradiation in each experiment. These are discussed in the section of experimental procedure. As you pointed out, the benzene or 1,3,5-TMB does not react away completely during irradiation, which means that SOA formation and particle growth are ongoing throughout the experiments. However, as described in page 291 lines 15-16, the O/C ratio of organics increased with time, whereas the H/C ratio decreased with time. The continuous increase in the O/C ratio of particulate organics measured by H-ToF-AMS shows SOA aging occurs continuously during experiments. This discussion is added in the section of van Krevelen diagram.

“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."

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. I agree with this. These oxocarboxylic acids will react with alcoholic products in the particle phase to form hemiacetal dimers with lower volatilities than those of monomeric oxocarboxylic acids. The reverse reactions of hemiacetal formation can occur to form oxocarboxylic acids and alcoholic products again. Particulate oxocarboxylic acids can proceed to the vaporization followed by the oxidation in the gas phase to form dicarboxylic acids which can be absorbed on particles again, or the particulate oxocarboxylic acids can be oxidized by reactions in the particle phase to form dicarboxylic acids. This oxidation to form carboxylic acids results in an increase in the O/C ratio of organics and should be classified as a SOA aging processes. Dicarboxylic acids can react with alcohols in the particle phase to form ester-type oligomers. These are discussed in the manuscript.

"p. 286, line 24. Was the added NOx in the form of NO or NO2? Why was it added?"

It is already stated in the caption of Table 1. NOx is needed for OH radical formation

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from the photooxidation of methyl nitrite. The reaction scheme of OH radical formation from the photooxidation of methyl nitrite is explained in the text.

“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?”

The rate of particle wall deposition loss is 3 × 10ˆ-5 s-1 (Sato, 2008). Using this rate, the yields listed are corrected to 2.2% (Run 1), 8.3% (Run 2), 32.0% (Run 3), 2.9 % (Run 4), 4.1% (Run 5), and 16.5% (Run 6). These are described in the caption of Table 1. We did not assess the effect of vapor-phase wall loss on SOA growth.

“p. 289, sentence starting on line 13. At the hydrocarbon and NOx concentrations in the present experiments, do you expect RO2 + HO2 to be competitive with RO2 + NO or RO2 + RO2? It seems unlikely that hydroperoxide formation would be significant under high-NOx conditions.”

I define the total peroxide concentration by “RO2 concentration + HO2 concentration” here. “RO2 + HO2” does not mean the RO2 + HO2 reaction. To avoid reader’s misunderstanding, I revise this to “RO2 and HO2.” I reply to the second sentence of your comment as follows: As you describe, the RO2 + NO reaction (k= 7.7 x 10ˆ-12 cm3 molec-1 s-1 (DeMore et al., 1997)) is major RO2 sink when NO concentration is sufficiently high. However, the RO2 + HO2 reaction (k = 5.6 x 10ˆ-12 cm3 molec-1 s-1 (DeMore et al., 1997)) will also occur under <1 ppb NO levels. These conditions can be achieved after most NO is converted to NO2. You can find similar discussion elsewhere (Ng et al., 2007; Johnson et al., 2004, 2005).

“p. 316 (Fig. 4). To be precise, the benzene reactive intermediates react with NO to form ring-opened products, not NOx in general. Also, gas-particle partitioning of the firstgeneration 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

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products?”

I substitute “NOx” with “NO” in Fig. 4. First-generation dicarbonyl products cannot be detected by present negative mode LC/TOF-MS because the sensitivities of these products are very low. Glyoxal polymers are known to be produced by the particle phase reactions of the absorbed first-generation products (Kalberer et al., 2004). We don’t have any evidence to exclude these processes.

“p. 317 (Fig. 5) Why does the HRNO3/HROrg start higher for the experiments with higher initial NOx? 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 NOx concentration increase the background HRNO3 before the onset of SOA growth?”

The background of HRNO3 is very small (basically zero) as shown in Fig. S1a. The start value of the HRNO3/HROrg is not influenced by any background signal. I describe these in the caption of Fig. 5.

“Additional comments:”

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

I fix it.

“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.”

I reword this sentence.

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

The original description in the manuscript is incorrect. The mixing ratio of H2O was 1ppm (which corresponds to 0.003%RH). I revise this sentence using %RH.

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“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.”

I revise this sentence following your comment.

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

Unfortunately, W-mode data weren’t available.

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

One sample for iodometric spectrophotometry was collected in each of Runs 1 and 4, or two samples (i.e., one for iodometric spectrophotometry and the other for LC/TOF-MS analysis) were collected in each of the other runs. This is explained in the text.

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

The SOA yield was calculated using the data when the volume concentration reached a maximum. This is added in the text.

“p. 289, line 9. Why was a density of 1.4 g cm?1 used?”

Alfarra et al. (2006) determined the density of 1,3,5-TMB SOA to be 1.35-1.40 g cm-3, whereas Martine-Reviejo and Wirtz (2005) determined the density of benzene SOA to be 1.35 +/-0.04 g cm-3. I cite these references.

“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.”

I fix this sentence to explain correctly the results. I don’t know a clear reason why Run 3 overlaps Run 2. Low-volatility species may be saturated in Runs 2 and 3, or the difference in the hydrocarbon concentration (i.e., RO2 chemistry) between Runs 2 and 3 may affect these results.

“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?”

What I mean here is that the f44 values of low-volatility SOVCs are likely to be higher than those of high-volatility SVOCs. I rewrite this sentence.

“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).”

The intensities of m/z 18 and 28 organic fragments were modified in the new table (Aiken et al., 2008). Results of f44 decreased <2% by this modification. I describe these in the text. The modification of the fragment table is not original work of this study. I don’t include the fragment table in the supplement, but I cite the reference instead.

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

This sentence is removed. (Please see also reply to the comments of referee #3.)

“p. 290, sentence beginning on line 27. This trend is not readily apparent from Fig. 1. Runs 2 and 3 have f44 similar to or lower than that of toluene and ethylbenzene. The range of f44 for benzene also overlaps that observed for p-xylene and m-xylene. The f44 for m-xylene, 1,2,4-trimethylbenzene, and run 4 are all approximately the same.”

I revise the sentence. I compare only results of benzene and 1,3,5-TMB in the new manuscript. The corresponding sentence in the conclusions is also revised.

“p. 291, line 15. Were HR-AMS ions NO+ and NO+2 included in O/C and H/C calculations?”

No, they weren’t. The O/C and H/C ratios were calculated for organics, while the NO+ and NO2+ ions are treated as being formed from nitrates. It is explained in the text.

“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

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do not form directly from benzene. Both benzene and 1,3,5-trimethylbenzene form dicarbonyl products. This sentence is confusing and should be reworded."

The sentence is rewarded to "Since the oxidation of ketone groups is slow, formation of dicarboxylic acids from ketoaldehyde products is much slower than from dialdehyde products of benzene."

"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."

I revise this sentence as "The laboratory chamber experiments under dry conditions are not be able to simulate. . ." The corresponding sentences in the abstract and in the conclusions are also revised. In the conclusions, I suggest that the understanding of aqueous-phase SOA chemistry is necessary in the future.

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

Yes, I do. I fix it.

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

The equilibrium of gas/particle partitioning is held between particulate nitrophenol (NPh(p)) and gaseous nitrophenol (NPh(g)). NPh(g) is photolyzed under this equilibrium:

NPh(p) <-> NPh(g)

$NPh(g) + hv \rightarrow products$

If NPh(g) decrease by the photolysis, NPh(p) is vaporized to maintain the equilibrium. Thus, the concentration of NPh(p) can decrease by the gas-phase photolysis. This is briefly explained in the text.

"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."

This sentence was inserted by my mistake. I remove it.

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

I add Delta-HC and uncertainty of the SOA yields in the table.

"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."

I revise the legends of these figures.

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

I fix it.

References:

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Sincerely,

Kei Sato

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 283, 2012.