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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:

"1. Page 286, 2.1 Experimental procedure: (a) Line 26 could use a reference for the CH3ONO oxidation chemistry to provide OH or an overview of the reaction scheme expected would be helpful to improve understanding of what NOx comes from CH3ONO upon photolysis."

The reaction scheme of OH radical formation from the methyl nitrite-NO photooxidation is explained in the text.

"(b) How was the CH_3ONO obtained? Was it synthesized? Is there any initial NOx introduced from CH_3ONO impurities, and how much if so?"

The method for preparation is explained in the text. Prepared methyl nitrite was purified by vacuum distillation, and no NOx impurity was detected by FT-IR when 1 ppm methyl nitrite was introduced (NO detection limit was 8 ppb and NO_2 detection limit was 1 ppb). This is explained in the text.

"(c) Table 1: Would any of the $[NOx]_0$ include NOx from CH_3ONO ? It is unclear if this $[NOx]_0$ was obtained from NO and NO_2 injections to achieve the NO_2/NO ratios discussed in footnote a. An explanation for why the NO_2/NO ratios were 0 or ∼3 would aid in understanding the experimental design for the chemistry desired."

As described above, there was no detectable NOx impurity even though 1 ppm methyl nitrite was used. The NO_2/NO∼0 conditions were employed for low mass loading experiments, whereas the NO_2/NO∼3 conditions were employed for high mass loading experiments. These are explained in the caption of Table 1.

"2. Page 289, line 9 and Table 1: Provide a reference as to why 1.4 g cm?3 was used as the density or if it was measured and how."

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.

"3. Page 289, line 13 and overall chemistry regimes: Can the RO_2, HO_2, NO, NO_2 concentrations and their time profiles over time be estimated? The chemical regimes seem unclear as to how much of the fate of RO_2 is via reaction with HO_2 and with NOx since you discuss hydroperoxide and nitrophenol products. Can you quantify expected contributions to the RO2 + RO2 channel since you run at ppm levels of the precursor?”

Thank you for the comment. It is difficult to determine the time profiles of the RO2, HO2, NO concentrations from available experimental data. NO was measured by FT-IR, but its concentration was lower than a detection limit (∼several ppb) during SOA formation. In addition, we don’t have any chemical box model software appropriate for predictions of the RO2, HO2, NO concentrations. I discuss the fate of RO2 radicals based on available data as follows:

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 <1ppb 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).

The RO2 + RO2 reaction can occur, but it will be minor compared with the RO2 + NO reaction even after NO decreased. The concentration of total peroxy radicals (HO2 and RO2) is generally 10ˆ8 molec cm-3 (40ppt) at maximum. When [RO2] is 40ppt and the RO2 + RO2 reaction (k = 4.7 x 10ˆ-13 cm3 molec-1 s-1 (DeMore et al., 1997)) is competitive with the RO2 + NO reaction (k = 7.7 x 10ˆ-12 cm3 molec-1 s-1 (DeMore et al., 1997)), [NO] should be 6.1x10ˆ6 molec cm-3 (= 2.4 ppt). Such conditions will not be achieved in the presence of NOx.

“4. Page 289, lines 17-26: I find the comparison of the yields somewhat misleading. While the mentioned studies and the current study all report SOA yields for benzene in the presence of NOx, there are obvious differences in NOx levels and NO2/NO ratios between the studies which presumably could have an impact on the SOA chemistry and formation as well as the mass loadings. Can the authors comment if the comparisons of growth curves made in Figure S2 by mass loading are comparable by NOx condition as well or at least if differences in NOx levels can explain some of the differences in yield for similar aerosol mass loading?”

These sentences are rewritten. In the new manuscript, I compare only the results with comparable mass loadings. Discussion on the relationships between the SOA yield and the NOx level is added.

“5. Page 290, lines 20-21: The asserted statement seems too strong here without having discussed yet the chemistry of benzene that supposedly provides lowvolatility SVOCs that would contribute to m/z 44. What specific low-volatility SVOCs are produced from benzene photooxidation that are comparable to the low-volatility behavior of those observed in the case of -pinene ozonoylsis in Schilling et al. (2009)?”

This section is moved after the section of reaction schemes for SOA formation and aging. Low-volatility SVOCs found in SOA from alpha-pinene ozonolysis are multifunctional species such as dicarboxylic acids (Shilling et al., 2009). As described in the section of LC/TOF-MS analysis, dicarboxylic acids were found to be present in SOA from the benzene photooxidation. These are also explained in the text.

“6. Page 290, lines 24-27 and Figure 1: The use of “data migration” is confusing. Initial impression of Figure 1 is to see the spread in the data in the f44 vs. f43 space based on increasing methyl groups on the aromatic ring. I think, as in line 13, you are referring to the progression of the data over one run migrating to lower f43 and higher f44. Are you essentially arguing that f43 and f44 from the beginning to end point is greater with more alkyl substituted aromatics compared to benzene? If this is what you mean, then I would recommend 1) making certain that the starting and end points for oxidation for each run are visually known in Figure 1, and 2) pointing out a specific example comparison (e.g. “For example, the benzene runs show data migration in a merely vertical direction towards increasing f44 over time, whereas 1,3,5-TMB shows greater shifts in f43 while moving towards increased f44.”). I believe comparing Run 2 benzene and Run 4 1,3,5-TMB at similar mass loadings would make sense for this type of comparison if you are trying to compare data migration due solely to chemical structure, though the NOx conditions are different so it seems misleading to explain f44 and f43 character solely by mass loading or chemical structure. Argument of chemical structure being the major factor behind SOA aging would be strengthened if you could compare experiments with same mass loading and same NOx condition."

It seems that this sentence misleads you. I remove this sentence and explain f44 and f43 character by chemical structure, NOx level, and mass loading as follows:

Previous experiments of Sato et al. (2010) are conducted at the initial NOx concentrations of ∼100ppb. 1,3,5-TMB data of Sato et al. (2010) are added in Figure 1. The data obtained at the NOx concentration of ∼100ppb (Run 1 and experiments of Sato et al. (2010)) are compared each other. The mass loadings measured for these data are 2-32 microgram m–3. By selecting these data, data obtained under extremely high mass loadings (>32 microgram m–3) can be excluded. From these comparisons, I discuss f43 and f44 character by chemical structure.

"7. Page 291, lines 2-4: This seems to be more a conclusive statement that is better understood after the chemistry in Figure 4 is discussed. I feel that the chemistry explanations given to explain the f43 and f44 triangle plot are better understood if this section is moved after the chemistry discussions. This line seems to generally suggest that using the f43 vs. f44 plot can show that any decrease in f43 for an increase in f44 means the chemical pathway is oxidation of carbonyls to carboxylic acids. While this is supported by the current work, I would add additional references of other systems that support this statement or state it less matter of factly. For example, propose it as a tool to identify this route of oxidation in other systems, but it is stated too ubiquitously with the current wording."

The section of triangle plot is moved after the section of reaction scheme for SOA formation and aging. To state the conclusion of this section less matter of factly, I add a sentence, "The triangle plot may also be used in other reaction system as a tool to identify the carbonyl to acid oxidation route." The section of iodometric spectrophotometry is also moved after the section of triangle plot because the relationship between peroxides and the f44 value is newly discussed in the section of iodometric spectropho-

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Interactive Discussion

Discussion Paper

tometry following the comments of the other referees (please see also the replies to comments of referees #1 and #2).

“8. Figure 1: It might be informative to note that despite benzene being a higher volatility precursor compared to the other aromatics with additional methyl groups, it seems that the higher volatility precursors generate the more highly oxidized, presumably low volatility products (higher f44) products. This seems somewhat contrary to what one might expect just looking at the structures.”

I note what you mentioned in the text.

“9. Page 291, line 6-7: The authors may consider citing additional references (e.g. Chhabra et al, 2011) in support of this statement.”

I cite references (Chhabra et al., 2010, 2011) here.

“10. 4.2 Van Krevelen diagram; Figure 2: (a) Why does it seem like run 6 starts off with higher O:C than that of runs 4 and 5?”

Because of the overlapping of data of different runs, the start point of Run 6 cannot be seen. The O/C ratios of start points are 0.62 (Run 1), 0.64 (Run2), and 0.70 (Run 3) for experiments with benzene and 0.25 (Run 4), 0.27 (Run 5), and 0.31 (Run 6) for experiments with 1,3,5-TMB. These results are described in the text.

“(b) It appears that increased NOx and increased mass loading go with increased O:C and OSc for the runs shown. Can the authors comment on the role of each of these and their relation to O:C, H:C, and OSc?”

Chhabra et al. (2011) measured SOA from aromatic hydrocarbons by H-ToF-AMS and showed that the O/C of SOA was independent of the NOx level. The O/C ratio of start point increased with increasing the mass loading. I discuss this in the text. In contrast, the f44 was constant or decreased with increasing the mass loading. These results suggest that the O/C ratio of the organics present in high mass loading SOA is determined by the amount of the oxygenated organics other than carboxylic acids.

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Interactive Discussion

Discussion Paper

These are discussed in the section of triangle plot (which is moved to the last of section 4 (see also the reply to comment 7)). The relationship between OSc and O/C (or H/C) is evident if the definition of the oxidation state of carbon (OSc = 2 O/C − H/C) is described. The definition of the oxidation state is described at the place where it is first stated in the text.

"11. Page 292, lines 2-6: It seems that run 4 also veers towards the -0.5 slope line as well. Can the authors comment? Is this really only a mass loading dependence?"

Run 4 data point deviations from the -1 slope are within the experimental fluctuations. However, such a mass loading dependence is not seen for benzene data, indicating that carboxylic acid or hydroxy carbonyl formation is limited not only due to an increase in mass loading but also due to the reactant chemical structure. These are stated in the text.

"12. Page 292, lines 13-14: Isn't the H/C ratio of benzene lower than that of 1,3,5-TMB?"

Yes, it is. It's my mistake. I revise the sentence.

"13. Page 294, lines 1-10: Are the average points of OSc using LC/TOF-MS comparable to the average AMS OSc at the same time? That is, how do these oxidation states compare during the filter sampling period only?"

Even if these oxidation states are compared during the filter sampling period only, the result is the same as that described in the original manuscript. The text is rewritten, and the comparison during the filter sampling period only is described.

"14. Page 294, lines 16-18: This sentence is extremely confusing. Clarify."

What I mean here is that the signals in the 200 - 500 region were detected by using H-ToF-AMS in both experiments with benzene and 1,3,5-TMB. I revise the text.

"15. Page 294, line 19: Can any discussion of chemical strucutres or chemistry of oligomerization be discussed or referenced to explain the expectation that >200 m/z oligomer structures may span the listed 200-600 region?”

I add discussion on chemistry of oligomerization and cite appropriate references.

“16. Page 294, line 26: Authors should elaborate on the effect of organic peroxides on f44. There is no connection made between the estimate of SOA mass contributions from peroxides measured to the f44.”

It is discussed in the text as follows:

The organic peroxides to SOA ratio measured for the photooxidation of aromatic hydrocarbons in this study were lower than that measured for the ozonolysis of α-pinene. If organic peroxides affect the f44 value obtained by AMS, the f44 value of SOA from α-pinene would be higher than that of SOA from aromatic hydrocarbons. However, the f44 values measured for SOA from the α-pinene ozonolysis (0.042 (Bahreini et al., 2005)) were close to or lower than those measured in this study (0.038-0.17). Although organic peroxides from aromatic hydrocarbon are present in SOA, the effect of these peroxides on the AMS data will be limited.

“17. Page 295, lines 10-12: Can the authors comment on how much/when in the experiment RO2 + HO2, RO2+ NOx, and RO2+ RO2 are taking place? While the premise for peroxide formation is based on expected higher HO2 and higher RO2 concentrations, why are RO2 self reactions not considered as a sink of RO2?”

The RO2 + RO2 reaction can occur, but it will be minor compared with the RO2 + NO reaction even after NO decreased. Please see also the reply to comment 3.

Peroxides will be produced by the RO2 + HO2 reactions or the RO2 + RO2 reactions. The RO2 + HO2 reactions will be major pathways rather than the RO2 + RO2 reactions because the rate constant for the RO2 + HO2 reaction (k = 5.6 x 10ˆ-12 cm3 molec-1 s-1 (DeMore et al., 1997)) is higher than that for the RO2 + RO2 reaction (k = 4.7 x 10ˆ-13 cm3 molec-1 s-1 (DeMore et al., 1997)), and the HO2 concentration is generally higher than the RO2 concentration during the hydrocarbon photooxidation.

“18. Section 4.5 Reaction schemes for SOA formation and aging and Figure 4: (a) Looking at the [NOx]0 in Table 1 and the mechanism in Figure 4, it seems initially contrary that in explaining increased f44 due to carbonyl oxidation, that the f44 decreases with increasing [NOx]0 across runs. It might be helpful to point out that with decreasing NO2/NO ratio in Figure 1, the f44 is increased, so fragmentation and carbonyl oxidation is enhanced with greater NO.”

Thank you for the comment. As discussed in the section of triangle plot and the reply to comment 10b, the f44 is dependent on the mass loading rather than the [NOx]0. No further discussion is added.

“(b) Is the reaction scheme on the right for functionalization to the hydroxy carbonyl supposed to be RO2 with alcohol production rather than “NOx/O2”?”

No, it isn’t. The RO2 + RO2 reaction can occur, but it will be minor compared with the RO2 + NO reaction even after NO decreased. The concentration of total peroxy radicals (HO2 and RO2) is generally 10ˆ8 molec cm-3 (40ppt) at maximum. When [RO2] is 40ppt and the RO2 + RO2 reaction (k = 4.7 x 10ˆ-13 cm3 molec-1 s-1 (DeMore et al., 1997)) is competitive with the RO2 + NO reaction (k = 7.7x10ˆ-12 cm3 molec-1 s-1 (DeMore et al., 1997)), [NO] should be 6.1 x 10ˆ6 molec cm-3 (= 2.4 ppt). Such conditions will not be achieved in the presence of NOx. I state this process in the figure caption following the comment, but I don’t revise the figure.

“(c) Can the authors comment on any possible contributions from the formation of PAN compounds or peracids from reaction of the acylperoxy radical with HO2 or NOx in the carbonyl oxidation scheme? Again, understanding the expected fate of the RO2 radical could be clarified. For example, why is the fate of the alkyl peroxy radical under SOA aging scheme (c) considered only as reaction with NOx/O2 and RO2, but the acylperoxyradical reaction fate is shown only as reaction with HO2?”

Organic acid can also be produced via PAN compounds (Surratt et al., 2010). This is explained in the caption of Figure 4. Figure 4 is depicted in order to explain formation processes of major non-nitro products detected by LC/MS (i.e., oxocarboxylic acids and dicarboxylic acids with carbonyl and/or hydroxy groups). To reflect this comment, I note in the figure caption that peroxy and acylperoxy radicals shown in figure can react with oxidants which are not depicted.

"19. Page 298, lines 21-23: What chemical reactions are being referred to as decreasing organic peroxides with time?"

What I mean here is organic nitrates (NOT organic peroxides). It's my mistake. I revise it.

"20. Page 299, line 12: Instead of "increased" should this read "decreased"?"

The HRNO3/HROrg ratio decreased with time in experiments with 1,3,5-TMB. I fix this sentence.

"21. Page 299, lines 3-11: This section is problematic. I find that the discussions throughout the paper thus far try to point at SOA mass loading or NOx concentration in isolation to explain the trends. I think the arguments could be strengthened if experiments were compared when only one of these variables was changed (NOx changes with same mass loading vs. varying mass loading with same NOx) by altering initial HC loading. Can the experiments be designed differently?"

Very recently, we measured the HRNO3/HROrg ratio of SOA from the toluene photooxidation as a function of initial NOx concentration using the same instruments as this study (Nakayama et al., 2012). The HRNO3/HROrg ratio increased with increasing the initial NOx level in the range 100-600 ppb, supporting the present conclusion. These are explained in the text. I will send the draft of this reference as additional information for the editor.

"22. Page 300, lines 7-9: Is there a reference that can support this chemistry?"

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Discussion Paper

No, there isn't. I don't add any reference, but I tone down this description instead.

"23. Figure 5: It becomes clear here that the runs vary by duration based on the onset of nucleation. Is it possible to comment on the efficiency of SOA aging across systems on similar timescales? That is, using the metrics of examining aging that you propose (e.g. f44, HRNO3/HROrg) how do they compare across runs for the same time of irradiation or same HC reacted? Can results be examined on a normalized basis of NOx or SOA mass loading?"

Thank you for the comment and the suggestion. The HRNO3/HROrg can be used as a metric of SOA aging among the data measured in each experiment. However, the HRNO3/HROrg ratios observed at the same irradiation time cannot directly be compared across runs conducted under different NOx and SOA mass loading conditions. Your suggestion on the examination on a normalized basis of NOx or SOA mass loading is interesting. Such an examination is useful for better understanding of SOA aging. However, it will be the beyond of a scope of this study.

"Technical Corrections:"

"1. Page 284, line 7: The use of "attempted" here is poor word choice. The paper shows experimental results from benzene and 1,3,5-TMB, so it seems odd to have "attempted to select benzene and 1,3,5-trimethylbenzene.""

I revise the sentence to "…, we selected benzene and 1,3,5-trimethylbenzene…"

"2. Page 285, line 15: The use of Jimenez et al., 2009 as the only "e.g." reference seems weak. Add other references."

I add the references (Kroll and Seinfeld, 2008; Wang et al., 2012; Zhang et al., 2011).

"3. Page 286, line 13: No need to repeat the "H-ToF-AMS" acronymn here again since already defined on line 9."

I fix it.

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Interactive Discussion

Discussion Paper

“4. Page 287, line 12 and Page 288, line 7: Inconsistency with use of “mass resolution.” Provided units page 288, line 7. Is this more properly named as limit of detection rather than mass resolution?”

The value described in page 288, line 7 is named “mass accuracy” by users of this instrument. I substitute “mass resolution” by “mass accuracy.”

“5. Page 289, line 17: Martin-Reviejo and Wirtz “(2006)” should be “(2005)” to be consistent with the references listed.”

The reference list is correct. I revise the text.

“6. Page 290, line 13: Awkward phrasing “with elapse of time”. Consider replacing with “...also migrated over time, toward the top...””

I fix it.

“7. Page 291, line 11: Awkward wording. Replace “with” with “that of” instead.”

I fix it.

“8. Page 291, line 27: Should change “data point migrates” to “data points migrate.””

I fix it.

“9. Page 293, line 27: Cross-reference should be to “Photo S1” rather than “Fig. S1.””

I fix it.

“10. Figure 3: It might be helpful if the color scheme for these runs are consistent with that used in Figures 1 and 2 so the LC/MS average point O:C and the AMS Van Krevelen average O:C can be compared more easily.”

I fix it.

“11. Figure S1: Please define OM.”

I define OM.

“12. Figure S2: The “(%)” should be omitted from the y-axis label.”

I revise it.

“13. Figure S6: The caption highlights m/z 200-500 for oligomers, though the text page 294, lines 11-13 refer to a different m/z range.”

I revise the m/z range of the caption of Figure S6 to “m/z 200-600” as referred in the text.

References:

DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A., R., Kolb, C. E., and Molina, M. J.: Chemical kinetics and photochemical data for use in stratospheric modeling, JPL Publication 97-4, 1-266, 1997.

Nakayama, T., Sato, K., Matsumi, Y., Imamura, T., Yamazaki, A., and Uchiyama, A.: Wavelength and NOx dependent complex refractive index of SOAs generated from the photooxidation of toluene, Atmos. Chem. Phys. Discuss., in preparation, 2012.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, P. Natl. Acad. Sci. USA, 1007, 6640–6645, 2010.

Wang, Y., Arellanes, C., and Paulson, S. E.: Hydrogen peroxide associated with ambient fine-mode, diesel, and biodiesel aerosol particles in Southern California, Aerosol Sci. Tech., 46, 394-402, 2012.

Sincerely,

Kei Sato

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

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Discussion Paper