Atmos. Chem. Phys. Discuss., 12, C292–C299, 2012
www.atmos-chem-phys-discuss.net/12/C292/2012/

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 #3

Received and published: 28 February 2012

General Comments:

This paper discusses experimental results from the photooxidation of benzene and 1,3,5-trimethylbenzene (TMB) in the presence of NO$_x$ to evaluate the chemistry affecting SOA aging in a laboratory setting. They present these results within the context of previous studies on other aromatic compounds using H-ToF-AMS data displayed in an H:C vs. O:C Van Krevelen diagram to argue that aromatic systems tend to be rich in carboxylic acids or hydroxy carbonyls. They also argue that H-ToF-AMS data in an f_{44}

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

vs. f_{43} triangle plot suggest a trade-off between high f_{44}, low f_{43} (carboxylic acid enhanced, more aged, for the case of benzene) and low f_{44}, high f_{43} (carbonyl enhanced, less aged, for the case of 1,3,5-TMB), which is dependent on chemical structure of the starting hydrocarbon. Suggested chemical structures from LC/MS filter data support the conclusion that aging is limited by the slow oxidation of ketocarboxylic acids for aromatics as seen in the case of 1,3,5-TMB versus continued oxidation of aldehydic carboxylic acids in the case of benzene. The paper proposes that chamber experiments cannot simulate the oxidation to the same extent as ambient SOA not only due to insufficient duration, but also because laboratory experiments cannot simulate well ketocarboxylic acid oxidation in the aqueous phase. Overall, the paper provides newly identified compounds in SOA from 1,3,5-TMB and insight into the chemical factors affecting SOA aging for aromatics. The presentation of the experimental conditions and protocols affecting the chemistry could use improvement. The current presentation inhibits full understanding of the chemical regimes that this study operates under, which may affect the SOA chemical character that leads to the conclusions reached. Better treatment in explaining the dynamics of aerosol mass loading with varying NO_x and varying initial hydrocarbon is needed. The order of topics discussed could be better arranged for clarity of the argument development. Starting with elemental composition analyses followed by mechanism and chemical identification to explain the chemistry observed in the elemental composition analyses is backwards. It is difficult to understand the basis of the chemical arguments discussed early on without reference to any mechanisms or chemical structures.

Major Comments:

The following items need to be addressed satisfactorily before this paper can be published in ACP.

1. Page 286, 2.1 Experimental procedure:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

(a) Line 26 could use a reference for the CH_3ONO oxidation chemistry to provide OH or an overview of the reaction scheme expected would be helpful to improve understanding of what NO_x comes from CH_3ONO upon photolysis.

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

(c) Table 1: Would any of the $[NO_x]_0$ include NO_x from CH_3ONO ? It is unclear if this $[NO_x]_0$ 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.

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.

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 NO_x since you discuss hydroperoxide and nitrophenol products. Can you quantify expected contributions to the RO_2 + RO_2 channel since you run at ppm levels of the precursor?

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 NO_x, there are obvious differences in NO_x levels and NO_2/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 NO_x condition as well or at least if differences in NO_x levels can explain some of the differences in yield for similar aerosol mass loading?

5. Page 290, lines 20-21: The asserted statement seems too strong here without having discussed yet the chemistry of benzene that supposedly provides low-volatility 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 α-pinene ozonoylsis in Schilling et al. (2009)?

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 f_{44} vs. f_{43} 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 f_{43} and higher f_{44}. Are you essentially arguing that Δf_{43} and Δf_{44} 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 f_{44} over time, whereas 1,3,5-TMB shows greater shifts in f_{43} while moving towards increased f_{44}."). 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 NO_x conditions are different so it seems misleading to explain f_{44} and f_{43} 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 NO_x condition.

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 f_{43} and f_{44} triangle plot are better understood if this section is moved after the chemistry discussions. This line seems to gener-

ally suggest that using the f_{43} vs. f_{44} plot can show that any decrease in f_{43} for an increase in f_{44} 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.

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 f_{44}) products. This seems somewhat contrary to what one might expect just looking at the structures.
9. Page 291, line 6-7: The authors may consider citing additional references (e.g. Chhabra et al, 2011) in support of this statement.
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?
    (b) It appears that increased NO_x and increased mass loading go with increased O:C and OS_c for the runs shown. Can the authors comment on the role of each of these and their relation to O:C, H:C, and OS_c?
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?
12. Page 292, lines 13-14: Isn't the H/C ratio of benzene lower than that of 1,3,5-TMB?

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

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

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?

16. Page 294, line 26: Authors should elaborate on the effect of organic peroxides on f_{44}. There is no connection made between the estimate of SOA mass contributions from peroxides measured to the f_{44}.

17. Page 295, lines 10-12: Can the authors comment on how much/when in the experiment RO_2 + HO_2, RO_2+ NO_x, and RO_2+ RO_2 are taking place? While the premise for peroxide formation is based on expected higher HO_2 and higher RO_2 concentrations, why are RO_2 self reactions not considered as a sink of RO_2?

18. Section 4.5 Reaction schemes for SOA formation and aging and Figure 4:

    (a) Looking at the $[NO_x]_0$ in Table 1 and the mechanism in Figure 4, it seems initially contrary that in explaining increased f_{44} due to carbonyl oxidation, that the f_{44} decreases with increasing $[NO_x]_0$ across runs. It might be helpful to point out that with decreasing NO_2/NO ratio in Figure 1, the f_{44} is increased, so fragmentation and carbonyl oxidation is enhanced with greater NO.

    (b) Is the reaction scheme on the right for functionalization to the hydroxy carbonyl supposed to be RO_2 with alcohol production rather than “NO_x/O_2”?

    (c) Can the authors comment on any possible contributions from the formation of PAN compounds or peracids from reaction of the acylperoxy radical with HO_2 or NO_x in the carbonyl oxidation scheme? Again, understanding the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

expected fate of the RO_2 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 NO_x/O_2 and RO_2, but the acylperoxyradical reaction fate is shown only as reaction with HO_2?

19. Page 298, lines 21-23: What chemical reactions are being referred to as decreasing organic peroxides with time?
20. Page 299, line 12: Instead of "increased" should this read "decreased"?
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 NO_x 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 (NO_x changes with same mass loading vs. varying mass loading with same NO_x) by altering initial HC loading. Can the experiments be designed differently?
22. Page 300, lines 7-9: Is there a reference that can support this chemistry?
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. f_{44}, $HRNO_3$/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 NO_x or SOA mass loading?

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."

2. Page 285, line 15: The use of Jimenez et al., 2009 as the only “e.g.” reference seems weak. Add other references.
3. Page 286, line 13: No need to repeat the “H-ToF-AMS” acronymn here again since already defined on line 9.
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?
5. Page 289, line 17: Martin-Reviejo and Wirtz “(2006)” should be “(2005)” to be consistent with the references listed.
6. Page 290, line 13: Awkward phrasing “with elapse of time”. Consider replacing with “...also migrated over time, toward the top...”
7. Page 291, line 11: Awkward wording. Replace “with” with “that of” instead.
8. Page 291, line 27: Should change “data point migrates” to “data points migrate.”
9. Page 293, line 27: Cross-reference should be to “Photo S1” rather than “Fig. S1.”
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.
11. Figure S1: Please define OM.
12. Figure S2: The “(%)” should be omitted from the y-axis label.
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.