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Discussions

Interactive comment on "A study of volatility by composition, heating, and dilution measurements of secondary organic aerosol from 1,3,5-trimethylbenzene" *by* Kei Sato et al.

Anonymous Referee #2

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Summary and Recommendation:

This study examines the volatility distribution of secondary organic aerosol (SOA) produced from the photooxidation of 1,3,5-trimethylbenzene (TMB) under dry conditions (RH < 1%) and in the absence of pre-existing aerosol particles. The volatility distribution was determined from chemical composition data obtained by LC/MS and AMS as well as from heating and dilution experiments. With the LC/MS data, the authors used models to predict the volatility distribution of the SOA and compared this with the heating and dilution measurements. The LC/MS data revealed the presence of $C_9H_{14}O_x$ monomers (x= 4-7) and $C_{18}H_{26}O_x$ dimers (x = 8-12). The combined results from the

LC/MS, heating, and dilution measurements may suggest that TMB-derived SOA has constituents that have volatilities less than those predicted from conventional SOA yield curve analyses. Overall, the approach is quite nice and I find that this paper will be of interest to readers of ACP. I have a number of specific questions below that the authors need to address before publication can be fully considered in ACP. Due to the nature of these comments, I most recommend this paper be accepted with major revisions.

Specific Comments:

1.) Concentrations of TMB: The concentrations of TMB are quite high; specifically ppm levels. Do the authors have concerns about the RO2 radical dynamics being relevant to ambient atmospheres? Are there any concerns that RO2 + RO2 reactions could become more dominate than what might be expected in actual urban atmospheres? Basically, why are the concentrations of VOC and NO selected for these experiments? It seems unclear from the experimental description.

2.) RH Conditions: It appears from the experimental description that the RH was < 1% in all experiments conducted. Do the authors have any concerns for the lack of possible aqueous-phase chemistry? Previous work by the Kamens group (e.g., Zhou et al., 2011, Atmos. Environ.; Kamens et al., 2011, Atmos. Environ.) showed that aromatic VOCs oxidized in the absence of particle water produced less SOA than those with particle water at higher RH conditions. Do you worry your reaction conditions may not capture what could occur in more humid urban atmospheres? Related to my concerns about having particle-associated water to help further promote SOA, it appears your experiments relied on nucleation mechanisms to yield SOA. Can the authors clarify in the experimental approach why this condition was selected?

3.) HOMs: The authors mention HOMs in their paper and this is likely associated with the high oxygen atom content of your monomer and dimer species measured by LC/MS. Related to my comment above about the lack of particle-associated water, couldn't this potentially prevent HOMs from further reacting to make particle-phase re-

action products like peroxyhemiacetals? I'm assuming some of these HOMs may contain hydroperoxide functionalities and thus may be able to react with carbonyl species in the aqueous phase to form such products. I would suggest to the authors that they at least acknowledge that this is one drawback from their study; specifically, the lack of examination of the volatility distribution at higher RH conditions and that further work is warranted at these conditions.

4.) Dilution measurements: For your dilution experiments you added 20 ppm of CO. How much of this could have reacted away with OH radicals in your chamber? I'm assuming the OH levels are low enough to not matter in converting large quantities to CO2? It would be good to know in the text that you considered how much of the loss of CO was due to dilution rather than reaction with OH radicals.

5.) LC/ESI-TOFMS: Can the authors clarify how exactly the calibration of the LC/ESI-TOFMS system was done? Did you use a commercially available turning mixture? If so, what compounds are in this mixture and does it cover your entire mass axis? What was your mass resolution during your LC/ESI-TOFMS runs? Did you use a lock-mass correction approach for more accurately calculating elemental formulas of observed ions reported in Tables S1 and S2?

6.) Page 5, Lines 27-29: How do you know for sure that "the decrease in mass concentration was not only due to particle wall loss but also the photolysis of organic compounds in the particle phase or dissociative photooxidation of semivolatile compounds in the gas phase?" I don't see any clear data yet to back up this conclusion from the results presented in Figure 1.

7.) On Page 6, Line 10, the authors note that they didn't add sodium to their mobile phase or analytical samples. I'm curious why they didn't? Would adding some constant amount of sodium salt improve the ionization efficiency of such compounds, thus improving your detection sensitivities with ESI-MS? Are you at risk for missing any compounds in your SOA samples? Is it also possible the ESI-MS missed some of your

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compounds? Or what I mean is does ESI make you blind to other potentially present SOA constituents?

8.) Can the authors be more clear about what they mean by blank samples? Were these blank filters that were extracted in the same fashion as the filter samples collected from the chamber experiments?

9.) For Table S2, should you normalize the EIC peak areas for each ion by the volume of air sampled through the filter in order to compare each experiment? Or did you collect the same volume of air for each experimental filter?

10.) I noted that the LC/MS data presented in the SI (Tables S1 and S2) don't provide any suggestions on chemical structures. This is reasonable at this stage of your work, as in order to propose reasonable structures a combination of tandem MS experiments and synthesis of putative structures would be needed to really propose reasonable structures. However, without knowing actual structures, do the authors worry about how certain organic functionalities differ in their contribution to vapor pressures? That is, if you only use the total number of Cs, Hs, Os, etc., how uncertain is this prediction for volatility?

11.) Seeing that RO2+RO2 reactions may have dominated in your experiments owing to the high levels of VOC used, do the authors have any questions about whether this allowed for enough RO2 autooxidation to happen? What I mean is could there have been more oxygeanted products formed if the VOC concentrations were closer to atmospheric mixing ratios?

Minor Comments:

1.) Page 9, Line 33: Correct the spelling of "Kalbere et al." to "Kalberer et al."

2.) Page 10, lines 20 and 21: "Baltenspelger et al. 2005" is misspelled. It should be "Baltensperger et al."

3.) Conclusions, Line 21-22: Please provide citations to the published literature to

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support the statement "in accordance with previous results of heating measurements."

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