

Interactive comment on “Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products” by Z. Li et al.

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We thank the reviewer for his or her insightful comments. We address specifics below. (Reviewer comments in quotation marks, responses below)

"1.) Do you have any concerns with the high concentrations of these cVOCs (i.e., 0.018- 0.54 M) that you used to examine this process? Maybe certain reactions are favored that are not representative of atmospheric aerosol processes due to these high concentrations employed in this study? Should any caution be made to the readers of your manuscript about this issue?"

We have added the following paragraph into the discussion to better describe the con-
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centrations of these cVOCs. "Ambient aerosol concentrations of formaldehyde and acetaldehyde have been measured up to $0.26 \mu\text{g m}^{-3}$ formaldehyde and $0.4 \mu\text{g m}^{-3}$ acetaldehyde in Los Angeles (Grosjean, 1982). Using a specific aerosol volume of $10^{-10} \text{ m}^3 \text{ m}^{-3}$ (Noziere et al., 2010), these ambient in-particle concentrations of formaldehyde and acetaldehyde correspond to 0.088M and 0.092M respectively, which are well within the concentration ranges used in this study. At these realistic ambient aerosol concentrations, we observed non-negligible surface tension depression by formaldehyde and acetaldehyde (7.1% and 9.5%, respectively). The extended concentration range used here was chosen to enable us to characterize the surface tension behavior using the Szyszkowski-Langmuir equation."

"2.) With the volatilization step in your Aerosol-CIMS technique, do you fear that there could be the potential of chemical artifacts dominating your mass spectra? Thus, in these mass spectra are you observing what is actually present in the aqueous solutions?"

Aerosol-CIMS has been used extensively by us and others for the characterization of organic aerosols with known and unknown composition (Hearn et al., 2005; Hearn et al., 2007; Hearn and Smith, 2004a; Hearn and Smith, 2004b; Hearn and Smith, 2005; Hearn and Smith, 2006a; Hearn and Smith, 2006b; Hearn and Smith, 2007; McNeill et al., 2007; McNeill et al., 2008; Renbaum and Smith, 2009a; Renbaum and Smith, 2009b; Sareen et al., 2010; Schwier et al., 2010). The volatilization temperature is selected while monitoring the mass spectrum such that the organics of interest are fully evaporated, but not degraded by overheating. Once in the gas phase, the analytes are detected via chemical ionization, a soft ionization technique which results in little to no fragmentation.

The atomization and volatilization of these aerosols does result in dehydration and concentration of the solution. The aerosol exists in this concentrated state for <3.5 seconds; fast concentration-dependent chemistry could occur on these time scales. However, the oligomerization chemistry we expect to see with these compounds occur

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on the timescale of hours to days, so we expect these products to have been formed in the bulk solution (Noziere et al., 2010; Sareen et al., 2010). Therefore, we believe that the mass spectrum does represent the species that would be present in the bulk aqueous solutions.

"Additionally, do you have any concerns about the ions you interpret as SOA products being artifacts of the ionization? How do you know some of the ions you suggest as products of these reactions are not just fragment ions of the H_3O^+ reagent ion chemistry?"

While the reviewer brings up a valid point about the ionization techniques of many mass spectrometers, Aerosol-CIMS is a soft ionization technique, so fragmentation of organics is typically not a concern.

"...In the case of the latter, as an example, you found it difficult to explain the production of some of the tentatively identified organosulfates. As the authors indicated in the Discussion section, these could have formed due to the atomization process. I agree with this especially since you subsequently heat up the aerosol. Could this remove enough water to favor sulfate esterification? There is now some debate developing within the community that surfactants, such as organosulfates, might help to remove water from the system to help enhance the organosulfate reactions (or other condensation reactions)."

We refer the reviewer to the above comment and response for the use of the volatilization flow tube in performing Aerosol-CIMS. We did mention in the discussion manuscript the possibility of the atomization step enhancing alcohol sulfate esterification, however the reviewer is correct that the dehydration continues for a short time inside the VFT before volatilization occurs. We have modified our discussion of this in the manuscript to read "This suggests that either a) the kinetics of sulfate esterification for paraformaldehyde are significantly faster than for alcohols b) SO_4^{2-} or HSO_4^- is the active reactant, contrary to the conclusions of Deno and Newman, or c) sulfate esterification

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fication is enhanced by the solution dehydration that accompanies the atomization and volatilization steps in our detection technique.”

“I think the authors might want to be clear on this by saying in the Discussion or Conclusions section that further work is needed to really know the detailed reaction pathways that explain these compounds they seem to be observed by Aerosol-CIMS.”

We have added the following statement to the CIMS results discussion, “Several of the products identified in both positive- and negative-ion modes for formaldehyde and acetaldehyde have unknown chemical structures and formation mechanisms; these identifications will require further mechanistic studies in the future.”

“Even though the authors say “tentative structures” in the text, they might want to also consider adding the word “tentative” in their Table headings, especially since many readers these days don’t carefully read all of the text and usually go right to figures and tables to understand the results of a study.”

The tentative nature of our peak assignments is not different from other mass spectrometry studies using unit mass resolution, so we believe that our use of “tentative structures” in the text and “possible structures” in the tables is descriptive enough for the reader.

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