

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.

Anonymous Referee #1

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This work uses surface tension and chemical ionization mass spectrometry (CIMS) measurements on high-concentration bulk solutions (meant to emulate the environment of an aerosol particle) to show that acetaldehyde and formaldehyde can produce surface-active secondary organic aerosol (SOA) material. This conclusion will be of interest to the atmospheric science community because these aldehydes have been largely ignored as SOA precursors, and because of the importance of surface tension in controlling particle – cloud interactions. The authors wisely avoid making any quantitative statements about the importance of acetaldehyde and formaldehyde aerosol-phase reactions in the atmosphere, since their data does not allow it. However, if the experimental conditions are indeed typical for atmospheric aerosol, then

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it is reasonable that these reactions could significantly influence the surface tension of atmospheric aerosol. While the use of nearly saturated ammonium sulfate (AS) seems justified to simulate the environment of an aerosol particle, there should be some discussion of how the aldehyde concentrations (0.02 to 2 M) were chosen, how this compares to typical aldehyde concentrations in atmospheric aerosol, and whether any extrapolation between experimental and atmospheric conditions is necessary in order to assess the significance of the results.

The authors have done a tremendous amount of work tentatively identifying many reaction products from the mass spectra, including some unexpected products of oxidation and an organosulfate compound. When reaction mixtures contain MG, cross products are observed incorporating MG and other aldehydes present. In these systems the surface tension depression measured exceeds the sum of its parts, likely due to the surfactant natures of the cross products formed. However, more explanation is needed as to why the same base compounds are often identified at different m/z in different runs, even though the same CIMS ionization conditions are used. For example, formic acid shows up at m/z 82 and 209 in Figure 5, but at 173 and 209 in Figure 6, where the organics are at higher concentration and MG is also present. Why should this affect the ionized form of formic acid detected? Similarly, formaldehyde acetal oligomers are identified in both Figure 5 and 6, but there are (surprisingly) almost no common m/z values. In this case, different formaldehyde acetal oligomers are identified, suggesting a complex influence of MG and concentration on acetal formation. If these issues could be addressed in the manuscript, it would only increase confidence in the product identifications.

Detailed comments:

Abstract line 13: The abstract should make clear what the changes in surface tension were for both acetaldehyde and formaldehyde, rather than just listing the depressed surface tension values.

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Page 19480 line 18: The solution pHs are quoted as being near 3. Does this apply to the solutions in both AS and in water? If in water, what is the source of the acidity?

Page 19482 line 15: Could the text state either the surface tension of pure water, or the percent reduction caused by acetaldehyde?

Page 19484 line 14: The earlier cited work on acetaldehyde-AS and acetaldehyde-H₂O systems should be discussed in comparison to the products identified in this work. Were some of the same products observed in the earlier work as with the acetaldehyde-methylglyoxal (MG)-AS mixture in the present work?

Page 19485 line 15: The manuscript notes that organosulfate species have not been observed before by proton-transfer MS methods. However, this statement may cause some to doubt that organosulfates were indeed detected in this study. Can the authors make an argument based on the literature that organosulfates should be expected to survive the analytical process – heating to 135 C to volatilize from aerosol particles? Alternatively, can an organosulfate standard be run to demonstrate that it is indeed possible?

Page 19486 line 1: Can the authors use their previously published MG-AS CIMS data to more conclusively identify the m/z 272 peak?

Page 19488 line 3: Presumably the solutions equilibrated with headspace in capped bottles, but this statement made me wonder about the nature of this equilibration. No details are given in the Methods section.

Page 19488 line 11: This statement is almost certainly correct. However, it could be strengthened by including some references to atmospheric measurements.

Page 19489 line 1: Chemical name appears to be missing the term “sulfate.”

Page 19489 line 23: “Low solubility” seems like the wrong term here, since formaldehyde is highly soluble in water. The authors appear to be discussing the Henrys law coefficients and the transfer of aldehydes from the gas phase.

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Page 19490 line 1: Is it possible to harmonize the cited results of Kroll et al. and Romakkaniemi et al.? If surface-active species enhanced SOA production, why wouldn't growth be observed in the experiments described in Kroll et al.?

Figure 2 c: It is not clear how formaldehyde can increase from 0 to 0.4 M while MG decreases from 1.5 to 0.4 M while the total organic concentration stays constant at 0.5 M in all experiments. Are there huge differences in solution density?

Table S3 and S4: The C₂H₄O₃ molecule is listed as appearing at m/z 95 in Table S3 but at m/z 96 in Table S4.

Page S6: equation S4 is unbalanced. The last paragraph mentions C₂H₆O₅S on two occasions, when the correct formula is probably C₂H₆O₆S.

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