

# ***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 helpful comments. We address these comments below (Reviewer comments in quotation marks, responses below).

"Noteworthy, no surface tension change was observed in the case of formaldehyde in water and a better theoretical justification is needed for this observation."

We have changed the text in the discussion to read, "Both formaldehyde and acetaldehyde, and their aqueous-phase reaction products, were found to depress surface tension in AS solutions. However, surface tension depression was not observed in aqueous formaldehyde solutions containing no salt, due to the hydrophilic character

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of hydrated formaldehyde and its oligomer products. Net surface tension depression by acetaldehyde was greater in the AS solutions than in pure water. These differences for both organics are likely due to chemical and physical effects of “salting out” (Setschenow, 1889), which may enhance organic film formation on the surface of a pendant drop (or aerosol particle).”

“Page 19478 Line 12 (Abstract): The statement about identifying a hemiacetal sulfate ester for the formate-ammonium sulfate system does not seem to belong to the abstract. Although the word “tentatively” is used, based on the results section of the manuscript that reports products that are not completely identified, this statement should be reserved only for the discussion section. Further input on this issue is given below.”

We agree that this was not a main conclusion of the paper and it has been removed from the abstract.

“Page 19480 Line 13: The manuscript will benefit if an explanation for the concentrations used is given. This could be included in the introduction or in the discussion section. In addition, there is no indication of the concentration of formaldehyde used in the experimental section.”

We have added the following statement to show the experimental concentration of formaldehyde used, “Aqueous solutions containing varying concentrations of organic compounds (acetaldehyde, formaldehyde and/or methylglyoxal) with near-saturation concentrations (3.1 M) of AS were prepared in 100 mL Pyrex vessels using Millipore water. The concentration of formaldehyde used was 0.015 – 0.21 M. The concentration of acetaldehyde was 0.018 M – 0.54 M.”

In addition, in the discussion, we have added the following paragraph: “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

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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.”

“Page 19481 Lines 10-15: A control experiment using freshly prepared solution should be included in the supplement and cited here. In addition, a calculation should prove the statement that  $< 3.5$  s is a shorter time than required for reaction to occur at 135 °C. How long does it take for product formation to occur?”

Aerosol-CIMS experiments were performed to identify the organic compounds capable of surface tension depression, so the reaction time of 24 hours was kept consistent between all experiments performed in this study. The time from atomization of the solution until detection of the organic species is  $< 3.5$  seconds; of this time, the aerosols are in a volatilization flow tube held at 135 deg C for  $< 1$  s. The timescale for these organics to oligomerize in the presence of AS is on the order of hours to days (Sareen et al., 2010; Noziere et al., 2010). We currently state in the paper “The time between atomization and detection ( $\leq 3.5$  s) is too short for detectable quantities of the expected reaction products to form, therefore the detected molecules are most likely formed in the bulk aqueous solutions.”

“Page 19482 Lines 13-15: Unify the way of expressing surface tension changes. For example use the corresponding percentage change after the reported values for acetaldehyde “(20.6%)” and the measured change followed by “(9 %)” for formaldehyde.”

We have updated the surface tension changes to include surface tension values and the corresponding percentage change per the reviewer’s request.

“Page 19482, Line 16: Why is the concentration of formaldehyde in Figure 1B studied up to 0.20 mol C/kg H<sub>2</sub>O while acetaldehyde concentration was 5-times larger in Figure

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1A? Would you expect to see any change in surface tension at larger formaldehyde concentration in water? A dashed line may be used to distinguish that formaldehyde-water is not a Szyskowski-Langmuir fitting in Figure 1B."

The concentrations used in Figure 1 were chosen to determine the maximum surface tension depression possible from each individual organic. Formaldehyde was not observed to be surface active in pure water, so there should be no change in surface tension outside of the standard deviation at larger concentrations of organic. We have updated Figure 1B to use a dashed line for the formaldehyde-water data.

"Page 19484 Line 19-25: What is the concentration of formic acid (impurity) in the stock solution? What is the concentration of this impurity in the dilution of Figure 5? A typical 37% formaldehyde solution has < 0.03% formic acid. Peaks at  $m/z$  81.7 and 208.7 amu appear to be too intense (Figure 5) to be due to a very small impurity of formic acid. It is mentioned in the next page that the most common stabilizer in 37% formaldehyde water solution from Sigma-Aldrich is Methanol ( $\sim 15\%$ ). A better justification of the peaks and/or a clarification of the composition of the reagent are necessary."

While formic acid is added only through the formaldehyde reagent (as an impurity), it is possible that there are unknown pathways for the formation of formic acid in the reaction mixture. This is currently stated in the manuscript in the CIMS discussion (section 3.2.3), "Formic, glyoxylic, and glycolic acids correspond to the peaks at 84.4, 93.5, and 95.5 amu, respectively. Since no significant source of oxidants exists in the reaction mixtures, the formation mechanisms for these species in this system are unknown." Methanol is in our reaction mixtures due to its stabilization of formaldehyde, however it is not predicted to cluster with  $I^-$ . We have mentioned its possible role within the text (section 3.2.1), "Within our instrument resolution, these peaks are consistent with methanol, present in our system due to its use as a stabilizer in formaldehyde solutions. However, methanol is not predicted to form stable clusters with  $I^-$ ."

"The assigned hemiacetals clusters (peaks at  $m/z$  223.3, 291.1, 325.5 amu) are of very

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low intensity in the mass spectrum of Figure 5. Are they important to the composition of the mixture? Low intensity peaks at 273.8, 291.1, and 304.7 amu appear to be related to peaks at 176.7, 193.8, 208.7 amu. There is a difference of 97, 97, and 96 amu. How was the spectrometer calibrated? What masses were used for calibration? Is it possible to have a >0.5 Da amu error compared to previous work published by this group?"

We have performed peak identification on every peak that was outside the standard deviation of the N2 background spectra, including the low signal intensity products, to show a complete picture of the types of products that form in complex carbonyl mixtures.

The CIMS was calibrated using succinic acid (for details, see (Sareen et al., 2010)). The resolution for the spectra (i.e. the maximum standard deviation used for  $m/z$  when assigning peaks) is variable depending on the tuning of the mass spectrometer, and we calculate it based on the full width at half maximum for peaks visible in the spectra. The resolution for all CIMS data presented here was  $m/z \pm 1.0$  amu. We have added the following text to the CIMS results (section 3.2), "The CIMS data show products of self- and cross-reactions of formaldehyde, acetaldehyde and MG in pure water and 3.1 M AS. The resolution for all CIMS data presented here was  $m/z \pm 1.0$  amu."

"Page 19485 Lines 9-12: It is not possible to distinguish if the peak at 193.8 uma was assigned correctly. A blow up is needed to distinguish if there is a satellite peak (+2 uma). Based on the spectrum shown in Figure 5 the species of 176.7 amu appears to be C<sub>6</sub>H<sub>9</sub>O<sub>6</sub><sup>-</sup> instead of C<sub>2</sub>H<sub>7</sub>O<sub>6</sub>S<sup>-</sup> H<sub>2</sub>O because there is no satellite peak. Otherwise a blow up of this peak will also be needed. This issue is critical to the discussion and the output will considerably affect the abstract by confirming or rejecting the assignment."

We have included a figure of  $m/z$  193.8 amu with the satellite peak (+2 amu) in the supplement for the reader's benefit. In looking very closely at the spectra, there does not appear to be a satellite peak at 176.7, so we have also changed our discussion

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of  $m/z$  176.7 amu in the paper. We have added the following discussion to the CIMS results (section 3.2.1), "The peak at 193.8 amu is consistent with an organosulfate species formed from a formaldehyde hemiacetal dimer ( $C_2H_5O_6S \cdot 2H_2O$ ) and a satellite peak is also visible at 195.6 amu (see Supporting Information). The abundance of these peaks should be consistent with a 96:4 ratio of stable sulfate isotopes ( $^{32}S$  and  $^{34}S$ ), and instead this ratio is found to be 86:14. This is not inconsistent with the identification of the species at 193.8 amu as an organosulfate, but additional compounds could also be present at 195.6 amu. The peak at 176.7 amu matches an ion formula of  $C_6H_9O_6^-$ , but the structure and formation mechanism is unknown."

"Lines 13-14 (also applies to for page 19486, lines 16-17, and page 19487, line 1): A short statement should be included in the conclusions to summarize that the chemical structures and formation mechanisms of several products are unknown and that this task will require mechanistic studies."

We have added the following statement as per the reviewer's request: "Future mechanistic studies are needed in order to resolve the products with unknown chemical structures and/or formation mechanisms."

"Page 19486 Line 6-8: Figure 7 does not have any label to indicate a peak at 98.4 amu. It is listed in table 4. In addition, Table 4 is too small and the font size should be larger. Preferably use the font size of Table 2 for all tables."

We were unable to label every peak within the CIMS spectra due to space limitations and in order to have visual clarity for the reader. We have tried to label the major peaks. The font size of Table 4 has been increased.

"Line 26: Could other possible assignments for peak at 314.3 amu be two formic acid molecules, one sulfate, clustered with iodide?"

While this molecule is consistent with the  $m/z$  for this peak assignment, there is no satellite peak in our spectrum, so we would not feel confident assigning a sulfate-

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containing cluster to this mass.

"Line 28: The peak at 194.6 amu listed in Table 5 is absent in Figure 8. The same satellite peak analysis would apply here to confirm or discard the formation of possible products. Consider rewording the beginning of the sentence. It is likely that the supplement will be unnecessary if this species is for example C<sub>6</sub>H<sub>10</sub>O<sub>6</sub> in its undissociated form."

Please see the above response regarding the inclusion of all labeled peaks in the figures. In looking at the spectra closely, there is no observable satellite peak approximately 2 amu distance from the peak ( $m/z$  194.6 amu), so we have changed the manuscript accordingly to remove this organosulfate reference. We thank the reviewer for bringing this point to our attention.

"Tables 2 and 3 and Figures 5 and 6: Why there is no peak for sulfate or sulfate-iodide cluster? What were the conditions of the mass spectrometer? Can they be included in the experimental section or in the supplement?"

Sulfate and iodide are both negative ions, hence a stable cluster would not form between these two species. However, it is possible to detect a HSO<sub>4</sub><sup>-</sup> peak ( $m/z$  96). To better describe the mass spectrometer conditions, we have added the following sentence, "The resolution for all CIMS data presented here was  $m/z \pm 1.0$  amu." to the CIMS discussion (section 3.2).

"Figures 2A and 4A-D: Figures will look considerably better by removing the exponent and using a  $10^{\pm 2}$  multiplication factor in the respective concentration label. Fig. 2A is too small and it is very difficult to read it."

We have updated these figures per the reviewer's request.

References:

Grosjean, D.: Formaldehyde and other carbonyl in Los Angeles ambient air, Environmental Science & Technology, 16 (5), 254-262, 1982.

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2011

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Noziere, B., Dziedzic, P., and Cordova, A.: Inorganic ammonium salts and carbonate salts are efficient catalysts for aldol condensation in atmospheric aerosols, *Physical Chemistry Chemical Physics*, 12 (15), 3864-3872, 2010.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D. M., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, *Atmos.Chem.Phys.*, 10, 997-1016, 2010.

Setschenow, J. Z.: Über Die Konstitution Der Salzosungen auf Grund ihres Verhaltens zu Kohlensäure, *Z.Physik.Chem.*, 4, 117-125, 1889.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 19477, 2011.

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