

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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Received and published: 12 October 2011

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

"...the use of very high organic concentrations, coupled with the likely second order kinetics for the oligomerization processes, seems to suggest that these processes would be much, much slower on actual atmospheric aerosols than the one day timescale of the present experiments. In this vein, the authors should clarify the rationale for the choices for the organic concentrations (and why they are different for the different organic systems)."

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We have added the following paragraph to the discussion to clarify this point: "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."

"Were higher concentrations sometimes used to produce higher concentrations of products so that the CIMS analysis was easier to perform, or was it to drive the kinetics of the chemical reactions so that analyses could be performed relatively quickly?"

Higher concentrations were used in order to enhance the signal of the products for easier CIMS analysis.

"It's also not clear why the authors did not perform explicit concentration dependent measurements for the CIMS analysis aspect of the project since such reaction mixtures were prepared for the surface tension experiments. The concentration dependence information would have helped immeasurably in the CIMS assignment process, as it would aided in distinguishing impurities from reaction products, and first order forming products (such as the sulfate ester) from second order forming products (such as the oligomers)."

For this study, Aerosol-CIMS was used to determine the organic compounds that were possibly causing the surface tension depression in the bulk solutions. The kinetics experiments proposed were outside of the scope of this experiment, but could be the topic for future research. However, to distinguish impurities in the samples, background N2

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samples and organic/H₂O mixtures in the absence of salt were run. These additional spectra were used to help determine which peaks could be due to or enhanced by the presence of ammonium sulfate.

"1) There are many "assigned" peaks that have no logical chemical mechanism to explain their presence and many completely unassigned peaks. Approximately what fraction of the total CIMS products signal do these "unexplained" peaks represent for each system?"

We apologize to the reviewer for the confusion. If the peaks were left completely unassigned, the peak signal was not higher than the background N₂ spectra, and these peaks were not included in the peak assignment analysis. We have added the following statement to the CIMS discussion (section 3.2) to clarify this point, "All the peaks identified in the following sections have signal higher than that present in a N₂ background spectrum. Any unlabeled peaks are within the background, and have not been included in the peak assignment analysis."

"2a) Why would the "minor" impurity formic acid be a large peak?"

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."

"2b) Why would the hemiacetal sulfate ester be a large peak, when the authors' own kinetic analysis indicates that it should be 3000x below the detection level of the CIMS method?"

The goal of the modeling exercise was to demonstrate that the kinetic model based

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on the mechanism and rates of Minerath et al. may not accurately describe the formation of this species. As we stated in the discussion, the discrepancy that the reviewer noted "... suggests that either a) the kinetics of sulfate esterification for paraformaldehyde are significantly faster than for alcohols b) SO₄²⁻ or HSO₄⁻ is the active reactant, contrary to the conclusions of Deno and Newman, or c) sulfate esterification is enhanced by the solution dehydration that accompanies the atomization and volatilization steps in our detection technique." We have reworded this section in order to reduce possible reader confusion.

"2c) Why would some members of the oligomer series be present (for example, formaldehyde in AS forms the n = 2, 6, and 9 hemiacetals), but not others?"

This would be an interesting topic for a density functional theory study to determine the thermodynamic landscape of this reaction network, along the lines of that done by Kua et al. (2008) for glyoxal and Krizner et al. (2009) for methylglyoxal. A study of this type is outside the scope of this work.

"2d) Why are different ions detected for the same chemical species under the same CIMS conditions (for example Figures 5 and 6 show apparently quite different CIMS spectra, but since different m/z carriers are assigned to the same neutral species, many of the assigned products are actually the same)?"

We have added the following text to better explain this phenomenon in the CIMS discussion, "While the negative-ion spectra of the formaldehyde-AS and formaldehyde-MG-AS mixtures share many similar peaks, there are some differences in the spectra. Small variations in pressure and flow rates within the declustering region can affect the clustering efficiency between the analyte and the parent ions, and surrounding water molecules, resulting in the same analyte compound appearing at different m/z values"

"3) The authors should give example reactions (perhaps as a figure) for representative products according to each of the chemical mechanism types identified (aldol, hemiacetal (of which there is more than one type), esterification, etc.). This would also serve

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as a good visual way of organizing and summarizing the complex chemical reactions observed."

We have added a figure to the supplement to show the different chemical reaction pathways. We have also added the following text to the introduction, "In aqueous solution, both formaldehyde and acetaldehyde become hydrated and form acetal oligomers, similar to methylglyoxal and glyoxal (Loudon, 2009) (see Figure S2 in the Supplemental Information for the different reaction mechanisms in this study)."

"4) In a similar vein, they should compare these mechanisms to those they have previously identified for the methylglyoxal system."

Please see the above comment in reference to information already within the text. In addition, each product identification table shows the reaction pathways by which each product is formed.

"Page 19477, line 13-15: Please report all surface tension depressions as percentages."

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

"Page 19490, line 1: Typo: "dimer" should be replaced with "sulfate.""

We have updated the chemical name to include "sulfate" throughout the manuscript.

"Tables 4 and 5: It would be beneficial to combine this information into one table so that it would be obvious which species were identified with both ionization methods (thus giving more weight to these assignments) and which species were only identified with one of the ionization methods."

While the reviewer brings up an interesting point, whether species are identified in one mode, or in both positive- and negative-ion mode, bears no significance as to the weight of the peak assignments. Organic species are identified with either mode based

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on favorable reaction of the reagent ion (either I^- or H_3O^+) with the organic compound. Clustering in either mode depends on the different moieties of the organic species. If an organic species is identified in both positive and negative mode, this merely indicates favorable reaction of both reagent ions with the compound.

"Supplement S6: 1) I don't understand the first sentence in the second paragraph. It seems most likely that the sulfate esterification process is acid catalyzed and that either HSO_4^- or SO_4^{2-} is the nucleophile, both of which are provided by the 75 wt% H_2SO_4 solution used in the Minerath et al rate constant determination. In the present case, the solutions have much lower acidity, but comparable sulfate levels. Therefore, it is the difference in acid catalysis that will likely make the reactions much slower in the present case. I do think that authors have actually calculated their rates based on the acidity difference, but they discuss the dominant form of sulfate as a relevant difference, which I don't think it is."

This proposed mechanism does seem reasonable, in fact we also initially thought that bisulfate or sulfate would be the most likely reactant. However, we kindly refer you to the classic work of Deno and Newman (1950). They conclusively showed that the formation of alcohol ester sulfates occurs via the reaction with H_2SO_4 , not HSO_4^- . We have reworded that passage to reduce possible reader confusion. We also had mentioned this alternative pathway in the discussion of the kinetic model in the main text.

"2) Equation S4 is not balanced."

This equation has been balanced per the reviewer's request. We have updated the supplement to include the correct molecular formula for the organosulfate.

References:

Deno, N. C. and Newman, M. S.: Mechanism of Sulfation of Alcohols, *Journal of the American Chemical Society*, 72 (9), 3852-3856, 1950.

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

Kua, J. et al.: Thermodynamics and Kinetics of Glyoxal Dimer Formation: A Computational Study, *J. Phys. Chem. A*, 112, 66-72, 2008.

Krizner, H. E. et al.: Thermodynamics and Kinetics of Methylglyoxal Dimer Formation: A Computational Study, *J. Phys. Chem. A*, 113 (25) 6994-7001 2009.

Loudon, G. M., *Organic chemistry*, Roberts and Co, Greenwood Village, Colo, 2009.

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.

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