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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 #3

Received and published: 12 August 2011

General comments

This manuscript describes the measurements of the surface tension properties of formaldehyde, acetaldehyde, and methylglyoxal dissolved individually and as binary and ternary mixtures in pure water and saturated ammonium sulfate solutions. These mixtures are also subjected to chemical ionization mass spectrometric (CIMS) analysis in order to identify the particular chemical species that are formed. The results indicate that surface active species are formed, and that the surface tension lowering effects are larger for the binary and ternary systems than expected from a purely additive model. Many chemical species resulting from self- and cross-oligomerization processes are

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identified, as well as a previously unidentified hemiacetal sulfate ester derived from formaldehyde. These experiments are potentially of interest to the ACPD readership because if this type of chemical processing is actually occurring on ambient atmospheric aerosols, it would undoubtedly affect the physical properties (such as CCN ability) of those aerosols.

Unfortunately, however, the manuscript provides no quantitative evidence for the potential relevance of these processes on ambient atmospheric aerosols. In particular, 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). 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? 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).

Qualitatively, the manuscript has value as far as it is able to address the mechanisms of the reactions studied. As such, this aspect of the manuscript needs to be significantly strengthened so that it is more definitive. The following are some specific suggestions/questions: 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

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represent for each system? 2) For the fully assigned peaks, there are several ambiguities. For example, many aspects of the assignment of Figure 5 (the other Figures raise similar questions) deserve elaboration: a) Why would the “minor” impurity formic acid be a large peak? b) 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? c) 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? d) 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)? 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 as a good visual way of organizing and summarizing the complex chemical reactions observed. 4) In a similar vein, they should compare these mechanisms to those they have previously identified for the methylglyoxal system.

Specific comments

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

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

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.

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^- is the nucleophile, both of which are provided by the 75 wt% H_2SO_4

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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. 2) Equation S4 is not balanced.

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

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