

Interactive comment on “Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics” by E. L. Shapiro et al.

E. L. Shapiro et al.

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Response to Reviewer 4

We thank Reviewer 4 for his or her insightful and constructive comments. We respond to the Reviewer's specific comments and technical corrections below.

Organo sulfates: Minerath et al. recently showed that alkylsulfates are only formed under very acidic conditions. Galloway et al. state that glyoxalsulfate was only observed under irradiated conditions. The glyoxalsulfates identified in the work by Liggio et al. corresponded to glyoxal oligomers in the Galloway study. Given that these recent findings, which were not available at submission of this paper, cast in doubt the formation of glyoxalsulfates, the role of sulfate should be revisited.

We have expanded the discussion of previously observed products in the

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Interactive Discussion

Discussion Paper



glyoxal/ $(\text{NH}_4)_2\text{SO}_4$ system to include the points made by the reviewer above, and to include the references cited. We have added the following passage to the discussion section: "Galloway et al. (2008) recently showed that irradiation was necessary for organosulfate formation in the glyoxal/ammonium sulfate system. This, together with the results of our control experiments, which demonstrate that light is not required for the light-absorbing reaction products to form in our system, suggests that it is not likely that the light-absorbing molecules in our system are organosulfate species." Following this reasoning, we have removed structure (h) in Table 1 of the original manuscript from our list of possible light-absorbing products.

Aldol condensation: A reference that describes a study of self-aldol condensation for glyoxal is required, as it does not lend itself well to self-aldol condensation. For example, this was not included in the work by Barsanti and Pankow on dicarbonyl accretion reactions. To check the plausibility of this proposed reaction, a reaction scheme (perhaps in the supplementary material), possibly for the formation of product (h) in Table 1, should also be included. Specifically, the enol form of unhydrated glyoxal does not exist in aqueous solution (it would be a ketene). For the enol form of the singly hydrated glyoxal, the reactivity of the unhydrated aldehyde carbon is expected to be significantly higher for three related reasons: 1. it is sterically more approachable; 2. it is more nucleophilic 3. the carbo-cation formed on the other carbon after nucleophilic attack on another glyoxal molecule is more stabilized due to the presence of two OH groups. Thus, the proposed aldol self reaction would be more likely to result in a different product and terminate at a trimer (a dicarboxylic acid). The calculated spectrum for this species likely is similar to product (h) in Table 1, but it is unclear how the larger molecular weight compounds observed in MALDI could be formed via self aldol reaction, if it exists for glyoxal.

We thank the reviewer for sharing these insights. We have expanded our discussion of the possible products and mechanisms based on this comment and those of the other reviewers, as well as recent publications on this topic that came out while this

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manuscript was in the submission process.

Following the reviewer's logic, we agree that self-aldol condensation of singly hydrated glyoxal will terminate at a 3-mer for glyoxal, with 3 possible isomers formed. Based on our DFT calculations, we predict that the carboxylic acid dimer that would result from aldol addition at the unhydrated aldehyde carbon is 31 kcal/mol more stable than the aldehyde-terminated dimer that would result from addition at the hydrated carbon. We predict that the resulting dicarboxylic acid products will absorb at 300 nm. However, our calculations also suggest that addition at the hydrated carbon is thermodynamically favorable for glyoxal with imine substitutions, which may occur when ammonium is present in aqueous solution (Galloway, et al., 2008; Nozière et al., 2009a). If we begin with the singly hydrated iminium ion, the Gibbs free energy of the iminic acid dimer that would result from addition at the unhydrated carbon is 6.3 kcal/mol higher than that of the aldehyde-terminated dimer that would result from aldol-type addition at the hydrated carbon. Subsequent additions to the aldehyde-terminated dimer could lead to the formation of high molecular weight, light-absorbing species. We have included this discussion in the revised text.

MALDI mass spectra:

1. The observed mass ranges for glyoxal in NaCl and Ammonium sulfate are both very narrow; the entire distribution is less than +/- the mass added for each oligomer (m/z 58) whether it is an acetal or proposed aldol oligomer. If the appearance of the spectrum is not due to an instrument response function a scheme should be proposed why such a narrow product distribution is formed. If the appearance of the spectrum is due to the instrument response function, can one speculate what the real distribution might look like, are unobserved larger or smaller oligomers more likely?

Based on measurements of other systems that we have made with the same MALDI instrument that showed wider mass ranges, we do not believe that the spectrum we observe is due to the instrument response function. In polymerization reactions, average

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Discussion Paper



chain length is determined by the reaction kinetics. A narrow chain length distribution is to be expected for polymerization reactions that follow an ionic mechanism (Rosen, 1993). We have added this point to the revised manuscript.

2. What findings support that the absorptive species at 550 nm are due to the high molecular weight species found in the MALDI spectrum, as the NaCl/glyoxal and ammonium sulfate/glyoxal mass spectra look very similar, except for a signal near m/z 510? A discussion, which likely would have to remain speculative, of the small difference (including the m/z 510 signal), in light of the difference in the absorption spectra, should be added.

There are several possible explanations for our observation via MALDI of high-molecular-weight products in the glyoxal-NaCl solution, which were not strongly light absorbing, at similar masses to those observed in the glyoxal-ammonium sulfate solutions. The high-molecular-weight material in both systems could be acetal oligomers of similar structure, which we do not expect to absorb at visible wavelengths based on the results of our ab initio calculations. This would suggest that the light-absorbing products in the glyoxal-ammonium sulfate solutions are of lower molecular weight and were not detected via MALDI. Another possibility is that imine substitutions can lead to molecules that absorb at higher wavelengths but are similar in mass; the mass of a carbonyl and a =NH group (or a hydroxyl group and -NH₂) differs by 1 amu, so these structures may not be readily distinguished via our MALDI spectra. We have included this discussion in the revised text, and provide specific examples of proposed structures supported by predictions of their UV-Vis absorption based on ab initio calculations.

3. It would also be instructive to put the molecular weights observed in this study in context with those observed in other studies, e.g. Liggió et al. or Hastings et al.

Such a discussion has been added. The sentence "to our knowledge. . ." was replaced with "Acetal oligomer formation has been commonly reported for glyoxal in aqueous systems (Fratzke and Reilly, 1986; Hastings et al., 2005; Galloway et al., 2008; Liggió

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Interactive Discussion

Discussion Paper



et al., 2005b; Loeffler, et al., 2006; Nozière, et al., 2009a), with the highest masses (up to 475 amu) observed by Hastings et al (2005) using electrospray ionization/ion trap mass spectrometry.”

Absorptive properties and kinetic scheme:

Do the spectral changes, especially in the visible, occur in absence and presence of oxygen?

All experiments were done in the presence of ambient air. We believe that the observed reactions are not photochemical in nature based on control experiments in which the samples were protected from light until analysis. The UV/Vis data from these experiments are very similar to the rest of our data, in which the samples were not protected from light. However we cannot rule out a possible role for dissolved oxygen.

It would be useful to see a comparison between a calculated and measured absorption of a species with known absorption, such as crotonaldehyde. The spectrum of the glyoxal solution shows a band at 275-285 nm. However the calculated values of structure (e) in table 1 are between 100-160 nm. Does this provide a gauge for the accuracy of the calculation?

The excitation energies calculated using CIS using similarly sized basis sets to the ones used here are typically biased high by 1 eV compared to experimental values (Dorogan, 2008). And it is true that our calculations were made for gas-phase molecules and do not include solvent effects. However, we do not feel comfortable assigning the 275-285 absorption peak of the glyoxal solution to the predicted 160 nm absorbance of species (e) and (f) for the following reasons: the aqueous solution of glyoxal absorbs strongly at all measured wavelengths below 250 (see Figure S1), and our measurements do not extend to 160 nm. Also, the unhydrated glyoxal monomer in the gas phase exhibits absorption in the 275-285nm region (Volkamer et al., 2005). That being said, to reflect the reviewer's concerns, we have included the following line in our discussion: "Additional significant deviation between the theoretical results, which

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Interactive Discussion

Discussion Paper



are for gas-phase molecules, and experiment may result from solvent effects” and we have moved the discussion of the errors to immediately after where Table 1 is first introduced.

If there are other studies that have observed changing optical properties of organic aerosol or organic aerosol mimics over similar reaction times or similar conditions, they should be included in a discussion to provide a broader context of this important finding.

In response to the reviewer’s suggestion, we have added the following passage to the Discussion: “Field measurements have shown that the optical properties of ambient aerosols can change with photochemical aging (Moffet, et al., 2008; Lyamani, et al., 2008). Other groups have reported changes in the optical properties of reactive aerosol mimics over time (Nozière et al., 2007; Nozière and Esteve, 2007; Casale, et al., 2007). Nozière et al. (2009a) reported an increase in the absorption at 209 nm with time for the aqueous glyoxal/ammonium sulfate system at lower glyoxal concentrations (0.1 M) than those used in this study. They attributed the observed absorbance to a second-generation oligomerization product containing a C=N or C=C bond.”

In order to compare the results of the kinetic scheme with the observed data, it would be useful to see the evolution of the 277 nm band at longer times. In the kinetic scheme the compounds corresponding to this band appear to decrease at long times. As the reactions appear to be slow the measurements could be done by diluting a small amount of sample thus bringing the absorbance back into the dynamic range of the spectrophotometer.

We agree with the reviewer that 277 nm data at longer times would allow for a more direct comparison between our model and the experiment. However, dilution of our reaction mixtures may cause an equilibrium shift, making the results difficult to interpret. We believe at least some of the reactions are likely to be reversible upon dilution based on the observations of Galloway et al. (2008) for this system and our own unpublished data.

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Interactive Discussion

Discussion Paper

How does the rate constant used here, compare with that found for glyoxal dimer formation in aqueous solution determined by Fratzke et al. as well as the rates found for reaction of glyoxal with ammonium sulfate by Nozière et al?

The rate constant we used in our qualitative kinetics analysis ($5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) is roughly 100x lower than that reported by Nozière et al. (2009) ($8(\pm 4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) for the evolution of an absorption peak at 209 nm in the aqueous glyoxal/ $(\text{NH}_4)_2\text{SO}_4$ system at low glyoxal concentrations. It is roughly 30x lower than the pseudofirst order rate constant reported by Fratzke and Reilly (1986) for glyoxal dimerization at pH 5 and 25 C ($5 \times 10^{-4} \text{ s}^{-1}$). We have included this information in the discussion.

Technical corrections:

Page 61 line 2: Glyoxal is often a higher generation product of oxidation of biogenic VOCs (see for example Fu et al.)

In response to this suggestion, we have modified the passage to simply say "Glyoxal is a gas-phase oxidation product of many biogenic and anthropogenic VOCs"

Page 61 line 25: It might be clearer to first state "terms oligomer and HULIS are both used in the literature to refer to moderately large (300-600 Da) organic" and then state "further evidence."; Otherwise no evidence for HULIS has previously been stated.

This passage has been clarified as per the reviewer's suggestion.

The traditional glyoxal oligomers are acetals, not esters. I believe this is true for: Page 61 line 16 Page 66 line 23 Page 67 line 4-5 Page 68 line 11 and line 13

We thank the reviewer for pointing this out, the correction has been made.

Page 65 line 17-18. I am not sure that the UV/Vis spectrum of control experiment 4 (glyoxal/ Na_2SO_4) is shown in the supplemental material.

This omission has been corrected and the spectrum has been added to Figure S1. The legend on Figure S1 has also been corrected.

Page 63 line 9: *achieve is misspelled*

The correction has been made.

Supplement: Figure S2: the x-axis label should be changed to m/z and the y-axis label also should be corrected

The correction has been made.

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Interactive Discussion

Discussion Paper



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