

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 David DeHaan (Referee)

We thank Prof. DeHaan for his thorough and helpful review of our manuscript. We address his specific comments and answer his questions below.

Strangely, while almost identical-looking high molecular weight (MW) products are observed by MALDI-MS for solutions containing glyoxal and either ammonium sulfate or sodium chloride (with higher quantities seen with sodium chloride), only the glyoxal + ammonium sulfate solutions turn brown. Why don't the glyoxal + sodium chloride products turn brown, too? The authors posit that different products are formed, but this does not address the overwhelming similarity of the mass spectra (one of which is shown only in the supplementary material).

The paper would be improved by more extensive use of the MALDI data, such as an attempt to match structures to the observed masses. Without this connection, any product structures shown are highly speculative, given that UV-Vis spectra are nowhere near structurally specific.

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.

Adjacent peaks in the MALDI spectra of both the glyoxal/NaCl and glyoxal/ammonium sulfate solutions were separated by 14 amu on average. This separation is consistent with loss of a -CH₂, or as may be the case in the (NH₄)₂SO₄ system, the difference between a =NH group and a hydrogen. It follows that nonadjacent peaks were separated roughly by multiples of 14 amu: 28 amu, 42 amu, 56 amu, 70 amu, 84 amu. A monomer unit in the case of an acetal oligomer corresponds to 78-80 amu. In the aldol condensation products suggested in this work the monomer unit is 42 amu, and for an imidazole polymer (Galloway et al., 2008) it would be 95 amu. We have added a passage to this effect in the revised manuscript.

This reviewer was concerned that the MALDI matrix compound (2,5-dihydroxybenzoic acid, DHB) is structurally similar to aromatic diols used to create condensation poly-

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mers with glyoxal. [Maravigna, 1988; Tunca et al., 1995; Vigo et al., 1992] However, in a control experiment shown in the supplement, it can be seen that glyoxal, in the absence of sodium chloride or ammonium sulfate, does not produce large MW products. This seems to indicate that the conditions used in preparing samples for MALDI analysis are not amenable to polymer formation between glyoxal and DHB. On the other hand, the lack of ions to catalyze the reaction may also explain the MALDI control experiment results. Might the high molecular mass products seen in MALDI in the presence of sodium chloride and ammonium sulfate be glyoxal - DHB copolymers whose formation is catalyzed by ionic substances? A sodium sulfate control experiment might answer this question, but only if large-mass MALDI peaks are not detected. Can the authors make the case the DHB is not involved?

The reviewer raises an interesting point for discussion. In the references cited here by the reviewer, a strong acid catalyst such as sulfuric acid or methane sulfonic acid was required for DHB-glyoxal copolymer formation. Additionally, the polymerization reactions were carried out in an acetic acid medium. There is no evidence in the literature that ions such as Na⁺ or Cl⁻ in a mildly acidic aqueous environment act to catalyze DHB-glyoxal copolymer formation. Also, there is no evidence in the MALDI mass spectra for DHB-glyoxal copolymer formation. However, we have mentioned this alternative theory in the discussion section.

p. 66 line 6: It looks like one extra MS peak group (m/z 510) appears with glyoxal + ammonium sulfate as compared to glyoxal + NaCl. Is this true? If so, saying that most, but not all peaks overlap would be more accurate.

The change in the wording has been made as per the reviewer's suggestion.

p. 67 line 6 and Table 1 structures g and h: Usually in an aldol condensation the product loses OH groups as the C-C double bonds form. It is not clear what mechanism could form the structures shown.

Structures (g) and (h) were arrived at based on aldol condensation of singly hydrated

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glyoxal, with addition at the hydrated carbon of the enol. We have revisited the mechanism and products of aldol condensation involving the singly hydrated glyoxal monomer based in part on the comments of Reviewer 4 and the recent publications on this topic that came out while this manuscript was in the submission process. We propose alternate products and discuss the mechanism in more detail in the revised version.

Based on (1) the results of Galloway et al. (2008), who showed that irradiation was necessary for organosulfate formation in the glyoxal/ammonium sulfate system, (2) the results of our control experiments, which demonstrate that light is not required for the light-absorbing reaction products to form in our system, and (3) the fact that our control experiments with Na_2SO_4 and NH_4NO_3 indicate that the presence of ammonium, not sulfate, is the requirement for light-absorbing products to form, we conclude that it is not likely that the light-absorbing molecules in our system are organosulfate species. Therefore we have removed structure (h) from our lineup of possible light-absorbing products.

p. 68 lines 17 to 27: The product suggestions based on the kinetics data should reference structures shown in Table 1, since the authors have already shown that most of the known products of glyoxal self-reactions (or glyoxal - sulfate reactions) cannot be responsible for development of the observed absorbance. Do the authors mean to suggest that the aldol condensation of two glyoxal molecules could be responsible for the growing absorbance feature at 277 nm?

We have used this helpful suggestion to clarify our discussion of the kinetics analysis. The linear (first-order) dependence of the signal at 277 nm on initial glyoxal concentration for low concentrations is consistent with a product or products resulting from the direct reaction of glyoxal with ammonium sulfate. Its prompt evolution upon mixing is also consistent with a first generation reaction product. An example of such a product is the imine analog of glyoxal, which was predicted via DFT calculations to absorb at 252 nm. The product or products absorbing at 355 nm exhibits a linear dependence on the square of the initial glyoxal concentration ($R^2 = 0.957$) (i.e., second-order), consistent

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with glyoxal self-reaction or glyoxal reacting with the first-generation glyoxal/ $(\text{NH}_4)_2\text{SO}_4$ reaction product. However, the signal at 355 nm appears after a delay of roughly 3 hours, consistent with a second-generation product rather than glyoxal self-reaction. An imine-substituted aldol condensation dimer would be a product of this type; we predicted a representative molecule to absorb at 336 nm. We have added this discussion to the text.

p. 63 line 21: the recipe for MALDI samples needs to be clarified.

We thank the reviewer for pointing this out. The text has been modified to read: "5-dihydroxybenzoic acid (DHB) was used to make the matrix for all solutions following Karas et al. (1993). Briefly, 1 mg of DHB was added to 100 μL of a 9:1 (v/v) water to ethanol mixture. 1 μL each of the sample and matrix mixtures were deposited onto the MALDI target (i.e. on-spot mixing). The mixture was allowed to dry for ten minutes before analysis."

p. 65 line 18: The authors refer to a glyoxal + sodium sulfate control experiment for UV-Vis, but do not show the results in the supplement (Fig. S1).

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

Fig S2: Both axes are mislabeled.

The correction has been made.

Fig. S3b: Are these calculations for 24 h reaction times?

Yes. This has been clarified in the caption of that figure.

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