

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 Anonymous Referee 1

We thank Anonymous Referee 1 for his or her insightful and helpful comments and suggestions. We address the specific points raised by the Referee below.

1. As the authors are probably well aware, two papers studying the glyoxal/ammonium sulfate system have been published while this manuscript was in the submission process. The first is Nozière et al., 2008 which addresses the reaction kinetics of aqueous glyoxal and ammonium ions. Using UV absorption and LC-HRMS, they find the reaction occurring in their solutions to be second order and propose an iminium pathway to form larger glyoxal oligomers. Nozière et al. were also able to determine the effect of pH and the counterion on the reaction rate. How does this study compare with Nozière

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et al., 2008, considering both use similar experimental techniques?

We have added discussion of the two new papers by Nozière and coworkers to the revised manuscript. The following passages were added:

"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. The maximum concentration of glyoxal used in our study corresponds to ~25 wt% organics in the solute; typical tropospheric aerosols contain 10-90 wt% organic material (Kanakidou et al., 2005). It is possible that light-absorbing products such as those observed in this study are formed at the low glyoxal concentrations used by Nozière et al. (2009a), but at quantities which were too small to detect. Alternatively, different products may be thermodynamically favored when the initial glyoxal concentration is high, as suggested by Barsanti and Pankow (2005)."

"Consistent with the recent results of Nozière et al. (2009a,b) and Galloway et al. (2008), our observation that light-absorbing products form in the presence of ammonium sulfate and ammonium nitrate (but not NaCl or Na₂SO₄) suggests a mechanism involving the participation of the ammonium ion, and possibly a product or products containing C-N bonds."

Can the authors determine the reaction order or propose reaction products with the given data?

Upon the reviewer's suggestion we have included a reaction order analysis with our discussion of the kinetics model. The linear (first-order) dependence of the signal at 277 nm on initial glyoxal concentration for low concentrations (see Figure 2(b)) is consistent with a product or products resulting from the direct reaction of glyoxal with ammonium sulfate. Its prompt evolution upon mixing (see Figure 1(b)) is also consistent with a first generation reaction product. The product or products absorbing at 355

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nm exhibit a linear dependence on the square of the initial glyoxal concentration ($R^2 = 0.957$) (i.e., second-order), consistent 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. The signals at $\lambda > 500$ nm appear after a delay of ~ 12 hrs, suggesting higher-order products. We have expanded our discussion of the possible products in the revised manuscript.

it Can the conclusions of this study be applied to field investigations such as Volkamer et al., 2007?

The chemistry observed here represents new potential pathways for SOA formation by glyoxal in aqueous aerosols, and therefore this work does support the conclusions of Volkamer et al. (2007). The atmospheric significance of the SOA formation pathways we have identified will depend on the gas-aerosol mass transfer of glyoxal, which is the subject of active research. Assuming that glyoxal uptake to atmospheric ammonium sulfate aerosols follows Henry's Law with $H_{eff} \sim 5 \times 10^7 \text{ M atm}^{-1}$ (Kroll et al., 2005; Galloway et al., 2008), and using our estimated rate constant data, we can calculate a reactive uptake coefficient due to the bimolecular glyoxal-ammonium sulfate reaction of $\gamma \sim 10^{-6}$. This value will increase if other glyoxal reactions are included in the first order loss constant. We have included a detailed description of this calculation, which followed the method of Hanson et al. (1994), in the revised manuscript. Volkamer et al. (2007) inferred a higher value of $H_{eff} \sim 4 \times 10^9 \text{ M atm}^{-1}$ based on ambient glyoxal concentrations and SOA loadings in Mexico City, and found that the gas-particle partitioning of glyoxal could be modeled equally well as irreversible uptake. If $H_{eff} = 4 \times 10^9 \text{ M atm}^{-1}$ we find that $\gamma \sim 10^{-4}$ for the bimolecular reaction. If glyoxal uptake is effectively irreversible, as suggested by Volkamer et al. (2007), then the reactive uptake coefficient won't be directly dependent on the aqueous phase kinetics.

2. *The second publication is Galloway et al., 2008, a chamber study which finds that the glyoxal sulfates proposed by Liggio et al., 2005 are not formed in uptake experi-*

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ments in the absence of light and were not measured by the Aerodyne Aerosol Mass Spectrometer. The current study should be revised to acknowledge this. Galloway et al. found, however, that organosulfates were formed in the presence of UV light. How much light were the samples exposed to before measurement?

We have added discussion of the findings of Galloway et al. (2008) to the introduction and Discussion sections, and have revised our discussion of glyoxal sulfates to reflect this and other recent work.

Control experiments were performed 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. Therefore we conclude that the chemistry leading to light-absorbing material in this system does not require exposure to light. No conclusion can be drawn from these results as to whether or not the observed reactions would proceed in the presence of UV light, since the Pyrex reaction vessels used in this study filter UV light. Data from these experiments has been added to the supplementary material and the experiments have been referenced in the Results and Discussion sections. More detail about the reaction vessels and the light exposure of a typical experiment are given in the Experimental section. We have also 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.

3. The authors need to state the duration at which the control solutions were analyzed with the UV/Vis spectrophotometer to allow comparison to the glyoxal/(NH₄)₂SO₄ solutions since both absorb at 277 nm.

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We thank the reviewer for pointing out this omission. The control solutions were analyzed at 24 hr to allow direct comparison with the glyoxal/ammonium sulfate solutions. This has been noted in the text.

4. The authors note that absorbance at 277 nm can be attributed to a π - π^ transition and propose molecules (g) and (h) in Table 1 that can undergo this transition. Low level DFT calculations support this claim. However, to the reviewers knowledge, there is no evidence to suggest a glyoxal/ $(\text{NH}_4)_2\text{SO}_4$ solution can form these products. Mechanisms should be referenced to lend support to these structures.*

We have expanded our discussion of the possible products and mechanisms based on the recent publications on this topic that came out while this manuscript was in the submission process, and the helpful comments of all the reviewers. Glyoxal has been reported to be a retroaldol condensation product of glucose (Thornalley et al., 1999), however, glyoxal self-aldol condensation has not previously been reported. Pathways for glyoxal self-aldol condensation in the presence of ammonium sulfate are most likely to initiate with the singly hydrated form of glyoxal or its imine analog (Galloway et al., 2008; Nozière et al. 2009a). In the enol form of singly hydrated glyoxal, the hydrated carbon is expected to be less reactive than the unhydrated carbon, resulting in the formation of carboxylic acid groups upon aldol addition. 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. Therefore, the aldol condensation pathway may terminate at a 3-mer for glyoxal, with 3 possible isomers formed. The resulting dicarboxylic acid products are predicted to absorb at $\lambda \sim 300$ nm, but they would not contribute to the observed MALDI mass spectrum. 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

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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.

5. When the authors state glyoxal can form "ester products," I believe they mean "acetal products."

We thank the reviewer for pointing this out, the error has been corrected.

6. In Figure 3, a MALDI-MS shows the possible masses of products formed in solution. It is odd though that the peaks start at 500 amu and only go as far as 600 amu. This distribution suggests that the products consist of many glyoxal units and only vary within 1 or 2 glyoxal units. Mass spectra from the AMS (Liggio et al., 2005; Galloway et al., 2008) show peaks as high as 175 to 192 amu, and Nozière et al., using a much softer ionization method, identify compounds at 228 amu. Can the authors identify the peaks that occur in Figure 3 to at least unit mass resolution? Do the differences in the mass spectrum peaks suggest losses of monomer units?

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 $-\text{CH}_2$, or as may be the case in the $(\text{NH}_4)_2\text{SO}_4$ system, the difference between a $=\text{NH}$ 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.

Does the spectrum vary with glyoxal or $(\text{NH}_4)_2\text{SO}_4$ concentrations? Does the spectrum vary with how long the solution sits before measurement?

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We did not obtain MALDI mass spectra as a function of solution composition or time. The MALDI spectra shown were taken several days after mixing. The main focus of this work was to characterize the light-absorbing properties of the product mixtures. It was our intention to use MALDI simply as a yes/no test for the presence of high molecular weight material. However we agree that more detailed measurements of this type would be interesting for a future study.

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