

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

Anonymous Referee #4

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This paper presents observation of high molecular weight compounds and changes in optical properties as well as surface tension measurements of solutions of glyoxal in (mainly) ammonium sulfate. Glyoxal has gained much interest due to its role in secondary organic aerosol formation and the observation of compounds at molecular weight higher than previously observed certainly lends further evidence for this. In addition, the observation of a change in optical properties upon "aging"; of these solutions is interesting, particularly if it has more general implications for the change in optical properties in aging organic aerosol. The paper virtually coincides with a number of other related studies (see first 4 references given below). As result of this timing, the authors could not include the other findings in their work presented here. The work presented here could likely benefit from inclusion of relevant new findings, in particular

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about chemical processes, such as the proposed organosulfate formation and the role of ammonium in the glyoxal/ammonium sulfate/H₂O system. The paper adds to our understanding of the processing of glyoxal in aqueous ammonium sulfate as well as changes in optical properties of organic aerosol and is likely publishable after revisions suggested below.

Specific comments:

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.

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.

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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 \pm 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?

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.

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.

Absorptive properties and kinetic scheme:

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

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

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should be included in a discussion to provide a broader context of this important finding.

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.

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 Noziere et al?

Technical corrections:

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

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.

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

Page 65 line 17-18. I am not sure that the UV/Vis spectrum of control experiment 4 (glyoxal/Na₂SO₄) is shown in the supplemental material.

Page 63 line 9: achieve is misspelled

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

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Noziere, B., et al., Products and Kinetics of the Liquid-Phase Reaction of Glyoxal Catalyzed by Ammonium Ions (NH₄⁺) *J. Phys. Chem. A* 2009, 113, 231-237.

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Barsanti, K.C., and Pankow, J.F., Thermodynamics of the formation of atmospheric organic particulate matter by accretion reactions - 2. Dialdehydes, methylglyoxal, and diketones *Atmos. Environ.* 2005 39, 6597-6607.

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Hastings, W. P., et al., Secondary organic aerosol formation by glyoxal hydration and oligomer formation: humidity effects and equilibrium shifts during analysis. *Environ. Sci. Technol.* 2005, 39, 8728-8735.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 59, 2009.

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