

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

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General comments

This work presents interesting and puzzling data on bulk-phase reactions of glyoxal with aerosol materials ammonium sulfate and sodium chloride, certainly a relevant topic for this journal. The reaction products are analyzed by ultraviolet-visible absorbance spectroscopy (UV-Vis), matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), and pendant-drop tensiometry. The evolution of reaction solution absorbance towards longer wavelengths as the reaction progresses is carefully documented. The authors use ab initio calculations to show that all previously reported glyoxal oligomers cannot be responsible for the observed absorbance spectra. Instead, oligomers with conjugated bonds, such as might be formed in aldol reactions, could

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be causing the observed increases in absorbance by the addition of glyoxal subunits with increased reaction time. While the results are clearly presented, there are major differences between the MALDI-MS and the UV-Vis results that are not adequately explained.

Specific comments

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.

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

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p. 66 line 6: It looks like one extra MS peak group ($m/z \sim 510$) 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.

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.

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?

Technical notes

p. 63 line 21: the recipe for MALDI samples needs to be clarified. 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). Fig S2: Both axes are mislabeled. Fig. S3b: Are these calculations for 24 h reaction times?

References

Maravigna, P. (1988), Thermally stable polymers by condensation of diphenols with glyoxal., *J. Polym. Sci. A: Polym. Chem.*, 26(9), 2475-2485. Tunca, A. A., et al. (1995), Condensation polymers from diphenols and glyoxal, *Eur. Polym. J.*, 31(1), 9-14. Vigo, T. L., et al. (1992), Temperature-adaptable glyoxal-modified fibers and method of preparing them, *U. S. Pat. Appl.* 92-863274 19920403 (CAN 118:193595).

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