

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 2

We thank Reviewer 2 for his or her constructive comments.

“Two recent studies of the same reaction of glyoxal in ammonium sulfate are not mentioned (Nozière et al., JPCA, 113, 231, 2009 and Galloway et al., ACPD, 8, 20799, 2008). This is perhaps understandable because of the short delay between these papers and the present one, but would not be acceptable in a final version.”

We have added discussion putting our work in the context of Galloway et al (2008) and the two new papers by Nozière and coworkers in the revised version.

“there is not a single word on any of the previous studies of these light-absorbing products in the same reactions . . .”

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The papers by Nozière and coworkers which were most relevant for this aqueous system were referenced in the original manuscript (Nozière and Esteve, 2007, Nozière et al., 2007). We have added Nozière and Esteve (2005) and Casale et al. (2007) in the revised version, thank you for pointing out that omission.

"...neither Nozière et al., 2009 or Galloway et al., 2009 report such light-absorbing compounds."

Galloway et al (2008) did not measure aerosol optical properties during their experiments, and so it is not possible to compare our results and theirs in that respect. Our measurements were made at higher glyoxal concentrations than those used by Nozière et al. (2009) and therefore it is possible that similar light-absorbing products are formed at the low concentrations used by Nozière et al. but in quantities which were too small to detect, or that different products are formed when the concentration is sufficiently high, as suggested by Barsanti and Pankow (2005). We have included a discussion of this matter in the revised manuscript.

"There is no mechanistic explanation for the formation of the pi-conjugated products proposed in this manuscript from glyoxal ..."

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, as the reviewer pointed out, 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

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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 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 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.

"they should discuss the atmospheric relevance of these results, as the above-mentioned previous works did (discussing absorption cross-sections, concentrations, and the general relevance of the results for aerosols)."

We have included more discussion of the atmospheric significance of our findings in the revised version. We have modified the passage regarding absorption cross-sections as follows: "Based on the data shown in Figure 1 for solutions initially containing 2.21 M glyoxal and 3.11 M $(\text{NH}_4)_2\text{SO}_4$ after 4 days, and assuming that the species absorbing at $\lambda > 500$ nm consist of at least 3 glyoxal monomer units, following Beer's law we obtain a lower-bound estimate of the molar absorptivity at 550 nm of $\epsilon \geq 1 \text{ Lmol}^{-1}\text{cm}^{-1}$. Following the approach of Nozière et al. (2009a,b), the extinction coefficient of the solution at 550 nm is $\epsilon_{550} \geq 0.71 \text{ cm}^{-1}$ and the dimensionless absorption index, $A_{550} = \lambda \epsilon_{550} / 4\pi \geq 3.1 \times 10^{-6}$. This chemistry may represent a mechanism by which the absorption index of aqueous inorganic atmospheric aerosols may increase with aerosol age."

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