

Interactive comment on “Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 1: Surface tension depression and light-absorbing products” by A. N. Schwier et al.

Anonymous Referee #2

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This manuscript describes the measurements of the optical and surface tension properties of methylglyoxal dissolved in various salt solutions thought to be representative of tropospheric aerosols. Since methylglyoxal is potentially an important secondary organic aerosol precursor, the physical and chemical interaction of methylglyoxal with preexisting aerosols is currently of great interest in the field. Two main results are reported in the present manuscript: 1) methylglyoxal lowers the surface tension of aqueous solutions (and the effect is greater in the presence of salts) and 2) methylglyoxal apparently undergoes aldol condensation reactions in ammonium salt solutions.

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However, for this second aspect of the manuscript, I find that the experimental design and results analysis to be lacking. The ultimate goal here is to develop a chemical mechanism (including kinetics information) that can be used to assess the potential importance of these reactions on tropospheric aerosols. One problem is that the UV-Vis data do not allow for the specific chemical identification of any of the reaction products (more on this later). However, I do not understand why the authors did not control and vary the pH, and vary the salt concentrations. Since their proposed mechanism involves NH₄⁺ (or NH₃) and both the salt concentration and pH affect these concentrations, it seems that a lot more mechanistic information could have been obtained from pH and salt dependent experiments. Can the authors provide a rationale for the lack of experiments of this type?

In general, I find the discussion of the mechanism to be quite confused, and I don't think that it is very useful in its present form. Some specific problems are listed below:

1) The authors go back and forth between referring to NH₄⁺ (which should be dominant at pH = 2) or NH₃ as the key species in the mechanism. As I mention above, pH dependent experiments could shed some light on this issue. In any case, for the pH = 2 conditions used in the experiments they did perform, it seems that NH₄⁺ must be the active species.

2) On p. 15548, starting on line 3, the authors entertain two possible mechanisms, 1) formation of species with C-N bonds and 2) aldol condensation. Again, if the authors had performed salt (NH₄⁺) dependence experiments, they might have been able to determine whether NH₄⁺ participates stoichiometrically (the expectation for mechanism 1), or catalytically (the expectation for mechanism 2). However, since NH₄⁺ must be the dominant species, can't one rule out an ininium intermediate mechanism anyway?

3) On p. 15549, starting on line 24, the authors entertain two possible rate-limiting steps: 1) the reaction of NH₄⁺ with methyl glyoxal, or 2) methylglyoxal self reaction. Again, NH₄⁺ dependence experiments could have helped to resolve this issue.

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4) The discussion of the methylglyoxal rate order needs to be unified and much more clearly described. It seems to me that the linear dependence of the 282 nm species absorption on methylglyoxal concentration suggests the product kinetics are characterized by a process that is first order in methylglyoxal (such as $\text{NH}_4^+ + \text{methylglyoxal}$). However, the authors use a spectroscopic argument (on p. 1549, starting on line 24) to conclude that the rate limiting step must be second order in methylglyoxal. Since the atmospheric significance of these processes is much more likely if the rate is only first order in methylglyoxal, this is a crucial point. In any case, the authors assumptions (and resulting kinetics equations used) need to be much carefully described and developed.

5) With respect to the kinetic analysis for the 550 nm species, again the authors need to be more specific. Here, they are (correctly, in my opinion) assuming that the rate-limiting step is first order in methylglyoxal (likely: dimer + methylglyoxal) because of the linear dependence of the 550 nm absorption on methylglyoxal. The apparent pseudo first order behavior is presumably due to conditions of $[\text{dimer}] \ll [\text{methylglyoxal}]$; this should be specifically pointed out.

Other comments (in manuscript order):

1) p. 15542, starting on line 4: The time scales cited are not directly related to how fast these processes might be on actual tropospheric aerosols and should be removed from the abstract.

2) p. 1554, line 5. I assume that these salt concentrations were chosen because they are saturated solutions. This should be specifically indicated. It would have been informative to have used $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 solutions that had identical $[\text{NH}_4^+]$ concentrations to see if the sulfate or nitrate counter ion has any effect.

3) p. 1554, line 10. Why would the methylglyoxal solution be acidic? Why wasn't the actual pH for the reactions solutions measured accurately?

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4) p. 15549, starting on line 13. Since there is certainly some computational inaccuracy in the calculated wavelengths, and the solvent effects for these highly concentrated ionic solutions could be quite large, can one really used the calculated wavelengths to distinguish between two species with wavelengths that differ by only 30 nm?

5) p. 15549, starting on line 19. The weird initial effect of the entire baseline shifting must be due to a bulk optical effect – I don't see how it could be due to the discrete dimer absorption spectrum. I think this discussion should be removed.

6) p. 1552, starting on line 22. The authors should be able to do a semi-quantitative estimate of the kinetics of these processes for actual tropospheric aerosols. By starting with the Henry's law coefficient for methylglyoxal, they can calculate an equilibrium aerosol methylglyoxal concentration. From there, they can use whatever kinetic model they decide to settle on (first or second order in methylglyoxal) to see if these reactions would be expected to proceed significantly during the average lifetime of a tropospheric aerosol.

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