

## ***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.***

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Received and published: 10 November 2009

We thank Reviewer 2 for his or her insightful review of our manuscript. We address specific comments below:

*I do not understand why the authors did not control and vary the pH, and vary the salt concentrations. Since their proposed mechanism involves  $\text{NH}_4^+$  (or  $\text{NH}_3$ ) 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*

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*experiments. Can the authors provide a rationale for the lack of experiments of this type?*

In our study we chose the composition of our bulk aqueous aerosol mimics to be as atmospherically relevant as possible, using near-saturation salt concentrations and atmospherically realistic pH in our experiments (Tang and Munkelwitz, 1994; Zhang et al., 2007; Keene et al., 2004). Upon the reviewer's suggestion we performed further studies exploring the dependence of the formation of light-absorbing products on initial ammonium sulfate and solution pH and this did indeed provide additional insight into the mechanism. Results and discussion of these experiments are included in the revised manuscript.

The following comments regarding the mechanism and the role of ammonium are answered jointly below:

*1) The authors go back and forth between referring to  $\text{NH}_4^+$  (which should be dominant at  $\text{pH} = 2$ ) or  $\text{NH}_3$  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  $\text{pH} = 2$  conditions used in the experiments they did perform, it seems that  $\text{NH}_4^+$  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 ( $\text{NH}_4^+$ ) dependence experiments, they might have been able to determine whether  $\text{NH}_4^+$  participates stoichiometrically (the expectation for mechanism 1), or catalytically (the expectation for mechanism 2). However, since  $\text{NH}_4^+$  must be the dominant species, can't one rule out an inimum intermediate mechanism anyway?*

*3) On p. 15549, starting on line 24, the authors entertain two possible rate-limiting steps: 1) the reaction of  $\text{NH}_4^+$  with methyl glyoxal, or 2) methylglyoxal self reaction. Again,  $\text{NH}_4^+$  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  $\text{NH}_4^+$  + 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.

Upon the reviewer's suggestion the discussion of the kinetics of the fast initial signal increase at 550 nm for high initial methylglyoxal concentrations has been eliminated. The  $\text{NH}_4^+$  dependence experiments taken together with our other kinetic data has shown that the reaction of  $\text{NH}_4^+$  with methylglyoxal is the rate-limiting step. This is discussed in detail in the revised manuscript.

We agree with the reviewer that  $\text{NH}_4^+$  would be the dominant species at the low pH values used in this study. The most likely point of participation of both  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  in the mechanism is the initial step when the carbonyl is protonated before attack by the enol. Our Aerosol-CIMS observations also suggest the formation of species containing C-N bonds in this reactive system. Two recent studies report the formation of C-N compounds by glyoxal when  $\text{NH}_4^+$  is present in the aqueous phase under acidic conditions (Nozière et al., 2009; Galloway et al., 2009), and both propose mechanisms

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involving ammonia and iminium intermediates. The low pH in this study will result in low equilibrium  $\text{NH}_3$  concentrations, but the protonation of a carbonyl by  $\text{NH}_4^+$  as proposed here and by Nozière et al. (2009) will result in the generation of a short-lived  $\text{NH}_3$  molecule proximal to the reaction site. Nozière et al. reported that the iminium pathway was active for glyoxal in ammonium-containing solutions down to pH 4.8 (the lowest pH studied).

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.*

The reviewer is correct, this sentence has been removed.

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  $\text{NH}_4\text{NO}_3$  solutions that had identical  $[\text{NH}_4^+]$  concentrations to see if the sulfate or nitrate counter ion has any effect.*

Upon the reviewer's suggestion, we have indicated the rationale behind our choice of salt concentrations in the experimental section of the revised manuscript. While our results have clearly shown that  $[\text{NH}_4^+]$ , not  $[\text{SO}_4^{2-}]$ , is the active species, studies of the effect of counter ion may be recommended for future studies.

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

Aqueous methylglyoxal solutions typically contain a small amount of pyruvic acid. Pyruvic acid, an oxidation product of methylglyoxal, is a relatively strong organic acid, with  $\text{pK}_a = 2.49$ . Therefore, the fact that our stock solution is pH =2 corresponds to a very small (0.07%) impurity of pyruvic acid in the methylglyoxal stock solution.

More accurate pH measurements were used to confirm the pH values previously mea-

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sured using pH paper, and as mentioned, additional experiments were performed in order to characterize the effect of pH on the kinetics of formation of light-absorbing compounds.

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 use the calculated wavelengths to distinguish between two species with wavelengths that differ by only 30 nm?*

We thank the reviewer for this helpful observation. Our calculations were made for gas-phase molecules. Meller et al. (1991) reported that gas-phase methylglyoxal has an absorption peak at 280 nm. Our B3LYP/ccpvtz(-f) calculations predict that gas-phase, unhydrated methylglyoxal has an absorption peak at 291.1 nm. Therefore we estimate that our predictions for these molecules in the absence of solvent effects are accurate to within 12 nm.

Further deviation between the theoretical results (which were for gas-phase molecules) and experiment may result from solvent effects. The  $n$  to  $\pi^*$  excitation band which appears at 290 nm and is characteristic of carbonyl compounds is known to shift toward lower wavelengths for a molecule in aqueous solvent compared to the gas phase (Skoog et al., 1997). For acetone this shift is approximately 12 nm, and for crotonaldehyde the shift is 30 nm (Bayliss and McRae, 1954) (note that aqueous methylglyoxal solutions will contain a mixture of mono- and di-hydrated methylglyoxal, aldol condensation products, and hemiacetal oligomers (Krizner et al., 2009), so it is less straightforward to map the observed spectrum of aqueous methylglyoxal to the gas-phase absorbance of a single molecule for purposes of this discussion). Therefore, we can provide a rough estimate of (-12 nm, +42 nm) for the error range of our predicted absorbances compared to the observed aqueous-phase spectra. Solvent effects due to the presence of ions in the solution could extend this range.

As the reviewer suggests, based on our error estimate in the theoretical calculations

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(discussed above), the difference is not enough to rule out product (h) as the absorber. We have modified the discussion accordingly to read: "Our observation of increasing absorbance at 286 nm with time indicates a shift in equilibrium towards species predicted to absorb near that wavelength. As described in section 3.1, we estimate the error range of our theoretically predicted absorbances compared to the observed aqueous-phase spectra to be roughly (-12 nm, +42 nm). Therefore the absorbance band at 286 nm could correspond to a species predicted to absorb within the range  $274 \text{ nm} < \lambda < 328 \text{ nm}$ . Species which lie within this range include the pathway (2) aldol addition product species (h), which is predicted to absorb at 320 nm. Given the approximate nature of this error estimate the possible range may be extended to include species (c), which is the aldol condensation product corresponding to species (f) ( $\lambda_{\text{predicted}} = 271.1$ )."

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.*

We thank the reviewer for bringing this to our attention. We have changed the discussion of the baseline shift in our manuscript to include the possibility of a bulk optical effect, and removed the kinetic analysis.

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.*

We have added the following passage to the revised manuscript:

To our knowledge, the concentrations of the methylglyoxal reaction products we have

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proposed here have not been measured in atmospheric aerosol samples. Kawamura and coworkers have measured methylglyoxal monomer and related compounds (glyoxal, ketocarboxylic acids, and dicarboxylic acids) in ambient aerosols (Sempere and Kawamura, 1994; Kawamura et al., 1996; Kawamura and Yasui, 2005; Ho et al., 2007; Kundu et al., 2009). Methylglyoxal was found to comprise roughly 0.005-0.05% of aerosol mass in urban environments (Kawamura and Yasui, 2005; Ho et al., 2007). However, since methylglyoxal is highly reactive, this value underestimates the total methylglyoxal taken up by the particles. Assuming that all pyruvic acid, glyoxylic acid, and oxalic acid in the aerosol was formed via methylglyoxal oxidation (Carlton et al., 2006) provides a rough upper bound for methylglyoxal uptake of 2% of aerosol mass (Kawamura and Yasui, 2005; Ho et al., 2007). Assuming a particle density of  $1 \text{ g cm}^{-3}$  this corresponds to an in-particle initial methylglyoxal concentration range of 0.7 mM to 0.28 M.

A typical ammonium sulfate concentration in an aqueous atmospheric aerosol particle at 60% RH is 65 wt% (Tang and Munkelwitz, 1994), or 14 M, with  $0 \leq \text{pH} \leq 5$  (Keene et al., 2004) (Zhang et al., 2007), resulting in pseudo-first-order rate coefficients of  $k_A^I = 1.4 \times 10^{-4} \text{ min}^{-1}$  and  $10^{-8} \text{ min}^{-1} \leq k_B^I \leq 10^{-3} \text{ min}^{-1}$  for the loss of methylglyoxal through reaction with  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$ , respectively. Given a lower-bound aerosol-phase methylglyoxal content of 0.7 mM, this corresponds to a production rate of  $10^{-7} \text{ M min}^{-1}$  (at  $\text{pH} = 5$ ) to  $8 \times 10^{-7} \text{ M min}^{-1}$  (at  $\text{pH} = 0$ ). Based on our reaction model this corresponds to 0.07 to 0.6 mM of light-absorbing products formed after 12 hours (up to 43% conversion of methylglyoxal to products).

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