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Atmospheric
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Discussions

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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We thank Reviewer 1 for his or her insightful and helpful comments. We respond to specific comments below.

The authors provide helpful comparisons with computational results in an attempt to interpret the absorbance spectra. These comparisons would be more meaningful if there were some discussion of their expected accuracy.

We thank the reviewer for this helpful observation. Our calculations were made for gas-

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Interactive Discussion

Discussion Paper

phase molecules. Meller et al. (1991) reported that gas-phase methylglyoxal has an absorption peak at 280 nm. Our B3LYP/ccptvz(-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 $\sim$12 nm.

Further deviation between the theoretical results (which were for gas-phase molecules) and experiment may result from solvent effects. The n to π^* excitation band which appears at $\sim$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 $\sim$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.

We have included this passage in Section 3.1 and expanded the discussion of the UV-Vis results accordingly.

The observation of a temporarily high baseline upon mixing methylglyoxal and ammonium sulfate solutions (Fig 1B) is attributed to the fast formation of an intermediate. However, I cannot imagine any chemical compound, much less a methylglyoxal dimer, that would have essentially flat (featureless), high absorbance at every wavelength above 500 mn. Furthermore, the temporary existence of such a strong absorber would likely be incompatible with the observation that the mixture turned darker with time. Baseline shifts are usually caused instead by optical / physical processes such as changes in solution density, temperature, and/or refractive index.

We thank the reviewer for pointing out this issue. We have changed the discussion to include the possibility that this observed signal change is a baseline shift cause by a transient change in bulk optical properties.

There are some issues regarding pH that should be addressed to maximize the usefulness of this work to the community. First, why does a methylglyoxal stock solution have a pH = 2? One would not expect methylglyoxal to be particularly acidic, so this low pH suggests that impurities are present. Can the authors identify likely acids present, and can they rule out that they are affecting their results (beyond lowering the pH)?

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 pKa = 2.49. Therefore, the fact that our stock solution is pH =2 corresponds to a very small (0.07%) impurity of pyruvic acid.

Second, since the proposed reactions (aldol condensation and imine formation) are both highly pH dependent, running all experiments at pH = 2 limits the applicability of the results. Is it possible to check the formation of light-absorbing products at other atmospherically relevant pHs, for example?

Upon the reviewer's suggestion we performed further studies of the formation of light-absorbing products as a function of pH. Results and discussion of these experiments are included in the revised manuscript.

Finally, the authors point out once that the concentration of imine-substituted species should be low because their formation requires an ammonia molecule, whose existence is rare at pH 2. However, in several other places they postulate imine intermediates and C-N bond formation. This is confusing. Can the authors clearly and convincingly state their preferred explanation for how ammonium salts promote the formation of light-absorbing products?

We also performed additional studies of the dependence of the rate of formation of

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Interactive Discussion

Discussion Paper

light-absorbing products on initial NH_4^+ concentration. The NH_4^+ dependence experiments taken together with our other kinetic data has shown that the reaction of NH_4^+ with methylglyoxal is the rate-limiting step. This is discussed in detail in the revised manuscript. The most likely point of participation of both NH_4^+ and H_3O^+ in the mechanism is the initial step when the carbonyl is protonated before attack by the enol.

Our Aerosol-CIMS observations (included in the revised manuscript) 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 NH_4^+ is present in the aqueous phase under acidic conditions (Noziere et al., 2009;Galloway et al., 2009), and both propose mechanisms involving ammonia and iminium intermediates. The low pH in this study will result in low equilibrium NH3 concentrations, but the protonation of a carbonyl by NH_4^+ as proposed here and by Nozière et al. (2009b) will result in the generation of a short-lived NH3 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).

Detailed comments. p. 15542 line 6: Is the ammonium ion or ammonia involved? If it is the ammonium ion, what is the mechanism?

Please see our response to your general comment above.

p. 15543 line 8: The recent work of Galloway et al (2009) should also be cited here.

We did not cite Galloway et al. (2009) at this point in the manuscript because the discussion here was solely on light-absorbing compounds, which were not studied within the Galloway work. We cite Galloway et al. (2009) in other relevant sections within the manuscript.

p. 15543 line 20: Zhao (2006) measured non-zero methylglyoxal uptake onto aqueous surfaces in a flow tube, and should be cited here.

The citation has been added.

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p. 15544 eq 1: The variable g should also be identified. Acceleration due to gravity?

The variable *g* is now identified within the manuscript as the acceleration due to gravity.

p. 15547 line 23: It is not clear what is being alluded to in the Altieri reference. They used oxidants. Is this a valid comparison?

We agree with the reviewer that the comparison is not entirely accurate. The citation has been removed.

p. 15548 line 1: Technically, ammonia (rather than the ammonium ion) is required to form an imine.

Yes, the reviewer is correct. The description of the mechanism has been revised along the lines of our response to your general comment above.

p. 15548 line 18: Ketone moieties can form enols (Aldol pathway 2), so such a group need not be "terminal" in terms of oligomerization.

We thank the reviewer for bringing this unclear language in the manuscript to our attention. This passage has been reworded for clarification in the revised manuscript as follows: "Aldol addition via pathway (1) is likely to terminate after dimer or trimer formation due to the formation of organic acid or ketone end groups (e.g. species (c)-(g), Table 1). It is not energetically favorable for aldol addition at ketone end groups to continue via pathway 1 due to steric hindrance from the methyl group. Instead, these ketones may form an enol and follow pathway (2) for continuing aldol addition. . .."

p. 15549 line 15: An equilibrium shift to unhydrated methylglyoxal as the reaction progresses does not make sense.

We thank the reviewer for correctly pointing this out. We have eliminated that passage from the discussion.

p. 15549 line 18: The text mentions that product (h) absorbs at 320 nm, compared to the observed band at 286 nm. Is this difference enough to rule out product (h) as the

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Interactive Discussion

Discussion Paper

absorber?

As the reviewer suggests, based on our error estimate in the theoretical calculations (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 nm $< \lambda <$ 328 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) ($\lambda_{predicted}$ = 271.1)."

The following four comments are answered jointly below:

p. 15549 line: This inference is likely false, for reasons stated above. No plausible dimer structure can explain the observed featureless spectrum. I do not recommend a kinetic analysis based on a shifting baseline.

p. 15550 eq 3: I cannot determine where the "2" in "2kt" comes from. The point is moot if this kinetic analysis is dropped. The rest of the equation makes sense based on my derivation.

p. 15550 line 9: What is the basis of the assumption that 90consumed to form the intermediate? (Again, a moot point if this analysis is dropped.)

p. 15550 line 15: It should be made clear that the product P2 cannot be formed from the intermediate P1 (were P1 to exist), based on the incompatibility of its steady production compared to the brief appearance of P1.

In agreement with the reviewer, we have removed this kinetic analysis of the initial baseline shift.

p. 15551 line 20. Some context is necessary for these extinction coefficients and absorption indices. Would the products at expected concentrations contribute significantly to observed levels of light absorption by atmospheric aerosol?

We agree with the reviewer that more atmospheric context was needed here. We estimated the production rate of light-absorbing products from methylglyoxal in atmospheric aerosols (details of the calculation are given in the revised manuscript) and revised the passage to read: “These results add to the growing body of evidence that SOA formation and aging may be a source of “brown carbon” in atmospheric aerosols. Brown carbon, including the products observed here, does not absorb as strongly as black carbon at high wavelengths (550 nm and higher) and therefore its contribution to aerosol absorption in this range may be minor in comparison (Andreae and Gelencser, 2006). However, the absorption of UV radiation by brown carbon has the potential to reduce tropospheric O3 levels (Jacobson, 1999; Jacobson, 2002). Based on our calculated molar absorptivity of $\epsilon_{282} \geq$ 4938 Lmol^{-1}cm^{-1} and our estimated production rate of 0.07 to 0.6 mM products formed after 12 hours, we estimate that the contribution to the dimensionless absorption coefficient at 282 nm from methylglyoxal reaction products is $A_{282,MG} = \lambda\epsilon_{282}/4\pi \sim 10^{-6}$.”

p. 15552 line 5: Methylglyoxal concentrations in excess of 1 M are required to reach the surface tension depression levels described. How does this compare with measured and/or expected methylglyoxal concentrations in atmospheric aerosol?

To our knowledge, the concentrations of the methylglyoxal reaction products we have 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 (Kawamura et al., 1996; Kawamura and Yasui, 2005; Ho et al., 2007; Sempere and Kawamura, 1994;

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Interactive Discussion
Discussion Paper

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 g cm^{-3} this corresponds to an in-particle initial methylglyoxal concentration range of 0.7 mM to 0.28 M.

Since both methylglyoxal and its reaction products are surface-active, the relevant concentration for estimating particle surface tension is the total methylglyoxal uptake. However we also note that the relevant surface tension is that of the droplet at the moment of activation, at which point the surfactant concentration will be lower than that in the aqueous aerosol at lower relative humidities, especially for larger particles. Therefore, using 0.28 M methylglyoxal as an upper bound, we estimate a lower bound of $\sigma/\sigma_w >$ 0.67, which corresponds to a critical supersaturation as low as 54% that of a particle with $\sigma = \sigma_w$. CCN activation measurements are planned in order to confirm this effect.

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