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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 #1

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This paper describes UV-Vis absorbance and pendant drop tensiometry measurements on bulk aqueous solutions containing methylglyoxal and various salts intended to simulate atmospheric aerosol. This is a system of high interest to the atmospheric chemistry community since methylglyoxal may be capable of producing significant amounts of secondary organic aerosol. Two important conclusions are drawn. First, like glyoxal, methylglyoxal forms light-absorbing products in the presence of ammonium-containing salts. Second, unlike glyoxal, methylglyoxal lowers the surface tension of aqueous droplets, an effect that can increase the CCN activity of atmo-

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Discussion Paper



Interactive
Comment

spheric aerosol. The surface tension lowering increases similarly in the presence of the salts NaCl and $(\text{NH}_4)_2\text{SO}_4$. The authors point out that any products formed by chemical reactions between methylglyoxal and $(\text{NH}_4)_2\text{SO}_4$ are evidently not having a significant impact on the overall surface tension lowering.

Few other conclusions can be made, since neither of the experimental methods have much chemical specificity. 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. In the end it is not clear that any particular structure, or even class of structures, is responsible for a particular absorbance band.

Some rate constant upper limits are pulled from time-dependent absorbance data, but their usefulness is marginal because the identity of the detected absorbers and even the overall kinetic scheme remain a mystery. 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 nm. 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.

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 $\text{pH} = 2$? 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)? Second, since the proposed reactions (aldol condensation and imine formation) are both highly pH dependent, running all experiments at $\text{pH} = 2$ limits the applicability of the results. Is

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it possible to check the formation of light-absorbing products at other atmospherically relevant pHs, for example? 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?

Detailed comments.

- p. 15542 line 6: Is the ammonium ion or ammonia involved? If it is the ammonium ion, what is the mechanism?
- p. 15543 line 8: The recent work of Galloway et al (2009) should also be cited here.
- p. 15543 line 20: Zhao (2006) measured non-zero methylglyoxal uptake onto aqueous surfaces in a flow tube, and should be cited here.
- p. 15544 eq 1: The variable g should also be identified. 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?
- p. 15548 line 1: Technically, ammonia (rather than the ammonium ion) is required to form an imine.
- p. 15548 line 18: Ketone moieties can form enols (Aldol pathway 2), so such a group need not be “terminal” in terms of oligomerization.
- p. 15549 line 15: An equilibrium shift to unhydrated methylglyoxal as the reaction progresses does not make sense.
- 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 absorber?

Interactive
Comment

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 90% of the monomer is consumed 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.

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?

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15541, 2009.

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