

Interactive comment on “The optical, physical and chemical properties of the products of glyoxal uptake on ammonium sulfate seed aerosols” by M. Trainic et al.

Anonymous Referee #2

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This manuscript presents the changes in optical properties, chemical composition, reactivity and particle size of (effloresced) ammonium sulphate seed aerosol resulting from uptake of gas-phase glyoxal and subsequent aerosol-phase reactions. The study presents very interesting results, especially on the effect of relative humidity and aerosol seed diameter. The work is timely, and the manuscript is suitable for ACP after addressing the following comments.

My overall comment is that it would be helpful to make clearer what the phase-state, i.e. effloresced or deliquesced, of aerosol in this and other studies was, especially when results are compared. In particular, many other studies (Liggio et al., 2005, Volkamer

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et al., 2009, Kroll et al., 2005) discuss uptake on deliquesced aerosol and some have found that uptake scales with liquid water content (in particular Volkamer et al., 2009 as well as Liggio et al., 2005 after taking the effect of acidity into account). However, Corrigan et al. (2008) found uptake on dry aerosol, as did this study. I believe that the question of uptake on dry versus liquid aerosol and both of these as a function of RH is central to the manuscript and a very important aspect for SOA formation. This manuscript presents important contributions to this aspect. The individual comments below mainly address different aspects of this major point.

1. It would be useful to state very clearly that the experiments presented in this work are largely on effloresced seed particles, unless I misunderstood. The work that it is directly compared to, is, from my reading of the papers, largely for deliquesced particles. Specifically, in my opinion, this should be stated/made clear (a) in the abstract, (b) in section 2.1 and (c) in the comparison of Table 3 (e.g. at 50% RH).
2. It would be beneficial for the manuscript (and the community) if the authors in the introduction briefly summarized what effect of RH on glyoxal uptake was found for liquid aerosol by previous studies and the same for dry aerosol.
3. It would be helpful to clarify the following point: The authors state (e.g. at P. 19238 lines 10-19 and other places) that (a) lower water content speeds up the observed reactions, and (at P. 19236 L. 28-P19237 L. 6) that (b) higher water content enhances imidazole formation. These two statements, at the surface, appear contradictory, and it should be made clear in statement (a) how statement (b) fits into this, in particular if the imidazoles or similar compounds give rise to the enhanced optical activity.
4. The work of DeHaan et al., 2011 shows that the drying process itself greatly accelerates the formation of carbon-nitrogen compounds. One critical question, which the DeHaan et al. work raises with respect to the work presented here, is, to what degree the actual drying of the aerosol could have resulted in the observed behaviour in this work. In my opinion a control experiment using the AMS without drying the aerosol is

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important to ensure that the observed behaviour did not result from the drying process, i.e. the dryer used directly before sampling by SMPS or AMS.

5. The work of Corrigan et al., 2008 deserves more discussion, as it explicitly states the hypothesis of the role of water limitation and surface water driving reactions.

6. P. 19235, lines 14-18. A comparison is made between HULIS and the results obtained here. Are the authors implying that the chromophores for the glyoxal/ammonium sulfate system are similar to HULIS? Glyoxal acetal oligomers do not have any chromophores in the 355 nm range, aldol condensation is highly unlikely and the carbon-nitrogen compounds are the most likely carriers of the enhancement of optical activity. Does this imply that HULIS also has carbon-nitrogen compounds as chromophores? If not, the statement of similarity between HULIS and the system studied here should perhaps be phrased more carefully.

7. P. 19236 L. 28-P19237 L. 6. I think it would be helpful to make clear whether higher liquid water content enhances the absolute yield or rate of imidazole formation or only relative to oligomers, but not the absolute values. The reaction shown by Galloway et al., 2009, requires two ammonium and two glyoxal molecules. My guess would have been that going to dilute conditions (i.e. higher liquid water content, such as cloud processing) slows the rates down considerably.

Technical Comments:

P. 19225, Line. 13-14. "Aging occurs via oxidation reactions by abundant radicals. . . , as well as by gaseous organic oxidants, such as gas-phase glyoxal," Glyoxal is not really an oxidant. Do the authors mean VOC oxidation product?

P. 19226, Line 15-16: In my opinion it would be useful to reference the primary sources on the rural measurements in Fu et al. as the two Fu et al. papers present the results of glyoxal modelling studies. An additional rural measurements is given in Huisman et al., ACPD 11, 13655-13691, 2011.

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P. 19228, Line 10-12: The statement "reaction of glyoxal with ammonia is induced by hydration of the ammonium ion" confused me. I looked up the mentioned mechanism and it appears to start with a deprotonation of the ammonium ion.

P. 19229, line 10: As RH plays such a central role. What is the RH before entry to the nafion humidifier?

P. 19229, lines 15- 20: What is the RH of aerosol before entering the SMPS and AMS?

P. 19231, Line 12-13: There are earlier references for glyoxal preparation (Harries, C. et al., 1907 and Steacie, E. W. R. et al., 1935) and more recently Volkamer et al., 2005. However, I believe only one or two are necessary rather than the large number already listed and listing one early one could be useful.

P. 19233, Line 11: Typo: obsreve

Figure 2a should have uncertainties/error bars

References:

Corrigan, A.L., Hanley, S.W., DeHaan, D.O., Uptake of Glyoxal by Organic and Inorganic Aerosol, Environ. Sci. Techn. 4428-4433 (2008).

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Galloway, M.M., Chhabra, P.S., Chan, A.W.H., Surratt, J.D., Flagan, R.C., Seinfeld, J.H., Keutsch F.N., Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331 (2009).

Harries, C., Temme, P., Uber monomolekulares und trimolekulares Glyoxal, Berichte der deutschen chemischen Gesellschaft 40, 165-172 (1907).

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Kroll, J.H., Ng, N.L., Murphy, S.M., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, 110, D23207, 10.1029/2005JD006004 (2005).

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Steacie, E.W.R., Hatcher, W.H., Horwood, J.F., The Kinetics of the Decomposition of Gaseous Glyoxal, *J. Chem. Phys.* 3, 291-295 (1935).

Volkamer, R., Spietz, P., Burrows, J., Platt, U., High-resolution absorption cross-section of glyoxal in the UV-vis and IR spectral ranges, *J. Photochem. Photobio. A* 172, 35-46 (2005).

Volkamer, R., Ziemann, P.J., Molina, M.J. Secondary Organic Aerosol Formation from Acetylene (C₂H₂): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, *Atmos. Chem. Phys.* 9, 1907-1928 (2009).

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 19223, 2011.