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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.

M. Trainic et al.

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Reply to referee #2:

We thank the Reviewer for the positive review of our paper, for the thoughtful comments and for raising the issue of the state of the aerosol. The corrections and replies to all the issues are given below, each of the comments is followed by our reply (highlighted in bold letters).

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 parti-

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cles. 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).

From the literature it seems that Galloway et al. 2009 conducted their study at 50% RH with a hydration system and not dehydration, so their particles were hydrated. The particles we worked with were dry particles going through a hydration process, and consequently dried for the final analysis. Galloway et al. also measured the particle mass after drying, therefore the two studies can be compared. Therefore we adopt the suggestion by the Reviewer and we now clarify the fact that the process we are describing is one of hydration followed by efflorescence before analysis. Thank you for bringing this point to our attention.

(a) Line 5 page 19224 has been changed to: ‘Our experiments imitate an atmospheric scenario of particle hydration at ambient RH conditions in the presence of glyoxal gas followed by efflorescence due to decrease of the prevalent RH. The reactions were studied under different relative humidity (RH) conditions, starting from dry conditions (~20% RH) and using a hydration process to reach up to 90% RH, covering conditions prevalent in many atmospheric environments, and followed by consequent drying of the reacted particles before their analysis by the CRD and SMPS systems.’ (b) Line 5 page 19229 describes the entire process: ‘...after which the nearly monodisperse aerosol flow is directed into a humidification stage consisting of a nafion humidifier with a temperature controlled bath. This setup allows the RH of the aerosol flow to be controlled by varying the bath temperature. The hydrated aerosol flow enters a 30L reaction vessel into which gas phase glyoxal is introduced. The residence time of the particles with the gaseous glyoxal is approximately 1 hour, after which the aerosol population is dried by two additional silica gel diffusion dryer columns’ (c) Line 10 page 19238 was changed to: ‘Our experiments were conducted for the hydration process of AS aerosols (i.e. while increasing the RH), followed by drying and consequent efflorescence of the reacted particles.’ In addition, we changed line 22 page 19238 to: ‘Due to reaction on hydrated AS particles followed by drying and efflorescence, there is forma-

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tion of secondary organic material composed of glyoxal oligomers and C-N containing products that result in particle growth.'

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.

Previous studies did not provide the dependence of the reaction on RH. Since they did not restrict the conditions of the reaction, such as initial particle size or volume when changing the RH, there is no basis for comparison. Therefore, this is the first study which provides information on RH dependence of the reaction. For this purpose, we used the same initial monodisperse particle size distribution while changing only the RH in the system. By only changing this variable and keeping all the rest constant, we obtained the effect of RH. This is explained in the introduction.

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.

Thank you for the comment. Both the glyoxal fragments and the C-N compounds show a decrease with increasing RH. However, the relative decrease in glyoxal products is larger than in C-N compounds. That is why the ratio between the C-N compounds and the glyoxal oligomers shows an opposite trend of increase with increasing RH values. Therefore, the relative contribution (and not the absolute value) of C-N compounds increases with increasing RH values. Following the comment we changed the text in Line 28 page 19236 for clarification to: 'There is an increase in the relative contribution of the absorbing C-N compounds compared to the glyoxal products with increasing RH values.'

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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 behavior in this work. In my opinion a control experiment using the AMS without drying the aerosol is important to ensure that the observed behavior did not result from the drying process, i.e. the dryer used directly before sampling by SMPS or AMS.

The observed behavior is a result of the process of a reaction occurring under hydrated conditions and the consequent drying. This entire process leads to our results, so the consequent drying after the reaction may have an effect of accelerating the reaction. However, the residence time of the particles in the dryers is very short (approximately 20 sec), and another 10 sec until they reach the CRD and SMPS systems, which may limit the effect of the drying process. However, we do not rule out that the drying process does play a part in the results. Therefore, the measurements describe an atmospheric condition of a hydrated aerosol reacting with glyoxal and then dried. Regarding the suggestion to conduct an experiment with the AMS using hydrated particles, since the particles in the AMS undergo fast drying it will not resolve the issue. This comment and the ones above are very important and we changed the description of the reaction in the sections you mentioned above accordingly.

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.

Since Corrigan et al. did not conduct experiments with ammonium sulfate seed aerosols we did not elaborate more on their work since we had no direct comparison with their experiments, and could not infer from their results any assumptions regarding the current study.

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

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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.

Thank you for the comment. HULIS is probably not a good choice for comparison. The sentence in P. 19235, lines 14-18 has been deleted.

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.

We agree with this statement, and have changed the explanation in line 28 page 19236 according to comment 3.

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?

We agree and therefore P. 19225, Line. 13-14 was changed to: 'as well as by reactive organic gases, such as glyoxal'

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.

Thank you. We changed the references accordingly.

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.

Agreed. The wording in P. 19228, Line 10-12 was changed accordingly, to: ‘Galloway et al. [2009] demonstrate that the reaction of glyoxal with ammonia is induced by the deprotonation of the ammonium ion in the AS particle by a water molecule, and leads to imidazole formation [Galloway et al., 2009]. ‘

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

It was measured to be ~15%.

P. 19229, lines 15- 20: What is the RH of aerosol before entering the SMPS and AMS? It was measured to be ~5%.

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.

Thank you. We changed the references accordingly.

P. 19233, Line 11: Typo: obsreve

Corrected.

Figure 2a should have uncertainties/error bars

Corrected.

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