

Interactive comment on “Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions” by M. M. Galloway et al.

Anonymous Referee #2

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General Comments:

This paper utilizes the results from laboratory chamber studies in an attempt to understand the uptake of glyoxal to ammonium sulphate seed aerosol in a qualitative sense. In particular, the authors highlight some interesting mechanistic pathways with respect to uptake of glyoxal such as imidazole and organosulfate formation. More importantly, they contrast the uptake of glyoxal during irradiated (without oxidants) and dark experiments, showing that they are distinctly different, while highlighting some unexplainable results. This paper certainly adds to our understanding of the uptake of alpha-dicarbonyls (and potentially others) to aerosols and is likely publishable after

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some revisions. However, some assertions are not fully backed up by evidence, and should be examined more closely or removed all together. That being said, the paper is fairly well written, concise and easy to understand. There are some general issues which should be addressed, and are discussed below.

Generally, there seems to be too few experiments actually conducted. According to Table 3 there were only 3 experiments performed, although the authors appear to refer to quite a few more. If there are more they should all be included in Table 3. If truly there were only 3 experiments done, then drawing any conclusions from these is not easily done. The authors should be clear on how many were actually conducted, as 3 is not enough in my view to warrant publication.

The authors state in the introduction (20804, line 4) that they aim to determine the relative contribution of the 'individual processes'. Do they mean in a quantitative sense? If so, they do not do this in the paper. They do show that there are a number of processes occurring all at the same time but there is no attempt to determine a relative contribution from these to the total, or at least it is not clear. Given that they have W-mode AMS data it may be somewhat possible, based on the different temporal profiles of various m/z 's and the results of dilution.

This paper asserts that there is a reversible mechanism which they probe by diluting the chamber. To me, it is not clear from their results how important this equilibrium really is or if it is happening at all. Firstly, the equilibrium is only achieved after about 10 hrs. This is quite a long time. For the purpose of the atmosphere, 10hrs is a long enough time that perhaps this so-called reversibility can be considered irreversible. What is more important is how quickly this equilibrium is re-established after being perturbed (ie: relaxation time). From Figure 5 it looks like it takes a long time for equilibrium to be re-established. This is important, in relation to other atmospheric processes.

Furthermore, why are only 25-40% of the organics lost to the gas phase? In essence what is the dilution factor that was used? The authors should be able to calculate what

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the gas phase glyoxal concentration is after dilution and compare the organics at this GL value to that before dilution. They may even have GL values (ppb) before and after dilution in some experiments that are near equivalent. In that case are the organics in these situations the same (ie: diluted GL at some ppb vs undiluted GL in a different experiment at the same ppb level)? The question here is does 25-40% make sense based on the dilution used? It would seem that 25% is not enough material lost, but one cannot assess this without knowing the dilution factors and the measured or calculated gas phase glyoxal. These numbers should be put into Table 3. Based on how much organics are lost in figure 5 vs how much might be expected based on dilution, the authors should have an idea of how important a reversible mechanism really is. (ie: is it fully reversible? Partially reversible?).

Perhaps more puzzling is the fact that the authors state that the walls of the chamber are a source of glyoxal on its own, resulting in a steady state gas phase concentration during experiments. If that is the case, then it should be a very fast equilibrium based on adsorption, or at least much faster than any equilibrium observed during the experiments (ie: 10hrs). In this case, dilution should only perturb the gas phase for a very short time before it is at equilibrium with the walls again. Under these conditions why would the uptake to aerosols be reversible at all since you have essentially not changed the gas phase GL concentration, especially over such a long time scale? In order to answer this question we need to see the glyoxal concentration as a function of time before and after dilution. Presumably it was measured, and so should be included. If the gas phase is constant (as might be expected) then what is driving the loss of material from the aerosol phase? Essentially the authors have not shown that there truly is a reversible process occurring. This needs to be cleared up in the paper significantly or removed, since the qualitative identification of imidazoles and organosulfates as well as light vs dark experiments might be enough for a paper.

There is also the issue of using high gas phase concentrations in the first place. Although Henry's law should apply at higher concentrations, it is not clear if irreversible

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Comment

reactions of some sort are second order in the liquid phase. Therefore higher order products may only be observed at the high liquid phase concentrations of these experiments and probably not relevant to the atmosphere. This should be discussed in the paper. The same argument could be made for the high seed concentrations. In this regard, the initial seed concentration ($\mu\text{g}/\text{m}^3$) should be included in table 3, as well as final organic/ SO_4 fractions.

The authors state that the GL-sulphate under irradiated conditions is likely due to organic acid catalysis. There is no evidence of this in their experiments, and in fact is likely not correct. The formation of organosulphates under strongly inorganic acidic conditions (H_2SO_4) has been observed (Minerath et al, 2008) but only under these strong acid conditions (>50 wt%). Weak organic acids probably don't provide enough acidity on their own. If this were true, then dark experiments would also yield organosulphates with acidic inorganic seed. In fact, it would be nice if the authors had done such an experiment as confirmation.

The authors also state that there is evidence that the aerosols are oxidized under irradiated conditions, based mostly on m/z 44. Oxidation implies the addition of oxygen from some oxidant. Since they did not add any oxidants, where is this extra oxygen coming from? In order to oxidize anything one needs an oxidizing agent. It is not clear what that might be here. Since they have the W-mode AMS data they should calculate the O/C ratio to determine if they truly are oxidizing anything. It is possible that photolysis of glyoxal is producing radicals which participate in some very complicated chemistry, but even so, that is not a source of extra oxygen. Some discussion of this should be included, but as a first step O/C should be calculated.

More specific Comments:

Pg 20808, line 6: Figure 4b is not a blank in this case.

Pg 20810, lines 10-12: It is not clear what the authors are trying to say here. What does photo-chemistry have to do with acid catalysis?

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Pg 20811, line24: 'judged' , do you mean 'as measured' by the AMS?

Pg 20813, lines 10-14: It is not entirely clear from figure 5 that it is not linear before 4 hrs. Certainly it looks linear before about 2 hrs. The data in the figures from Liggio et al., are quite a bit noisier, so it is difficult to say what kind of curvature exists there.

Pg 20813, line 25: since the authors abruptly shift to discussing henry's law calculations there should be some sort of sub-heading here.

Pg 20815, lines 1-10: The density of the commercially available glyoxal trimer by my recollection is less than 2.14. Hence the density used in the calculated (1.94) is probably too high. Also, the entire volume of the particle may not be aqueous. I agree with the previous reviewer in that the authors could calculate the water content.

Pg 20818, line 3: 'high' should be 'low' ie: more acidic

Table 3: As noted previously, include all experiments, which ones were dark?, what was the seed aerosol mass? Etc.

Figure 5: Clearly state in the caption what 'a' and 'b' show. Also show at what point dilution occurred in the experiment.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20799, 2008.

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