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Atmospheric
Chemistry
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Discussions

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.

M. M. Galloway et al.

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The authors would like to thank this reviewer for their careful review and helpful comments and suggestions to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. The referee's comments are listed in italics, followed by the authors' responses.

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.*

There were more experiments conducted, and they will be added to Table 3, along with more information on the experiments currently in the table.

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.

We are following the reviewer's helpful advice, and are analyzing the W-mode AMS data to explore the individual processes occurring within the aerosol and strengthen this aspect of the paper. We will add our findings to the final version of the paper. We have a standard for the 1H-imidazole-2-carboxaldehyde and have synthesized an organosulphate standard and are awaiting analytical results.

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, 10 hrs 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.

As the referee correctly points out, reversibility is often a question of timescale. 10 hours can be a long time on atmospheric timescales. However, atmospheric aerosols have a lifetime of several days, so the reversibility observed here can become important over long time periods. Production of gas phase glyoxal generally decreases rapidly

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after sunset and concentrations decrease rapidly. This time period (∼8-14 hours) is comparable to the equilibration time in this study. Another example is transport away from a pollution source. As an air mass moves into an area with low gas phase glyoxal concentrations, reversibility can have an effect on concentrations within the aerosol. In addition, temperature increases can occur rapidly, potentially repartitioning glyoxal to the gas phase. It should however be kept in mind that if photochemical processing in the aerosol phase is rapid, the importance of reversibility of (unreacted) glyoxal could be reduced.

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 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 asses 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 that 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

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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.

We will add the glyoxal gas phase concentrations during the dilution experiments to Fig. 5, and will change the wording in the text to be clearer about our observations. Figure 9 shows that the organic mass in the aerosol at equilibrium depends linearly on gas-phase glyoxal concentration (Henry8217;s law). In order for glyoxal uptake to be reversible, Henry8217;s Law thus requires that a reduction in gas phase concentrations be reflected proportionally in the condensed phase. In our experiments, gas phase glyoxal was reduced by 25–40% during dilution, as the chamber walls present a large, but limited, reservoir of glyoxal. As would be expected for a reversible system, the 30% decrease in condensed phase glyoxal is proportional to this drop in gas phase glyoxal.

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 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 $(\mathrm{ug}/\mathrm{m}^3)$ *should be included in table 3, as well as final organic/*SO_4 *fractions.*

The referee's point is well taken. The concentrations are high and the formation of 1H-imidazole-2-carboxaldehyde requires two glyoxal molecules. Therefore, under atmospheric conditions, this product will be formed in lower yields. However, the imi-

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dazole reaction proceeds efficiently with just one glyoxal (or any other α-dicarbonyl), one aldehyde species (formaldehyde is often used in synthetic organic chemistry) and ammonium sulfate. Thus this type of reaction, not necessarily the specific product reported here, can be atmospherically relevant.

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 (H2SO4) 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 referee's comment is on point, and, we have in fact since proven that glyoxal sulphate formation under irradiated conditions is due to a (unknown) photochemical mechanism. In our original draft, we believed that there was less of a foundation for photochemical processing than for organic acid catalysis, as acid catalysis has been proposed as a sulfate ester formation mechanism. Our recent studies show that organosulphates do not form even in the presence of very acidic (pH 1) ammonium sulphate/sulphuric acid aerosol. These experiments will be presented in Table 3 and discussed in the final version of our paper.

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

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should be included, but as a first step O/C should be calculated.

We thank the referee for this helpful comment and have analyzed our data accordingly. During the irradiated experiments, the N:C and H:C ratios increase while the O:C ratio decreases, even as the contribution of *m/z* 44 increases to just under 6%of the total organic aerosol mass. The AMS data also show that glyoxal, which has an O:C ratio of 1:1, is re-volatilized (likely because the chamber temperature increases by 5-10C), and that the imidazole (O:C=0.25, N:C=0.5 and H:C=1) is not re-volatilized. We also believe that the higher molecular weight ester products (giving *m/z* 44) remain in the aerosol. The net effective likely explains the observed trends in the above ratios. The increasing *m/z* 44) and observation of organic acids (via filter sample analysis) demonstrate that some oxidation process is present although no OH source was added during the irradiated experiments.

More specific Comments:

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

This has been fixed, and now states that it is an experiment in the absence of light.

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?

We intended to state that given that organic acids were observed and that acid catalysis had been proposed previously for sulfate ester formation, the acid catalysis via organic acids was a more plausible mechanism than a speculative photochemical mechanism. Our studies since have revised this (see reply on previous page).

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

Yes, and this has been fixed

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

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al., are quite a bit noisier, so it is difficult to say what kind of curvature exists there.

One close inspection non-linearity is clearly observable after ca. 2 hours, but the referee is correct that non-linearity cannot clearly be identified for the first two hours. We will revise our description accordingly.

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

This will be included in the final version

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.

Please see the reply to the comment by Referee #1.

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

We were not able to find this.

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

The table will list all experiments and include irradiation information as well as other data.

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

This will be fixed and the figure will be revised.

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

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