**Atmospheric
Chemistry
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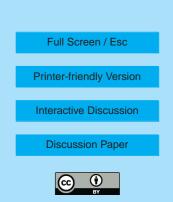Discussions**

Interactive
Comment

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.

The most surprising result is the AMS detection of the irreversible production of small amounts of C-N-containing molecules. The only nitrogen source in the experiment is the AS aerosol itself, suggesting a direct reaction between glyoxal and particle-phase ammonia. The authors do not directly address whether the rate of this reaction is enhanced by irradiation, but note that the C-N products are seen both in the dark and dur-

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ing irradiation. The authors hypothesize that an imidazole derivative has formed based on a similar, known glyoxal + ammonia + formaldehyde reaction. While the product exact mass (and therefore formula) is confirmed by HR-ToF-AMS, the fragmentation pattern, which is often not structurally specific, is the only direct experimental evidence presented in support of this particular product structure. A bit more evidence would nail it.

We have confirmed the assignment of the specific imidazole via comparison of filter samples of the chamber experiments with a standard, which will be discussed in the final version of the paper.

Specific comments and questions:

There are two issues with the calculation of the Henry's law constant. The calculated glyoxal aerosol-phase density is far higher than the MSDS-reported density of the commercially available trimer, biasing the calculated Henry's law constants upward by almost a factor of 2. Secondly, the authors treat the entire aerosol volume as the aqueous phase. While this is likely the correct approach, the authors could report the water content of the aerosol (before glyoxal uptake, using Chak Chan's data, for example) in support.

We could not find a reference for an experimentally measured density of glyoxal oligomers, which is why we originally used the calculated densities. In response to the comments, the density of glyoxal trimer dihydrate (in our lab) and glyoxal aerosol derived from drying aerosolized glyoxal solutions (David De Haan, personal communication) have been measured. The densities were determined to be 1.67 g/cm^3 and 1.71 g/cm^3. We will use an averaged value of 1.69 g/cm^3 in our updated calculations in the final paper.

Following the suggestions of both reviewers, we will report the liquid water content of the aerosol in these studies.

On page 20815 line 21, the authors make the odd claim that the difference between the Henry's law constants measured in water and in AS aerosol is due to the low amount of water in AS aerosol. Doesn't Henry's law by definition normalize for the amount of water?

There is no evidence for phase separation of the glyoxal/ammonium sulphate/ water system and a recent paper by Shapiro et al. (2009) shows no effect of glyoxal on surface tension. Henry's Law normalizes for the volume of solution, not the amount of water in the solution. Therefore, in this work Henry's Law normalizes for the volume of water and ammonium sulphate and organics, not the amount of just the water in this solution. We will reword this statement to make our intended statement clearer, which was referring to the dependence of the Henry's law constant on sulfate. This dependence has since been published by Ip et al. (2009)

While the authors call the imidazole product non-volatile, they estimate the vapor pressure using an on-line calculator to be 1.43×10^3 Torr. This is at the high end of the "semi-volatile" range, certainly high for a particle-phase compound. Wouldn't partitioning theory predict that most of this imidazole would evaporate?

The referee is correct. However under the conditions of the aerosol (pH $\sim$ 4), essentially all of the imidazole will be protonated, thereby reducing the volatility of the compound. We will adjust our wording in the final version to clarify this.

It is not clear what additional information is provided by Figure 9b. Since 9a and 9b are graphical expressions of two different forms of the same equation, why wouldn't they produce similar values for KH?

We will remove one of these plots.

Technical corrections:

P20808 line 6: Figure 4b can't really be called a blank experiment.

This will be corrected in the final version.

Line 21: typo "wass"

Thank you. This has been corrected.

P20811: The peak at m/z 96 is referred to as a molecular ion, but how do the authors know that it is not a fragment of a larger molecule?

Since we have access to a standard of 1H-imidazole-2-carboxaldehyde, we have been able to verify the presence of this compound in the aerosol using the UPLC-HR-TOF-MS method. As this compound has the same fragmentation pattern as the *m/z* 96 ion, which has the same chemical formula as determined by the high-resolution AMS data, it is reasonable to assume that the latter is the molecular ion corresponding to 1H-imidazole-2-carboxaldehyde.

P20819 line 20. Without warning the text suddenly switches from discussing glyoxal reactions to discussing other aldehyde reactions with ammonia. The switch is confusing.

We will clarify this transition.

Table 3 should include the control experiments. Many more experiments seem to be described in the Experimental section than are listed here. This table should also show which experiments were irradiated.

This will be corrected in the final version.

The Fig 5 caption has a typo: the authors meant to refer to m/z 68 behaving differently than the others, not m/z 58, it appears.

Thank you. This has also been corrected.

References

Ip, H. S. S., Huang, X. H. H. and Yu, J. Z.: Effective henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, doi:10.1029/2008GL036212, 2009.

Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R. and McNeill, V. F.: Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, Atmos. Chem. Phys. Discuss., 9, 59-80, 2009.

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