Atmos. Chem. Phys. Discuss., 12, C550–C553, 2012
www.atmos-chem-phys-discuss.net/12/C550/2012/
© Author(s) 2012. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Identification and characterization of aging products in the glyoxal/ammonium sulfate system – implications for light-absorbing material in atmospheric aerosols" *by* C. J. Kampf et al.

Anonymous Referee #1

Received and published: 13 March 2012

This manuscript discusses reaction products of glyoxal in aerosol mimics, i.e., aqueous ammonium sulfate solutions, within the context of aerosol optical properties. The role of glyoxal for secondary organic aerosol formation, in particular via aqueous systems, and the optical properties of the resulting aerosol are a topic of intense current research. The manuscript adds chemical detail to the rapidly increasing understanding of the role of glyoxal in aerosol. In particular the determination of the 2,2'-biimidazole and its formation kinetics as well as observation of numerous low polarity compounds with absorptions in the near-UV visible range are valuable additions to previous work. The

manuscript discusses a timely topic and adds considerable detail to our understanding of chemical control of aerosol optical properties. Therefore, I recommend this article for publication in ACP after consideration of the following points.

1. The authors synthesized 2,2'-biimidazole (BI) via reaction of glyoxal and ammonia. This is in essence the same as the reaction studied in this work, i.e., glyoxal + $(NH_4)_2SO_4$. Therefore the proof that the compound observed via MS is BI is a little cyclical: the synthesized standard was analyzed via MS and made via analogous chemistry to that of the system being studied. The compound likely is BI, but at present the results only show that the two compounds are the same and have the mass of BI. It would be useful to show a NMR spectrum of the synthesized BI, as that is the commonly used method to characterize organic compounds (structurally). It is consistent that MS/MS has losses of 27, e.g., HCN. However, the fragmentation pattern (MS/MS) should be explained in more detail and/or shown that it is consistent with the literature one. BI is also available commercially.

2. It would be helpful to show/discuss control experiments, i.e., experiment 9-11 listed in Table S1, for the discussion in section 3.1.

3. How certain are the authors of the suggested di-amide structure of m/z 219 (Figure 6) containing a formamide and a glyoxylamide. I am not suggesting it is not, but assigning structures from masses is difficult and this case seems speculative: A) A loss of 28 amu was also observed for IC, which is not a formamide. B) Was there any evidence of glyoxylic acid formation, e.g. in negative mode ESI? C) It is surprising that no other amides, especially formamides (e.g., imidazole formamide, i.e. 1H-imidazole-1-carbaldehyde) were observed? It is especially surprising that the only amide is a double amide of BI with a carboxylic acid (glyoxylic acid) not mechanistically explained. Also, a technical correction: the loss from 219 to 135 (delta mass=84) corresponds to C_3O_3, not $C_3H_4O_3$ (mass 88). However, C_3O_3 does agree with loss of CO from the formamide and C_2O_2 from the glyoxylamide shown in Figure 6. 84 could however also correspond to $C_3H_4N_2O$ or $C_3H_2NO_2$? I recommend considering other possibilities

or finding proof for additional amides.

4. The authors mention a potential contribution to overall absorption from formamide(s) p.6245 line 29 and p.6248 line 14. This is very reasonable, but can the authors synthesize or purchase formamide standards and quantify this aspect?

5. The authors suggested that m/z 127 in Figure 2 is unhydrated N-glyoxal substituted 1H-imidazole (GI). However, the work presented shows that hydration of the aldehyde group is quite favored. In addition, both reaction solvent and LC eluent are either water or mainly water. Specifically, the fact that m/z 127 (unhydrated GI) is missing in the MS spectrum of Figure S2 supports that hydration is highly favorability for GI, e.g., compare Figures S4, S6 that show both forms. A MS/MS spectrum analogous to the hydrated GI (Figure S2) for m/z 127 that shows the same fragment as from m/z 145, i.e., m/z 69, would be reassuring.

6. The authors mentioned low polarity products eluting between 9 to 15 min, which is very interesting, but they could not elucidate structural information. Would it help if the authors collected the 9-15 min eluate and apply a high resolution ESI-TOF MS characterization?

7. Could GBI also be a ring-closed (6-memberde C4N2) form in which the carbonyl group reacts with the single-bonded nitrogen on the other imidazole ring? How can this be excluded?

Technical comments: 8. The axes of the 3D chromatogram in the supplement are hard to read. The figures are very interesting and thus it would be helpful to improve the clarity. As mentioned in the text it seems IC has a BI impurity.

9. It would be helpful if the authors could show a full UV-Vis spectrum of BI, which is one of the major findings of the paper.

10. Page 6242, line 24-27: “Yu et al. (2011) measured a decreasing pH . . . and proposed the formation of formic acid ...” The decrease of pH could also be due to

reaction of NH4+ to H+, a much stronger acid than NH4+.

11. Figure S2, S3 have the same caption. S3 should be HGGI.

12. Figure S7, caption should be HGHIC

13. Figure S15: please change “3M” to “3M AS” and add reaction time. Is it really 0.01M GL?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6235, 2012.