

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.

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The authors thank referee #1 for the thorough reading of the manuscript and will respond to all comments in detail:

Referee #1, 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 + (NH₄)₂SO₄. 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

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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.

Reply: The referee points out an interesting issue. We believe that even though the proof of identification seems a little cyclical, it is true nevertheless. As pointed out in the short comments from Barbara Nozière there is also an U.S. patent describing the production of 2,2'-bi-1H-imidazole from glyoxal and an ammonium salt (and is now referenced in the text). In addition also the MS/MS-spectrum shown in the supplemental material strongly points on an aromatic compound. In summary, we believe that it is not the formation of BI itself which is the central message of this paper, however, the focus is on the identification of this compound under atmospherically relevant conditions (acidic pH). Therefore, we think there is little doubt that the compound identified here really is BI.

Referee #1, 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.

Reply: A statement on the control experiments has been added to the discussion in section 3.1: “Control experiments (Experiments 9 – 11 in Table S1 in the Supplement) were conducted to obtain chromatograms of water, ammonium sulfate and glyoxal backgrounds. No imidazole signals were observed in those chromatograms.”

Referee #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

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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 (Δ mass=84) corresponds to C3O3, not C3H4O3 (mass 88). However, C3O3 does agree with loss of CO from the formamide and C2O2 from the glyoxylamide shown in Figure 6. 84 could however also correspond to C3H4N2O or C3H2NO2? I recommend considering other possibilities or finding proof for additional amides.

Reply: The authors want to thank the referee for this valuable comment. A) The referee is right pointing out that IC also shows the loss of 28 amu and is not a formamide. B) We didn't observe any proof for glyoxylic acid formation. However, the samples were not measured in negative ion mode ESI after an aging time of about 16 h. Additionally, the high concentration of sulfate ions in the sample solutions produced a high background signal in negative ion mode ESI, suppressing a potential detection of glyoxylic acid. Nevertheless, we agree that other potential structures might be responsible for the observed signal and included a corresponding discussion in the revised manuscript. Fig. 6 has been corrected: "C3O3" instead of "C3H4O3" and "Tentative structure" instead of "Proposed structure".

Referee #1, 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?

Reply: We think it would be possible to synthesize formamide standards. However, we think this should be done in further studies regarding the identification of the observed low-polarity products.

Referee #1, 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

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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.

Reply: We thank the referee for the thorough reading of the manuscript. Indeed, m/z 127 visible in Fig. 2 most likely does not correspond to unhydrated GI due to the reasons mentioned by the referee. It appears that m/z 127 in the MS shown here is caused by the instrument during this specific run, since it does not appear in other chromatograms we have checked. Therefore, we changed the paragraph as follows: "All mono-imidazole products described in Figure 1 are visible at this point except IC and GI, which likely are completely hydrated under the analytical conditions applied here. This includes m/z 69 = 1H-imidazole (IM), m/z 115 = hydrated 1H-imidazole-2-carbaldehyde (HIC), m/z 145 = hydrated N-glyoxal substituted 1H-imidazole (HGI),...".

Referee #1, 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?

Reply: We thank the referee for this suggestion. We also consider high resolution mass spectrometry to be helpful for further studies on the identity of these products. This should be further investigated in future studies.

Referee #1, 7.: Could GBI also be a ring-closed (6-membered C4N2) form in which the carbonyl group reacts with the single-bonded nitrogen on the other imidazole ring? How can this be excluded?

Reply: We would expect the MS/MS of such a compound to look different from what we observed for GBI, i.e. the exclusive loss of m/z 58 likely corresponding to a molecule

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of glyoxal. A loss of m/z 18 corresponding to a molecule of H_2O should also be visible for a ring-closed compound as proposed by the referee. Additionally, the retention time should also shift compared to BI, which is not the case for GBI.

Technical comments:

Referee #1, 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.

Reply: We have tried to improve the quality of the graphs in Figs. S14 and S15. We hope the quality is now sufficiently high to be able to read the numbers when zooming in.

Referee #1, 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.

Reply: We agree and included a full UV-Vis spectrum of BI in the Supplement (Fig. S16), which is referenced in the text in section 3.2. The spectrum is also attached to the response on the short comments of Barbara Nozière (Fig. 3).

Referee #1, 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 NH_4^+ to H^+ , a much stronger acid than NH_4^+ .

Reply: A corresponding statement has been included in the discussion: "In addition, the removal of ammonia from the corresponding equilibrium reaction (see Equation 1) by its reactions with glyoxal will influence the pH (transformation of NH_4^+ to H^+)."

Referee #1, 11.: Figure S2, S3 have the same caption. S3 should be HGGI.

Reply: Has been corrected.

Referee #1, 12.: Figure S7, caption should be HGHIC

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Reply: Has been corrected.

Referee #1, 13.: Figure S15: please change "3M" to "3M AS" and add reaction time. Is it really 0.01M GL?

Reply: The missing "AS" and reaction time have been inserted. The chromatogram shows a mixture of 3M AS and 1.5 M Gly. We apologize for the typos in the Supplement.

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

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