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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.

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The authors want to thank referee #2 for his review and specifically respond to each of the comments below:

Specific Comments

Referee #2, 1.: The idea that minor products are mostly responsible for absorbance of visible light in biogenic SOA systems due to aldehyde + ammonia reactions has been put forth by Bones, et al. (2010) and this work could be cited here.

Reply: The authors agree with the referee and included the suggested reference in the introduction of the revised manuscript.

Referee #2, 2.: p. 6238 line 1: Formic acid production during imidazole formation was proposed by De Haan, et al. (2009) and confirmed experimentally by Yu, et al (2011).

Reply: We agree with the referee and changed the corresponding sentence in the revised manuscript.

Referee #2, 3.: p. 6243 line 13: This work finds biimidazole formation to be first order with respect to glyoxal. Yu et al. (2011) found imidazole formation to be 2nd order with respect to glyoxal. Can the authors highlight and discuss possible reasons for the discrepancy?

Reply: An interesting point, however, in both studies the data available for such a discussion are really limited. Therefore, we prefer not to discuss the possible reasons for this discrepancy.

Referee #2, 4.: p. 6243 line 20: many of the glyoxal – imidazole adducts identified in this work may be in rapid equilibrium in aqueous systems, hence would not be separable by the chromatographic methods used. Do all species expected to be in equilibrium indeed coelute? If so, this is more indirect evidence that the product identifications are correct, and may make it possible to extract more equilibrium constants from the data.

Reply: Yes, all the species which are suspected to be subject to these equilibrium reactions co-elute.

Referee #2, 5.: p. 6244 line 10: How far into higher wavelengths could the line broadening discussed here extend? How does this relate to the potential absorbances of the low-polarity compounds discussed in the next section?

Reply: If one looks at the data from Shapiro et al. (2009) for example the line broadening can reach up to 550-600 nm. So far we cannot say something quantitative about the relative importance of the low polarity compounds discussed in this paper. However, it appears that the majority of the line broadening is related to the absorption band at 280 nm (Shapiro et al. 2009, Fig. 1a).

Referee #2, 6.: p. 6247 line 20: I would hope that no one would try to quantitate imidazole compounds in aerosol using UV-Vis absorbance alone. This cautionary statement is unnecessary in my opinion.

Reply: We indeed hope no one would try to do so, too. However, the cautionary statement is not limited to UV-Vis detection alone, but also points to potential artifacts from such transition metal complexes using mass spectrometric detection.

Referee #2, 7.: p. 6248 line 14: The claim of formamide formation seems to rest on very little evidence. None of the products shown in Table 1 are formamides (or any kind of amides). The only formamide structure is the speculative structure in Figure 6, based largely, it seems, on the loss of m/z 28 from the parent molecule. CO loss is non-specific, occurring in carboxylic acids, ketones, and aromatic aldehydes (Laskin, et al. 2010). Since the loss of $C_3H_4O_3$ (or C_3O_3) is very difficult to reconcile with the suggested structure, and since loss of m/z 28 could happen from many possible structures, I argue that claims of formamide production are dubious, and should either be removed from the manuscript or backed up with further evidence.

Reply: This valid concern has been addressed as pointed out in the response to the comments/review of referee #1.

Referee #2, 8.: Supplement Figure S8: Do the authors have ESI-MS-MS data showing that their biimidazole standard fragments in the same way?

Reply: Figure S8 represents the chromatographic and mass spectrometric characterization of the biimidazole standard. However, the same fragmentation pattern is obtained during analysis of Gly/AS mixtures.

Technical Corrections

Referee #2, 9.: p. 6238 line 10: “glycin” should be “glycine”

Reply: Has been corrected.

Referee #2, 10.: p. 6239 line 25: do the authors mean “adduct” instead of “educt”?

Reply: No, since the formation reactions of glyoxal substituted imidazoles are equilibrium reactions also the free imidazoles and glyoxal are detectable in these mixtures, i.e. the educts.

Referee #2, 11.: Section 2.4: the DAD abbreviation is never defined.

Reply: The DAD abbreviation was defined on p. 6240 in line 5.

Referee #2, 12.: p. 6246 line 11: I suggest that the authors substitute “cannot be made” for “is not given”

Reply: Has been replaced.

Referee #2, 13.: p. 6247 line 15: To lesson confusion, substitute “formation of transition metal complexes” for “complex formation of transition metals”

Reply: Has been replaced.

Referee #2, 14.: Supplement Figure S14 and S15: As pointed out by Reviewer 1, the numbers on the scales cannot be read no matter how much you zoom in, limiting the utility of these otherwise beautiful graphs.

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.

References cited:

Bones, D. L.; Henricksen, D. K.; Mang, S. A.; Gonsior, M.; Bateman, A. P.; Nguyen, T. B.; Cooper, W. J.; Nizkorodov, S. A., Appearance of strong absorbers and fluorophores in limonene-O_3 secondary organic aerosol due to NH_4^+-mediated chemical aging over long time scales. J. Geophys. Res. - Atmos. 2010, 115, (D5), D05203/1-14.

De Haan, D. O.; Corrigan, A. L.; Smith, K. W.; Stroik, D. R.; Turley, J. T.; Lee, F. E.; Tolbert, M. A.; Jimenez, J. L.; Cordova, K. E.; Ferrell, G. R., Secondary organic aerosol-forming reactions of glyoxal with amino acids. Environ. Sci. Technol. 2009, 43, (8), 2818-2824.

Laskin, J.; Laskin, A.; Roach, P. J.; Slysz, G. W.; Anderson, G. A.; Nizkorodov, S. A.; Bones, D. L.; Nguyen, L. Q., High-resolution desorption electrospray ionization mass spectrometry for chemical characterization of organic aerosols. Anal. Chem. 2010, 82, (5), 2048-2058.

Shapiro, E. L.; Szprengiel, J.; Sareen, N.; Jen, C. N.; Giordano, M. R.; McNeill, V. F., Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics. Atmos. Chem. Phys., 9, 2289-2300, 2009.

Yu, G.; Bayer, A. R.; Galloway, M. M.; Korshavn, K. J.; Fry, C. G.; Keutsch, F. N., Glyoxal in aqueous ammonium sulfate solutions: products, kinetics, and hydration effects. Environ. Sci. Technol. 2011, 45, 6336-6342.

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