

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 #2

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General Comments

This paper reports new, strongly absorbing biimidazole products in the glyoxal / ammonia reaction under conditions relevant to atmospheric aerosol. Although the concentrations are 100 times lower than the major products (with single imidazole rings), the high molar absorptivities and longer wavelengths of absorption make biimidazole the dominant absorber at 280 nm. The proposed structures of glyoxal – biimidazole adducts seem reasonable given what is known about the reactivities of these molecules. Other low-polarity N-containing compounds are seen (but not identified) at long reaction times

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in the chromatograms, suggesting these may be responsible for some absorbance in the visible range. The suggestion that the chemistry described may be happening over northern India because of alkaline aerosol particles and high ammonia emissions is intriguing. This work will be of interest to those studying brown carbon and its formation pathways. This discussion paper is clearly written, and is appropriate for ACP after addressing the following comments.

Specific Comments

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.

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).

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?

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 co-elute? 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.

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?

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.

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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.

Supplement Figure S8: Do the authors have ESI-MS-MS data showing that their biimidazole standard fragments in the same way?

Technical Corrections

p. 6238 line 10: "glycin" should be "glycine"

p. 6239 line 25: do the authors mean "adduct" instead of "educt"?

Section 2.4: the DAD abbreviation is never defined.

p. 6246 line 11: I suggest that the authors substitute "cannot be made" for "is not given"

p. 6247 line 15: To lesson confusion, substitute "formation of transition metal complexes" for "complex formation of transition metals"

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.

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-O₃ secondary organic aerosol due to NH₄⁺-mediated chemical aging over

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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.

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.

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