

## ***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.***

**B. Noziere**

barbara.noziere@ircelyon.univ-lyon1.fr

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We read this paper with great interest. To our opinion it is a good work and we only wanted to share a few comments/questions on the results and experimental conditions. Some of them, however, have important implications for the kinetic results.

### 1) Bi-imidazole as main product of glyoxal

The fact that bi-imidazole is a main condensation product of glyoxal with  $\text{NH}_3/\text{NH}_4^+$  is also fully supported by our studies and LC/MSMS analyses (paper in preparation). But

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it should probably be mentioned in this manuscript that this fact is somewhat known in the literature, as shown by the papers describing its synthesis from glyoxal (Fiesemann et al., 1978; Mao et al., 2003). We also would like to mention on this point the US patent 6 713 631 by Cho et al. “preparation method of 2,2-bis-1H imidazole using glyoxal and an ammonium salt” (the method that we chose to synthesize the bi-imidazole). Mentioning this previous knowledge would reinforce the results and make the reader understand that the specificity of this work is to identify this compound for atmospherically relevant conditions (i.e. not basic pH).

### 2) Kinetic studies – or diffusion ?

It would be essential to indicate if the 10 mL samples used in the kinetic studies were stirred (or shaken) because the medium in which these measurements were made,  $(\text{NH}_4)_2\text{SO}_4$  3 M, is very viscous and diffusion in it is thus VERY slow. Without stirring the reactions would be limited by diffusion, not kinetics, which would explain the very slow rates obtained and the fact that they are all similar (Figure 4 of the paper). Yu et al., ES&T 2011 clearly state that their solutions were not stirred, thus probably explaining the very slow kinetics obtained. By contrast, our previous work (Nozière et al., JPC A, 2009) where the solutions were stirred, clearly shows that the simple imidazole is produced first, and within a timescale of an hour.

### 3) UV absorption and absolute calibration

There are some inconsistencies between the UV absorption reported in this paper (and in Yu et al. 2011) and our own measurements, both in term of general shape of the spectra, and of the absolute calibrations of the absorption.

- First, it would be very useful to present on a Figure the spectra of each of the imidazoles studied in water. Attached are the spectra recorded at our laboratory for these imidazoles, in water (Fig. 1) and in  $(\text{NH}_4)_2\text{SO}_4$  (Fig. 2). Some of the main peaks are a little shifted compared to what reported here and in Yu et al.: 287 nm instead of 273 nm for the main peak of Imidazole carboxaldehyde, and 275 nm instead of 280 nm for the

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bi-imidazole. But, most importantly, we find that the peaks for Imidazole carboxaldehyde at short wavelength is small, smaller or comparable to the peak at 275/280 nm. Could the strong peak observed in this work and in Yu et al. be due to some impurities of bi-imidazole ?

- second, the range of concentrations on which the absorption of Imidazole carboxaldehyde and of bi-imidazole are supposed to have been calibrated (up to 1 mM) is surprising because both compounds are very insoluble in water. We have not been able to dissolve more than 0.3 mM of Im. Carboxaldehyde and 0.2 mM of bi-imidazole in water. Was something else used in this study to help dissolve these compounds (adjusting the pH. . .) ? If not, could there be a mistake in the range of concentrations reported ?

- Finally, we obtain a different molar extinction for bi-imidazole. For the two other imidazoles, we obtain values comparable to those reported (except for the bands at short wavelength, as commented above): 5290 M<sup>-1</sup> cm<sup>-1</sup> for Imidazole at 205 nm (instead of 4462), and 625 M<sup>-1</sup> cm<sup>-1</sup> for imidazole carboxaldehyde at 289 nm (instead of 273) (see Fig. 3 attached). There might be a factor ln10 (~2.3) to take into account depending on the output of the spectrometer (ln or log) and the definition. However, for bi-imidazole at 275 nm we find about 3985 M<sup>-1</sup> cm<sup>-1</sup>, which is about a factor 10 lower than reported in this work. This result is directly impacted by the values used for the concentrations and the pathlength (for instance if 0.1 cm is used instead of 1 cm). Could this factor have been forgotten along the way ?

Beside these comments, we emphasize that this work is interesting and brings useful information on this complex reaction system, and we congratulate again the authors on this good work.

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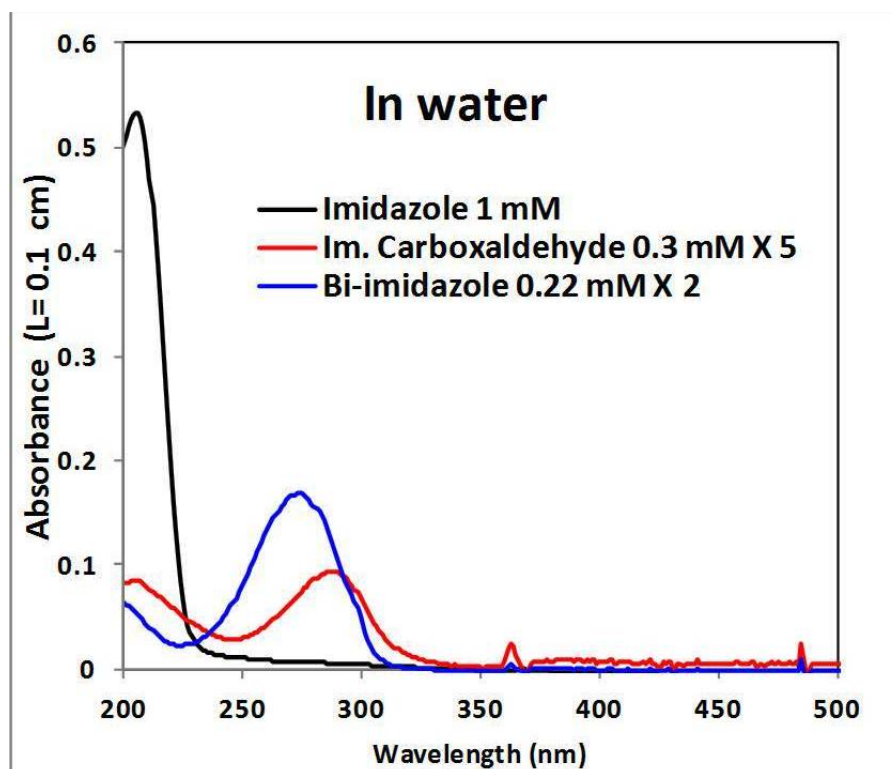


Fig. 1.

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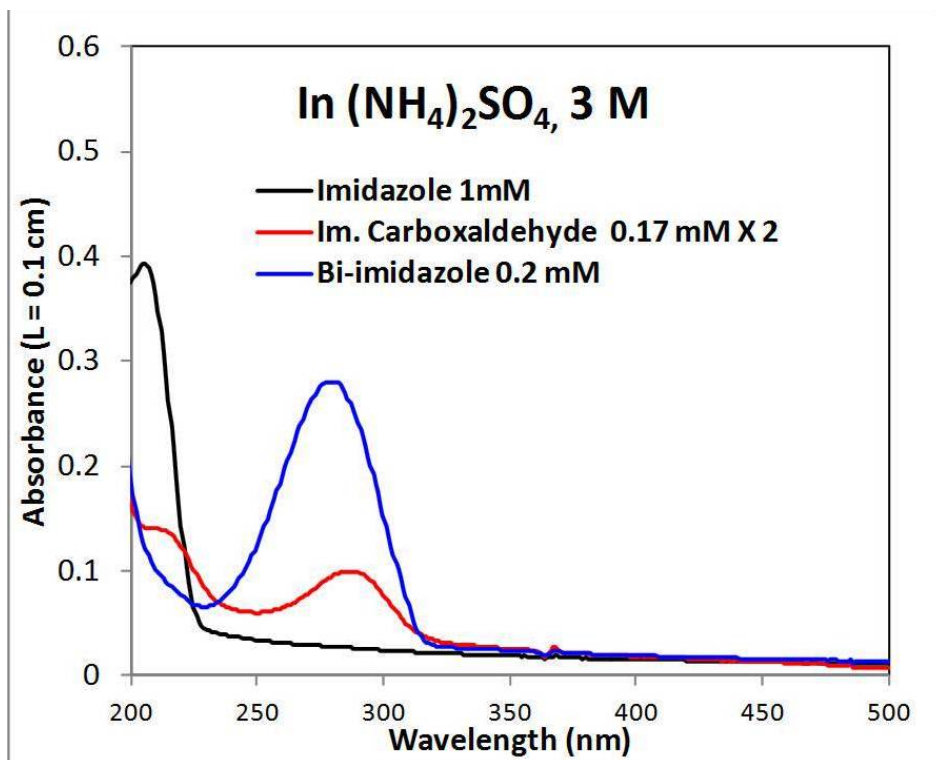


Fig. 2.

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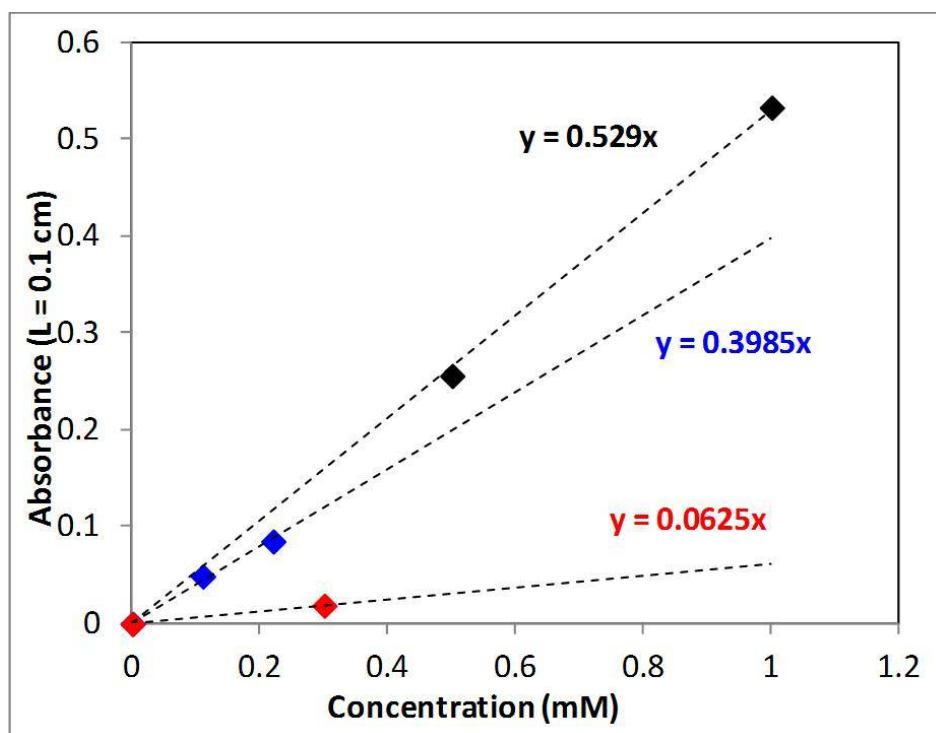


Fig. 3.

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