

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.

C. J. Kampf et al.

hoffmant@uni-mainz.de

Received and published: 21 June 2012

The authors want to thank Barbara Nozière for her valuable comments and specifically respond to each of them below:

1) Bi-imidazole as main product of glyoxal

Barbara Nozière: 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 it should probably be mentioned in this manuscript that this fact is

C3881

somewhat known in the literature, as shown by the papers describing its synthesis from glyoxal (Fieselmann et al., 1978; Mao et al., 2003). We also would like to mention on this point the US patent 6713631 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).

Reply: We agree that the specificity of the of this work can be pointed out more clearly and included a corresponding statement in section 3.1: “This product is already known in the literature (Mao et al., 2003; Fieselmann et al., 1978) and its formation from the reaction of glyoxal with an ammonium salt has also been described in US patent 6713631 (Cho et al., 2003). Here we report the formation of BI under atmospherically relevant conditions, i.e. not basic pH.”. The authors thank Barbara Nozière for this valuable comment.

2) Kinetic studies – or diffusion ?

Barbara Nozière: 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.

Reply: We thank Barbara Nozière for bringing up this interesting point. Our solutions were not stirred. A corresponding statement has been added in section 2.2 in the revised manuscript. However, in this study we wanted to investigate aerosol mimics by

C3882

scaling up the concentrations, which are assumed to be relevant for atmospheric (wet) aerosols or cloud droplets.

3) UV absorption and absolute calibration

Barbara Nozière: 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.

Barbara Nozière: - First, it would be very useful to present on a Figure the spectra of each of the imidazoles studies in water. Attached are the spectra recorded at our laboratory for these imidazoles, in water (Fig. 1) and in (NH₄)₂SO₄ (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 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?

Reply: We agree that the UV/Vis spectra of the imidazole standards are useful information and have included them here and in the Supplement to the revised manuscript (Figs. S16 – S18). Note that for the calculations of the extinction coefficients the time integrated absorbance at the respective wavelength from the LC-UV/Vis measurements was used. The figures are referenced in section 2.3 of the text. With regard to the question about the bi-imidazole impurity in the imidazole carboxaldehyde standard: Yes, there is an impurity of bi-imidazole in our standard. However, since we used HPLC-UV/Vis detection we can separate the spectra of the two compounds (the retention times differ by more than one minute). There must be another explanation for the observed differences. Our UV-Vis spectrum of IC shows another maximum at 225 nm. However, we didn't quantify its contribution because we think that this absorption might be related to an impurity co-eluting in our standard.

C3883

Barbara Nozière: - 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?

Reply: Yes, the ultrapure water was acidified with a small amount of 1 M hydrochloric acid, as is pointed out in section 2.3. Nevertheless, we can confirm that without this mild acidification only small amounts of the imidazoles are soluble in water. The concentrations of our IM, IC and BI standards were 0.02 M, contrary to what was written in text. This has been corrected.

Barbara Nozière: - 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⁻¹ cm⁻¹ for Imidazole at 205 nm (instead of 4462), and 625 M⁻¹ cm⁻¹ 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⁻¹ cm⁻¹, 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?

Reply: All molar extinctions for the different imidazoles presented in this work were measured using the same instrument and applying the same mathematical equations. Therefore, any factor that might not have been taken into account should apply to all our measurements in the same manner. The path length of our instrument was 1 cm. This length was also used for the calculations of the molar extinctions. We used the log definition of the molar extinction coefficient in the Beer-Lambert law. We have

C3884

re-checked all calculations for bi-imidazole molar extinction and confirm the result of 36990 M⁻¹ cm⁻¹ at 280 nm based on our measurements.

References cited:

Cho, J. R., Cho, S. G., Goh, E. M., and Kim, J. K: Preparation method of 2,2'-bi-1H-imidazole using glyoxal and an ammonium salt, United States Patent, 6713631, 2003.

Noziere, B., Dziedzic, P., and Cordova, A.: Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH₄⁺), J. Phys. Chem. A, 113, 231-237, 2009.

Yu, G., Bayer A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects, Environ. Sci. Technol., 45, 6336-6342, 2011.

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

C3885

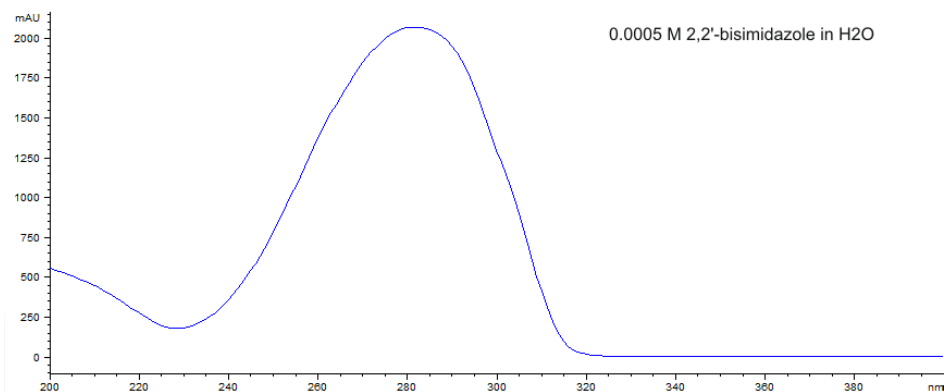


Fig. 1. UV-Vis spectrum of BI (at 3.5 min retention time)

C3886

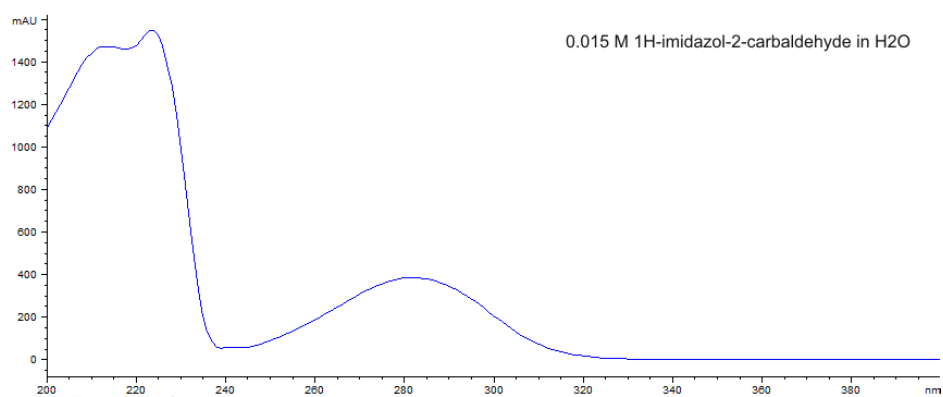


Fig. 2. UV-Vis spectrum of IC (at 2.3 min retention time)

C3887

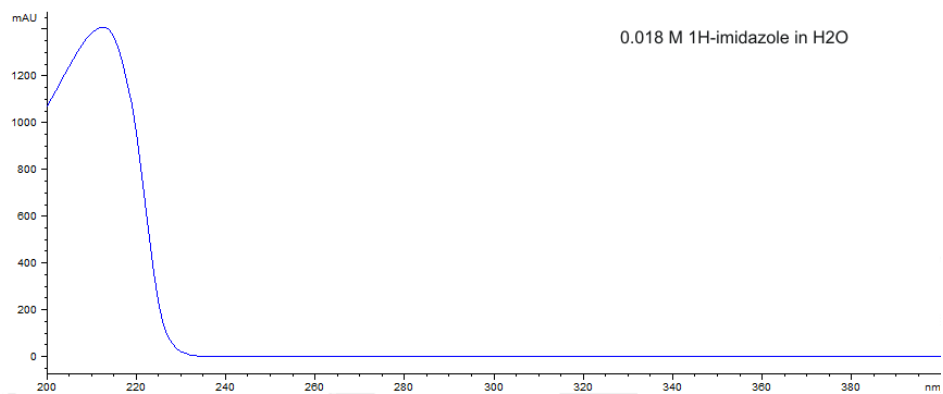


Fig. 3. UV-Vis spectrum of IM (at 2.2 min retention time)

C3888