Identification and characterization of aging products in the glyoxal/ammonium sulfate system – implications for light-absorbing material in atmospheric aerosols

C. J. Kampf, R. Jakob, and T. Hoffmann

Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, 55128 Mainz, Germany

Received: 7 February 2012 – Accepted: 8 February 2012 – Published: 29 February 2012

Correspondence to: T. Hoffmann (hoffmant@uni-mainz.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

In this study we report the identification of bicyclic imidazoles in aqueous aerosol mimics using HPLC-ESI-MS/MS. 2,2′-Biimidazole was identified to be a major contributor to the 280 nm absorbance band observed in mixtures of glyoxal and ammonium sulfate, despite the fact that its production rate is two orders of magnitude lower than the previously reported production rates of imidazole or imidazole-2-carboxaldehyde. The molar absorptivity of 2,2′-biimidazole was determined to be \((36 690 \pm 998) \text{ M}^{-1} \text{ cm}^{-1}\). This demonstrates the necessity of molecular product identification at trace levels to enable a better understanding of relevant absorbing species. Additionally the formation of lower polarity products including formamides of imidazoles is proposed. The role of imidazoles and other light-absorbing species in the formation of SOA and optical properties of SOA is discussed and potentially interesting fields for future investigations are outlined.

1 Introduction

Atmospheric aerosols impact global and regional climate, air quality and human health (Seinfeld and Pandis, 2006). Fine mode atmospheric aerosols (submicron particles) are comprised of organic aerosols (OA) as a major fraction (Zhang et al., 2007). The organic matter in those submicron particles is mostly secondary in nature (Jimenez et al., 2009). Over the past years the perception that secondary organic aerosols (SOA) are formed only by gas to particle conversion of low volatility products from atmospheric oxidation processes of volatile organic compounds (VOC’s) (Pankow 1994; Odum et al., 1996) has changed and now also involves heterogeneous chemistry and particle phase chemistry of more volatile oxidation products (Hallquist et al., 2009; Lim et al., 2010; Ervens et al., 2011). Prominent examples of such compounds are the two simplest and most abundant \(\alpha\)-dicarbonyl compounds glyoxal (Gly) and methylglyoxal (Mgly), which remain at least partly in the particle phase through a number of
possible reaction pathways in the condensed phase. Briefly, these pathways include self-oligomerization (Kalberer et al., 2004; Hastings et al., 2005; Liggio et al., 2005a,b; Loeffler et al., 2006; Zhao et al., 2006), aldol condensation (Schwier et al., 2010; Sarrein et al., 2010; Yasmeen et al., 2010), formation of nitrogen containing compounds and nitrogen containing oligomers (De Haan et al., 2009a,b, 2011; Noziere et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; Yu et al., 2011; Kua et al., 2011) as well as organosulfates (Liggio et al., 2005a; Surratt et al., 2007, 2008; Galloway et al., 2009). Furthermore, oxidation of Gly and Mgly in the particle phase by OH radicals resulting in the formation of lower volatility carboxylic acids (e.g. oxalic acid or pyruvic acid) (Carlton et al., 2007; Tan et al., 2009, 2010; Lim et al., 2010; Altieri et al., 2008) are also discussed as sources of SOA from small $\alpha$-dicarbonyl compounds.

Another important aspect of aqueous phase chemistry besides SOA formation is the potential influence of the respective products on aerosol properties, e.g. optical properties. In recent studies the formation of light-absorbing material in aqueous aerosol mimics containing $\alpha$-dicarbonyl compounds and ammonium sulfate was observed and nitrogen containing compounds were identified as products in both bulk and chamber experiments (Shapiro et al., 2009; Galloway et al., 2009; De Haan et al., 2009, 2011; Yu et al., 2011; Trainic et al., 2011; Trainic et al., 2012). Light-absorbing material was formed when glyoxal was introduced into ammonium ion containing solutions, i.e. ammonium sulfate or ammonium nitrate solutions, while no such light-absorbing species were observed when glyoxal was introduced into salt solutions without ammonium ions, i.e. sodium sulfate, sodium chloride. Imidazoles were identified as major products from the reaction of $\alpha$-dicarbonyl compounds and ammonium ions or primary amines, e.g. methyamine and amino acids (De Haan et al., 2009a,b, 2011; Yu et al., 2011; Trainic et al., 2012). Yu et al. (2011) identified imidazole and imidazole-2-carboxaldehyde, which was identified as a product in the glyoxal/ammonium sulfate system (Gly/AS system) before by Galloway et al. (2009), as major carriers of the absorption observed in the Gly/AS system and confirmed nitrogen containing compounds to be responsible for the light absorption in this system by studying solutions of glyoxal and ammonium,
methylamine, and dimethylamine salts. They also proposed the formation of formic acid in one of two major pathways of the reaction of glyoxal with ammonia or primary amines, thus reducing the pH value in solution and consequently reducing the rate of the formation of imidazoles. However, they were not able to explain the observed absorbance in Gly/AS mixtures completely. Very recently, Trainic and colleagues report the formation of a particle phase product absorbing at \( \lambda = 290 \text{ nm} \) in ammonium sulfate seed aerosols exposed to gas phase glyoxal for a wide range of RH values (Trainic et al., 2011). They also report a higher ratio of C–N oligomers to glyoxal oligomers in AS/glycine (100 : 1) seed particles, likely due to an acid catalyzed imine formation from glycine and glyoxal (Trainic et al., 2012).

The purpose of this paper is to further complete the understanding of the product spectrum of the reaction of glyoxal and ammonia in aqueous aerosol mimics through the identification of several new imidazole products and kinetic investigations. Therefore, we use high performance liquid chromatography coupled with UV-Vis and mass spectrometric detection (Electrospray Ionization Ion Trap Mass Spectrometry, ESI-IT-MS). The time resolved chromatographic separation of the reaction mixture combined with the use of reference compounds is a powerful tool for the assignment and structural identification of reaction products in a dynamic aqueous phase reaction like the Gly/AS system. Additionally, we report the formation of species absorbing at near visible wavelengths, which are of low polarity and relatively high molecular weight and discuss the implications for light-absorbing material in SOA from glyoxal.

2 Experimental

2.1 Chemicals and materials

Ammonium sulfate (> 99.5%), ammonium hydroxide solution (28%), formic acid (> 99%), 1H-imidazole (> 99%) and glyoxal (40% wt. solution) were obtained from Acros Organics, ammonium nitrate (> 99%) from Fluka, hydrochloric acid (30%) from Merck
2.2 Aqueous aerosol mimics

In order to achieve the best possible approximation of aqueous atmospheric aerosols with batch experiments and to be able to compare the results of this study with literature data (Shapiro et al., 2009; Noziere et al., 2009; Yu et al., 2011) 3 M solutions of (NH₄)₂SO₄ (ammonium sulfate, AS) were prepared containing initial glyoxal concentrations ranging from 0.01 to 1.5 M. Sample solutions were prepared in batches of 10 ml. All samples read pH=4 (±1), achieving a pH relevant to tropospheric aerosols. All mixtures were stored in brown glass auto sampler vials until analysis. The brown glass auto sampler vials are expected to provide a good shielding from UV, thus the samples were not otherwise protected from light. A selected list of experiments is available in the supporting information (Table S1).

2.3 Reference compounds

2-(1H-imdazol-2-yl-)-1H-imidazole (2,2'-bisimidazole, 2,2'-biimidazole, BI) was synthesized using a modification of a method of Debus (1858) and Fieselmann et al. (1978) by Mao et al. (2003), who substituted the ammonia gas with concentrated NH₄OH (28–30 %) solution. HPLC-DAD-ESI-MS showed that the product was pure. 1H-imidazole (IM) and 1H-imidazole-2-carboxaldehyde (IC) were commercially available in >99.5 % purity. 0.2 M solutions of IM, IC and BI were prepared by dissolving the solids in 10 ml ultrapure water acidified with 20 µl of 1 M hydrochloric acid. To characterize the glyoxal substituted imidazoles, samples were prepared to be 0.2 M with respect to Gly and IM, IC or BI, respectively. These samples were analyzed immediately after preparation and showed the respective educts as well as the N-glyoxal substituted imidazoles.
2.4 HPLC-DAD-ESI-MS/MS measurements

All samples were analyzed by HPLC-DAD-ESI-MS measurements using a HCT-Plus ion trap mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with a HPLC-System (Agilent 1100 series, auto sampler, gradient pump, degasser and diode array detector (DAD), Agilent Technologies GmbH, Germany) and an Atlantis T3 150 mm × 2.0 mm column with 3 µm particle size (Waters, Germany). The eluents were ultrapure water with 0.1 % formic acid and 2 % acetonitrile (eluent A) and acetonitrile with 2 % water (eluent B). The gradient of the mobile phase, with a flow of 0.2 ml min⁻¹, was chosen as follows: Starting with 1 % B, gradient to 100 % B in 30 min, isocratic for 5 min and gradient to 0 % B in 5 min. The column was equilibrated at 1 % B for 20 min. The HPLC system was connected to the MS via a DAD equipped with a 500 nl flow cell. The electrospray ion source of the MS was operated using the following setup: nebulizer pressure 2200 mbar, dry gas flow 91 min⁻¹, dry gas temperature 300 °C and spray voltage 4500 V.

3 Results and discussion

3.1 Imidazole formation in the glyoxal/ammonium sulfate system

The reaction of glyoxal with ammonia, which is present in ammonium sulfate solutions in concentrations depending on the pH value of the solution, yields a variety of different imidazoles. Figure 1 depicts proposed pathways for the formation of imidazoles in the Gly/AS system as discussed by Yu et al. (2011), who concluded the formation of 1H-imidazole (IM), hydroxyl(1H-imidazol-1-yl)acetaldehyde or N-glyoxal substituted 1H-imidazole (GI), its hydrated form (HGI), 1H-imidazole-2-carbaldehyde (IC) and its hydrated form (HIC) from NMR studies on the Gly/AS system. In addition to these products we propose the formation of 2-(1H-imidazol-2-yl)-1H-imidazole (or 2,2'-bisimidazole, 2,2'-biimidazole, BI) from further reactions of IC with ammonia. We
believe BI is a major contributor to light-absorbing material formed in the Gly/AS system although it is only produced in small amounts as will be discussed in the following Sect. 3.2.

The HPLC-DAD-ESI-MS/MS analysis of Gly/AS mixtures at different times after mixing reveals two main features in their temporal product evolution. The first feature is observed in the chromatograms between 2.0 and 2.5 min retention time. It is accompanied by an increase of several UV signals at 210 nm and 280 nm absorption. A typical mass spectrum of this feature from a solution of 1.5 M Gly in 3 M AS is shown in Fig. 2 (69.7 h after mixing, retention time of 2.3 min). All mono-imidazole products described in Fig. 1 are visible at this point except IC, which likely is 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 127 = N-glyoxal substituted 1H-imidazole (GI), m/z 145 = hydrated N-glyoxal substituted 1H-imidazole (HGI), m/z 173 = N-glyoxal substituted hydrated 1H-imidazole-2-carbaldehyde (GHIC), m/z 203 = hydrated glyoxal dimer substituted imidazole (HGGI). The second feature is visible at around 3.5 min retention time, where an increase in one specific UV signal at 280 nm absorption is observed. Figure 3 shows a typical mass spectrum of this feature from a solution of 0.01 M Gly in 3 M AS (23.46 h after mixing, retention time of 3.4 min). The two prominent signals correspond to BI (m/z 135) and its glyoxal substituted analog GBI (m/z 193). The identity of these products was confirmed through reference compounds. A detailed characterization in terms of chromatograms, MS and MS/MS spectra is available in the supporting information (Figs. S1–S9). Retention times, protonated ion masses and abundant fragments for the observed products are listed in Table 1.

3.2 Characterization and kinetic investigations of BI in the Gly/AS system

All previous studies on the formation of light-absorbing material in the Gly/AS system involving UV-Vis analysis observed an increasing absorption at around 280 nm with increasing time after mixing. Yu et al. (2011) were able to determine IC as one
carrier of this absorption band and quantified its contribution. They concluded that additional unknown absorbing species must be present in the mixture to explain the actual absorbance at this wavelength. They calculated a lower limit for the molar absorptivity of 3100 M$^{-1}$ cm$^{-1}$ (in water) for a single compound contributing to this absorption band to explain the remaining absorbance. Their calculation was based on the assumption that no unidentified signals at concentrations higher than 0.1 mM were observed at 190.5 min after mixing of a 3.3 M AS/0.17 M Gly solution in their NMR spectra. After calibration of the HPLC-DAD-ESI-MS system with the synthesized standard we were able to determine the molar absorptivity of BI in water at 280 nm to be (36 690 ± 998) M$^{-1}$ cm$^{-1}$ (see Supplement for more details). BI therefore seems to be a major contributor to the 280 nm absorption band observed in the recent studies (Shapiro et al., 2009; Noziere et al., 2009; Yu et al., 2011). At a comparable time (176 min) after mixing of a 3 M AS/0.3 M Gly solution we found a BI concentration of 0.013 mM, supporting the calculations of Yu et al. (2011). This clearly demonstrates the importance of the molecular identification of products in the investigated aerosol mimics at trace levels for a better understanding of the absorbance of the reaction mixtures. BI is not a major product of these reactions, however, due to its high molar absorptivity it is an important contributor to the observed absorbance features.

The concentration of BI in the reaction mixtures was monitored over a timescale of one week simulating the estimated mean residence time of sulfur compounds in the troposphere (Seinfeld and Pandis, 2006) as a measure for the mean lifetime of secondary aerosols. Figure 4 shows the concentrations of BI as a function of time after mixing of the Gly/AS solution. It was observed that the formation of BI decreases after the first several hours of each experiment. Yu et al. (2011) measured a decreasing pH value over the course of their experiments using an in situ NMR technique and proposed the formation of formic acid during the formation of IM as the potential reason for this observation. A lower pH value decreases the amount of available ammonia in solution due to the pH dependent equilibrium of ammonium ions and ammonia (see
Eq. 1).
\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \tag{1}
\]

Yu et al. (2011) concluded an exponential dependency between available ammonia and pH value and report a first order dependency of the production rate of formic acid/(\text{IM + GI}) and IC from \([\text{H}^+]\). This dependency applies in a similar way for the production rate of BI, since its formation also involves the nucleophilic attack of ammonia at the carbonyl carbon atom of IC, resulting in a similar temporal behavior.

A stronger decrease of the production rate of BI \((R_{\text{BI}})\) was observed at higher initial glyoxal concentrations, which reflects a stronger decrease of the pH value as a result of increased IM and formic acid production under these conditions. Thus, to stay in a regime of linear correlation between BI concentration and reaction time only data from the first \(\sim 10\) h of the reaction were used to determine the production rates of BI. \(R_{\text{BI}}\) ranged from \(0.07\) to \(7.19 \times 10^{-9}\) \(\text{M s}^{-1}\) depending linearly on the initial glyoxal concentration (see Table 2). Detailed information on the calculations can be found in the Supplement. Compared to the reported production rates of formic acid, IM and IC in 1.6 M AS/1.5 M Gly solutions (Yu et al., 2011) the initial production rate of BI is approximately two orders of magnitude lower (3 M AS/1.5 M Gly solution). Mass spectrometric detection revealed that \((11 \pm 1)\%\) of BI was present as GBI over the timescale investigated for the determination of \(R_{\text{BI}}\) \(([\text{Gly}]_{\text{init}} = 0.01\) M\) assuming similar ionization efficiencies for BI and GBI. This indicates a fast equilibrium between BI and GBI depending on the initial Gly concentration. At a given glyoxal concentration \([\text{GBI}]/[\text{BI}]\) remains constant for the initial phase of the reaction and correlates linearly with the initial glyoxal concentration (Figure S13, Supplement). At the highest concentration of \([\text{Gly}]_{\text{init}} = 1.5\) M a \([\text{GBI}]/[\text{BI}]\) of 5.17 was observed. However, over the course of the reaction \([\text{GBI}]/[\text{BI}]\) increases slightly with the decreasing pH value suggesting the equilibrium to favor GBI at higher proton concentrations.
3.3 Characterization of mono-imidazole products

The molar absorptivities of IM and IC reported by Yu et al. (2011) are supported by our measurements within the uncertainties of the measurements. We calculated the molar absorptivities in water for: IM at 207 nm: $4462 \pm 245 \text{M}^{-1}\text{cm}^{-1}$, IM at 300 nm: $18 \pm 2 \text{M}^{-1}\text{cm}^{-1}$, IC at 213 nm: $6004 \pm 638 \text{M}^{-1}\text{cm}^{-1}$, IC at 273 nm: $273 \pm 28 \text{M}^{-1}\text{cm}^{-1}$. Our values for IC tend to be a bit lower. This observation might be due to a minor BI contamination we observed in the IC standard (see Supplement, Fig. S15). However, at higher concentrations, which can be present e.g. in evaporating wet aerosols or cloud droplets, the absorption bands of all imidazoles are subject to a substantial broadening process. This broadening of the absorption bands potentially explains the delayed increase of the absorbance at higher wavelengths in Gly/AS mixtures reported in the literature, e.g. by Shapiro et al. (2009).

The effect of suppressed ionization in the ESI source due to the high ammonium sulfate concentrations in the reaction mixtures made it difficult to determine the concentrations of the mono-imidazoles since their retention time was within the ammonium sulfate signal in the chromatograms. Additionally, a UV based determination of the concentrations was not possible due to the low chromatographic resolution of the mono-imidazoles hindering a reasonable integration of the respective peaks. Therefore, no kinetic analysis was carried out for these compounds.

3.4 Characterization of low polarity products

In addition to the mono- and bicyclic imidazole products of the reaction of glyoxal and ammonia in the investigated Gly/AS mixtures a number of products with a lower polarity were observed that absorb at wavelengths between 350–400 nm. Their retention times ranged from 9 to 15 min as illustrated in Fig. 5. MS analysis suggests that at least some of these products contain nitrogen atoms since their protonated molecular ions exhibited even $m/z$ ratios pointing to an odd number of nitrogen atoms in the molecules. However, products with an even number of nitrogen atoms in the molecule...
would be observed at odd $m/z$ ratios. Therefore, it cannot be excluded that compounds observed at odd $m/z$ ratios during that retention period contain nitrogen atoms. Noziere et al. (2009) proposed the oligomerization of the iminium intermediates after the nucleophilic attack of ammonia at the carbonyl C-atom as a potential pathway for the formation of higher molecular weight compounds other than heterocycles containing C–N bonds. Such compounds potentially contribute to the observed signals in our chromatograms. However, this would have to be confirmed through the measurement of reference compounds.

A prominent example of a compound eluting during this specific retention period is a compound with $m/z$ 186 eluting at 10.9 min retention time and strongly absorbing at a wavelength of 350 nm. The even $m/z$ ratio of this signal indicates that the corresponding protonated molecular ion contains an odd number of nitrogen atoms. Additionally, the MS/MS of this compound shows the loss of a neutral compound with a mass of 27 Dalton, likely corresponding to hydrogen cyanide (HCN). However, it is not possible to elucidate structural information from this data except for the presence of a functional group containing a C–N bond.

Furthermore, esterification or other reactions increasing the molecular weight and lowering the polarity potentially occur in the reaction mixture. Formic acid, which is produced during the formation of IM, is capable of forming formic acid esters and formamides by reacting with alcohols and (secondary) amines present in the reaction mixture, respectively. A compound with $m/z$ 219 eluting at a retention time of 10.6 min absorbs at 280 nm. The MS/MS of this compound reveals fragments of $m/z$ 191 and $m/z$ 135, corresponding to neutral losses of CO or $C_3H_4O_3$, respectively. Additionally, the UV absorbance at 280 nm hints towards a structure similar to BI. The MS/MS spectrum of this compound and its proposed structure are shown in Fig. 6.

The production rates of these compounds seem to be small as they only appear in detectable amounts after several hours after mixing of Gly and AS. However, the variety of potential products including non-imidazole compounds containing C–N bonds, formamides or formic acid esters in sum could contribute to a considerable amount
of the light-absorbing material formed in the Gly/AS mixtures. This demonstrates the complexity of aqueous phase chemistry even in the relatively simple mixture of glyoxal and ammonium sulfate. In ambient aerosols the number of potential reaction partners is much higher and an identification of appropriate tracer compounds is necessary to estimate the organic carbon production or the impact on aerosol optical properties from distinct precursors.

Interestingly, the low polarity products absorbing at wavelengths between 350 and 400 nm might explain the gap Yu et al. (2011) found between known contributors to the 350 nm absorption band and the actual measured absorption in glyoxal/ammonium sulfate solutions. However, due to the lack of appropriate reference compounds a quantitative statement is not given at this point.

### 3.5 Implications for light-absorbing material from glyoxal in SOA

The major contributors to light-absorbing material from glyoxal in SOA were identified in recent studies (Galloway et al., 2009; Yu et al., 2011) and extended in this work. The formation of imidazoles including IM, (H)IC and BI strongly depends on the pH value and the concentrations of glyoxal and ammonium ions, or ammonia, respectively (Noziere et al., 2009; Yu et al., 2011; this work). The conditions investigated in the recent studies focused on conditions relevant for aerosols over North America or Europe. However, the formation of imidazoles under these conditions was reported to be of minor importance (Galloway et al., 2009; Ervens and Volkamer, 2010; Yu et al., 2011; Trainic et al., 2011, 2012). This study adds to this point of view, since all additionally identified products were produced in even smaller amounts as the previously reported products.

However, there are regions in the world where SOA formation or changes in aerosol optical properties from nitrogen containing oligomers of glyoxal might be more important. As discussed above imidazole formation from glyoxal and ammonia in aerosols should be favored in regions with aerosols exhibiting more alkaline pH values and higher ammonium ion concentrations. Therefore, regions such as Northern India are of
special interest. Due to regional soil characteristics mineral dust particles in extended Indian regions are alkaline in nature (e.g., Kulshrestha et al., 1998; Parashar et al., 2001). Recent studies also revealed high emissions of ammonia from livestock waste, its application in agriculture and the application of inorganic fertilizers (Clarisse et al., 2009). As a consequence, certain organic multiphase processes, e.g. the uptake and further reactions of organics and ammonia leading to secondary light-absorbing products (formation of brown carbon), can be expected to be strongly enhanced. Therefore, dedicated experimental studies under such conditions and ambient measurements in India would enable a much better understanding of the regional SOA formation and aging.

Additionally, the identification of BI as a product in aqueous aerosol mimics containing glyoxal and ammonium sulfate brings up another interesting aspect in connection to light-absorbing material in atmospheric aerosols. 2,2′-biimidazole and other bicyclic heteroaromatic compounds are long known to act as bi- or multidentate ligands in the complex formation of transition metals (e.g., Holmes et al., 1961; Chiswell et al., 1964). Complexes formed in these reactions are generally colored (i.e. red-shifted absorption behavior relative to the parent compounds). Therefore, bicyclic imidazoles acting as bidentate chelating ligands of transition metals (for example in combustion aerosols) might enhance their impact on aerosol optical properties on a regional scale. However, such complexes could also hinder the correct quantification of imidazoles in atmospheric aerosols with common analytical techniques involving UV-Vis spectrometric or mass spectrometric detection. This should be further investigated in future studies.

4 Conclusions

The spectrum of products formed in mixtures containing glyoxal and ammonium sulfate was extended in this work. The major reaction products monocyclic imidazoles, including imidazole, imidazole-2-carboxaldehyde and their N-glyoxal substituted analogs, as well as formic acid were identified in recent studies (De Haan et al., 2009b, 2011;
Galloway et al., 2009; Yu et al., 2011). We report the formation of 2,2′-biimidazole and confirm it as a major contributor to the absorption band at 280 nm measured in Gly/AS mixtures. The production rates of 2,2′-biimidazole are approximately two orders of magnitude smaller than for major reaction products. However, its molar absorptivity at 280 nm is two orders of magnitude higher than for imidazole-2-carboxaldehyde. This demonstrates the necessity of the molecular identification of products of the reactions in the Gly/AS system at trace levels to enable a better understanding of the observed absorbance features. Very recently, the formation of a product absorbing at a wavelength of 290 nm was observed in chamber experiments on AS seed particles affecting the radiative properties of the product aerosols by Trainic and coworkers (Trainic et al., 2011). Very likely 2,2′-biimidazole contributes significantly to this absorption behavior. Additionally, we report the formation of lower polarity products in Gly/AS mixtures, likely also containing C–N bonds and at least partly having structural similarity to imidazoles. Formamides and formic acid esters of imidazoles potentially explain some of the observed signals, which were not previously reported. Most of these lower polarity products absorb light at near visible wavelengths and thus potentially contribute to the light-absorbing material formed in the Gly/AS mixtures.

As pointed out by Shapiro et al. (2009) and Yu et al. (2011) all those products mentioned before do not contribute substantially to SOA mass. However, we were able to demonstrate that even non-major reaction products in Gly/AS mixtures can be major contributors to the observed absorbance behavior. Therefore, due to the high absorption coefficients of some nitrogen containing reaction products, an important influence on the optical and radiative properties of ambient aerosols cannot be excluded. Especially in regions with conditions potentially favoring the formation of imidazoles, i.e. a higher pH value and high ammonium ion concentrations in aerosols (e.g. reported by Kulshrestha et al. (1998) and Parashar et al. (2001) for Northern India), this influence could be very strong.

Additionally, the absorption characteristics of aerosols containing imidazoles, especially bicyclic imidazoles, and transition metals (e.g. iron, copper or manganese in
urban and combustion aerosols as reported e.g. by See et al., 2006) are potentially influenced by the formation of colored transition metal complexes. 2,2’-Biimidazole is known to act as a chelating bidentate ligand in metal complex formation (Holmes et al., 1961). Depending on the respective stability constants and concentrations, those complexes might not only influence the optical properties of the aerosols but also have to be considered as a source of negative artifacts for a potential quantification of imidazoles in ambient aerosols.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/6235/2012/acpd-12-6235-2012-supplement.pdf.

Acknowledgements. This work was supported by the EC project POLYSOA (Polymers in secondary organic aerosols) and the EU-IP EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality Interactions). The authors thank the German Research Foundation (DFG: Deutsche Forschungsgemeinschaft) for their financial support within the Research Training Group 826: Trace Analysis of Elemental Species: Development of Methods and Applications.

References


Identification and characterization of aging products

C. J. Kampf et al.


Table 1. HPLC-ESI-MS/MS characterization of imidazole products in the Gly/AS system.

<table>
<thead>
<tr>
<th>Product abbreviation</th>
<th>Structure</th>
<th>Sum formula</th>
<th>$m/z$ of $[M + H]^+$</th>
<th>$m/z$ of fragments</th>
<th>Retention time/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="image1" alt="Structure" /></td>
<td>C$<em>6$H$</em>{10}$N$_2$</td>
<td>69.1</td>
<td>–</td>
<td>2.2</td>
</tr>
<tr>
<td>HGI</td>
<td><img src="image2" alt="Structure" /></td>
<td>C$_9$H$_8$O$_3$N$_2$</td>
<td>145.1</td>
<td>69.1</td>
<td>2.3</td>
</tr>
<tr>
<td>HGII</td>
<td><img src="image3" alt="Structure" /></td>
<td>C$<em>7$H$</em>{12}$O$_5$N$_2$</td>
<td>203.0</td>
<td>185.0, 69.1</td>
<td>2.4</td>
</tr>
<tr>
<td>IC</td>
<td><img src="image4" alt="Structure" /></td>
<td>C$_4$H$_6$ON$_2$</td>
<td>97.1</td>
<td>69.1</td>
<td>2.3</td>
</tr>
<tr>
<td>HIC</td>
<td><img src="image5" alt="Structure" /></td>
<td>C$_4$H$_8$O$_2$N$_2$</td>
<td>115.1</td>
<td>97.1</td>
<td>2.2</td>
</tr>
<tr>
<td>GHIC</td>
<td><img src="image6" alt="Structure" /></td>
<td>C$_6$H$_8$O$_4$N$_2$</td>
<td>173.1</td>
<td>155.1, 115.1, 97.1</td>
<td>2.4</td>
</tr>
<tr>
<td>HGHIC</td>
<td><img src="image7" alt="Structure" /></td>
<td>C$<em>9$H$</em>{10}$O$_5$N$_2$</td>
<td>191.1</td>
<td>no data</td>
<td>2.4</td>
</tr>
<tr>
<td>BI</td>
<td><img src="image8" alt="Structure" /></td>
<td>C$_6$H$_8$N$_4$</td>
<td>135.0</td>
<td>108.1, 81.0</td>
<td>3.5</td>
</tr>
<tr>
<td>GBI</td>
<td><img src="image9" alt="Structure" /></td>
<td>C$_8$H$_8$O$_2$N$_4$</td>
<td>193.0</td>
<td>135.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 2. Initial production rates of BI depending on initial Gly concentration.

<table>
<thead>
<tr>
<th>[Gly]_{init}/M</th>
<th>0.01</th>
<th>0.3</th>
<th>0.9</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{BI}/10^{-9}$ M s$^{-1}$</td>
<td>0.074 ± 0.002</td>
<td>1.58 ± 0.14</td>
<td>5.0 ± 0.26</td>
<td>7.19 ± 0.44</td>
</tr>
</tbody>
</table>
Figure 1. Proposed reaction pathways for imidazole formation in the glyoxal/ammonium sulfate system are shown. Green colored compounds were previously described in literature (Yu et al., 2011; Galloway et al., 2009); orange colored compounds were identified in this work.
Figure 2. Typical MS of 1.5 M Gly in 3 M AS at 2.3 min retention time.
Figure 3. Typical MS of 0.01 M Gly in 3 M AS at 3.4 min retention time.
Figure 4. Concentration of BI in 3 M AS at different initial glyoxal concentrations is shown as a function of reaction time. Concentrations were determined via 280 nm absorption band at 3.5 min retention time using HPLC-DAD.
Figure 5. Temporal evolution of relatively apolar products in a Gly/AS mixture (1.5 M Gly, 3 M AS). The blue chromatogram was recorded immediately after mixing and the red chromatogram 116.05 h after mixing (sum of absorbances at wavelengths between 350 and 400 nm).
Figure 6. MS/MS of a compound with m/z 219 eluting at 10.6 min retention time. Proposed structure and neutral losses are shown.