

Letter

# pH Dependence of the Imidazole-2-carboxaldehyde Hydration Equilibrium: Implications for Atmospheric Light Absorbance

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## **Supporting Information**

**ABSTRACT:** Imidazole-2-carboxaldehyde (IC) has been identified as an aqueous "brown carbon" absorber and a possible atmospheric photosensitizer. IC exists in a pH-dependent equilibrium between its aldehyde and geminal diol form; the diol form is the dominant species in solution at pH <5. Calculated molar absorptivity coefficients are  $13700 \pm 200 \text{ cm}^{-1} \text{ M}^{-1}$  at 287 nm for the aldehyde and  $7800 \pm 100 \text{ cm}^{-1} \text{ M}^{-1}$  at 212 nm for the diol. This shift from aldehyde to diol changes the peak light absorption of the aqueous solution from 287 to 212 nm, which is beyond the actinic range and may have implications for radiative forcing. The observed pH-dependent shift in the hydration equilibrium of IC is driven by the interaction between its



hydration and protonation equilibria. Calculated  $pK_a$  values are 2.5  $\pm$  0.4 and 5.94  $\pm$  0.05 for the aldehyde and diol, respectively, and are consistent with the trend toward increasing diol as the pH decreases. The acid–base equilibrium affects both the solubility and the major species in solution depending on the protonation state of IC and may affect atmospheric light absorption, brown carbon, and photosensitization under acidic conditions. These findings indicate a need for a greater level of attention to the effect of the matrix in aqueous atmospheric systems, particularly concerning species affected by multiple equilibria.

# INTRODUCTION

Imidazoles make up one class of light-absorbing ("brown carbon") compounds formed in secondary organic aerosol (SOA) through the reaction of ammonium salts with  $\alpha$ -dicarbonyls (Figure 1).<sup>1,2</sup> Of the imidazole derivatives identified as reaction products of ammonium and glyoxal, only imidazole-2-carboxaldehyde (IC) has been observed in ambient aerosol (at <4 ng/m<sup>3</sup>).<sup>3</sup> IC has significant molar absorptivity



**Figure 1.** Formation of IC and the associated protonation and hydration equilibrium reactions that occur in aqueous solution. A reaction scheme describing the role of IC as a photosensitizer is shown in Figure S1.

coefficients; published values range from 229 to 6100 cm<sup>-1</sup>  $M^{-1}$ , indicating that IC could contribute to radiative forcing via its brown carbon nature even at low atmospheric concentrations.<sup>1,2,4–7</sup>

Aregahegn et al.<sup>7</sup> showed that several imidazole compounds (imidazole, 2,2'-bi-1H-imidazole, and IC) act as photosensitizers in the presence of ultraviolet light and certain volatile organic compounds (VOCs). Atmospheric photosensitizing compounds within the condensed phase absorb light and then transfer the energy to VOCs at the surface of a particle (Figure S1).<sup>8,9</sup> This photoinitiated VOC oxidation has been identified as a possible source of missing ambient aerosol mass.<sup>7,8,10-12</sup> Of the imidazoles studied, IC contributed to the greatest amount of aerosol growth. However, further studies of the significance of IC photosensitization as a source of aerosol mass have called into question the magnitude of this contribution.<sup>8,9,13</sup> Tsui et al.<sup>9</sup> modeled photosensitized aerosol growth via the triplet excited state of IC (<sup>3</sup>IC\*) under laboratory and ambient conditions and found that <sup>3</sup>IC\* contributes <0.3% by mass of total aqueous SOA growth, while humic-like substances may be a more significant source.

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The surrounding solution affects the chemistry of both the aldehyde and the basic nitrogen (N3) on IC. Aqueous carbonyls exist in a hydration equilibrium between a carbonyl and a geminal diol (Figure 1). In a neutral solution, a small amount of IC exists as its diol [1-(1*H*-imidazol-2-yl)-methanediol], while the majority is in the aldehyde form.<sup>14</sup> Water availability in solution is a factor in this equilibrium under atmospheric conditions.<sup>15</sup> The aldehyde could be favored in particles with a lower liquid water content (LWC), while some atmospheric droplets (clouds and fog) contain a higher LWC that may favor diol formation.<sup>16</sup>

Atmospheric pH varies widely and affects the chemical form of acidic compounds; a compound will protonate if the surrounding pH is lower than its  $pK_a$ . SOA is acidic, with recently measured particle pH values between -0.51 and  $4.00.^{17-22}$  However, primary sea spray aerosol is likely to initially be basic,<sup>23-26</sup> and pH values for cloud and fog droplets have been observed between 3.00 and 7.50.<sup>27-29</sup> Therefore, organic compounds within an atmospheric droplet may be exposed to a range of pH conditions during their lifetime.

The chromophoric nature of a compound is highly dependent on its chemical structure. For compounds at equilibrium, such as those described above for IC, hydration or protonation of a molecule will change the electronic structure and possibly the optical properties. This is especially important for brown carbon and photosensitizing compounds. Most brown carbon compounds are classified as such because although their wavelength of maximum absorbance  $(\lambda_{max})$  is in the ultraviolet (UV) region, their molar absorptivity "tails" into the visible region, giving the molecule a brown color.<sup>30</sup> If protonation or hydration of a molecule results in blue-shifted absorbance, this tail may shift too far into the UV region to contribute to visible light absorbance and be considered brown carbon. This can also affect photosensitization; a photosensitizing compound must absorb light and then come into contact with a VOC at the surface of a droplet to which it can transfer a specific quanta of energy.8 This requires an atmospheric photosensitizer to absorb light in the actinic region, so chemical reactions resulting in blue-shifted absorbance may also change the effectiveness of a molecule as a photosensitizer. In this work, we present a systematic study of the pH dependence of the IC protonation and hydration equilibria in aqueous solution and the optical properties thereof.

#### MATERIALS AND METHODS

All chemicals were used as received from Sigma-Aldrich unless otherwise designated. The solution pH was measured with an Accumet Basic pH meter. All data were taken in triplicate.

Nuclear Magnetic Resonance (NMR) Spectroscopy. <sup>1</sup>H NMR measurements were taken with a Joel 400 MHz spectrometer (see the Supporting Information for further details). Saturated IC solutions were buffered with 100 mM oxalic acid (pH <6) or sodium bicarbonate (pH >6, Fisher); the pH of each solution was adjusted down with sulfuric acid or up with sodium hydroxide and each solution was allowed to equilibrate overnight. Deuterium oxide (99.9%) was added to each solution to allow the spectrometer to lock on the signal, and dimethyl sulfoxide was added for quantitative purposes. Analogous experiments were conducted using solutions containing 13 mM IC. Relative peak areas of the NMR spectra were used to determine the concentrations of aldehyde and diol in solution.

UV–Visible (UV–vis) Spectroscopy. For the light absorption experiments, solutions of ammonium sulfate, succinic acid, and IC were mixed to produce a solution containing each at a concentration of 1 mM. The pH was adjusted down with sulfuric acid or up with ammonium hydroxide and then allowed to equilibrate overnight. The UV– vis absorbance was measured using a NanoDrop spectrophotometer (Thermo Scientific, 1 mm optical path length), with 2  $\mu$ L samples blanked against solutions containing 1 mM ammonium sulfate and 1 mM succinic acid. Absorbance data were taken over the working range of the instrument (200–800 nm).

#### RESULTS AND DISCUSSION

IC Concentration. A sample NMR spectrum at pH 5.23 is shown in Figure S2 along with peak assignments.<sup>1</sup> Maxut et al.<sup>2</sup> determined the IC solubility to be ~15 mM under neutral conditions via NMR. To ensure that the differences observed in the relative concentrations of aldehyde and diol were not due to changes in overall solubility, the molar solubility of IC was calculated over a range of pH values (Figure S3; see the Supporting Information for further details). The IC solubility at pH >5.50 is  $36 \pm 2$  mM. The solubility increases significantly as the pH drops below 5 to 4.86 M at pH 2.63. This solubility trend can be explained by considering the  $pK_a$  of IC.  $pK_a$  values for the aldehyde and diol were calculated for each compound by monitoring changes in chemical shift values with pH (Figure S4). Calculation details are given in the Supporting Information. pK<sub>a</sub> values are 2.5  $\pm$  0.4 and 5.94  $\pm$  0.05 for the aldehyde and diol, respectively. These are in agreement with the values of 2.46  $\pm$  0.69 and 6.20  $\pm$  0.70, respectively, predicted by ACDLabs.<sup>31,32</sup> The protonated cation would be significantly more soluble than the deprotonated neutral molecule, which explains the rapid decrease in solubility as the pH increases above 5 and the molecules are deprotonated.

At low pH, nearly all IC molecules are in the hydrated diol form. Under more basic conditions (pH >5), the aldehyde becomes the more abundant species in solution with only 3% of IC in the diol form at pH 8.92. The same trend occurs in experiments in which the total IC concentration was 13 mM, indicating that this is not a concentration-dependent equilibrium. While the hydration of the aldehyde can be acidor base-catalyzed, the catalysis itself should not change the equilibrium concentrations of aldehyde and diol in solution, only the rate at which the system reaches equilibrium. Therefore, the acid-catalyzed hydration cannot be the driving factor in the shift from aldehyde to diol with increasing acidity. However, the coexisting acid-base equilibrium does affect hydration, and the gap between the  $pK_a$  values explains this shift to the diol. At pH <4.94, most diol molecules will be protonated. Following Le Châtelier's principle, the neutral IC equilibrium will then shift toward the diol. As the pH decreases and more diol becomes protonated, the neutral hydration equilibrium continues to shift toward the diol and the total diol concentration (neutral + protonated) increases. The imidazolium cation also increases the electrophilicity of the aldehyde carbon. Therefore, as the pH approaches 2.5 and the fraction of protonated aldehyde increases, so does the rate of hydration, and the protonated equilibrium shifts further toward the diol. This essentially traps the IC in the diol form as the acidity increases, which can be seen in Figure 2 as the fraction of diol begins to increase significantly as the pH drops below 5.94. Under the acidic pH conditions found in fine atmospheric



**Figure 2.** Relative contributions of aldehyde (red circles) and diol (blue squares) forms to the total IC concentration as a function of pH. The diol becomes the dominant form under acidic conditions (pH <5, blue shaded area). Chemical structures show the dominant species in each pH range denoted by the shaded areas (neutral aldehyde in red and protonated diol in blue). Vertical lines give the  $pK_a$  values for the aldehyde (red dashed–dotted line) and diol (blue dashed line) species. Error bars show a  $1\sigma$  error.

aerosol (pH -0.5 to 3),<sup>20</sup> the IC hydration equilibrium strongly favors the hydrated diol.

The hydration equilibrium constant  $(K_{hyd})$  for the equilibrium between the neutral IC aldehyde and diol (top equilibrium, Figure 1) can be estimated from these data. Details about the calculations are given in the Supporting Information. Because some of the IC molecules are protonated at the highest pH value tested here,  $K_{hyd}$  cannot be precisely determined for this equilibrium. However, the estimated upper bound for the hydration constant is calculated to be 0.043. For the neutral IC hydration equilibrium, the aldehyde is strongly favored. The presence of the basic nitrogen (N3) on the imidazole ring leads to an increase in the apparent  $K_{hyd}$  at lower pH values as the imidazole is protonated and the cationic diol becomes the favored species (Figure S5).

**UV–Vis Absorbance.** Two peaks are observed in the UV– vis absorption spectra of aqueous IC. As the pH decreases, the absorbance at 212 nm increases while the peak at 287 nm decreases (Figure 3 and Figure S6). On the basis of a similar trend in the NMR data, we can conclude that the aldehyde absorbs at 287 nm and the diol absorbs at 212 nm. Because the carbonyl group is part of the conjugated  $\pi$ -electron system, its presence may be the driving factor in the absorbance at wavelengths closer to the visible region.

Via combination of the NMR and absorbance data, molar absorptivity coefficients were calculated for the aqueous diol and aldehyde species. The molar absorptivity coefficients are  $7800 \pm 100$  cm<sup>-1</sup> M<sup>-1</sup> for the diol at 212 nm and 13700 \pm 200  $\mbox{cm}^{-1}\ \mbox{M}^{-1}$  for the aldehyde at 287 nm. These calculations include only data from pH values at which the individual species contributes >75% of the total IC concentration. Errors given are  $1\sigma$ . Previously published aqueous molar absorptivity coefficients assume the IC is in the aldehyde form and that one compound contributes to both absorption peaks. Yu et al.<sup>1</sup> calculated molar absorptivity coefficients of  $6119 \pm 302$  cm<sup>-1</sup>  $M^{-1}$  at 213 nm and 229.9 ± 3.0 cm<sup>-1</sup>  $M^{-1}$  at 273 nm. Kampf et calculated molar absorptivity coefficients of 6004  $\pm$  638 al.<sup>6</sup>  $cm^{-1} M^{-1}$  at 213 nm and  $273 \pm 38 cm^{-1} M^{-1}$  at 273 nm. These numbers are significantly lower than those calculated in this



**Figure 3.** IC absorbance overlaid with solar spectral flux densities calculated with the Quick TUV calculator corresponding to Los Angeles, CA, at noon on the summer solstice.<sup>33</sup> Note the lack of overlap between the solar spectrum and the absorbance peak at 212 nm.

study; however, the numbers presented here take into account the actual concentration of each species in solution.

Atmospheric Implications. IC has been identified as a possible atmospheric brown carbon and photosensitizing compound. This work indicates that there may be atmospheric conditions under which the optical properties of IC are significantly altered. Wavelengths of <300 nm do not reach the lower troposphere (Figure 3, dotted line),<sup>33</sup> so IC may not absorb significant atmospheric radiation to act as a photosensitizer or contribute to brown carbon if it is in the diol form  $(\lambda_{max} = 212 \text{ nm})$ . Structurally, there is evidence that the carbonyl acts to enhance the photosensitizing ability of IC.<sup>7,11</sup> If the diol is the dominant species in solution, which is likely under acidic conditions, the absence of the carbonyl would diminish the photosensitizing capability of the compound. These results add to previous work studying the impacts of photosensitization reactions on overall ambient SOA growth.<sup>8,9,13</sup> Tsui et al.<sup>9</sup> did not consider the pH dependence of the <sup>3</sup>IC\* photosensitization reaction and studied acidic particles (1 < pH < 4). More than 90% of the IC is in the diol form under these conditions, indicating that the <sup>3</sup>IC\* concentration, and therefore the kinetics, used in that study may have been overpredicted. Therefore, the contribution to SOA growth from <sup>3</sup>IC\* chemistry is likely smaller than the predicted value of 0.3% by mass.

The results of this work can be applied to many aqueous atmospheric droplets and highlight the need to understand the solution matrix within the droplets, especially given the variety of conditions that may be present. Atmospheric droplets exist under conditions different from the bulk conditions studied here, but parallels can be drawn. The LWC is significantly lower in droplets than in bulk solutions, which would likely shift the IC hydration equilibrium toward the aldehyde. However, the LWC increases in cloud and fog droplets, which could lead to an increased level of diol.<sup>16</sup> Because atmospheric water can exist in a variety of LWC regimes,<sup>16</sup> and a droplet may cycle through several regimes during cloud processing events,<sup>34</sup> a compound may shift hydration states several times during its atmospheric lifetime. These changing regimes would change the optical properties, and possibly the reactivity, of compounds within the droplets.

In the pH range of cloud and fog droplets, it is possible that the hydration equilibrium will favor the neutral aldehyde.<sup>27–29</sup>

This would be in competition with the LWC-driven hydration, which makes prediction of  $K_{\rm hyd}$  difficult under the range of LWC and pH conditions that may be present in the atmosphere. The sea surface microlayer is also basic, and sea spray aerosols are likely basic upon formation before the acidity decreases due to partitioning of gaseous species.<sup>23–26</sup> Therefore, the optical properties of similar compounds within these droplets may change over time as their surrounding matrix is altered.<sup>23–26</sup> These findings indicate that we must be thoughtful about the assumptions we make concerning atmospheric systems and that the surrounding matrix may play a greater role than previously considered in the chemical and optical properties of atmospheric droplets. We must also consider the evolution of the droplet matrix with time, as this can shift equilibria.

In broader terms, the pH-dependent light absorbance described herein has implications for compounds within atmospheric droplets beyond IC. If atmospheric IC is in the diol form, it is not likely to absorb light in the actinic region and may not be considered brown carbon, but the low atmospheric concentrations (<4 ng/m<sup>3</sup>) of IC make this unlikely to significantly change global predictions of brown carbon radiative forcing.<sup>3</sup> However, many atmospheric compounds are multifunctional, and this interplay between the basic nitrogen atom and carbonyl group indicates that acid-base chemistry can play an important role in governing the hydration equilibria of nearby functional groups. This may affect optical properties, as seen here, or could affect the reactivity of the molecule. This can be more generally applied to any chemical equilibrium where structural changes cause a significant difference between the  $pK_a$  of the resulting species, which is more likely to occur in small molecules or those in which the protonation site is close to the functional group undergoing the equilibrium reaction, because proton affinity will change as the nearby electronic structure changes. Further studies are needed to look at these and similar compounds in the droplet phase to determine the importance of this interplay between acidity and other chemical equilibria.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00486.

NMR data collection parameters; a sample <sup>1</sup>H NMR spectrum of IC, showing peak assignments; further information about the  $pK_a$  and  $K_{hyd}$  calculations; and UV–vis absorbance data for IC across the pH range (PDF)

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## Notes

The authors declare no competing financial interest.

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