

# Evidence for the Formation of Imidazole from Carbonyls and Reduced Nitrogen Species at the Individual Particle Level in the Ambient Atmosphere

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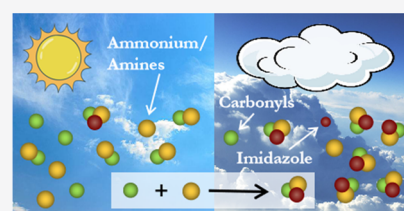


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Supporting Information

**ABSTRACT:** While laboratory studies have demonstrated that aqueous reactions between carbonyls and reduced nitrogen species may contribute to the production of N-heterocycle brown carbon (BrC) such as imidazole, there is currently a lack of evidence for this in the atmosphere. We investigated the mixing state of carbonyls, ammonium, amines, and imidazole (as a surrogate of BrC) in cloud residual, interstitial, and cloud-free particles by single-particle mass spectrometry. The results provide the first ambient evidence of the formation of imidazole through reactions between carbonyls and ammonium/amines at the individual particle level. The key evidence for this is that 60% of the imidazole particles are internally mixed with carbonyls and ammonium/amines. The number fraction of imidazole is significantly enhanced in particles with internally mixed carbonyls and ammonium (7.8%)/amines (26.7%), compared with that (1.4%) in all of the cloud-free particles. Furthermore, a higher number fraction of imidazole is observed in all cloud residual and interstitial particles (2.9%) than in the cloud-free particles (1.4%). This is due to the enhancement of amines and/or the synergistic effect of ammonium and amines in the formation of imidazole in cloud residual and interstitial particles. These findings extend the current understanding of the formation and evolution of imidazole-based BrC.



## 1. INTRODUCTION

Brown carbon (BrC) plays a considerable role in the aerosol radiative forcing of the Earth's climate.<sup>1</sup> Secondary BrC produced from the aqueous-phase reactions of carbonyls (e.g., methylglyoxal and glyoxal) and reduced nitrogen species ( $\text{NH}_3$ ,  $\text{NH}_4^+$ , amines, and amino acids) has therefore attracted an increasing amount of attention.<sup>2–4</sup> Laboratory simulations show that these BrC products are highly light absorptive at wavelengths of 207–230 and 280–330 nm.<sup>5–10</sup> Among secondary BrC products, N-heterocyclic compounds, such as imidazoles, contribute the most to light absorption and are active photosensitizers.<sup>11</sup>

Several imidazoles have been identified in solutions of carbonyls and reduced nitrogen species. For instance, 1*H*-imidazole-2-carboxaldehyde, 1*H*-imidazole, and 2,2-bisimidazole have been detected in glyoxal and ammonium sulfate bulk solutions.<sup>12,13</sup> Moreover, 1,3-dimethylimidazole has been identified in the aqueous-phase reactions of glyoxal with amino acids<sup>14</sup> and methylamine.<sup>15</sup> The browning reactions of carbonyls and ammonium or amines occur slowly in bulk solutions (hours to days).<sup>4,16–18</sup> However, these processes take only tens of seconds to minutes in simulated cloud evaporation.<sup>14,19–21</sup> The reactions are expected to be accelerated in highly concentrated solutions due to evaporating droplets<sup>16</sup> and/or the autocatalytic photosensitization of radical species generated by the photolysis of BrC.<sup>20</sup> Prior studies have shown that BrC from these solutions can be

quickly photobleached.<sup>10,22</sup> However, recent studies have shown the regeneration of BrC in simulated cloud processes after photobleaching.<sup>20</sup>

Imidazoles are commonly found as byproducts of cooking activities.<sup>23,24</sup> However, few studies have identified or quantified imidazoles in ambient aerosols; their concentrations have been reported to be in the range of 0.1–14 ng m<sup>-3</sup> in the atmosphere of Germany, Japan, and China.<sup>25–27</sup> Until now, very little about the direct formation of imidazoles or about the direct link of the laboratory-hypothesized precursors to imidazole formation in the real atmosphere is known. On the basis of the ubiquitous presence of carbonyls, ammonium, and amines in the troposphere, especially in wet aerosols and fog/cloud droplets,<sup>28,29</sup> we speculate that imidazole can be formed in the troposphere, yet this needs to be confirmed.

To better understand the evolution of imidazole, we investigated the detailed mixing state of ambient and cloud-processed (cloud residual and interstitial) particles containing imidazole, carbonyls, and ammonium/amines, based on single-

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particle mass spectrometry (SPMS). The objective of this work is not to establish a quantitative relationship between imidazole with carbonyls and ammonium/amines but rather to explore the evidence of the production of imidazole from carbonyls and ammonium/amines in the real atmosphere. In addition, the factors influencing the formation of imidazole, including cloud processing and the abundance of ammonium and amines, are discussed.

## 2. MATERIALS AND METHODS

**2.1. Data Collection.** The main data used in this study were the measurements of individual particles by single-particle aerosol mass spectrometry (SPAMS). A detailed description of the operational principle of SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China) has been provided previously<sup>30</sup> and is outlined in the [Supporting Information](#). The data sets, including the size and chemical compositions of individual particles, were collected in urban Guangzhou and at the Mt. Tianjing remote site (24° 41' 56" N, 112° 53' 56" E; 1690 m above sea level) in southern China. Herein, we primarily show the results obtained at the Mt. Tianjing site, from May 9 to June 4, 2018. Other data, including those collected in Guangzhou and at the Mt. Tianjing site, used to support the discussion are also described in the [Supporting Information](#).

At the Mt. Tianjing site, separate inlets were employed to collect ambient and cloud-processed particles. During cloudy periods (an upper limit visibility threshold of 5 km and a lower limit relative humidity threshold of 95%<sup>31</sup>), a ground-based counterflow virtual impactor (model 1205, Brechtel Manufacturing Inc.) inlet was used to collect cloud residual (RES) particles,<sup>31</sup> as detailed in the [Supporting Information](#). A PM<sub>2.5</sub> cyclone inlet was used to deliver ambient particles under cloud-free conditions and cloud interstitial (INT) particles during cloud events. Only cloud-free particles with aerodynamic diameters ( $d_a$ ) of <2.5  $\mu\text{m}$  were collected at the Guangzhou site. The size and chemical composition of the sampled particles were obtained using downstream SPAMS.

**2.2. Data Analysis.** Data analysis was performed by importing single-particle size and mass spectra into MATLAB (The MathWorks, Inc.) using the FATES toolkit.<sup>32</sup> Particle types were classified according to whether a particle contained one or more specific chemical components, with a peak area that is >3 times the noise level of SPAMS. Imidazole (IM)-containing particles were identified with an ion peak at  $m/z$  69  $[\text{C}_3\text{H}_4\text{N}_2 + \text{H}]^+$  by SPMS and electrospray ionization mass spectrometry.<sup>13</sup> Laboratory generation of various imidazole compounds followed by SPAMS detection identified several representative peaks for imidazoles, including 1*H*-imidazole, 1,3-dimethylimidazole, 2,2-bisimidazole, 2,4-dimethylimidazole, and 4-methylimidazole. All of the imidazoles exhibit similar characteristic peaks at  $m/z$  68  $[\text{C}_3\text{H}_4\text{N}_2]^+$  and  $m/z$  69  $[\text{C}_3\text{H}_4\text{N}_2 + \text{H}]^+$  ([Figure S1](#)). Therefore, we use the peak at  $m/z$  68 or 69 to represent substances containing imidazole rings. Peaks for imidazole-based products at  $m/z$  81  $[\text{C}_4\text{H}_5\text{N}_2]^+$ ,  $m/z$  83  $[\text{C}_4\text{H}_7\text{N}_2]^+$ ,  $m/z$  95  $[\text{C}_5\text{H}_7\text{N}_2]^+$ , and  $m/z$  97  $[\text{C}_5\text{H}_9\text{N}_2]^+$  are also enriched in the IM-containing particles, with a number fraction of ~20–40%.

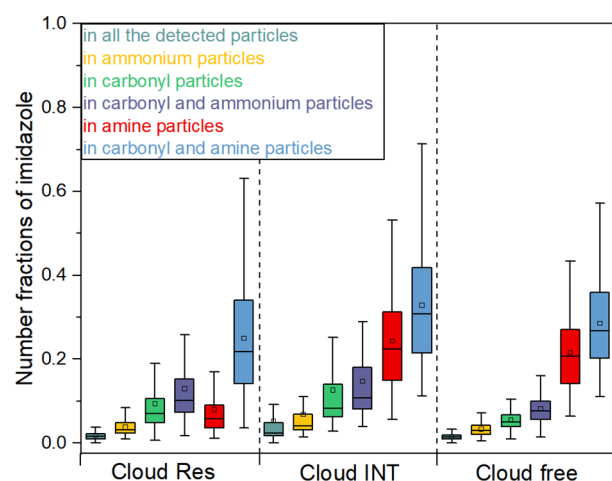
We note that this is the most probable assignment of imidazole-based products because other interference from various organics cannot be eliminated through such a technique. The peak at  $m/z$  68 is also considered to be a fragment from zinc when it appears with peaks at both  $m/z$  64

and 66; however, it is not the case for most of the particles (95.8% by number) in this study. In our field observations, acceptable correlations exist among the temporal trends of the hourly number count of the peak  $m/z$  68- and 69-containing particles in the cloud RES ( $r = 0.91$ ;  $p < 0.01$ ), cloud INT ( $r = 0.89$ ;  $p < 0.01$ ), and cloud-free particles ( $r = 0.88$ ;  $p < 0.01$ ) ([Figure S2](#)), confirming the correct assignment of imidazole. In this scenario, 36015 IM-containing particles were identified, including 18907 cloud RES, 9733 cloud INT, and 7375 cloud-free particles in the size range ( $d_a$ ) of 0.2–2.0  $\mu\text{m}$ .

Carbonyl-containing particles are represented by peaks at  $m/z$  -71  $[\text{C}_3\text{H}_3\text{O}_2]^-$  (methylglyoxal or acrylate) or  $m/z$  -73  $[\text{C}_3\text{H}_5\text{O}_2]^-$  (glyoxylate).<sup>33,34</sup> Methylglyoxal and glyoxal, as the most abundant carbonyls in the environment, usually coexist in the atmosphere. Glyoxylate is a major oxidation product of glyoxal, and its number fraction is well correlated ( $r = 0.91$ ;  $p < 0.01$ ) with the ion peak at  $m/z$  -71 throughout the sampling period. Ammonium- and amine-containing particles were identified with ion peaks at  $m/z$  18  $[\text{NH}_4]^+$  and  $m/z$  59  $[(\text{CH}_3)_3\text{N}]^+$  or  $m/z$  86  $[(\text{C}_2\text{H}_5)_2\text{NCH}_2]^+$ , respectively.<sup>30,35,36</sup> An illustration showing the mixing state among carbonyls, imidazole, and amines/ammonium is provided in [Figure S3](#).

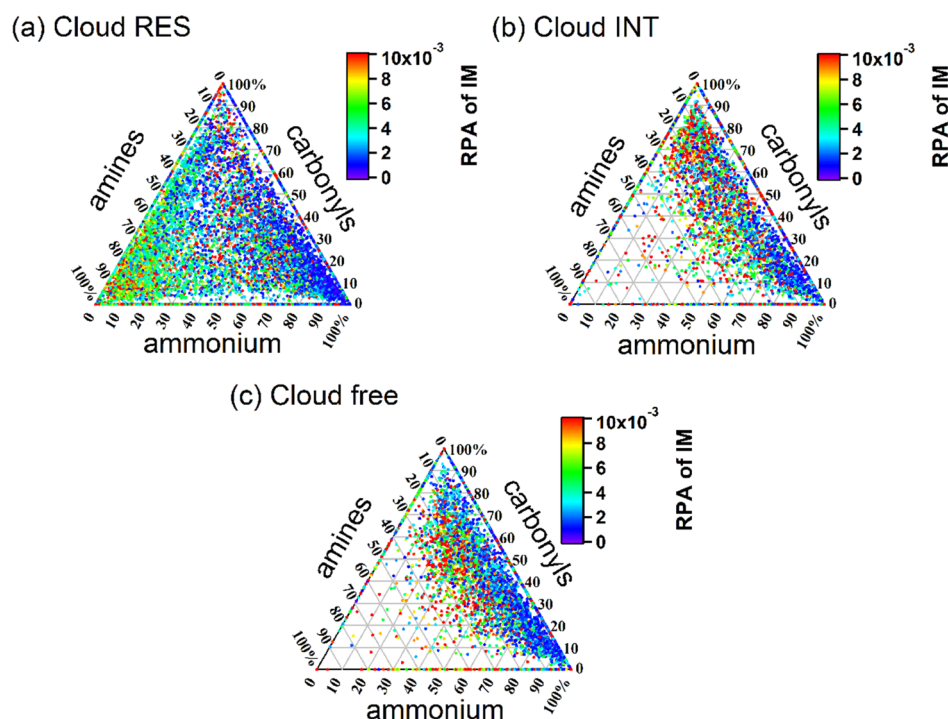
## 3. RESULTS AND DISCUSSION

### 3.1. Imidazole Derived from Reactions between Ammonium/Amines and Carbonyls. [Figure 1](#) shows a



**Figure 1.** Number fractions of imidazole in each particle type for the cloud RES, cloud INT, and cloud-free particles in June 2018.

considerable difference in the number fraction of imidazole in various particle types, with different mixing states between ammonium/amines and carbonyls. The average number fractions (3.3–32.8%) of imidazole in the particles containing amines, ammonium, or carbonyls are considerably higher than those in all of the detected particles (1.5–5.2%). Moreover, higher number fractions of imidazole are found in the internally mixed carbonyls and ammonium/amine particles. Approximately 60% of imidazole is mixed with carbonyls and ammonium and/or amines, with only 10% of the imidazole externally mixed with these species in four data sets ([Figure S3](#)). Less imidazole mixed with carbonyls, amines, or ammonium in January 2016 may be due to the influence of air mass.<sup>36,37</sup> However, the air mass does not have a significant influence on the number fraction and chemical composition of particles during the sampling period from May to June of 2018



**Figure 2.** Ternary plots showing the relative distributions of RPA of imidazole, amines, ammonium, and carbonyls for the IM-containing particles in June 2018.

(Figure S4). Additionally, there are significant correlations ( $r = 0.16$ – $0.61$ ;  $p < 0.01$ ) between the hourly number fractions of ammonium-, amines-, or carbonyl-containing particles and IM-containing particles in June 2018 (Table S1); the mixing state characteristics suggest that most of the imidazole is derived from reactions between carbonyls and ammonium or amines in the atmosphere.<sup>34,38–40</sup>

Laboratory simulations have shown that carbonyls can potentially generate imidazole and other N-heterocyclic compounds in the presence of amines or ammonium by nucleophilic attack<sup>4,12,14,15,41–43</sup> or be oxidized to organic acids (such as oxalic acid).<sup>44,45</sup> In the troposphere, carbonyls dissolved in cloud droplets can potentially form nitrogen-containing organics in the presence of ammonium or amines or produce organic acids in the presence of oxidants (ozone, hydroxyl radicals, etc.).<sup>46,47</sup> Consequently, these N-heterocyclic compounds could be assumed to be internally mixed with organic acids and other low-volatility organics.<sup>14,48</sup> Consistently, organic acids<sup>25,40</sup> (47–78%) and nitrogen-containing organics<sup>40,49,50</sup> (~70%) are frequently observed in IM-containing particles. In addition, the number fractions of ammonium, amines, nitrogen-containing organics, and organic acids are also remarkably higher in the IM-containing particles than in all of the detected particles (Figure S5). Field measurements show results that are consistent with studies that suggest imidazole as a tracer for the browning reactions of carbonyls and reductive nitrogen,<sup>5,12,42</sup> helping to confirm the mechanism of imidazole formation in the ambient atmosphere.

Further evidence supporting this mechanism is the detection of the concurrent products with imidazoles, such as  $m/z$  87 [IM + H<sub>2</sub>O + H]<sup>+</sup>,  $m/z$  135 [C<sub>6</sub>H<sub>7</sub>N<sub>4</sub>]<sup>+</sup>, and  $m/z$  –45 [HCO<sub>2</sub>]<sup>–</sup>.<sup>13</sup> These products account for 36%, 6%, and 72% of the IM-containing particles, respectively, and for 2%, 0.2%, and 19% of all of the detected particles, respectively. In addition, the concurrent products with ion peaks at  $m/z$  87 or –45 show

temporal profiles similar to those of imidazole ( $r = 0.27$ – $0.60$ , and  $r = 0.48$ – $0.56$ ) (Table S2), consistent with previous laboratory simulations.<sup>13</sup> These formic acids derived from carbonyl–ammonium/amine reactions may affect the acid–base balance of the IM-containing particles.<sup>51,52</sup> Other suspected concurrent products such as those at  $m/z$  104, 125, 149, 165, and 184 (peak assignments and references in Table S3) also occur more frequently in IM-containing particles (5.0–19.9%) than in all of the detected particles (0.1–3.3%).

This finding represents ambient observational evidence of the formation of imidazole via interactions between carbonyls and ammonium/amines at the level of individual particles. Low imidazole concentrations (0.2–14 ng m<sup>–3</sup>) have been observed in ambient aerosol samples of different environments in Europe, Japan, and China.<sup>25–27</sup> Our data show that the number fraction of IM-containing particles varied over a wide range (1–27%) (Figure S6a). While prior laboratory studies have shown that amine/ammonium-BrC can be quickly photobleached,<sup>10,22</sup> no significant diurnal variations of imidazole were observed (Figure S6b), which may indicate an unresolved process of imidazole-related chemistry in the atmosphere.

It should be noted that it is still quite challenging for SPAMS to provide quantitative information about chemical compositions.<sup>53–55</sup> Despite this, the number fraction and relative peak area (RPA) are still suitable indicators for investigating the atmospheric processing of various species in individual particles.<sup>34,56</sup> RPA is defined as the fractional peak area of each  $m/z$  peak relative to the sum of peak areas in the mass spectrum, which is applied to represent the relative amount of a species in a particle.<sup>53,54</sup> Although they are insufficient to provide a quantitative assessment of imidazoles, our results successfully identify the mixing state of imidazole and provide evidence for the possible pathways of imidazole production in

the ambient atmosphere and, thus, can help achieve a qualitative understanding of the formation and evolution of imidazoles in individual particles.

**3.2. Cloud Processing Enhanced the Formation of Particulate Imidazole.** The average number fractions of the IM-containing particles in all of the measured cloud RES (2.1%) and INT particles (2.9%) (Figure 1) are significantly higher than those in all of the measured cloud-free particles (1.4%) throughout the sampling period. Similar patterns are also found for the RPA of imidazole and the RPA ratio of imidazole to carbonyls. Consistently, the marker ion peaks of the concurrent products ( $m/z$  104, 125, 149, 165, and 184) found in carbonyl and ammonium or amine solutions occur more frequently in the cloud-processed particles (Figure S7). These results indicate that cloud processing may facilitate the formation of imidazole from carbonyls.

Factors affecting the formation of imidazole in cloud droplets may include reactant concentrations, liquid water content, etc.<sup>57–60</sup> Figure 2 depicts the ternary plots of relative distributions of amines, ammonium, and carbonyls in the cloud-free, cloud INT, and cloud RES particles. Most of the data points are distributed along the carbonyl–ammonium axes in the cloud-free and cloud INT particles, indicating the limited involvement of amine in the formation of imidazole. In contrast, there are more data points distributed toward amines in the cloud RES particles, with relatively higher RPAs of imidazole. These results suggest that more amines and carbonyls in the cloud RES particles contribute to the enhanced imidazole. Because of the high aqueous solubility, the concentrations of amines and ammonium, as indicated by the average RPAs (Figure S8), are expected to be higher in wet aerosol and cloud droplets.<sup>39,61–65</sup> It is, therefore, inferred that the additional amines in the cloud RES particles may directly contribute to the additional imidazole or enhance the formation of imidazole via a synergistic effect (more light-absorbing products can be produced when carbonyls react with an ammonium/amine mixture, rather than with ammonium or amine alone<sup>2,66</sup>) of ammonium and amines. However, such chemistry cannot explain the difference in imidazole between the cloud-free and cloud INT particles. While imidazole may accumulate in the older activated aerosol, our data are still limited in presenting the influence of cloud cycling or cloud droplet age on the formation of imidazole.

Laboratory simulations of cloud evaporation suggest that the cloud processes may be more critical because of the increased reaction rates during cloud evaporation and the high content of carbonyls in cloud droplets.<sup>21,67</sup> Our results partly support this hypothesis, showing the enhancement of imidazole in evaporated cloud droplets (i.e., cloud RES particles). However, imidazole represents only a part of the reaction products from reactions between carbonyls and reduced nitrogen species. Further studies are still required to quantify the contribution of these reactions to aqueous secondary organic aerosols and BrC.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.0c00722>.

Detailed information about field sampling (S-1), correlation analysis and peak assignments for SPAMS (Tables S1–S3), mass spectra of various detected

particle groups, number fractions of IM-containing particles and the major ion peaks, diurnal patterns of imidazole, and the mixing state among amines/ammonium, carbonyls, and imidazole (Figures S1–S8) (PDF)

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## Notes

The authors declare no competing financial interest.

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