CO₂ in 1-Butyl-3-methylimidazolium Acetate. 2. NMR Investigation of Chemical Reactions

Marcel Besnard,*+ M. Isabel Cabaço,†,‡ Fabián Vaca Chávez,⊥ Noël Pinaud,‖ Pedro J. Sebastião,†,⊥ João A. P. Coutinho,# Joëlle Mascetti,† and Yann Danten†

†GSM Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération 33405 Talence Cedex, France
‡Departamento de Física, Instituto Superior Técnico, UTL, Av. Rovisco Pais 1049-001 Lisboa, Portugal
§Centro de Física Atómica da UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal
⊥Centro de Física da Matéria Condensada da UL, Av. Prof. Gama Pinto 2, 1694-003 Lisboa, Portugal
‖CESAMO Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération 33405 Talence Cedex, France
#CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Supporting Information

ABSTRACT: The solvation of CO₂ in 1-butyl-3-methylimidazolium acetate (Bmim Ac) has been investigated by ¹H, ¹³C, and ¹⁵N NMR spectroscopy at low CO₂ molar fraction (mf) (xCO₂, ca. 0.27) corresponding to the reactive regime described in part 1 of this study. It is shown that a carboxylation reaction occurs between CO₂ and Bmim Ac, leading to the formation of a non-negligible amount (~16%) of 1-butyl-3-methylimidazolium-2-carboxylate. It is also found that acetic acid molecules are produced during this reaction and tend to form with elapsed time stable cyclic dimers existing in pure acid. A further series of experiments has been dedicated to characterize the influence of water traces on the carboxylation reaction. It is found that water, even at high ratio (0.15 mf), does not hamper the formation of the carboxylate species but lead to the formation of byproduct involving CO₂. The evolution with temperature of the resonance lines associated with the products of the reactions confirms that they have a different origin. The main byproduct has been assigned to bicarbonate. All these results confirm the existence of a reactive regime in the CO₂–Bmim Ac system but different from that reported in the literature on the formation of a reversible molecular complex possibly accompanied by a minor chemical reaction. Finally, the reactive scheme interpreting the carboxylation reaction and the formation of acetic acid proposed in the literature is discussed. We found that the triggering of the carboxylation reaction is necessarily connected with the introduction of carbon dioxide in the IL. We argue that a more refined scheme is still needed to understand in details the different steps of the chemical reaction in the dense phase.

I. INTRODUCTION

In a recent study (part 1), we have investigated by Raman spectroscopy the dense phase of the mixture of carbon dioxide in 1-butyl-3-methylimidazolium acetate (Bmim Ac) in a large concentration range (xCO₂, molar fraction (mf) up to 0.49) at 313 K.¹ We have shown that two distinct solvation regimes occur. The first one, corresponding to CO₂ concentration extending to ca. 0.35 mf, was found to be characterized by sizable perturbations of the ionic liquid (IL) and by the absence of the strongly active CO₂ Fermi dyad always observed for this molecule diluted in organic or ionic liquids.²–⁴ We came to the conclusion that carbon dioxide reacted with the cation, leading to the carboxylation of the imidazolium ring and concomitantly to the formation of acetic acid. In the course of these studies, we also found that the Raman spectra performed on diluted CO₂–Bmim Ac mixture (xCO₂ < 0.25) did not evolve with time even after a 6 month period, indicating that the carboxylation reaction is irreversible. In contrast, the second regime (xCO₂ > 0.35) was found to be characterized by a very weak perturbation of Bmim Ac compared to the differences detected in the first regime and by the observation of the carbon dioxide Fermi dyad, showing that the reaction has been strongly moderated. It has been interpreted as resulting from the interaction of the nascent acetic acid with the oxygen atom of the acetate group involved in a single interaction with the proton bonded to the C₂ atom of the imidazolium ring (see Figure 1). The detection of the Fermi dyad shows that CO₂ interacts in the second regime in a softer way with the variety of
Bmim TFA5,6 is a consequence of the carboxylation reaction been assessed by DFT modeling showing that CO2, in a liquid phase using Raman and NMR (1H, 13C, and 15N) spectroscopy and DFT calculations.8 This preliminary study showed that the main features observed in the liquid mixture (carboxylate and acetic acid formation) are also observed in the solid state. Our aim now is to investigate in depth the existence of the carboxylation reaction proposed in our former investigation and in particular, the triggering of the carboxylation reaction by CO2. Furthermore, we want to assess the consequence of the acetic acid formation which has been put indirectly in evidence in our previous Raman study.

We have also addressed here the issue concerning the influence of water traces on the carboxylation reaction.9 As far as we know, its role in assisting this reaction has been evoked but never discussed in depth at the molecular level.5,7 Therefore, a complete characterization of the products formed in the CO2−Bmim Ac−H2O system remains to be done and is aimed at the current study. This investigation led us to characterize the byproduct formed due to the water presence and how their formation can compete with the carboxylation reaction.

II. EXPERIMENTAL SECTION

II.1. Experimental Details. The ionic liquids Bmim Ac, Bmim TFA, 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim BF4, purity >98%) originated from Solvionic, the CO2 from Air Liquide (purity 99.995%), and the 13C labeled CO2 from Aldrich (99 at. %). Additional glacial acetic acid (Riedel-de Hain, >99.8%), sodium hydrogenocarbonate (Aldrich, >99.5%), sodium carbonate (Aldrich, >99.995%), and heavy water (Aldrich, >99.990) were used without further purification. The ILs were put in a glass container connected to a vacuum line and dried at 353 K under a primary vacuum during more than 48 h, with a continuous stirring performed with a magnetic rotating agitator. The water content was measured by Karl Fischer titration and found to be 530 ppm, much lower than the value measured for the undried ionic liquid (~5000 ppm). Carbon dioxide was then introduced under a 0.1 MPa pressure in the Bmim Ac and the solution was stirred for a further period of about 30 h. After the container with the mixture under its vapor pressure was isolated, a Raman spectrum was taken to check for the presence of the strong perturbations observed in the spectral domain 1200−1800 cm−1 and the absence of the characteristic dyad of CO2 that we have reported in the Raman study, ensuring that the first solvation regime was reached.1 Then, the mixture was transferred into a standard NMR glass tube (5 mm inner diameter) and tapped with an inner Teflon cap and the standard outer plastic tap. Parafilm was subsequently used to isolate the extremity of the tube. This sealing method was used to avoid any contact with the atmosphere. During the very short time corresponding to the filling of the tube under the atmosphere, we did not observe any bubbling of the liquid, thus excluding a degassing of CO2 from the liquid phase. The integrity of the solution prepared using this protocol was checked by further comparative Raman measurements. We emphasize that the NMR spectra of the samples did not evolve in time as seen from the comparison of the spectra recorded for fresh solutions, just after filling the tube, with those measured at regular interval periods during more than 6 months at the exception of the resonance line assigned to the acetic acid (see section III).

A number of CO2−Bmim Ac solutions aimed at performing complementary tests have been prepared by keeping the undried IL in a stainless steel vessel in which carbon dioxide (at pressure ca. 6 MPa) was introduced at 298 K. After the mixture

Figure 1. 1H NMR spectra of Bmim BF4, Bmim TFA, and Bmim Ac. The schematic representation of the Bmim Ac ion pair with the labeling of the carbon atom used in the assignment is displayed.
was allowed to equilibrate for at least 2 h, the cell was opened and the pressure released to 0.1 MPa. The mixture was then immediately transferred in a NMR tube sealed as described above. NMR measurements have shown that the solutions prepared that way led to spectra displaying the same relevant line signatures as those prepared under the controlled conditions previously described. The molar fraction of CO2 in the mixtures at 298 K and under 0.1 MPa has been deduced from data reported previously 5 and corresponds to a CO2 concentration of ca. 0.27 mf.

<table>
<thead>
<tr>
<th>atom</th>
<th>1H</th>
<th>13C</th>
<th>1H secondary lines</th>
<th>13C secondary lines</th>
<th>1H</th>
<th>13C</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.72</td>
<td>13.10 (124)</td>
<td>0.72</td>
<td>13.10 (125)</td>
<td>0.84</td>
<td>12.69 (125)</td>
</tr>
<tr>
<td>8</td>
<td>1.13</td>
<td>19.14 (126)</td>
<td>1.13</td>
<td>19.16 (127)</td>
<td>1.27</td>
<td>19.04 (126)</td>
</tr>
<tr>
<td>12</td>
<td>1.64</td>
<td>25.53 (124)</td>
<td>1.69</td>
<td>24.81 (125)</td>
<td>114.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.74</td>
<td>32.22 (128)</td>
<td>1.75</td>
<td>32.13 (128)</td>
<td>116.7 (298)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.11</td>
<td>35.49 (143)</td>
<td>4.08</td>
<td>35.43 (143)</td>
<td>118.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.37</td>
<td>48.54 (143)</td>
<td>4.35</td>
<td>48.54 (143)</td>
<td>120.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8.52</td>
<td>121.1 (204)</td>
<td>8.36</td>
<td>124.2 (204)</td>
<td>122.2 (204)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.67</td>
<td>121.1 (204)</td>
<td>8.51</td>
<td>123.1 (204)</td>
<td>122.2 (204)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.88</td>
<td>138.6 (220)</td>
<td>10.67</td>
<td>138.9 (222)</td>
<td>137.8 (222)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>175.1</td>
<td></td>
<td></td>
<td>174.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 1H NMR and 13C NMR chemical shifts measured in this work for pure 1-butyl-3-methylimidazolium trifluoroacetate (Bmim TFA) are displayed for comparison. The coupling constants J (Hz) are given in parentheses. 6COO group of the carboxylate formed upon the reaction. 6COOH group of the acetic acid formed upon the reaction. 6The assignment of these lines is supported by the 2D 1H−13C HMQC and 1H−13C HMBC NMR sequences (Supporting Information). 6The position of this resonance line evolves from 15.95 ppm (3 days) to 12.3 ppm (40 days after preparation of the mixture).

The NMR measurements were performed on Bruker AVANCE III spectrometer operating at 600 MHz Larmor frequency for 1H, 150 MHz for 13C and 60 MHz for 15N (France). The 1H spectra were collected after a 30° pulse with a 90° pulse (τ90) of 8 μs. The number of scans was ranging from 512 to 1024 with a relaxation delay (d1) of 1 s. The 13C spectra have been acquired after a single pulse with τ90 = 11 μs and d1 = 3 s. The 15N proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. The samples were contained in standard 5 mm tubes filled with an external lock solvent of D2O and calibrated with the H2O signal at 4.8 ppm. The temperature of the samples was regulated and stabilized to within ±0.5 K using gas flow.

II.2. Results. Assignment of the NMR Spectra of Pure Bmim Ac and Bmim TFA. On Figure 1, we compare the 1H spectra measured for pure Bmim Ac with that of pure Bmim BF4 whose assignment is well-known.9 Moreover, the 1H spectrum of pure Bmim TFA that has been recently reported is displayed on this figure.12 Thus, it becomes a simple matter to assign from this comparison the peaks belonging to the Bmim cation common to the three compounds and from the difference between the spectra of Bmim Ac and Bmim TFA the peaks belonging to the acetate anion. The assignment of the protons of Bmim Ac is reported in Table 1 according to the reference between the spectra of Bmim Ac and Bmim TFA. The peaks belonging to the acetate anion. The assignment of the protons of Bmim Ac is reported in Table 1 according to the reference between the spectra of Bmim Ac and Bmim TFA.

Measurements were also performed in a Bruker AVANCE II spectrometer at 300 MHz Larmor frequency for 1H, 75 MHz for 13C (Portugal). The 1H spectra were recorded after a single pulse, τ90 = 14 μs and d1 = 5 s. The number of scans has been ranging from 512 to 1024. The 13C spectra have been acquired after a single pulse with τ90 = 11 μs and d1 = 3 s. The 13C proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. The samples were contained in standard 5 mm tubes filled with an external lock solvent of D2O and calibrated with the H2O signal at 4.8 ppm. The temperature of the samples was regulated and stabilized to within ±0.5 K using gas flow.
spectrum of Bmim Ac\textsuperscript{14} although the chemical shifts values that we have obtained are systematically slightly greater.

**NMR Spectrum of the CO\textsubscript{2}–Bmim Ac Mixture.** The proton decoupled $^{13}$C spectrum of the CO\textsubscript{2}–Bmim Ac mixture having a CO\textsubscript{2} molar fraction close to ca. 0.27 is displayed in comparison with that of the pure IL (Figure 3). From this comparison, two main observations can be readily made. A new line centered at ca. 155 ppm is observed having no counterpart in the spectrum of the pure IL. In addition, the main intense lines of Bmim Ac are accompanied by secondary lines of lower intensity (as well as in the $^{1}$H spectrum) (Table 1 and Supporting Information). The origin of the new peak is clearly connected with carbon dioxide. However, the isolated CO\textsubscript{2} has a single resonance line situated at 125.4 ppm\textsuperscript{15} and therefore the new peak, although correlated to the presence of this molecule, cannot correspond to the spectral signature of the CO\textsubscript{2} solvated in the IL. Therefore, we may conclude that CO\textsubscript{2} has reacted with the IL. In our previous investigation, we have put in evidence the existence of an irreversible chemical reaction occurring between the carbon dioxide and the Bmim cation to form a carboxylate species.\textsuperscript{1} For this purpose, we have proposed a reactive scheme in which CO\textsubscript{2} triggers the carboxylation reaction through two concerted mechanisms which are respectively an isomerization process (chemical exchange of the acidic proton between the imidazolium ring and the acetate anion) and the formation of a “transient” CO\textsubscript{2}–carbene (1-butyl-3-methylimidazole-2-ylidene carbene) complex (Figure 4).

In step 1, the carbon atom of CO\textsubscript{2} is transiently “bonded” to the imidazolium ring after the release of the proton of carbon 2 of the ring. Such a concerted mechanism takes place on a very short time scale (subpicosecond range) during which the deprotonated C\textsubscript{2} site can be considered as a “carbene” species, avoiding to suppose the formation of a long-lived carbene entity, questionable in dense phase. Then, such a “transient” CO\textsubscript{2}–carbene association can be considered as an intermediate.
precursor leading toward a definitive CO$_2$ capture by imidazole-2-ylidene carbene species (step 2 of the reaction).

If this reaction occurs and is not total, we should expect that the spectrum is a composite one resulting from the addition of the spectrum of the Bmim Ac and of the carboxylate species. In that case, we should detect in the vicinity of each main resonance lines of the IL, secondary lines of lesser intensity corresponding to the carboxylate. This is exactly what can be observed on the $^{13}$C spectra presented in Figure 3 and also on the 2D $^1$H–$^{13}$C HSQC and $^1$H–$^{13}$C HMBC NMR sequences (Supporting Information). To ground firmly this conclusion, we have measured the $^{15}$N spectra of pure Bmim Ac and of its mixture with carbon dioxide (Figure 5a,b). In the pure IL, this spectrum presents two intense resonance lines centered at about 183.7 and 171.6 ppm assigned to the nitrogen atoms of the ring core. The assignment of these lines is supported by 2D $^1$H–$^{15}$N HMBC NMR sequence which shows that the proton bonded to carbon atom 10 is correlated with the nitrogen atom N$_3$ (Figure 5c). We note that this assignment is different with that reported in the literature.$^{16}$ In the mixture, two additional resonances lines flanking each of the previous peaks are observed at 182.1 and 170.0 ppm, respectively (Figure 5b), and confirmed by the 2D $^1$H–$^{15}$N HMBC NMR sequence (Figure 5d). The proportion of the new species estimated from the integrated intensity of the secondary lines of the cation in $^1$H, $^{13}$C and $^{15}$N NMR spectra is about 0.16 molar fraction. This result confirms that the addition of carbon dioxide to the IL leads to the formation of a carboxylate molecule. This finding also supports our previous conclusion concerning the origin of the observed secondary lines.

Having shown that the carboxylation reaction occurs, we may wonder about the favored chemical site among the three possible carbons 2, 4, and 5 of the cation ring. A first answer to this question is provided by the comparison of the decoupled versus non decoupled $^{13}$C spectra in natural abundance in the mixture in the region of carbon 2 (Figure 3b,c). On the nondecoupled spectrum, the doublet line characteristics of the resonance of carbon 2 ($C_2$) is observed at about 137.6 and 139.0 ppm and is accompanied by a single line at about 141.6 ppm. Upon proton decoupling, we notice as expected that the doublet line gives rise to a singlet (at about 138.3 ppm) whereas the other line is not affected by the decoupling. Clearly, the structure of the doublet line is indicative of the existence of the scalar interaction between the spin of $C_2$ of the Bmim cation and the spin of the bonded proton. Therefore, this doublet can be assigned to the Bmim Ac species that have not reacted with carbon dioxide. In contrast, the observation of a single line not affected by the proton decoupling reveals the existence of a molecular species in which $C_2$ is not bonded to a proton as expected for the carboxylate. Such an analysis is confirmed by considering the spectrum of the mixture with labeled carbon dioxide $^{13}$CO$_2$. Indeed, we observed on the $^{13}$C spectrum a doublet centered at about 141.6 ppm that is not affected by the proton decoupling (Figure 3, top). The doublet structure can be therefore interpreted as the signature of the scalar interaction of the spin of $C_2$ (in natural abundance) with the spin of the labeled carbon atom of the bonded carbon dioxide. A final piece of evidence has been provided by measuring the 2D spectrum using the INADEQUATE sequence (Figure 6). It appears immediately that the peak of

The Journal of Physical Chemistry A

Figure 5. Comparison of the spectra of the pure Bmim Ac (with that of the CO$_2$–Bmim Ac mixture): $^{15}$N NMR (a) and (b); 2D HMBC $^1$H–$^{15}$N NMR sequence (c) and (d).

Figure 6. 2D NMR spectrum obtained from the INADEQUATE sequence on the $^{13}$CO$_2$–Bmim Ac mixture: the correlation observed between the C atom of the bonded CO$_2$ of the new species (155.3 ppm) and the $C_2$ atom (141.6 ppm) proves that these carbon atoms are covalently bonded.

dx.doi.org/10.1021/jp211689z | J. Phys. Chem. A 2012, 116, 4890–4901
moiety is bonded on C2. This conclusion is in agreement with the Raman results that we have previously reported.1,8 We note that the synthesis of 1,3-dialkylimidazolium-2-carboxylates by direct carboxylation is a subject of a strong current interest.17–19 Among the motivation is the use of 1,3-dialkylimidazolium-2-carboxylates in organic synthesis and in synthesis of halogen-free ionic liquids20 or as air- and moisture-stable species to transfer N-heterocyclic carbene (NHC) to a variety of metal salts with release of CO2.21,22 In this context it was found that NHCs freely add CO2 to form (reversibly under certain conditions) the corresponding imidazolium carboxylate.23

The synthesis and characterization of 1-butyl-3-methylimidazolium-n-carboxylates (with n = 2, 4, and 5) using a number of physical–chemical techniques including 13C NMR spectroscopy (D2O solution, 500 MHz) has been reported.18 The comparison of the chemical shifts of the resonance lines that these authors have reported for the n = 2 carboxylate is in a good agreement with those we have measured (Table 2). The

<table>
<thead>
<tr>
<th>atom</th>
<th>1-butyl-3-methylimidazolium-2-carboxylate</th>
<th>1-butyl-3-methylimidazolium-4-carboxylate</th>
<th>1-butyl-3-methylimidazolium-5-carboxylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>13.25</td>
<td>13.08</td>
<td>13.09</td>
</tr>
<tr>
<td>8</td>
<td>19.32</td>
<td>19.16</td>
<td>19.16</td>
</tr>
<tr>
<td>7</td>
<td>32.88</td>
<td>32.27</td>
<td>31.55</td>
</tr>
<tr>
<td>10</td>
<td>36.65</td>
<td>36.88</td>
<td>36.06</td>
</tr>
<tr>
<td>4</td>
<td>48.8</td>
<td>49.57</td>
<td>49.67</td>
</tr>
<tr>
<td>123.4f</td>
<td>122.4</td>
<td>131.38</td>
<td>126.66</td>
</tr>
<tr>
<td>5</td>
<td>122.2f</td>
<td>123.39</td>
<td>125.26</td>
</tr>
<tr>
<td>2</td>
<td>141.6</td>
<td>140.29</td>
<td>137.53</td>
</tr>
<tr>
<td>COO</td>
<td>155.3</td>
<td>158.15</td>
<td>163.03</td>
</tr>
</tbody>
</table>

“*This work. b*Literature values.18 The assignment of these lines is supported by the 2D 1H−13C HSQC and 1H−13C HMBC NMR sequences (Supporting Information).

peak reported at 158.15 ppm corresponds to the new line observed here at 155.3 ppm and assigned to the carbon atom of the carboxylate group of the 1-butyl-3-methylimidazolium-2-carboxylate. The 13C NMR spectra reported for the two other compounds (i.e., 1-butyl-3-methylimidazolium-n-carboxylate with n = 4 and 5), possess a resonance line at about 163 ppm that is not observed here. Moreover, the chemical shifts of the resonance lines of carbons 4 and 5 for n = 4 are respectively 131.4 and 125.3 ppm, whereas these values are 126.7 ppm and 130.8 ppm for n = 5, which are clearly different from the corresponding values reported for n = 2 (122.4 and 123.4 ppm, respectively) (Table 2). Because these values (for n = 2) agree with those obtained in the present work (124.2 and 122.2 ppm), we can conclude that a selective carboxylation of the ring occurred. It is noteworthy that these results justify the point of view of a greater reactivity of site 2 due to the greater acidic character of the proton bonded to this site.

It was established that CO2 dissolved in imidazolium-based ILs is found preferentially interacting with the anion. The hydrogen bonding of the anion to the “acidic” C2 proton of the imidazolium ring prevents CO2 from associating with the cation.24−26 DFT and NMR studies in diluted solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate (Emim BF4) in dichloromethane showed that the equilibrium existing between the structures in which the anion is located near the C2 atom of the ring (mainly favored) or close to C4 or C5 atoms was found to be influenced by the concentration/polarity of the solvent.27 Moreover, neutron diffraction and molecular simulation studies of 1-ethyl-3-methylimidazolium acetate (Emim Ac) revealed that acetate anions are hydrogen-bonded to the hydrogen atoms of the cation rings (mainly with the proton bonded to C2).28 The carboxylation reaction observed in the present study marks a great contrast with the general behavior reported for ILs based ionic liquids.

III. DISCUSSION

Carboxylation Reaction. The eventuality of a chemical reaction occurring in CO2−Bmim Ac mixtures has been first invoked by Maginn et al.29 from NMR results. Such a reaction would proceed according to a two stages process. In a first step, it is assumed that the proton bonded to C2 of a Bmim cation is transferred to the acetate anion, to form an acetic acid molecule whereas the deprotonated Bmim cation becomes a transient imidazole-2-ylidene carbene species. In a second step, the carbene species reacts with carbon dioxide to lead to the formation of an imidazolium-2-carboxylate. Incidentally, we note that the signature of an isolated carbene has been recently reported by Holloczki et al. in Emim Ac under very stringent thermodynamical conditions (423 K, 1 Pa),30 which are very different from those considered here in the dense phase. The carboxylation reaction has been critically discussed by Shiflett et al.31 in their study of the solvation of CO2 in Bmim Ac. Because the presence of neither the carboxylate nor the acetic acid was put in evidence, these authors concluded that if the reaction occurs, it should be considered as marginal.

In marked contrast, we have shown that an irreversible chemical reaction takes place from the formation of a transient CO2−carbene species leading to quantifiable amounts of carboxylate species.1,8 In our investigations the amount of formed carboxylate species is estimated to be about 16 mol % of the total mixture which is far from negligible. In other words, the introduction of CO2 in the IL strongly disturbs the existing equilibrium between the Bmim and acetate ions by triggering the carboxylation reaction. Clearly, the detection of acetic acid becomes of importance to discuss the proposed scheme.

Formation of Acetic Acid. The detection of the proton released by the imidazolium ring upon carboxylation is rather delicate as the existence of a “free” proton in solution can only be put in evidence indirectly. For this purpose, we have first measured the proton NMR spectrum of glacial (i.e., highly concentrated acid, purity >99.8%) acetic acid, which displays two resonance lines situated at about 10.74 and 2.06 ppm assigned to the proton of the COOH and CH3 groups, respectively (Figure 7). To “track” the signature of the proton, we have added increased amounts of glacial acetic acid to Bmim Ac and considered the resonance line of the proton of the COOH group. At low acidic concentration (0.08 mf), an extremely weak and broad feature, which was absent in the spectrum of the pure ionic liquid, is observed at about 16.2 ppm. Upon increasing the acid concentration (0.16 mf), we notice that this feature becomes more pronounced and is slightly upfield shifted by at ca. 0.5 ppm. Clearly the local ordering of the acetic acid is strongly perturbed upon dilution in the IL. This modification of the state of aggregation of
carboxylic acids and in particular of acetic acid upon dilution in organic liquids, is well documented.\textsuperscript{31–35} In mixtures with polar solvents, the population of cyclic dimers decreases at the expense of monomers and linear forms that may form complexes with the solvent. This situation occurs as well for acetic acid diluted in Bmim Ac. Let us recall that in Emim Ac the most probable short-ranged local structure consists of anions in which an oxygen atom of the COO\textsuperscript{−} group interacts in a monodentate configuration with a proton of the imidazolium ring (mainly with the proton bonded to C\textsubscript{2}), leaving the other oxygen atom available for other interactions.\textsuperscript{28} Thus, we may infer that the COOH group of monomers as well as linear dimers of acetic acid molecule interact through hydrogen bond with the available oxygen atom of the COO\textsuperscript{−} group of nearby acetate anion, whereas the other oxygen atom is hydrogen bonded to the imidazolium ring. Such a proposition is reinforced and attested by both spectral signatures and vibrational DFT modeling.\textsuperscript{1}

In CO\textsubscript{2}−Bmim Ac, a resonance line not observed in the pure IL, is detected at about 15.95 ppm (Figure 7) and assigned to the COOH group of the acid molecule interacting with “free” atom oxygen atom of the COO group of the ion pair. It was found to correspond to an acidic Bmim solution in which the acid molar fraction is close to 0.12. Therefore, by analogy, we can estimate the molar fraction of nascent acetic acid to be ca. 0.12 in CO\textsubscript{2}−Bmim Ac solutions. This estimate nicely matches the estimated concentration of carboxylate formed during the reaction as obtained from the \textsuperscript{15}N spectra. From the previous discussion, we conclude not only that acetic acid molecules are formed in this mixture due to the carboxylation reaction but also that these nascent molecules interact in turn to form the bidentate species discussed before.

A further indirect confirmation of this conclusion can be obtained by considering the \textsuperscript{13}C resonance line of the methyl groups of the acetate anion of Bmim Ac and of acetic acid, which are detected at 26.1 and 20.8 ppm, respectively (Figure 8). Upon dilution of acetic acid in the IL, the resonance line of the methyl group of the acetate anion shifts progressively upfield with the acid concentration. This trend shows that the methyl group of the anion feels the perturbation of the COO group of the acetate upon their hydrogen bonded interaction with the acid molecules. In CO\textsubscript{2}−Bmim Ac, the resonance line of the methyl group of the acetate anion is centered at about 25.5 ppm and corresponds to the line observed for the mixture Acetic acid−Bmim Ac with an acid molar fraction close to 0.12. We note that this value is close and consistent with those reported previously for the estimated concentration of carboxylate.

All these findings confirm that acetic acid is produced as a consequence of the carboxylation reaction. It should be pointed out that they also support the indirect inference which has been reached in our Raman study concerning the acid production.\textsuperscript{1,8}

A final piece of information has been obtained from the long time evolution of the \textsuperscript{1}H spectra of CO\textsubscript{2}−Bmim Ac. We found that the position of the new line observed in \textsuperscript{1}H NMR at about 16 ppm changes with time to reach 12 ppm in a 40 day time period (Figure 9). This latter value being close to that observed for pure acid (10.74 ppm) suggests that, with elapsed time, the...
acid molecules in CO$_2$–Bmim Ac tend to form again cyclic dimers mostly existing in the pure acid. This result indicates that the interaction between acetate anion and Bmim cation is slightly more attractive as it is not affected in the same time by a secondary interaction of an acetic acid molecule with the COO group of the anion. Thus, the subtle competition between monodendate and bidentate associations of acetate with Bmim cations (without and with the presence of acetic acid, respectively) leads to favor the former ones (monodendate associations) through a self-association (dimerization) of acetic acid. This dimerization mechanism of acetic acid takes place upon a long time scale (approximately a few days) because the interaction strengths between a pair of acetic acid molecules and between acetic acid-acetate anion are nearly iso-energetic. This finding confirms that the hydrogen bonded structure of liquid acetic acid is strongly modified upon dilution in the IL, even if such a “destruction” is only a metastable process.

Although the formation of acetic acid and carboxylate molecule in the CO$_2$–Bmim Ac mixture can now be taken for granted, we may question if the carboxylation reaction takes place according to the two steps mechanism proposed in the literature. Indeed, in this scheme, it is the acid production that triggers the reaction by leading to the formation of a carbene species. The formation of acetic acid is considered as resulting from the interaction of the acetate anion with the Bmim cation independently of the presence of carbon dioxide. This assumption seems to be contradicted by the fact that the presence of acetic acid is only detected after the introduction of CO$_2$ in the IL and, therefore, appears as a consequence of the release of the proton after the carbene formation. Moreover, we do not detect the presence of acid in the pure ionic liquid either in our NMR measurements or in our Raman study.7 As a consequence, the triggering of the reaction cannot be attributed to the formation of acetic acid. This finding reinforces two points. First, the relevance of the role played by CO$_2$ in triggering the reaction. Then, the dynamical aspect of the reactive process in the liquid phase through concerted mechanisms leading to the formation of “transient” CO$_2$ carbene complexes and acetic acid molecules as proposed in the reactive scheme discussed before. The two concerted mechanisms which are the chemical exchange of the acidic proton between the imidazolium ring and the acetate anion and the formation of a “transient” CO$_2$–1-butyl-3-methylimidazol-2-ylidene carbene complexes, respectively (step 1), can be viewed as a cooperative process taking place on a short time scale governed by the deprotonation of the C$_2$ site of the imidazolium cation interacting with acetate species. Indeed, the time scale of this latter elementary process (certainly in the subpicosecond range) avoids supposing the existence of long-lived carbene species formed in the mixture. Moreover, such a scenario is not unrealistic considering the order of magnitude of the values of the energy barriers of the isomerization process (step 1, 13.6 kcal/mol) and of the carboxylation reaction involving the transient CO$_2$ carbene species proposed here (step 2, 1.5 kcal/mol), which are likely significantly lowered in the dense phase due to the stabilization by the environment.8

**Influence of Water Traces on the Carboxylation Reaction.** Ionic liquids are generally hygroscopic and the presence of water traces that possibly influence their thermodynamical and physical chemical properties is a matter of concern.4–6,36–38 This applies equally well for the CO$_2$–Bmim Ac system for which we may wonder if water traces have any influence on the carboxylation reaction, either as a catalyst or in hampering the reaction by opening new byproduct pathways.5

In a series of experiments, we have considered the influence of water on the CO$_2$–Bmim Ac system. We have used dried Bmim Ac and prepared two mixtures containing 0.05 and 0.15 water molar fraction, respectively. The former concentration can be considered as the typical water content of undried ILs, whereas the latter clearly corresponds to an unrealistic amount but it is aimed at magnifying any possible effect of water in the reactive processes occurring in the mixture. We have then introduced carbon dioxide in these mixtures under a pressure of 0.1 MPa, as described in the Experimental Section. The $^{13}$C NMR spectra of these two ternary mixtures are compared with the spectrum of the CO$_2$–Bmim Ac dried mixture in Figure 10.

![Figure 10. Influence of added water on the $^{13}$C NMR spectrum of the mixture CO$_2$–Bmim Ac.](https://dx.doi.org/10.1021/jp211689z)
and 5 for \( n = 4 \) and \( n = 5 \) are clearly different from the corresponding values reported for \( n = 2 \), we have established above that only the 1-butyl-3-methyl-imidazolium-2-carboxylate has been formed. Therefore, we can conclude that the line at about 160 ppm cannot be associated to a carboxylate species.

To assign the new line observed at about 160 ppm, we have performed measurements on an undried Bmim Ac–CO\(_2\) mixture (water less than 0.05 mf) using labeled \(^{13}\)CO\(_2\) to increase the intensity of the lines detected upon the introduction of carbon dioxide in the IL (Figure 11). As expected, we notice that the lines at about 155 and 160 ppm are strongly enhanced compared to those of the ionic liquid. Moreover, we detect a new line at 157.7 ppm having an intensity of about 3% of the sum of the intensities of the other two lines and which was not obviously detected before using natural carbon dioxide.

This chemical shift domain is typical for formates, carboxylates, carbamates, carbonates, and hydrogen carbonates.\(^{39-44}\) On the basis of literature information, we have assigned the line at 160.2 ppm to the presence of a bicarbonate-like ion. To check this assignment, we have measured the \(^{13}\)C NMR spectrum of sodium bicarbonate (NaHCO\(_3\)) diluted at saturation in D\(_2\)O which con...
moiety bonded to the imidazolium group. It has been shown above that the carboxylate molecule remains stable upon heating to temperatures ca. 413 K and becomes degraded by a further increase of the temperature (presence of the new line at 167.2 ppm).

It was shown that the decarboxylation temperature can be correlated with the frequency of the $v_{\text{COO}}$ asymmetric vibration and with the dihedral angle between the planes of the COO group and the imidazolium ring. The experimental value of the $v_{\text{COO}}$ asymmetric vibration and the calculated value for the dihedral angle that we obtained and reported in our Raman-DFT study allowed estimating that the decarboxylation temperature falls in the range 413–433 K. These results allow inferring that the reduction of the intensity of the line at 155 ppm is correlated with a partial decarboxylation.

Therefore, we expect that the line remains first almost unaffected upon heating until some temperature value beyond which the line progressively vanishes, indicating that the compound becomes degraded. Indeed, the line at 155 ppm, almost unaffected up to 373 K, progressively vanishes up to 413 K. We note that the temperature range during which the degradation process is initiated and becomes effective is rather modest (about 40 K). The proof of the degradation of the carboxylate species is completed by considering the fact that cooling the sample to room temperature reduces the intensity of the 155 ppm line by about 30%. This shows that the carboxylate group of the 1-butyl-3-methylimidazolium-2-carboxylate to which this line is assigned has been partially removed from the ring during the temperature study. In addition, the concomitant observation of the new stable line at ca. 167.2 ppm should be correlated with this process. The value of this chemical shift suggests that a carbonate adduct has been formed in the course of the degradation. This assignment is supported by the $^{13}$C NMR spectrum of sodium carbonate diluted at saturation in D$_2$O, which shows that the single resonance line of this compound is observed at 168.1 ppm (Figure 12), a value in good agreement with that reported above.

We may wonder if the partial decarboxylation of the imidazolium carboxylate could produce imidazolium–carbene or even imidazolium–carbene dimer. The existence of these species would lead to resonance lines situated at 210–220 ppm and 124–130 ppm, respectively. We do not detect the weak resonance lines of these not $^{13}$C labeled species at these chemical shifts. Therefore, in the absence of such signature we can discard the hypothesis of the existence of such species. We note that it was reported on a study about the reversible carboxylation of N-heterocyclic carbenes that the addition of $^{13}$CO$_2$ to the 1,3-diosopropyl-4,5-dimethylimidazol-2-carboxylate formed, directly by addition of CO$_2$ to the carbene or by deprotonation of the corresponding salt, led to an enhancement of the line assigned to the carbonyl group of the carboxylate. This finding suggested to the authors that the bound CO$_2$ was equilibrating the free $^{13}$CO$_2$, which was confirmed by the attenuation of the signal with the reintroduction of CO$_2$. Louie et al. have also observed that in solution the carboxylate group could be exchanged between some imidazolylidenes carboxylates and imidazolylidenes leading to more stable imidazolylidenes carboxylates. Although we deal with a different system we may also question if equilibrium occurs between the imidazolium carboxylate and their fragments, carbene and CO$_2$. The existence of this equilibrium should lead to the appearance of the lines of the “free” CO$_2$ (at 125.4 ppm which is not observed) and of the lines of an imidazolium carbene (not observed too, as referred before) under the hypothesis of a slow exchange, compared with the NMR time scale. The hypothesis of a very fast exchange does not appear probable taking into account the small value of the shift of the line at 155 ppm (about 1 ppm for 423 K). The broadening and shift of this line should be connected with the approach of the decarboxylation temperature (estimated to be in the range 413–433 K, as referred before). Therefore, under our experimental conditions such an equilibrium does not appear likely to occur and if it exists it is hard to put it in evidence taking also into account that CO$_2$ is involved in other reactions (formation of bicarbonate).

Considering now the resonance lines at 160 and 158 ppm, we noticed that these two lines are strongly affected by the temperature and almost vanish with a modest temperature increase (40 K). At last, considering the temperature evolution of the three lines, the difference between the broadening of the lines at 160 and 155 ppm and the fact that it is only at high temperature that a covalent bonding is expected to break, we may surmise that the species giving rise to the 160 and 158 ppm lines are certainly more labile and presumably involved in noncovalent type of interactions. This conclusion is consistent with the assignment to bicarbonate species proposed for the resonance line at 160 ppm.

**Formation of Bicarbonate Species.** We may now explain the origin of the resonance line observed at 160 ppm that we have assigned to a bicarbonate-like ion. For that purpose, we must recall that carbon dioxide in the presence of water produces carbonic acid (H$_2$CO$_3$), which in turn leads to the formation of hydrogen–carbonate ions (i.e., bicarbonate ions HCO$_3^-$). An acid–base equilibrium exists between bicarbonate ions with its conjugated base constituted by carbonate ions (CO$_3^{2-}$) according to the well-known chemical reaction

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad (1)$$

In $^{13}$C NMR spectroscopy, because the interchange between these two species is fast on the observation time scale, only a sharp resonance is observed at a position corresponding to the concentration weighted average of the chemical shifts of the species in the absence of exchange, namely 169.4 and 161.4 ppm for the carbonate and bicarbonate ions, respectively. Moreover, the equilibrium is pH dependent and is displaced in favor of the formation of bicarbonate species under acidic conditions. As a consequence, upon increasing the pH of the solution, the single resonance line shifts continuously between the values of the chemical shifts mentioned before (for the sites in the absence of chemical exchange) with typical values ranging from 162 ppm at pH ~ 6 to about 166 ppm at pH ~ 10. On this ground, we may argue that the condition of observation of bicarbonate ions are gathered as we have traces of water and we also know that protons originating from the carboxylation reaction are present in large excess (compared to the water content), leading to the acetic acid formation. Indeed, the previous equilibrium must be displaced toward the bicarbonate formation. This conclusion allows interpreting both the presence of bicarbonate ions and the absence of the carbonate ions.

**IV. CONCLUSION**

As a final conclusion, we emphasize the richness of the solvation process of carbon dioxide in Bmim Ac, which appears
as a unique system that should deserve further consideration. The solvation process involves two distinct regimes as we pointed out before and which can be considered as a chemical and a physical regime, respectively. Our study agrees with the original proposition of Shiflett et al.\(^{50}\) but, nevertheless, with marked differences concerning the nature of the processes involved in these regimes. Our results show that the chemical regime is not due to a chemical complexation in the sense of the formation of a reversible molecular complex between CO\(_2\) as was proposed but corresponds to a true chemical reaction. Incidentally, it has been reported using electrochemistry techniques that the chemical absorption of CO\(_2\) in Bmim Ac is not easily reversible.\(^{51}\)

Several important issues have been covered here concerning the carboxylation reaction. The first one deals with the synthesis of the carboxylate itself. We found that this chemical can be obtained using simple and mild conditions consisting in a simple mixing of the reactants under very low pressure at room temperature. We found that the carboxylation reaction is highly selective and limited to the carboxylation of C\(_2\) of the IL. This study has also allowed discussion of the chemical scheme proposed in the literature,\(^{49}\) giving support not only to the existence of an irreversible carboxylation reaction taking place in the CO\(_2\)−Bmim Ac mixture but also to the predicted acetic acid formation that results from the introduction of the CO\(_2\) in the IL. We have shown that nascent acetic acid molecules produced by the carboxylation reaction group interact with the acetate anion to form bidentate species. In these species, the COOH group of the acid interacts through a hydrogen bond with the available oxygen atom of the COO\(^−\) group of the nearby acetate anion, having the other oxygen atom hydrogen bonded to the imidazolium ring. These results support the indirect inference reached in our Raman study and confirmed by DFT calculations.\(^1\) The long time evolution (40 day time period) of the CO\(_2\)−Bmim Ac mixture shows that the acid molecules tend to form again the cyclic dimers predominant in the pure acid.

Finally, we have discussed the first step of the carboxylation reaction as proposed in the literature on the ground of recent investigations on the Emim Ac.\(^{30}\) We argued that this step is only valid in the vapor phase (at high temperature and very low pressure) in conditions very different from those involved in the liquid state. We came to the conclusion that the formation of carboxylate species, which is only observed after the introduction of carbon dioxide in the IL, could be possible if the CO\(_2\) molecule interacts with the C\(_2\) site during the time lapse in which the proton, exchanging between two sites, the Bmim Ac ion pair (I) and the N HC acetic acid complex (II), is preferentially located on site II. This led to a picture that demands consideration of the cooperativity of the processes between CO\(_2\) and the moieties constituting the IL, as well as the time scale associated with the molecular interactions to explain the reaction triggering. Such a viewpoint, taking into account all the main features of chemical reactions in a dense phase, is more satisfying than a description of the elementary act of reaction as proposed in the literature which is only valid in the gas phase.

In the second part of this study, we have addressed the question of the influence of water traces, often present in "real" systems, on the carboxylation reaction. The presence of water leads to the formation of bicarbonate species at the expense of the carboxylate molecules. We have shown that even at unrealistic content (15% mf), water does not hamper the carboxylation reaction to proceed, although a quite large amount of bicarbonate is formed.

In addition, a temperature study has shown that the carboxylate molecule is rather stable whereas the bicarbonate is more fragile. We also found that at high temperatures (433 K), these species are partially decomposed and that, after cooling at room temperature, they are again present in reduced proportion. Moreover, we detected that carbonate species is formed.

In spite of all the investigations that we have performed, we believe that a full understanding of the complete reactive scheme remains to be done, not only in the dried CO\(_2\)−Bmim Ac but also in the ionic liquid when water traces are present. In this context, kinetics studies appear important to shed light on the existence of a cooperative process taking place between carbon dioxide and the moieties constituting the IL to lead to the carboxylation, as we have suggested here.

We also believe that a close exploration of the possible chemical pathways, using the methods of quantum chemistry, would be an important step to perform investigation, in particular the question of the selectivity of the carboxylation reaction. In this context, we also surmise that these calculations should consider the influence of the supramolecular organization of the ionic liquid itself, which should play an important role. Indeed, in such highly organized complex liquids, it seems to us that an approach strictly limited to a few interacting species, although providing some clues, would possibly lead to an oversimplified picture of this remarkable system.

As a final comment, we note that the results presented here have also some incidence in the context of the solute recovery from ILs using supercritical CO\(_2\) in the domain of the green chemistry.\(^{52}\) In this process, the ionic liquid is a priori supposed to not suffer degradation and could be recycled for further chemical operations. Clearly, the current study shows that this view should be taken with some caution for the present system, which would imply certainly further processing treatment, as pointed out by Baroste-Antle et al.\(^{51}\)

### ASSOCIATED CONTENT

#### Supporting Information

\(^{1}\)H NMR spectra, \(^{1}\)H−\(^{1}\)H COSY NMR spectra, and \(^{1}\)H−\(^{13}\)C HSQC and HMBC NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

**Corresponding Author**

Tel: +33 5 40006357. Fax: +33 5 4000 8402. E-mail: m.besnard@ism.u-bordeaux1.fr.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors are pleased to thank Mr Jean-Michel Lasnier (CESAMO) for his help in NMR measurements. Marcel Besnard is also pleased to acknowledge Pr. M. Luisa de Carvalho for the facilities during his long time duration stay at the Centro de Fisica Atomica da Universidade de Lisboa. The authors are indebted to Pr E. Gomes de Azevedo and Dr Miguel Rodrigues of the Centro de Quimica Estrutural do Instituto Superior Tecnico da Universidade Tecnica da Lisboa for providing facilities in high pressure samples preparation.