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## COMMUNICATION

## On the spontaneous carboxylation of 1-butyl-3-methylimidazolium acetate by carbon dioxide†

Marcel Besnard,<sup>\*a</sup> M. Isabel Cabaço,<sup>bc</sup> Fabián Vaca Chávez,<sup>d</sup> Noël Pinaud,<sup>e</sup> Pedro J. Sebastião,<sup>bd</sup> João A. P. Coutinho<sup>f</sup> and Yann Danten<sup>a</sup>

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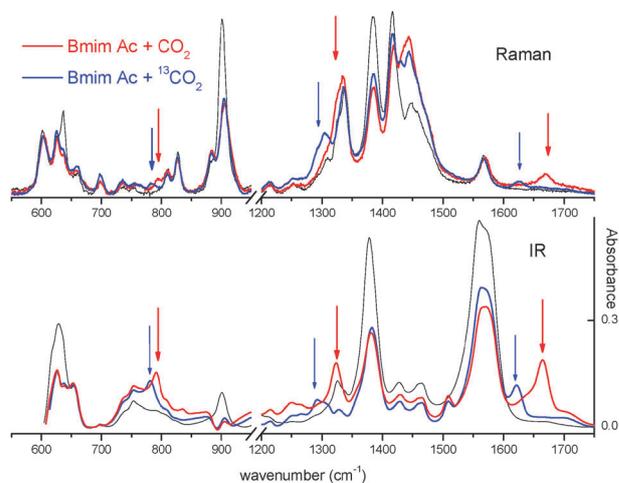
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**The formation of 1-butyl-3-methylimidazolium-2-carboxylate in the mixture of CO<sub>2</sub> with 1-butyl-3-methylimidazolium acetate under mild conditions (298 K, 0.1 MPa) has been put in evidence in the liquid phase using Raman and infrared spectroscopy complemented by DFT calculations and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N) spectroscopy.**

The capture and sequestration of CO<sub>2</sub> and its conversion into stable useful adducts for further reutilization is a topic of paramount concern in green chemistry. Nowadays, a wealth of investigations have been devoted to study the solubility of this compound in ionic liquids which offer due to their remarkable physical and chemical properties a promising route.<sup>1–8</sup> This area concerns the design of task-specific ionic liquids by adding functionalities, either on the anion or the cation, to introduce specific and tunable chemical reactivity of carbon dioxide.<sup>9–11</sup> The synthesis of ionic liquids themselves *via* cleaner, efficient and less waste productive methods is also of interest in green chemistry. In this context, the unexpected synthesis of an ionic liquid precursor, namely 1,3-dimethylimidazolium-2-carboxylate, using dimethyl carbonate as an environmentally benign reagent has been proposed.<sup>12–14</sup> The current investigation can be situated at the intersection of these two issues. We have studied, at the molecular level, the solubility of CO<sub>2</sub> in 1-butyl-3-methylimidazolium-acetate, which has been found to be unusually high.<sup>15,16</sup> Shiflett *et al.* concluded that a reversible 1:2 molecular complex (1 being

the CO<sub>2</sub> and 2 the IL) was formed.<sup>17</sup> The eventuality of a chemical reaction leading to the carboxylation of the imidazolium cation by CO<sub>2</sub> accompanied by formation of acetic acid was proposed<sup>15</sup> but ruled out after.<sup>16,18</sup> Surprisingly, we found that upon mixing CO<sub>2</sub> with this ionic liquid, at room temperature and under modest pressure (0.1 MPa), a spontaneous, selective and irreversible reaction occurs leading to the formation of 1-butyl-3-methylimidazolium-2-carboxylate.<sup>19</sup> This communication addresses this issue using vibrational (Raman and infrared) and NMR spectroscopy and DFT modeling.

The Raman and infrared (IR) spectra of a CO<sub>2</sub>-Bmim Ac mixture (CO<sub>2</sub> molar fraction *ca.* 0.27, 0.1 MPa, 298 K) are compared with those of pure Bmim Ac in Fig. 1. Sizeable perturbations of the spectra of the ionic liquid are observed upon mixing with CO<sub>2</sub>. In Raman spectroscopy, the strongly active  $2\nu_2 - \nu_1$  Fermi dyad of CO<sub>2</sub> generally observed at about 1280 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> is totally absent in the spectrum of the mixture. Three new bands are clearly detected (Table 1). A strong intensity enhancement of the broad, composite band centered at about 1450 cm<sup>-1</sup> resulting from the overlapping of four ring modes is observed (Table S11, ESI†). A strong perturbation of the  $\nu_{CC}$  stretching mode of the anion (about 900 cm<sup>-1</sup>) is also observed.



**Fig. 1** Comparison of the Raman and infrared spectra of Bmim Ac (black) with its mixture in CO<sub>2</sub> (red) and in <sup>13</sup>CO<sub>2</sub> (blue). The arrows pinpoint the three new bands.

<sup>a</sup> GSM Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération, 33405 Talence Cedex, France. E-mail: m.besnard@ism.u-bordeaux1.fr, y.danten@ism.u-bordeaux1.fr

<sup>b</sup> Centro de Física Atómica da UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa. E-mail: isabel@cii.fc.ul.pt

<sup>c</sup> Departamento da Física, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: Pedro.jose.sebastiao@ist.utl.pt

<sup>d</sup> Centro de Física da Matéria Condensada da UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa. E-mail: fychavez@cii.fc.ul.pt

<sup>e</sup> CESAMO Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération, 33405 Talence Cedex, France. E-mail: noel.pinaud@u-bordeaux1.fr

<sup>f</sup> CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: jcoutinho@ua.pt

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**Table 1** Assignment of the bands detected in CO<sub>2</sub>-Bmim Ac and <sup>13</sup>CO<sub>2</sub>-Bmim Ac (in parentheses) mixtures compared with those reported in the literature for 1-butyl-3-methylimidazolium-2-carboxylate.<sup>20</sup> The values obtained from DFT calculations are also displayed (values in cm<sup>-1</sup>)

	CO <sub>2</sub> -BmimAc		1-Butyl-3-methylimidazolium-2-carboxylate <sup>20</sup>	DFT
	Raman	IR	IR	
δ COO	794 (783)	792 (781)	794	778 (768)
ν sym	1323	1323	1323	1326
COO	(1294)	(1293)		(1315)
ν asym	1672	1665	1662	1748
COO	(1631)	(1622)		(1700)

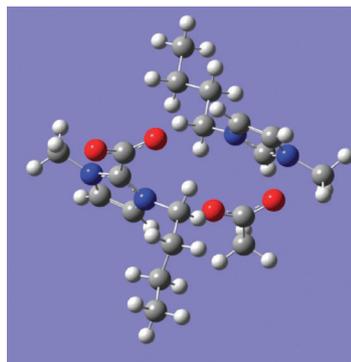
Upon using <sup>13</sup>CO<sub>2</sub>, these sizeable perturbations are still present in the spectrum but the three new bands are found to be affected by the isotopic substitution and red shifted (Table 1).

Infrared spectroscopy confirms the existence of these new bands, detected at about the same wavenumber and exhibiting the same red shift upon isotopic substitution (<sup>13</sup>CO<sub>2</sub>) as in Raman. We also observe that the symmetric (1382 cm<sup>-1</sup>) and asymmetric (1582 cm<sup>-1</sup>) stretching and bending (637 cm<sup>-1</sup>) vibrations of the acetate anion are perturbed.

These observations show that both anions and cations of the IL are perturbed upon dilution. Of utmost importance is to notice that the three new bands are associated with CO<sub>2</sub> as testified by the isotopic substitution. The isolated CO<sub>2</sub> molecule has four vibrational modes namely, the doubly degenerated bending (667 cm<sup>-1</sup> Raman inactive),<sup>21</sup> the OCO symmetric stretch (1337 cm<sup>-1</sup>, infra-red active giving rise in Raman to the Fermi doublet)<sup>22</sup> and the OCO asymmetric stretch (2349 cm<sup>-1</sup>, infrared active).<sup>21</sup> For CO<sub>2</sub> diluted in the IL, we found that the three modes are active in both Raman and IR spectroscopy and that the Fermi dyad is absent. These findings are characteristic of a strongly perturbed carbon dioxide molecule which loses its linear structure (*D*<sub>∞h</sub> symmetry) to become bent (*C*<sub>2v</sub> symmetry).

To validate this hypothesis, we have performed DFT calculations using the B3LYP functional with the 6-31+G(d,p) basis set and considered a carboxylate molecule interacting with a Bmim Ac ion pair. After optimization of the structure (Fig. 2), we have calculated the main IR and Raman fundamental transitions and their activities. We found that the frequencies of the three vibrations of the carboxylate group (considering COO and <sup>13</sup>COO groups) agree nicely with the experimental values (Table 1). The success of such a modeling provides a further strong indication that a carboxylate molecule is present in the IL and interacts with the ions.

Recently, the synthesis of 1,3-dialkylimidazolium-*n*-carboxylate (*n* = 2, 4, 5) was performed and these molecules were characterized using standard laboratory techniques including in particular infrared and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.<sup>20</sup> The frequencies of the new Raman and IR bands measured in our study are compared with the IR bands reported for 1-butyl-3-methylimidazolium-2-carboxylate<sup>20</sup> (Table 1). We find that there is a perfect agreement and we can conclude that carbon dioxide is bonded to the imidazolium ring after substitution of the hydrogen atom of its carbon 2. Therefore, the three new vibrations cannot be considered as those of a

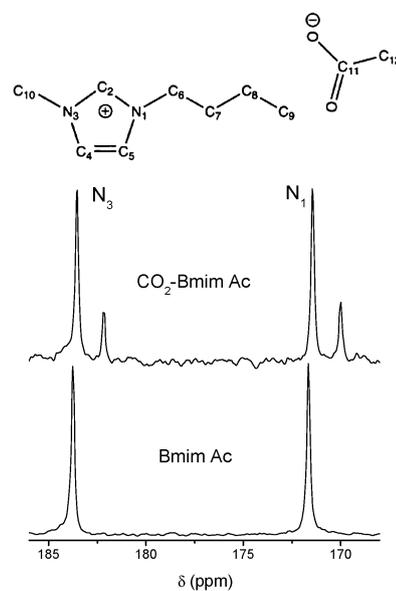


**Fig. 2** Structure calculated at the B3LYP/6-31+G\*\* level for one 1-butyl-3-methylimidazolium-2-carboxylate molecule interacting with a single Bmim Ac ion pair.

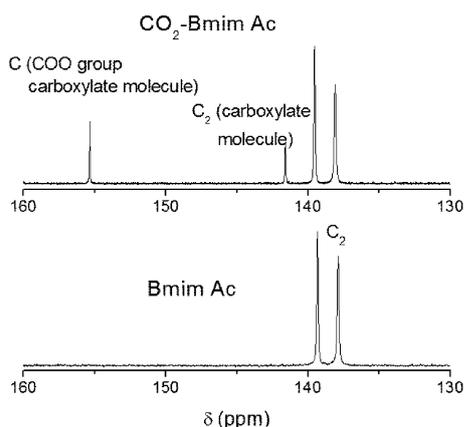
CO<sub>2</sub> molecule interacting with the IL but corresponding to the vibrations of the functional COO group of the carboxylate molecule. We can then interpret the strong perturbation of the cation observed at about 1450 cm<sup>-1</sup> as resulting from the ring carboxylation. This is confirmed by a recent Raman study showing that a new and intense Raman band centered at 1499 cm<sup>-1</sup>, assigned to a NC(CH<sub>3</sub>)N CC stretching mode, appears upon the methylation of the carbon 2 (C<sub>2</sub>) position in 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide.<sup>23</sup>

We have measured the <sup>15</sup>N NMR spectra of pure Bmim Ac and its mixture with carbon dioxide (Fig. 3). In the pure IL, the spectrum presents two intense resonance lines centered at about 183.7 and 171.6 ppm assigned, from the <sup>1</sup>H-<sup>15</sup>N HMBC NMR sequence, to the non-equivalent nitrogen 3 and 1 of the ring core, respectively. In the mixture, two additional resonance lines flanking each of the previous peaks are observed at 182.1 and 170.0 ppm, respectively.

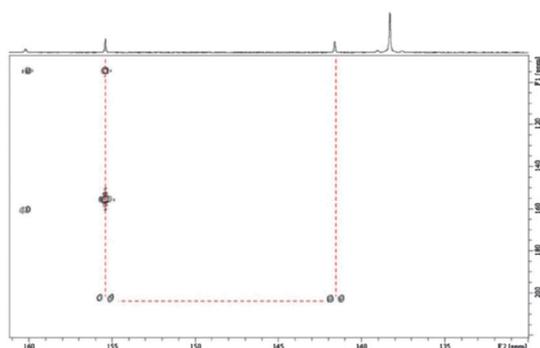
The <sup>13</sup>C spectrum of a CO<sub>2</sub>-Bmim Ac mixture is compared with the spectrum of the pure IL (Fig. 4). Two main findings are apparent. A new line centred at 155.3 ppm is observed and all the



**Fig. 3** Comparison of the <sup>15</sup>N NMR spectra of the pure Bmim Ac with that of a CO<sub>2</sub>-Bmim Ac mixture. The schematic representation of the Bmim Ac molecule is presented.



**Fig. 4** Comparison of the  $^{13}\text{C}$  NMR spectra of pure Bmim Ac with that of a  $\text{CO}_2$ -Bmim Ac mixture.



**Fig. 5** 2D NMR spectrum using the INADEQUATE sequence on the  $^{13}\text{CO}_2$ -Bmim Ac mixture under 0.1 MPa at 298 K.

intense lines of the Bmim cation are found to be accompanied by secondary lines of lower intensity (Table SI2 in ESI $^\dagger$ ). In particular the doublet *ca.* 138 ppm assigned to the  $\text{C}_2$  of the ring (Table SI2 in ESI $^\dagger$ ) is accompanied by a secondary line at 141.6 ppm.

The new secondary lines observed on  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR spectra confirm that carbon dioxide has reacted with Bmim Ac to form a new species having spectral signatures close to those of the Bmim cation. Moreover, the  $^{13}\text{C}$  line at 155.3 ppm should be associated with the carbon atom of  $\text{CO}_2$  which has reacted to form the new species. The proportion of the new species estimated from the integrated intensity of the secondary lines of the cation in  $^{15}\text{N}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra is about 0.16 molar fraction.

To assess the origin of the line at 155.3 ppm the 2D INADEQUATE sequence was measured (Fig. 5). It is found that this line is correlated with the secondary line of the  $\text{C}_2$  (141.6 ppm) and not with the resonance line of  $\text{C}_2$  of the Bmim Ac (138 ppm). This result shows that the carbon atom of carbon dioxide became covalently bonded to the  $\text{C}_2$  of the new species.

The presence of nascent acetic acid due to the release of the proton of the  $\text{C}_2$  consequent of the carboxylation reaction has been put in evidence from the  $^1\text{H}$  spectrum of the mixture. The resonance line corresponding to this nascent acid was

found to evolve in time showing that its state varies from monomer (nascent) to aggregated forms (acid interacting with the acetate anion) (Table SI2, ESI $^\dagger$ ).

In conclusion, all these results show that under mild conditions (298 K, 0.1 MPa)  $\text{CO}_2$  has reacted with Bmim Ac to form 1-butyl-3-methylimidazolium-2-carboxylate accompanied by the formation of nascent acetic acid originated from the release of the proton bonded to carbon 2 of the imidazolium ring.

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- 19 In the course of the submission of this communication, direct experimental evidence has been obtained from the X-ray structure of the solid-state products resulting from the reaction of  $\text{CO}_2$  with acetate ILs [G. Gurau, H. Rodriguez, S. P. Kelley, P. Janiczek, R. S. Kalb and R. D. Rogers, *Angew. Chem., Int. Ed.*, 2011, **50**, DOI: 10.1002/anie.201105198]. The present study shows that the main features observed in the liquid mixture (carboxylate and acetic acid formation), which involve the finite time scale of interaction and also the observation time of the techniques (vibrational and NMR spectroscopy) are also observed in the solid state.
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