

# On the chemical reactions of carbon dioxide isoelectronic molecules CS<sub>2</sub> and OCS with 1-butyl-3-methylimidazolium acetate†

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**Raman and NMR spectroscopies show that CS<sub>2</sub> and OCS react spontaneously with 1-butyl-3-methylimidazolium acetate [C<sub>4</sub>mim][Ac] in the liquid phase. The formation of [C<sub>4</sub>mim] CO<sub>2</sub>, [C<sub>4</sub>mim] COS, CH<sub>3</sub>COS<sup>−</sup> and gaseous CO<sub>2</sub> and OCS in both systems demonstrates that the anion plays an unexpected role not observed in the CO<sub>2</sub>–[C<sub>4</sub>mim][Ac] reaction.**

Characterizing the solvation of carbon dioxide in ionic liquids (IL) and understanding the physisorption and chemisorption processes at the molecular level leading to its capture is an actual extensive research area in both fundamental and applied investigations motivated particularly by environmental concerns.<sup>1–4</sup> In this context, imidazolium based acetate ionic liquids have been the subject of substantial studies recently due to their role as model systems for which an unusually high solubility of CO<sub>2</sub> is achieved.<sup>5,6</sup> In these systems, the chemisorption process results from the interaction of the CO<sub>2</sub> molecule with the carbene formed after abstraction of proton 2 of the imidazolium ring leading to the formation of imidazolium-2-carboxylate and acetic acid.<sup>7–9</sup> The presence of the carbene, which has never been spectroscopically observed in the pure liquid IL, is indirectly detected in the mixture *via* carboxylate formation.<sup>7–15</sup> It was found that the presence of CO<sub>2</sub> in the IL triggers this reaction.<sup>13,14</sup> A reactive scheme involving concerted

mechanisms has been proposed. The proton exchanges between the cation and the acetate anion leading to the formation of a transient CO<sub>2</sub>-1-butyl-3-methyl imidazole 2-ylidene carbene and the carboxylation reaction is initiated.<sup>13,14</sup> More recently, a theoretical study concluded that in the CO<sub>2</sub>–IL mixture more carbene are formed than in the pure IL due to the way CO<sub>2</sub> is solvated.<sup>15,16</sup> The introduction of neutral molecules like CO<sub>2</sub> in the IL charged network partially cancels the existing charge-stabilizing effect shifting the single solvating anion away from CO<sub>2</sub>. Concomitantly, more solvating cations approach CO<sub>2</sub>. This so-called inverse ionic liquid effect facilitates carbene formation, giving rise to chemical absorption.<sup>15</sup> Although it is not straightforward to compare these studies, they confirm that the presence of CO<sub>2</sub> and a subtle interplay of the IL cation–anion allows the chemisorption of CO<sub>2</sub>. From these studies, one might question if the isoelectronic molecules of CO<sub>2</sub>, carbon disulfide (CS<sub>2</sub>) and carbonyl sulfide (OCS) react spontaneously with [C<sub>4</sub>mim][Ac] as observed for CO<sub>2</sub>. If so, can we also anticipate that a similar synergy between the ions and the solute exists, leading only to 1-butyl-3-methylimidazolium-2-dithiocarboxylate [C<sub>4</sub>mim] CS<sub>2</sub> (1) and 1-butyl-3-methylimidazolium-2-thiocarboxylate [C<sub>4</sub>mim] COS (2), respectively, and acetic acid production (ESI<sup>+</sup>)? Indeed a number of groups have shown that stable zwitterionic adducts, [C<sub>4</sub>mim] CS<sub>2</sub> and 1-butyl-3-methylimidazolium-2-carboxylate [C<sub>4</sub>mim] CO<sub>2</sub> (3), can be formed in solutions by the direct reaction of free N-heterocyclic carbene with CS<sub>2</sub> and CO<sub>2</sub>.<sup>17</sup> However, the role of the anion and the solute (CS<sub>2</sub> and OCS) in triggering possible reactions in the IL is still an open question. Moreover, the capture of CO<sub>2</sub> isoelectronic molecules also deserves more in depth investigation. OCS plays an important role in the global cycling of sulfur, being the most abundant sulfur compound in the atmosphere released by oceans, biomass, oxidation of CS<sub>2</sub> and industrial activities.<sup>18–21</sup> Our attempts to provide answers to these questions are the subject of the present communication.

Upon mixing CS<sub>2</sub> in dried [C<sub>4</sub>mim][Ac] (system I), under ambient conditions, an exothermic reaction accompanied by degassing and an almost instantaneous red-blood coloration is observed (ESI<sup>+</sup>). As OCS is gaseous under ambient conditions the preparation of solution II was different (ESI<sup>+</sup>) and only a faint yellowish colouring was noticed. The signature of these chemical reactions is confirmed

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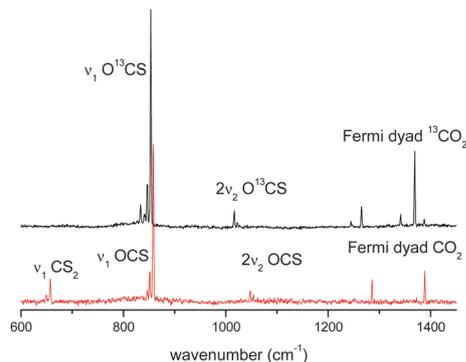
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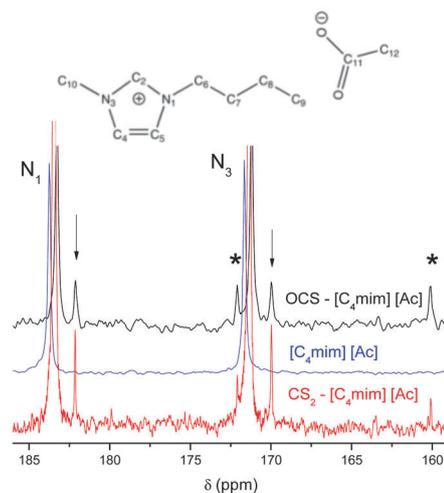
**Fig. 1** Raman spectra of the vapour phase of  $\text{CS}_2$ -[C<sub>4</sub>mim][Ac] (red,  $x_{\text{CS}_2} = 0.30$ ) and  $\text{O}^{13}\text{CS}$ -[C<sub>4</sub>mim][Ac] (black) mixtures.

by UV-visible spectroscopy which shows two new transitions in system I which are not observed in the pure compounds (about 514 nm and 430 nm) and ascribed to the presence of [C<sub>4</sub>mim] CS<sub>2</sub> (1).<sup>22–24</sup> In mixture II the strongly enhanced intensity observed in the UV domain is ascribed to the presence of [C<sub>4</sub>mim] COS (2) (ESI<sup>†</sup>). Additional experiments performed using [C<sub>4</sub>mim] ILs having different anions (trifluoroacetate [TFA], tetrafluoroborate [BF<sub>4</sub>], bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>]) do not show any traces of reaction (ESI<sup>†</sup>). However with carboxylate type anions (lactate, malonate and hexanoate) a red-coloration similar to that observed in [C<sub>4</sub>mim][Ac] was noted (ESI<sup>†</sup>).

To characterize the nature of the constituents of the gas released during the chemical reactions of the two systems, we used Raman spectroscopy (Fig. 1). In the CS<sub>2</sub> mixture, the  $\nu_1$  symmetric stretching vibration of CS<sub>2</sub> (657 cm<sup>-1</sup>), the  $\nu_1$  (symmetric stretch, 858 cm<sup>-1</sup>) and  $2\nu_2$  (bending first overtone, 1047 cm<sup>-1</sup>) of OCS<sup>25</sup> and the Fermi dyad of CO<sub>2</sub> (1285 cm<sup>-1</sup>, 1388 cm<sup>-1</sup>)<sup>26</sup> are observed. In the OCS mixture (with labeled O<sup>13</sup>CS) we observe the  $\nu_1$  (853 cm<sup>-1</sup>) and  $2\nu_2$  (1016 cm<sup>-1</sup>) of O<sup>13</sup>CS and the Fermi dyad of <sup>13</sup>CO<sub>2</sub> (1265 cm<sup>-1</sup>, 1369 cm<sup>-1</sup>) which are slightly shifted towards lower frequency due to the isotopic effect.

In both systems, CO<sub>2</sub> was produced in the course of the chemical reaction. As the only “source” of oxygen atoms in system I is the anion, it can be inferred that it plays an important role in the reaction which could not be *a priori* anticipated from the previous discussion (ESI<sup>†</sup>). Moreover, the presence of labeled <sup>13</sup>CO<sub>2</sub> in system II indicates that this molecule originates from a <sup>13</sup>CO fragment of the labeled O<sup>13</sup>CS and that the other oxygen atom must come from the acetate anion (ESI<sup>†</sup>). It could be speculated that in system I the CO<sub>2</sub> originates from the COO group of the acetate. This hypothesis will be ruled out as demonstrated below, confirming that in both systems one of the oxygen atoms of CO<sub>2</sub> comes from the acetate anion.

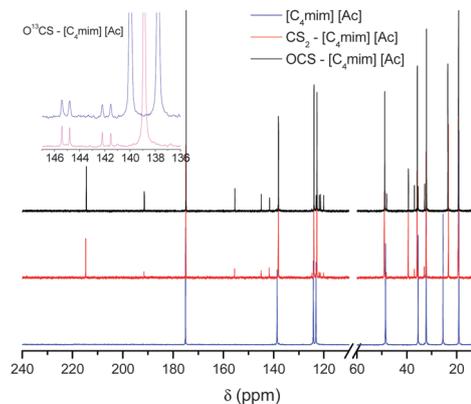
The <sup>15</sup>N NMR spectra of the pure IL and its mixture with CS<sub>2</sub> and OCS are shown in Fig. 2. In the pure liquid, the two resonance lines at 171 and 183 ppm assigned to the nitrogen atom N<sub>1</sub> and N<sub>3</sub> of the cation ring are observed.<sup>12</sup> These intense lines are accompanied by two pairs of new weaker resonance lines observed at the same chemical shifts in the two mixtures. These lines are due to the two nitrogen atoms of two new species involving the imidazolium ring as confirmed by the 2D HMBC <sup>1</sup>H–<sup>15</sup>N NMR sequence (ESI<sup>†</sup>). The lines marked by arrows (170 and 182 ppm) can be readily assigned to the



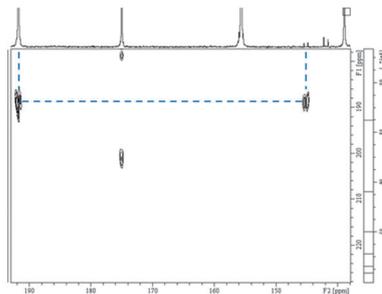
**Fig. 2** Comparison of the <sup>15</sup>N NMR spectra of  $\text{CS}_2$ -[C<sub>4</sub>mim][Ac] (red,  $x_{\text{CS}_2} = 0.08$ ) and  $\text{O}^{13}\text{CS}$ -[C<sub>4</sub>mim][Ac] (black) mixtures with that of pure [C<sub>4</sub>mim][Ac] (blue).

presence of the carboxylate [C<sub>4</sub>mim] CO<sub>2</sub> (3)<sup>12</sup> (ESI<sup>†</sup>). In the OCS mixture, the second pair of lines (172 and 160 ppm) can be assigned to the formation of [C<sub>4</sub>mim] COS (2). We note that these lines are also present in system I and allow us to conclude that [C<sub>4</sub>mim] COS is formed in this system. Surprisingly, the [C<sub>4</sub>mim] CS<sub>2</sub> is not detected.

A comparison of the proton decoupled <sup>13</sup>C NMR spectra shows new secondary lines observed at the same chemical shifts in both mixtures (Fig. 3). This confirms the formation of the same adducts in the two systems. We also note that the characteristic line of the carbon of the CSS group of the [C<sub>4</sub>mim] CS<sub>2</sub> (226–229 ppm)<sup>17,27,28</sup> is not detected. Moreover the presence of the resonance lines at 142 ppm and 155 ppm can be assigned to carbon 2 and to the carbon atom of the COO group of the [C<sub>4</sub>mim] CO<sub>2</sub> (3), respectively.<sup>12,14</sup> This result agrees with the conclusion of the <sup>15</sup>N NMR study. The other main secondary lines are observed at about 40, 145, 192 and 215 ppm. The single line observed at 145 ppm is a secondary line of carbon 2 of the new species (2). It becomes a doublet when <sup>13</sup>C is used in OCS and CS<sub>2</sub> and is not affected by the proton decoupling (inset, Fig. 3) as observed for carbon 2 of [C<sub>4</sub>mim]



**Fig. 3** Comparison of the proton decoupled <sup>13</sup>C NMR spectra of  $\text{CS}_2$ -[C<sub>4</sub>mim][Ac] (red,  $x_{\text{CS}_2} = 0.20$ ) and  $\text{OCS}$ -[C<sub>4</sub>mim][Ac] (black) mixtures with that of pure [C<sub>4</sub>mim][Ac] (blue). The inset shows a magnification of the spectra (with and without proton decoupling) of  $\text{O}^{13}\text{CS}$ -[C<sub>4</sub>mim][Ac].



**Fig. 4** 2D NMR INADEQUATE sequence of the  $^{13}\text{C}_{52}$ -[C<sub>4</sub>mim][Ac] mixture ( $x_{13\text{CS}_2} = 0.08$  m.f.).

$\text{CO}_2$  in previous studies.<sup>14</sup> This carbon atom is therefore not covalently bonded to protons. This line is correlated with the one appearing at 192 ppm, as shown from the INADEQUATE sequence (Fig. 4).

Because the intensity of the 192 ppm line strongly increased upon  $^{13}\text{C}$  isotopic substitution, it can be inferred that carbon 2 of the new species is covalently bonded to a carbon atom belonging to OCS or  $\text{CS}_2$ . The formation of the [C<sub>4</sub>mim] COS in the OCS mixture can be understood if proton 2 of the cation ring is replaced by the OCS molecule (ESI<sup>†</sup>). Such an interpretation closely follows the one proposed for carboxylate formation in the [C<sub>4</sub>mim][Ac]- $\text{CO}_2$  system.<sup>9</sup> However, in the  $\text{CS}_2$  mixture the formation of the [C<sub>4</sub>mim] COS cannot be understood without considering the exchange of an oxygen atom of the acetate anion by a sulfur atom of the  $\text{CS}_2$  molecule. Consequently, a thioacetate anion  $\text{CH}_3\text{COS}$  (**4**) should be formed (ESI<sup>†</sup>). Indeed, the remaining resonance lines at about 40 and 215 ppm are shown to belong to this new adduct, as demonstrated using  $^1\text{H}$  NMR spectra and  $^1\text{H}$ - $^{13}\text{C}$  sequences. The  $^1\text{H}$  spectra of mixtures I and II display the line corresponding to the formation of nascent acetic acid (18–14 ppm range) and a new line at 2.3 ppm (ESI<sup>†</sup>). Using the HSQC sequence, this latter line is correlated with the carbon line at about 40 ppm assigned to the methyl group of the acetate (ESI<sup>†</sup>). Using the HMBC sequence, the proton line at 2.3 ppm is correlated with the line observed at 215 ppm (ESI<sup>†</sup>). Therefore, this line belongs to the carbon atom of the acetate group in which one of the oxygen atoms has been substituted by a sulfur atom. Additional experiments with sodium acetate in the presence of crown ether, producing ‘naked’ acetate, show that  $\text{CS}_2$  reacts with the anion. The same result was observed for a mixture of  $\text{CS}_2$  with a quaternary ammonium acetate (ESI<sup>†</sup>).<sup>29</sup>

In summary, in both systems, [C<sub>4</sub>mim] COS (**2**), [C<sub>4</sub>mim]  $\text{CO}_2$  (**3**) and  $\text{CH}_3\text{COS}$  (**4**) are formed in the liquid phase and the presence of OCS and  $\text{CO}_2$  in the gaseous phase in system I and  $\text{CO}_2$  in system II is noted. The [C<sub>4</sub>mim]  $\text{CS}_2$  (**1**) could not be observed by NMR and it is only in IL- $\text{CS}_2$  mixtures that the presence of this adduct as traces could be inferred (estimated  $<0.01$  mol  $\text{l}^{-1}$  for a solution 0.03  $\text{CS}_2$  m.f.) due to the very high sensitivity of UV-visible spectroscopy (ESI<sup>†</sup>). This might be understood by arguing that the thiolate (**1**) is formed but is not stable in the IL. The formation of  $\text{CO}_2$  in the gas phase indicates that one of the oxygen atoms of  $\text{CO}_2$  comes from an oxygen atom of an acetate anion. Therefore, in IL- $\text{CS}_2$  such a mechanism should involve two oxygen atoms originating from two different acetate anions. Clearly, the anion plays an important and complex role in the interpretation of these results.

Concerning the cation, we may infer that it reacts in a similar way to that found in  $\text{CO}_2$ -[C<sub>4</sub>mim][Ac].<sup>9,11–14</sup> Indeed, as in this latter system, the carbene species plays a role which can be inferred *via* the formation of (**2**) and (**3**) and of nascent acetic acid. However the  $\text{CS}_2$  system shows that there is an interplay between the cation and the anion, as the expected [C<sub>4</sub>mim]  $\text{CS}_2$  (**1**) is absent in adduct formation. Elucidating the reactive scheme in these coupled chemical reactions still certainly demands the assessment of the interplay among the ions and the solute in these more complex systems. Finally, we hope that this experimental study which provides new insight into the complex processes taking place between IL and  $\text{CO}_2$  isoelectronic molecules will motivate more studies in particular in the theoretical domain to consistently elucidate the subtle role and interplay of the cation and anion of the IL in the complex chemical reactions reported here at the molecular level.

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