Understanding chemical reactions of CO2 and its isoelectronic molecules with 1-butyl-3-methylimidazolium acetate by changing the nature of the cation: The case of CS2 in 1-butyl-1-methylpyrrolidinium acetate studied by NMR spectroscopy and density functional theory calculations

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NMR spectroscopy ($^{1}$H, $^{13}$C, $^{15}$N) shows that carbon disulfide reacts spontaneously with 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) in the liquid phase. It is found that the acetate anions play an important role in conditioning chemical reactions with CS$_2$ leading, via coupled complex reactions, to the degradation of this molecule to form thioacetate anion (CH$_3$CO$_2$), CO$_2$, OCS, and trithiocarbonate (CS$_3^{2-}$). In marked contrast, the cation does not lead to the formation of any adducts allowing to conclude that, at most, its role consists in assisting indirectly these reactions. The choice of the [BmPyrro]$^{+}$ cation in the present study allows disentangling the role of the anion and the cation in the reactions. As a consequence, the ensemble of results already reported on CS$_2$-[Bmim][Ac] (1), OCS-[Bmim][Ac] (2), and CO$_2$-[Bmim][Ac] (3) systems can be consistently rationalized. It is argued that in system (1) both anion and cation play a role. The CS$_2$ reacts with the acetate anion leading to the formation of CH$_3$CO$_2$-, CO$_2$, and OCS. After these reactions have proceeded the nascent CO$_2$ and OCS interact with the cation to form imidazolidine-carboxylate ([Bmim]CO$_2$) and imidazolidine-thiocarboxylate ([Bmim]COS). The same scenario also applies to system (2). In contrast, in the CO$_2$-[Bmim] [Ac] system a concerted cooperative process between the cation, the anion, and the CO$_2$ molecule takes place. A carbene issued from the cation reacts to form the [Bmim]CO$_2$, whereas the proton released by the ring interacts with the anion to produce acetic acid. In all these systems, the formation of adduct resulting from the reaction between the solute molecule and the carbene species originating from the cation is expected. However, this species was only observed in systems (2) and (3). The absence of such an adduct in system (1) has been theoretically investigated using DFT calculations. The values of the energetic barrier of the reactions show that the formation of [Bmim] CS$_2$ is unfavoured and that the anion offers a competitive reactive channel via an oxygen-sulphur exchange mechanism with the solute in systems (1) and (2).

I. INTRODUCTION

Understanding at the molecular level the solvation and capture of carbon dioxide in ionic liquids (IL) is an active field of researches strongly motivated by their environmental incidences. $^{1-11}$ In this context, imidazolium acetate based ILs were proposed as systems able to capture comparatively to other ionic liquids, unusual amounts of carbon dioxide. $^{12,13}$ A number of investigations by us and others have shown that carbon dioxide dissolved in dried 1-butyl-3-methylimidazolium acetate [Bmim] [Ac] reacts spontaneously leading to the formation of 1-butyl-3-methylimidazolium-2-carboxylate and acetic acid. $^{14-23}$ A reactive mechanism has been proposed in which the proton bounded to carbon atom 2 of the imidazolium cation is released leading to the generation of a carbene intermediate, whereas the proton interacts with the acetate anion to form acetic acid (Fig. 1). $^{14-16}$

This description led to conclude to the presence of carbene species in this ionic liquid, the concentration of which is controlled by the nature of the anion. Other works, although considering the formation of carbene and acetic acid, differ slightly from this initial interpretation, arguing that the reactions are triggered by the introduction of carbon dioxide itself in the IL and that the carbene and carboxylate formation results from a concerted cooperative process.

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between the cation, the anion, and the CO$_2$ molecule.$^{20-22}$ More recently, it was theoretically inferred that it is the introduction of neutral molecules like CO$_2$ in the IL charged network which cancels partially the charge-stabilizing effect existing in the neat IL and that this so-called inverse ionic liquid effect facilitates the carbene formation and, thus, the chemical absorption.$^{24,25}$ Very recently, new insights in the understanding of solute-solvent interactions within IL were provided from a theoretical study on the solvation of a carbene 1-ethyl-3-methylimidazole-2-yldiene in 1-ethyl-3-methylimidazolium acetate.$^{26}$ It was shown that the lack of strong hydrogen bonding between the hypovalent carbon atom of the carbene and the ring hydrogen atoms of the cation prevents the stabilization of this species explaining its high reactivity in acetate-based ILs. Overall, these studies converge towards a common recognition about the existing synergy between the cation and anion of the IL in the chemisorption of CO$_2$. Recently, the solvation of CS$_2$ (system 1) and OCS (system 2), which are isoelectronic molecules of CO$_2$, has been studied in [Bmim] [Ac].$^{27}$ Based upon the considerations above and the fact that long-lived carbene are known to react with CS$_2$,$^{4,28-31}$ it could be anticipated that a dithiocarboxylate and a thiocarboxylate, respectively, could be formed in these mixtures together with the production of acetic acid. Surprisingly enough, it was shown that the same adducts, namely, thiocarboxylate, carboxylate, thioacetate anion, and acetic acid are formed in the liquid phase, whereas the presence of CO$_2$ was detected in the gaseous phase of both mixtures.$^{27}$ This result allowed us to infer that, besides the almost predictable role of the cation in the carboxylate and thiocarboxylate formation, the anion plays a relevant and unexpected role in the chemisorption of solute in the IL. In order to have a better insight on the respective role of the IL ions into chemical reactions, we have thus investigated the solution of 1-butyl-1-methylpyrrolidinium acetate [BmPyro] [Ac] with CS$_2$. This particular ionic liquid was selected because it shares, in common with the previous systems, the acetate anion but differs from them in the nature of the [BmPyro] cation constituted by a five-member saturated ring having a quaternary ammonium group on which the methyl and butyl chain are bonded as schematic represented in Fig. 2. The pure IL is known to exist under slightly ionized forms and in contrast to imidazolium ILs, the cation is not expected to form a carbene.$^{32}$ Thus, by using this specific IL, the role of the anion and cation can be somehow “decoupled” compared to [Bmim] [Ac] and if reactions occur with CS$_2$, they could be ascribed either to the acetate anion only or, possibly, to a cooperative cation-anion process differing from those reported previously. This work is aimed at providing new insights on these issues.

II. EXPERIMENTAL

A. Experimental conditions

The ionic liquid was obtained from Iolitec (stated purity greater than 97%), CS$_2$ (purity greater than 99.9%), and $^{13}$C labelled CS$_2$ (99 atom%) from Aldrich. The IL was dried at 323 K under a primary vacuum during more than 48 h under continuous stirring. The water content measured by Karl-Fisher titration was 530 ppm.

Na$_2$CS$_3$ was synthesized by mixing Na$_2$S with CS$_2$ in excess in aqueous solution according to the protocol of reference.$^{33}$

NMR measurements were performed on a Bruker AVANCE II spectrometer operating at Lambor frequency of 600 MHz for $^1$H, 150 MHz for $^{13}$C, and 60 MHz for $^{15}$N. The $^1$H spectra were collected after a 30° pulse with a 90° pulse ($t_{90}$) of 8 μs. The number of scans was ranged from 512 to

![Fig. 1. Formation of carbenes from [Bmim] [Ac].](image)

![Fig. 2. $^{15}$N NMR spectra of CS$_2$-[BmPyro] [Ac] solutions ($x_{CS_2} = 0.05$, red, $x_{CS_2} = 0.20$, blue) and of pure [BmPyro] [Ac] (black).](image)
1024 with a relaxation delay (d1) of 1 s. The $^{13}$C spectra was acquired after a $t_{90} = 15 \mu$s and d1 = 5 s. The $^{13}$C proton decoupled spectra were measured using the standard WALTZ-16 decoupling sequence. These measurements have been completed by performing 2D $^1$H−$^1$H COSY, $^1$H−$^{13}$C HSQC, and $^1$H−$^{13}$C HMBC sequences. The samples were contained in standard 5 mm tubes and an external D$_2$O lock was used. Measurements were also performed in a Bruker AVANCE II spectrometer at 300 MHz Larmor frequency for $^1$H, 75 MHz for $^{13}$C. The $^1$H spectra were recorded after a single pulse, $t_{90} = 14 \mu$s and d1 = 5 s. The number of scans was ranged from 512 to 1024. The $^{13}$C spectra have been acquired after a single pulse with $t_{90} = 11 \mu$s and d1 = 3 s. The $^{13}$C proton decoupled spectra were measured using the standard WALTZ-16 decoupling sequence. The temperature of the samples was regulated at 298 K and stabilized to within ±0.5 K using gas flow.

Raman spectra were measured on a Horiba Xplora spectrometer with 6 cm$^{-1}$ resolution using a back-scattering geometry with a laser excitation at 638 nm.

UV-Visible spectra were measured on a double-beam spectrometer (Hewlett-Packard 8452A) using standard 1 mm quartz cells.

B. DFT calculations details

Density Functional Theory (DFT) calculations have been carried out using the program GAUSSIAN-09. The open shell energy calculations have been achieved from the unrestricted DFT procedure using the hybrid functional B3LYP (DFT-UB3LYP) with the 6-31+G(d,p) basis set except for sulphur (S) atoms for which the MQZVP (Modified QZVP) basis set was used.

At this computational level, the reactive paths are evaluated from the examination in a restricted domain of the relaxed Potential Energy Surfaces (PES) calculated from initial (local energy minimum) structures involving only one CO$_2$, OCS, or CS$_2$ triatomic molecule interacting with the 1-butyl-3-methylimidazolium acetate ion pair ([Bmim] [Ac]), respectively. The location of a transition state linking two consecutive anchored local energy minima along the calculated PES is obtained using Synchronous Transit-Guided Quasi-Newton (STQN) method. Full optimization and vibrational analysis have been carried out for the stationary points (i.e., local energy minima and transition states) determined from the pathway experienced along of the PES. Then, the reaction path is evaluated from a given transition state using the Intrinsic Reaction Coordinate (IRC) integration method implemented in the program GAUSSIAN.

C. Experimental results

Upon dissolution of CS$_2$ in dried [BmPyro] [Ac], a blood-red solution is obtained showing that a reaction occurs.

The $^{15}$N NMR spectrum of the cation of pure [BmPyro] [Ac] exhibits a single resonance line at about 74 ppm which broadens upon addition of CS$_2$ (0.05 and 0.20 CS$_2$ mole fraction) and remains almost centered at the same chemical shift value (Fig. 2). This observation together with the absence of new resonance lines allows inferring that the cation is not involved in the adducts of the chemical reactions. Therefore, the reaction only takes place between the acetate anion and CS$_2$.

The $^{13}$C (in natural abundance) NMR spectrum of the pure IL was assigned from the comparison of the proton decoupled and un-decoupled spectrum using also 2D sequences (COSY $^1$H−$^1$H, HSQC $^1$H−$^{13}$C, and HMBC $^1$H−$^{13}$C) (Table I and supplementary material in Ref. 39). Upon mixing CS$_2$ in the IL new resonance lines have been observed in the solutions investigated (Fig. 3, Table I). The resonance line of

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Resonance lines of the formed thioacetate.
Resonance lines of the formed carbon disulfide.
Resonance lines of the formed carbonyl sulfide.
Resonance lines of the formed trithiocarbonate anion.

FIG. 3. Proton decoupled $^{13}$C NMR spectra of CS$_2$-[BmPyro] [Ac] solutions ($x_{CS2} = 0.05$, red, $x_{CS2} = 0.20$, blue) and of pure [BmPyro] [Ac] (black). The inset shows a magnification of the spectra (with and without proton decoupling) of the new resonance line (about 40 ppm) of the concentrated solution.
CS₂ at 193 ppm⁴⁰ was not observed indicating that this compound has been fully consumed by the chemical reaction. The absence of new secondary lines on the spectra of the cation together with the fact that only slight perturbations of the resonance lines of the carbon bonded to the nitrogen atom are observed confirm that the CS₂ molecule does not attack the cation (Table I, Fig. 3).

Two main new resonance lines (at about 40 and 213 ppm) inexistent in the pure IL are detected in the proton decoupled ¹³C spectra (Fig. 3, Table I). For the more concentrated solutions (xCS₂ = 0.20) a resonance line at about 125 ppm is also detected. The assignment of these lines is readily done considering that CS₂ reacting with the acetate anion leads to the formation of thioacetate anion (40 and 213 ppm) and solvated carbon dioxide (125 ppm) as it was shown in the CS₂⁻-[Bmim] [Ac] system. The formation of thioacetate in the present system is also confirmed by the presence of a new line detected at 2.4 ppm in the ¹H NMR spectra of the solutions that is assigned to the protons atoms of the methyl group of the thioacetate anion (Table I and supplementary material³⁹). The examination of correlations in the HSQC ¹H-¹³C sequence corroborate this conclusion (supplementary material³⁹). The formation of thioacetate is also confirmed from the ¹H and ¹³C NMR spectra of aqueous solutions of potassium thioacetate (supplementary material³⁹).

The formation of CO₂ has been confirmed from the Raman spectrum of the vapor phase of the CS₂⁻-[BmPyrro] [Ac] solution which displays the characteristic Fermi doublet transitions (1282 and 1385 cm⁻¹) and the asymmetric stretch vibration (2330 cm⁻¹) of this species (Fig. 4). We have also observed in the ¹³C NMR spectra two weak resonance lines centered at 159 and 269 ppm. Measurements using labeled ¹³CS₂ reveal that the intensity of these lines is strongly enhanced by the isotopic substitution, whereas the intensity of the lines of the thioacetate anion (40 and 213 ppm) remains unaffected (Fig. 5).

The enhancement of the 159 and 269 ppm resonance lines indicates that they should involve at least a ¹³CS moiety. The line at 159 ppm can be assigned to the formation of carbonyl sulfide (OCS) which was previously found in the CS₂⁻-[Bmim] [Ac] system at 156 ppm.²⁷ We surmised that the line at 269 ppm could be due to the formation of trithiocarbonate anion (CS₃²⁻). The ¹³C spectrum of sodium trithiocarbonate (Na₂CS₃) in aqueous solution was measured (Fig. 6) and a single line found at about 269 ppm confirms this assignment.

The blood-red color of the CS₂⁻-[BmPyrro] [Ac] solutions should be due to the presence of CS₃²⁻ as the other species formed, namely, thioacetate anion and CO₂, do not display absorption in the visible domain (supplementary material³⁹). Indeed, the aqueous solutions containing the CS₃²⁻ anion have a red-blood color. The UV-Visible of the CS₃²⁻ aqueous solution displays two bands at 416 and 502 nm ascribed to the signatures of the n → π* transition of sulfur (Fig. 7).⁴⁴-⁴⁶
FIG. 7. UV-Visible spectrum of aqueous solutions of Na$_2$CS$_3$ (0.07 mol l$^{-1}$, black; 0.014 mol l$^{-1}$, red).

These features are consistent with those observed on the UV-Visible spectrum of CS$_2$-[BmPyrro] [Ac] solutions in which two transitions at about 447 nm and 538 nm, inexistent in the pure reactants, are detected (Fig. 8). Concomitantly, the intensity of the wing of the strong transition in the UV-region below 400 nm observed for the solution is strongly enhanced compared to that of the pure liquids. Therefore, the two bands observed in the present system may be assigned to the $n \rightarrow \pi^*$ transition of sulfur involved in a new adduct.

It is noteworthy that ionic liquid ([Bmim] [BF$_4$]) used as a phase-transfer catalyst in the synthesis of the trithiocarbonate anion led to greater yield keeping in addition the trithiocarbonate ion stable. This ensemble of evidences gives strong supports to the existence of such CS$_3^{2-}$ anion in the present solutions.

III. INTERPRETATION AND DISCUSSION

The acetate anions in [BmPyrro] [Ac] play an important role in conditioning chemical reactions with CS$_2$, via coupled complex reactions, to the degradation of this molecule to form several main adducts, namely, CO$_2$, OCS, thioacetate anion (CH$_3$COS$^-$), and as a minor species the trithiocarbonate anion (CS$_3^{2-}$). The products formed in this system have been already found in the solution of CS$_2$ in [Bmim] [Ac]. This ensemble of consistent results definitively establishes the role of the acetate anion in the interaction with carbon disulfide. In view of this complexity, establishing a complete reactive scheme is quite challenging and beyond the scope of this study without having more experimental and theoretical supports. Nevertheless, a number of insights on this scheme have been previously presented in Ref. 27 and related ESI. The first issue concerns the formation of thioacetate anion. This species can be only formed via the exchange of an oxygen atom of the acetate anion with a sulfur atom of CS$_2$ leading also to the formation of the OCS molecule according to the proposed reaction (Fig. 9).

This is further supported by the fact that using labelled $^{13}$CS$_2$, the formation of O$^{13}$CS is observed as described above. The formation of CO$_2$ in the solution, which is also detected in the vapour phase, can be understood by taking into account the presence of nascent OCS according to the proposed reaction (Fig. 10):

The formation of the minor species trithiocarbonate anion CS$_3^{2-}$ in CS$_2$-[Bmim] [Ac] was not discussed in the previous study although a resonance line at 269 ppm was detected (Fig. 6). The blood-red color of this solution and the observation in UV-Visible spectroscopy of two $n \rightarrow \pi^*$ transitions of sulfur$^{27,31,39,43-45}$ close to those found in the CS$_2$-[BmPyrro] [Ac] solutions (Fig. 8) would indicate the formation of trithiocarbonate anion. In previous study, these transitions have been tentatively assigned to the presence of traces of 1-butyl-3-methylimidazolium-2-dithiocarboxylate [Bmim] CS$_2$ although the resonance line of the carbon atom of the dithiocarboxylate $\sim$220-225 ppm was not detected by NMR.$^4,28,31$ Therefore, it can be inferred from the present results that it is the trithiocarbonate anion which has been formed and not the dithiocarboxylate. Although the formation of the latter species cannot be totally ruled out, the present analysis shows that if formed it suffered such degradation in a short time scale (typically less than 15 min) that it could not be observed experimentally.

It clearly appears that the [BmPyrro]$^+$ cation does not participate to the formation of any adducts and at most its role (if any) is in assisting the reactions indirectly. In contrast, the [Bmim]$^+$ cation plays the main role in the CO$_2$-[Bmim] [Ac]
The carbene issued from the H\(^+\) exchange between acetate and imidazolium cation reacts with CO\(_2\) to form the imidazolium carboxylate and acetic acid. In the CS\(_2\)-[Bmim] [Ac] system, both the anion and cation play a role. The current study suggests that the thioacetate anion, CO\(_2\), and OCS have been produced by the reaction between CS\(_2\) with the acetate anions. It is only after these reactions have proceeded that the nascent CO\(_2\) and OCS will cooperatively interact with the [Bmim] [Ac] ion pair to produce the imidazolium-carboxylate and imidazolium-thiocarboxylate. This scenario also applies to the OCS-[Bmim] [Ac]. It remains to understand why the presence of imidazolium-dithiocarboxylate was not observed in CS\(_2\)-[Bmim] [Ac].

For that purpose, DFT-calculations were carried out to evaluate from the Potential Energy Surface the values of the energy barrier and of the reaction energy associated with the insertion of the molecules OCS, CS\(_2\) (thio- and dithiocarboxylation), and CO\(_2\) (carboxylation) on the imidazolium ring. It is shown that the insertion of the triatomic molecule is started from specific configurations with respect to the pair imidazolium cation-acetate anion and after the release of the acidic proton of the imidazolium ring (the predicted reactive pathways are further discussed elsewhere\(^{37}\)). From these "pre-reactive" structures (p-R Str1) (Fig. 11), the capture phenomenon by the imidazolium 2-ylidene carbene species is mainly governed by the electro-reduction of the solute (OCS, CS\(_2\), CO\(_2\)). The later process is revealed by the appearance of a bending of the triatomic molecule along the calculated reactive pathways (cf. activated complex at the transition state TS2 in Fig. 11). The comparison of the calculated pathways

![Predicted structures associated with the stationary points along the capture process of the triatomic molecule by the imidazolium 2-ylidene carbene species (last step of the reactive mechanism of the carboxylation and thio- and dithiocarboxylation) calculated, respectively, for the systems (CO\(_2\), OCS, and CS\(_2\)) + the ion pair (IP) at the UB3LYP/6-31+(d,p):MQZVP(S) level.](image)
allows us determining a well-defined hierarchy between these three systems. From the calculated pathways obtained for the systems (CO₂, OCS, CS₂) + IP, we can estimate the energy barriers associated with the carboxylation, thiocarboxylation, and dithiocarboxylation reactions at values about 15, 21, and 27 kcal mol⁻¹, respectively (Fig. 12 and Ref. 47). The reaction energies are evaluated at about −8.8, −5.4, and −10.4 kcal mol⁻¹, respectively.

These calculations show that the energetic barrier values of the reaction between the cation and the solute molecules follow a hierarchy (CO₂ < OCS < CS₂) indicating that the formation of [Bmim] CO₂ is favoured compared to that of [Bmim] COS and [Bmim] CS₂. Moreover, the magnitude of the energetic barriers for the thio- and dithiocarboxylation reactions indicates why the anion can offer a competitive reactive channel. This inference is supported by two facts. The first one concerns the fact that the dithiocarboxylate is not observed in the CS₂ - [Bmim] [Ac] system. The second one is supported by the observation of adducts resulting from the solute-anion reaction.

The existence of a sulfur-oxygen (S-O) exchange mechanism between the molecule CS₂ and acetate appears as an alternative to the reaction involving the “transient” formation of the imidazolium-2-ylidene carbene-acetic acid pair. To rationalize this assertion, we have determined by DFT-calculations a three-step pathway associated with the S-O exchange between CS₂ and acetate. Thus, the degradation of the CS₂ needs to cross a first barrier to lead to a first intermediate (Int1.2) species (Fig. 13) under anionic form [CH₃COO-CS₂] (energy barrier about 18.5 kcal/mol) (Fig. 14). This reaction is followed by the so-called S-O exchange mechanism to form the second intermediate anionic species [CH₃COS-OCS] (Int2.2) (Figs. 13 and 14). This second step involves the highest energy barrier (22.7 kcal/mol). The last step is related to the dissociation of this intermediate species to product the two stable adduct issues from this degradation mechanism, the thioacetate anion, and OCS. Of course, the existence of the S-O exchange mechanism introduces a set of possible competitive reactions from these adducts.

The complete predicted reactive scheme leads to a set of coupled reactions more or less probable according to the values of the energy barriers and reaction energy taking place in both imidazolium and pyrrolidinium-acetate based IL which will appear in a companion paper.47

FIG. 12. Energy diagrams associated with carboxylation (CO₂), thiocarboxylation (OCS), and dithio carboxylation (CS₂) reactive mechanisms (including the proton transfer, first step). For each system the reference energy is that of the global energy minimum structure 1 (Str.1) calculated for the systems (CO₂, OCS, and CS₂) + ion pair (IP) at the UB3LYP/6-31+(d,p):MQZVP(S) level. The “pre-reactive” structures (p-R Str.1, shown in Figure 11) correspond with the calculated configurations of the solute (with respect to the imidazolium-2-ylidene carbene-acetic acid pair) triggering its selective insertion on the imidazolium ring. The calculated energy values associated with the stationary points transition states (TS), intermediate structures (Int), and final structures of the adducts (Prd1) along the reactive pathways are given in kcal/mol.

FIG. 13. Predicted structures associated with S-O exchange mechanism between CS₂ and acetate calculated for the system CS₂ + ion pair (IP) (Structure 2), intermediate structures (Int), and final structures with the adducts (Prd2) calculated at the UB3LYP/6-31+(d,p):MQZVP(S) level.
IV. CONCLUSION

This study shows that the acetate anions in 1-butyl-1-methylpyridinium acetate play an important role in conditioning chemical reactions with CS₂ leading, via coupled complex reactions, to the degradation of this molecule to form thioacetate anion ((CH₃)₂CO⁻), CO₂, OCS, and triothiocarbonate (CS₃²⁻). Because, the cation does not lead to the formation of any adducts, we conclude that it can play only an indirect role in assisting these reactions. These results should be contrasted with the CO₂-[Bmim][Ac] system in which the formation of carboxylic acid and acetic acid is almost driven by the cation.

The current study suggests that in the solutions of CS₂ in [Bmim][Ac], the thioacetate anion, CO₂, and OCS species have been produced by the reaction between CS₂ with the acetate anions. It is only after these reactions have proceeded that the CO₂ and OCS just formed will cooperatively interact with the [Bmim][Ac] ion pair to produce the imidazolium-carboxylate and imidazolium-thiocarboxylate. This scenario also applies to OCS in [Bmim][Ac]. Finally, the choice of the [BmPyrr]+ cation in this study allowed to somewhat disen- tangle the role of the anion and the cation simplifying the rationalisation of the chemical reactions in these three systems. These findings have motivated a theoretical investigation aimed at determining the complete reactive scheme taking place in both imidazolium and pyridinium-activated IL solutions with CO₂ and its iso-electronic molecules.

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