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On the reactivity and stability of electrogenerated N-heterocyclic carbene in parent 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate: Formation and use of N-heterocyclic carbene-CO_2 adduct as latent catalyst

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ABSTRACT

A simple electrolysis (under galvanostatic conditions) of the room temperature ionic liquid 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate, BMIm-BF_4, yields, after bubbling CO_2 into the catholyte, the adduct NHC-CO_2. The considerable stability of this NHC-CO_2 adduct, at room temperature, in the parent ionic liquid as solvent, has been compared with the one of free NHC in the same BMIm-BF_4. The BMIm-BF_4 solution containing NHC-CO_2 adduct, suitably triggered (US irradiation or 120 °C), is able to release free NHC. The NHC-CO_2 adduct usefulness has been demonstrated using it as efficient latent catalyst, in BMIm-BF_4 as solvent, in the benzoin condensation and in the oxidative esterification of cinnamaldehyde with benzyl alcohol.

1. Introduction

The synthesis of efficient catalysts and/or the set up of latent catalysts (i.e. of systems, stable at room temperature and able, suitably triggered, to release the catalyst) [1,2] may be regarded as a significant target in modern organic chemistry.

Since the pioneering investigations of the last century [3–7], N-heterocyclic carbenes (NHCs) have been frequently utilized as ligands in organometallic catalysis [8–10] and as organocatalysts [11–17,9] in organic synthesis. Owing to the ability of NHCs to induce the inversion of the polarity (umpolung) in the structure of aldehydes, considerable results have been achieved in NHC catalyzed procedures of carbon-carbon bond formation via generation of NHC-aldehyde adduct (Breslow intermediate): benzoin condensation, Stetter reaction, 1,2-addition reactions, etc. [11–13].

At present, considerable investigations are carried out to synthesize further, more efficient NHCs, as well as to identify new and more intriguing applications [18–23]. The structure of a NHC strongly affects its efficiency as organocatalyst in a peculiar reaction; moreover solvent and temperature could play a remarkable role. Hypothesis of possible correlations have been reported by different authors [24–26].

Although some NHCs have been synthesized and isolated [6,7,27,28], as a general rule NHCs (air and moisture sensitive) are notably unstable even at room temperature and any hypothesis of storage of NHCs can be ruled out. Therefore, in the NHCs catalyzed syntheses, the generation in situ of the catalyst is often required. On this subject, NHCs can be obtained from suitable pre-catalysts (i.e. the parent azolium salts: imidazolium, thiazolium, oxazolium, etc.) in organic solvents, in the presence of proper bases or reducing agents (Scheme 1, reactions 1 and 2). Nevertheless, the use of bases and reducing agents could be inconsistent with acidic substrates or substrates containing reducible functional groups. To circumvent this difficulty, as well as to avoid the utilization of volatile and toxic organic solvents, NHCs have been obtained by us via cathodic reduction of imidazolium room temperature ionic liquids (RTILs) in the absence of organic solvents, bases, etc. (Scheme 1, reaction 3). The double role of solvent and pre-catalyst of the imidazolium ionic liquids has been frequently emphasized [29–37].

As an alternative route, the possible set up of systems able to catch and release NHCs has been investigated [38,39]. Intriguing results have been obtained studying the reactivity of NHCs versus carbon dioxide. NHC-CO_2 adducts (imidazolium carboxylate, stable at room temperature) have been obtained, in organic solvents,

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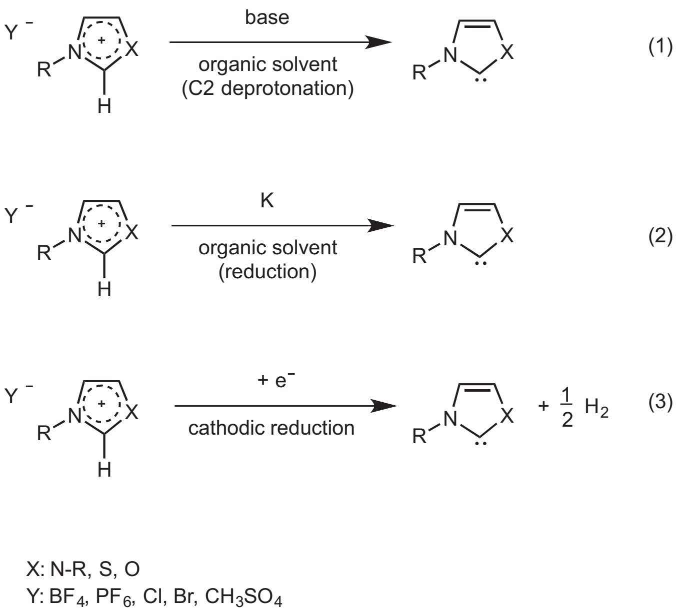


Scheme 1. Chemical and electrochemical generation of N-heterocyclic carbenes.

by simple bubbling CO_2 in a solution containing imidazolium salt and a suitable base (i.e. containing NHCs). NHC-CO_2 adducts have been isolated as white solids, stable at room temperature, and able, heated at proper temperature, to release NHCs and carbon dioxide (Scheme 2).

Therefore, carbon dioxide is able to catch NHC, at room temperature, yielding a stable NHC-CO_2 adduct, and to release NHC if heated at higher temperature.

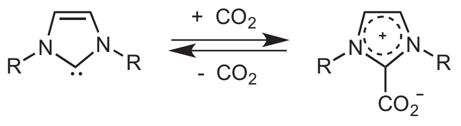
The NHC-CO_2 adducts could be regarded as “latent pre-catalysts”. The stability of the adduct and the release-temperature, extensively investigated via thermogravimetric analysis (TGA), are strongly affected by the structure of the NHC and, for the NHC-CO_2/organic solvent solutions, by the nature of the solvent [38,39].

Recently, syntheses of cyclic carbonates, via reaction of carbon dioxide (2.0–4.5 M Pa) and epoxides or propargylic alcohol, have been reported [40–42]. The syntheses have been carried out in the presence of NHC-CO_2 adducts and the role of the adduct versus the one of free NHC as catalyst has been discussed [43]. The utilization of imidazolium hydrogen carbonate versus imidazolium carboxylate as organic precatalysts for NHC catalyzed reactions carried out in organic solvents has been performed [44]. Last, the formation of dialkyl carbonate from carbon dioxide and alcohols, in the presence of electrogenerated NHC has been hypothesized [45].

Spurred from these results, as a continuation of our previous investigations concerning the use, as catalysts, of electrogenerated NHCs in the parent ionic liquid, we have studied the reactivity of CO_2 in a pre-electrolyzed 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate BMIm-BF_4 (i.e. RTIL 1a containing NHC 1b; Scheme 3, reaction 1).

Aim of this investigation was:

- to prove the actual formation of the NHC-CO_2 adduct by simple bubbling of CO_2 in pre-electrolyzed BMIm-BF_4 (chosen as model pre-catalyst as the most extensively utilized RTIL in organic synthesis) and to control the stability of this adduct in RTIL compared to the one of the free NHC (i.e. 1-butyl-3-methylimidazol-2-ylidene) in RTIL;
- to verify the possible utilization of a CO_2-saturated electrolyzed BMIm-BF_4 solution as a system able to catch electrogenerated NHC (as stable, at room temperature, NHC-CO_2 adduct) and to release free NHC when heated at a suitable temperature, in the absence of any base and organic solvent (Scheme 3, reaction 2);
- to ascertain the possible utilization of NHC-CO_2 adduct as a latent catalyst in NHC catalyzed reactions (e.g. the benzoin condensation – Scheme 3, reaction 3-and the oxidative esterification of cinnamaldehyde – Scheme 3, reaction 4).



Scheme 2. Catch and release of carbon dioxide by N-heterocyclic carbenes.

The behavior of this electrogenerated system has been studied by cyclic voltammetry, thermogravimetry and chemical reactivity, using the NHC both as reagent and as catalyst.

2. Experimental

2.1. Starting material

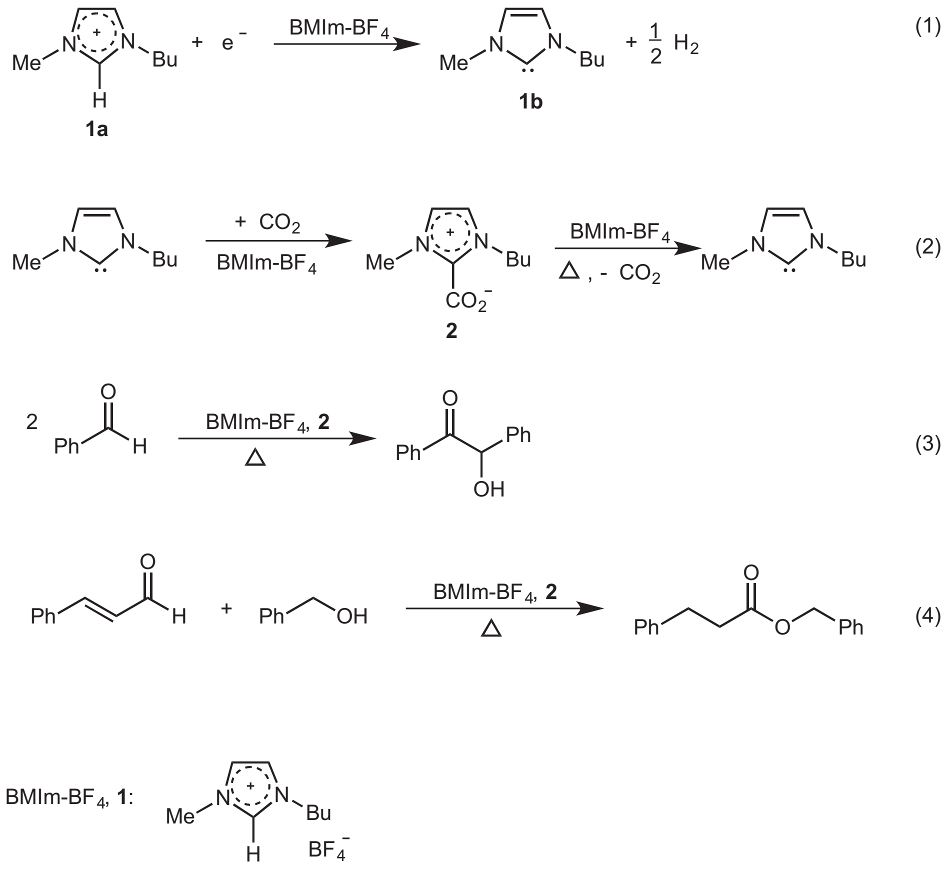
Ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (IoLiTec) was commercially available and used as pure compound (impurities reported: water < 0.02%, chloride < 100 mg/kg), after being kept at reduced pressure at 70 °C for 24 h. Sulfur, cinnamaldehyde and benzyl alcohol (Aldrich) were commercially available and used as received. Benzaldehyde (Aldrich) was commercially available and used after distillation.

2.2. Instrumentation

^1H and ^{13}C NMR spectra were recorded using a Bruker AC 200 spectrometer using $CDCl_3$ as internal standard. Voltammetric measurements were performed with an Amel 552 potentiostat equipped with an Amel 566 function generator and an Amel 563 multipurpose unit in a three-electrode cell; the curves were displayed on an Amel 863 recorder. A 492/GC/3 Amel microelectrode was employed, using a Pt counter electrode and an Ag quasi reference electrode (q.r.e.), $\nu = 0.2\ V\ s^{-1}$. Electrolyses under galvanostatic control were carried out (using an Amel 552 potentiostat equipped with an Amel 771 integrator) in a two compartment home-made glass cell. The anolyte and catholyte (1.0 and 2.0 ml, respectively) were separated by a glass disk (porosity 3). The electrode surface areas (flat Pt spirals, 99.9%) were ca 1.0 cm^2 for the cathode and 0.8 cm^2 for the anode. The cell was kept at 60 °C, if not otherwise specified. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum-One spectrophotometer equipped with an ATR detector, band frequencies are given in wave number (cm^{-1}). Thermogravimetry (TG) experiments were carried out at a heating rate of 10 K min^{-1} on a Stanton-Redcroft 625 simultaneous apparatus at flow rate of 50 ml min^{-1} using open cylindrical aluminum crucibles with a cross sectional area of $2.0 \times 10^{-5}\ m^2$.

2.3. Electrochemical synthesis of NHC and NHC-CO_2 in BMIm-BF_4

A galvanostatic electrolysis was carried out on BMIm-BF_4 (catholyte: 2 ml; anolyte: 1 ml) under N_2 atmosphere at 60 °C. The current density was 20 mA cm^{-2}. After 97 C, the current was switched off, the anodic compartment removed and the catholyte kept as it was (obtaining the NHC-BMIm-BF_4 solution) or CO_2 was bubbled into the catholyte for 15 min (obtaining the NHC-CO_2-BMIm-BF_4 solution). The two solutions were kept at room temperature under air for the time reported in Table 1 or used immediately after their preparation (Tables 2 and 3).



Scheme 3. Electrochemical generation of NHC-CO_2 adduct and its use as latent catalyst.

Table 1

Reactivity of elemental sulfur with BMIm-BF_4 solutions containing 1b (sample *A*) or 2 (sample *B*), freshly prepared or used after the time interval Δt^*.[a]

Sample[b]	Δt^*/day[c]	Products (yields, %)[d]	
		Imidazole-2-thione	Imidazole-2-one
A	0[e]	99	–
B	0	99	–
A	1	89	11
B	1	98	–
A	2	56	10
B	2	95	–
A	3	28	12
B	3	87	–
A	4	11	12
B	4	71	–
A	7	3	11
B	7	28	9

[a] Galvanostatic reduction of BMIm-BF_4 (97 C), CO_2 bubbling in the catholyte (15 min), then, under open air and moisture conditions, 0.5 mmol of S_8 were added and the catholyte sonicated for 10 min.

[b] Sample *A*: electrolyzed BMIm-BF_4; sample *B*: electrolyzed BMIm-BF_4, subsequently saturated with CO_2.

[c] Days passed between the preparation of samples *A* and *B* and their use in this synthesis (see Section 2).

[d] Yields of isolated products, based on starting sulfur.

[e] This result is identical to the one obtained by us in the published paper [51].

Table 2

Reactivity of benzaldehyde with 2-BMIm-BF_4 solutions under different activation temperatures: benzoin condensation.[a]

Release conditions[b]	Benzoin (yields, %)[c]
T = 60 °C	–
T = 100 °C	49
T = 120 °C	75
T = 65 °C, literature[d]	85
T = 100 °C, literature[d]	72
US irradiation	63
US irradiation, literature[d]	80

[a] Galvanostatic reduction of BMIm-BF_4 (193 C), CO_2 bubbling in the catholyte (15 min), then, under open air and moisture conditions, 10 mmol of benzaldehyde were added and the catholyte kept at the indicated temperature for 1 h.

[b] Temperature at which the catholyte was kept for 1 h after the addition of benzaldehyde; in the case of ultrasound irradiation, the catholyte was irradiated for 30 min at 22.5 kHz, 4 W.

[c] Yields of isolated products, based on starting benzaldehyde.

[d] Yields taken from our published work [33].

Table 3

Reactivity of cinnamaldehyde and benzyl alcohol with adduct 2-BMIm-BF_4 solutions under two different activation conditions: oxidative esterification reaction.[a]

Release conditions	Ester (yields, %)[b]
T = 120 °C, 0.7 F/mol	65
T = 60 °C, 0.7 F/mol, literature[c]	91

[a] Galvanostatic reduction of BMIm-BF_4 (70 C, 0.7 F/mol aldehyde), CO_2 bubbling in the catholyte (15 min), then, under open air and moisture conditions, 1 mmol of cinnamaldehyde and 3 mmol of benzyl alcohol were added and the catholyte kept at the indicated temperature for 1 h.

[b] Yields of isolated benzyl hydrocinnamate, based on starting cinnamaldehyde.

[c] Yields taken from our published work [31].

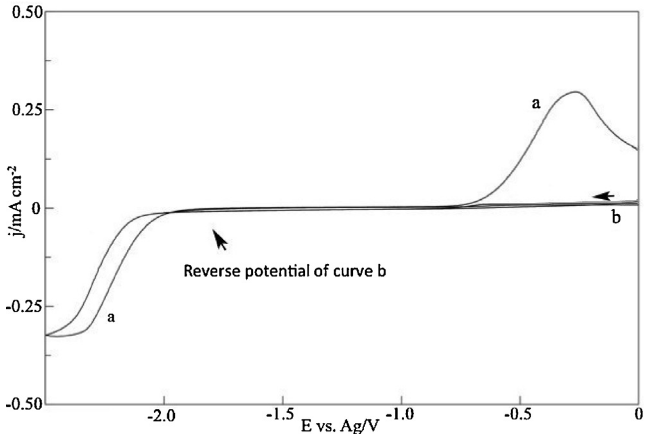


Fig. 1. Cyclic voltammetric curves of BMIm-BF$_4$ (vitreous carbon cathode, $\nu = 0.2\,V\,s^{-1}$, Ag as pseudoreference electrode, $T = 60\,°C$). Scanning reversed at $E = -2.5\,V$ (curve a) or $E = -1.8\,V$ (curve b). At $E < -2.0\,V$, the current reaches the upper limit of the instrument.

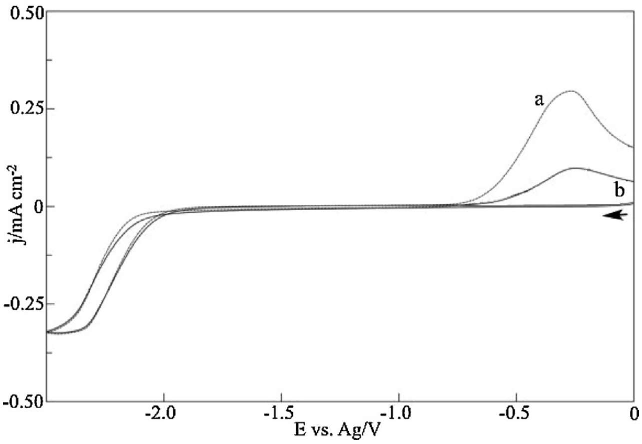


Fig. 2. Cyclic voltammetric curves (vitreous carbon cathode, $\nu = 0.2\,V\,s^{-1}$, Ag as pseudoreference electrode, $T = 60\,°C$) of BMIm-BF$_4$ (curve a) and of BMIm-BF$_4$ after 15 min CO$_2$ bubbling (curve b). At $E < -2.0\,V$, the current reaches the upper limit of the instrument.

2.4. *Synthesis of 1-butyl-3-methylimidazole-2-thione*

The NHC-BMIm-BF$_4$ or NHC-CO$_2$-BMIm-BF$_4$ solution was added to 0.5 mmol of elemental sulfur and the mixture subjected to ultrasound irradiation (4 W) for 10 min. Then usual workup [49] gave the product in the yields reported in Table 1.

2.5. *Benzoin condensation*

The NHC-CO$_2$-BMIm-BF$_4$ solution was added to 5.0 mmol of freshly distilled benzaldehyde. The solution was kept for 2 h under stirring at 60 °C (or 100 °C or 120 °C). Otherwise the mixture subjected to ultrasound irradiation (22.5 kHz, 4 W) for 30 min. Then usual workup [33,36] gave the product in the yields reported in Table 2.

2.6. *Oxidative esterification of cinnamaldehyde*

The NHC-CO$_2$-BMIm-BF$_4$ solution (after the consumption of 70 C) was added to 1.0 mmol of cinnamaldehyde and 3.0 mmol of benzyl alcohol. The solution was kept for 1 h under stirring at 120 °C. Then usual workup [31] gave the product in the yields reported in Table 3.

3. Results and discussion

3.1. *Voltammetric behavior of BMIm-BF$_4$: the role of CO$_2$ and of temperature*

The voltammetric curves recorded at a glassy carbon cathode for BMIm-BF$_4$ under N$_2$ bubbling ($\nu = 0.2\,V\,s^{-1}$, potential window from 0.0 V to −2.5 V, Ag pseudo reference electrode [46,47], 60 °C) show a rapid increase in the cathodic current ($E_{red.} \leq -2.1\,V$) and an oxidation peak ($Ep_{ox.} = -0.3\,V$) related to the reduction of the BMIm$^+$ cation 1a to NHC 1b (Scheme 3, reaction 1) and to the oxidation of 1b (electrogenerated at Ep_{red}) [48], respectively. This hypothesis is confirmed by the fact that if the scanning is reversed at a less negative potential than −2.1 V, the oxidation peak $Ep_{ox.}$ disappears (Fig. 1).

The voltammetric curve of CO$_2$-saturated BMIm-BF$_4$ shows a value of the current of the oxidation peak ($ip^*_{ox.}$) significantly smaller than the one ($ip_{ox.}$) in the absence of CO$_2$ (Fig. 2).

These results suggest that the reaction of electrogenerated 1b versus carbon dioxide in the parent ionic liquid can be operative as well as in organic solvents, yielding the electroinactive adduct NHC-CO$_2$ 2 (Scheme 3, reaction 2). The stability of the NHC-CO$_2$ adducts, i.e. their ability to relase free NHC and CO$_2$, is strongly affected by the temperature as well as by the structure of the NHC and by the solvent (as previously reported) [38,39].

To inquire the stability, in the parent BMIm-BF$_4$, of the adduct 2 with the temperature, we have compared the voltammetric curves of BMIm-BF$_4$ (at different temperatures) with those of CO$_2$ –saturated BMIm-BF$_4$.

In Fig. 3 the voltammetric curves for CO$_2$ saturated BMIm-BF$_4$ solutions, recorded at different temperatures (60–120 °C) have been reported. The $ip^*_{ox.}$ current increases on increasing of the temperature. At $T > 120\,°C$, the values of $ip^*_{ox.}$ and $ip_{ox.}$ (not in Fig. 3) are equal. As the decrease of $ip^*_{ox.}$ (with respect to $ip_{ox.}$) is related to the formation of the electroinactive adduct 2, the catch of CO$_2$ by electrogenerated 1b in BMIm-BF$_4$ is reversible and the adduct is able to relase completely free NHC and CO$_2$ at $T > 120\,°C$ (Scheme 3, reaction 2).

3.2. *Analysis of electrolyzed BMIm-BF$_4$ and of CO$_2$-saturated electrolyzed BMIm-BF$_4$*

To prove the initial hypothesis (i.e. the formation of the adduct 2), IR spectra have been recorded for a sample of BMIm-BF$_4$

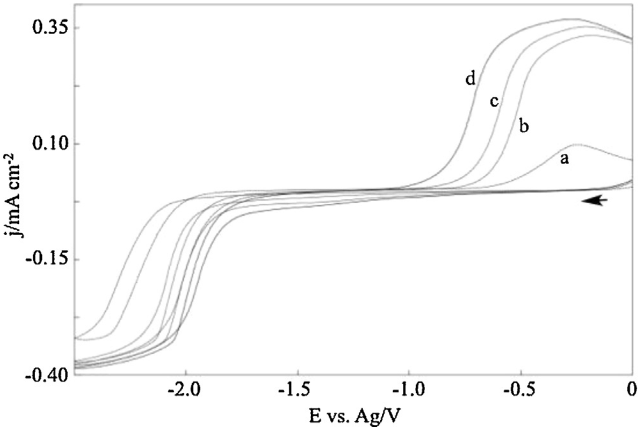


Fig. 3. Cyclic voltammetric curves (vitreous carbon cathode, $\nu = 0.2\,V\,s^{-1}$, Ag as pseudoreference electrode,) of BMIm-BF$_4$ after 15 min CO$_2$ bubbling. Curve a: $T = 60\,°C$; curve b: $T = 80\,°C$; curve c: $T = 100\,°C$; curve d: $T = 120\,°C$. At $E < -2.0\,V$, the current reaches the upper limit of the instrument.

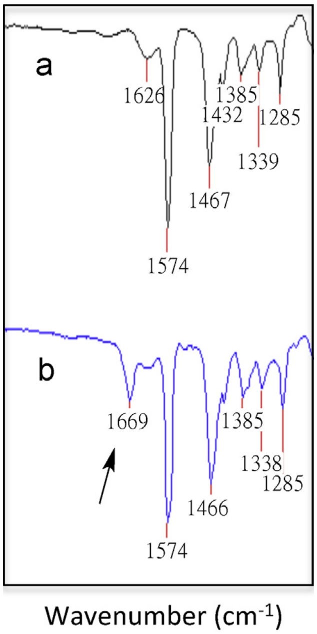


Fig. 4. IR spectra of BMIm-BF$_4$ (curve a) and of electrolyzed BMIm-BF$_4$ and subsequently saturated with CO$_2$ (curve b).

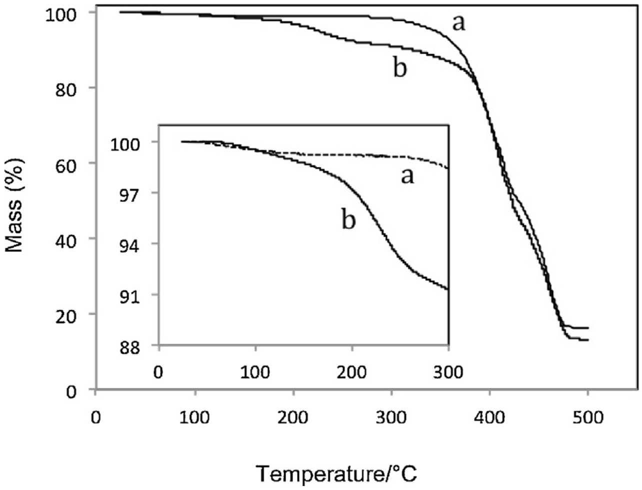


Fig. 5. TGA of BMIm-BF$_4$ (curve a) and of electrolyzed BMIm-BF$_4$ and subsequently saturated with CO$_2$ (curve b). Heating rate: 10 K min^{-1}.

electrolyzed and subsequently bubbled with CO$_2$ for 15 min and compared with the one of BMIm-BF$_4$. The first sample displays the distinct carbonyl stretching frequency of adduct 2, $\nu = 1669\ \text{cm}^{-1}$, absent in BMIm-BF$_4$ (Fig. 4) [38].

In addition, electrolyzed BMIm-BF$_4$ solution subsequently saturated with CO$_2$ (containing the adduct 2) and pure BMIm-BF$_4$ were monitored via thermogravimetric analysis (TGA) (Fig. 5). Starting from about 120 °C the electrolyzed sample begins to decompose in several steps, the first of which is ascribable to the evolution of CO$_2$, similarly to what it was found for other imidazolinium-2-carboxylate derivatives [49,50].

3.3. *Reactivity of electrolyzed BMIm-BF$_4$ and of CO$_2$-saturated electrolyzed BMIm-BF$_4$*

The effective reactivity and stability of this particular NHC-CO$_2$ adduct in BMIm-BF$_4$ can be demonstrated using it as latent catalyst, which releases NHC upon thermal or ultrasound activation; the released NHC can be used as reagent or as catalyst in classical chemical reactions.

Recently, we have reported that the reaction of NHCs, electrogenerated via electrolysis of the parent 1,3-dialkylimidazolium ionic liquid, with elemental sulfur under ultrasound irradiation yields 1,3-dialkylimidazole-2-thiones in very high yields (Scheme 4) [51].

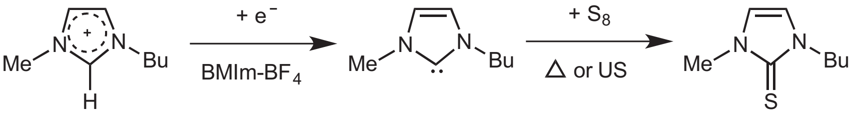
According, to realize a comparison between the stability of adduct 2 and free carbene 1b (both in BMIm-BF$_4$), we have investigated the reactivity of sulfur with an electrolyzed BMIm-BF$_4$ solution (containing 1b, sample *A*) and with an electrolyzed BMIm-BF$_4$ solution subsequently saturated with CO$_2$ (containing the adduct 2, sample *B*).

The two solutions were prepared and used after prefixed intervals of time (Δt^*); to them S$_8$ was added and the mixture was subjected to ultrasound irradiation. Usual workup gave the corresponding imidazole-2-thione. The yields of isolated thione are strongly affected by the nature of the initial solution (thus containing 1b or 2) and by the time interval Δt^* between the preparation of the solution and its use (Table 1), thus reflecting the stability of the reagent in the parent ionic liquid.

From both the solutions (samples *A* and *B*) the corresponding imidazole-2-thione was obtained. Nevertheless, the yield of thione isolated from sample *A* fast decreased on increasing Δt^*, according to a significant instability of 1b in the parent ionic liquid at room temperature (isolated imidazole-2-thione: 11%, $\Delta t^* = 4$ days; 3%, $\Delta t^* = 7$ days). On the contrary, the decrease with Δt^* of thione isolated from the sample *B* is slow, according to a considerable stability of the adduct 2 in the parent ionic liquid at room temperature.

The adduct is able (conveniently trigged) to release 1b with elevated yields (71% of isolated imidazole-2-thione, $\Delta t^* = 4$ days). As the two solutions were stored without any precaution to preserve them by air and moisture (in order to demonstrate the ability of the ionic liquid solvent to protect the reagent because of its high viscosity), imidazole-2-one was isolated in addition to the formation of imidazole-2-thione in some cases, due to the reaction of free carbene with oxygen [51]. This is the demonstration that no free carbene is present in the sample with the adduct (no imidazole-2-one formation within the first four days), confirming the stability of 2 in BMIm-BF$_4$. These results show that it is possible to produce a 1b-BMIm-BF$_4$ solution and protect the carbene under the adduct 2 form, in order to use it in a later time, without loss of reactivity for the first 2–3 days (period in which the 1b-BMIm-BF$_4$ solutions lose more than half of their reactivity).

In order to study the reactivity of 1b released from adduct 2 (in BMIm-BF$_4$) as organocatalyst, we have synthesized the adduct in ionic liquid and let it react with benzaldehyde in the benzoin reaction (Scheme 3, reaction 3). The yields in benzoin rely on the procedure of release of the catalyst (Table 2), indicating again that



Scheme 4. Electrogeneration and reaction of N-heterocyclic carbene with elemental sulfur.

for the optimal release, a temperature of 100 °C or higher is necessary, as a confirmation of the findings of TGA results (see Fig. 5).

The yields in benzoin (not optimized) are comparable to those obtained in a previous work using a BMIm-BF_4 solution of free carbene, indicating a good yield in the release of 1b from adduct 2 [33,36].

To confirm the ability of 2 to behave as latent organocatalyst, we have used it in the oxidative esterification of cinnamaldehyde with benzyl alcohol, reaction in which benzyl hydrocinnamic ester is formed via umpolung of the aldehyde and internal reduction of the double bond catalyzed by 1b (Scheme 3, reaction 4) [31]. The results are reported in Table 3.

The not optimized yield, reported in this paper (electrogenerated NHC-CO_2 adduct as latent catalyst), is smaller than the one reported by us in a previous work (*free* electrogenerated NHC as catalyst; 65% versus 91%) [31]. Nevertheless, this last result suggests a possible general utilization of electrogenerated NHC-CO_2 adduct as latent catalyst in the NHC-catalyzed organic reactions (it should be noted, however, that the literature yields are relative to reactions carried out at 60 °C, while the yield of this paper – first line of Table 3 – is for a reaction carried out at 120 °C, so the yields are not strictly comparable).

4. Conclusions

The stability of electrogenerated N-heterocyclic carbene in the parent ionic liquid BMIm-BF_4 (studied by cyclic voltammetry) can be enhanced by reaction with carbon dioxide to form an NHC-CO_2 adduct. In this way a latent catalyst is obtained, able to re-produce NHC upon thermal or ultrasonic stimulation. The production of NHC from the adduct has been confirmed by reaction with elemental sulfur to yield the corresponding imidazole-2-thione. A comparison between the behavior of an adduct-containing BMIm-BF_4 and an NHC-containing BMIm-BF_4 has been carried out, both of freshly prepared and of aged (days) solutions and the higher stability of the adduct solution confirmed. This latent catalyst has been employed in two exemplifying organocatalyzed reactions, the benzoin condensation and the oxidative esterification of cinnamaldehyde with benzyl alcohol, showing the ability of the re-generated NHC to efficiently catalyze these reactions.

Supplementary materials

Supplementary materials are available with the on-line version only.

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