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Special Issue

Cathodic Behaviour of Dicationic Imidazolium Bromides: The Role of the Spacer

Daniele Rocco,[a] Isabella Chiarotto,[a] Francesca D'Anna,[b] Leonardo Mattiello,[a] Fabiana Pandolfi,[a] Carla Rizzo,[b] and Marta Feroci*[a]

The cathodic reduction of dicationic imidazolium bromides, whose spacer is either an aliphatic chain or a xylyl group, leads to the formation of the corresponding N-heterocyclic carbenes (NHCs), which were isolated as the corresponding thiones, after reaction with elemental sulfur. The behaviour of the dications was compared with the corresponding monocations. The behaviour of dicarbenes depends on the nature of the spacer. This study evidenced that dicarbenes deriving from xylyl dications are less stable than the corresponding aliphatic ones (giving lower yields in thiones), due to a debenzylation reaction. On the other hand, the yields in thiones starting from aliphatic dications are higher than the corresponding monocations, suggesting a cooperative reduction at the electrode of the two imidazolium moieties. The cathodic process was confirmed using the co-electrogenerated hydrogen to reduce 2,2,2-trifluoroacetophenone to the corresponding alcohol.

1. Introduction

Ionic liquids, salts formed by organic or inorganic anions and large organic cations very slightly, or not coordinated at all,[1] are usually liquid at (or near) room temperature. They have gained large popularity during the last two decades, due to their many interesting properties, which render them attractive reagents and solvents: a very low vapour pressure (they are not air pollutant), which frequently facilitates their recycling, the possibility to modulate their properties almost at will by varying the structure of anion and cation, good thermal and electrical conductivity, and so on. Among ionic liquids, imidazolium derivatives belong to the most studied class of such compounds, also because they are easily synthesized, often cheap and they have many application fields, from solvents in synthesis, to reagents, to electrolytes in electrochemistry, etc.[2]

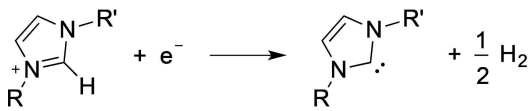
More recently, dicationic imidazolium ionic liquids (DILs) were examined in a natural evolution in the modulation of the structure of imidazolium ionic liquids (ILs). DILs are formed by two positively charged imidazolium groups, kept together (usually at nitrogen atoms) by a spacer of variable length and structure (aliphatic, xylyl, aromatic).[3] The main advantage in using DILs instead of the corresponding ILs lies in the possibility of further modulating their properties varying the nature of the spacer.[4]

In fact, imidazolium DILs have been successfully used as electrolytes in dye sensitized solar cells (DSSCs),[5] as efficient replacements of organic phase-change materials (the heat capacity of DILs is noteworthy higher than that of the corresponding monocations),[6,7] as solvents for the controlled pyrolysis of cellulose,[8] as templates for the synthesis of ZnO nanostructures in water,[9,10] as surfactants (due to a better capacity of aggregation with respect to monocationic analogues),[11] as efficient extractors of phenolic compounds from oil mixtures[12] or of triazole fungicides from contaminated water,[13] etc.

One of the main objections to considering imidazolium ionic liquids as "green" reagents is their possible toxicity.[14–16] Recent studies have reported that imidazolium DILs show an increase in biocompatibility and cytocompatibility,[17] demonstrating that DILs are less toxic than the corresponding imidazolium ILs, as the introduction of a second charged part renders the DIL more hydrophilic and thus less toxic, although their biodegradability remains low.[18]

During the last ten years we have studied the electrochemical characteristics of imidazolium ionic liquids. Our main interest in imidazolium ionic liquids is their use in electroorganic synthesis, as solvents and precursors of N-heterocyclic carbenes (NHCs). In fact, the monoelectronic electrochemical reduction of an imidazolium cation leads to the formation of the corresponding NHC (Scheme 1),[19–25] which can behave as a base and/or as a nucleophile depending on the reaction partner.[26–27]

NHCs are among the most popular organocatalysts,[28–29] mainly when an aldehyde is involved. In fact, the reaction of a



Scheme 1. Electrochemical generation of NHC.

[a] Dr. D. Rocco, Prof. I. Chiarotto, Prof. L. Mattiello, Dr. F. Pandolfi, Prof. M. Feroci
Department Scienze di Base e Applicate per l'Ingegneria (SBAI)
Sapienza University of Rome
via Castro Laurenziano, 7, 00161, Roma, Italy
E-mail: marta.feroci@uniroma1.it
[b] Prof. F. D'Anna, Dr. C. Rizzo
Università degli Studi di Palermo
Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche
Viale delle Scienze, Ed. 17, 90128, Palermo, Italy

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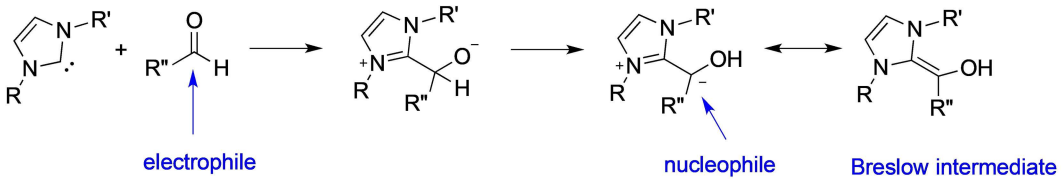


Scheme 2. Umpolung of the aldehyde carbonyl carbon atom. Formation of the Breslow intermediate.

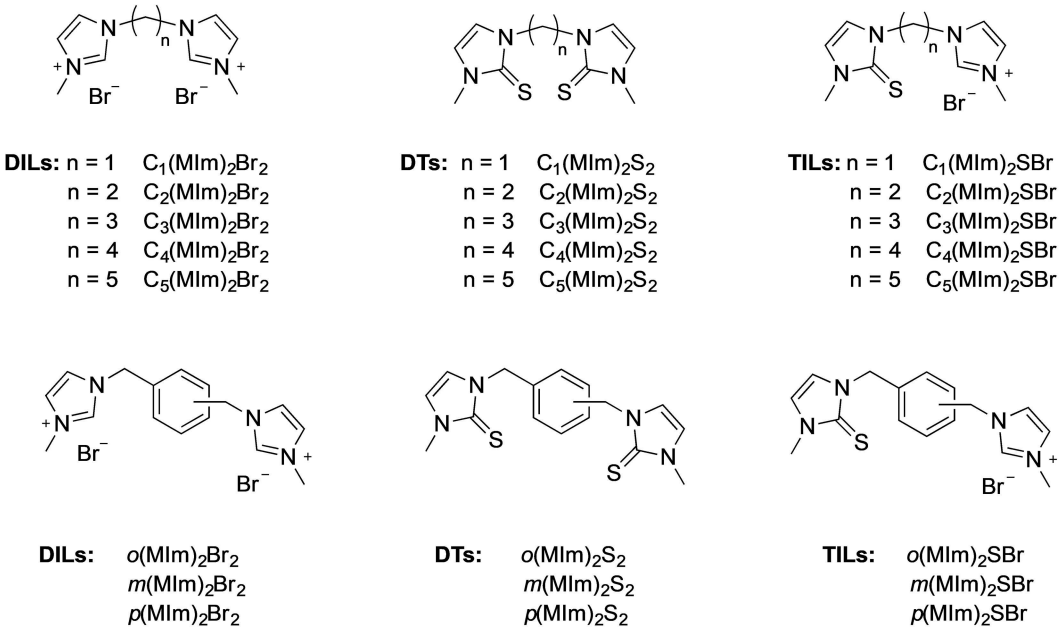


Figure 1. Reagents (DILs) and products (DTs and TILs) for this work.

suitable NHC with an aldehyde can lead to the formation of the "Breslow intermediate",[30] in which the carbonyl carbon atom undergoes an "umpolung", a polarity reversal from electrophilic to nucleophilic character (Scheme 2).

This organocatalytic strategy was successfully applied to many organic reactions, including for example the benzoin condensation,[31–33] esterification and amidation of benzaldehydes and cinnamaldehydes,[34–41] synthesis of γ-butyrolactones,[42–43] synthesis of 1,3-diketones,[44] etc..

With the advent of DILs, the possibility to obtain, by deprotonation with strong bases, dicarbene species was exploited, mainly oriented to the synthesis of complexes.[45–48] Very few papers concern the use of dicarbenes in organocatalysis.[49]

Scope of this work was to study the possibility to obtain dicarbenes starting from DILs, by cathodic reduction, and to carry out a comparison with the electrochemical behaviour of the corresponding imidazolium salts.

2. Results and Discussion

Figure 1 illustrates the structures of the imidazolium bromides (DILs) studied in this paper. In particular, two classes of DILs were analysed: the first class contains two 3-methylimidazolium cations separated (at 1-position) by a linear alkyl chain, in the second the two 3-methylimidazolium cations are separated (at 1-position) by a xylyl group (*ortho*, *meta* or *para*).

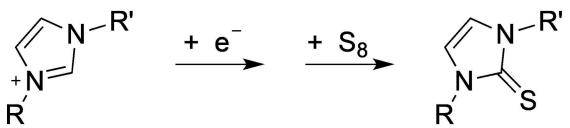
Cyclic voltammetric curves of imidazolium ionic liquids, pure or in DMF, show the presence of one cathodic peak, which corresponds to the monoelectronic cleavage of the C–H bond in 2-position, with the formation of the corresponding carbene (NHC) and molecular hydrogen (Scheme 1). The cathodically formed NHC is then oxidised at a potential near 0 V on the return scan. The peak potential depends on the structure of the imidazolium cation and of the anion. As a useful comparison, we carried out the voltammetric study also on two monocationic ILs, 1-butyl-3-methylimidazolium bromide (BMImBr, to be compared with the electrochemical behaviour of DILs with an aliphatic spacer) and 1-benzyl-3-methylimidazolium bromide (BzMImBr, to be compared with the electrochemical behaviour of DILs with a xylyl spacer). The peak potentials corresponding to their cathodic reduction are reported in Table 1.

The same voltammetric analysis was carried out with DILs (Table 1), but in this case the anodic peak current (in the return scan) was very low or even absent. Nonetheless, the cathodic behaviour of DILs was very similar to the one of the corresponding ILs, rendering the cyclic voltammetry of DILs difficult to explain. In fact, the cathodic peak potentials of DILs in which the spacer is a xylyl group are comparable to the one

Table 1. First reduction peak potentials for DILs and ILs (by voltammetric analysis)[a] and thione current yield after cathodic reduction and subsequent reaction with elemental sulfur.[b]

DIL	E_{pred}	Thione[c]	DT/TIL[d]	IL[e]	E_{pred}	Thione[c]
$C_1(MIm)_2Br_2$	−1.84 V	13%	nd	BMImBr	−2.58 V	29%
$C_2(MIm)_2Br_2$	−2.17 V	<5%	nd			
$C_3(MIm)_2Br_2$	−2.30 V	47%	67/33			
$C_4(MIm)_2Br_2$	−2.68 V	43%	62/48			
$C_5(MIm)_2Br_2$	−2.70 V	44%	63/37			
$o(MIm)_2Br_2$	−2.26 V	16%	nd	BzMImBr	−2.37 V	38%
$m(MIm)_2Br_2$	−2.32 V	30%	57/44			
$p(MIm)_2Br_2$	−2.28 V	31%	62/38			

[a] DMF-0.1 mol L^{-1} Et_4NBF_4, rT, N_2 atmosphere, GC electrode, SCE reference electrode, $[DIL]=2.5\cdot10^{-3}$ mol L^{-1}, $[IL]=5.0\cdot10^{-3}$ mol L^{-1}. Voltammetric curves in Supporting Information. [b] DMF (5 mL) solution of DIL (0.25 mmol) or IL (0.50 mmol), divided cell, rT, N_2 atmosphere, Pt electrodes, mSCE reference electrode, galvanostatic conditions ($I=15$ mA cm^{-2}), electrolysis stopped after 31 C. Then S_8 added (0.13 mmol) to the catholyte and sonicated (22.5 kHertz) for 5 min. [c] Current yields in thione were calculated from the ^{1}H-NMR spectrum of the crude catholyte (after solvent elimination under vacuum), considering the single imidazolium group transformation (1 F/mol imidazolium group, 31 C: 0.32 mmol thione group, for 100% current yield). [d] Mole ratio between dithione and monothione-monoimidazolium, in case it was possible to obtain it from the ^{1}H-NMR or ^{13}C-NMR spectrum of the crude catholyte. [e] 1-Butyl-3-methylimidazolium bromide (BMImBr) and 1-benzyl-3-methylimidazolium bromide (BzMImBr) were taken as reference monoimidazolium salts.



Scheme 3. Electrochemically generated NHC transformation into the corresponding thione by reaction with elemental sulfur.

of BzMImBr (−2.26 ÷ −2.32 V vs −2.37 V, Table 1), while those of DILs with an aliphatic spacer strongly depend on the spacer length (Table 1).

In order to better understand the voltammetric behaviour of DILs, with particular reference to the very low peak current or absence of NHC anodic oxidation, we carried out the cathodic reduction of DILs in DMF, followed by the addition of sulfur, which is reported to react with NHC and give the corresponding imidazole-2-thione (Scheme 3).[50–51] We fixed the amount of charge (31 C) in order to compare the behaviour of different DILs, with no intention of carrying out the synthesis of imidazole-dithiones, but only to take advantage of this reaction to quantify, if possible, electrogenerated NHCs. The results are reported in Table 1.

DILs contain two identical imidazolium cation groups, so it is possible that the cathodic reduction leads to the formation of two varieties of carbenes: a dicarbene, formed by the cathodic reduction of both the imidazolium groups of DIL (leading to the corresponding dithione), and a monocarbene-monoimidazolium bromide, derived from the cathodic reduction of only one of the two imidazolium groups of DIL (leading to the corresponding monothione-monoimidazolium bromide). In order to understand which thione products were obtained from the cathodic reduction of DILs and subsequent reaction with elemental sulfur, we synthesized (following literature methods) both dithiones (DTs) and monothione-monoimidazolium bromides (TILs). Then we compared the NMR signals of the crude catholyte with the signals of synthesized products (DTs are neutral molecules and can be extracted from the crude reaction with a suitable solvent, but TILs are charged and it is really difficult to separate them from the charged DILs). The results are reported in Table 1.

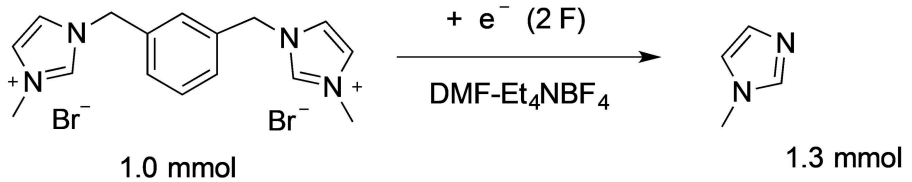
A rapid comparison between the efficiency of thione formation for ILs and DILs (Table 1) shows that xylyl DILs yielded lower amounts of thione than the corresponding monocationic BzMImBr, while the opposite behaviour was obtained with DILs with a linear aliphatic spacer >C2, for which the yields in thione were higher than the corresponding monocation BMImBr.

In order to understand the low thione yields obtained from DILs with a xylyl spacer, we carried out a complete reduction of $m(MIm)_2Br_2$ (in this case in the presence of the supporting electrolyte Et_4NBF_4, as the scope of the electrolysis was the total consumption of the DIL). At the end of the electrolysis (2 F), starting from 1.0 mmol of $m(MIm)_2Br_2$, 1.3 mmol of methylimidazole were obtained, demonstrating the formation of an electrogenerated diNHC and its decomposition (Scheme 4).

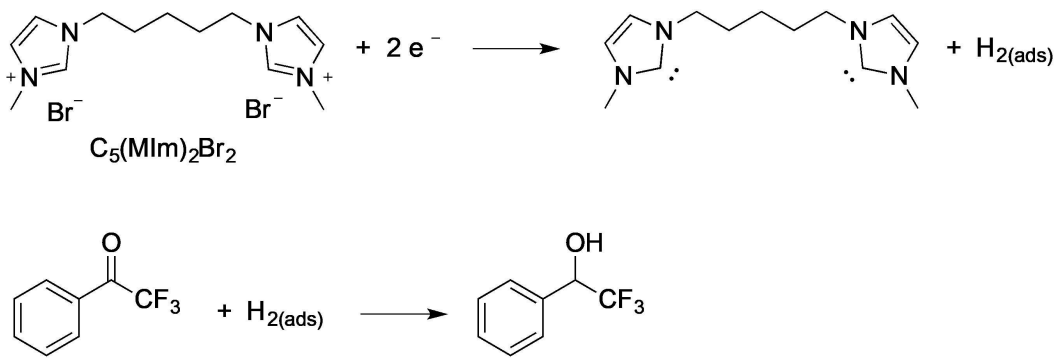
The instability of electrogenerated carbene could account for the low current yield in the synthesis of the corresponding thione after addition of elemental sulfur.

In contrast, thione yields from the electroreduction of aliphatic DILs are higher than those obtained from the monocations, indicating a higher efficiency in the electrogeneration of NHC from the corresponding dication. Moreover, the amount of dithione is often higher than the amount of monothione-monocation (Table 1). From these results it can be suggested that the electroreduction of an imidazolium cation favours the electroreduction of the other cation of the same molecule, in what could be defined a cooperative effect (probably simply due to the proximity to the electrode of the second imidazolium moiety when the first is being reduced).

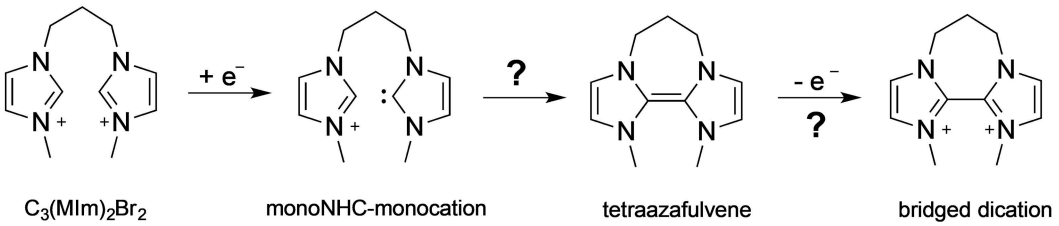
The same effect is probably active with xylyl DILs, but their tendency to debenzylation lowers the final yield in thione.



Scheme 4. Complete electrochemical reduction of $m(MIm)_2Br_2$.



Scheme 5. Reduction of trifluoroacetophenone by electrochemically generated molecular hydrogen during the reduction of the imidazolium cation. For simplicity, the cathodic reduction product is indicated as di-NHC, not excluding the formation of monothione-monocation.



Scheme 6. Possible formation of tetraazafulvene and its subsequent oxidation, after electrochemical reduction of $C_3(MIm)_2Br_2$.

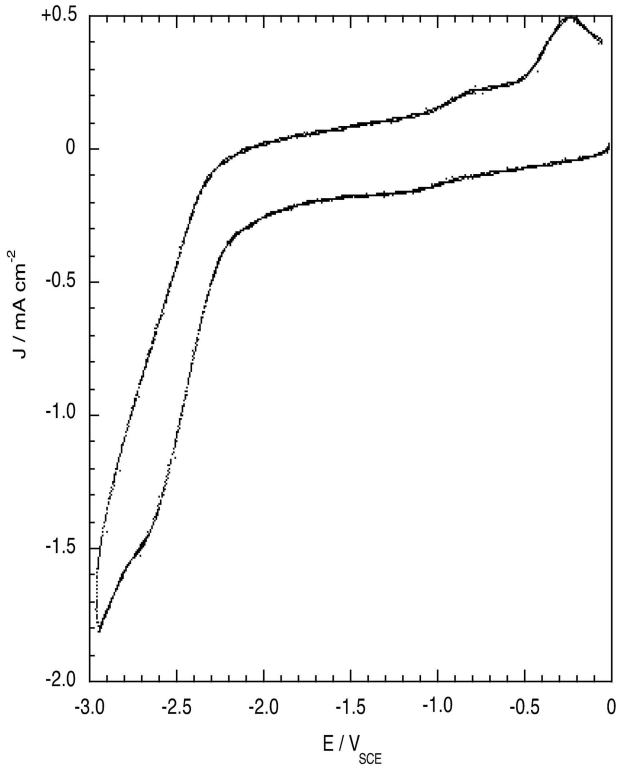


Figure 2. Cyclic voltammetry of a DMF-0.1 M Et_4NBF_4 solution of $C_3(MIm)_2Br_2$ after reduction at −2.3 V (2 F) and subsequent oxidation at +0.5 V (0.15 F). GC working electrode, SCE reference electrode, room temperature, nitrogen atmosphere. Scan rate: 200 mV s^{-1}. Potential scan: 0 to −3.0 to 0 V.

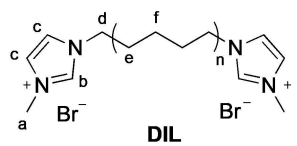
In order to confirm that the cathodic process is the reductive scission of the C–H bond in the 2-position of the imidazolium cation (yielding molecular hydrogen), we carried out the cathodic reduction of $C_5(MIm)_2Br_2$ (or of $BMImBr_2$) and we added 2,2,2-trifluoroacetophenone to the catholyte (in which the platinum cathode was present) after current flow interruption. After 2 h at 60 °C, the corresponding alcohol was isolated in 22% (or 19%) current yield (Scheme 5). If the same experiment was carried out adding the ketone to the catholyte in the absence of the platinum cathode, only starting material was recovered in quantitative yield.

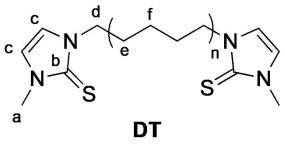
These experiments confirm the presence of hydrogen (adsorbed on the electrode) in the catholyte when the platinum electrode is present, but not when it is absent.

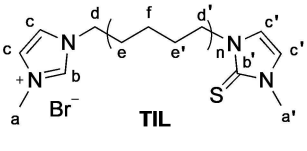
We were interested in determining if, under our electrochemical conditions, it was possible to obtain tetraazafulvene dimers of the di-NHCs derived from our DILs. In fact, the literature reports this possibility,[52–56] also if it is somehow controversial (Scheme 6). In fact, while Thummel and coworkers [55] were not able to obtain tetraazafulvene by chemical deprotonation of an imidazolium DIL, Murphy and coworkers[52] reported a chemical deprotonation of imidazolium DIL in liquid ammonia to the corresponding tetraazafulvene. In particular, in order to check for the formation of highly unstable tetraazafulvene, we looked for its oxidation product at the electrode, the bridged dication, whose reduction potential is reported to be about −1.3 V in DMF.

Toward this end, we examined cyclic voltammograms between −2.5 V (potential at which NHC should form) and +0.5 V (potential at which NHC or its dimer tetraazafulvene should be oxidised). In any cases we could not see a reduction

Table 2. NMR data for aliphatic DILs, DTs and TILs.

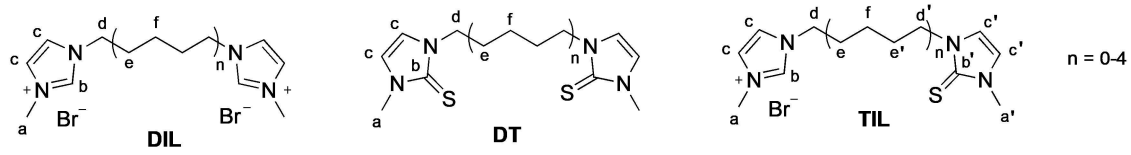




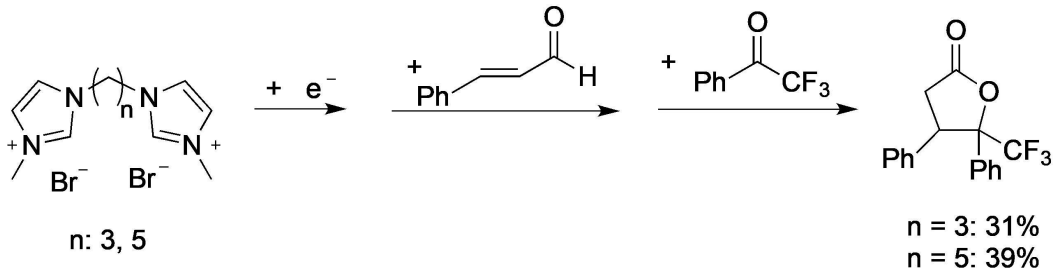


	a	b	c	d	e	f	f′	e′	d′	c′	b′	a′
^{1}H-NMR for DILs (CD_3SOCD_3)												
$C_1(MIm)_2Br_2$	3.90	9.43	8.00 7.80	6.69								
$C_2(MIm)_2Br_2$	3.85	9.14	7.74 7.66	4.71								
$C_3(MIm)_2Br_2$	3.87	9.31	7.85 7.76	4.27	2.41							
$C_4(MIm)_2Br_2$	3.85	9.12	7.78 7.73	4.22	1.77							
$C_5(MIm)_2Br_2$	3.86	9.24	7.82 7.73	4.19	1.83	1.22						
^{13}C-NMR for DILs (CD_3SOCD_3)												
$C_1(MIm)_2Br_2$	36.2	138.0	124.2 121.9	57.8								
$C_2(MIm)_2Br_2$	36.4	137.6	124.3 122.8	48.8								
$C_3(MIm)_2Br_2$	35.8	136.8	123.6 122.1	45.6	29.5							
$C_4(MIm)_2Br_2$	35.8	136.6	123.7 122.2	47.9	26.0							
$C_5(MIm)_2Br_2$	36.6	136.8	124.4 123.0	49.5	29.4	22.8						
^{1}H-NMR for DTs ($CDCl_3$)												
$C_1(MIm)_2S_2$	3.58		7.61 6.61	6.32								
$C_2(MIm)_2S_2$	3.58		6.60 6.56	4.46								
$C_3(MIm)_2S_2$	3.61		6.92 6.69	4.11	2.32							
$C_4(MIm)_2S_2$	3.62		6.80 6.68	4.11	1.83							
$C_5(MIm)_2S_2$	3.61		6.72 6.69	4.04	1.85	1.39						
^{13}C-NMR for DTs ($CDCl_3$)												
$C_1(MIm)_2S_2$	35.1	163.7	118.6 117.7	56.1								
$C_2(MIm)_2S_2$	35.1	162.2	117.7 117.7	45.5								
$C_3(MIm)_2S_2$	35.1	162.2	117.8 116.9	45.1	28.1							
$C_4(MIm)_2S_2$	35.1	162.2	117.8 116.9	47.1	25.8							
$C_5(MIm)_2S_2$	35.1	162.0	117.7 116.7	47.5	28.2	23.1						
^{1}H-NMR for TILs (CD_3OD)												
$C_1(MIm)_2SBr$	4.01	9.39	7.92 7.61	6.44						7.41 7.11		3.65
$C_2(MIm)_2SBr$	not obtained[65]											
$C_3(MIm)_2SBr$	3.96	9.08	7.73 7.61	4.33	2.44			2.25	4.16	7.16 7.07		3.60
$C_4(MIm)_2SBr$	3.93	8.99	7.67 7.59	4.31	2.08			1.85	4.11	7.08 7.05		3.57
$C_5(MIm)_2SBr$	3.98	9.06	7.71 7.63	4.28	2.20	1.27	1.32	1.98	4.03	7.08 7.07		3.57
^{13}C-NMR for TILs (CD_3OD)												
$C_1(MIm)_2SBr$	35.6	137.3	123.9 121.8	57.7						117.6 116.8	161.4	34.1

Table 2. continued



	a	b	c	d	e	f	f′	e′	d′	c′	b′	a′
$C_2(MIm)_2SBr$	not obtained[65]											
$C_3(MIm)_2SBr$	35.7	136.9	123.5 122.1	46.4	28.9			28.2	46.2	118.8 117.1	161.1	35.3
$C_4(MIm)_2SBr$	35.2	136.6	123.6 122.2	46.3	26.4			25.2	46.3	118.5 117.2	159.8	35.1
$C_5(MIm)_2SBr$	35.4	136.6	123.6 122.3	47.0	29.1	22.5	22.7	28.0	46.7	118.3 117.3	160.6	35.4



Scheme 7. Synthesis of γ-butyrolactone by organocatalysis of electrogenerated NHC.

peak at −1.3 V, corresponding to the bridged dication reduction potential. Unfortunately this result is not conclusive, confirming only the absence of the bridged cation but not excluding the formation of tetraazafulvene in our experimental voltammetric conditions.

In order to have insights on the possible formation of tetraazafulvene by cathodic deprotonation of an imidazolium DIL, we carried out the cathodic reduction of $C_3(MIm)_2Br_2$ (2 F) in DMF-Et_4NBF_4 and at the end of the electrolysis we carried out the cyclic voltammetry, which showed an oxidation peak, most probably due to electrogenerated NHC. Then, we carried out a subsequent oxidation at 0.0 V; in this second electrolysis the amount of electricity flown through the cell was low (0.15 F), indicating a minimum amount of residual carbene. At the end of electrolysis we registered a cyclic voltammetry (Figure 2) in which no evident reduction peak at about −1.3 V was visible.

Due to the absence of peak current, we cannot assert the presence of the bridged dication (whose reduction potential is about −1.3 V), but its presence in solution cannot be excluded.

Finally, we checked the possibility to use electrogenerated di- or monocarbenes as organocatalysts in a classical organocatalysed reaction, the synthesis of γ-butyrolactone starting from cinnamaldehyde and 2,2,2-trifluoroacetophenone[57] (Scheme 7). The reaction was not optimized, but γ-butyrolactone was obtained starting from $C_3(MIm)_2Br_2$ or $C_5(MIm)_2Br_2$ in 31% and 39% yield, respectively, indicating the organocatalytic behaviour of these electrochemically reduced dication.

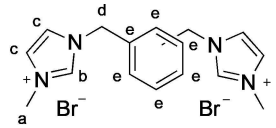
3. Conclusions

Imidazolium dicationic ionic liquids are a recent evolution of more common and classical monocationic imidazolium salts, one of the most studied class of ionic liquids. The advantage in using such dicationic salts resides in the possibility of further modulation of the chemical and physical properties of these salts with the variation of the spacer between the two imidazolium heads. This paper reports the study of the electrochemical behaviour of dicationic imidazolium bromides, whose spacer is either an alkyl chain or a xylyl group. We have demonstrated that the cathodic reduction of these species leads to the formation of the corresponding N-heterocyclic carbenes, which were evidenced after transformation into the corresponding thiones. The current efficiency of thione formation is higher for dications with an aliphatic spacer, with respect to the corresponding monocations, indicating that the reduction of an imidazolium head facilitates the reduction of the other (probably by proximity to the electrode). Moreover, the presence of a xylyl spacer enhances the instability of the corresponding dicarbene, leading to a benzylic elimination of both imidazole rings.

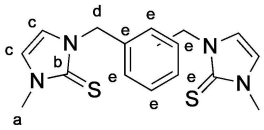
The cathodic process (formation of NHC and dihydrogen) was confirmed using electrogenerated dihydrogen as reductant of 2,2,2-trifluoroacetophenone, yielding the corresponding alcohol.

The possibility to use electrogenerated diNHCs as organocatalysts was demonstrated carrying out the synthesis of γ-butyrolactone, a classical reaction catalysed by NHC.

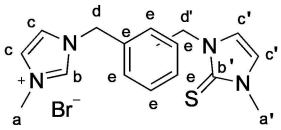
Table 3. NMR data for xylyl DILs, DTs and TILs.



DIL



DT



TIL

1H-NMR for DILs (CD_3SOCD_3)	a	b	c	xylyl	d	d′	c′	b′	a′
o(MIm)$_2$Br$_2$	3.88	9.26	7.48 7.32	7.79–7.78	5.68				
m(MIm)$_2$Br$_2$	3.87	9.25	7.78 7.75	7.54–7.38	5.44				
p(MIm)$_2$Br$_2$	3.85	9.27	7.79 7.72	7.48	5.44				
^{13}C-NMR for DILs (CD_3SOCD_3)									
o(MIm)$_2$Br$_2$	36.2	136.9	123.9 122.5	132.9;129.7;129.6	49.0				
m(MIm)$_2$Br$_2$	36.4	136.8	124.0 122.3	135.6;129.7;128.6;128.3	51.5				
p(MIm)$_2$Br$_2$	36.6	136.7	124.1 122.3	135.5;129.8	51.3				
^{1}H-NMR for DTs ($CDCl_3$)									
o(MIm)$_2$S$_2$	3.66		6.72 6.61	7.33–7.15	5.29				
m(MIm)$_2$S$_2$	3.66		6.69 6.61	7.27	5.25				
p(MIm)$_2$S$_2$	3.65		6.67 6.57	7.29–7.27	5.24				
^{13}C-NMR for DTs ($CDCl_3$)									
o(MIm)$_2$S$_2$	35.3	162.9	118.2 116.6	133.9;129.4;128.7	48.8				
m(MIm)$_2$S$_2$	35.3	162.9	118.1 116.4	136.5;129.4;127.8;127.9	51.0				
p(MIm)$_2$S$_2$	35.3	162.9	118.0 116.4	135.8;128.6	50.9				
^{1}H-NMR for TILs (CD_3OD)									
o(MIm)$_2$SBr	3.96	9.03		7.67–7.51	5.42	5.28	7.06 6.98		3.59
m(MIm)$_2$SBr	3.88	8.77		7.63–7.28	5.59	5.31	7.01 6.85		3.54
p(MIm)$_2$SBr	3.93	9.02		7.65–7.52	5.41	5.29	7.04 6.97		3.60
^{13}C-NMR for TILs (CD_3OD)									
o(MIm)$_2$SBr	35.5	136.2	123.6 122.0	135.5;134.3;131.2;129.1;128.5; 128.1	50.3	49.9	119.0 117.1	161.2	34.2
m(MIm)$_2$SBr	35.5	135.8	125.3 123.6	139.2;135.8;129.3;129.2;128.6; 128.4	51.5	51.4	120.2 118.6	162.7	35.5
p(MIm)$_2$SBr	35.8	133.7	124.0 122.3	133.7;128.9;128.6;128.0	49.9	49.0	118.8 117.2	161.6	34.2

Experimental Section

Materials

DILs and reference DTs and TILs were synthesized following literature methods.[58–59] Their spectral data (Tables 2 and 3) were in accordance with those reported in the literature.[60] BMImBr and BzMImCl were purchased from Iolitec and used after being kept at reduced pressure at 70 °C for 24 h. BzMImBr was obtained from BzMImCl using an ion exchange resin (Amberlite® IRA-400 chloride form) pre-treated with NaBr.[61] The resulting white solid was kept at reduced pressure at 70 °C for 24 h.

Voltammetric Measurements

Voltammetric measurements were performed using 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; acquisition software was a CorrWare for windows version 2.8d1 Scribner, elaboration

software was a CorrView for windows version 2.8d1 Scribner. A 492/GC/3 Amel microelectrode was employed, using a Pt wire counter electrode and a modified saturated calomel electrode (mSCE) as reference electrode. The oxidation peak potential, on GC electrode, of ferrocene in DMF-0.1 M Et_4NBF_4 with modified saturated calomel electrode reference electrode is $E_{oxFc} = +0.516$ V. The scan rate was $\nu = 0.2\ V\,s^{-1}$. All cyclic voltammetries were recorded at room temperature on 5 mL of DMF-0.1 M Et_4NBF_4.

Electrolyses: Synthesis of Thiones

Constant current electrolyses ($I = 15\ mA\,cm^{-2}$) were performed under a nitrogen atmosphere, at room temperature, using an Amel Model 552 potentiostat equipped with an Amel Model 731 integrator. All the experiments were carried out in a divided glass cell separated through a porous glass plug filled up with a layer of gel (i.e., methyl cellulose 0.5% vol dissolved in DMF-Et_4NBF_4 1.0 $mol\,L^{-1}$); Pt spirals (apparent area 0.8 cm^2) were used as both cathode and anode. Catholyte: 5 mL of DMF containing 0.50 mmol of IL or 0.25 mmol of DIL. Anolyte: 2 mL of the same solvent of catholyte. After 31 C, the current flow was stopped, the electrodes removed and 0.13 mmol of S_8 was added to the catholyte, which was subsequently sonicated for 5 min (22.5 kHertz).[51] Usual workup and flash column chromatography (eluent: AcOEt to AcOEt/MeOH 9/1) yielded the corresponding products (DTs and TILs). The spectral data of DTs and TILs were identical to those of the same compounds purposely prepared in a chemical way following literature methods (see Table 2).[62]

Electrolyses: Reduction of 2,2,2-Trifluoroacetophenone

Constant current electrolyses ($I = 15\ mA\,cm^{-2}$) were performed under a nitrogen atmosphere, at room temperature, as previously described. Catholyte: 5 mL of DMF containing 1.0 mmol of BMImBr or 0.5 mmol of $C_5(MIm)_2Br_2$. Anolyte: 2 mL of the same solvent of catholyte. After 97 C, the current flow was stopped, the electrodes removed and 0.5 mmol of trifluoromethylacetophenone was added to the catholyte, which was subsequently heated at 60 °C for 2 h. After usual workup yielded only starting material in quantitative yield. When the same reaction was carried out leaving the platinum cathode into the solution, 2,2,2-trifluoro-1-phenylethan-1-ol was obtained in 19% and 22% current yields starting from BMImBr or $C_5(MIm)_2Br_2$ respectively. Alcohol spectral data were identical to those reported in the literature.[63]

Electrolyses: Synthesis of γ-Butyrolactone (4,5-Diphenyl-5-(trifluoromethyl)dihydrofuran-2(3*H*)-one).

Constant current electrolyses ($I = 15\ mA\,cm^{-2}$) were performed under a nitrogen atmosphere, at room temperature, as previously described. Catholyte: 5 mL of DMF containing 0.50 mmol of IL or 0.25 mmol of DIL. Anolyte: 2 mL of the same solvent of catholyte. After 31 C, the current flow was stopped, the electrodes removed and 0.60 mmol of cinnamaldehyde and 1.20 mmol of trifluoromethylacetophenone were added to the catholyte, which was subsequently heated at 60 °C for 2 h and then kept 12 h at room temperature. Usual workup yielded the corresponding γ-butyrolactone,[57,64] whose spectral data were identical to those reported in the literature.[43]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cathodic reduction · cyclic voltammetry · dicationic imidazolium bromide · imidazole-2-thione · ionic liquids

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