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STABILITY AND ORGANOCATALYTIC EFFICIENCY OF *N*-HETEROCYCLIC CARBENES ELECTROGENERATED IN ORGANIC SOLVENTS FROM IMIDAZOLIUM IONIC LIQUIDS



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ABSTRACT

The kinetic of degradation of 1-butyl-3-methylimidazole-2-ylidene (selected as model *N*-heterocyclic carbene - NHC), generated in organic solvents by cathodic reduction of the parent 1-butyl-3-methylimidazolium salts BMIm-X, was studied by a simple voltammetric analysis. The effect of NHC degradation rate on the efficiency of an organocatalyzed reaction (the synthesis of γ -butyrolactone from cinnamaldehyde and trifluoromethylacetophenone) was investigated. The nature of the solvent and of the anion X⁻ have a remarkable effect on the stability of the NHC, the bis(trifluoromethylsulfonyl) imide anion being the best for a long lasting carbene (while acetonitrile seems to be the worst solvent). The role of X⁻ has been related to a competition between NHC and X⁻, in the hydrogen bonding interaction with BMIm⁺. The higher the stabilization of NHC by hydrogen bond, the lower its degradation rate. These hydrogen bonding interactions, previously reported in pure BMIm-X, seem to be operative even in organic solvents containing BMIm-X at low concentrations (c < 0.1 mol L⁻¹). The effect of the nitrogen alkyl substituents on the degradation of NHC (and thus on its efficiency as organocatalyst) is also pointed out.

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1. Introduction

The urging need for removing or reducing any waste in chemical processes forces modern organic synthesis to seek for catalysts able to increase both the efficiency and the sustainability of the procedures [1–5].

N-Heterocyclic carbenes (NHCs), a new generation of organocatalysts, possess both these requirements and represent a significant alternative to organometallic catalysts as regards cost and environmental impact [6,7].

NHCs are cyclic carbenes bearing at least one α -amino substituent, frequently utilized as versatile ligands for transition metals [8–10] and more recently as catalysts in metal-free polymer synthesis [11]. In the last two decades NHCs have attracted considerable interest as powerful nucleophilic organocatalysts in molecular chemistry [12–17]. This attention is due to the versatility and high activity of NHCs to catalyze, under mild reaction

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conditions, several processes involving C–C, C–O and C–N bond formation: benzoin condensation, Stetter reaction, NHC-redox acylation, synthesis of oxygen and nitrogen containing heterocycles, etc. The ability of NHCs to activate aldehydes, via inversion of their polarity (umpolung), is an intriguing reaction extensively investigated.

Owed to their possible instability, NHCs are frequently generated in situ by deprotonation or reduction of suitable precursors (e.g., imidazolium, pyrazolium, thiazolium based salts) [18].

The efficiency of a catalyst is certainly affected by its affinity with the substrate and by its ability to trigger the substrate structure, but also by its lifetime if it is not a stable molecule. A significant decrease of the catalyst concentration during the reaction could indeed negatively affect its outcome.

Therefore the lifetime of a NHC in the reaction conditions should be regarded as a key-feature of organocatalysis and quantitative investigations on the kinetic of NHC degradation are of interest.

In a previous communication we reported an electrochemical methodology for the generation of NHCs and for the evaluation of their stability in the parent ionic liquid as solvent, emphasizing the possible influence of the anion on their lifetime [19].

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Fig. 1. 1-Butyl-3-methylimidazolium salts (BMIm-X) used in this investigation.



Scheme 1. Electrochemical reduction of BMIm⁺ 2 and oxidation of NHC 3.

Subsequently, the very extensive utilization of NHCs in catalyzed syntheses carried out in organic solvents spurred us to investigate the stability of NHCs in organic solvents, according to the assumption that the NHC lifetime might be affected also by the nature of the medium. 1-Butyl-3-methylimidazole-2-ylidene was chosen as reference NHC, owing to the availability of its BMIm-X salts (1-butyl-3-methylimidazolium salts, **1a-h**; Fig. 1).

NHC was generated by cathodic reduction of BMIm-X **1a-h** in organic solvent (DMF, MeCN, DME, DMSO). The concentration of free NHC was evaluated by simple voltammetric analysis, measuring the height of the NHC oxidation peak, as reported in our previous papers [19,20].

Aim of the present investigation was:

- i) to verify and quantify the dependence of the stability of 1butyl-3-methylimidazole-2-ylidene 3 (Scheme 1) on the nature of the solvent and of the anion of the parent imidazolium salt;
- ii) to ascertain the correlation between the NHC lifetime and its efficacy in a NHC catalyzed reaction (the synthesis of γ-butyrolactone, via NHC-catalyzed umpolung of cinnamaldehyde, was taken as reference reaction);
- iii) to obtain indications for a substantial choice of the proper solvent and anion for a NHC catalyzed reaction, in order to increase its efficiency.

2. Experimental

2.1. General Remarks

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 counter electrode and modified saturated calomel electrode as reference electrode. Electrolyses under galvanostatic control were carried out with an Amel 552 potentiostat equipped with an Amel 721 integrator. A two-compartment cell was used. The electrode apparent surface areas (flat Pt spirals, 99.9%) were ca 1.0 cm² for the cathode and 0.8 cm² for the anode. ¹H and ¹³C NMR spectra were recorded using a Bruker AC 200 spectrometer using CDCl₃ as internal standard.

MeCN was distilled twice from P_2O_5 and CaH_2 ; *N*,*N*-dimethylformamide (DMF) was distilled from activated alumina under reduced pressure; dimethylsulfoxide (DMSO) and 1,2dimethoxyethane (DME) were used without any further purification. 1-Methyl-3-octylimidazolium bis-(trifluormethylsulfonil) imide was obtained by anion metathesis from the corresponding chloride according to a previously reported procedure [21]. 1-Benzyl-3-methylimidazolium bis-(trifluoromethylsulfonil) imide and 1-benzyl-3-butylimidazolium bis-(trifluoromethylsulfonil) imide were synthesized according to the previously reported procedure [22]. All other ionic liquids were purchased from lolitec and used after being kept at reduced pressure at 70 °C for 24 h. All other reagents were purchased from Aldrich and used as received.

2.2. Cyclic voltammetries of ionic liquids 1a-h in organic solvents

Catholyte (0.10 mol L⁻¹ of ionic liquid **1a–h** in 5.0 mL of organic solvent) and anolyte (2.0 mL same solvent/electrolyte) were separated through a porous glass frit filled with methylcellulose in DMF-Et₄N-BF₄. The electrolysis was carried out, under N₂ atmosphere at 25 °C, at a constant current (J = 15 mA · cm⁻²). After the consumption of 31 C, the current was switched off, the anodic compartment removed and the catholyte analyzed by cyclic voltammetry at different time intervals from the end of the electrolysis.

2.3. Electrolyses of 1a in organic solvents followed by addition of cinnamaldehyde 4 and trifluoromethylacetophenone 5

Catholyte (1.0 mmol of BMIm-BF₄ **1a** in 3.0 mL of organic solvent) and anolyte (2.0 mL same solvent/electrolyte) were separated through a porous plug filled with methylcellulose in DMF-Et₄N-BF₄. The electrolysis was carried out, under N₂ atmosphere at 25 °C, at a constant current (J = 15 mA · cm⁻²). After the consumption of 31 C, the current was switched off. Cinnamaldehyde **4** (0.5 mmol) and trifluoromethylacetophenone **5** (1.5 mmol) were added to the catholyte immediately or after 40 minutes (in which the catholyte was kept under nitrogen at room temperature) and the mixture was stirred at 60 °C for 2 h and at r.t. for 12 h.

The solvent was evaporated under reduced pressure and the residue extracted with Et₂O (3×20 mL). The ethereal layers were combined, the solvent was removed and the crude reaction mixture analyzed by ¹H NMR. The mixture was purifed by flash chromatography, using *n*-hexane/ethyl acetate 95/5 as eluent to afford the pure 4,5-diphenyl-5-trifluoromethyl- γ -butyrolactone **6** in the yields reported in Table 1. γ -Butyrolactone **6** is a known compound and gave spectral data in accordance with those reported in the literature [23].

3. Results and Discussion

The voltammograms recorded for solutions of BMIm-X **1a-h** in organic solvents (DMF, MeCN, DME, DMSO) show a behavior

Table 1

Yields of γ -butyrolactone **6** from the reaction of electrogenerated NHC, cinnamaldehyde and trifluoromethylacetophenone in different solvents. Reaction carried out after 0 minutes (t=0 min) or 40 minutes (t=40 min) from the NHC generation.^a

| Entry | Solvent | 6 , yield (t=0 min) | 6 , yield (t = 40 min) |
|-------|---------|----------------------------|-------------------------------|
| 1 | DMF | 75% | 63% |
| 2 | DME | 59% | 21% |
| 3 | DMSO | 58% | 5% |
| 4 | MeCN | 15% | - |

^a1 mmol of BMIm-BF₄ in 3.0 mL of solvent was reduced on a Pt cathode (divided cell, r.t., N₂ atmosphere, $J = 15 \text{ mA} \cdot \text{cm}^2$, 31 C). At the end of the electrolysis or after 40 minutes from the end, 0.5 mmol of cinnamaldehyde and 1.5 mmol of trifluoromethylacetophenone were added to the catholyte and the solution kept at 60 °C for 2 h and then at r.t. for 12 h. Usual workup gave the corresponding γ -butyrolactone **6** (isolated yields) [23].

(Fig. 2) similar to the one of pure BMIm-X (previously reported [19,24]):

- i) an increase of the cathodic current at E < -2.0 V (vs SCE) due to the monoelectronic reduction of the imidazolium cation 2 to NHC 3 and hydrogen (Scheme 1, reaction 1);
- ii) an irreversible anodic peak, at E > -0.6 V, in the reversed anodic scanning due to the monoelectronic oxidation of NHC (generated during the cathodic scanning at E < -2.0 V) (Scheme 1, reaction 2) [25].

The structure of the cation and the anion of BMIm-X, as well as the presence and the nature of the organic solvent, might affect the values of the electrochemical parameters of the specific salt (the peak potential *Ep* and the peak current *ip*).

Electrolyses of BMIm-X **1a–h**, under galvanostatic conditions in a divided cell, yield the corresponding NHC **3** as product of the cathodic reduction of the imidazolium cation **2** (Scheme 1, reaction 1). Voltammograms recorded on the catholyte at the end of the electrolysis, show an anodic peak (scanning potential -1.0 to +0.1 V vs SCE) related to the oxidation of electrogenerated NHC. The value of the oxidation peak current increases on increasing the number n of Faradays consumed during the electrolysis, i.e. on increasing the concentration of **3** in the catholyte. Due to the proportionality between the peak current and the NHC concentration, it is possible to follow the decrease of the NHC concentration as a decrease in the corresponding oxidation peak current.

Since the lifetime of the NHC in solution could be affected by its initial concentration¹, the lifetime of the NHC generated from the ionic liquids **1a–h** in different solvents, DMF, MeCN, DMSO, and DME, was determined at an identical concentration of 0.10 mol L⁻¹, the ionic liquid playing also the role of supporting electrolyte.

Therefore, these solutions (5.0 mL) were electrolyzed under galvanostatic conditions in a divided cell (Pt catode and anode, $J = 15 \text{ mA} \cdot \text{cm}^{-2}$, $T = 25 \,^{\circ}\text{C}$). After the consumption of 31 coulombs, the current was switched off ².

We evaluated the kinetic of degradation of **3** in the different organic solvents recording the voltammetric curves on the catholyte at prefixed intervals of time t^n from the end of the



Fig. 2. Cyclic voltammetric curves of **1a** (0.10 mol L⁻¹) in DME (curve a), MeCN (curve b), DMF (curve c) and DMSO (curve d). Vitreous carbon cathode, $\nu = 0.2 \text{ V s}^{-1}$, T = 25 °C. Scanning potential +0.6 to -3.0 V (where the current reaches the upper limit of the instrument).

electrolysis by measuring the NHC oxidation peak current ip^{n}_{ox} (Fig. 3; apex n: increasing times from the end of electrolysis).

The behaviour of NHC **3** in different conditions (solvent, IL anion) can be compared by plotting ip_{ox}^n vs tⁿ. For a correct comparison, a plot of the normalized value ip_{ox}^n/ip_{ox}^0 vs tⁿ is reported, as the voltammetric peak current is dependent on the dielectric constant and the viscosity of the solvent (besides other factors) and therefore it is different in different solvents for the same NHC concentration.

3.1. Stability of 1-butyl-3-methylimidazole-2-ylidene 3 electrogenerated from $BMIm-BF_4$ 1a. The effect of the solvent

Taking **3** as model carbene, we studied the NHC degradation process in four classical solvents: acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1,2-dimethoxyethane (DME). Plots of ip^{n}_{ox} and ip^{n}_{ox}/ip^{0}_{ox} vs t^{n} are reported in Fig. 4.

The variation of ip^{n}_{ox} or ip^{n}_{ox}/ip^{0}_{ox} as function of time suggests that:

i) the nature of the organic solvent considerably affects the NHC degradation rate³ [28]. The values of the half-life time $(\tau_{1/2})$ for **3** in the various solvents indicate that the degradation of NHC in

¹ The assumption that the initial NHC concentration is the same in all the electrolyses is not strictly correct, as the rate of NHC disappearance depends on the solvent and the anion. This means that there could be a different NHC consumption during the electrolysis time, which would lead to a slightly different initial NHC concentration.

² Assuming a current yield r = 1 to the editorial staff: in this equation r must be the greek letter r, which I cannot find here the concentration of the electrogenerated NHC and of the BMIm+ cation in the cathodic solutions (not considering the NHC degradation during the electrolysis time) at the end of the electrolysis can be evaluated as: $[NHC]^0 = \frac{31 \cdot 10^2}{96500 \cdot 5} = 6 \cdot 4 \cdot 10^{-2} \text{molL}^{-1}$; $[BMIm^+]^0 = 1 \cdot 0 \cdot 10^{-1} - 6 \cdot 4 \cdot 10^{-2} = 3 \cdot 6 \cdot 10^{-2} \text{molL}^{-1}$

³ The high viscosity of DMSO and DME (respect to MeCN and DMF) could account for the low initial oxidation peak current in these solvents.



Fig. 3. Voltammetric curves of **1a** (0.10 mol L⁻¹) in DMF recorded on a vitreous carbon cathode ($\nu = 0.2 \text{ V s}^{-1}$, T = 25 °C), scanning potential -1.0 to +1.0 V. Curve a*: before the electrolysis; curve a°: immediately at the end of the electrolysis (31 C); curves a¹-a³: after 30, 50 and 73 minutes from the end of electrolysis.

MeCN ($\tau_{1/2}$ = 28') and in DMSO ($\tau_{1/2}$ = 24') is more significant than in DME ($\tau_{1/2}$ = 93') or in DMF ($\tau_{1/2}$ = 69'). The half-life of **3** was evaluated as the time required to halve the initial NHC oxidation peak current ip⁰_{ox} (recorded immediately after the end of the electrolyses, i.e. from ip⁰_{ox} to ipⁿ_{ox} = 0.5 ip⁰_{ox}). Among the properties of the solvents (dielectric constant, viscosity, polarity, etc.), polarity rather than viscosity seems to have a noteworthy effect on the lifetime of NHC; in fact, an increase in polarity leads to a decrease of $\tau_{1/2}^{4}$.

ii) degradation of NHC occurs irrespective of the nature of the solvent and, 200 minutes after the end of the electrolyses, the NHC concentration is negligible in the cathodic solutions.

In order to verify the results obtained from the voltammetric analysis, we carried out a classical NHC-catalyzed reaction, comparing the yields obtained using electrogenerated NHC immediately after its generation with those obtained using NHC after 40 minutes from its generation.

The synthesis of γ -butyrolactone **6** from cinnamaldehyde **4** and trifluoromethylacetophenone **5** (Scheme 2) was chosen as model reaction [23].

⁴ Values of viscosity and polarity $E_T(30)$ of the solvents are reported, together with the halflife time $_{1/2}$ of NHC **3** (this paper).

| Solvent | η•(mPa•s) | $\tau_{1/2}$ (min) | E _T (30) (kcal/mol) ^a |
|---------|------------------------|--------------------|---|
| DMSO | 1.948 ^[26] | 24 | 45.1 |
| DMF | 0.796 ^[26] | 69 | 43.8 |
| ACN | 0.361 ^[26] | 28 | 45.6 |
| DME | 0.4089 ^[27] | 93 | 35.8 |

 $^{a}\text{The}\ E_{T}(30)$ value for a solvent is simply defined as the transition energy of a dissolved betaine dye measured in kcal/mol [28].

The results are reported in Table 1. The yields of lactone **6** using **3** immediately after its generation are, as expected, higher than those obtained using **3** after 40 minutes, confirming the validity of the voltammetric results. Moreover, 1–3 hours (depending on the solvent) after the end of the electrolysis the catholytes are no more able to significantly support the catalytic synthesis of γ -butyrolactone from cinnamaldehyde (too low NHC concentration).

3.2. Stability of 1-butyl-3-methylimidazole-2-ylidene 3 electrogenerated from BMIm-X 1a-h. The effect of the anion

In order to assess the influence of the BMIm-X anion on the stability of NHC **3** in organic solvents, we studied the NHC degradation process in DMF, electrogenerating the carbene from different BMIm-X salts. Plots of ip^{n}_{ox} and ip^{n}_{ox}/ip^{0}_{ox} vs t^{n} are reported in Fig. 5.

The data show that the NHC degradation rate is strongly dependent on the nature of the anion which surrounds the carbene in solution (being the cation identical for all salts).

The curves allow to determine the values of NHC half-life time $\tau_{1/2}$ in DMF in the presence of different anions X⁻ and of the cation BMIm⁺ (Table 2).

As it can be derived from Fig. 5 and Table 2, the stabilizing action of the anion $N(SO_2CF_3)_2^-$ (as previously reported by others [29,30]) with respect to other anions is considerable and the same effect is obtained when the solvent is the parent ionic liquid (Table 2, entries 9–12).

As an example, the value of the half-life time of NHC in DMF is eight times higher in the presence of $N(SO_2CF_3)_2^-$ than in the presence of Cl⁻.

The remarkable reactivity of NHC depends on its nucleophilicity and its strong basicity (pKa = 22–24 in DMSO) [11] and its possible



Fig. 4. NHC generated by cathodic reduction (31 C) of 1a in different solvents. t = 0: end of the electrolysis. Left: NHC oxidation peak current ipⁿ_{ox} vs time. Right: ratio between NHC oxidation peak current and initial NHC oxidation peak current ip^{n}_{ox}/ip^{0}_{ox} vs time.



Scheme 2. NHC-catalyzed synthesis of γ -butyrolactone 6.

instability in organic solvent containing an imidazolium salt can be possibly related to (Scheme 3):

i) an exchange of proton with the solvent (reaction 1),

As the voltammetric analyses were carried out in dry solvents, under continuous N₂ bubbling, reactions (3) and (4) can be ruled out. In any case, the reactivity of NHC is due to the availability of its lone pair, so the more this lone pair is free to react, the shorter the half-life time of the carbene.

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Recently, the stability and the reactivity of 1,3-dialkylimidazole-2-ylidenes, in the presence of the parent ionic liquid, were extensively investigated [29] and the formation of a hydrogenbonded adduct I was hypothesized (Scheme 4, reaction 1).

As the reactivity of NHC depends mainly on the availability of the lone pair localised in an sp²-orbital of the C2 atom, the formation of adduct I should decrease the NHC reactivity while



Fig. 5. NHC generated by cathodic reduction (31 C) of different BMIm-X in DMF. t=0: end of the electrolysis. Left: NHC oxidation peak current ipⁿ_{ox} vs time. Right: ratio between NHC oxidation peak current and initial NHC oxidation peak current ipⁿ_{ox}/ip⁰_{ox} vs time.

Table 2

Stability of 1-butyl-3-methyl-2-ylidene **3**. Effect of the counterion on NHC half-life time $\tau_{1/2}$. Data from Fig. 5.

| Entry | Anion X | Solvent | $\tau_{1/2}/min^a$ | β ^b |
|-------|---------------------------------|--------------------------------------|--------------------|----------------|
| 1 | MeOSO ₃ | DMF | 14 | 0.75 |
| 2 | Cl | DMF | 30 | 0.95 |
| 3 | OTf | DMF | 37 | 0.57 |
| 4 | PF ₆ | DMF | 43 | 0.44 |
| 5 | CF ₃ CO ₂ | DMF | 52 | 0.74 |
| 6 | BF_4 | DMF | 69 | 0.55 |
| 7 | Ι | DMF | 194 | 0.75 |
| 8 | NTf ₂ | DMF | 262 | 0.42 |
| 9 | BF_4 | BMIm-BF ₄ | 20 ^c | 0.55 |
| 10 | CF ₃ CO ₂ | BMIm-CF ₃ CO ₂ | 50 ^c | 0.74 |
| 11 | PF ₆ | BMIm-PF ₆ | 80 ^c | 0.44 |
| 12 | NTf ₂ | BMIm-NTf ₂ | 220 ^c | 0.42 |

^a $\tau_{1/2}$ of **3** was evaluated by voltammetric analysis as the time required to halve the initial NHC oxidation peak current ip^{0}_{ox} (recorded immediately after the end of the electrolyses, i.e. from ip^{0}_{ox} to $ip_{ox} = 0.5$ ip^{0}_{ox}).

 b Kamlet-Taft β ; parameter as a measure of the Hydrogen Bond Accepting ability of anions [31].

^c Data from ref. [19].

increasing its stability.

Nevertheless, anions as Cl⁻, with high hydrogen bond accepting ability (measured from the Kamlet-Taft β parameter, Table 2) [31], could yield the more stable adduct **II** (Scheme 4, reaction 2), displacing the equilibrium (1) to left by removing BMIm⁺. Accordingly, the concentration of free carbene, which is more reactive than the bonded carbene **I** [29], increases.

The results of Table 2 attest that anions X⁻ play a significant role in the kinetic of NHC degradation, giving very different $\tau_{1/2}$ for different salts. The same effect of the bis(trifluorosulfonil) imide anion on $\tau_{1/2}$ was observed in pure BMIm-X, i.e. in the absence of organic solvents [19]. Consequently, the role of X⁻ was related to a competition in the hydrogen bonding interaction (effective in solution of organic solvent as well as in BMIm-X as solvent)



Scheme 3. Possible NHC degradation reactions.





between NHC and BMIm⁺ (adduct I) or between X⁻ and BMIm⁺ (adduct II). Nonetheless, the hydrogen bonding effect does not seem to be the only parameter in NHC stability (see for example entry 7 vs entry 10, Table 2). The anion effect could be due in fact to a combined influence of hydrogen bond ability and ionic dimension (for the same β value, the stabilization of larger anions seems to be more important. As an example, PF₆⁻ and NTf₂⁻ anions have the same β value -0.44 and 0.42, respectively -, but very different ionc radius -3.44 and 4.39 Å, respectively [32] -, with a $\tau_{1/2}$ of 43 and 262 minutes, respectively). Further studies will be devoted to this subject.

The voltammograms in Fig. 2 show that the values of Ep_{ox} (the peak potentials for the oxidation of **3** at the electrode surface) are not significantly affected by the nature of the solvent (as well as by the anion X⁻). This result could appear rather unexpected, if compared with the strong influence of X and of the solvent on the reactivity and stability of NHC in the bulk of the solution, and it deserves a specific study.

In addition, several authors reported NHC catalyzed reactions performed using imidazolium-X salts (X: Cl, CH₃COO) in the absence of any base purposely added to the reaction mixture [33,34]. The results of these reactions were justified admitting the formation of NHC by an equilibrium of proton exchange between the imidazolium cation and X^- (X^- as endogenic base). Nevertheless, no direct experimental support of the presence of free NHC in the ionic liquid or in organic solvent was given [29] (NHCcontaining hydrogen bonded structures were, on the contrary, evidenced in the gas-phase by spectroscopic analysis [35]).

About this subject, we never observed the NHC oxidation peak in the voltammetric curves recorded for BMIm-Cl or BMIm-CH₃COO (pure or in solution). These results suggest that X^- (chloride or acetate anions) is unable to generate NHC from BIMm⁺ to a significant concentration to be revealed by cyclic voltammetry (a technique which is indeed quite sensitive).

3.3. Stability of electrogenerated 1,3-dialkylimidazole-2-ylidenes. The effect of the alkyl substituents

Finally, we studied the effect, on the stability of the corresponding NHC, of different alkyl substituents on the nitrogen atoms of the imidazolium cation for two series of salts in DMF: tetrafluoroborates (Fig. 6, upper plots) and bis(trifluoromethyl-sulfonyl) imides (Fig. 6, lower plots).

The behavior of these NHCs is quite similar (stabilizing effect of NTf_2^- with respect to BF_4^-), with the striking exception of BMIm- NTf_2 (as previously pointed out), whose stability is much higher than that of the other NHC. When aromatic substituents on the nitrogen atoms are considered, the NHC behavior is not clear. Studies are currently ongoing to understand this reactivity.



Fig. 6. NHC generated by cathodic reduction (31 C) of imidazolium salts in DMF. t = 0: end of the electrolysis. Left: NHC oxidation peak current ip^{n}_{ox} vs time. Right: ratio between NHC oxidation peak current and initial NHC oxidation peak current ip^{n}_{ox}/ip^{0}_{ox} vs time. Imidazolium cations: BMIm = 1-butyl-3-methylimidazolium; OMIm = 1-methyl-3-octylimidazolium; BnMIm = 1-benzyl-3-methylimidazolium; BnBMIm = 1-benzyl-3-met

4. Conclusions

The degradation of NHCs in organic solvents has a remarkable effect on their efficiency as organocatalysts. A simple voltammetric methodology allows to investigate the stability of NHCs generated in organic solvents (by cathodic reduction of the corresponding BMIm-X salts) and to determine their lifetime, which is critical for the proper utilization of these solutions for NHC-catalyzed syntheses. The nature of the solvent and of the anion X⁻ has a considerable effect on the kinetic of degradation of NHC (due to dimerization, protonation or ring opening reactions). The role of X⁻ was related to a competition in the hydrogen bonding interaction between NHC and BMIm⁺ (adduct I) and

between X⁻ and BMIm⁺ (adduct **II**). These hydrogen bonding interactions, previously reported in pure BMIm-X, seem to be operative also in organic solvents containing BMIm-X at low concentration (c < 0.1 mol L⁻¹). The efficiency of the NHC-catalyzed synthesis of γ -butyrolactones, used as a test for the stability of NHCs, confirmed the results of the voltammetric analysis.

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