catalysts

Review

Advances in the Knowledge of *N*-Heterocyclic Carbenes Properties. The Backing of the Electrochemical Investigation

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Abstract: In the last twenty years, *N*-heterocyclic carbenes (NHCs) have acquired considerable popularity as ligands for transition metals, organocatalysts and in metal-free polymer synthesis. NHCs are generally derived from azolium based salts $NHCH^{+}X^{-}$ by deprotonation or reduction (chemical or electrochemical) of $NHCH^{+}$. The extensive knowledge of the physicochemical properties of $NHCH^{+}$/NHC system could help to select the conditions (scaffold of NHC, nature of the counter-ion X^{-}, solvent, etc.) to enhance the catalytic power of NHC in a synthesis. The electrochemical behavior of $NHCH^{+}$/NHC system, in the absence and in the presence of solvent, was extensively discussed. The cathodic reduction of $NHCH^{+}$ to NHC and the anodic oxidation of NHC, and the related effect of the scaffold, solvent, and electrodic material were emphasized. The electrochemical investigations allow acquiring further knowledge as regards the stability of NHC, the acidic and nucleophilic properties of $NHCH^{+}$/NHC system, the reactivity of NHC versus carbon dioxide and the effect of the hydrogen bond on the catalytic efficiency of NHC. The question of the spontaneous or induced formation of NHC from particular ionic liquids was reconsidered via voltammetric analysis. The results suggested by the classical and the electrochemical methodologies were compared and discussed.

Keywords: *N*-heterocyclic carbene (NHC); cyclic voltammetry; electrolysis; NHC stability; NHC nucleophilicity; azolium acidity; electrogenerated NHC; hydrogen bond; carbon dioxide; NHC–CO_2 adduct

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1. Introduction

The advantages in the use of catalysts in chemistry are well known; nevertheless, some drawbacks in their use should be kept in mind. As an example, the possible toxicity of some catalysts could affect the sustainability of such syntheses. In addition, the instability of some catalysts prevents their generation long before the catalytic step, requiring their formation directly in the reaction mixture.

Therefore, the discovery of new classes of "greener" and efficient catalysts (e.g., organocatalysts vs. metal catalysts) and the set up of mild conditions for their generation in the reaction mixture are regarded as significant targets in modern organic synthesis. Anyway, the reported drawbacks (toxicity and instability) require the knowledge of the overall chemistry of the catalyst, beyond its peculiar catalytic activity.

In the field of organocatalysis, *N*-heterocyclic carbenes (NHCs) take on a dominant position.

1.1. Carbenes

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valency shell [1,2]. The linear (as an extreme case) and the bent geometries of carbene structure are related to the different possible hybridization of the carbene carbon atom. The sp-hybrid orbitals, coupled with two energetically degenerated p orbitals, and the sp^2-hybrid orbitals (δ orbitals), coupled with a p orbital (pπ orbital), promote the linear or bent geometry, respectively (Figure 1).

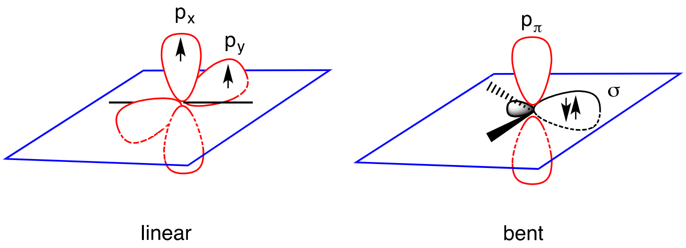


Figure 1. Geometry at the carbene carbon atom: linear and bent. Arrows: electrons.

The reactivity and the properties of carbenes (with bent geometry) are strongly affected by the arrangement of the two nonbonding electrons (triplet or singlet carbenes):

- triplet ground state, the two nonbonding electrons occupy the two empty orbitals δ and pπ with parallel or antiparallel spin orientation: δ^1 $p\pi^1$ ($^3B_1$ or $^1B_1$ state); and
- singlet ground state, the two nonbonding electrons occupy only the empty δ orbital as a lone pair, being empty the pπ orbital: δ^2 $p\pi^0$ ($^1A_1$ state). The δ^2 $p\pi^0$ ($^1A_1$ state) is generally regarded as more stable than the δ^0 $p\pi^2$ ($^1A_1$ state) in which the lone pair occupies the pπ orbital (Figure 2).

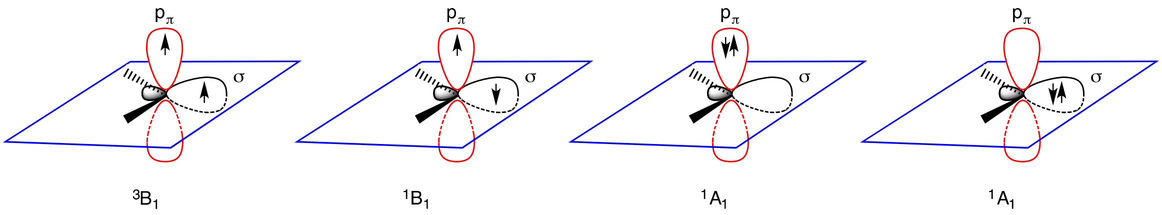


Figure 2. Triplet and singlet carbenes: electronic configurations. Arrows: electrons.

The singlet ground state is supported by a significant difference between the energies of the δ and pπ orbitals (>2.0 eV) [1]. The ambiphilic behavior (nucleophilic and electrophilic character) of singlet carbenes is due to the presence of an sp^2-hybridized lone pair and of an unoccupied p-orbital.

1.2. N-Heterocyclic Carbenes (NHCs)

N-Heterocyclic carbenes (NHCs) are neutral species containing a carbene carbon and at least one adjacent nitrogen atom within a ring structure. In addition to the nitrogen atom, NHCs could be marked by the presence of other heteroatoms (sulfur and oxygen).

The considerable role of NHCs as ligands for transition metals [3] and as catalysts in metal-free polymer synthesis [4] has been frequently emphasized. In addition, NHCs are often utilized as green and cheap organocatalysts in many C–C bond-forming reactions (benzoin condensation, Stetter reaction, etc.) [5–11].

At the beginning, NHCs were studied as mere curiosities. Nevertheless, since the investigations of Wanzlich in 1968 [12], the subsequent studies of (Bertrand and coworkers, 1998) [13] and especially thanks to the isolation and characterization of 1,3-di(adamantyl)imidazole-2-ylidene (Arduengo and coworkers, 1991) [14], NHCs are regarded as organic structures of considerable significance.

As regards the NHC electronic configuration, the singlet ground state of 1,3-di(adamantyl)imidazole-2-ylidene could be assumed as reference and some significant conclusions are generally accepted. In the single ground state, the two nitrogen atoms adjacent to the carbene atom C2 could be regarded as δ-electron-withdrawing as well as π-electron-donating atoms. As a consequence, the overall structure is stabilized both inductively and mesomerically. The inductive effect lowers the energy of the occupied δ-orbital. Likewise, the nitrogen atoms are able, via the mesomeric effect, to delocalyze their lone pair involving the carbene empty p-orbital, i.e., to push their lone pair into the empty p-orbital of the carbene (Figure 3) [2]. Accordingly, Taton have summarized a significant result: the interaction between nitrogen atoms and C2 atom destabilizes the pπ orbital, resulting in a large δ-pπ gap [4]. Therefore, NHCs must be regarded as strong nucleophilic agents and not as electrophilic ones. In addition, owing to this interaction, a four-electrons-three π-system and a partial multiple bond character of C–N bond could be considered.

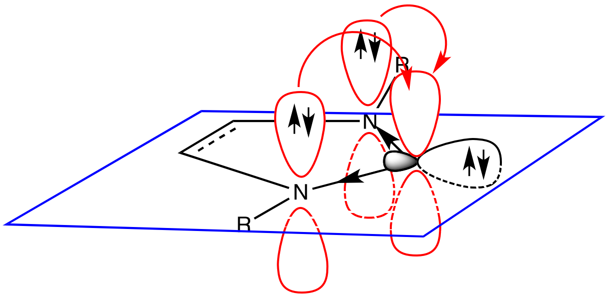


Figure 3. *N*-Heterocyclic carbenes: stabilization via δ-withdrawing and π-donating effects. Arrows: electrons.

1.3. Umpolung and the Peculiar Chemistry of NHCs

Many authors discussed the catalytic activity of NHCs and suggested their ability to induce umpolung in suitable functional group (e.g., aldehydic group). The umpolung is an intriguing question concerning a nucleophilic addition of NHC (or other nucleophilic agent) to an electrophilic center, causing an inversion of the classic polarity of the acceptor group (polarity reversal).

Usually, an NHC is generated via deprotonation of the azolium salt precursor by a suitable base. According to the hypothesis of Breslow, the heart of the mechanism is the nucleophilic attack of NHC to the carbonyl function of an aldehyde yielding a zwitterionic structure, which is converted (by an intramolecular proton transfer) into an acylanion equivalent (the Breslow intermediate). The coupling of the Breslow intermediate with a second aldehyde molecule yields the product (α-hydroxyketone, benzoin) and regenerates the NHC [15–18].

The benzoin condensation was labeled by some authors as a "biomimetic reaction". In fact, the enzyme transketolase, in the presence of vitamin B_1 (thiamine), catalyzes (via a nucleophilic acylation reaction) the transfer of a two-carbon unit from a carbohydrate to another (transketolase process). The transformation of thiamine into its active carbene suggests a Benzoin-like mechanism [19].

The possible utilizations of NHCs (generated from azolium salts and bases) as organocatalysts in organic synthesis is reported in a plethora of papers, summarized in classical and more recent significant reviews [5–11]. On the other hand, some authors suggested the electrochemical generation of NHCs by cathodic reduction of azolium cations. This procedure allows obtaining NHCs in situ, even in the presence of base-sensitive substrates. The related papers are reported in a recent review [20].

Nevertheless, beyond the question of umpolung and the related synthetic applications, the NHC-chemistry is very peculiar und affected by several factors:

- the structure of the cycle and the presence of other hetero-atoms (S, O) in addition to nitrogen atom;
- the nature of the substituents at the hetero and carbon atoms;
- the presence, in the reaction mixture, of the parent azolium cation and of the counter ion; and
- the presence and the nature of the solvent.

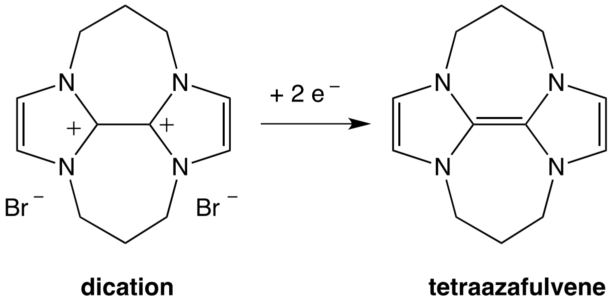
Systematic studies are carried out to clarify the peculiar chemistry of NHCs (in any case related to the presence of a lone pair in the δ-orbital and to an empty pπ orbital) and of the parent cation $NHCH^+$. A very extensive investigation was performed by both classical and electrochemical procedures. In the present mini-review, we wish to emphasize the results derived by electrochemical techniques and to compare them with those derived via classical methodologies. The backing of the electrochemical investigation results from the possibility to obtain NHC from electrolysis of the corresponding ionic liquid [20].

Since the end of the past century, some authors, spurred by a possible non innocent nature of azolium based ionic liquids due to the acidity of the C2-H group, investigated the voltammetric behavior of these structures ($NHCH^+$). In this contest, azolium based ionic liquids (neat salts or their solutions in organic solvents) were systematically electrolyzed and their electrolysis products identified. Thanks to these studies, the electrodic activity of the system $NHCH^+$/NHC (parent/electrogenerated son) was considerably clarified and efficient electrochemical methodologies for NHC generation were reported.

2. Electrodic Activity of the System $NHCH^+$/NHC

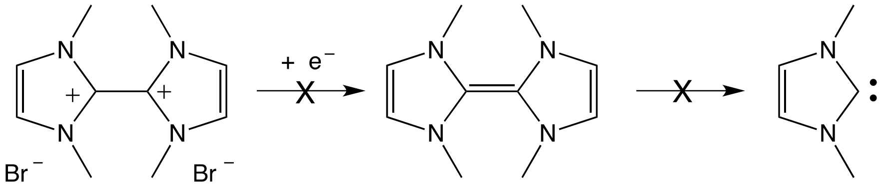
The electrochemical generation of NHC derives from early investigations on the electrodic activity of ionic liquids.

In 1994, the electrodic activity of 1,3-bis-(4-methylphenyl)imidazolium chloride was proven by voltammetric analysis [21]. Actually, the curves revealed a single reduction at −2.32 V in forward scan and two oxidations at −0.89 and −0.54 V in the following scan reversal. Afterwards, Thummel and coworkers [22] emphasized the presence of a single irreversible reduction peak in the voltammograms of dication 1,1′;3,3′′-bistrimethylene-2,2′diimidazolium dibromide recorded in CH_3CN solution (E = −1.4 V). Nevertheless, the authors reported that bulk electrolyses of solution of dication (carried out at a potential which would ensure its complete reduction) provides tetraazafulvene (Scheme 1).



Scheme 1. Electrochemical reduction of dication to tetraazafulvene.

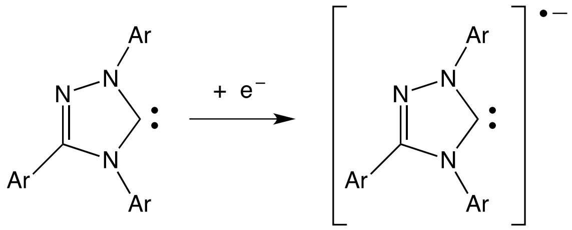
Contrary, electrolysis of solution of simple tetramethyl dication did not provide the corresponding tetraazafulvene (Scheme 2). This was especially disappointing for the authors since they expected that the formation of tetraazafulvene might in turn lead to the stable carbene (i.e., an electrogenerated NHC).



Scheme 2. Electrochemical reduction of tetramethyl dication.

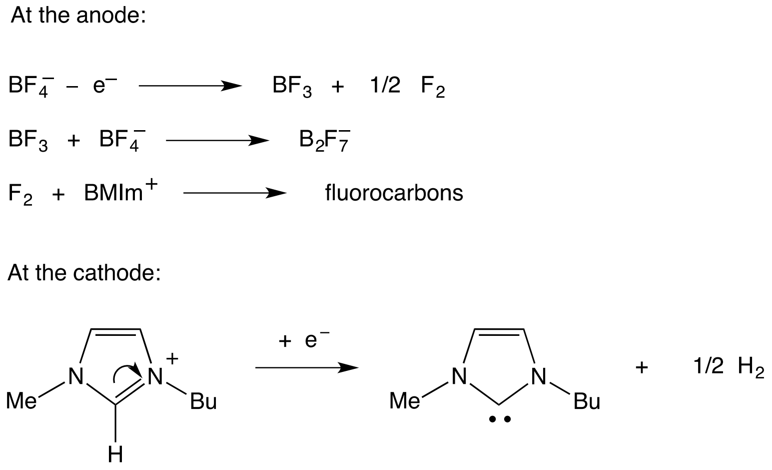
Voltammetric measurements proved that the electrochemical window of dialkyl-imidazolium tetrafluoroborate or hexafluorophosphate is wide and affected by the nature of the electrodic material [23].

As regards *N*-heterocyclic carbenes, their electrodic activity was first pointed out by Enders and Simonet [24]. Cyclic voltammetric curves of a triaryl-triazol-5-ylidene (Scheme 3) in DMF-0.1 M solution (Hg cathode; room temperature (rT); ν = 0.5 V·s^{-1}; $c = 2\times10^{-3}$ M) showed a reversible reduction peak (Ep = −1.8 V vs. Ag/AgI) related to the monoelectronic reduction of the carbene to the corresponding radical anion, which was characterized by electron spin resonance (ESR) measurements. On the other hand, Clyburne and coworkers reported that no one-electron oxidation of NHCs was identified [25].



Scheme 3. Electrochemical reduction of a triaryl-triazol-5-ylidene to radical anion.

Johnson reported an investigation aimed, inter alia, to identify the cathodic and anodic products of the electrolysis of 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate (BMImBF$_4$) [26]. The study was carried out by cyclic voltammetry and Osteryoung square wave voltammetry. The electrolysis was performed under constant current conditions and the products were analysed but not isolated. The authors hypothesized the formation of BF$_3$ and fluorocarbons (as anodic products) and dimerization and dealkylation reactions after reduction of BMIm$^+$ to NHC (as cathodic process) (Scheme 4). As regards the voltammetric curves, sweeping negatively from 0.0 V, there are no reduction peaks until −2.0 V, but after reversal at $E < -2.0$ V, an oxidation peak appears at ≈−0.13 V. The authors concluded that the peak is due to the oxidation of the reduction product of BMIm$^+$.



Scheme 4. Electrolysis of BMImBF$_4$. Reproduced with permission from [26]. Copyright The Electrochemical Society, 2003.

According to Clyburne and coworkers [27], the voltammetric curves of 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride in DMF show an irreversible reduction peak at −2.28 V vs. SCE (ν = 0.3 V·s^{-1}) related to the monoelectronic reduction of the azolium cation. In addition, the cyclic voltammetry (CV) shows the presence of an oxidation peak at −0.20 V corresponding to the oxidation of chemical species generated in the cathodic reduction of the azolium cation (Figure 4).

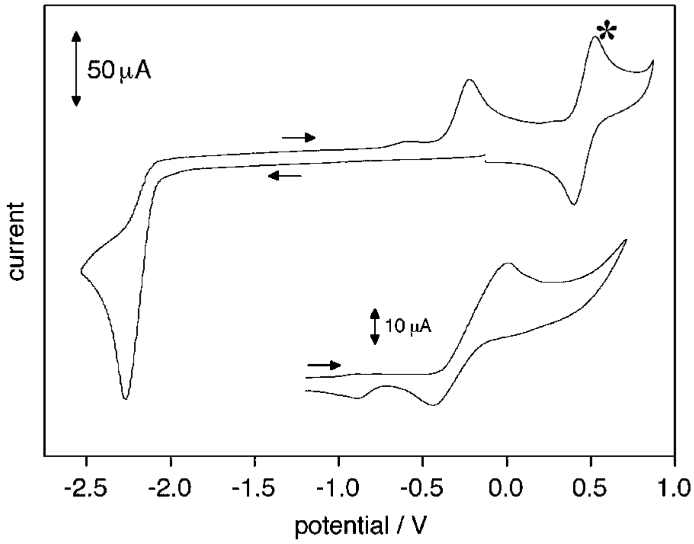


Figure 4. Cyclic voltammetry of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride in DMF. Arrows define the scan direction. Reproduced with permission from [27]. Copyright The Royal Chemical Society, 2004.

The authors note that this peak has the same potential as the one they measured for the electrochemical oxidation of the corresponding carbene, 1,3-bis(2,4,6-trimethylphenyl) imidazole-2-ylidene. Owing to the overlapping of these two peaks, the authors suggested that the cathodic reduction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride produces NHC. In addition, the authors emphasized that the electrochemical and the chemical (by potassium metal) reductions lead to the same radical intermediate. The decomposition of this radical produces 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene and H_2 [25,27].

More recently, the voltammetric behavior of neat azolium salts (imidazolium-, triazolium-, and thiazolium-based) or of their solutions (*N*,*N*-dimethylformamide (DMF), and MeCN as solvents) was reconsidered [28–32]. The $NHCH^+$ reduction and NHC oxidation potentials are obviously dependent on structure of the azolium cation, of the counter-ion, the presence and the nature of the solvent, and the electrode material (Figure 5).

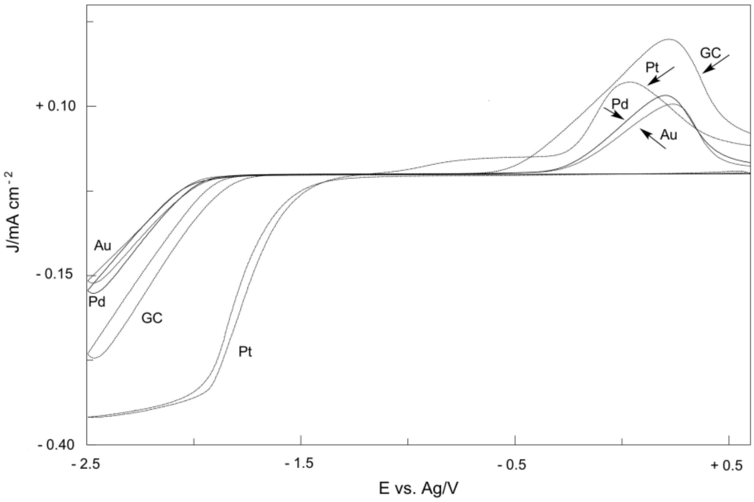


Figure 5. Voltammetric curves of $BMImBF_4$ on different cathodes. Starting potential: +0.8 V, reversal potential: -2.5 V. ν = 0.2 V·s^{-1}, Ag quasireversible electrode, T = 60 °C. Arrows define the scan direction. Reproduced with permission from [31]. Copyright Elsevier, 2016.

On a glassy carbon electrode (ν = 0.2 V·s^{-1}), the voltammetric curves of these ionic liquids show a significant cathodic current at $E < -1.9$ V and an anodic peak around 0.0 V in the reversed anodic scanning. The cathodic current and the anodic peak were related to the reduction of the NHCH$^+$ azolium cation to NHC and H_2 and to the oxidation of the NHC, generated during the direct cathodic scanning at $E < -1.9$ V [32].

As regards the anodic peak, the voltammetric parameters affects both the current and the potential values. In fact, the peak current decreases on increasing the value of the reversal potential from −2.5 to −1.9 V, according to a different pilling up of the electroactive species (NHC). No oxidation peak is present in the voltammogram if the value of the reversal potential is >−1.8 V (Figure 6) [31].

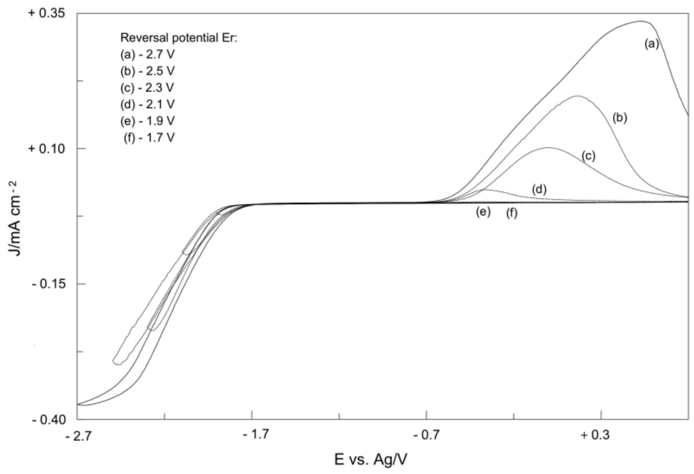


Figure 6. Voltammetric curves of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$). Starting potential: +0.8 V, reversal potential: as reported. GC cathode, ν = 0.2 V·s^{-1}, Ag quasireversible electrode, T = 60 °C. Reproduced with permission from [31]. Copyright Elsevier, 2016.

The presence of the anodic peak around 0.0 V is particularly important, as it could be regarded as a distinguishing mark of the presence of NHC and of its oxidation. Moreover, this peculiar anodic peak is present both in pre-electrolyzed $BMImBF_4$ ($E < -1.9$ V) and in DBU-$BMImBF_4$ solution, being DBU a strong organic base (1,8-diazabicyclo[5.4.0]undec-7-ene). Therefore, NHC can be generated by both cathodic reduction and chemical deprotonation of NHCH$^+$ [31]. The NHC oxidation peak current increases on increasing the concentration of NHC, i.e., on increasing the concentration of added DBU or of the number of Faradays consumed during the electrolysis of $BMImBF_4$, as expected. This is thus a confirmation that the electrochemical methodology is able to generate NHC by cathodic reduction of NHCH$^+$. Therefore, in NHC-catalyzed syntheses involving base sensitive substrates and requiring the generation of NHC in situ, the electrochemical procedure could be a unique alternative.

Moreover, a prefixed concentration of NHC is easily obtained by planning the number of Faradays consumed during the electrolysis. In addition, the simple recording of a voltammetric curve allows to verify the presence of NHC (oxidation peak) and to evaluate its concentration (peak current). Therefore, we underline that the electrochemical methodology can be useful not only in NHC-catalyzed syntheses, but even in any investigation requiring a measurement of NHC- concentration.

3. NHC Stability

The catalytic power of an NHC is mostly related to its ability to trigger the substrate. This ability is mainly shaped by the whole scaffold of NHC. On the other hand, the complex reactivity of NHC could also affect considerably its stability and cause a fast decrease of free NHC really present in the reaction mixture and hence prejudice the catalytic efficiency.

In a recent paper Gronert and coworkers discussed the strategies for assessing the stability of various classes of carbenes and the relevant experimental and computational procedures which were used [33]. The carbene stabilization energy (CSE) and the singlet-triplet gaps (DE_{ST}) were even reported. The authors emphasized that assessing the carbene stability is a richly rewarding but could be a frustrating endeavor. In fact, a precise description of stability in practical application is problematic as appropriate, universal reference state cannot always be defined [33]. Accordingly, any definition of stable carbene is subjective.

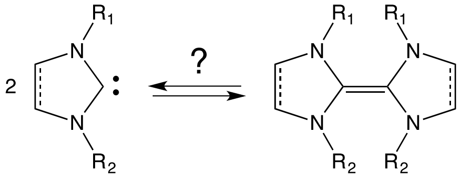
Generally, a stable carbene is a carbene, which can be isolated in pure form. Instead, a persistent carbene is a carbene that can be observed by experimental techniques (e.g., spectroscopic analysis), but not isolated [34].

Arduengo synthesized for the first time a stable *N*-heterocyclic carbene: 1,3-di(adamantyl)imidazole-2-ylidene [14]. This NHC was isolated and could be stored. However, this considerable result could not be generalized. Some authors remind that NHCs must be considered in any case as sensitive species [35].

As regards the most frequently utilized NHCs dialkylimidazole-2-ylidenes, their significant reactivity (even in the total absence of dioxygen and moisture) involves a limited lifetime and prevents from isolating them.

At the same time, we must keep in mind that carbene lifetime is affected not only by their peculiar structure, but even by the overall experimental conditions. The presence and the nature of solvent, counter ion, parent azolium salt, acidic substrates could play a significant role.

The limited lifetime of many NHCs could be related to the formation of dimeric structures, according to the Wanzlick equilibrium (Scheme 5). Steric and electronic effects in the dimerization process were discussed. [36] The stronger tendency to dimerize of saturated NHCs, compared with unsaturated ones, was correlated to electronic effects [37,38].



Scheme 5. Possible Wanzlick equilibrium.

The efficiency of a catalyst is affected, ceteris paribus, by its lifetime. Therefore, the knowledge of NHC lifetimes and of the influence of the experimental conditions on these values is significant, helping to define the optimum conditions of an NHC-catalyzed synthesis.

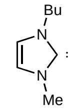
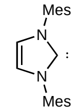
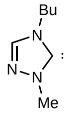
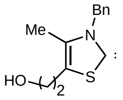
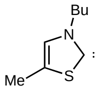
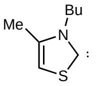
The measurement of NHC-lifetimes (in different conditions: scaffold, solvent, counter ion) could be carried out by simple electrochemical procedures. As above reported, the voltammetric curves, recorded in a medium containing NHC, show the corresponding oxidation peak. The peak current is directly related to the NHC concentration and thus this peak analysis allows to verify the presence and the concentration of NHC. The stability of several NHCs was studied defining their half-life ($\tau_{1/2}$) by voltammetric analysis [32,39–41]. NHCs were generated by electrolysis of neat azolium salts (system A) or solutions of azolium salts in organic solvents (system B). In system A the ionic liquid performs the double role of NHC parent and solvent.

The voltammograms on the catholyte of systems A and B were recorded as a function of the time from electrolysis end. The half-life $\tau_{1/2}$ is defined as the time to halve NHC concentration (i.e., the anodic peak current) with respect to the initial one. Therefore, the factor $\tau_{1/2}$ could be considered as measure of NHC stability in that experimental conditions. From the electrochemical investigation, some preliminary considerations were possible:

- The investigated NHCs (imidazole-, triazole-, and thiazole-based) are involved in a remarkable degradation process.
- The NHC half-life is strongly affected by NHC scaffold (Table 1) [32].

- The NHC degradation rate increases on increasing NHC concentration. Accordingly, the degradation process could be associated, inter alia, with a coupling reaction between two NHC molecules.
- The NHC half-life is influenced by the nature of the counter ion X^- of the parent azolium salt and by the presence and nature of organic solvents (Table 2) [39,40]. In fact, $\tau_{1/2}$ for an NHC is quite different when measured in ionic liquid or in organic solvent. As regards this question, many authors have investigated the role of hydrogen bond between NHC, $NHCH^+$, or X^- and the solvent (see Section 6).
- The presence of an acidic substrate (CH_3COOH) influences the NHC $\tau_{1/2}$ values and generally the acid increases the NHC degradation rate. In this regard, the role played by the proton exchange equilibrium between NHC and the acid was discussed in terms of pK_a of NHC and acid (Table 1) [32,41].

Table 1. $\tau_{1/2}$ Values for NHCs in the absence and in the presence of acetic acid. Reproduced with permission from [32]. Copyright Wiley-VCH, 2016.

Entry	**NHC**	**$\tau_{1/2}$ [1] (min)**	**$\tau_{1/2}/CH_3COOH$ [2] (min)**
1		70	8
2		133	17
3		>>300	>>300
4		>>300	>300
5		>>300	>>300
6		175	275

[1] Time necessary to halve the oxidation peak current registered at the end of 31 C electrolysis (t = 0); [2] time necessary to halve the oxidation peak current registered at the end of 31 C electrolysis (t = 0) when 1.0 eqiv. of CH_3COOH (with respect to NHC) is added to the solution at t = 0.

Table 2. Stability of 1-butyl-3-methyl-2-ylidene. Effect of the counterion on NHC half-life time $\tau_{1/2}$. Reproduced with permission from [40]. Copyright Elsevier, 2016.

Entry	**Anion X**	**Solvent**	**$\tau_{1/2}$/min [1]**
1	$MeOSO_3$	DMF	14
2	Cl	DMF	30
3	OTf	DMF	37
4	PF_6	DMF	43
5	CF_3CO_2	DMF	52
6	BF_4	DMF	69
7	I	DMF	194
8	NTf_2	DMF	262
9	BF_4	BMIm-BF_4	20
10	CF_3CO_2	BMIm-CF_3CO_2	50
11	PF_6	BMIm-PF_6	80
12	NTf_2	BMIm-NTf_2	220

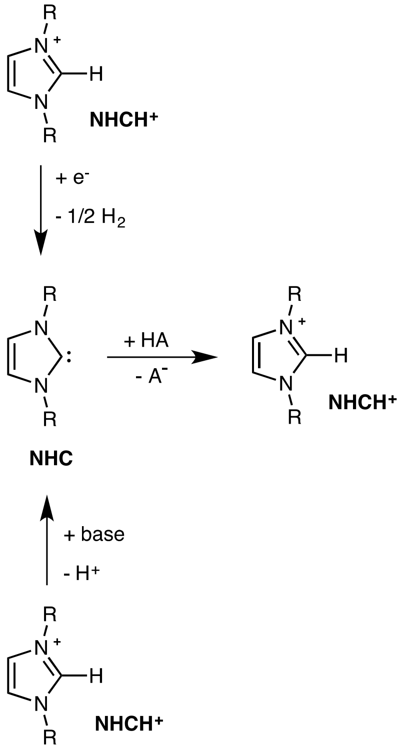
[1] $\tau_{1/2}$ of NHC was evaluated by voltammetric analysis as the time required to halve the initial NHC oxidation peak current ip^0_{ox} (recorded immediately after the end of 31 C electrolyses, i.e., from ip^0_{ox} to $ip_{ox} = 0.5\ ip^0_{ox}$).

The correlation between $\tau_{1/2}$ and NHC efficiency as catalyst was ascertained considering the synthesis of γ-butyrolactones via NHC-catalyzed umpolung of cinnamaldehyde [40]. In fact, the yields of the isolated γ-butyrolactones increased on increasing the values of $\tau_{1/2}$ (derived from the voltammetric analysis) of the selected NHC.

Therefore, a simple voltammetric analysis could suggest the best experimental conditions (counter ion and solvent for a fixed NHC) to increase NHC $\tau_{1/2}$ in a reaction and, consequently, to increase the efficiency of the synthesis.

4. The Acidic and Nucleophilic Properties of $NHCH^+$/NHC System

NHCs can be generated by deprotonation or reduction of their conjugate acids, $NHCH^+$s (Scheme 6). Therefore, the chemical behavior of NHC (often unstable) could be in part derived from the study of its conjugate acid $NHCH^+$.



Scheme 6. Generation of NHC from $NHCH^+$ and its behavior as a base.

The chemistry of $NHCH^+$ and NHC is mainly centered on the carbon atom in 2-position, i.e., on the C2-H group and on the lone pair for $NHCH^+$ and NHC, respectively. The pK_a of $NHCH^+$ and the nucleophilicity of NHC are significant features of this chemistry and should be evaluated. In particular, acidity and nucleophilicity are dependent on $NHCH^+$/NHC structures, but also the solvent plays a significant role.

As regards the evaluation of pK_a of the azolium based cation $NHCH^+$, extensive investigations were carried out by many authors. Experimental pK_a values and those calculated by computational methods are consistent, e.g., in DMSO as solvent: 1,3-dimethylimidazolium trifluorosulfonylimide, pK_a 22.0 (exp), pK_a 21.1 (calcd); 1,3-dibutylimidazolium trifluorosulfonylimide, pK_a 23.2 (exp), pK_a 22.6 (calcd). The results of these experimental and theoretical studies are reported by O'Donoghue and Massey in a very exhaustive review [42]. As $NHCH^+$ is a weak acid, the evaluation of the equilibrium concentration of its conjugate base NHC could be problematic. To circumvent this trouble the overlapping indicator method is frequently utilized. The acid–base equilibrium between the weak acid $NHCH^+$ (of unknown pK_a) and an indicator (of known pK_a) is investigated via UV–vis or ^{1}H

NMR spectrometry [43,44]. The reported pK_a are affected by the structure and substituents of $NHCH^+$, the counter ion, the nature of the solvent [45,46].

Weak acids pK_a can be determined also by electrochemical techniques. In this regard, potentiometric and voltammetric approaches were described [47,48], but, to the best of our knowledge, in no case the pK_a of azolium cations or the nucleophilicity of their conjugate bases NHC were reported.

Although absolute pK_a values for azolium cations obtained by electrochemical means were never reported, some authors ordered different $NHCH^+$s and NHCs according to their acidity and nucleophilicity (respectively) by cyclic voltammetry [32]. The structures considered are reported in Figure 7.

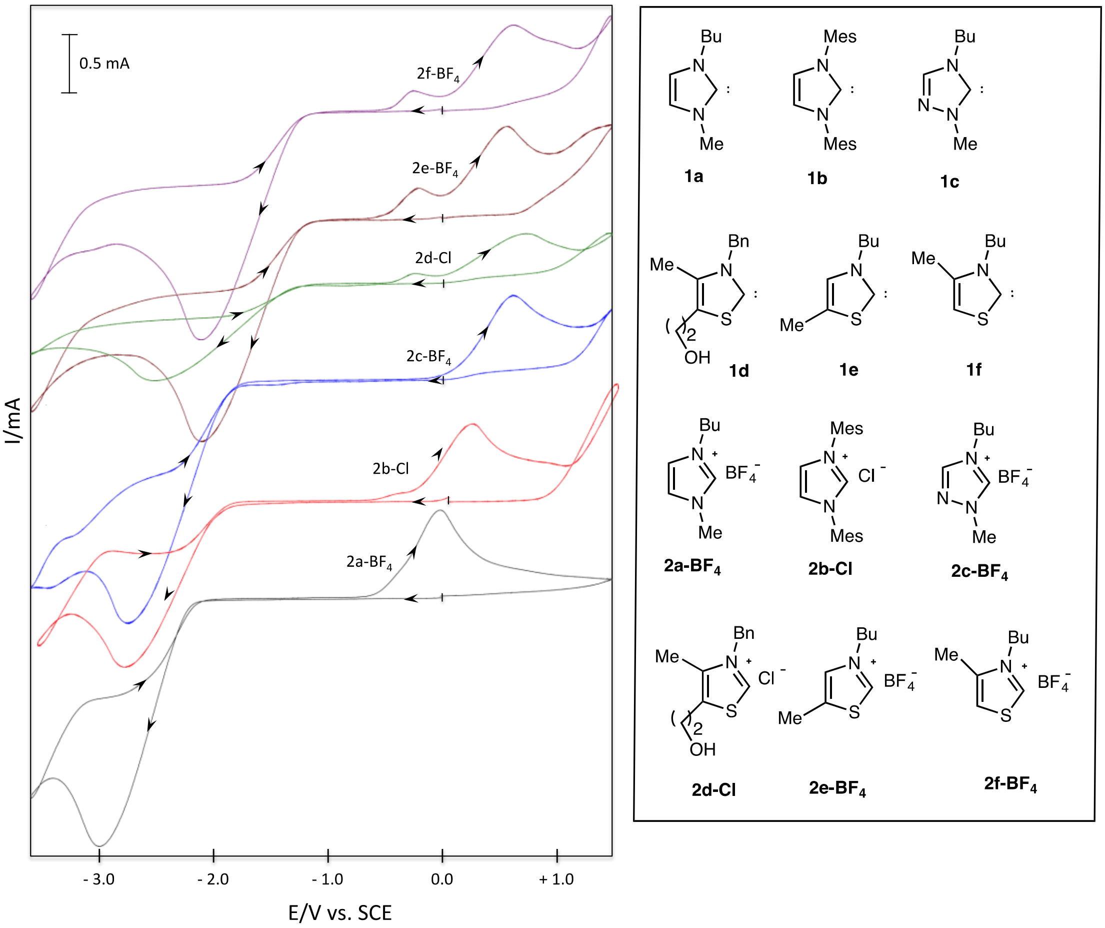


Figure 7. Cyclic voltammetries of DMF solutions of azolium salts (0.1 M). Vitreous carbon cathode, $\nu = 0.2\ V{\cdot}s^{-1}$, $T = 25\ ^{\circ}C$. Scan potential: 0.0 to −3.6 to +1.5 to 0.0 V vs. SCE. Reproduced with permission from [32]. Copyright Wiley-VCH, 2016.

As regards these structures, it is pointed out that:

- imidazolium cations (as **2a–b**, Figure 7) are the least acidic azolium cations (pK_a = 22–24 in water and 22 in DMSO), while triazolium (as **2c**) and thiazolium ones (as **2d–f**) are the most acidic (pK_a = 16–19 in water and 14 in DMSO) [4,49]; and
- the nucleophilicity of imidazole NHC (as **1a–b**, Figure 7) is three orders of magnitude greater than the thiazole based NHC (as **1d–f**) [50].

The voltammetric curves (azolium salts in DMF, vitreous carbon electrode) show a reduction peak in the direct scanning and an oxidation peak in the reverse one. These peaks are related to the reduction of $NHCH^+$ to NHC and to the oxidation of the electrogenerated NHC (Figure 7). The reduction peak potential of $NHCH^+$ (Ep_{red}) as well as the oxidation peak potential (Ep_{ox}) of NHC are affected by the structure of the electroactive species (Table 3).

Table 3. Cyclic voltammetries of **2a–f** (0.10 M) in DMF (Figure 7). Reduction and oxidation peak potentials vs. SCE. Vitreous carbon cathode, $\nu = 0.20\ V \cdot s^{-1}$, $T = 25\ °C$. Reproduced with permission from [32]. Copyright Wiley-VCH, 2016.

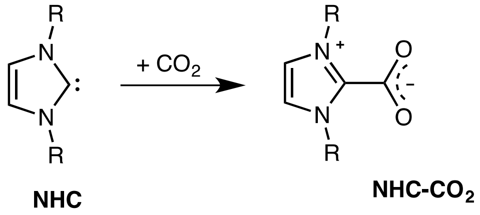
Entry	Salt	Ep_{red}/V	Ep_{ox}/V
1	**2a**-BF_4	−3.00	0.00
2	**2b**-Cl	−2.87	+0.22
3	**2c**-BF_4	−2.76	+0.60
4	**2d**-Cl	−2.47	+0.75
5	**2e**-BF_4	−2.11	+0.58
6	**2f**-BF_4	−2.09	+0.64

The Ep_{red} values increase on increasing the acidity of $NHCH^+$, i.e., on decreasing the energy for the electrochemical cleavage of the C2–H bond. The Ep_{ox} values decrease on increasing the NHC nucleophilicity, the nucleophilicity being evaluated versus the anodic vitreous carbon surface regarded as a conventional electrophilic agent.

The authors suggested that Ep_{red} and Ep_{ox} could be thus considered as indicative of the acidity of $NHCH^+$ and of the nucleophilicity of NHC, respectively, and they ordered the substrates according to their voltammetric potentials, i.e., to their acidity or nucleophilicity. These data could be particularly important as the ease of a carbene generation is usually connected with the acidity of the parent molecule, while a carbene reactivity is usually connected with its nucleophilicity (lone pair availability). A simple voltammetric analysis can thus compare different $NHCH^+$/NHC systems.

5. NHC and Carbon Dioxide

Due to their nucleophilicity, NHCs are able to add to carbon dioxide to yield imidazole-2-carboxylates (NHC–CO_2 adducts, Scheme 7).



Scheme 7. Reaction between NHC and CO_2 to yield NHC–CO_2 adduct.

An NHC–CO_2 adduct was firstly obtained by Kuhn and coworkers by direct coupling of free NHC (2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with CO_2 [51]. Later, Louie and coworkers reported a different synthesis, carried out bubbling CO_2 into an imidazolium salt and potassium *tert*-butoxide solution [52]. The various syntheses of NHC–CO_2 adducts as well as their chemistry are discussed in both classical and more recent reviews [53–55].

Two topics could be emphasized:

- the small NHC–CO_2 bond dissociation energies suggested an extensive investigation on the possible utilization of NHCs as means to catch and release carbon dioxide; and
- the considerably higher stability of NHC–CO_2 adducts than free NHCs spurred many authors to verify the possible use of these adducts as catalysts (or, rather, as latent catalysts) instead of NHCs.

5.1. Catch and Release of CO_2: Role of NHCs

The investigations of the last decades suggest that carbon dioxide can be considered both as a problem and as a resource. Concerning this, two questions should be underlined:

- The control of the global climate change is, at present, a very serious problem [56,57]. Carbon dioxide is the most significant greenhouse gas responsible of this change [58]. Global emissions of carbon dioxide reached 34 billion tons in 2011, up 3% relative to 2010. If the increase in CO_2 emissions continues at this rate, within the next two decades global carbon dioxide cumulative emissions will reach levels that will make it impossible to hold the increase in global temperature below 2 °C every year [59]. Therefore, any possible attempt must be oriented to reduce (or at least to stabilize) the levels of carbon dioxide in the atmosphere.
- On the other hand, the reaction of CO_2 with organic substrates to form new C–C bonds is a goal pursued by many authors. In fact, carbon dioxide is a non-toxic, abundant, low cost C1 building block in organic synthesis [60].

The two topics go hand in hand; in fact, the capture and storage of CO_2, while decreasing the CO_2 level in atmosphere, allows the availability of a reservoir of C1 building block.

At present, the most frequently used industrial technology for CO_2 capture is based on amine solutions, due to its efficiency. However, the capture of CO_2 with amines involves a chemical reaction with a large enthalpy [61]. Consequently, a large amount of heat is required to release the captured CO_2 in the regeneration step. In addition, some drawbacks as reagent volatility and instrument corrosion were reported [62–64]. Other promising methodologies, recently suggested, are related to the use of room temperature ionic liquids [65–67], task-specific ionic liquids [68,69], ionic liquid (IL)-based mixture [70,71], and polyionic liquids [72,73].

Due to its ability to form adducts with carbon dioxide, even NHC was considered to lower the level of carbon dioxide in the atmosphere. An efficient systems for CO_2 capture and release via NHC, generated in situ from imidazolium salts and organic superbases, was reported by Dai and coworkers [70]. The captured CO_2 was released by heating or N_2 bubbling and recycled. Suresh and coworker rationalized the capture ability of NHC on the basis of the electronic and steric properties of the *N*- and *C*-substituents, in terms of molecular electrostatic potential minimum observed of the carbene lone pair region of NHC and at the carboxylate region of the NHC–CO_2 adduct [74].

Recently, papers described the electrochemical synthesis of NHC–CO_2 adducts for the CO_2 catch and release [29,31,39]. A simple electrolysis of neat liquid imidazolium salts (e.g., 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate) generated NHC in the catholyte and, after carbon dioxide bubbling, the NHC–CO_2 adduct. The adduct could release CO_2 after physical stimulation (120 °C), regenerating NHC. Cooling down the solution to 60 °C and adding carbon dioxide, the adduct was regenerated. This system is able to catch and release CO_2 cyclically and in mild conditions. After a single electrolysis, in a series of 10 cycles the solution (electrogenerated NHC in imidazolium salt as solvent) was able to catch and release 4 mol of CO_2 per Faradays consumed during the electrolysis [31]. These investigations, extended to different ionic liquids BMImX, proved that the rate of CO_2 capture is affected by the nature of the counter ion X^- [39].

Simple cyclic voltammetries allowed to evidence and quantify the presence of NHC after every heating cycle (presence of its oxidation peak).

5.2. NHC–CO_2 Adducts as Latent Catalysts

In spite of NHCs catalytic ability, their instability could in some cases render their use problematic. In this contest, the use of "latent catalysts", i.e., stable structures able-suitably triggered-to release catalysts, could be a solution [75]. As NHC–CO_2 adducts, triggered by heating (120 °C) or US irradiation, are able to release free NHC [30], these structures may be regarded as latent catalysts. In fact, recently many groups reported the use of NHC–CO_2 adducts as source of NHCs in organic synthesis [76,77] and references therein.

The lower stability of electrogenerated NHCs than electrogenerated NHC–CO_2 adducts (both in the parent imidazolium salt as solvent) was proved according to a voltammetric investigation [30]. As a consequence, the lower catalytic efficiency of free NHC than NHC–CO_2 latent catalyst was ascertained using the benzoin condensation and the oxidative esterification of cinnamaldehyde with benzyl alcohol as test reactions.

6. Hydrogen Bond and Catalytic Activity of NHC

As frequently reported, the chemistry of NHCs is strongly dependent on the lone pair hydrogen bond with donors (Figure 8) [7,16,78–82].

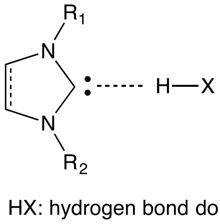


Figure 8. NHC hydrogen bond.

In fact, the NHC lone pair availability influences the NHC catalytic effectiveness (e.g., in an umpolung process); in an isolated NHC this lone pair availability is conditioned exclusively by the NHC-scaffold, but the presence of isolated NHCs (i.e., of NHCs free from any interaction) in the reaction mixtures is questionable. In solutions containing NHC, hydrogen bonds with its parent $NHCH^+$, substrates, or solvent could be effective and the presence of hydrogen bonded aggregates could not be rejected. When the hydrogen bond donor is the parent $NHCH^+$, the aggregate could be regarded as a dimeric structure (Figure 9).

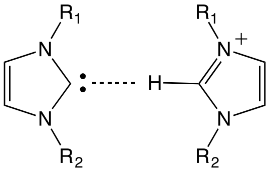


Figure 9. NHC–$NHCH^+$ dimer.

The possible formation of such dimeric structures opens to some intriguing questions about:

- the effective presence of dimeric structures instead of (or in addition to) free NHC;
- the influence of the dimeric partner on the NHC lone pair availability (i.e., on the catalytic efficiency) [16,19,82–84];
- the higher stability of the dimeric structure than that of free NHC; and
- the nature of the "effective" catalyst, i.e., the attack to the active site of the substrate is carried out by free NHC (being the dimeric structure a precursor of free NHC) or by the dimer? In fact, a direct interaction between substrate and dimeric structure could not be rejected.

As a consequence, reaction conditions favoring the formation of dimeric structures could modify the reaction kinetics and the catalytic power of an NHC in a synthesis.

Recently the role of the solvent, of the parent ionic liquid and of the nature of the anion of the ionic liquid in the hydrogen bonds involving NHC was extensively discussed.

It was reported that NHC-catalyzed C–C coupling reaction yielding γ-butirolactones procedes with lower rate and selectivity in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as solvent than in tetrahydrofuran [85].

Hollóczki [7,16] emphasized that this result is related to the formation of a hydrogen bond between NHC and the ring hydrogen atom of $NHCH^+$ (present in IL but not in tetrahydrofuran, Figure 9). Accordingly, NHC should be deactivated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide but not in tetrahydrofuran.

Nevertheless, in 1-ethyl-3-methylimidazolium acetate ionic liquid as solvent, NHC (available from a proton transfer between cation and anion of IL) is relatively highly active in the benzoin condensation and hydroacylation reaction. Hollóczki and coworkers refer to the high hydrogen bond affinity of acetate anion [7,16,86]. Owing to this high affinity, the ring hydrogen atom of $NHCH^+$ is involved in a hydrogen bond with acetate anion instead of NHC. Therefore, in IL containing acetate anion, NHC is free from interactions with the parent cation and could be regarded as free NHC, retaining its high catalytic activity.

Last, we must keep in mind that:

- NHCs could form unexpected hydrogen bonds, as weaker interactions, with the alkyl side chain of imidazolium cation; and
- in organic solvents (such as toluene and tetrahydrofuran (THF)), NHCs are able to form hydrogen bonds with each other, via the ring hydrogen atoms and the divalent carbon atom, yielding short lived dimeric structures (Figure 10) [7].

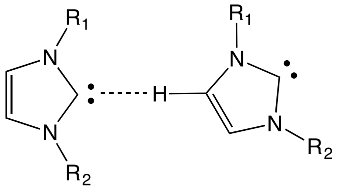
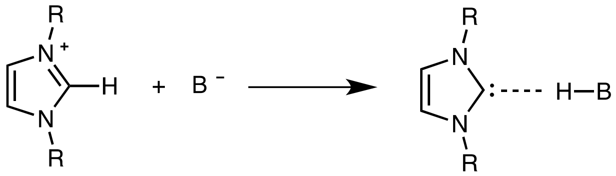


Figure 10. NHC–NHC dimer.

As previously stated, in NHC-catalyzed syntheses, owing to their possible instability, NHCs are often generated in situ via deprotonation of the imidazolium cations by suitable bases purposely added to the reaction mixture.

Hydrogen bond between NHC and the conjugate acid (HB) of the added base could be hypothesized. The presence, in the reaction mixture, of NHC trapped as a hydrogen bonded adduct with HB (instead of free NHC) should be considered (Scheme 8).



Scheme 8. Formation of NHC–HB hydrogen bonded adduct.

In a recent paper, Hollóczki reports an interesting conclusion: "the hydrogen bond between the protonated base and the NHC does not need to cleave before the NHC could attack the electrophilic site of the substrates … the NHC can access the substrate in a manner that the bond between the catalyst and the substrate can be formed parallel to the cleavage of the hydrogen bond … " [7]. As a consequence, the catalytic efficiency of NHC is affected by the presence of the hydrogen bond with the protonated base HB.

The electrochemical methodology allows to generate NHC by direct reduction of $NHCH^+$, avoiding the presence of a base and, consequently, the formation of the hydrogen bonded adduct between NHC and the conjugate acid HB. In this regard, the electrochemical methodology allows thus to simplify the study of the reactivity of NHC, limiting the hydrogen bond formation possibility to the parent cation and the solvent.

Recently, in order to assess the presence or absence of electrogenerated NHCs as hydrogen bonded $NHCH^+$–NHC adducts in solution, NHC-azolium salt-DMF solutions were investigated theoretically via DFT.

A few azolium salts of different structures were selected as model compounds (Figure 7). The values of the binding energies and distances of the hydrogen bonded adducts are reported in Table 4 [32].

Table 4. $NHCH^+$–DMF and $NHCH^+$–NHC adducts calculated binding energies and H-bond distances. Reproduced with permission from [32]. Copyright Wiley-VCH, 2016.

$NHCH^+$/NHC	Binding Energies (kJ/mol)		$NHCH^+$–NHC [1] H-Bond Distance [2] (Å)
	$NHCH^+$–DMF	$NHCH^+$–NHC	
2a/1a	−76.75	−88.41	2.00
2c/1c	−84.88	−88.51	1.96
2e/1e	−78.65	−92.59	2.03
2f/1f	−79.78	−93.34	2.03

[1] Substrates as reported in Figure 7; [2] calculated by DFT.

The values of the reported binding energies suggest the formation of dimers $NHCH^+$–NHC (instead of $NHCH^+$–DMF adducts) in the case of azolium and thiazolium cations (**2a**, **2e**, and **2f**) and related carbenes (**1a**, **1e**, and **1f**), but not in the case of triazolium cation **2c** and the related carbene **1c**. Accordingly, in DMF solutions triazole carbene **1c** is free from hydrogen bond with the parent cation $NHCH^+$. These results are significant enough, as the catalytic activity of free NHC should be higher than one of the hydrogen bonded dimer $NHCH^+$–NHC.

The authors are now engaged in a further investigation to verify the role of the scaffold and of the solvent in the formation of hydrogen bonded $NHCH^+$–NHC adducts, i.e., to clarify the experimental conditions able to support the presence of free NHC.

7. Spontaneous or Induced Formation of NHC

As above reported, the formation of NHC from azolium salts $NHCH^+X^-$ requires the presence of deprotonating or reducing agents purposely added to the reaction mixture. In this context, the literature reports a few cases of NHC-catalyzed reactions performed using azolium salts $NHCH^+X^-$ without addition of any deprotonating or reducing agent. We wish to summarize these reactions:

- The Claisen rearrangement (reaction of kojic acids with ynals yielding dihydropyranones; yields 75%–98%) was carried out using azolium salts as precatalysts in the absence of added base [87]. The authors suggest that the counter-ion X^- (Cl^- or CH_3COO^-) plays the role of base generating a trace amount of NHC, which quickly attacks the aldehyde to initiate the catalytic cycle. Azolium salts with less basic counter-ions such as SbF_6^- or ClO_4^- are unreactive.
- The benzoin condensation was carried out by adding a benzaldehyde to neat 1-ethyl-3-methyl- or 1-butyl-3-methylimidazolium acetate in excess. Benzoins were isolated in good yields (60%). No products were isolated with ionic liquids containing non-basic anions such as methanesulfonate ion. The efficiency of $NHCH^+X^-$ as precatalyst was related to the ability of the counter-ion CH_3COO^- to deprotonate $NHCH^+$ to NHC [86].
- 1-ethyl-3-methylimidazole-2-thione was isolated from an equimolar mixture of S_8 and 1,3-dialkylimidazolium acetate (24 h at 25 °C; yield 50%) [88]. No reaction was observed with S_8 using 1,3-dialkylimidazolium salts containing other anions as Cl^-, HSO_4^-, SCN^-. According to the opinion of the authors, imidazolium acetate acts as base yielding NHC, which reacts with S_8 giving thione.

Theoretical calculations showed that, in $NHCH^+CH_3COO^-$, the acetate anion deprotonates the imidazolium cation yielding NHC and acetic acid (AcOH). Spectroscopic analyses report results depending on pressure and temperature. As an example, photoelectron spectroscopy shows presence of the hydrogen bonded complex NHC-AcOH as the dominant structure in 1-ethyl-3-methylimidazolium acetate EMIM-OAc vapor phase, while the mass spectrum shows the presence of both NHC and AcOH (in agreement with the low pressure during this analysis) [89].

Sander et al. reported that, if the vapor of EMIM-OAc is trapped in solid argon or nitrogen at 9 K, only AcOH and NHC are detected by IR spectroscopy, but no ionic species. This result could indicate that, during the evaporation of EMIM-OAc, a proton transfer occurs between acetate anion and $NHCH^+$ yielding NHC [90].

The topic of the "spontaneous, induced, or prohibited NHC formation in neat $NHCH^+X^-$ ionic liquids" was further tackled in recent papers [91,92]. $NHCH^+OAc^-/CO_2$ systems were investigated and the formation of *N*-heterocyclic carbene–carbon dioxide adducts ($NHC–CO_2$) was discussed. The authors inferred that "the occurrence of trapping and catalytic reactions in $NHCH^+OAc^-$ that represent NHC reactivity does not necessarily mean that NHCs are actually present in the neat $NHCH^+X^-$, it means only that they are accessible".

In fact, NHC formation in neat $NHCH^+OAc^-$ could be not spontaneous, but induced by the reactants and the overall kinetics of the process should be reconsidered.

As regards the question of the spontaneous formation of NHC, we should consider the values of the pK_a of NHC ($pK_a > 14$ in dimethylsulfoxide -DMSO) and of acetic acid ($pK_a = 12$ in DMSO) [45]. These pK_a values suggest that the proton exchange equilibrium between $NHCH^+$ and CH_3COO^- is strongly shifted to left (Scheme 9). Therefore, to verify the presence and the concentration of NHC via conventional methodology could be questionable.

$$\mathrm{NHCH^{+} + CH_3COO^{-} \rightleftharpoons NHC + CH_3COOH}$$

Scheme 9. Proton exchange equilibrium between azolium cation and acetate anion.

As regards this proton exchange equilibrium and the related kinetic parameters, the electrochemical methodologies allow investigating the effect of:

- the addition of CH_3COOH to solutions containing NHC; and
- the addition of CH_3COO^- to solutions containing $NHCH^+$.

7.1. Effect of the Addition of Acetic Acid to Solutions Containing NHC

As previously reported [32], the voltammetric curves of DMF solutions of NHCs show an anodic peak related to NHC oxidation. Therefore, a simple voltammetric analysis allows to ascertain the presence of NHC in a solution. Moreover, the oxidation peak current is proportional to NHC concentration. It is thus possible to evaluate the life time of NHC and its kinetics of degradation simply repeating the voltammetric analysis during time and measuring the NHC anodic peak current.

The NHC solutions were obtained by cathodic reduction of DMF solutions containing $NHCH^+X^-$ ionic liquids, under galvanostatic conditions. The obtained NHCs **1a–f** (Figure 7) are marked by different scaffolds and different pK_a values. The NHC life time is strongly dependent on the NHC structure. The addition of an acid (acetic acid) or a base (acetate ion) to NHC solutions has a great impact on NHC life time.

Comparing the behavior of NHC solutions in the absence and in the presence of acetic acid, it can be noted that in the presence of CH_3COOH the degradation rate of imidazole based NHCs (**1a** and **1b**) increases significantly, while the ones of triazole- (**1c**) and thiazole- (**1d–f**) based NHCs are less influenced. In any case, the voltammetric curves show that, 100 min after the addition of acetic acid to the NHC solutions, 10% of **1a** and **1b** and >60% of **1c–f** (with respect to the NHC amount initially electrogenerated) were still involved in the oxidation process at the anodic surface. These surprising results suggest that the efficiency of the protonation process of NHC by acetic acid is affected not only by the pK_a values of NHCs, but also by the kinetics of the proton exchange reaction. The presence of NHC 100 min after the addition of acetic acid can in fact be explained by slow kinetics.

Moreover, it should be kept in mind that the rate of NHC degradation is evaluated measuring the current of NHC anodic peak. This current is due to the oxidation of both the NHC initially present in the solution and the NHC instantly regenerated at the anodic surface from $NHCH^+$ by the proton exchange equilibrium in Scheme 9. In these experimental conditions $NHCH^+$ can thus be regarded as an "NHC reservoir". Accordingly, the anodic current could not be suppressed even by addition of acetic acid.

7.2. Effect of the Addition of Acetate Anion to Solutions Containing NHCH+

The effective ability of the voltammetric methodology to study the proton exchange reaction between $NHCH^+$ and CH_3COO^- was also demonstrated analyzing the voltammetric behavior of DMF solutions containing these two reactants [93]. Moreover, the same study was carried out using a base, DBU, which was reported to be strong enough to deprotonate $NHCH^+$. The considered azolium salts $NHCH^+X^-$ **2a** and **2b** and **2d–f** are reported in Figure 7.

Voltammetric curves ($-1.0 \div +2.0$ V vs. SCE) recorded on $NHCH^+X^-$/DMF solutions in the absence and in the presence of DBU or CH_3COO^- (tetrabutylammonium acetate as acetate ion source) were compared. A different behavior was observed between imidazolium and thiazolium salts.

The addition of DBU to imidazolium salts solutions (**2a** and **2b**) caused the appearance of the anodic current corresponding to the oxidation of NHC (otherwise absent), in accordance with the ability of this strong base to deprotonate the imidazolium cation. Contrary, the addition of CH_3COO^- did not modify the voltammograms of these solutions. When the same analysis was carried out with thiazolium salts **2d–f**, both bases caused the appearance of the anodic peak.

Accordingly, in the investigated conditions, DBU is able to deprotonate both imidazolium (**2a** and **2b**) and thiazolium (**2d–f**) cations, while CH_3COO^- can deprotonate only the more acidic thiazolium ones.

In azolium salt-DMF solutions, the proton exchange equilibrium reported in Scheme 9 is certainly affected by the addition of the base CH_3COO^- or of the acid CH_3COOH, and NHC concentration is obviously affected by $NHCH^+$ pK_a. In addition, the kinetics of this equilibrium certainly plays a significant role.

Last, the differences between the analytical methodologies must be kept in mind. In particular, the voltammetric methodology for NHC analysis, due to an EC process of the oxidation peak, could shift to right the proton exchange equilibrium at the interface electrode/solution. Accordingly, the oxidation peak current could involve $NHCH^+$, in addition to the NHC initially present. Therefore the voltammetric analysis is able to prove the effectiveness of the equilibrium involving the presence of NHC by the appearance of its oxidation peak in the recorded voltammograms. Nevertheless a direct knowledge of the NHC concentration from the values of the current of the anodic peak could be questionable.

8. Conclusions

Different authors investigated the electrodic activity of the Bronsted acid–base system $NHCH^+$/NHC and reported the cathodic reduction of $NHCH^+$ to NHC and the anodic oxidation of NHC. The reduction and oxidation peak potentials are affected by the structure of the acid–base system, by the presence and nature of the solvent, and by the electrodic material. The values of the cathodic and anodic current could be assumed as an indirect measurement of the concentration of $NHCH^+$ and NHC, respectively. Therefore, the electrochemical methodology allows achieving two targets:

- NHC generation by electrolysis of $NHCH^+X^-$ ionic liquids (neat or in solution), i.e., by cathodic reduction of $NHCH^+$. This procedure, alternative to the deprotonation of $NHCH^+$ via a suitable base B^- purposely added to $NHCH^+X^-$, allows to avoid the presence of the base conjugate acid BH in the final mixture. The presence of the acid HB could strongly decrease the catalytic activity of NHC, owing the possible formation of the hydrogen-bond adduct NH–HB.

- NHC presence determination, by the appearance in the voltammograms of its oxidation peak. The NHC concentration is evaluated from the current of this peak.

Some results, related to electrochemical procedures, seem significant.

Electrolyses of $NHCH^+X^-$ and subsequent voltammetric analyses allow evaluating the stability of NHC. The effect of the structure, solvent, and nature of the counter ion X^- on the half-life of NHC was investigated.

Conventional acidity and nucleophilicity scales of $NHCH^+$ and NHC were suggested using the reduction and oxidation potentials obtained from the voltammetric curves. The results are consistent with previously reported data and qualitative indications.

Recently, a procedure able to catch and release CO_2 cyclically via electrogenerated NHCs was reported. As regards the question of the increase in the CO_2 emission and control of the global climate change, we must keep in mind that NHC forms adducts with CO_2 (60 °C) and releases the caught CO_2 by heating (120 °C). The procedure is able, in a series of 10 cycles, to catch and release 4 mol of CO_2 per Faraday consumed during the electrochemical generation of NHC.

The chemistry of NHCs and of their precursors $NHCH^+$s is affected by the possible presence of hydrogen bond. In neat $NHCH^+X^-$ or in organic solvent (e.g., DMF), the formation of hydrogen bonded $NHCH^+$-solvent and $NHCH^+$–NHC adducts was suggested. In this regard, the role of NHC structure, solvent, and counter ion X^- is significant. The formation of $NHCH^+$–NHC adducts decreases the catalytic power of NHC. Concerning this, the voltammetric analysis provides a picture consistent with the results derived from ab initio calculations.

Last, the intriguing question of spontaneous or induced formation of NHC from particular ionic liquids may be regarded from "the viewpoint of the voltammetric measurements". In neat $NHCH^+OAc^-$, an acid–base equilibrium, if operative, is strongly shifted towards the reagents and is unable to generate a significant concentration of NHC, according to the pK_a values of $NHCH^+$ and CH_3COOH. Nevertheless, the voltammetric analysis can evidence the presence of NHC via its oxidation peak and the influence, on this equilibrium, of acetic acid or acetate anion can be studied. The anodic surface draws NHC from $NHCH^+$ via the described equilibrium. The authors hypothesize that this draw could help the recording of the anodic current relate to the oxidation of NHC, i.e., the check of NHC, even at very moderate equilibrium concentration.

Some authors reported the significant catalytic activity of the azolium salt $NHCH^+OAc^-$ in the absence of any base purposely added to the reaction mixture. The presence of NHC, derived from the acid–base equilibrium involving $NHCH^+$ and OAc^-, was never directly ascertained in the reaction mixture with classical methodologies. Therefore, the substrate, involved in the catalytic process, could play a role similar to that one of the anodic surface in electrochemical measurements. The substrate draws NHC from $NHCH^+$ via the equilibrium. This draw enables the catalytic action of NHC even at very low equilibrium concentrations.

In conclusion, simple electrochemical methodologies could be a powerful support to the knowledge of the chemistry of $NHCH^+/NHC$ system. Significant results could be achieved in synthetic investigations as regards the generation of NHC in green conditions at prefixed and controlled concentration, and in kinetic investigations as regards the problem of checking the presence of NHC and verifying its concentration.

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