



# Azolium and acetate ions in DMF: Formation of free N-heterocyclic carbene. A voltammetric analysis



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## ABSTRACT

In order to reveal the possible formation of free N-heterocyclic carbene (NHC) in DMF-azolium and acetate solutions, the proton exchange equilibrium between azolium cations and  $\text{CH}_3\text{COO}^-$  was investigated (by cyclic voltammetry) by adding  $\text{CH}_3\text{COOH}$  or tetrabutylammonium acetate to DMF solutions of imidazolium or thiazolium salts of different acidity.

The voltammetric analysis confirms that the deprotonation of the azolium cation by  $\text{CH}_3\text{COO}^-$  (with the formation of free NHC) is significant in the case of the more acidic thiazolium cations, while it is not effective with the less acidic imidazolium ones.

Accordingly, the NHC-catalyzed benzoin condensation was carried out in DMF solutions of azolium salts, tetrabutylammonium acetate, and benzaldehyde. Benzoin was isolated only starting from the more acidic thiazolium salts.

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## 1. Introduction

During the last decades, N-heterocyclic carbenes (NHCs) have been frequently utilized as cheap and environmental friendly organocatalysts in a plethora of organic syntheses [1–6].

Owing to their possible instability, NHCs are often generated in situ by deprotonation of the parent azolium salts with suitable bases.

Although the addition of a base to the reaction mixture could be regarded as necessary, some authors reported NHC-catalyzed syntheses using imidazolium acetate in the absence of any exogenous base [7–11].

The possible presence of free NHC in dialkylimidazolium acetate (due to the ability of  $\text{CH}_3\text{COO}^-$  to deprotonate the imidazolium cation, which can be seen as the protonated carbene,  $\text{NHCH}^+$ ) was extensively discussed [12].

Although the formation of NHC from dialkylimidazolium acetate was proven in the gas phase, no NHC was directly detected in pure IL or in solution, but its presence was inferred by its catalytic activity in neat IL [13,14]. In fact, the values of  $\text{pK}_a$  of dialkylimidazolium cation and of acetic acid in DMSO ( $\text{pK}_a$ : 22 and 12 respectively [15,16]) make questionable the presence of a detectable amount of free NHC in a

solution of dialkylimidazolium acetate in the absence of an exogenous base.

Recently, we reported a simple electrochemical procedure to ascertain the presence of free NHC in organic solvents [17]. Cyclic voltammeteries of solutions containing an NHC (in a detectable amount) showed the carbene presence by its oxidation peak. The absence of NHC in 1-butyl-3-methylimidazolium acetate ( $\text{BMIm}^+\text{CH}_3\text{COO}^-$ )-DMF solution without an exogenous base was emphasized. Nevertheless, it cannot be excluded that DMF solutions of more acidic azolium acetates could contain a small amount of free NHC.

In the present communication, we wish to report that cyclovoltammetric measures are able to reveal the possible presence of NHC **1a-e** (also in small amount) in DMF solutions of azolium and  $\text{CH}_3\text{COO}^-$  and to investigate the different behavior of imidazolium or thiazolium and  $\text{CH}_3\text{COO}^-$  in the proton exchange equilibrium reaction.

## 2. Experimental

Ionic liquids **2a**<sup>+</sup>**BF**<sub>4</sub><sup>-</sup>, **2b**<sup>+</sup>**Cl**<sup>-</sup>, **2c**<sup>+</sup>**Cl**<sup>-</sup>, and  $\text{Bu}_4\text{N}^+\text{AcO}^-$  were purchased from Iolitec, **2d**<sup>+</sup>**BF**<sub>4</sub><sup>-</sup> and **2e**<sup>+</sup>**BF**<sub>4</sub><sup>-</sup> were synthesized according to the literature [18,19]. ILs were used after being kept at reduced pressure at 70 °C for 24 h. The cyclic voltammetry instrument was previously described [17]. A 492/GC/3 Amel microelectrode was employed, using a Pt wire counter electrode and modified saturated calomel electrode as reference electrode [20]. The scan rate was  $\nu = 0.2 \text{ V s}^{-1}$ .

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All cyclic voltammeteries were recorded on 5 mL of DMF-0.1 M azolium salt at 25 °C.

Electrolyses were carried out in the same conditions as the voltammeteries, under galvanostatic conditions ( $I = 20 \text{ mA cm}^{-1}$ ) in a divided cell, and stopped after 31 C. Then the catholyte was analyzed by voltammetry.

### 2.1. Benzoin condensation

0.5 mmol of azolium salt, 1.0 mmol of  $\text{Bu}_4\text{N}^+ \text{AcO}^-$  (or DBU), and 1.0 mL of DMF were stirred at rt for 5 min, then benzaldehyde (2.0 mmol) was added and the solution was kept at 65 °C for 2 h [21]. Usual workup gave the results reported in Table 1.

## 3. Results and discussion

Cyclic voltammetry is a technique able to evaluate in which cases the acetate ion is a base strong enough to deprotonate an azolium cation. For this purpose, imidazolium (less acidic) and thiazolium (more acidic) salts were considered. The structures of carbenes **1a–e** and of the corresponding azolium salts are reported in Fig. 1.

The extent of the deprotonation of azolium cations (**2a–e**<sup>+</sup>) by acetate ion to yield the corresponding NHCs **1a–e** and acetic acid (in the equilibrium Reaction 1, see below) can be at first studied evaluating the effect on the cyclic voltammetry of the addition of acetic acid to a azolium salt–DMF solution.



In fact, the voltammetric curves of azolium salts in DMF (Fig. 2, black curves) are characterized by

- a reduction peak related to the monoelectronic reduction of the azolium cation to NHC and  $\text{H}_2$  ( $E_{p(\text{red})} < -2.5 \text{ V vs SCE}$ );
- an oxidation peak, in the reverse scan, related to the monoelectronic oxidation of NHC electrogenerated in the direct scan ( $E_{p(\text{ox})} > 0.0 \text{ V vs SCE}$ ) [22,23].

As regards **2b**<sup>+</sup>  $\text{Cl}^-$ , **2c**<sup>+</sup>  $\text{Cl}^-$ , **2d**<sup>+</sup>  $\text{BF}_4^-$ , and **2e**<sup>+</sup>  $\text{BF}_4^-$  DMF solutions, the voltammetric curves show a pre-peak in addition to the major oxidation peak. The current of these pre-peaks is dependent on the structure of the azolium salt. The presence of the two oxidation peaks required a further investigation to correlate them to the oxidation of the electrogenerated NHC.

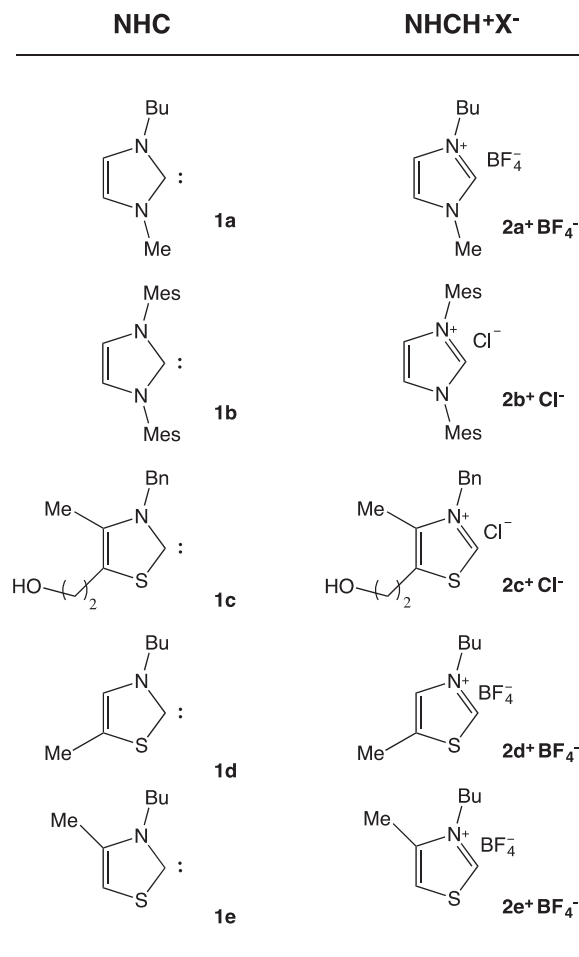
Azolium salts–DMF solutions were electrolyzed in a divided cell under galvanostatic conditions. The voltammetric curves recorded on the catholyte (starting potential  $-1.0 \text{ V}$ ) show, in the anodic scan, only one oxidation peak (no pre-peak, Fig. 2, inserts).

Therefore, the presence of a pre-peak could be related to the history of the electrodic surface during the cathodic scan. We suppose that the pre-peak and the major peak could be related to the oxidation of NHC both at the electrodic surface and in the bulk of the solution.

**Table 1**  
Benzoin condensation.\*

Entry	Azolium salt	Benzoin, yield
1	<b>2a</b> <sup>+</sup> $\text{BF}_4^-$	Traces
2	<b>2b</b> <sup>+</sup> $\text{Cl}^-$	2%
3	<b>2c</b> <sup>+</sup> $\text{Cl}^-$	46%
4	<b>2d</b> <sup>+</sup> $\text{BF}_4^-$	12%
5	<b>2e</b> <sup>+</sup> $\text{BF}_4^-$	13%

\* 0.5 mmol azolium salt, 1.0 mmol  $\text{Bu}_4\text{N}^+ \text{AcO}^-$ , 1 mL DMF, 5 min rt. Then 2.0 mmol benzaldehyde, 65 °C, 2 h.



**Fig. 1.** Structures of NHCs and azolium salts. ( $\text{NHCH}^+ \text{X}^-$ ) considered in this work (Bn:  $\text{CH}_2\text{Ph}$ ; Mes: 2,4,6-trimethylphenyl).

### 3.1. Addition of acetic acid

#### 3.1.1. Cathodic scan

The addition of acetic acid to the azolium salt–DMF solution has a remarkable effect on the peak current relative to the electrogeneration of NHC (cathodic scan). In fact, the reduction peak current in the presence of  $\text{CH}_3\text{COOH}$  ( $i_{p(\text{red})}$ , red and blue curves) is higher than that recorded in its absence ( $i_{p(\text{red})}^0$ , black curve, Fig. 2).

These higher values of peak current could be due to

- the direct reduction of  $\text{CH}_3\text{COOH}$  to  $\text{H}_2$  and  $\text{CH}_3\text{COO}^-$ ;
- a proton exchange between  $\text{CH}_3\text{COOH}$  and electrogenerated NHC, yielding again the azolium cation, the increase of the current being caused by the reduction of this re-formed azolium cation (reverse of Reaction 1).

Although the peak potential for the reduction of acetic acid in our experimental conditions is lower than  $-3.5 \text{ V}$ , we cannot exclude a minimal<sup>2</sup> cathodic reduction at higher potentials, especially at high concentrations. Moreover, according to the values of  $\text{pK}_a$  in DMSO (acetic acid: 12; imidazolium salts: 20–22; thiazolium salts: 16–19 [24]), the  $i_{p(\text{red})}/i_{p(\text{red})}^0$  ratio of imidazolium cations **2a**<sup>+</sup> and **2b**<sup>+</sup> is higher than that of thiazolium cations **2c**<sup>+</sup>, **2d**<sup>+</sup> and **2e**<sup>+</sup> (i.e., a higher protonation extent for the more basic NHCs), and this ratio increases on increasing the

<sup>2</sup> A substantial co-reduction of acetic acid during the cathodic scan of the cyclic voltammetry must be excluded, as the increase in the cathodic current is very different for the different salts in the presence of the same concentration of acetic acid.

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