Synthesis of a new 2,4,5-triphenyl-1H-imidazolium-paratoluenesulfonic acid salt: Thermal and electrochemical stability

Abdelwaheb Dhahri, Amel El Ghali, Mohamed Hassen V Baouab[*]

Laboratoire de Microélectroniques et Instrumentations, Université de Monastir, Faculté des Sciences de Monastir, Boulevard de l'environnement, 5019 Monastir, Tunisie

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Abstract: A new Imidazolium salt named 2,4,5-triphenyl-1H-imidazolium-paratoluen sulfonic acid have been synthesized from 2,4,5-triphenyl-1H-imidazole and paratoluen sulfonic acid. The structure of the obtained compound has been established on the basis of FTIR, ^{1}H NMR and ^{13}C spectral data. The stability of this novel product was confirmed by thermal and electrochemical characterizations.

Key words: Imidazolium salt; Anion Tosylate; Thermal and Electrochemical stability.

Résumé: Un nouveau sel d'imidazolium, l'acide 2,4,5-triphényl-1H-imidazolium-para-toluène sulfonique a été synthétisé à partir de l'acide paratoluène sulfonique et du 2,4,5-triphényl-1H-imidazole. La structure du composé obtenu a été caractérisée par les données spectroscopiques FTIR, RMN ^{1}H et ^{13}C. La stabilité de ce nouveau produit est confirmée par les caractérisations thermiques et électrochimiques.

Mots-clés: Sel d'Imidazolium; Anion Tosylate; Stabilité Thermique et Electrochimique.

INTRODUCTION

Ionic liquids (ILs) are defined as salts which exclusively consist of cations and anions, and which have a melting point at around the room temperature [1]. The field of ILs is growing at a very fast rate because of their unique chemical and physical properties over those of conventional solvents in many aspects. These include negligible volatility, inflammability, high thermal stability, high capacity of dissolving and easy recyclability [2]. ILs has been used in a broad variety of synthesis [3], separation [4], electrochemistry [5], fuel cells [6], etc. In addition to that, the majority of the research and industrial activities related to ILs were associated to their applications as environmentally friendly –green- organic solvents [7]. One of the hot topics in ILs research is to develop new types of ionic liquids with special physicochemical characteristics and special applications. Though thousands of ILs has been expanded, most of them are based on imidazolium. In this field, ILs containing imidazolium cations and anions received an important attention for application in electrolyte [8] materials as well as battery technology [6]. Imidazole functional group plays important roles in various bioactive products. In recent times, the attention in this heterocyclic system has widened as it is a precursor to a class of compounds called room temperature ionic liquids [9]. Ionic liquids, of which imidazolium salts are most widely used, have grown initial interest of synthetic chemists and continue to hold their attention as reaction catalysts or promoters [9]. The general syntheses of ionic liquids based on nitrogen-containing heterocycles, imidazolium, involve a consecutive quaternisation-anion metathesis procedure [10]. This induced the creation of undesirable by-products and impurities due to multiple reactions [11]. The main objectives of this work are as follows: (i) synthesis and characterization of 2,4,5-triph enyl-1H-imidazole via condensation reaction of benzil, aldehyde, ammonium acetate and catalyst [sulfuric acid immobilized onto silica gel]) (ii) synthesis of

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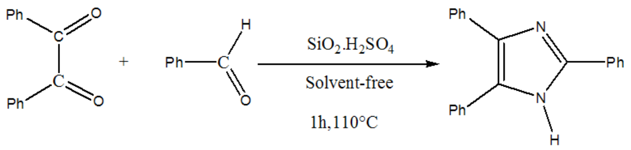
[*] Corresponding author, e-mail address : hbaouab@yahoo.fr



Scheme 1. Sulfuric acid immobilized on silica gel used for catalyzed synthesis of 2,4,5-triphenyl imidazole (a).

imidazolium salt, for the first time, from quaternisation reaction by paratoluen sulfuric acid (tosylate anion) (iii) characterization of 2,4,5-triphenyl-1H-imidazole and imidazolium obtained salt using FTIR, ^{1}H and ^{13}C NMR (iv) examination of thermal and electrochemical stability of salt were performed by TGA, DSC and cyclic voltammetry, respectively.

EXPERIMENTAL

1. Materials

All the reagents [Benzyl ($C_{14}H_{10}O_2$), Sulfuric acid (H_2SO_4), silica gel, acetonitrile (C_2H_3N), ethanol 96% (C_2H_6O), para toluene sulfonic acid ($C_7H_8O_3S$), ammonium acetate ($C_2H_7O_2N$), benzal -dehyde (C_7H_6O)] were supplied by Sigma Aldrich Company and used without further purification.

2. Preparation of the 2,4,5 triphenyl-1H-imidazole

The synthesis of 2,4,5 triphenyl-1H- imidazole was carried out in two steps using a similar method reported previously [12], as can be seen in (Figure 1). The first step dealt with the preparation of the $H_2SO_4{\cdot}SiO_2$ catalyst. For this, a concentrated H_2SO_4 solution (3 mL) was added to slurry of silica gel (10g, 200 - 400 mesh) in dry diethyl ether (50 mL). The mixture was shacked for 5 min. Afterwards, the solvent was evaporated under reduced pressure to obtain dry $H_2SO_4{\cdot}SiO_2$ catalyst which was then heated at 120 °C for 3 h. It can be noted that the H_2SO_4 immobilized on SiO_2 was used as a catalyst for synthesis of several organic compounds [13-18]. The second step (preparation of 2,4,5 triphenyl-1H- imidazole) was conducted as follows. In a round bottomed flask were placed 1 mol of benzaldehyde, 1 mol of benzyl, 5 mol of ammonium acetate and 0.1 g of $H_2SO_4{\cdot}SiO_2$, as a catalyst. The bottomed flask was stirred for 1h at 110 °C. After achievement of the reaction, the mixture was cooled to room temperature and the final product was washed with water and separated by filtration to give the crude product. The material was then recrystallized from ethanol 96% to afford a pure product. The resulting product was then dried at 60 °C under vacuum for 24 h.

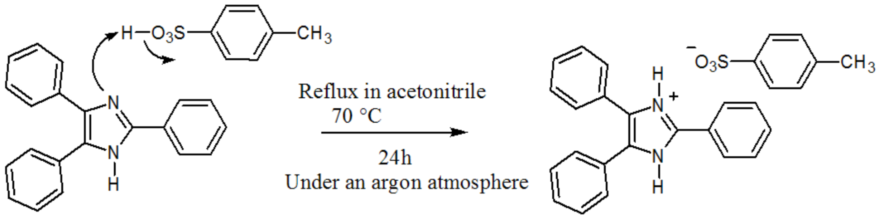
3. Synthesis of imidazolium salt

In a 100 mL three-necked flask fitted with a dropping funnel and reflux condenser are placed 1mol of 2,4,5-triphenyl-1H-imidazole that was dissolved in 20 mL of acetonitrile. The mixture is heated in an oil bath under reflux at 70°C for 1 h, and then 1mol of para-toluenesulfonic acid, which was dissolved in 20 mL of acetonitrile, is added drop wise, while stirring and maintaining the temperature at 70°C. When the addition was complete (after about 2h), the mixture was stirred for 24 h at reflux (70°C) under an argon atmosphere. After the desired reaction time, the material is removed and washed thoroughly with a diethyl ether anhydrous solution for its purification. The obtained product was then dried at 60 °C under vacuum for 24 h. The synthesis reaction of imidazolium salt is presented in (Figure 2).

CHARACTERIZATION OF THE PREPARED SUPPORTS

1. Fourier transform-infrared spectroscopy (FTIR)

IR analyses were carried out using Nicolet® 510M spectrophotometer, Faculty of Sciences of Monastir, Tunisia. About 1 mg of the sample was mixed with 100 mg of spectroscopic grade KBr, and the FTIR spectra were recorded from 4000 cm^{-1} to 500 cm^{-1} in transmission mode.



Scheme 2. Synthesis of imidazolium salts (b) using 2,4,5-triphenyl imidazole and p-toluenesulfonic acid.

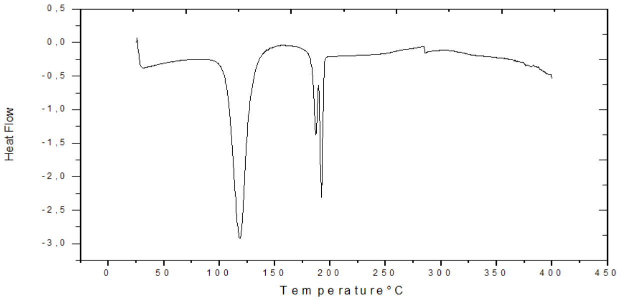


Figure 1. Thermogram DSC of imidazolium salt.

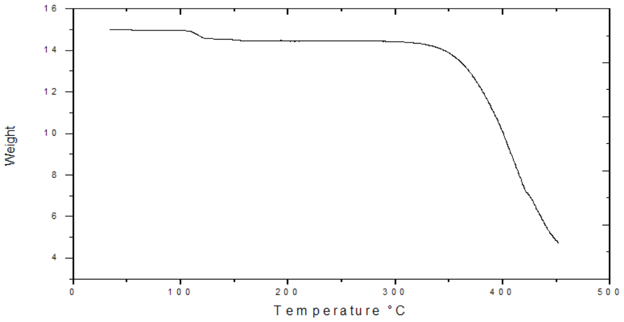


Figure 2. thermogram TGA of imidazolium salt.

2. Thermo Gravimetric (TGA) and Differential Scanning Calorimetry (DSC) analysis

The thermal behaviors of the synthesized compounds were examined by differential scanning calorimetry (DSC) under azote atmospheric conditions at a scanning rate of 10°C/ min. Each product was heated from 25 to 400° C.

3. Nuclear magnetic resonance (NMR)

^{1}H NMR and ^{13}C spectra in solution were obtained with a standard Bruker AV 300 MHz, Faculty of Sciences of Monastir, Tunisia. The spectrum of the salt is stored in $CDCl_3$. The positions of peaks (chemical shift) are δ scale data and expressed in parts per million (ppm).

4. Cyclic voltammetry

Cyclic voltammetry (CV) measurements of imidazolium salt were performed at room temperature with a scan rate of 100 $m.s^{-1}$ from -3 V to 3 V using an electrochemical analyzer including a potentiostat/galvanostat VoltaLab 10 assisted by a computer, Faculty of Sciences of Monastir, Tunisia. The product concentration was fixed to 0.1M. In this analysis, imidazolium salt was used as the supporting electrolyte.

RESULTS AND DISCUSSION

Several methods are used in the synthesis of the ILs and the imidazolium salts. Generally, the synthesis and purification of ILs are difficult [11]. The synthesis of this kind of products is usually performed using two steps namely quaternerisation and metathesis reactions of the anion and the halide salt [19-21]. This induced the formation of undesirable by-products and impurities due to multiple reactions. However, in this study, the proposed protocol used for the preparation of imidazolium salt was only based on a quaternisation [22-24] reaction. In fact, the protonation of the imidazole by a p-toluene sulfonic acid leads directly to imidazolium desired salt. In addition to that, the applied method gives reliable result as can be earlier shown in this paper.

1. Thermal stability of imidazolium salts

Typical DSC thermogram of the imidazolium salt is shown in (**Figure 1**). This Figure reveals the existence of an endothermic peak at 120 °C which could be attributed to the melting Temperature of the synthesized salts. The DSC curve illustrates a second endothermic peak at about 198°C corresponding to the rearrangement of the hydrogen atoms. The degradation of the imidazolium salt is beginning at 330°C.

(Figure 2) illustrates the dynamic TGA curve of the imidazolium salt which confirmed the DSC obtained results. It display a loss of mass in 100 °C due to moisture evaporation and about 0.81% mass disappears during this process. As can be seen, this loss is low and it could be attributed to the hygroscopic character of our salt since it absorbs the moisture. In addition to that, the TGA thermogram reveals the stability of the obtained product until a temperature of 330°C in which appears the degradation beginning of the imidazolium salt.

(Figure 3) shows cyclic voltammetry curves of the synthesized imidazolium salt. As can be seen, the oxidation and reduction voltammogram peak positions were observed at 2.34 V and 0.7 V, respectively. The obtained results revealed the stability of the prepared imidazolium salt [25, 26].

Generally, the application of imidazolium salts in electrochemistry requires good thermal and electrochemical stability. The results obtained in this study confirmed the thermal stability importance of synthesized imidazolium salt up

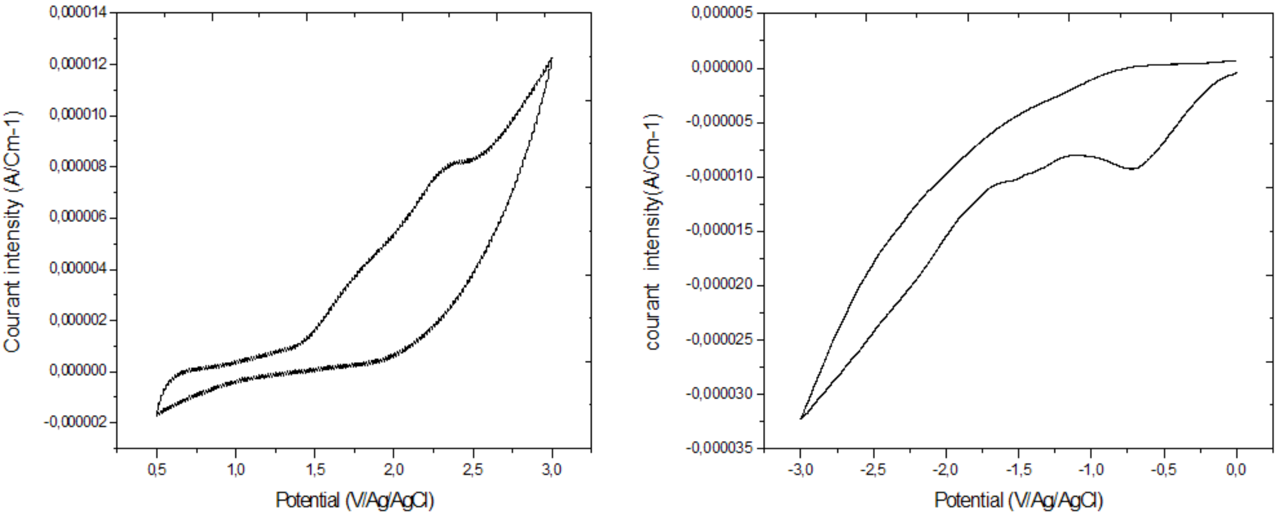


Figure 3. Cyclic voltammetry of imidazolium salts with V_b= 100 m/s and C= 0.1 M.

330 °C and electrochemical stability up 2.34 V. This stability depends on many factors such as the symmetry of the molecule, the structure of cation and anion [23]…, etc. In this case the thermal and electrochemical stability depends of size of cation and more precisely the effect of the phenyls group substituent.

2. The Spectral Data for imidazolium salt and the Selected Compound

2,4,5-Triphenyl-1H-imidazole (a): Yield=90%, Mp 272°C - 274°C. FTIR (KBr, cm^{-1}): 3450, 2961, 1635, 1590. ^1H NMR (300 MHz, DMSO-d6): δ = 12.70 (s, 1H), 8.09 (d, 2H), 7.38 - 7.66 (m, 13H). ^{13}C NMR (75 MHz, DMSO-d6) δ: 145.54, 137.12, 135.08, 134.66, 130.96, 130.22, 128.67, 128.33, 128.28, 128.17, 127.92, 127.76, 127.24, 127.09, 126.56, 125.19.

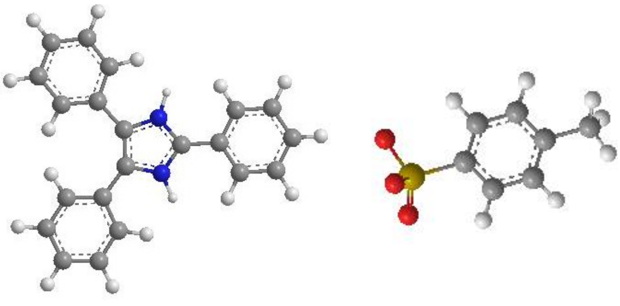
2,4,5-triphenyl-1H-imidazolium-paratoluen sulfonic acid salt (b): Yield=60%, Mp 120°C - 122°C. FTIR (KBr, cm^{-1}): 3393, 3067, 1850, 1649, 1229. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (S, 1H), 7.09 - 7.36 (m, 13H), 6.99 (d, 2H), 7.46 (d, 2H), 8.17 (d, 2H), 13.96 (d, 2H).

3. Proposal of 3D schematic structure of the imidazolium salt

The Possible 3D structures of the cation 2,4,5-triphenyl-1H-imidazolium (a') salt and the anion Tosylate (b') are shown in (Figure 4) and regularly shows the position of atoms in space. It can be noted that the carbon, the nitrogen, the hydrogen, the oxygen and the sulpher atoms are presented in grey, blue, white, red and yellow colors, respectively.

CONCLUSIONS

A specific imidazolium salt was prepared by the reaction at reflux of 2,4,5-triphenyl-1H-imidazole and paratoluen sulfonic acid in acetonitrile. The applied procedure is very important and provides a new idea for the synthesis of a new imidazolium salt without passing through an ion exchange step namely the quaternisation by paratoluen sulfonic acid. The DSC and TGA studies indicate that the imidazolium salt based anion tosylate has an excellent thermal stability until a temperature of 330°C. The study of electrochemical caracterisation by Cyclic Voltammetry also shows a high stability of the product until a value of 2.34 V. The



(a’) (b’)

Figure 4. Proposal of 3D schematic structure of:
(a’) 2,4,5-triphenyl-1H-imidazolium cation
and (b’) Tosylate anion.

obtained results show the importance of the synthesized salt that make it good candidate for the application in many fields, in particularly their use in electrolytic systems.

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