Influence of the Electrode Material on the Electrochemical Behavior of 1H-3-Methyl-4-Ethoxycarbonyl-Benzylidene-Hydrazino-Pyrazole

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Abstract: 1H-3-methyl-4-ethoxycarbonyl-5-substituted-benzylidene-hydrazino-pyrazoles are valuable intermediates in obtaining various heterocyclic systems including pyrazolo triazoles. Literature on electrochemical studies of these compounds is rather scarce to our knowledge. We present the voltammetric behavior of 1H-3-methyl-4-ethoxycarbonyl-5-benzylidenehydrazono-pyrazole in nonaqueous media, using glassy carbon and platinum working electrodes respectively, in order to elucidate the influence of the various electrode materials on the process of anodic oxidation and cathodic reduction. The main goal in using the obtained data is optimizing the electro synthesis of the corresponding pyrazolo-triazoles.

Key words: Cyclic voltammetry, Electrochemistry, Heterocycles, Electrode material

1. Introduction

The scientific interest of 1H-3-aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[5,1-c][1,2,4] triazoles (I Scheme 1) relies mostly on their biological activity [1], their use as precursors in obtaining color photosensitive materials [2-4] as well as inks and toners [5].

Both ways of obtaining the 1H-3-aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[5,1-c][1,2,4] triazoles (I Scheme 1) reside on the cyclization reaction of 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazono-pyrazoles (II) by using either bromine in acetic acid in the presence of anhydrous sodium acetate [2] or using lead tetraacetate in acetic acid [6, 7] (Scheme 1)
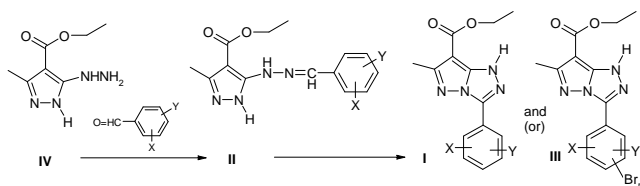
Scheme 1. Synthetic paths in the preparation of the 1H-3-aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[5,1-c][1,2,4] triazoles(I) (III). (Ia, IIa, X=Y=H)

The starting compounds bearing X = -Cl, -CH₃, -NO₂ [2] or -F, -CF₃, -4-pyridil [8] yield the desired pyrazolo-triazoles (I) while the compounds containing -OH, and -OCH₃ respectively give the brominated byproducts (III) [9]. Using lead tetraacetate, the pyrazolo-triazoles (I) bearing one -OH group could not be obtained at all [7].

In order to find a way to overcome these limitations and to electrochemically synthesize the pyrazolo-triazoles (I) with donating groups attached to the phenyl ring, we've studied the electrochemical synthesis of these compounds [10, 11]. Therefore the study of the electrochemical

behavior in nonaqueous media of the unsubstituted hydrazone (**IIa**) (X = Y = H) on Glassy carbon and Pt working electrodes is extremely important in order to get a better perspective on the electrochemical behavior of the latter.

2. Experimental

1H-3-methyl-4-ethoxycarbonyl-5-benzylidenehydrazino-pyrazole, (IIa, X =Y =H) and was obtained according to the literature [2, 7, 8]. Dimethylsulfoxide (DMSO) for synthesis (Fluka) as well as tetra-n-butylammonium tetrafluoroborate (Merck) were used as purchased.

Melting points were recorded with a Boetius PHMK (Veb–Analytik Dresden) apparatus; thin layer chromatography was performed using $60F_{254}$ silica gel plates (Merck) and a mixture of benzene : ethyl acetate = 1:1 as eluant. IR spectra were recorded with a JascoFT/IR-410 Infrared Spectrophotometer using KBr disks and Bruker Avance 300 spectrometers were used for ¹H-NMR and ¹³C-NMR spectroscopy. The characterization of the studied benzylidenehydrazino-pyrazole **IIa** was reported elsewhere [12].

Cyclic voltammetry experiments were performed using a Jaissle 1200PCT potentiostat / galvanostat, coupled to an Agilent 33120A signal generator and an Agilent 34970A data acquisition system using Glassy Carbon (GC) or Pt working electrodes and Pt auxiliary electrodes and were carried out in a single compartment cell with 7 cm⁻³ of electrolyte solution containing $c = 2 \cdot 10^{-3}$ mol·L⁻¹ of substrate at room temperature. No correction was applied to compensate for the solution resistance. The solvent-supporting electrolyte system consisted of dry DMSO and tetra-n-butylammonium tetrafluoroborate. Solutions for all voltammetric analyses were deoxygenated by bubbling

with dry nitrogen and an atmosphere of dry nitrogen was maintained throughout the experiments All potentials were quoted with respect to the Ag/AgCl electrode at room temperature, which corresponds to a potential difference from that of Fc/Fc^+ (Fc = ferrocene) standard redox couple [13] of +0.45 V in DMSO / tetra-n-butylammonium tetrafluororborate.

3. Results and discussion

The electrochemical behavior of the benzylidenehydrazino-pyrazole **IIa** in anhydrous dimethylsulfoxide was investigated by cyclic voltammetry in a three electrode cell using two different electrode materials: Glassy Carbon (GC) and Pt.

The first experiment involves the use of a GC working electrode under the above mentioned conditions. As the potential is scanned towards positive values, the cyclic voltammogram of compound **IIa** on the GC working electrode shows one well defined non-reversible oxidation peak at a potential of about E_{pa} = +1,18 V vs. ref. (Fig.1). Revesral of the scan direction does not reveal any corresponding reduction peaks suggesting that this peak might arrise due to a non-reversible oxidation with the formation of a positively charged intermediate (cation radical or cation depending on the reaction mecahanism). The latter could then react quickly resulting in compounds that are stable in the potential window of interest. This might be due to the fact that the intermediate formed does not undergo reduction processes on the studied potential range or the fact that this intermediate reacts quickly on the timescale of the experiment forming electrochemically stable compounds [14].
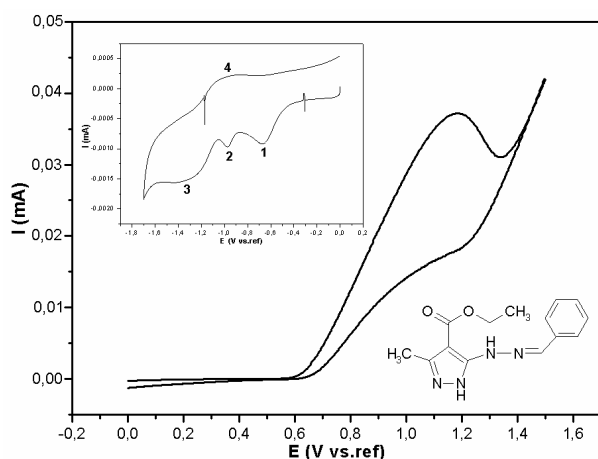

Figure 1. Cyclic voltammogram of **IIa** in anhydrous DMSO. Conditions: substrate concentration, $c = 2 \cdot 10^{-3}$ mol·L^{-1}; supporting electrolyte: tetra-n-butyl ammonium tetrafluororborate; working electrode: GC; auxiliary electrode: Pt; reference electrode: Ag/AgCl; scan rate $50 \cdot 10^{-3}$ V·s^{-1}. Inset: Cathodic scan of **1Ia** under the same experimental conditions.

Scanning towards negative potentials reveals a umber of four peaks all summarized in table 1. The first one appears at about -0.67 V vs. ref. (1 Fig.1 inset). No coupled oxidation peak is recorded on the voltammogram leading to

the assumption that, under the given conditions, a relatively stable anion radical is formed. A second smaller peak appears at -0.97 V vs. ref. possibly due to the reduction of the previously formed radical anion. A broader peak (3, Fig.1 inset) is observed at more negative potentials that may appear due to the adsorption of the previously formed intermediates onto the electrode surface. Sweep reversal shows a weakly defined peak (4 Fig.1 inset) at about -0.93 V caused probably by the cvasi-reversible oxidation of the previously formed intermediate.

The electrochemical behavior of compound **IIa** on the GC electrode reflects an irreversible anodic oxidation of the substrate, which, according to literature [15, 16] may generate a cation radical with the positive charge located at the hydrazonic carbon atom. This intermediate could rapidly form electrochemically stable compounds on the potential window of interest.

Scanning towards more negative potentials reveals four waves the data being summarized in table 1. The first one probably reflecting the formation of a radical anion [17, 18]. This step is followed by the presumable one electron reduction of the latter intermediate. The weakly defined third wave could arise because of adsorption phenomena at the working electrode [14, 19, 20].

In order to further investigate the mechanistic aspects revealed by the electrochemical study on the GC electrode, we studied the electrochemical behavior of compound **IIa** on a Pt working electrode, under the same experimental conditions (Fig.2).
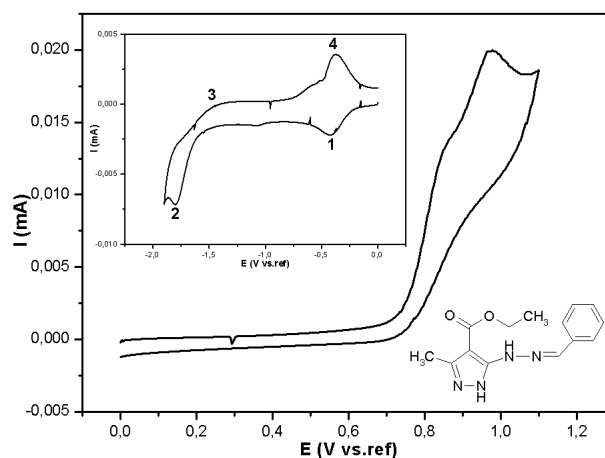

Figure 2. Cyclic voltammogram of **IIa** in anhydrous DMSO. Conditions: substrate concentration, $c = 2 \cdot 10^{-3}$ mol·L^{-1}; supporting electrolyte: tetra-n-butyl ammonium tetrafluororborate; working electrode: Pt; auxiliary electrode: Pt; reference electrode: Ag/AgCl; scan rate $50 \cdot 10^{-3}$ V·s^{-1}. Inset: Cathodic scan of **1Ia** under the same experimental conditions.

Scanning towards more positive potentials reveals a weakly defined peak at E_{pa1} = +0,860 V vs. ref. and a better outlined peak at E_{pa2} = +0,979 V suggesting a stepwise loss of charge. Sweep reversal does not show any reduction waves on the potential window of interest. This behavior might be due to the fact that the intermediate formed in the second oxidation step does not undergo reduction under the given conditions or due to a fast homogenous process

resulting in electrochemically stable products on the potential range of interest [21].

A significant difference could be observed between the potential of the oxidation peak on GC and the second oxidation peak recorded on Pt.

$$(E_{pa})_{GC} - (E_{pa2})_{Pt} = 0,207 \text{ V} \qquad (1)$$

This difference outlines the fact that, along the stepwise mechanism observed on Pt, the oxidation of the substrate occurs at a potential more positive on GC. Taking into account that all experimental conditions have been kept constant except for the working electrode material, we can conclude that the oxidation of compound **IIa** occurs far more easily on the Pt electrode [21].

*TABLE 1. Electrochemical data from cyclic voltammetry for compound **IIa** on various electrode materials [a]*

Electrode material	E_p/V
	+1,186
	-0,672
Glassy Carbon	-0,976
	-1,367
	-0,936
	+0,860
	+0,979
Pt	-0,424
	-1,801
	-1,400
	-0,371

[a]Conditions: compound concentration $c=2 \cdot 10^{-3}$ mol·L^{-1}, ref. Ag/AgCl, scan rate: $50 \cdot 10^{-3}$ V·s^{-1}

Knowing that one - electron anodic oxidations with the formation of radical cations occur more easily on Pt electrodes and two - electrode oxidations are more probable on GC [14] we can assume that the potential gap between the oxidation processes recorded on the two electrode materials resides mainly in the difference between the two reaction mechanisms. The above statement is backed up by the fact that the oxidation peak height on GC is about twice the height of the second oxidation peak recorded using the Pt working electrode. This finding leads to he assumption that in the first step, on Pt the substrate loses only one electron / molecule (Scheme 2) forming the corresponding radical cation [14, 21].
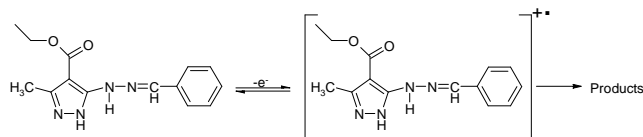
Scheme 2. Proposed anodic oxidation mechanism of compound **IIa** on a Pt working electrode in anhydrous DMSO

The cathodic scan (Fig.2 inset) shows four peaks, at potentials outlined in table 1. The first peak (1) appears at about - 0,4 V vs. ref., meaning that the first reduction step occurs at less negative potentials on the Pt working electrode than on GC. The second reduction peak (2) is situated at about -1,8 V.

Reversing the sweep direction reveals a third weakly defined wave (3) at about -1,4 V which can occur as a result of an oxidation process involving presumably a radical anion formed in the previous reduction step corresponding to peak 2. It is obvious however that at this scan rate the process involves some kinetic limitations taking into account the peak separation of about 380 mV between peaks 2 and 3 [14, 21]. This step which does not follow the cyclic voltammetric criteria of reversibility [22] is cvasi - reversible probably because the slow electron transfer between the electrode and the intermediate formed at the potential corresponding to peak 2 [14, 23].

A well defined peak (4 Fig.2 inset) appears at about - 0.37 V. It may reflect the reoxidation of the intermediate formed at the potential of the first cathodic peak (1). The two peaks fulfill the criteria of reversibility shown below at this scan rate [22, 24].

$$\Delta E_p = \left| E_{pc1} - E_{pc4} \right| = 52 \text{ mV} \qquad (2)$$

The difference between peak potential and half - peak potential (at $i = i_p/2$) can be expressed in the case of a reversible process as follows [21]:

$$\left| E_p - E_{p/2} \right| = 2,20 \cdot \frac{RT}{nF} \qquad (3)$$

At 25°C and assuming a transfer of n electrons / substrate molecule, the above formula can be rewritten as [22]:

$$\left| E_p - E_{p/2} \right| = 56.5/n \text{ mV} \qquad (4)$$

In this case, $\left| E_p - E_{p/2} \right| = 63.7$ mV, a value which, considering the experimental errors validates, along with the ratio of the anodic to cathodic peak currents ($i_{p4}/i_{p1} = 0.87$) the reversibility of the studied process under the given conditions reflecting the major mechanistic differences induced by the change of the electrode material.

4. Conclusion

Comparison of the cyclic voltammograms recorded using the two working electrode materials shows that the anodic oxidation of the substrate takes place in two separate steps on the Pt disk electrode. The first oxidation step occurs at a less positive potential on this material than on glassy carbon, leading to the assumption that on the latter support, the substrate loses only one electron per molecule in each step. Knowing the fact that on glassy carbon organic substrates usually undergo two electron oxidations [14] and taking into account the difference in peak heights, we can assume that on CG the substrate undergoes a two electron oxidation.

The differences in behaviour get even more outlined studying the cathodic reduction of the substrate on the two materials. The first reduction peak occurs at a more negative potential on GC that the corresponding one observed using the Pt electrode, mostly due to a possible

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kinetic limitation of the first reduction step on the GC electrode. The second reduction step takes place at a less negative potential on glassy carbon (Fig.1). The first reduction step on Pt support is totally reversible (Fig.2) while the second one is cvasi reversible. On GC we can observe that both reduction steps are irreversible. It is clearly shown that the reduction mechanism on GC support differs significantly from that on Pt under the same experimental conditions.

The above mentioned findings lead to the assumption that the oxidation as well as the reduction mechanisms and the intermediates formed vary largely depending on the electrode material.

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