Electrochemical properties of N'-ferrocenylmethyl-N'-phenylbenzohydrazide at glassy carbon electrode in aqueous and organic mediums

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ABSTRACT

We carried out a detailed study of the kinetics of oxidation of N'-ferrocenylmethyl-N'-phenylbenzohydrazide (FcX) to ferrocenium ion (FcX$^+$) in aqueous and organic mediums. This study using cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry showed that the FcX/FcX$^+$ redox couple is reversible. The N'-ferrocenylmethyl-N'-phenylbenzohydrazide and ferrocenium ion diffusion coefficients (D) were calculated from these results. In addition, the electron transfer rate constant and the exchange current density for the oxidation of ferrocene were determined. A comparison of the kinetic data obtained from the two electrochemical techniques appears to show that the data from the RDE experiments are more reliable because they are collected under strict mass transport control.

Keywords: Cyclic voltammetry, diffusion coefficient, ferrocene derivative, half-wave potential, Randles-Sevcik equation.
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INTRODUCTION

Many studies and analysis by electrochemical methods were effected on the oxido-reducing properties of ferrocene. In general, the cathodic behavior of ferrocene usual in organic media such as dichorométhane, acetonitrile and DMF can be described by a reversible reduction in an electron, leading to ion ferrocerium [1-2]. In the present work the oxidation of ferrocene, $Fe(C_5H_5)_2$, to the ferrocenium cation, $Fe(C_5H_5)_2{}^+$, was examined in the solvents dichloromethane solution containing tetrabutylammonium tetrafluoroborate and aqueous solution containing sulfuric acid using the technique of cyclic voltammetry[4-3]. The results indicated that redox reactions of ferrocene/ ferricenium couple were a reversible process of diffusion-controlled single electron transfer in both studied solutions.

One of the ferrocene derivatives is the compound N'-Ferrocenylmethyl-N'-henylbenzohydrazide , very important in electron-transfer systems for molecular electronics owing to its characteristic redox behaviors[6-5] and they could also be expected to play a key role of an electron chemical probe of the electron-transfer process in biological molecules [7-8]. It is well known that N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide easily undergoes one electron oxidation to form ferrocenium cation in a reversible manner [9-10] figure (1). Thus, we investigated the electrochemical N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide behaviors in aqueous media.
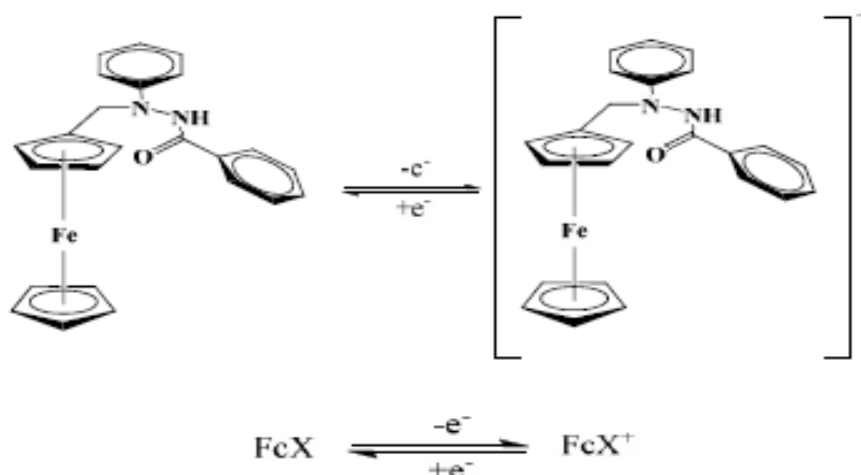
$$FcX \xrightleftharpoons[+e^-]{-e^-} FcX^+$$

Fig 1: Reversible mono electronic oxidation of N'-Ferrocenylmethyl-N'-
Phenylbenzohydrazide

MATERIALS AND METHODS

Instrumentation and software: Cyclic voltammetric measurements were performed using PGZ301 potentiostat (radiometer analytical SAS) and a voltammetric cell with a volumetric capacity of 25ml containing a glassy carbon electrode (GCE) working electrode (radiometer analytical SAS), a Pt wire counter electrode, and an Hg/Hg_2Cl_2 reference electrode (3.0M KCl). Solutions were deoxygenated with high purity nitrogen for 3 min prior to each experiment. Data acquisitions were accomplished with a Pentium IV (CPU 3.0 GHz and RAM 1 Gb) microcomputer using VoltaMaster software version 7.08 (radiometer analytical SAS). Graphs plot and calculus were carried out using Origin Lab software version 2.0 (Integral Software, France).

Chemicals: Electrochemical characterization was carried out on a potentiostat type voltalab 40 of radiometer, with a three-stand electrode cell. Cyclic voltammetric experiments were performed in deoxygenated CH_2Cl_2 and aqueous ethanol solutions of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide with 10^{-1} M of Bu_4NBF_4 and H_2SO_4 respectively as supporting electrolyte and N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide concentration of 10^{-3} M. The three electrodes used were glassy carbon disk as the working electrode, saturated calomel electrode as a reference electrode, and Pt wire as an auxiliary electrode. The working electrode was polished with 0.05 μm alumina slurry for 1–2 minutes, and then rinsed with double-distilled and deionized water. This cleaning process is done before each cyclic voltammetry experiment.

RESULTS AND DISCUSSION

Electrochemical measurement on a fixed electrode: The synthesized compound in previous work [5]. Cyclic voltammograms of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide at glassy carbon electrode were performed at concentration of 10^{-3} M of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in deoxygenated dichloromethane and in aqueous ethanol solutions with respectively 10^{-1} M of Bu_4NBF_4 and H_2SO_4 as supporting electrolyte, each solution was scanned at scan rate equal to 0.05, 0.10, 0.30 and 0.50 $V.s^{-1}$.the resultant CV curves and the electrochemical parameters are shown respectively in figure 2 and table 1.
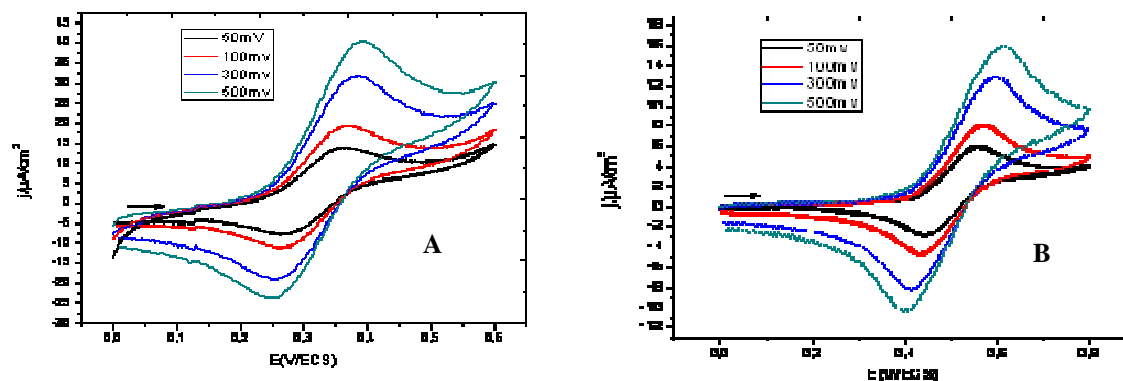
Fig.2 (A,B). cyclic voltammetry of 1 mM N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in (B) 100 mM Bu$_4$NBF$_4$ in CH$_2$Cl$_2$ and (A) in ethanol/aq.H$_2$SO$_4$ at 2 mm diameter glassy carbon working electrode, Pt counter electrode, and CSE reference electrode at (0.05, 0.10, 0.30, 0.50 V.s^{-1}).

Table 1: Electrochemical parameters obtained from voltammograms of figure 2

mediums	v mV/s	i_{pa} μA/cm^2	i_{pc} μA/cm^2	E_{pa} mV	E_{pc} mV	$E_{pa} - E_{pac}$ mV	$E_{\frac{1}{2}}$ mV	$\left\|\frac{i_a}{i_c}\right\|$
Bu$_4$NBF$_4$	50	11.51	-11.665	582.5	447	138.5	513.25	0.98
(0.5g)	100	15.76	-15.90	594	431	163	512.5	0.99
+	300	25.36	-25.76	630	405	225	517.5	0.98
CH$_2$Cl$_2$	500	31.68	-33.1	660	385	275	522.5	0.95
H$_2$SO$_4$ (0.1M)	50	13.93	-14.49	367.5	264.5	103	316	0.96
+ Ethanol	100	19.37	-19.54	372	258	114	315	0.99
(1/1) (v/v)	300	31.81	-33.58	381	258	123	319.5	0.94
	500	40.4	-42.52	395	250	145	322.5	0.95

The anodic and the cathodic peak heights as function of the square root of the scanning rate for glassy carbon electrode in different medium are shown in figure 3. The obtained linear relation ship indicates clear diffusion character. As it can be seen from figures 3, the ratio of the anodic and cathodic current peak heights is close to one for both solutions; this indicates the reversible character of the oxidation of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in both studied medium.
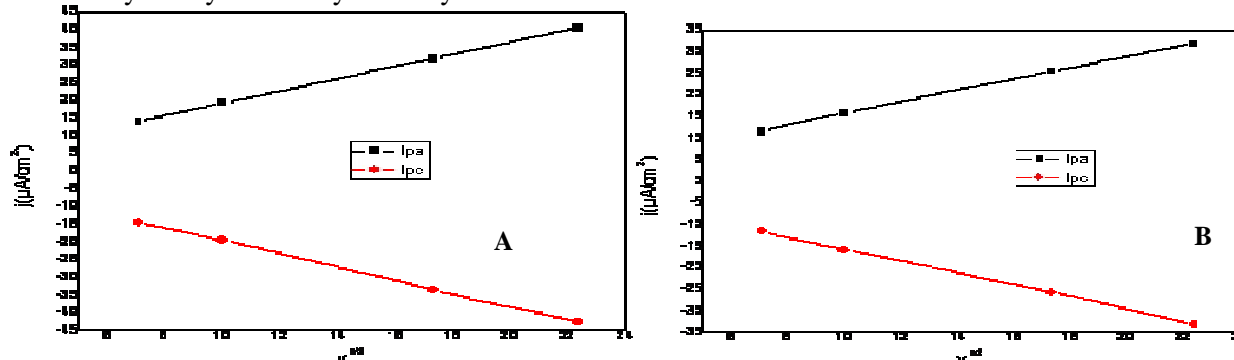

Fig. 3 The anodic and the cathodic peak heights as function of the square root of the scanning rate in CH$_2$Cl$_2$ (B) and in ethanol/H$_2$SO$_4$ (A) at 2 mm diameter glassy carbon working electrode.

Electrochemical measurement on rotating disk electrode: Rotating disk electrode is a hydrodynamic electrode technique which utilizes convection as the mode of mass transport as opposed to CV which is governed by diffusion. Convection is more efficient and is not diffusion limited with the result that the analytical data is more reproducible and precise. Thus a comparison of the kinetic parameters obtained from CV and RDE experiments is informative to elucidate the role of mass transport on electrode reaction kinetics. Fig. 4 A shows RDE voltammograms for N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide at a series of rotation rates. It is evident from the data that the current generated by the RDE method is much larger than that generated under diffusion control. The much larger current obtained using RDE reflects the efficiency of this method. Also notice that there is significant increase in anodic current while the amount of cathodic current is negligible, essentially making the cyclic voltammogram anodic.
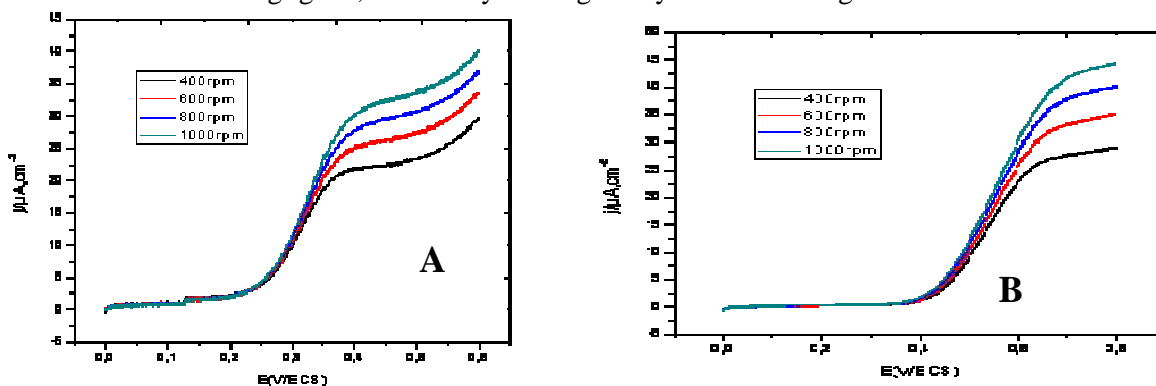

Fig.4(A,B) : Polarogramme of (B) 1 mM N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide and 100 mM Bu_4NBF_4 in CH_2Cl_2 and (A)1 mM of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in ethanol/H_2SO_4 at 2 mm diameter glassy carbon working electrode, Pt counter electrode, and CSE reference electrode at 0.50 $V.s^{-1}$. (Rotating rate 400, 600, 800, 1000 rpm)

The diffusion current limit, the current half-wave and half-wave potential are calculated at different rotation speed of the electrode, Table 2.

Table 2. Electrochemical parameters calculated from polarogammes obtained at glassy carbon electrode of different rotational speed in two media

ω tour/min	i_{lim} $\mu A/cm^2$		$i_{P/2}$ $\mu A/cm^2$		$E_{\frac{1}{2}}$ mV		$\sqrt{\omega}$
	org	aqu	org	aqu	org	aqu	
400	27.58	22.68	13.79	11.34	532	308	20
600	34.4	26.96	17.2	13.48	543.5	314.5	24.494
800	39.5	30.18	19.75	15.09	549.5	319.3	28.284
1000	42.96	32.96	21.48	16.48	550	322.7	31.622

 Calculation of diffusion coefficient: The Levich equation predicts the current observed at a rotating disk   electrode and shows that the current is proportional to the square root of rotation speed. The equation is:

$$\delta = 0.645 D_{Ox}^{\frac{1}{3}} \gamma^{\frac{1}{2}} \omega^{-\frac{1}{2}}$$

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Where D_{ox}: diffusion coefficient of the oxidant is expressed in $cm^2.s^{-1}$

ω: rotational speed of the electrode (rad s^{-1})

γ: kinematic viscosity in $cm^2. s^{-1}$

<u>Kinematic viscosity</u> is the ratio of the viscosity on the density, we have for dichloromethane

$$viscosity = 0.43 mPa. s \quad 25°c$$
$$density\ d = 1.328$$

$$\gamma = \frac{0.43}{1.328} \times 10^{-3} \frac{\frac{kg}{m.s}}{\frac{kg}{m^3}} = 0.323 \times 10^{-3} \frac{m^3}{m.s} = 0.323 \times 10^{-3} 10^4 cm^2. s^{-1} = 0.323 \times 10^{-1} cm^2. s^{-1}$$

$$= 0.0323 cm^2. s^{-1}$$

$$\gamma = 0.0323 cm^2. s^{-1}$$

The kinematic viscosity ($\approx 10^{-6}$ m^2 s^{-1}, for an aqueous solution at 25 ° c)

The relationship between i and the square root of rotation speed $P = \frac{i}{\omega^{\frac{1}{2}}}$ (2)

On another hand the limited current is given by,

$$i = \frac{nFADC}{\delta} \quad (3)$$

Where: n, number of electrons

F is the Faraday ($9.65.10^4$ C/mol)

A is the area of the working electrode (cm^2).

D is the coefficient diffusion ($cm^2.s^{-1}$)

C is the concentration (mol/cm^3), in our case is equal to10^{-3} mol L^{-1}

Replacing equations 2 and 3 in 4 gives,

$$D^{\frac{2}{3}} = \frac{P 1.61 \gamma^{\frac{1}{6}}}{nFAC\sqrt{2\pi}} \quad (4)$$

For a rotating rate of the working electrode equal to 400 t/min., the coefficient diffusion of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in dichlormethane is.

$$D = 13.2 \times 10^{-6} \ cm^2. s^{-1}$$

The coefficient diffusion of ferrocene in aqueous ethanol is calculated as above. Table 2 summarize the obtained values.

APPLICATION

The kinetic data obtained from the two electrochemical techniques appears to show that the data from the RDE experiments are more reliable because they are collected under strict mass transport control.

Table3: Diffusion coefficients of compound calculated from polarogramme of figure 5

Electrode/medium	p	$D \times 10^{-6}$ cm^2/s	δ(nm)
GC / CH_2Cl_2	1.4	**13.2**	**288**
GC /aq.ethanol	1.1	**2.6**	**70**

CONCLUSIONS

Voltammetry analysis on a fixed electrode of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in aqueous and organic solutions indicates that the electrochemical reaction of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in both studied solutions is a diffusion controlled process, namely, electrochemical process and,show that the electron withdrawing N'-Phenylbenzohydrazide group introduced to the ferrocene influences the redox potential of the iron centre. This is may be due to the non-insulating effect of methylene between the N'-Phenylbenzohydrazide group and the cyclopentadienyl ring of ferrocene. In addition ΔEp for the ferrocene in CH_2Cl_2 is grater than ΔEp in aq. ethanol, this difference can be

attributed to the difference in diffusion coefficient between ferrocene in each medium which is a major contributor. However there is a minor contributor which is related to the difference in the solution resistance of the two electrochemical medium.

ACKNOWLEDGMENTS

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