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ELECTROCHEMICAL STUDY OF 3,5 - DIMETHYLPYRAZOLE-PENTACYANOFERRATE (II) COMPLEXES AT GLASSY CARBON ELECTRODE.

V. López, M.M. Gómez and A.M. Arevalillo

Universidad Autónoma de Madrid, Dpto Química Física Aplicada. Facultad de Ciencias C(II). 28049 Madrid Spain

ABSTRACT

Electrochemical oxidation of 3,5 dimethylpyrazole-pentacyanoferrate (II) complexes at glassy carbon electrode has been determined from analyses of voltamperometric curves at different pH values. The complex species formed are dependent on the pH media. Voltammograms display only a well-defined wave but the peak potentials shift to less positive values as the pH medium increases. The possible mechanisms of the reaction have been discussed.

Key words: glassy carbon electrode; pyrazole complexes

INTRODUCTION

Several studies have been carried out on the behaviour of the nitrogen bases into different complexes with transition metal-ions in biological compounds.

The development of the pyrazoles chemistry is due to the importance of these substances as components of many drugs, herbicides and fungicides. Also, pyrazoles are known to coordinate with metal ions [1-5]

Pyrazole is a five-membered aromatic heterocycle with two vicinal N atoms in the position 1 and 2, known as pyrrole and pyridine nitrogen atoms, respectively. (Figure 1). It forms a variety of complexes with transition-metal ions. The formation of the metal to ligand bond takes place via pyridine nitrogen atom (5). Janina Goslar has studied the copper chloride methylpyrazole complexes and their quantitative composition and physical chemical properties have been determined. On the basis of spectroscopic, electron paramagnetic resonance (e.p.r.) and magnetic studies, the structures of the complexes occurring in solids and the ethanol solutions are discussed. Four- and six-coordinate Cu-pyrazole complexes have been distinguished and the budging properties of 3,5-dymethylpyrazole ligand have been rationalised (6). The pyrazole and pyrazolate anions can act either as monodentate or as binding ligands, and the two nitrogens can bond to different metal ions thus forming di- or trinuclear clusters (7-9); furthermore the chains can be present in solids (10). A wide range of pyrazole copper compounds have been studied as models for copper proteins (11). Four- and six-coordinate Cu-pyrazole complexes have been identified.

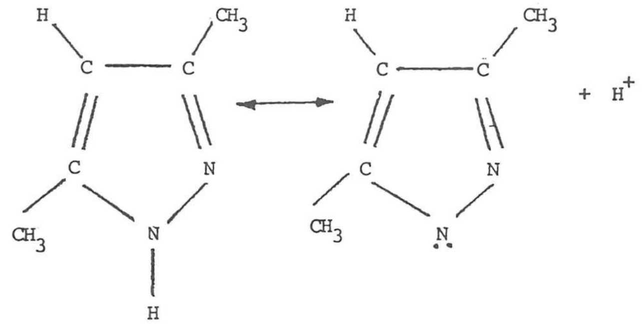

Figure 1.- Schematic structure of 3,5 dimethyl pyrazole molecule.

The strong affinity of pentacyanoferrate (II) ion for unsaturated ligands can be used to make another very interesting series of complexes with imidazol, pyridine, pyrazine and pyrazole as the sixth ligand. $Fe(CN)_5R$, where R refers to organic bases involving one or two nitrogen atoms, has been published in numerous papers, but the five membered heterocyclic molecules have received little attention. Some kinetic and electrochemical results referring to the imidazole ferrate can be found in a few papers (12-16)

In a previous paper we have determined the kinetic parameters for the reaction of pyrazole derivatives complexes at a platinum electrode (17). The aim of this research was to analyse the response of 3,5 dimethylpyrazole-pentacyanoferrate (II) (35DMPPCF) complexes on a glassy carbon electrode in order to contribute to a better understanding of the electrochemical behaviour of these compounds.

EX PERIMENTAL

The complexes were prepared *in situ* by dissolving solid $Na_3Fe(CN)_5(NH_3)$ and the appropriate ligand: 3,5Dimethylpyrazole, in a ratio close to 1:10 in a 0,5 M aqueous solution of $NaClO_4$. It is considered for the complexes generated *in situ* that a 1:10 ratio is sufficient for their formation. The complex formation is immediate and accompanied by a colour change.(12). The pH was varied by small additions of hydrochloric acid or sodium hydroxide and measured immediately after recording the voltammetric curves (18,19). The solutions pH was checked after each experiment and remained constant during the measurements. The electrode used for the electrochemical study was a glassy carbon electrode. The auxiliary electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE) Radiometer E-65 to which all potentials are referred.

The ligands and $Na_3Fe(CN)_5(NH_3)$ were prepared by standard methods (19). Voltammograms have been recorded using an Amel 563 Polarograph coupled to a Hewlett Packard 7047-A, X-Y recorder.

All the reagents used were of analytical grade. Ground electrolyte was 0,5 M of aqueous solution of sodium perchlorate. Solutions were prepared using twice-distilled water which had subsequently been passed through a Millipore Mili Q system. All solutions were previously deoxygenated.

RESULTS

Effect of the pH

The studied pH range was between 1,7 and 10,6. The colour of the solutions changes from green in acidic pH to yellow at pH > 7. Therefore, the complex species formed between 3,5 dimethylpyrazole and pentacyanoferrate (II) may be dependent on the pH media.

Cyclic voltammetry measurements of 3,5DMPPCF complexes were performed in aqueous solution of $NaClO_4$ 0,5 M at different pH values. For all the pH range, the 3,5DMPPCF complexes display only a well-defined wave. However, the voltammetric parameters are pH dependent. The experimental results for the anodic, E_{pa}, and cathodic peak potentials, E_{pc}, and the corresponding anodic, i_{pa}, and cathodic peak currents, i_{pc}, are given in Table 1 for solutions 10^{-3} M of 3,5DMPPCF complex and a scan rate of 50 mVs^{-1}. Values for peak currents increase as the pH increases. On the other hand, the peak potentials shift towards less positive values as the pH medium increases.

TABLE I

Voltammetric parameters for oxidation of 3,5 dimethylpyrazole 10^{-3}M in the presence of pentacyano ferrate (II) on a glassy carbon electrode at different pH values. T = 25°C. Scan rate = 50 mVs^{-1}

pH	E_{pa}/mV	E_{pc}	$\Delta E_p/mV$	$i_{pa}/\mu A$	$i_{pc}/\mu A$	$i_{pa}/i_{pc}/\mu A$
1,7	389	+135	254	27	19	1.42
2.4	346	+111	235	22	20	1.10
3.4	288	+43	245	23	20	1.15
5.4	259	+116	163	26	17	1.52
7.1	226	+96	130	26	22	1.18
8.2	212	+129	83	26	23	1.13
8.5	183	+91	92	30	25	1.20
9.4	183	+87	96	33	27	1.22
10.6	202	+87	115	37	25	1.48

The electrochemical order with respect to protons can be calculated from the results given in Table 1. At constant concentration of 3,5DMPPCF, the E_{pa} – pH dependence can be decribed by two segments of $\delta E_{pa} / \delta$ pH equal to 30 mV at pH < 7 and only 10 mV at higher pH values. These results seems to indicate that one proton takes part in the overall reaction in acidic media but this is pH independent in alkaline media. This means that the oxidation process is probably due to different species according to the pH value.

The peak current is also modified by the pH as it is shown in Table 1 At pH < 7 values of i_{pa}, remain practically constant. However at pH > 7 an increase in the current is observed as the pH increases.

Effect of the concentration

Voltammetric measurements were performed in aqueous solutions at different concentration of 3,5DMPPCF complexes (10^{-3} – 4,2 x10^{-2}M) at two values of pH: 1,7 and 10,6. These pH values remain constant during the measurements. The variation of the voltammetric parameters with the bulk concentration of complex is shown in Table 2. At acidic media, anodic peak potential are nearly independent on the concentration. However, in alkaline solutions, the obtained values for E_{pa} shift to less positive potentials as de bulk concentration of organic compound increases.

TABLE II

Voltammetric parameters for oxidation of 3,5 dimethyl pyrazole in presence of pentacyano ferrate (II) on a glassy carbon electrode at different concentrations. T=25°C. Scan rate = 50 mVs^{-1}

pH = 1.7						
Mol/	E_{pa}/mV	E_{pc}/mV	$\Delta E_p/mV$	$I_{pa}/\mu A$	$I_{pc}/\mu A$	I_{pa}/i_{pc}
10^{-3}	389	135	254	27	19	1.42
$2.7*10^{-3}$	385	144	241	26	19	1.36
$6.1*10^{-3}$	390	144	246	25	19	1.31
$8.3*10^{-2}$	390	135	255	23	20	1.15
pH = 10.6						
Mol/	E_{pa}/mV	E_{pc}/mV	$\Delta E_p/mV$	$I_{pa}/\mu A$	$I_{pc}/\mu A$	I_{pa}/i_{pc}
10^{-3}	200	85	115	39	23	1.69
$1.8*10^{-3}$	192	105	87	44	27	1.62
$4*10^{-3}$	188	91	87	41	26	1.57
$8*10^{-2}$	178	96	82	43	27	1.59
$1.2*10^{-2}$	175	98	77	36	25	1.44

Under the experimental conditions employed here, the obtained values for the separation between anodic and cathodic peaks, ΔE_p, are higher than 59 mV. Therefore, the reaction seems to be quasi-reversible or irreversible.

In presence of the studied compounds, the experimental values of the half peak potentials, $\Delta E_{p/2}$ and ΔE_p were within a range for which Nicholson's table of values could be utilised.

Therefore, the Nicholson method (20) was used to obtain kinetic parameters. The same procedure used in a previous paper (19) has been applied for these substances.

The electrode rate constant, k_0, could be obtained from the function of the current, ψ, which is given by the following equation (21):

$$\Psi = \left(\frac{D_O}{D_R}\right)^{1/2} k_0 \left(\frac{RT}{\pi nFvD_O}\right)^{1/2}$$

v is the scan rate, D is the diffusion coefficient and O and R stand for the oxided ans reduced forms respectively. The ψ values for each ΔE_p experimental were obtained from the Nicholson's tables. For a correct calculation of ψ we interpolated those values that do not exactly coincide with tabulated one at ΔE_p-ψ, where ψ shows a linear dependence on ΔE_p.

The obtained results for k_0 in the different studied media and its dependence on the concentration is shown in Tables 3 and 4. Values of k_0 are about 10^{-3} that indicate a process quasi-reversible. This is in agreement with the observed values for ΔE_p.

TABLE III

The electrode rate constant, k_0, for oxidation of 3,5 dimethyl pyrazole 10^{-3} M in presence of pentacyano ferrate (II) on a glassy carbon electrode at different pH values. T = 25°C. Scan rate = 50 mVs^{-1}.

pH	5.4	7.1	8.2	8.5	9.4	10.6
K_0	$9.8*10^{-3}$	$2.4*10^{-3}$	$3.5*10^{-2}$	$4.1*10^{-3}$	$3.6*10^{-3}$	$2.9*10^{-2}$

TABLE IV

The electrode rate constant, k_0, for oxidation of 3,5 dimethyl pyrazole in the presence of pentacyano ferrate (II) on a glassy carbon electrode at pH = 10,6. T = 25°C. Scan rate = 50 mVs^{-1}

$C/mol.l^{-1l}$	$1,8x10^{-3}$	$4x10^{-3}$	$8x10^{-3}$	$1,2x10^{-2}$	$4,2x10^{-2}$
K_0	$3,5x10^{-3}$	$5,7x10^{-3}$	$7,7x10^{-3}$	$7,5x10^{-3}$	$2,4x10^{-2}$

Effect of the potential scan rate

In order to analysed the mechanism of the oxidation process on a glassy carbon electrode, the peak currents and potentials measurements were made over a range of scan rate from 5 $mV.s^{-1}$ to 1 $V.s^{-1}$. Voltammograms of 3,5DMPPCF complexes at high scan rate are given in Figure 2.

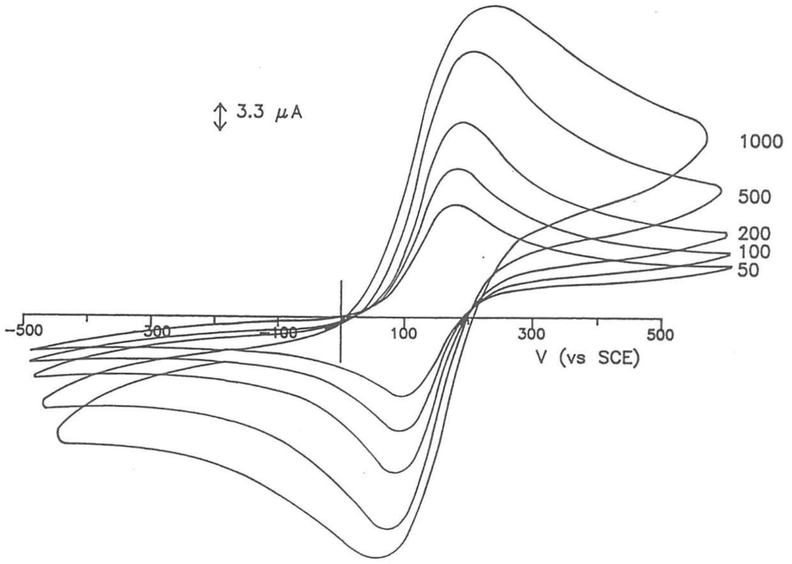

Figure 2 -. Voltammograms of 3,5 dimethyl pyrazole 1,8 x 10^{-3} M in presence of pentacyano ferrate (II) ion on glassy carbon electrode at different scan rate, v. Values of v in $mV.cm^{-1}$ are indicated on each voltammogram. pH = 10,6. T = 25°C.

In the studied pH range, the obtained voltammograms show an increase in i_p with sweep rate but is not proportional to $v^{1/2}$. This behaviour is characteristic of systems in the quasi-reversible region. From the experimental data, a value of about 49 mV was found for $\delta \log i_p/\delta \log v$ which corresponds to a diffusion-limited current. On the other hand, the relationship between $i_p/v^{1/2}$ and v depends on the pH. The obtained results are given in Figure 3. In acidic media, the term $i_p/v^{1/2}$ decrease slightly as v is increases. In alkaline media, $i_p/v^{1/2}$ decreases as v is increased. This fact indicates the presence of coupled chemical reactions.

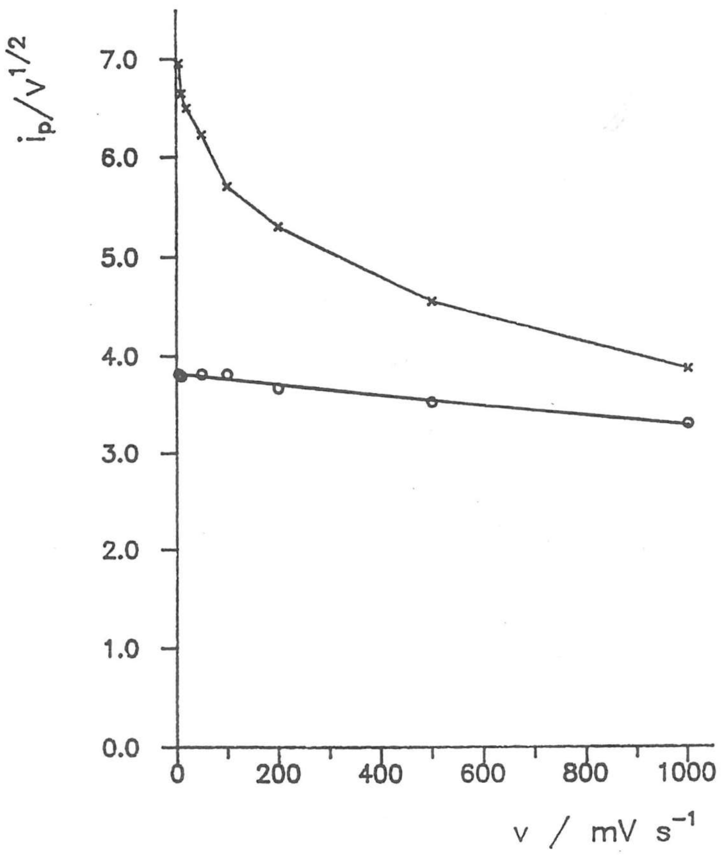

Figure 3.- Dependence of the parameter $i_p/v^{1/2}$ on the scan rate for solutions of 3,5 dimethyl pyrazole in presence of pentacyano ferrate (II) ion. (o) pH = 1,7; c = 5x 10^{-3} M: (x) pH =10,6; c = 10^{-3} M.

The ratios of cathodic to anodic peak currents, i_{pc}/i_{pa} display different dependence with v in the studied media as Figure 4 shows. At pH < 7, i_{pc}/i_{pa} is less than one but a pH > 7 values for i_{pc}/i_{pa} very close to the unity was found.

The peak potentials change with the sweep rate. In all media, E_{pa} and E_{pc} shifts always to more anodic and more cathodic values, respectively, as v is increased. Values for ΔE_p grater than 50 mV were observed and they increase with the scan rate. At pH = 1,7 E_{pa} shifts about 30 mV per tenfold increase in v. However, at pH = 10,6 higher shifts were observed.

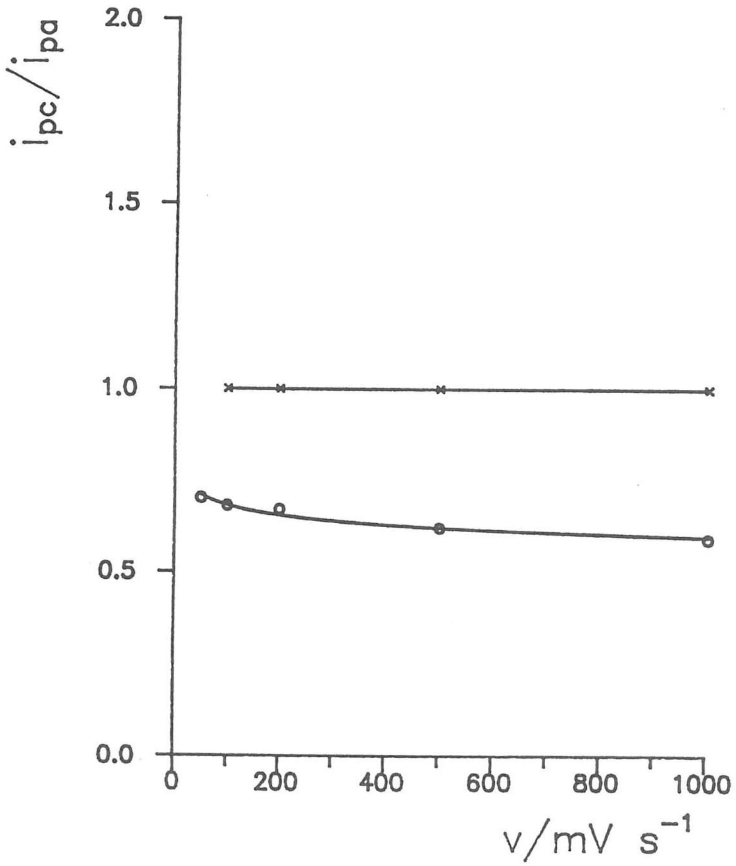

Figure 4.- Dependence of the ratio of cathodic to anodic peak currents, i_{pc}/i_{pa}, on the scan rate for solutions of 3,5 dimethyl pyrazole in presence of pentacyano ferrate (II) ion. (o) pH = 1,7; c = 5x10^{-3} M; (x) pH = 10,6; c = 10^{-3} M.

DISCUSSION AND CONCLUSIONS

Results obtained in the present work show the presence of an oxidation process in all studied media. However, the colour of the solutions and the voltammetric parameters indicate that the electroactive species are different in acidic and alkaline media. Therefore, electrochemical behaviour on a glassy carbon electrode depends on the pH.

The obtained values for the electrode rate constant indicate that the electrochemical oxidation corresponds to quasi-reversible systems in all the pH range is controlled by diffusion.

At pH = 1,7, the anodic peak potential is independent of the bulk concentration of pyrazole and the global electrochemical process is the first order respect to the protons. This seems to indicate no formation of a complex before the oxidation reaction. Therefore, the electroactive species is the organic substance.

Electrochemical oxidation of polymethylated derivatives of heterocyclic compounds has been examined (22). In all cases cation radicals were the primary oxidation products. With mono or di-Me-derivatives the process occurred via an ECE mechanism. In the presence of strong acids the protonation of the solute must be taken into account (23).

In the present work the results at pH = 1,7 seem to indicate the mechanism cannot be an ECE mechanism, in which the chemical reaction is irreversible, because the theory indicates that for this type of system the term i_{pc}/i_{pa} must increases. The 3,5-dimethyl pyrazole shows a decrease of this parameter. The effect of v on $i_p/v^{1/2}$ and E_{pa} corresponds to the characteristics of an EC mechanism. Therefore, the global reaction is probably the result of two successive steps. The first step could be due to the electrochemical oxidation of the organic compound with the formation of a cation radical. In this media, the dependence of E_{pa} on pH shows that one proton takes part in the overall reaction. Therefore, the proton transfer would take place in the subsequent chemical reaction.

The dependence of the anodic peak potentials with the bulk concentration increases with increasing pH. The formation of the complex species between 3,5 dimethyl pyrazole and pentacyano ferrate (II) seems to be more favourable in alkaline solutions where the concentration of pyrazolate anions increases.

At pH = 10,6 the voltammetric parameters display different behaviour with the scan rate than the observed at pH = 1,7. There are two mechanisms which can account for the values of the ratio of cathodic to anodic peak currents very close to the unity: charge transfer kinetics (quasi-reversible charge transfer) or a chemical reaction coupled to a charge transfer (CE mechanism). The decrease observed in the values of $i_p/v^{1/2}$ as v is increases, could indicate the presence of a chemical reaction. The formation of the complex between the pyrazolate anions and the pentacyano ferrate (II) may be the first step.

Thus the electrochemical reactions are presumed to be as follows:

$$Fe(II) - 1e^- \rightarrow Fe(III)$$

$$Fe(III) + p(3{,}5DMP) \rightarrow Fe(III)(3{,}5DMP)_p^{3-p}$$

$$\begin{tikzcd} Fe(III)(3{,}5DMP)_p^{3-p} \arrow[r] & Fe(III)(3{,}5DMP)_q^{3-q} + (p-q)(3{,}5DMP) \arrow[d, "+1e^-"] \\ & Fe(II)(3{,}5DMP)_q^{2-q} \end{tikzcd}$$

Only in alkaline media according to J.L. Brisset and M. Biquard other equilibria can appear following the reaction:

$$Fe(CN)_5L^{-3} + OH^- \rightarrow Fe(CN)_5OH^{-4} + L$$

being L = NH_3.

Another explanation could consist of an attack of the OH^- ion to the ligand L in a similar way to that observed for pyrazole-ferrate compounds (J.L. Brisset and V. Ilimbi,).

The difference between the coordination number of the oxidised and reduced forms, (p-q), of complex species may be calculated by using the Lingane equation (24):

$$E_{1/2} = E^0 - \frac{RT}{nF}\log\frac{\beta MX_p}{\beta MX_q} - (p-q)\frac{RT}{nF}\log(X)$$

where M is the metal and X is the ligand.

$E_{1/2}$ values were obtained from the E_p values measured in the voltamograms following the criteria used by R.S. Nicholson and Shain as well as the criteria reported in Electrochemistry at Solid electrodes by Adams (25,26)

Matsuda and Ayabe (27) established that for quasi-reversible reactions a similar study can be carried out like for reversible ones. Then the (p-q) value may be derived from the slope of the plot $E_{1/2}$ vs. Log [3,5DMP].

In the present system, the obtained half wave potentials are nearly independent on the 3,5 DMP concentration. The value of (p-q) = 0.3 was found. These value seems to indicate that the ligand number its the same for the oxided and reduced species. Therefore, it is reasonable to assume that the electrochemical reaction is due to the oxidation of Fe (II) at Fe(III) into pentacyanoferrate ions, and the structure of the complex does not change in this process (28).

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