

## ELECTROCHEMICAL STUDY OF CIS-DIFERROCENYLETHENE DERIVATES

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## ABSTRACT

Ferrocene derivatives have been used in the synthesis of polymeric materials with thermal resistance and nonlinear optical properties, and in the field of supramolecular electrochemistry as redox switching receptors. For these reasons, during the past few years the electrochemical studies on ferrocenyl derivatives have been growing up. In order to characterize molecules with potential uses in the synthesis of polymeric materials and to understand its electrochemical functioning, this paper presents electrochemical studies on these chemicals: 1) cis-diferrocenylethenes derivatives (Isopropyl *cis*-2,3-Diferrocenylacrylate; 2) *cis*-2,3-Diferrocenylacrylic Acid; 3) *cis*-2,3-Diferrocenylacrylohydrazide; 4) *cis*-2,3-Diferrocenylacrylic Acid Piperidide; 5) *cis*-3,4-Diferrocenyl-2-methylbut-3-en-ol, and 6) *cis*-1,1-Diphenyl-2,3-Diferrocenylprop-2-en-1-ol. All of the chemicals presented two oxidation processes (I-II), which were thought to be caused by the oxidation of the ferrocene groups,  $E_{1/2}(I)$ ,  $E_{1/2}(II)$ ,  $\Delta E_{1/2}(II-I)$ . The comproportionation constant  $K_{com}$  was calculated. According to this value, it can be proposed that the molecules containing a carbonyl group (1-4) present larger electronic communication compared to molecules with a hydroxy group (5-6). Uv-vis spectra of all compounds in butyronitrile solution were obtained. A correlation between  $K_{com}$  and  $\lambda_{max}$  was also observed.

**Key Words:** *Cis*-2,3-diferrocenylacrylates, *cis*-2,3-diferrocenyl allyl carbinols, cyclic voltammetry, diferrocene, electrochemistry, ferrocene.

## RESUMEN

Los derivados del Ferroceno han sido empleados en la síntesis de materiales poliméricos con resistencia térmica y con propiedades ópticas no lineales y en el campo de la electroquímica supramolecular como receptores de interruptores redox. Por estas razones los estudios electroquímicos de los derivados ferrocenil se han incrementado en los últimos años. Con la finalidad de caracterizar moléculas con potenciales usos en la síntesis de materiales poliméricos y entender su comportamiento electroquímico, este trabajo presenta estudios electroquímicos de derivados *cis*-diferrocenileno (*cis*-2,3-Diferrocenilacrilato de isopropilo (1), Ácido *cis*-2,3-Diferrocenilacrílico (2), *cis*-2,3-Diferrocenilacrilohidrazida (3), Piperidina del Ácido *cis*-2,3-Diferrocenilacrílico (4), *cis*-3,4-Diferrocenil-2-metilbut-3-en-ol (5), *cis*-1,1-Difenil-2,3-Diferrocenilprop-2-en-1-ol (6). Todos los compuestos presentan dos procesos de oxidación (I-II), atribuidos a la oxidación de los dos ferrocenos,  $E_{1/2}(I)$ ,  $E_{1/2}(II)$ ,  $\Delta E_{1/2}(II-I)$ . Se calcula la constante de desproporción  $K_{com}$ . De este valor se propone que las moléculas que contienen el grupo carbonilo (1-4) presentan una gran comunicación electrónica comparada con las moléculas que contiene un grupo hidroxil (5-6). El espectro UV-vis de todos los compuestos se obtuvo en butironitrilo. Se encontró también una correlación entre  $K_{com}$  y  $\lambda_{max}$ .

**Palabras Clave:** *Cis*-2,3-diferrocenilacrilato, *cis*-2,3-diferrocenil alilo carbinols, voltametría cíclica, diferrocenos, electroquímica, ferroceno.

## INTRODUCTION

**F**errocene molecule has an extraordinary thermal stability, its structure is retained up to 500°C, this fact has made ferrocene suitable for fire retardant applications<sup>1,2</sup>. For example, when used as fuel additive suppresses soot in several processes like acetylene pyrolysis, and poly(vinyl chloride) combustion<sup>2-6</sup>.

In the realm of materials science, several polymers containing ferrocene derivatives have been reported<sup>7-13</sup>. These polymeric materials present optical nonlinearities, magnetic, redox and electrical properties<sup>14-16</sup>. Several reports focus on the thermal stability of different ferrocene-containing polymers<sup>13,17-21</sup>.

Additionally ferrocene-containing polymers have been used as molecular building blocks, and in supramolecular electrochemistry as redox switching receptors<sup>22-26</sup>.

Ferrocene moieties in diferrocenylethenes derivatives that are separated by unsaturated carbon-carbon bonds present two separated electrochemical-reversible oxidation processes; the splitting can be attributed to the electronic communication of the two iron redox centers in the mixed valence state or simpler to the different environment; the comproportionation constant  $K_{com}$  indicates the degree of charge delocalization in the mixed-valence species within the Robin-Day classification<sup>27-29</sup>.

Klimova *et al.* reported a series of compounds (**1-6**) containing diferrocenyl moieties with different substituents (Scheme 1) with possible uses in the synthesis of polymeric materials<sup>30-31</sup>. Despite the well done characterization of these compounds no electrochemical studies were performed.

In order to characterize molecules with potential uses in the synthesis of polymeric materials and to understand the electrochemical behavior of *cis*-2,3-diferrocenyl derivatives, expecting a different electronic communication between ferrocene moieties due to the different substituents, this paper presents electrochemical studies of compounds (**1-6**) and their comproportionation constant  $K_{com}$ . A correlation between  $K_{com}$

and  $\lambda_{max}$  of the absorption bands, obtained from UV-Vis spectra, is also reported.

## EXPERIMENTAL SECTION

### Chemicals

The following reagents were purchased from Aldrich: tetrachlorocyclopropanone, 98%; ferrocene, 98%; aluminum chloride, 99.99%; hydrazine monohydrate, 98%; piperidine, 99%; methyl lithium, 1.6 M solution in diethyl ether; ethylmagnesium chloride, 2.0 M solution in diethyl ether; lithium aluminum hydride, powder, 95%; potassium tert-butoxide, 95%; deuterium oxide, 100.00 atom% D. Tetrafluoroboric acid-diethyl ether (50-52%) was purchased from Alfa AESAR. For electrochemical experiments, Tetra-N-butylammonium chloride (TBACl) was obtained from Fluka, and Tetra-N-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) was purchased from Aldrich Chemical Co.

Compounds **1-6** were synthesized from 2,3-diferrocenylcyclopropanone and their corresponding nucleophiles as it was described in literature<sup>30-31</sup>. The melting points of compounds **1-6** and the RMN spectra are according to those reported in literature<sup>30-31</sup>.

### Electrochemical studies

All electrochemical measurements were performed in butyronitrile (HPLC grade, in order to work with the minimum amount of water) solution containing 0.1 M tetra-N-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) as supporting electrolyte. A potentiostat/galvanostat EG&G PAR model 263 controlled by a PC software was used. A typical three-electrode array was employed for all electrochemical measurements: platinum disk as working electrode, platinum wire as counter-electrode, and a pseudo reference electrode of silver wire immersed in an butyronitrile solution with 0.1 M tetra-N-butylammonium chloride (TBACl). All solutions were bubbled with nitrogen prior each measurement. All voltammograms were initiated from open circuit potential ( $E_{ocp}$ ) and the scan potential was obtained in both positive and negative directions. All potentials were reported versus the couple Fc<sup>+</sup>/Fc according to IUPAC convention<sup>32</sup>.

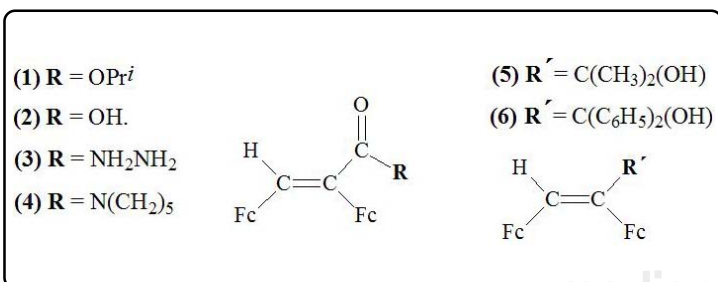
### UV-Vis spectra of compounds **1-6**

A Hewlett-Packard 5484A diode array spectrophotometer was used to acquire UV-Vis spectra. Sample concentrations of ca.  $1 \times 10^{-4}$  M in butyronitrile solution containing 0.1 M TBABF<sub>4</sub>.

## RESULTS AND DISCUSSION

### Electrochemical studies of compounds (**1-6**)

The electrochemical behavior of compounds **1-6** was investigated by cyclic voltammetry. In all experiments, a 1 mM solution of each compound in supporting electrolyte (0.1 M TBABF<sub>4</sub> in butyronitrile) was used. Figure 1 shows



Scheme 1. Compounds studied. Isopropyl *cis*-2,3-Diferrocenylacrylate (**1**), *cis*-2,3-Diferrocenylacrylic Acid (**2**), *cis*-2,3-Diferrocenylacrylohydrazide (**3**), *cis*-2,3-Diferrocenylacrylic Acid Piperidine (**4**), *cis*-3,4-Diferrocenyl-2-methylbut-3-en-ol (**5**), *cis*-1,1-Diphenyl-2,3-Diferrocenylprop-2-en-1-ol (**6**).

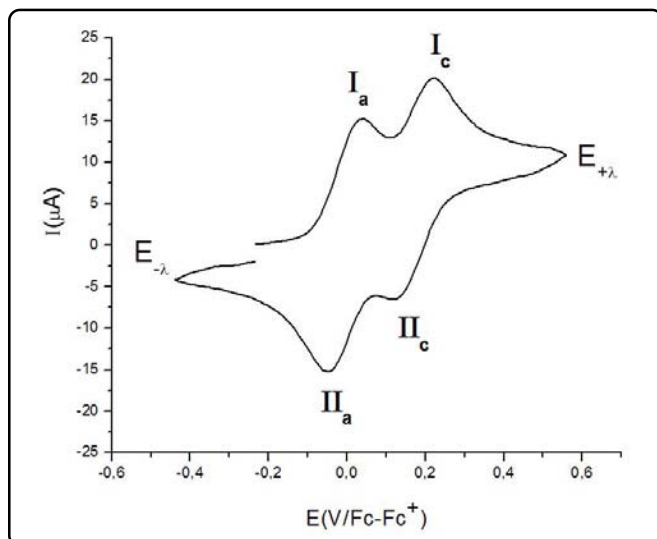


Figure 1. Cyclic voltammogram for 1.00 mM of compound **1** in the presence of 0.1 M TBABF<sub>4</sub> in butyronitrile. The scan potential was initiated from  $E_{opp}$  to positive direction. Scan rate 750 mV s<sup>-1</sup>. The working electrode used was platinum.

a typical voltammogram of compound **I** obtained in a platinum electrode. When the potential scan was initiated in the positive direction, two oxidation signals (**I<sub>a</sub>** and **II<sub>a</sub>**) were observed, and when the potential scan was reversed  $E_{+λ}$  two reduction signals (**I<sub>c</sub>** and **II<sub>c</sub>**) were detected. On the other hand, when the potential scan was started in the negative direction, the same behavior is presented. The independence of the oxidation signals (**I<sub>a</sub>**, **II<sub>a</sub>**) was established by modifying the switching potentials ( $E_{+λ}$ ), see Figure 2. Each oxidation signal has respectively a corresponding reduction signal (**I<sub>c</sub>**, **II<sub>c</sub>**).

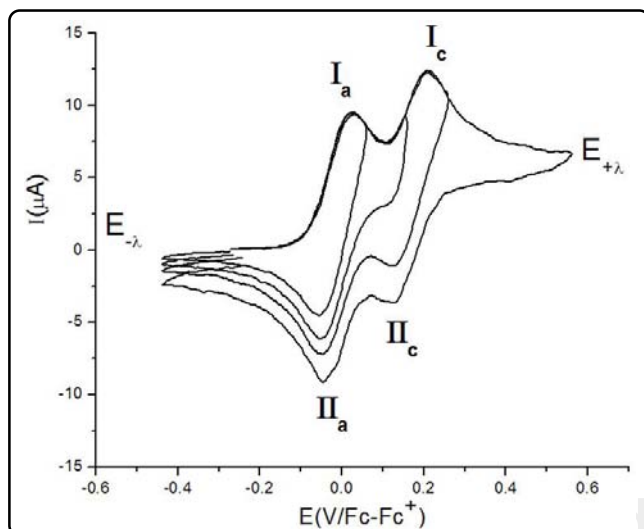


Figure 2. Cyclic voltammograms for 1.00 mM of compound **1** in presence of 0.1 M TBABF<sub>4</sub> in butyronitrile. The scan potential was initiated from  $E_{opp}$  to different inversion potentials ( $E_{+λ}$ ).

The anodic peak potential value  $E_{pa}$ (**I**) obtained for signal **I<sub>a</sub>** was 0.025 V/Fc-Fc<sup>+</sup>, and the corresponding cathodic peak potential value  $E_{pc}$ (**I**) for signal **I<sub>c</sub>** was -0.034 V/Fc-Fc<sup>+</sup>; a reversible electrochemical behavior is presented. The  $\Delta E_p$  was independent of scan rate (0.1-1 V s<sup>-1</sup>), and the cathodic peak current was proportional to  $v^{1/2}$ , indicating that process **I** is a diffusion-controlled process<sup>33</sup>.

The anodic and cathodic peak potential values for signals **II<sub>a</sub>** and **II<sub>c</sub>**  $E_{pa}$ (**II**) and  $E_{pc}$ (**II**) are 0.214 and 0.132 V/Fc-Fc<sup>+</sup>, respectively. The  $\Delta E_p$  was also independent of scan rate (0.1-1 V s<sup>-1</sup>), and the cathodic peak current was proportional to  $v^{1/2}$ .

A controlled potential coulometry established in both processes (**I** and **II**) an oxidation of one electron per molecule in each one. Processes **I** and **II** are attributed to a two consecutive one-electron transfer. A similar behavior was reported for diferrocenyl compounds<sup>17,28,34</sup>.

The half-wave potential was evaluated with the half sum of the anodic and cathodic peak potentials,  $E_{1/2} = 1/2(E_{pa} + E_{pc})$ , for the electrochemical processes **I** and **II**. The values obtained were  $E_{1/2}$ (**I**) = 0.006 V/Fc-Fc<sup>+</sup> and  $E_{1/2}$ (**II**) = 0.173 V/Fc-Fc<sup>+</sup>.

The comproportionation constant  $K_{com}$  from the  $\Delta E_{1/2}$ (**II-I**) was evaluated according to the literature for an EE mechanism<sup>33-34</sup>. According to the Robin-Day classification of mixed-valence compounds, a value of  $K_{com} < 10^2$  indicates that the charge of the electrochemical generated mixed-valence specie is localized in one redox center and no electronic communication between the redox centers is presented (**Class I**). Mixed-valence compounds electrochemically generated, with values of  $K_{com} > 10^6$ , belongs to **Class III**, where the charge is completely delocalized and a strong electronic communication is presented between the two redox centers. The intermediately range  $10^6 < K_{com} < 10^2$  corresponds to slightly charge delocalization and electronic communication between the two redox centers (**Class II**)<sup>29,35</sup>. The obtained value of 664.20 for  $K_{com}$  indicates that the mixed valence-compound generated electrochemically belongs to the class II according to the Robin-Day classification. A value of  $\Delta E_{1/2}$ (**II-I**) = 0 indicates that there are no effects affecting the oxidation of both ferrocene moieties (no electronic communication) the same redox potential is presented in both metal centers.

The electrochemical behavior for compounds **2-7** is very similar to that observed for **1**, though there are changes in the values of peak potentials. For all compounds, the half-wave potential of processes **I** and **II**, and the comproportionation constant  $K_{com}$  were evaluated (Table I).

The higher values of  $\Delta E_{1/2}$ (**II-I**) in compounds containing carbonyl group (**1-4**) suggests an increase electronic communication between the two ferrocenes, due to the

unsaturated character of carbon in carbonyl. The lower values of  $\Delta E_{1/2}$  (II-I) in compounds (5 and 6) can be attributed to a minor degree of communication of ferrocenes by the presence of a saturated carbon (Table I).

### $K_{\text{com}}$ WITH $\lambda_{\text{max}}$ CORRELATION

In order to obtain a correlation between a redox parameter with other property characteristic of the redox center, UV-Vis spectra was acquired (Figure 3). UV-Vis spectrum of compound 1 in butyronitrile solution containing 0.1 M TBABF<sub>4</sub> exhibits two spin allowed ligand field absorption transitions at 464 nm and 360 nm (<sup>1</sup>A<sub>1g</sub> → a<sup>1</sup>E<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → b<sup>1</sup>E<sub>1g</sub> respectively), and one charge transfer band at 305 nm. The assignment was made by analogy with ferrocene<sup>36-37</sup>. Table II shows the selected electronic spectra absorption data for compounds 1-6. The spectra for all complexes are similar to that observed for 1.

From tables I and II it is observed that  $K_c$  increases linearly as the  $\lambda_{\text{max}}$  of the absorption bands around 400 nm increase; particularly

Compd	$E_{1/2}$ (I)	$E_{1/2}$ (II)	$\Delta E_{1/2}$ (II-I)	$K_c$
1	0.006	0.173	0.167	664.20
2	-0.016	0.158	0.174	872.16
3	0.006	0.146	0.152	370.51
4	0.013	0.15	0.137	206.68
5	-0.075	0.049	0.124	124.62
6	-0.036	0.087	0.123	119.86

$E_{1/2} = (E_{pa} + E_{pc})/2$ , reported vs ferrocene in 0.1 M TBABF<sub>4</sub>-butyronitrile. Scan rate 0.75 V s<sup>-1</sup>.

Table I. Electrochemical potentials  $E_{1/2}$ (I),  $E_{1/2}$ (II) and  $\Delta E_{1/2}$ (II-I), and constant  $K_{\text{com}}$  for compounds 1-6.

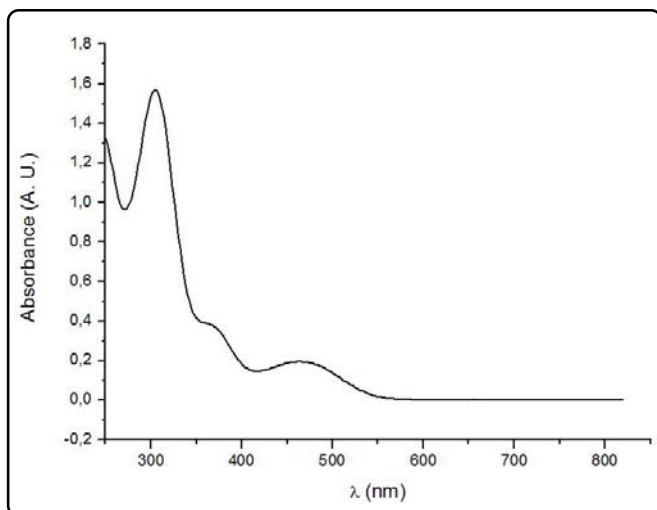


Figure 3. UV-Vis spectrum of compound 1 in butyronitrile solution containing 0.1 M TBABF<sub>4</sub>.

Compd	Charge Transf. $\lambda_{\text{max}}$ nm ( $\epsilon, M^{-1} \text{ cm}^{-1}$ )	<sup>1</sup> A <sub>1g</sub> → b <sup>1</sup> E <sub>1g</sub> $\lambda_{\text{max}}$ nm ( $\epsilon, M^{-1} \text{ cm}^{-1}$ )	<sup>1</sup> A <sub>1g</sub> → a <sup>1</sup> E <sub>1g</sub> $\lambda_{\text{max}}$ nm ( $\epsilon, M^{-1} \text{ cm}^{-1}$ )
1	305 (15658)	360 (3897)	464 (1936)
2	308 (14741)	362 (3639)	468 (1974)
3	290 (10721)	348 (2496)	458 (978)
4	283 (14239)	346 (3181)	456 (1015)
5	276 (15309)	no no	458 (727)
6	280 (12233)		458 (876)

Sample concentrations of ca.  $1 \times 10^{-4}$  M in butyronitrile solution containing 0.1 M TBABF<sub>4</sub>. no = not observed.

Table II. UV-Vis Spectroscopic Data for Compounds 1-6.

for compounds (1-4). This correlation between  $K_c$  and  $\lambda_{\text{max}}$  was found to have the equation  $K_{\text{com}} = 53.80 \lambda_{\text{max}} - 24301.40$ , with a correlation coefficient  $r = 0.9997$ . This can be explained in terms of a stronger delocalization (higher  $K_{\text{com}}$ ) resulting in a lower energy of the absorption band ( $1/\lambda_{\text{max}}$ ). For compounds 5-6 no correlation was found due to the same electrochemical behavior and the same  $\lambda_{\text{max}}$ .

### CONCLUSION

A different electronic communication between ferrocene moieties in all compounds was observed. High values of  $\Delta E_{1/2}$  (II-I) and  $K_{\text{com}}$  in vinylferrocene compounds containing carbonyl group indicates a high electronic communication between the two ferrocenes. Low values of  $\Delta E_{1/2}$  (II-I) and  $K_{\text{com}}$  in vinylferrocene compounds containing alcohol group indicates a low electronic communication between the two ferrocenes. This fact suggests that carbonyl group is a good substituent that allow the electronic communication.

A correlation of two experimental parameters, that are related to the electron density of the metallic center was obtained ( $K_{\text{com}}$  and  $\lambda_{\text{max}}$ ). This suggests that for a high value of  $\lambda_{\text{max}}$  (low energy) there is a low communication between the two redox centers.

Due to the fact that all compounds presented in this work are oxidized only in ferrocene moieties, they can be employed as polymeric materials that can present optical nonlinearities, magnetic, redox and electrical properties.

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