Materials, Nanoscience and Catalysis

The electrochemistry of some ferrocene derivatives: redox potential and substituent effects

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Fifteen ferrocene derivatives I–IX (four of which have been prepared for the first time: II, IIIf, V and VIII) have been prepared by Friedel–Crafts acetylation, Claisen condensation, Michael reaction, and ring closure by hydrazine hydrate. The anodic behaviour of these compounds has been studied by cyclic voltammetry at a platinum electrode in an aprotic solvent. All these substituted ferrocenes exhibit a reversible one-electron oxidation reduction centred at each iron centre, and the effect of substituents on the half-wave oxidation potential is discussed in terms of their electronic properties. Linear correlations have been observed between these potentials and the Hammett σ_x constant for the substituents. Cyclic voltammetry has been carried out for ferrocene derivatives IIIa, V and IX. Copyright © 2003 John Wiley & Sons, Ltd.

INTRODUCTION

Ferrocene and its derivatives undergo reversible oxidation. During the last three decades, numerous studies have been reported concerning the effects of the substituents on the properties of ferrocene.[1–11] Recently,[12] cyclic voltammetry of ferrocenylmethyl nucleo bases, e.g. thymine, cytosine, uracil, N_2-acetylguanine and 2-amino-6-chloropurine, revealed reversible redox processes and no significant changes in redox potentials of the ferrocene moiety by these substituents. Similar work has been carried out on tetrapyrrole derivatives substituted with ferrocenylethynyl moieties,[13] for which cyclic voltammetry revealed that the ferrocenyl moieties appear to be electrochemically independent in these complexes and that there is no significant electronic coupling among the Fe(II) centres.

In addition, the electrochemical behaviour of ferrocene was compared in the presence and absence of fluoride ions at three different electrodes, i.e. platinum, glassy carbon and graphite, using cyclic voltammetric technique.[14] The voltammetric behaviour is equal and similar on all three electrodes. In the absence of fluoride ions, the oxidation potential is generally independent of the electrode material. In the presence of fluoride ions the electrode exhibits a significant surface effect and the electrode activity is noticeably lower when compared with a fluoride-ion-free medium. Thus far, similar work has not been carried out on ferrocylidene acetophenones.

In the present work, we report the synthesis of some new ferrocene derivatives and the determination of their redox potentials. These compounds are *p*-methyl benzalacetylferrocene (**II**), ferrocylidene acetophenones (**III**) and their Michael adducts (**IV**), pyrazoline derivatives bearing a ferrocene moiety (**V**) and ferrocylidene acetyl ferrocene (**IX**) (See Scheme 1).

EXPERIMENTAL

Electrochemical studies

PAR 173, 175 and 176 instruments were used in conjunction with a Houston 2000 recorder to obtain cyclic voltammograms. IR compensation was employed in all cases. A one-compartment glass cell with nitrogen purge and three electrodes (reference, cathode and anode) was used. The cell has added side arms for introduction of the sample, nitrogen purge, and for the unfused Vycor-separated Ag–0.1 M AgNO$_3$ in acetonitrile reference electrode, carbon rod (counter electrode) and platinum electrode working electrode (anode). The latter was constructed by sealing a platinum wire in a

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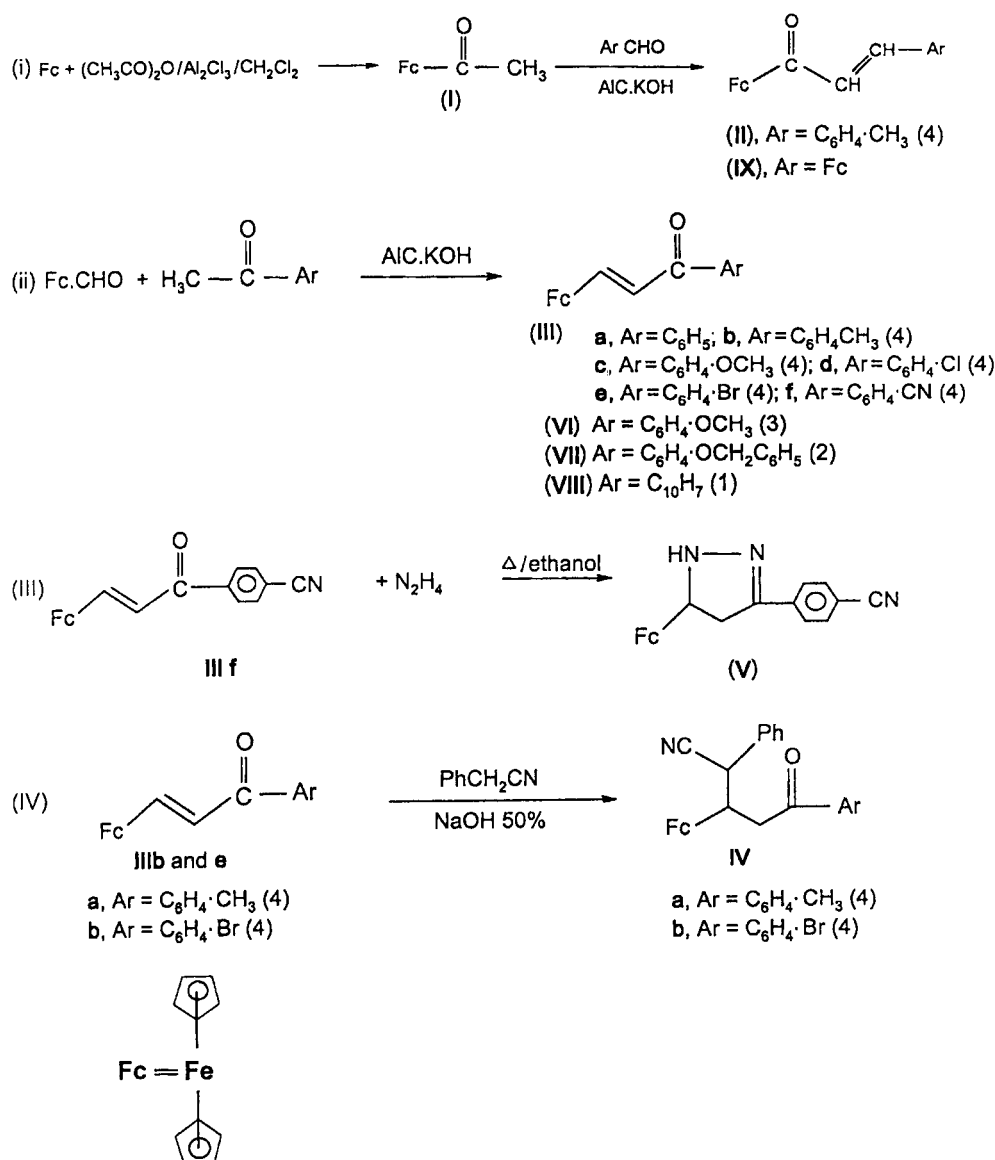
Scheme 1.

glass capillary tube. Acetonitrile (Baker, HPLC grade) was dried via double distillation over phosphorus pentoxide, and reagent-grade sodium perchlorate was used as received.

Spectroscopic studies

IR spectra were recorded on a Beckman ACCUILAB spectrometer, UV and visible spectra were measured on a Cary 219 spectrophotometer, and proton NMR spectra were measured on a JEOL-JNM-FX 200.

Preparation of starting materials

Compounds **I**, **III**, **VI**, **VII** and **IX**, which were prepared according to a literature procedure, gave analytical and spectral data in agreement with published data.[8,15–18] The synthesis of the ferrocylidine **IIIf** was carried out according to the literature.[8]

Synthesis of some ferrocene derivatives
Synthesis of 4-methylbenzalacetylferrocene (II)

A stirred mixture of acetylferrocene (0.01 mol) and 4-methylbenzaldehyde (0.01 mol) in 50 ml ethanol was treated with 20 ml of aqueous KOH (10%) dropwise over a period of 30 min; stirring was continued for 3 h. The solid that separated out was filtered off and recrystallized from *n*-hexane; m.p. 171 °C. Anal. Found: C, 72.27; H, 5.60. Calc. for $C_{20}H_{18}FeO$ (330): C, 72.72; H; 5.45%.

The structure of compound **II** was established as follows: (i) the IR spectrum showed absorption bands at 1110 cm^{-1} (characteristic of the unsubstituted ferrocene ring), 1265 cm^{-1} (substituted ferrocene ring), 1615 cm^{-1} ($\nu_{C=C}$), and 1660 cm^{-1} conjugated ($\nu_{C=O}$); (ii) the UV and visible spectrum (in *n*-hexane) exhibited absorption at 381 (ε, 4320 M^{-1} cm^{-1}) and

475 nm (ε, 3000 M^{-1} cm^{-1}); (iii) the proton NMR spectrum (CDCl$_3$) showed the following peaks at δ 2.3 (S, 3H, Ar–CH$_3$), 4.5–4.7 (m, 9H, cyclopentadienyl protons), two doublets at 6.8 and 7.0 (2H, AB system of olefinic protons), two doublets at 7.4 and 7.6 (4H, A$_2$B$_2$ system of phenyl moiety).

Synthesis of ferrocylidene-4-cyanoacetophenone (IIIf)

A stirred mixture of 4-cyanoacetophenone (0.01 mol) and ferrocenealdehyde (0.01 mol) in 50 ml ethanol was treated with 20 ml of aqueous KOH (10%) dropwise over a period of 30 min; stirring was continued for 3 h. The solid that separated out was filtered off and recrystallized from n-hexane; m.p. 171 °C. Anal. Found: C, 70.16; H, 4.65. Calc. for C$_{20}$H$_{15}$FeNO (341): C, 70.38; H, 4.39%.

The structure of compound **IIIf** was inferred from the IR spectrum, which exhibited strong absorption bands at 1120 cm^{-1} (characteristic of an unsubstituted ferrocene ring), 1260 cm^{-1} (for substituted ferrocene ring), 1620 cm^{-1} ($\nu_{C=C}$), 1665 cm^{-1} ($\nu_{C=O}$) and 2220 cm^{-1} ($\nu_{C\equiv N}$).

Synthesis of pyrazoline derivatives (V)

A mixture of **IIIf** (0.01 mol) and hydrazine hydrate (0.015 mol) in 30 ml ethanol was heated under reflux for 2 h. The solid that separated after cooling was filtered off and recrystallized from benzene to give **V** as pale yellow crystals; m.p. 131 °C. Anal. Found: C, 67.42; H, 4.58. Calc. for C$_{20}$H$_{17}$FeN$_3$ (355): C, 67.60; H, 4.78%.

The structure of compound **V** was inferred from the following: (i) the IR spectrum exhibited strong absorption bands at 1115 cm^{-1} (unsubstituted ferrocene ring), 1267 cm^{-1} (substituted ferrocene ring), 1620 cm^{-1} ($\nu_{C=N}$) and 3300 cm^{-1} (ν_{NH}); (ii) the UV spectrum (in ethanol) showed absorption at 267 (ε, 17 500 M^{-1} cm^{-1}, $\pi-\pi^*$) and 355 nm (ε, 1100 M^{-1} cm^{-1}, $n-\pi^*$); (iii) the proton NMR spectrum (CDCl$_3$) showed signals at δ 1.4 (methine proton), 2.1 (d, 2H, methylene protons), 4.3–4.5 (m, 9H, cyclopentadienyl protons) and doublets at 7.4 and 7.6 (4H, A$_2$B$_2$ system of penyl protons).

Synthesis of ferrocylidine-1-acetylnaphthalene (VIII)

A stirred mixture of ferrocenealdehyde (0.01 mol) and 1-acetylnaphthalene (0.01 mol) in 50 ml ethanol was treated with 20 ml of aqueous KOH (10%) drop wise over a period of 30 min; stirring was continued for 3 h. The solid that separated out was filtered off and recrystallized from n-hexane; m.p. 121 °C. Anal. Found: C, 75.24; H, 5.10. Calc. for C$_{23}$H$_{18}$FeO (366): C, 75.40; H, 4.91%.

The structure of compound **VIII** was deduced from the following: (i) the IR spectrum revealed strong absorption bands at 1125 cm^{-1} (unsubstituted ferrocene ring), 1255 cm^{-1} (substituted ferrocene ring), 1615 cm^{-1} ($\nu_{C=C}$), and 1670 cm^{-1} ($\nu_{C=O}$); (ii) the UV and visible spectrum in (ethanol) showed absorption at 265 (ε, 15 300 M^{-1} cm^{-1}), 340 (ε, 4370 M^{-1} cm^{-1}), 375 (ε, 1230 M^{-1} cm^{-1}) and 460 nm (ε, 730 M^{-1} cm^{-1}); (iii) the proton NMR spectrum (CDCl$_3$) exhibited signals at δ 4.3–4.5 (m, 9H, cyclopentadienyl protons), 6.6–6.8 (2d, 2H, AB system of olefinic protons) and 7.7–7.9 (m, 7H, aromatic protons).

RESULTS AND DISCUSSION

Table 1 lists the half-wave redox potentials $E_{1/2}$ for compounds **I–IX** at a scan rate 50 mV s^{-1}, for 10^{-3} M solutions of these compounds in pure acetonitrile[†] using 0.1 M sodium perchlorate as electrolyte. Generally, the redox potentials are better expressed by $E_{1/2}$ than by the anodic peak E_{pa} or cathodic peak E_{pc}, because both E_{pa} and E_{pc} change with scan rate, whereas $E_{1/2}$ is independent of the scan rate. Also, the half-peak or wave potential is often easier to measure experimentally than E_p, because of the broadness of the peak. The potentials were measured on platinum anode versus Ag/AgNO$_3$ as reference electrode.

Thus, in comparing $E_{1/2}$ **I** (0.317 V) with that of ferrocene (0.124 V), we can conclude that the iron atom in **I** is more difficult to oxidize. The above conclusion may be due to the following factors: (i) the shielding of the iron atom by the carbonyl group, and the steric bulk of the acetyl moiety render the interaction of the iron atom with the electrode difficult; (ii) the electron-withdrawing power of the acetyl group results in an increase in the positive charge on the iron atom and its oxidation becomes more difficult.

$E_{1/2}$ of compound **II** is decreased by a small amount ($E_{1/2} = 0.302$ V); this can be attributed to the decrease

Table 1. Compounds examined and corresponding electrochemical data[a]

Compound	E_{pa} (V)	ΔE_p	$E_{1/2}$ (V)	i_{pa} (μA)	i_{pa}/i_{pc}
I	0.355	0.075	0.317	1.15	1.09
II	0.345	0.085	0.302	2.65	0.98
IIIa	0.287	0.079	0.247	1.87	1.03
IIIb	0.282	0.079	0.242	5.07	1.15
IIIc	0.275	0.075	0.237	1.15	1.01
IIId	0.210	0.067	0.177	0.90	1.12
IIIe	0.222	0.072	0.186	1.30	1.04
IIIf	0.304	0.072	0.268	2.55	1.03
IVa	0.145	0.075	0.107	1.15	1.09
IVb	0.140	0.065	0.107	1.15	1.04
V	0.182	0.082	0.141	3.10	1.03
VI	0.295	0.080	0.255	3080	1.00
VII	0.285	0.085	0.242	1.92	1.01
VIII	0.272	0.072	0.236	2.22	1.03
IX	0.230	0.080	0.190	2.40	1.26
	0.395	0.070	0.360	1.82	1.25

[a] Potential versus [Ag]/[AgNO$_3$] in acetonitrile containing 0.1 M sodium perchlorate. E_{pa}: anodic oxidation potential (anodic peak potential); ΔE_p: separation between anodic oxidation potential and cathodic reduction potential; $E_{1/2}$: half-wave potential (average of oxidation and reduction potentials); i_{pa}: anodic peak current; i_{pa}/i_{pc}: ratio between anodic peak current and cathodic peak current.

[†] Double acetonitrile, b.p. 82 °C over P$_2$O$_5$; water concentration may be 10 mM or higher, as determined by Karl Fischer titration or gas chromatography.

of the electron-attracting power of the carbonyl group as a result of conjugation with the double bond, thereby rendering the iron atom in **II** less positive than in **I**.

For compounds **III** and **VI–VIII** the $E_{1/2}$ values were in the range 0.180 to 0.268 V, indicating that the iron atoms in **III** and **VI–VIII** are easily oxidized in comparison with **I** or **II**. The reasons could be that: (i) the shielding effect of the iron atom by the carbonyl group is strongly diminished; (ii) the electron-attracting power of the carbonyl group is decreased. In these compounds the drop in $E_{1/2}$ is large compared with that in **II**. This seems to be reasonable, because the electron-attracting power of the carbonyl groups in **III** and **VI–VIII** is still present via the conjugative effect, which does not decrease with the distance, although the carbonyl groups in these compounds are located far away from the ferrocene moieties.

Compounds **IV** have $E_{1/2} = 0.107$ V; this agrees well with their structure, in which both the shielding effect by the carbonyl group the and transmission of electrons through the α, β-unsaturated carbonyl moiety are neglected and the compounds become similar to alkylferrocenes.[19]

The $E_{1/2}$ (0.141 V) of compound **V**, which is higher than that of compound **IV**, is attributed to the electron deficiency on the pyrazoline ring, which is transmitted to the iron atom through the substituted cyclopentadienyl ring. On the other hand, compound **IX** exhibits two half-wave potentials: $E_{1/2}^1 = 0.190$ V and $E_{1/2}^2 = 0.360$ V. The first one is attributable to the absence of the shielding effect of the carbonyl group, because the ferrocene nucleus is far away from it; the second one is due to the presence of the shielding effect of the carbonyl group, because the ferrocene nucleus is adjacent to it. This suggests that the -I (inductive) effect of the carbonyl group is of greater importance than the -M (mesomeric) effect in determining the oxidation potentials.

Compounds **IIIa** and **IX** are structurally identical, except that the phenyl group of **IIIa** is replaced by a ferrocenyl group in **IX**; Fc^1 in **IX** is more easily oxidized than Fc of **IIIa**. This is due to the electron-attracting power of the carbonyl group being more compensated by the electron-repelling power of Fc^2, and consequently Fc^1 becomes less positive than Fc in **IIIa**; at the same time the Fc^2 in **IX** becomes more positive and more difficult to oxidize.

(IIIa)

$E_{1/2} = 0.247$ V

(IX)

$E_{1/2}^1 = 0.190$ V

$E_{1/2}^2 = 0.360$ V
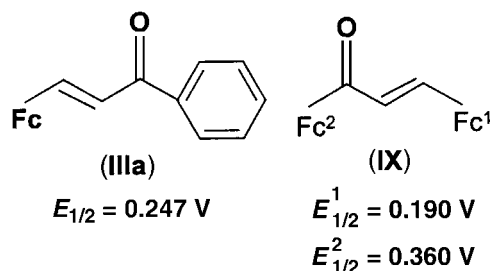
The plots of anodic peak current i_{pa} versus the square root of the scan rate for these compounds were linear, indicating that the reactions are diffusion controlled,[20] see Fig. 1a, b and c for **IIIf, V** and **VIII** respectively. The peak separations ΔE_p (67–80 mV) are just above the ideal value (59 mV), and hence the measurements, which were carried out in an organic solvent, seem to be adequate. The peak current ratios are
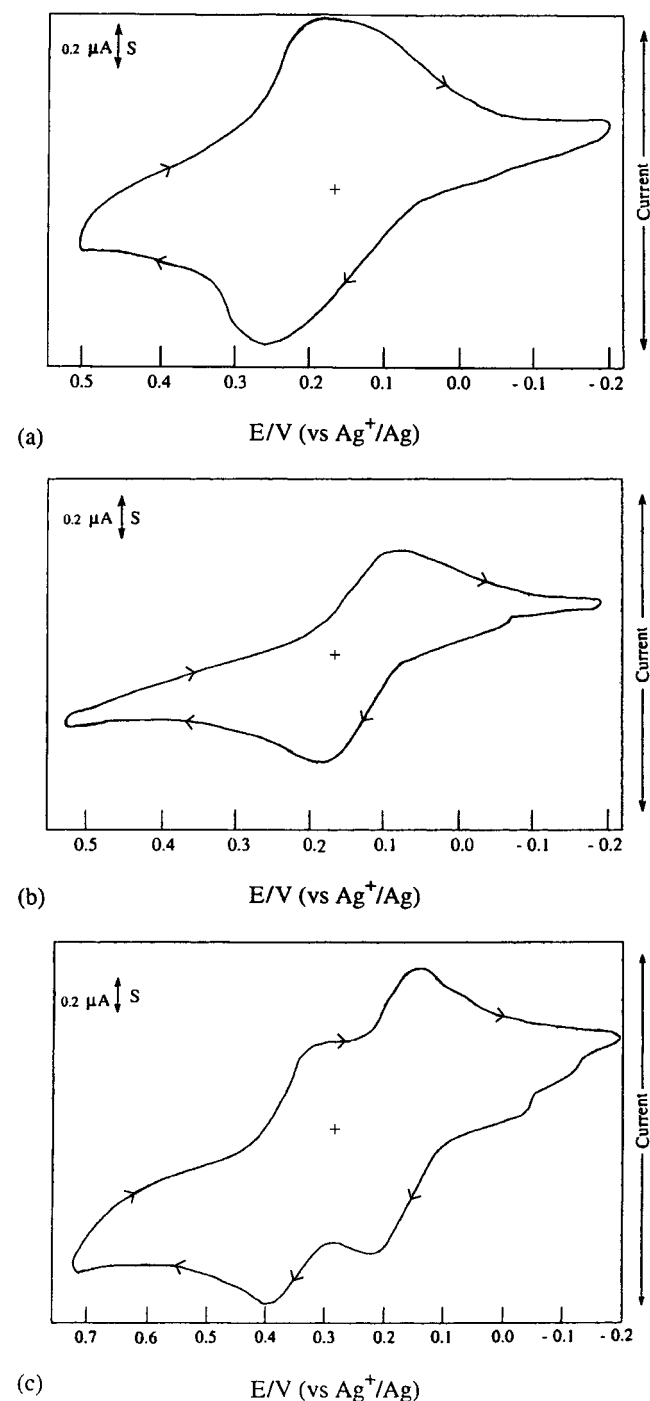

(a)   E/V (vs Ag^+/Ag)

(b)   E/V (vs Ag^+/Ag)

(c)   E/V (vs Ag^+/Ag)

Figure 1. i_{pa} versus square root of scan rate (20, 50, 100, 200 mV s^{-1}): (a) **IIIf**; (b) **V**; (c) **VIII**.

almost close to unity, which indicates that the redox reaction is reversible.

In compound **IX** the ratio between anodic peak current and cathodic peak current is $i_{pa}/i_{pc} \approx 1.25$ for the two peaks; this can be explained as follows. The Fc^1 group remains in solution for a long time after the oxidation process is completed; under these conditions, acetonitrile acts as a nitrogen nucleophile[21] and attacks the positively charged iron atom during cyclic voltammetry. Also, the electron-withdrawing groups on the Fc^2 cyclopentadienyl ring and $^+$Fc^1 lead to the destabilization of $^+$Fc^2. As a result, the positive charge on the iron atom is decreased and, therefore, its reduction becomes difficult, consequently, the cathodic peak current i_{pc} is decreased. This suggests that the reaction is a diffusional process (depending on the combined effect of the charge transfer between the electroactive molecules and counter ion)[22] and a wave with a 'diffusion-controlled' appearance is expected, with peak currents showing a proportionality to the square root of the scan rate.

The cyclic voltammograms of compounds **IIIa, V** and **IX** (Fig. 2 a–c) respectively), exhibit reversible electrochemical oxidation and reduction for a one-electron process of electroactive species. Furthermore, $i_{pa}/i_{pc} = 1.0$ for a reversible charge transfer in the absence of coupled chemical reactions. The voltage is scanned in the anodic direction. The broad ill-defined voltammograms, despite the use of *iR* compensation, suggest large background currents due to impurities (such as water must be present *in significant* amounts since very pure
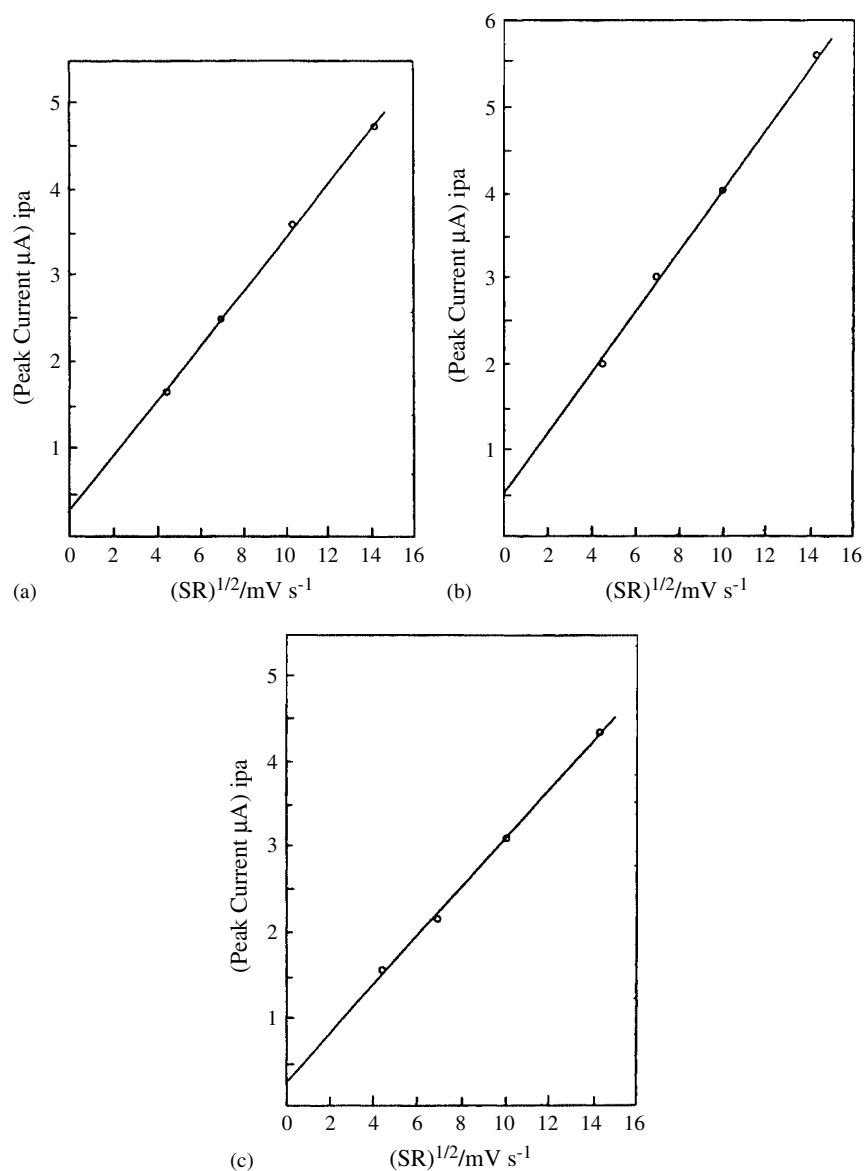

Figure 2. Cyclic voltammogram of ferrocene derivatives **IIIa, V** and **IX** in acetonitrile containing 0.1 M NaClO$_4$. Scan rate is 50 mV s^{-1}; potential versus [Ag]/[AgNO$_3$].

acetonitrile contains 10 mM or higher of water and NaClO$_4$ is very hygroscopic.
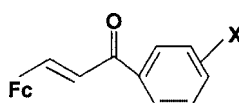
Correlation of ferrocene oxidation potentials with various Hammett-type sigma constants has suggested that the primary mode of interaction occurs through inductive effects rather than resonance or conjugation.[23]

In this work we have found that the α, β-unsaturated carbonyl system has the ability to transfer electrons from the iron atom of the ferrocenyl moiety through the cyclopentadienyl ring to the oxygen of the carbonyl group; consequently, the oxidation potentials increase (compound **IV** has $E_{1/2} = 107$ mV), i.e. there is no interaction between the carbonyl group and the ferrocene moiety. On the other hand, compound **IX** exhibits conjugation between Fc^1 and Fc^2 and the carbonyl group, which shifts the formal oxidation potentials to 190 mV and 360 mV respectively. Such electron transmission through the α, β-unsaturated moiety in ferrocene compounds prompted us to correlate the oxidation potentials of substituted ferrocylidene acetophenone derivatives with Hammett δ constants. Such work has not been carried out thus far on substituted ferrocylidene acetophenone. The $E_{1/2}$ values (measured versus ferrocene oxidation) for a series of substituted ferrocylidene acetophenone under investigation (Table 2) were plotted against the Hammett substituent constant[24] σ_x (Fig. 3). It can be observed (Fig. 3) that the correlation between $E_{1/2}$ and the Hammett substituent constant σ_x is quite good, with a correlation coefficient of 0.987; the exceptions are *p*-chloro- and *p*-bromo-ferrocylidene acetophenone, which fall significantly below the line (i.e. are easily oxidized in acetophenone solution). Here, we attempt to offer an explanation for these anomalies: (i) the *Z*-configuration of the zwitterion (**X**) is energetically profitable during the oxidation process due to the interaction between the positively charged iron atom and the non-bonding electrons of the carbonyl oxygen; (ii) the electromeric effect of the halogen atom plays a significant role during the oxidation process and reinforces the p–π conjugation effects of *p*-chloro and *p*-bromo derivatives, leading to the highly stabilized canonical form (zwitterion **X**) in which an internal solvation of the iron takes place by the carbonyl oxygen, which is the driving force for the ease of oxidation.

(**X**)
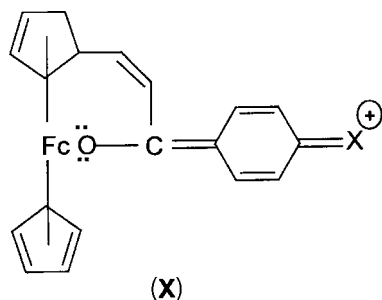
The data from Table 2 were utilized to establish the regression line in Fig. 3. The equation of the regression line, which

Table 2. Measured $E_{1/2}$ values and σ constants for compounds **IIIa–IIIf** and **VI**

Substituent	$E_{1/2}$ (mV)[a]	σ_x[b]
H	247	0.00
4-CH$_3$	242	−0.17
4-OCH$_3$	237	−0.27
4-Cl	177	0.23
4-Br	186	0.23
3-OCH$_3$	255	0.12
4-CN	268	0.63

[a] Versus [Ag]/[AgNO$_3$] in acetonitrile containing 0.1 M sodium perchlorate.
[b] Ref. 21.

was calculated using the Maple V[25] program (ferrocylidene *p*-chloro- or *p*-bromo-acetophenone not included) is $E^{\circ'} = 0.341\delta + 0.237$ V.

The $E^{\circ'}$ value, or the formal potential, is related to the polarographic half-wave potential as follows:

$$E_{1/2} = E^{\circ'} + RT/nF \ln(D_R^{1/2}/D_O^{1/2}) \qquad (1)$$

where D_R and D_O are the diffusion coefficients for the reduced and oxidized forms. Since the diffusion coefficients for the two forms are normally very close in magnitude, then the last term in Equation (1) equals zero and $E_{1/2} = E^{\circ'}$. This is the normal assumption, and allows direct comparison of polarographic E values and cyclic voltammetric values determined from the average of the oxidation and reduction peak potentials.

CONCLUSIONS

The conjugation effects of the carbonyl group adjacent to ferrocenyl and/or vinyl ferrocene moieties are the active mechanisms in determining formal oxidation values. For compound **IX** $E_{1/2} = 360$ mV for the ferrocenyl moiety and 190 mV for the vinyl ferrocene moiety; $E_{1/2} = 107$ mV for **IV**, which has no conjugation effect. For compounds **IIId** and **IIIe**, the combined electromeric effect and the p–π conjugation of the halogen atoms facilitate oxidation. On the other hand, conjugation of the double bond with a carbonyl group adjacent to the ferrocenyl moiety has only a small effect on the oxidation potential of Fc ↔ Fc$^+$ (ferrocene ↔ ferrocenium), as is the case for compound **II**, whereas conjugation of the carbonyl group with the vinyl ferrocene moiety has a pronounced effect. In Hammett-type correlations the inductive effect of the substituents plays a significant role.
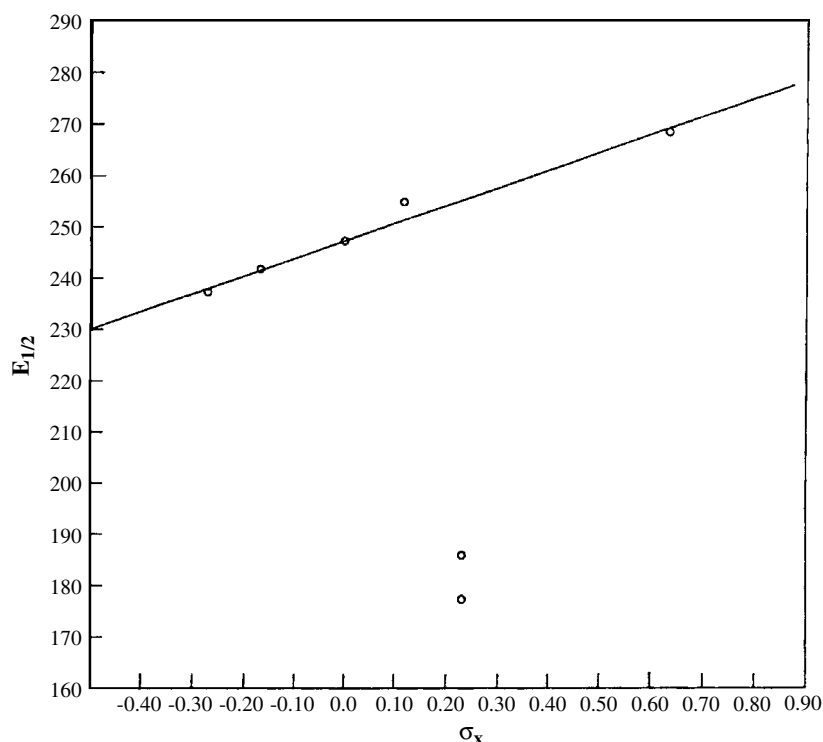
Figure 3. Oxidation potential of ferrocylidene derivatives versus Hammett constant σ_x.

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