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Electrochemical Studies of η^5-Cyclopentadienyliron Hexafluorophosphates of η^6-Substituted Arenes and η^6-Heterocycles

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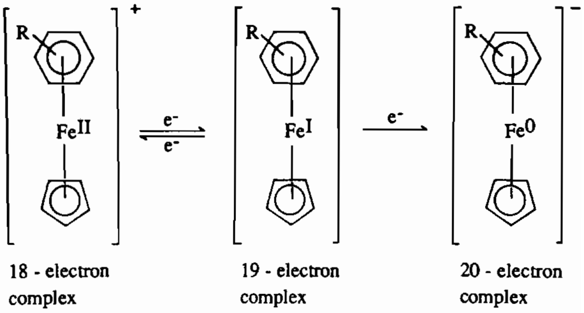
Abstract

Polarographic half-wave potentials for two reduction steps of 49 cyclopentadienyliron complexes of substituted arenes or heterocycles in dimethylformamide were determined. A fast cyclic voltammetry (10–40 V/s) was used to study the electron transfer kinetics of some of these complexes. After correction for the double layer effects, the rate constants of all the complexes studied show that the transfer of electrons in the second reduction step occurs significantly faster than in the first one. This was interpreted as a result of greater delocalization of electrons in the 20-electron complexes of iron compared to the 19-electron complexes.

Introduction

The concept of electron transfer catalysis is receiving growing attention both in inorganic and organic chemistry [1]. Its importance in organometallic chemistry has been stressed recently by Darchen [2] in the course of his study on mixed η^6-arene-η^5-cyclopentadienyliron complexes. Earlier work on such systems, involving mostly polarographic studies with some employing the more versatile cyclic voltammetric technique, has been reviewed [3–5]. Initial reports by Dessy *et al.* [6], Astruc and Dabard [7] and Nesmeyanov *et al.* [8] have shown the presence of two monoelectronic reduction waves for cyclopentadienyliron complexed arenes. It was specified later by El Murr [9] that the first electron-transfer step leading to the formation of electroneutral, 19-electron iron complexes is chemically reversible while transfer of the second electron to give a 20-electron anionic complex is chemically irreversible because of high reactivity of the complex (Scheme 1).



Scheme 1.

El Murr [9] and Solodovnikov *et al.* [10] have claimed that the second reduction step might be reversible under certain experimental conditions; the latter authors also claimed the formation of an extremely unstable 21-electron dianionic complex for the naphthalene–FeCp system. The stability of 19-electron complexes has been discussed by Bowyer *et al.* [11] in terms of the extent of overlapping of the metal and ligand orbitals.

The fate of the 19-electron complex has been studied in various media. Decomposition, dimerization and catalysis have been observed in water, water–alcohol and alcohol solutions [12, 13]; decomposition [2, 11, 14] as well as reduction [8, 10] in aprotic solvents have also been reported. In the case of solvating aprotic solvents exchange of the arene ligand for two molecules of the solvent (MeCN) with the formation of the 17-electron $(\text{solvent})_2\text{CpFe}^+$ complex was postulated by Darchen [2, 14]. When another two-electron ligand was present in solution, the formation of a $L_3\text{CpFe}^+$ complex was observed [$L = P(OMe)_3$], giving the free arene in a potentially very important route to ligand exchange coupled with the formation of a new complex. It is of interest to note that some studies on the dependence of the reduction potential on the structure of the arene CpFe^+ complex have been reported [2, 8, 13]. It was found that the presence of electrodonating substitutents would cause an increase in the magnitude of the reduction potential and Nesmeyanov *et al.* [8] have reported a correlation between $E_{1/2}$ potential and Hammett's σ_p parameter for (substituted arene) CpFe^+ and (arene) (substituted Cp)Fe^+ complexes. In the present work such dependencies were examined for a series of (monosubstituted benzene) CpFe^+ complexes as well as a

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number of previously unreported (heterocycle) $CpFe^+$ complexes. The only previously reported study on a heterocyclic complex involved the (thiophene) $CpFe^+$ hexafluorophosphate [15].

Experimental

Chemicals

Dimethylformamide (DMF) (analytical grade) was dried over calcium hydride for one day and then distilled under vacuum at 30 °C. Tetrabutylammonium perchlorate (Eastman Kodak) which was used as the supporting electrolyte, was dried under vacuum at the boiling point of xylene using a Dean-Stark stillhead. Triple distilled mercury (Fisher Scientific) was purified further in order to remove any base metals by the procedure suggested in the polarographic analyzer manual (EF & G Princeton Applied Research). Known η^6-substituted arene-η^5-cyclopentadienyliron hexafluorophosphates were prepared according to procedures given in previous reviews [4, 5] while the new complexes were prepared as follows.

η^6-Phenoxathiin-10,10-dioxide-η^5-cyclopentadienyliron hexafluorophosphate

The complex was obtained by oxidation of the phenoxathiin complex with *m*-chloroperbenzoic acid as described recently [16]. Yield, 70%. *Anal.* Calc. C, 40.89; H, 2.62. Found C, 40.60; H, 2.51%. IR (cm^{-1}): 1173, 1317 (SO_2). ^1H NMR (CD_3NO_2; δ, ppm; $\delta_{TMS} = 0$): 5.15 (s, Cp); 6.72 (bs, 2H) and 7.10 (m, 2H) (compl. arom.); 7.70 (m, 2H) and 8.15 (m, 2H) (uncompl. arom.). ^{13}C NMR (CD_3NO_2; δ, ppm): 80.99 (Cp); 93.87; 90.44; 87,21; 80.99; 80.44 (compl. arom.); 151.97; 137.52; 127.35; 124.82; 124.35; 120.94 (uncompl. arom.).

η^6-Indoline-η^5-cyclopentadienyliron hexafluorophosphate

The complex was obtained in a ligand exchange reaction [4, 5]. Yield 48%. *Anal.* Calc. C, 40.43; H, 3.65. Found C, 40.62; H, 3.70%. IR (cm^{-1}): 3415 (NH). ^1H NMR (CD_3CN; δ, ppm): 6.15 (s, 1H, NH); 4.88 (s, 5H, Cp); 6.00–5.66 (m, 4H, compl. arom.); 3.90–3.50 and 3.15–2.80 (two m's, 4H, $2CH_2$). ^{13}C NMR (CD_3CN; δ, ppm): 126.1; 90.3; 83.2; 81.2; 78.7; 66.3 (compl. arom.); 74.8 (Cp); 44.1 and 26.4 (2 CH_2).

η^6-2,3-Dihydrobenzofuran-η^5-cyclopentadienyliron hexafluorophosphate

The complex was obtained in a photochemically induced ligand exchange reaction as described recently [17]. Yield 54%. *Anal.* Calc. C, 40.45; H, 3.39. Found C, 40.20; H, 3.54%. ^1H NMR (CD_3CN; δ, ppm): 6.7–6.5 and 6.3–6.1 (two m's, 4H compl. arom.); 5.20 (s, 5H, Cp); 3.70–3.58 and 3.50–3.36 (two m's, 4H, $2CH_2$). ^{13}C NMR (CD_3CN; δ, ppm): 135.56; 93.55; 88.19; 85.69; 84.00; 83.29 (compl. arom.); 79.84 (Cp); 73.30 and 29.29 (2 CH_2).

Electrochemical Measurements

All electrochemical measurements were performed using an Ag/0.1 M $AgNO_3$ in DMF reference electrode. The reference electrode solution was separated from the analyzed solutions by a Vycor™ disk. The counter electrode was made of a platinum wire. The solutions were deaerated for 10 min with argon prior to the electrochemical experiments.

In polarographic measurements, and EG & G Princeton Applied Research (PAR) Model 364 Polarographic Analyzer and a PAR Model 303A Static Mercury Electrode were used. The surface area of the working electrode was approximately 0.076 cm^2, the drop time was 1 s and scan rate 5 mV/s. Cyclic voltammetry experiments were carried out with a computer controlled system consisting of an Apple IIe computer and a PAR Model 273 Potentiostat/Galvanostat. The system was able to provide scan rates of up to 50 V/s. In these measurements the Hanging Mercury Drop Electrode (Metrohm), 8.5×10^{-3} cm^2 in surface area, was used as the working electrode. The double layer capacitance measurements were obtained using a PAR Model 368 AC Impedance System. All computations were done on a Macintosh Plus microcomputer and programs were created using the ZBasic compiler.

Treatment of Data

The cyclic voltammetry data were acquired at the rate of 10 000 samples per second as a current *versus* time function. From these data the charging current was subtracted using a method similar to one described by Nadjo *et al.* [18].

The following algorithm was used

$$i_f = i_t - C_d n + C_d R_s (di_t/dt) \tag{1}$$

where i_f is the faradic current, i_t is the experimental (total) current, C_d is the double layer capacitance, R_s is the uncompensated solution resistance. R_s was determined from the ac impedance measurements. In the potential range of interest, the double layer capacitance was practically independent of potential and it was determined from the offset of current observed in cyclic voltammetric experiments in the absence of faradaic processes.

The convolution was done using the algorithm

$$I(t) = I(k\Delta t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{i=k} \frac{[i((j-1)\Delta t) + i(j\Delta t)]\Delta t}{\sqrt{4\Delta t(k-j) + 2\Delta t}} \tag{2}$$

where k is the number of a data point and Δt is the time period between two consecutive data points.

As it was shown by Oldham [19, 20] the convoluted current $I(t)$ is proportional to the surface concentration of oxidized and reduced forms of the depolarizer

$$C_{ox}(0,t) = \frac{I_l - I(t)}{nFA\sqrt{D_{ox}}} \tag{3}$$

$$C_{red}(0,t) = \frac{I(t)}{nFA\sqrt{D_{red}}} \tag{4}$$

and

$$I_l = nFA\sqrt{D_{ox}}C^*_{ox} \tag{5}$$

where A is the electrode surface, n is the number of electrons involved in the elemental process, D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced form of the depolarizer, respectively, I_l is the limiting value of the convoluted current and C^*_{ox} is the bulk concentration of the oxidized form of the depolarizer.

The potential dependence of the electron transfer rate constant for the first reduction step was calculated from the Butler–Volmar expression

$$k_{fh}(E) = \frac{i_f(t)}{nFA\left\{C_{ox}(0,t) - C_{red}(0,t)\exp\left[\frac{nF}{RT}(E - E^\circ)\right]\right\}} \tag{6}$$

where k_{fh} is the forward electron transfer rate constant, $i_f(t)$ is the faradaic current associated with the first reduction step and E° is the standard potential of the depolarizer.

In calculations of the second electron transfer rate constant an equation similar to eqn. (6) was used except that $i_f(t)$ was replaced with the current caused exclusively by second reduction step, $i_{sc}(t)$. Since the experimental current associated with the second peak is caused by both reduction steps the $i_{sc}(t)$ function must be calculated. Such calculations are quite simple with the use of the convolution method. One can notice that the convoluted current caused by the first reduction step becomes time independent soon after the first reduction peak is reached. Any increase in $I(t)$ function after the first peak can be attributed exclusively to the second reduction step. Therefore, the convoluted current caused by the second reduction step is

$$I_{sc}(t) = I_T(t) - I_{fl} \tag{7}$$

where $I_T(t)$ is the total convoluted current and I_{fl} is the limiting value of the convoluted current associated with the first reduction step.

Then $i_{sc}(t)$ can be obtained by the semidifferentiation of the $I_{sc}(t)$ function [20]

$$i(t) = i(k\Delta t) = \frac{2}{\sqrt{\pi\Delta t}} \times \left\{\frac{I(0)}{2\sqrt{k}} + \sum_{j=1}^{i=k}[I(j\Delta t) - I(j\Delta t - \Delta t)] \times [\sqrt{k-j+1} - \sqrt{k-j}]\right\} \tag{8}$$

The diffuse layer potential (ϕ_2 potential) was calculated from the differential capacitance data obtained for HMDE in 0.1 M TBAP in DMF.

$$\sigma_M(E) = \int_{E_{ZC}}^{E - \phi_2(E)} C_d(E)\,dE \tag{9}$$

and

$$\phi_2(E) = \frac{2RT}{zF}\sin h^{-1}\left[\frac{\sigma_M(E)}{\sqrt{8RT\epsilon\epsilon_0 C_s}}\right] \tag{10}$$

where σ_M is the charge on the electrode, E_{zc} is the zero charge potential, ϵ_0 and ϵ are the permittivity of vacuum and the relative permittivity of the solvent, C_s is the concentration of the supporting electrolyte and z is the magnitude of the charge on the ions.

In the present work $\phi_2(E)$ was calculated by a successive approximation method. First an approximate charge on the electrode was calculated from eqn. (9) assuming $\phi_2 = 0$, then the first approximation of ϕ_2 was obtained from eqn. (10) and this value was fed back to eqn. (9). The cycle was repeated several times until σ_M and ϕ_2 converged to exact values.

So-called true values of rate constant were obtained by applying Frumkin's correction

$$k^{app} = k_t\exp[(\alpha n - z)F\phi_2/RT] \tag{11}$$

where k^{app} is the apparent rate constant, k_t is the true (or corrected) rate constant, α is the electron transfer coefficient, n is the number of electrons transferred in the reduction process, and z is the magnitude of the charge on the reactant. Other symbols have their usual meaning. It is assumed in this correction that the reaction site coincides with the outer Helmholtz plane.

Results and Discussion

Polarography

Polarograpic half-wave potentials ($E_{1/2}$) have been reported for a number of arene CpFe$^+$ complexes bearing a substituent on the arene or cyclopentadienyl ring. The experiments were carried out in various solvents including DMF [6], DMF/THF (1:2) [10], MeCN [8, 21], H_2O [13, 22] or H_2O/EtOH (1:1) [7, 23]. As expected the half-wave potential varied with the solvent used. In the present work the half-wave potentials have been measured

TABLE I. Polarographic Half-wave Potentials for (Monosubstituted Benzene) (Cp)iron Hexafluorophosphates, $(C_6H_5X)(Cp)FePF_6$[a]

Complex	Substituent X	σ_p of X[b]	*para/ortho* ratio[c]	$-E_{1/2}$ (V)[d]	Reported $-E_{1/2}$ (V)
I	NMe_2	−0.83	0	1.95; 2.67	
II	OMe	−0.27	0.3	1.83; 2.60	
III	t-Bu	−0.20	0.39	1.82; 2.46	1.56[e, f]
IV	Et	−0.15	1.32	1.81; 2.62	1.64[g], 1.57[e, f]
V	OPh	−0.32	1.5	1.74; 2.49	
VI	Me	−0.17	1.57	1.71; 2.48	1.68[h], 1.63[f, g], 160[e]
VII	CH_2Ph		1.88	1.70; 2.49	
VIII	Ph	−0.01	2.33	1.66; 2.47	1.44[e, f], 1.30, 2.22[i]
IX	SPhMe-*p*		1.40	1.65; 2.37	
X	Cl	0.23	9	1.60; 2.25	
XI	CO_2Me	0.39	11.1	1.52; 2.21	
XII	COPh	0.46	36.9	1.46; 2.19	
XIII	CN	0.66	67.7	1.45; 2.12	
XIV	SO_2PhMe-*p*		116.7	1.45; 2.08	
XV	NO_2	0.78	∞	1.04; 1.49	

[a] Depolarizer concentration = 10^{-3} M; supporting electrolyte: 0.1 M Bu_4NClO_4 in DMF; $t = 22$ °C; ref. electrode: Ag/0.1 M $AgNO_3$ in DMF.
[b] From ref. 24.
[c] From ref. 25.
[d] Values for the first and second reduction step, this work.
[e] H_2O/EtOH (1:1); depolarizer concentration = 5×10^{-4} M; supporting electrolyte: 0.1 M $NaClO_4$ [7].
[f] H_2O/EtOH (1:1) [23].
[g] H_2O; depolarizer concentration = 5×10^{-4} M; supporting electrolyte: 0.1 M LiOH [13].
[h] H_2O; supporting electrolyte: 0.1 M LiOH [22].
[i] MeCN; depolarizer concentration = 2×10^{-3} M; supporting electrolyte: 0.1 M Bu_4NBF_4; $t = 25$ °C [8]. All potentials *vs.* SCE.

for a large number of complexes under one set of conditions. The results are given in Tables I and II. For comparison, the results reported by the other authors are also included.

As pointed out by Nesmeyanov *et al.* [8], and later confirmed by Darchen [2], the presence of electrondonating substituents on the benzene ring causes a change of the half-wave potential toward more negative values while electronwithdrawing substituents exert the opposite effect. For $CpFe^+$ complexes of *p*-substituted toluenes a relationship between $E_{1/2}$ and the Hammett σ_p parameter has been found [8]. Our study confirmed that finding on a wider range of monosubstituted benzene complexes (Table I). In another study recently reported from our laboratory, it was found that the ratio of *o*/*p* isomers obtained from hydride addition to the monosubstituted benzene complexes can also be correlated with the σ_p parameter [25]. The present results showed that changes in $E_{1/2}$ follow a similar correlation with the *ortho/para* isomer ratio (Table I).

The data thus further reaffirm the earlier conclusion [8] that the inductive component of the substituent's polar effect is transmitted through the aromatic ring to the iron atom, thereby influencing both the magnitude of the reduction potential and the chemical reactivity of the complex [27].

A similar trend on the polar effects of the substituents was observed for 1,2-disubstituted benzenes **XLIII**–**XLIX**. A comparison of the reduction potentials observed for complexes of polycyclic arenes **XXXVI**–**XXXIX** with those of the hydrogenated complexes **XL**–**XLII** also revealed a tendency of an decrease of reduction potentials upon hydrogenation. As the saturated ring could correspond to two electrodonating alkyl substituents, the decrease in $E_{1/2}$ upon hydrogenation in **XL**–**XLII** again fits the observed trend of polar effects.

For the complexes **XXXIII**, **XXXV**, **XLI** all of which are related to indane, the reduction potentials increase in the order of **XXXV** < **XLI** < **XXXIII**, for X = NH, CH_2 and O, respectively. Similarly, for complexes related to fluorene, the order of increasing reduction potential was **XXXIV** < **XXXIX** < **XXX** < **XXIV** < **XXVII**, for X = NH, CH_2, O, S, and CO. For complexes related to anthracene, such as **XX**, **XXIII** and **XXV**, with Y = S, the reduction potential also increases in the order of X = CH_2 < O < S, while for **XVIII**, **XXIII**, **XXIX**, **XXXI**, with Y = O, the reduction potential increases in the order of X = $C(CH_3)_2$ < O < S < SO_2. Thus for such 2- or 3-ring complexes if one of the groups bond to the complexed ring were the same, e.g. direct bond or bonding through S or O, changes in the second groups would cause an increase of the reduction potential in the order of NH < CR_2 < direct bond < O < S < SO_2 (see Fig. 1).

The trends, as discussed above, apply strictly to the $E_{1/2}$ of the one-electron reduction of the complexes as in Tables I and II. The $E_{1/2}$ values of the second reduction step are also included in these Tables and they were more negative by 0.5 to 0.8 V than the $E_{1/2}$ values associated with the first reduction step.

TABLE II. Polarographic Half-wave Potentials for (Disubstituted benzene); (Arene) or (Heterocycle)(Cp)iron Hexafluorophosphate

Complex	Ar in $ArCpFe^+$	$-E_{1/2}$ (V)[a]
XVI	9H-thioxanthene-10,10-dioxide	1.32; 184
XVII	dibenzothiophene-5,5-dioxide	1.34; 1.89
XVIII	phenoxathiin-10,10-dioxide	1.39; 1.91
XIX	9,9-dimethyl-9H-thioxanthene-10,10-dioxide	1.42; 1.84
XX	thianthrene	1.54; 2.22
XXI	2-methylthianthrene	1.57; 2.32
XXII	1,2-bis(*p*-tolylthio)benzene	1.58; 2.19
XXIII	phenoxathiin	1.62; 2.34
XXIV	dibenzothiophene	1.63; 2.37
XXV	9H-thioxanthene	1.69; 2.49
XXVI	9,9-dimethyl-9H-thioxanthene	1.70; 2.50
XXVII	fluorenone	1.21; 1.76
XXVIII	fluorene-9-ol	1.58; 2.42
XXIX	dibenzodioxin	1.68; 2.42
XXX	dibenzofuran	1.70; 2.44
XXXI	9,9-dimethyl-9H-xanthene	1.76; 2.54
XXXII	phenoxazine	1.82; 2.55
XXXIII	2,3-dihydrobenzofuran	1.82; 2.64
XXXIV	carbazole	1.78; 2.75
XXXV	indoline	1.79; 2.76
XXXVI	naphthalene[b, e, f]	1.42; 2.04
XXXVII	phenanthrene[c, g]	1.55; 2.15
XXXVIII	acenaphthene	1.55; 2.28
XXXIX	fluorene[d]	1.74; 2.48
XL	9H-10H-anthracene	1.82; 2.62
XLI	indan	1.84; 2.64
XLII	tetrahydronaphthalene	2.04; 2.92
XLIII	*o*-dichlorobenzene	1.43; 2.14
XLIV	*o*-chlorophenoxybenzene	1.54; 2.19
XLV	1,2-bis(phenoxy)benzene	1.62; 2.37
XLVI	1,2-bis(benzyloxy)benzene	1.80; 2.53
XLVII	2-methoxytoluene	1.84; 2.46
XLVIII	2-ethoxytoluene	1.84; 2.47
XLIX	1,2-dimethoxybenzene	1.84; 2.62

[a] Data for the first and second reduction cycle obtained in this work under conditions given in Table I. [b] -1.07; -1.75 V; depolarizer concentration = 2×10^{-3} M; 0.1 M Bu_4NBF_4 in MeCN; $t = 25$ °C [8, 10]. [c] -1.23; -1.80 V [8]. [d] -1.40; -2.23 V [8] (both c and d under the same conditions as b). [e] -1.01; -1.82 V (same conditions as b except BF_4^- was used instead of PF_6^-) [21]. [f] -1.00 V; 0.1 M TBAP in DMF; $t = -30$ °C [26]. [g] -1.07 V; same conditions as ref. 26.

Cyclic Voltammetry

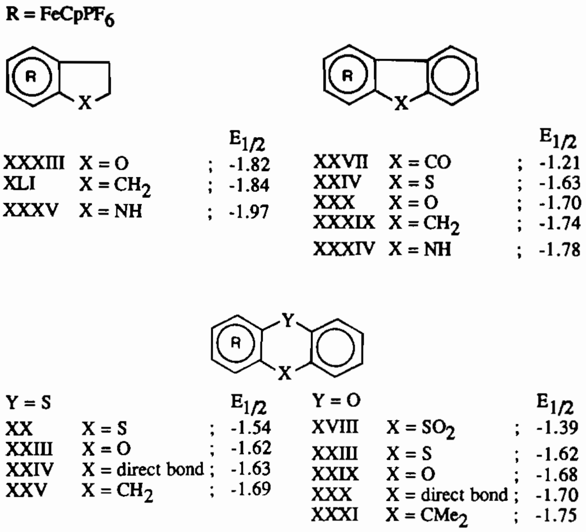

Fig. 1. Comparison of half-wave potentials for the first reduction step of ArCpFe complexes studied in this work.

Cyclic voltammetry was used to investigate chemical reversibility of electron addition and to determine the heterogeneous electron transfer rate constants of selected complexes. The measurements were carried out with HMDE. The sweep rate was varied from 1 to 40 V/s. In studies of kinetics the resistance polarization of solution (IR drop) causes a serious problem because it cannot be easily distinguished from the electrochemical irreversibility of a studied system. In order to avoid systematic errors in rate constant calculations the solution resistance was determined using the ac impedance method and the convoluted curves were numerically corrected for IR drop following the procedure described by Nadjo *et al.* [18]. In some experiments the electronic (positive feedback) IR compensation was also employed. Both methods produced comparable results (agreements of calculated rate constants being within 20%) however, electronic IR compensation usually caused a significant increase of the noise level. In addition to this, rate constants were determined for three different concentrations of depolarizer (1×10^{-3} to 5×10^{-3}) and different sweep rates (10 to 40 V/s) with agreements being within 20% again.

A current–potential curve recorded for the reduction of complex **IX** on HMDE is shown in Fig. 2. For this compound both reduction steps are chemically reversible. It can also be noticed that the potential difference between anodic and cathodic peaks for the second reduction step is greater than for the first one; this indicates that the apparent rate constant for the second electron transfer is lower than for the first one. This reduction pattern is typical of complexes containing sulfides as substituents of the benzene ring. The convoluted current plotted *versus* potential for both reduction steps is shown in Fig. 3. The height of the first step was used to calculate the diffusion coefficient of the depolarizer according to eqn. (5). For all complexes studied the diffusion coefficient was found to be practically independent of the kind of ligand (within 15%) and it was equal to about 5×10^{-6} cm^2/s. Since the convoluted current is proportional to the surface concentration of

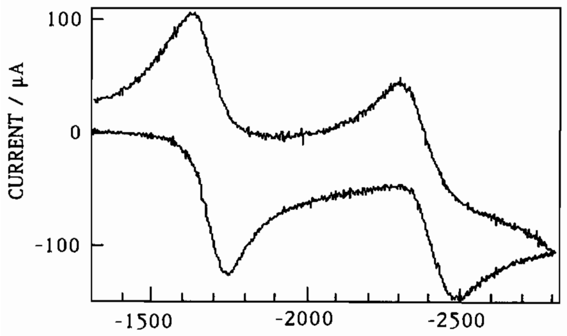

Fig. 2. Cyclic voltammogram recorded for the complex **IX** at concentration 2.5 × 10^{-3} M in DMF using the positive feed back IR compensation. The supporting electrolyte was 0.1 M TBAP, sweep rate was 40 V/s. The curve was corrected for capacitance current.

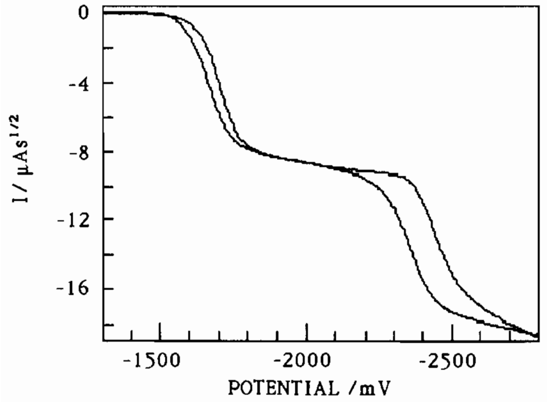

Fig. 3. Potential dependence of the convoluted current *I*, obtained by the semiintegration of the curve shown in Fig. 2.

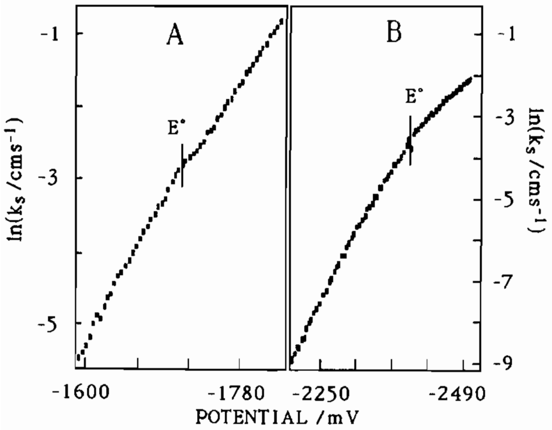

Fig. 4. Potential dependence of the forward rate constant of the electron transfer process calculated from the first (A) and the second (B) reduction step of complex **IX**. Data shown in Figs. 2 and 3 were used to obtain these results.

the depolarizer this function together with the current–voltage function can be used to determine the electron transfer rate constants. The potential dependence of the forward rate constant for the first and the second electron transfer is shown in Fig. 4. Both relationships exhibit some deviations from a straight line. For the first electron transfer, the deviation is comparable to random error, and therefore it is not significant. For the second electron transfer however, the change in the slope of the curve is quite large and it cannot be explained by variation in the ϕ_2 potential (detailed discussion of double layer effects will be presented later). The Marcus–Hush theory predicts a dependence of the electron transfer coefficient on potential [28, 29] and in fact such a dependence was observed in some electrochemical experiments (e.g. [30, 31]). However, as it was pointed out by Khan and Bockris [32], many systems strictly obey the Tafel equation in a very wide range of overvoltages. Thus, the observed potential dependence of the electron transfer coefficient may arise from some properties of the studied compounds rather than from fundamental properties of the electron transfer process. Remarkably, the curving of the potential dependence of the electron transfer rate constant for the second reduction step was observed for all complexes studied with the exception of complex **XX**.

The cyclic voltammograms of compounds containing a sulphonyl group are different from those described above. The second reduction step was chemically irreversible even at the highest sweep rates (Fig. 5). The most complex behavior was observed for compound **XIV**. In that case two cathodic and two anodic peaks were observed (Fig. 6, solid line). The potential dependence of the convoluted current for this compound is shown in Fig. 7. It is important to note that the height of the step associated with the second reduction process is twice as big as the first; this means that, according to eqn. (5), the second reduction process involves the transfer of two electrons per molecule. In the reversed cycle two one-electron oxidation steps are observed. The

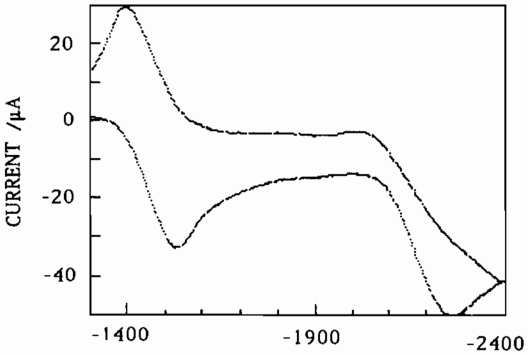

Fig. 5. Cyclic voltammogram recorded for a 1 × 10^{-3} M solution of complex **XIX** in 0.1 M TBAP in DMF. Sweep rate 40 V/s, the uncompensated solution resistance about 850 Ω. The curve was corrected for capacitance current.

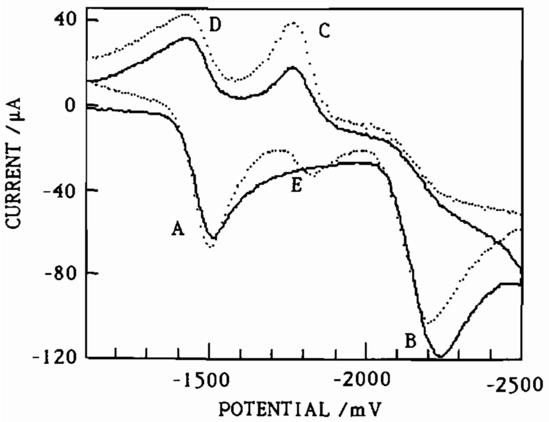

Fig. 6. Cyclic voltammogram recorded for a 2.5 × 10^{-3} M solution of complex **XIV** in 0.1 M TBAP in DMF. Sweep rate was 10 V/s, the positive feed back IR compensation was employed. Solid line represents the first sweep, broken line the second sweep. Both curves were corrected for capacitance current.

second oxidation peak (peak D in Fig. 6) is obviously the oxidation of the neutral complex observed in all cases studied and is directly related to the first reduction peak (A). However, it can be shown that the first oxidation peak (C) is not directly related to the second reduction peak (B). A broken line in Fig. 6

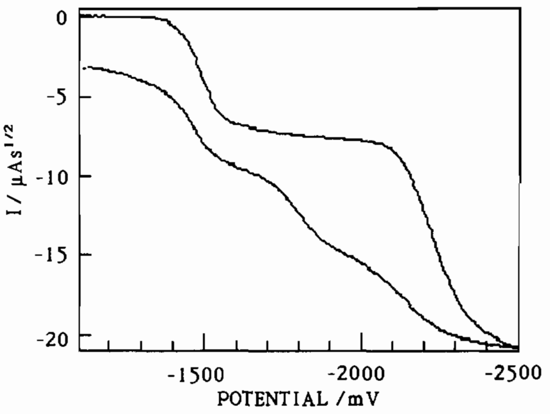

Fig. 7. Potential dependence of the convoluted current I, obtained by the semiintegration of the solid curve shown in Fig. 6.

shows the second sweep recorded immediately after the first one. In the second reduction cycle a new peak (E) most likely associated with the reduction of products formed in the first oxidation step of the first cycle appears. Thus peaks (C) and (E) most likely correspond to the same redox couple which is chemically different from the product of the first reduction step. This can be summarized as

$A^+ + e \longrightarrow A^\circ$ (peak A)

TABLE III. Cyclic Voltammetry Data

Compound	$E°$ (mV) *vs.* PZC	α^{app}	k_s^{app} (cm/s)	k_s^{corr} (cm/s)
XVI	−0.73 −1.28*	0.55 ± 0.02	0.07 ± 0.02	0.025
XVII	−0.77 −1.39*	0.55 ± 0.02	0.06 ± 0.02	0.021
XVIII	−0.79 −1.57*	0.51 ± 0.05	0.04 ± 0.01	0.013
XIX	−0.85 −1.66*	0.53 ± 0.05	0.09 ± 0.07	0.029
XIV	−0.87 −1.66*	0.55 ± 0.03	0.064 ± 0.06	0.021
IX	−1.08 −1.77	0.51 ± 0.05 0.49 ± 0.05	0.07 ± 0.05 0.02 ± 0.005	0.020 0.090
XX	−0.97 −1.63	0.49 ± 0.06 0.55 ± 0.03	0.09 ± 0.02 0.024 ± 0.007	0.025 0.12
XXII	−1.00 −1.59	0.48 ± 0.02 0.52 ± 0.03	0.06 ± 0.01 (8.1 ± 2) × 10^{-3}	0.016 0.038
XXIII	−1.05 −1.87*	0.42 ± 0.02	0.05 ± 0.02	0.011
XXIV	−1.05 −1.77	0.55 ± 0.01 0.55 ± 0.03	0.046 ± 0.02 (4.0 ± 1) × 10^{-3}	0.014 0.021
XXV	−1.12 −1.90	0.51 ± 0.05 0.52 ± 0.05	0.086 ± 0.02 0.024 ± 0.01	0.023 0.12

Starred items – peak potential for chemically irreversible process.

$A^\circ - e \longrightarrow A^+$ (peak D)

$A^\circ + 2e \longrightarrow B^n$ (peak B) (this step probably involves the ECE mechanism which leads to liberation of the ligand)

$B^n \longrightarrow B^{n+1} + e$ (peak C)

$B^{n+1} + e \longrightarrow B^n$ (peak E)

For compounds involved in the irreversible chemical reactions after or during the second reduction step, the rate constant of the second electron transfer cannot be determined. In Table III the kinetic parameters for the complexes studied are reported. In column II the formal potentials determined using the Saveant and Tessier method [30], are listed for chemically reversible systems (in cases of chemically irreversible reduction the cathodic peak potential at sweep rate 10 V/s is given). All potentials are given *versus* the zero charge potential of the dropping Hg electrode in 0.1 M TBAP in DMF. In column III the electron transfer coefficient calculated from the slope of $\ln(k_{\text{fh}})$ *versus* potential curve in the potential region $E^\circ \pm 59$ mV are given. In column IV and V the experimental values of the standard rate constants and the standard rate constants corrected for double layer effects are presented, respectively.

According to Marcus theory [28, 33] the activation energy for the electron transfer process at the standard potential can be expressed as

$$\Delta G^{\ddagger\circ} = \lambda/4 + 0.5 \times (W_{\text{ox}} + W_{\text{red}}) + (W_{\text{red}} - W_{\text{ox}})^2/4\lambda \qquad (12)$$

where λ is the reorganization energy, W_{ox} and W_{red} are works needed to transfer the oxidized and reduced form of the depolarizer, respectively, from the bulk of the solution to the reaction place. W_{ox} and W_{red} include electrostatic interactions between reacting species and the electrically charged electrode and accounting for the double layer effect.

The first reaction step involves a positively charged reactant and a neutral product, since the electrode has a negative charge; the double layer term in eqn. (10) is negative and the reaction is accelerated. The double layer effect on the electron transfer rate constant is quantitatively described by eqn. (9). The second reduction step involves a neutral reactant and a negatively charged product, consequently the double layer effect is opposite to that described above. It is important to notice that the corrected rate constants are practically independent of the kind of ligand and in all cases, the corrected rate constant for the second electron transfer is on average about 4 times greater than the first one. This value was obtained assuming that the reaction site coincides with the outer Helmholtz plane. In a DMF solution, Stokes' radius of TBA^+ ion is 3.83 Å [34] and it is much more than the average distance of the Fe–Cp ring (about 1.69 Å) or the Fe–benzene ring (about 1.56 Å). Therefore, the reaction site can be inside of the inner layer and if so the ratio k_s^{corr}(second)/k_s^{corr}(first) may be much larger than 4. This means that the total reorganization energy for the second reduction step is smaller compared to the first one. This conclusion is valid if the third term in eqn. (12) is negligible (*i.e.* $\lambda^2 \gg (W_{\text{red}} - W_{\text{ox}})^2$). This seems to be the case, since for all the processes studied the α coefficient was about 0.5. According to the Marcus theory the electron transfer coefficient at the standard potential can be expressed as

$$\alpha = 0.5 + (W_{\text{red}} - W_{\text{ox}})/2\lambda \qquad (13)$$

The reorganization energy can be expressed as the sum of reorganization energies for both the dielectric medium and the depolarizer molecule

$$\lambda = \lambda_0 + \lambda_i \qquad (14)$$

The outer sphere reorganization energy, λ_0, arises from the differences in the interaction of reactants and products with the solvent and the electrode. For the process involving one electron process it can be approximately described [33] as

$$\lambda_0 = \frac{e^2}{2}\left(\frac{1}{a} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \qquad (15)$$

where e is the charge of an electron, a is the radius of the reacting molecule, r is the double distance between the center of the reacting molecule and the electrode, n and ϵ are the refractive index and the relative permittivity of the solvent, respectively.

The inner sphere reorganization energy (λ_i) is defined as an energy needed to distort a reactant molecule into the configuration of the product.

The two reduction steps are in many aspects very similar: in the first step the charge on the molecule is changed from +1 to 0, in the second step it changes from 0 to −1; since the molecules undergoing reduction are large, one can expect that λ_0 is very similar for both reduction steps even if the description given by eqn. (15) is not exact. It follows that the distortion of the molecular configuration caused by the second electron transfer is smaller than that caused by the first electron transfer. This can be explained by assuming a greater delocalization of the second electron in the molecule than of the first one. This conclusion is intuitively expected and it is also in agreement with the observed lower stability of 20-electron complexes.

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