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Solvent and temperature effects on the electrochemical reduction of some η^5-cyclopentadienyliron hexafluorophosphates of η^6-polycyclic and η^6-heterocyclic complexes

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Abstract

Electrochemical reduction studies of a series of η^6-polycyclic and η^6-heterocyclic arene–η^5-cyclopentadienyliron cations were carried out in different solvents and at different temperatures. The complexes were reduced in two one-electron steps. Stability of the first reduction product was much higher than the second one. However, both undergo an irreversible chemical transition involving solvent molecules. The kinetics of the chemical reaction following the first reduction step were studied in detail. The rate constants in various solvents were determined by matching experimental curves with ones obtained by a numerical simulation.

Introduction

There have been numerous studies on the reduction of η^6-arene–η^5-cyclopentadienyliron complexes, which show that these types of complexes could be reduced electrochemically in two steps [1–4]:

$$[(\text{arene})\text{FeCp}]^+ \xrightarrow{e^-} (\text{arene})\text{FeCp} \xrightarrow{e^-} [(\text{arene})\text{FeCp}]^-$$

The first electron transfer involves the formation of the electrochemically neutral 19 e^-, d^7 complex, while the second electron transfer leads to the formation of the anionic 20 e^- complex. Solodovnikov *et al.* [5] have also observed the formation of an extremely unstable 21 e^-, dianionic naphthalene complex. The formation of the 19 e^- complex results in the change of the oxidation state of the iron from (II) to (I). The unusual Fe(I) oxidation state may be obtained by either one-electron oxidation of Fe(0) complexes, or by one-electron reduction of Fe(II) complexes. The latter is extremely useful because it can lead to 19 e^- structures without any decoordination [3]. Hamon *et al.*, isolated the 19 e^- peralkylated arene complexes [6]. The stability of these neutral complexes establishes the importance of the solvent used in the study [6, 7]. The stable neutral arene complexes are important electron reservoirs and could be useful as catalysts in the reduction of other species existing in the solution via homogeneous charge transfer [8]. X-ray studies have shown that $\text{CpFe(I)C}_6\text{R}_6$ are true 19 e^- complexes. Both rings are planar and parallel with the Cp–Fe bond (1.79 Å), longer than that found in 18 e^- complexes [3, 5, 9]. EPR studies of these 19 e^- complexes demonstrated the presence of an iron-d^7 configuration, with the unpaired electron in a mainly metal-centered (d_{xz}, d_{yz}) molecular orbital [10]. The formation of these 19 e^- complexes has been examined in various protic and aprotic media [3]. Decoordination of these complexes to liberate the arene ligands from their cyclopentadienyliron moiety has also been investigated [11].

Recently, we have reported the electrochemical studies of some substituted arenes, polycyclic and heterocyclic complexes [12]. The cyclic voltammetric studies of these complexes with a scan rate varying from 10 to 40 V/s showed two reduction waves. The first reduction step is chemically reversible, whereas the second step could also be reversible depending on the experimental conditions. We have also stated that the change of the electron-donating or withdrawing ability results in a change in the reduction potentials. The electron transfer kinetics of some arene complexes in *N*,*N*-dimethylformamide (DMF) at room temperature have been reported [12]. The cyclic voltammetric studies of

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dicyclopentadienyliron complexes of 9,10-dihydroanthracene and related heterocycles in dichloromethane and acetonitrile have also been investigated [13].

In this paper, we report the electrochemical studies and kinetic results of the chemical reactions following the first electron transfer reactions of some cyclopentadienyliron complex cations of a polycycle and some heterocycles in different solvents and at different temperatures.

Experimental

Chemicals

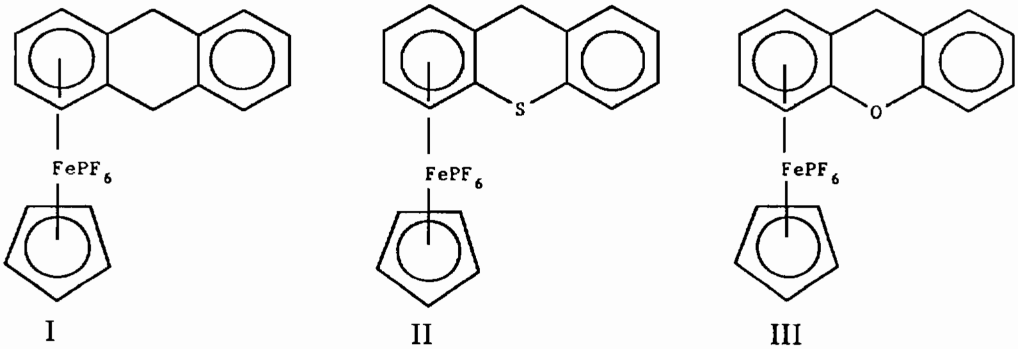
Organic solvents, *N,N*-dimethylformamide (DMF), propylene carbonate (PC), acetone (AC), acetonitrile (AN) and dimethyl sulfoxide (DMSO) were dried over calcium hydride for one day and then the solvents were purified by distillation under argon atmosphere. In the case of DMF, PC and DMSO, the distillations were carried out under reduced pressure. Tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium bromide (TBABr) were obtained from Eastman Kodak and used as supporting electrolytes after further drying. Triple distilled mercury (Fisher Scientific) was purified further in order to remove any base metals by the procedure suggested in the polarographic analyzer manual (EG & G Princeton Applied Research). The preparation of η^5-cyclopentadienyliron hexafluorophosphates of η^6-(9,10-dihydroanthracene), η^6-(thioxanthene) and η^6-(xanthene) were carried out according to literature procedures [14, 15].

Electrochemical measurements

Cyclic voltammetric experiments were performed using a conventional three electrode system. The hanging mercury drop electrode (HMDE) (Metrohm model no. 6.0335) was used as the working electrode. The surface area of this electrode was 0.0087 cm^2. The auxiliary electrode consisted of a platinum wire with surface area *c.* 0.5 cm^2. The reference electrode was made of a silver wire (about 0.1 cm^2 in surface area) placed in 0.1 M solution of $AgNO_3$ in DMF. Due to the instability of Ag^+ in DMF, the solution was prepared freshly prior to each experiment. The reference electrode compartment was separated from the cell by a vycor disk. This electrode was always kept at the same temperature as the studied solutions. Temperatures from 20 to −55 °C were obtained by means of methanol bath in a dewar flask cooled with an Immersion Chiller (Cole-Parmer model C1283-60). In order to do measurements below −60 °C the cell was cooled with liquid nitrogen and then slowly warmed up to a desired temperature. During the warming period the solution was stirred and the temperature was monitored using an internal thermometer. It was possible to keep an almost constant temperature in the cell for several minutes by placing it at a certain height above boiling liquid nitrogen in a dewar flask. Before measurements, solutions were deaerated by passing high purity argon through them for a period of 15 min. A potentiostat, EG&G model 273, interfaced with an AT&T PC 6300 microcomputer was used in all experiments. All computer programs for data acquisition, data processing and numerical simulations were written locally.

Results and discussion

We have previously shown that the cyclic voltammetric study at room temperature in DMF as a solvent is a convenient method for determining the heterogeneous electron transfer rate constants of some (arene)FeCp complex cations [12]. In the present study, we demonstrate that low temperature cyclic voltammetry and the use of a variety of organic solvents with different coordination abilities is a useful way to study the electrochemistry of arene complexes such as **I–III** (Fig. 1). Complexes **I–III** are soluble in various organic solvents. The solvents used included acetonitrile, acetone, *N,N*-dimethylformamide, propylene carbonate and dimethyl sulfoxide.



I II III

Fig. 1. Structures of η^6-arene–η^5-cyclopentadienyliron hexafluorophosphates.

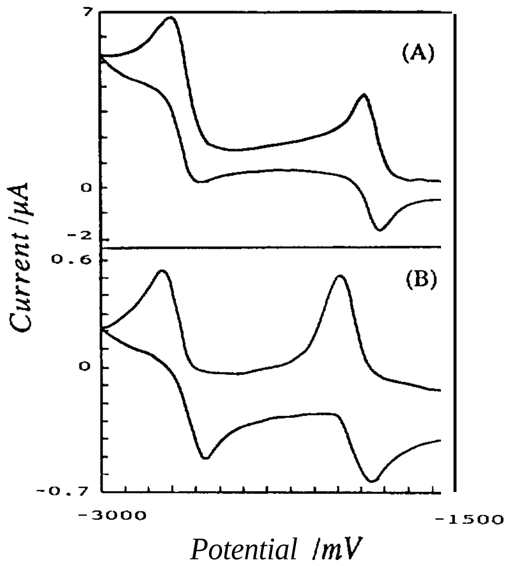


Fig. 2. Cyclic voltammogram at HMDE of 0.1 mM complex I in 0.1 M TBAP in DMF, ν=0.4 V/s, at 22 (A) and -60 (B) “C.

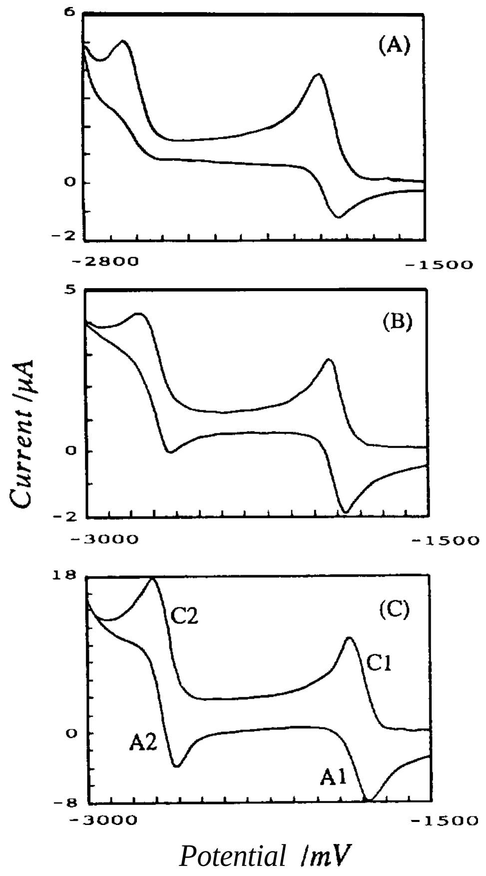


Fig. 3. Cyclic voltammogram at HMDE of 0.1 mM complex I, ν=1 V/s at 22 °C in: DmSO containing 0.1 M TBAP (A); PC containing 0.1 M TBAP (B); AC containing 0.1 M TBAP (C).

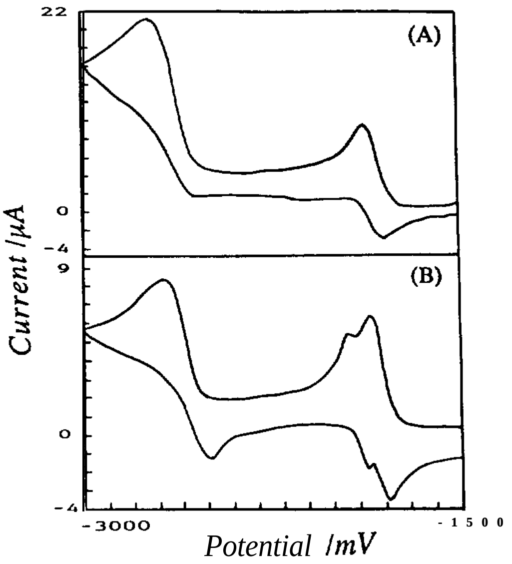


Fig. 4. Cyclic voltammogram at HMDE of 0.1 mM complex I in 0.1 M TBAP in AN, ν=1 V/s, at 22 (A) and -40 (B) “C.

Complexes I-III show similar electrochemical behaviour; all have two reduction steps. A typical cyclic voltammogram of the reduction of complex I in DMF at 22 and – 60 °C is shown in Fig. 2. The voltammogram recorded at room temperature (22 “C) exhibits two reduction steps. This shows the stability of the product from the first electron transfer, while the product from the second electron transfer is relatively unstable at this temperature. At a lower temperature (-60 “C), the product of the second electron transfer is relatively stable and the process is chemically reversible within the time frame of the experiment.

The reduction of complex I in DMSO, PC and AC at room temperature exhibits similar voltammograms, as shown in Fig. 3.

The cyclic voltammogram of complex I in DMSO shows two reduction steps. The product formed in the first reduction step is relatively stable within the time window used in this experiment. However, the product of the second reduction step undergoes fast chemical transformation leading to an irreversible behaviour. The rate of chemical processes associated with both reduction steps is strongly affected by the solvent. The effect is particularly strong in the case of the second reduction step, as shown in Fig. 3. In PC and AC, the second reduction step becomes chemically reversible. This behaviour can be explained in terms of different coordination abilities of various solvents. AN is known for its strong ability for coordination to iron complexes. The decomposition of the neutral complexes in AN at room temperature to produce the free arene ligands and ferrocene has also been reported [4, llc, 16]. Figure 4 shows the cyclic voltammogram of complex I in AN at two different temperatures. As expected, the stability of the reduction products increases with a decrease in temperature. At −40 °C both electrode reactions become chemically reversible. It is also important to point out that the voltammogram recorded at −40 °C exhibits an additional cathodic and anodic peak at potentials more negative than the standard potential of the redox couple. These are typical adsorption peaks and the negative potential shift indicates that the oxidized form of the depolarizer (the positively charged complex) undergoes the adsorption on the mercury electrode. To explain this phenomenon it should be noted that the reduction process takes place at potentials more negative than the zero charge potential of the mercury electrode, therefore the positively charged reactant is electrostatistically attracted by the negatively charged electrode. However, the adsorption must be relatively weak because it vanishes at higher temperatures.

In order to determine the kinetics of the chemical reaction following the first reduction step, a series of cyclic voltammograms were recorded in which the potential scan was reversed before reaching the second reduction step. In Fig. 5 the ratio of anodic to cathodic peak (i_{A1}/i_{C1}) is shown as a function of the sweep rate. The relation is clearly affected by the choice of solvent but it was found to be independent of the depolarizer concentration. This last observation is very significant because it indicates that the reaction is of the first order with respect to the arene complex.

By matching the observed ratios of anodic to cathodic peaks currents with theoretical ones obtained from numerical simulation, the rate constants of the chemical reaction were determined and listed in Table 1.

The rate constants determined in these various solvents for the reduction of complex I are of the first order with respect to the solvent. We can propose a mechanism for electron transfer reaction in this study:

$$[(\mathrm{DHA})\mathrm{Fe^{II}Cp}]^+ + e^- \rightleftharpoons [(\mathrm{DHA})\mathrm{Fe^{I}Cp}]$$

$$[(\mathrm{DHA})\mathrm{Fe^{I}Cp}] + \mathrm{S} \xrightarrow{k_f} [(\mathrm{DHA})\mathrm{Fe(Cp)(S)}]$$

$$[(\mathrm{DHA})\mathrm{Fe(Cp)(S)}] + n\mathrm{S} \longrightarrow \mathrm{DHA} + [\mathrm{CpFe^{I}S}_{n+1}]$$

$$2[\mathrm{CpFe^{I}S}_{n+1}] \longrightarrow \mathrm{Fe(Cp)_2} + \mathrm{FeS}_{n+1}$$

Scheme 1.

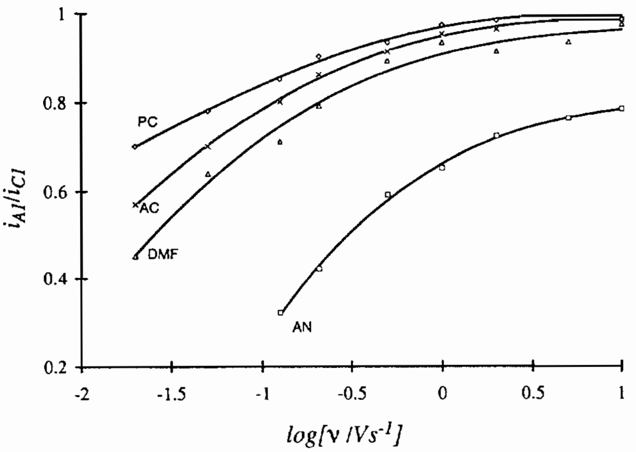


Fig. 5. The ratio of the first anodic peak current i_{A1}, to the first cathodic peak current, i_{C1} vs. the logarithm of the sweep rate, 0.1 mM complex I in different solvents containing 0.1 M TBAP.

TABLE 1. Standard potentials and rate constants of the following chemical reaction for complex I (0.1 mM) in different solvents. Supporting electrolyte: 0.1 M TBABr

Solvent	E_s (mV)	k_f (s^{-1})
DMF	−1830, −2640	0.08
AN	−1840, −2650	0.50
PC	−1830, −2640	0.02
DMSO	−1885, −2670	0.35
AC	−1780, −2610	0.04

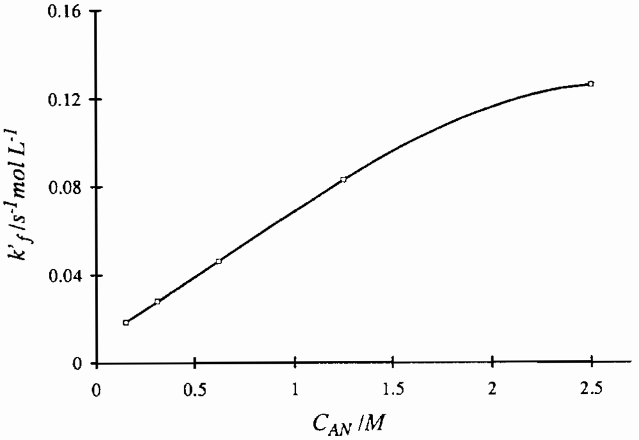


Fig. 6. The forward rate constant, k_f vs concentration of AN in PC, 0.1 mM complex I in different solvents containing 0.1 M TBAP.

These results show that the decomposition of the neutral complex (19 e^- complex) is faster when AN and DMSO are used as solvents. This behaviour could be explained in terms of the coordination ability of these two solvents [16]. In DMF, AC and PC, the process is quite slow. This also indicates the strong interaction between the product of the electrode reaction and the solvent. The order of the chemical reaction with respect to the solvent was determined by kinetic measurements carried out in the mixture of PC and AN. It should be emphasized that in these experiments, the concentration of AN was always at least 100 times greater than the concentration of the arene complex, therefore the kinetics remained to be the pseudo first order. Figure 6 shows the dependence of the rate constant on the concentration of acetonitrile in the mixture. The linear relation at low concentrations indicates that the reaction is first order with respect

TABLE 2. Standard potentials and rate constants of the following chemical reactions for complexes I–III (0.1 mM) in DMF. Supporting electrolyte: 0.1 M TBABr

Complex	E_s (mV)	k_f (s^{-1})
I	−1830, −2640	0.08
II	−1690, −2460	0.06
III	−1750, −2520	0.50

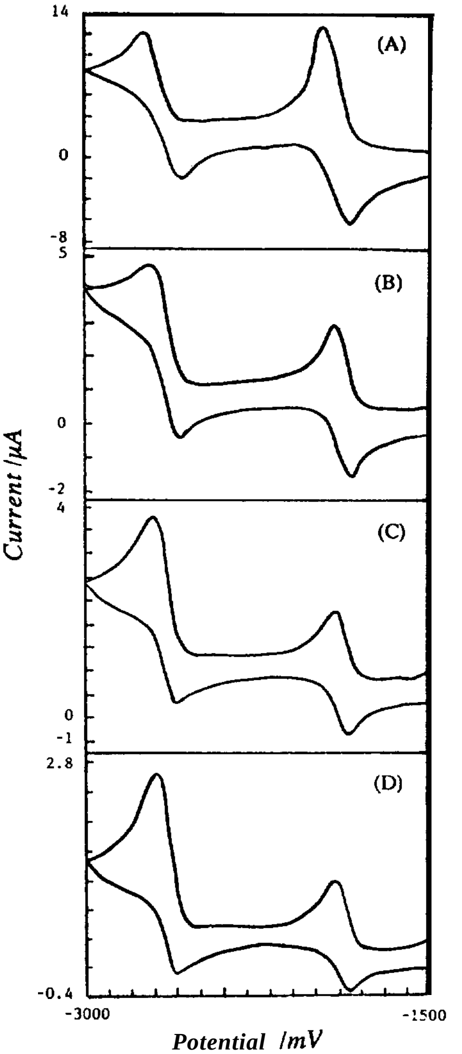


Fig. 7. Cyclic voltammogram at HMDE of 0.1 mM complex I in DMF containing 0. 1 M TBAP at 22 °C; ν(V/s) = 10 (A), 0.4 (B), 0.1 (C), 0.05 (D).

to the acetonitrile; a deviation at higher concentrations may be caused by a non-ideal behaviour of the mixture.

We have also studied the electrochemical properties of heterocyclic analogues, thioxanthene(II) and xanthene(III) complexes. The standard potentials and the rate constants of the following chemical reactions for these complexes in DMF, with tetrabutylammonium bromide as a supporting electrolyte, are listed in Table 2. In this study, we have observed that the rate constant of the following chemical reactions in the case of complex II is much lower than in complex III. This behaviour could be attributed to the d-orbital of the sulfur atom which is available for π delocalization of the added electron density in the case of the thioxanthene complex [13a].

The mechanism of chemical reactions following the second reduction step are much more complicated. In Fig. 7 cyclic voltammograms of complex I recorded at sweep rates 0.05 to 10 V/s in DMF at -26 °C are shown. With a decrease in the sweep rate the ratio of cathodic peaks i_{C2}/i_{C1} increases and the ratio of the second anodic peak to the first cathodic peak (i_{A2}/i_{C1}) decreases.

This may suggest that there are at least two chemical processes associated with the second reduction step: a catalytic process and an irreversible chemical reaction following the charge transfer step. In addition, the ratios of peaks strongly depend on the concentration of the complex in the solution. This indicates that the reactions are second or higher order with respect to the iron complex. Most likely, some products of the decomposition of the negatively charged complex (perhaps metallic iron) are deposited on the electrode surface. The chemical reactions are accelerated on the electrode modified in this manner, which gives an appearance of higher order kinetics.

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