Electroanalytical Studies of Ferrocene and Substituted Ferrocene in Non-aqueous Solvents by Rotating Disc Voltammetry

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Ferrocene, ferrocene carboxyaldehyde, acetylferrocene and benzoylferrocene were investigated by anodic rotating disc voltammetry at platinum, gold and glassy carbon electrodes in dimethyl sulphoxide and acetonitrile. All displayed a single wave and obeyed the Levich plots. The limiting current is linearly proportional to concentration, affording an excellent and rapid determination of these compounds in the presence of tetraethylammonium perchlorate (0.1 M) as supporting electrolyte. The electrode kinetic parameters were determined and mechanisms are suggested.

Keywords: *Ferrocene; substituted ferrocene; dimethyl sulphoxide; acetonitrile; rotating disc voltammetry*

Ferrocene and its derivatives are employed as homogeneous catalysts, anti-knock additives in fuels and for preparing metal film coatings in the gaseous phase.[1,2] Some studies on the electrochemical behaviour of ferrocene and its substituted derivatives in aqueous and mixed solvents have been reported.[1,3–5] Very little information is available on their behaviour in non-aqueous solvents and as far as we know there have been no studies involving rotating disc electrodes. Accordingly, we decided to study the electrochemical behaviour of ferrocene [$(\pi\text{-}C_5H_5)_2Fe$], ferrocene carboxyaldehyde [$(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4CHO)$], acetylferrocene [$(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4COCH_3)$] and benzoylferrocene [$(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4COC_6H_5)$] with the aim of obtaining some information about solvent and substituent effects on the electrode potential, kinetic parameters and mechanisms, and also on the use of rotating disc voltammetry for the determination of these complexes.

Experimental

Chemicals and Reagents

Acetonitrile (ACN) was purified for electrochemical measurements by distillation over phosphorus pentoxide as described by Donnell *et al.*[6] Dimethyl sulphoxide (DMSO) was obtained from Fluka and dried over molecular sieve type 4A.

Preparation of Complexes

Ferrocene carboxyaldehyde was obtained from Fluka and used without further purification. Ferrocene was first prepared and converted into the monoacetyl derivative by a literature method.[7] The monobenzoyl derivative was prepared as described by Weliky and Gould[8] with slight modification as follows.

A solution of ferrocene (0.56 g, 3 mmol) in dichloromethane (5 ml) was added to a stirred mixture of anhydrous $AlCl_3$ (0.42 g, 3.1 mmol) and benzoyl chloride (0.42 g, 3 mmol) in dichloromethane (10 ml) under nitrogen at room temperature. Immediate evolution of HCl gas and formation of an intensely violet - indigo solution was observed. The mixture was stirred for *ca.* 4 h, then cooled, decomposed with ice and filtered through silica gel. The silica gel was washed with chloroform until colourless. The separated blue aqueous layer was extracted with chloroform and combined with the organic layer. The latter was washed several times with distilled water. The deep red organic layer was evaporated under vacuum until the volume became *ca.* 5 ml. Light petroleum (b.p. 40–60 °C) (5 ml) was added and the mixture was kept in a refrigerator overnight. Deep-red needle-like crystals were obtained, m.p. 106–108 °C (lit.[8] m.p., 108–109 °C). The product was also confirmed by ^1H NMR spectroscopy.

Apparatus

All electrochemical measurements were carried out using a potentiostat (Gerhard Bank Electronik, Model ST72).

A Type R.B.2 waveform generator, supplied by Chemical Electronics, was used. The voltammograms were recorded using a Braynas 29000A *X* - *Y* recorder. A three-electrode cell was used; the working electrode was a Brucker ERS1 rotating disc with platinum, gold and glassy carbon electrodes (electrode area = 0.28 cm^2), the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum plate. All measurements were carried out at room temperature (20 °C).

Results and Discussion

Voltammetry

In DMSO

Current - potential curves for the oxidation of ferrocene and its derivatives were recorded at platinum, gold and glassy carbon electrodes at different rotation speeds. Figs. 1 and 2 show typical examples of the voltammograms obtained. All

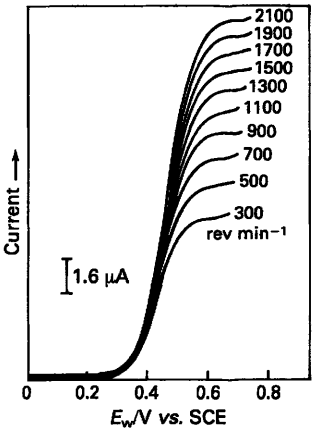

Fig. 1. Anodic oxidation of 10^{-3} M ferrocene in DMSO at a platinum electrode. Scan speed = 10 mV s^{-1}. Tetraethylammonium perchlorate (TEAP) = 0.1 M

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compounds studied gave a good single anodic wave with a well defined limiting current, which was proportional to the square root of the rotation speed and to concentration with a zero or near-zero intercept. Examples of Levich plots[9] are given in Fig. 3. The linearity of these plots indicates that the electrode process is mass transfer dependent and no other complicated processes such as adsorption of reactants or chemical reactions are involved in the electrode reaction.

In ACN

Current - potential curves were obtained for the oxidation of 10^{-3} M solutions of ferrocene, ferrocene carboxyaldehyde, acetylferrocene and benzoylferrocene in ACN. Figs. 4 and 5 illustrate the curves obtained for ferrocene and acetylferrocene. A very well defined limiting current was obtained for all compounds at platinum, gold and glassy carbon electrodes. There was no noticeable difference in the shape of the voltammograms compared with those obtained in DMSO. The Levich plots, shown in Fig. 6, are straight lines passing through the origin, which indicates a simple mass transfer electrode process.

Cyclic voltammetry of the compounds

The reversibility of the system was checked by using cyclic voltammetric measurement at the platinum electrode using a scan speed of 10 mV s^{-1}. Typical results for acetylferrocene are shown in Fig. 7, which indicates a well defined cyclic process with $n = 1$.

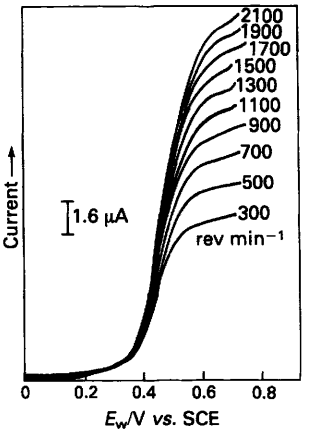

Fig. 2. Anodic oxidation of 10^{-3} M ferrocene in DMSO at a gold electrode. Scan speed = 10 mV s^{-1}. TEAP = 0.1 M

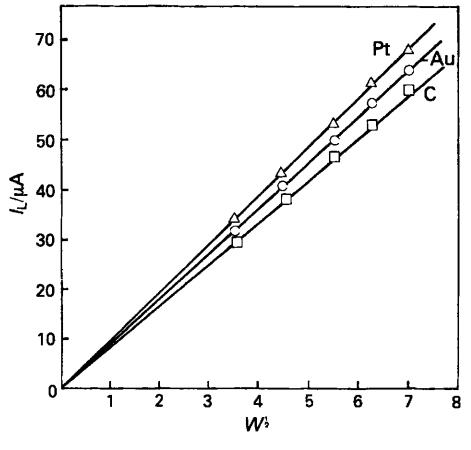

Fig. 3. Levich plots for oxidation of ferrocene in DMSO

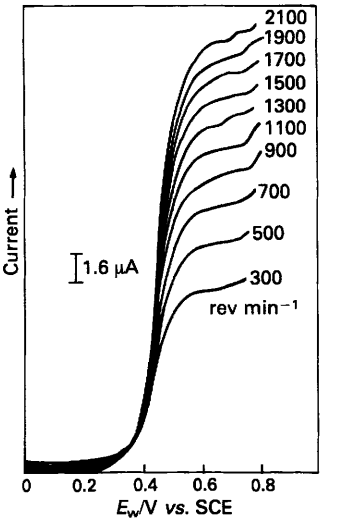

Fig. 4. Anodic oxidation of 10^{-3} M ferrocene in acetonitrile at a platinum electrode. Scan speed = 10 mV s^{-1}. TEAP = 0.1 M

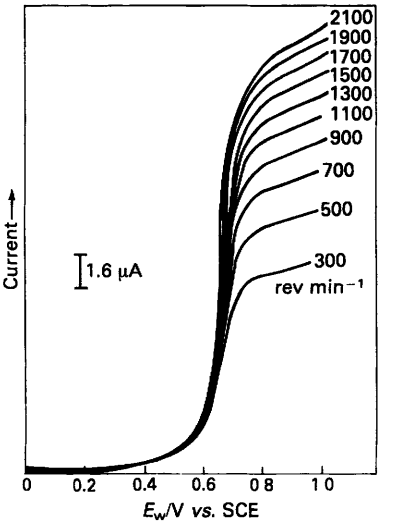

Fig. 5. Anodic oxidation of 10^{-3} M acetylferrocene in acetonitrile at a gold electrode. Scan speed = 10 mV s^{-1}. TEAP = 0.1 M

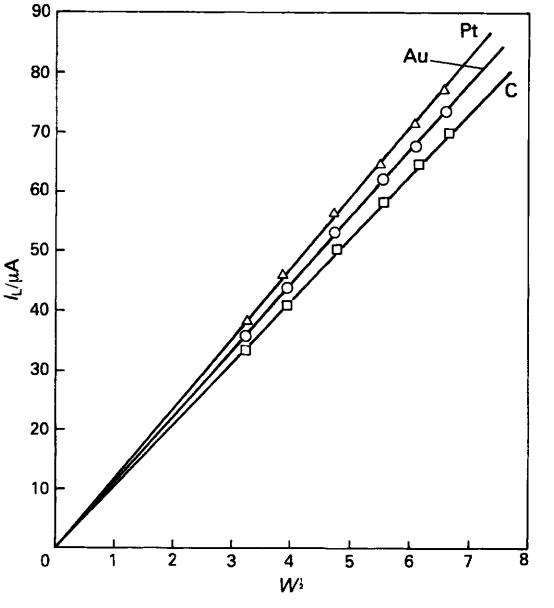

Fig. 6. Levich plots for oxidation of acetylferrocene in acetonitrile

Table 1. Half-wave potentials of ferrocene and its derivatives in DMSO

Substituent on cyclopentadienyl ring	$E_{\frac{1}{2}}$/V *vs.* SCE
H	0.42
COH	0.71
$COCH_3$	0.72
COC_6H_5	0.73

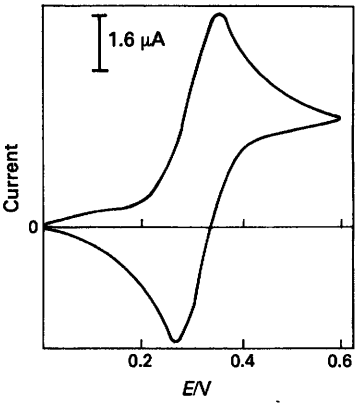

Fig. 7. Cyclic voltammogram for oxidation of 10^{-3} M acetylferrocene in acetonitrile at a stationary glassy carbon electrode. Scan speed = 10 mV s^{-1}

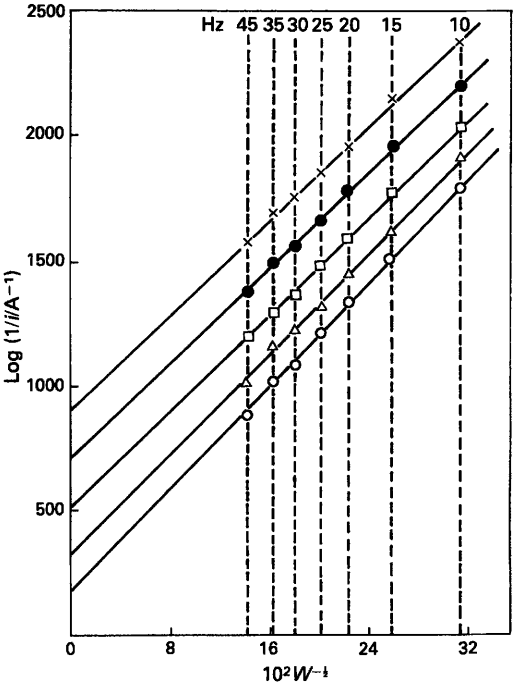

Fig. 8. Mass extrapolation graph following equation (1), for oxidation of ferrocene in DMSO. Each line corresponds to a different electrode potential

Substituent and Solvent Effects on the Half-wave Potential

The half-wave potentials are similar for the platinum, gold and glassy carbon electrodes. Ferrocene showed a well defined anodic wave, with a half-wave potential of 0.42 V *versus* SCE, and no change in potential was observed on going from DMSO to ACN. The introduction of substituents into ferrocene did not alter its reversibility, whereas the half-wave potential was found to be affected by the substitutent, as shown in Table 1.

This difference in half-wave potentials on going from ferrocene to its substituted derivatives could be explained on the basis of the electron-withdrawing inductive effect of the substituents, *i.e.*, COX, where X = H, CH_3 or C_6H_5, whereas the small differences in half-wave potentials on going from X = H to X = C_6H_5 could be attributed to the bulk of the group X attached to a carbonyl group. Similar observations have been obtained by using single-scan voltammetric and polarographic techniques.[1]

Kinetic Parameters

During the calculation of charge-transfer constants we used the half-wave potentials ($E_{\frac{1}{2}}$) as a reference instead of conditional potentials, because the latter are difficult to obtain for these systems. The half-wave potentials are similar for the platinum, gold and glassy carbon electrodes and show a small increase with increasing rotation speed and concentration.

The charge-transfer rate constants (K^0) and the charge-transfer coefficients (α cathodic; β anodic) were determined

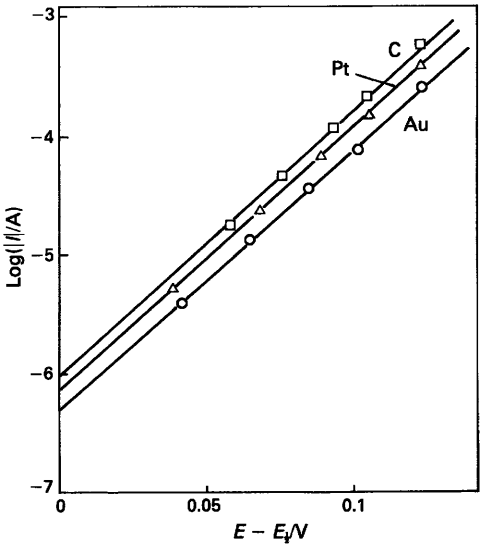

Fig. 9. Graphs used to evaluate K^0 and β by the diffusion extrapolation method

Table 2. Kinetic parameters for 10^{-3} M solutions of the complexes studied in tetraethylammonium perchlorate

		Ferrocene		Ferrocene carboxyaldehyde		Acetylferrocene		Benzylferrocene	
Solvent	Electrode	$K^0/10^{-4}$ cm s^{-1}	β	$K^0/10^{-4}$ cm s^{-1}	β	$K^0/10^{-4}$ cm s^{-1}	β	$K^0/10^{-4}$ cm s^{-1}	β
DMSO	Pt	3.1	0.38	3.0	0.37	2.9	0.37	2.7	0.37
	Au	3.3	0.39	3.2	0.39	3.1	0.38	2.9	0.39
	C*	2.9	0.36	3.1	0.35	2.8	0.35	2.5	0.36
ACN	Pt	2.6	0.35	2.5	0.34	2.4	0.35	2.2	0.36
	Au	2.8	0.38	2.7	0.37	2.6	0.39	2.6	0.37
	C*	2.5	0.34	2.5	0.32	2.5	0.35	2.1	0.33

* Glassy carbon.

by the mass transport extrapolation method using the relationship[10,11]

$$\frac{1}{i_A} = \frac{1}{I_A} + \frac{K}{w^{\frac{1}{2}}} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where i (A) is the current for a particular electrode, w (rad s^{-1}) is the electrode rotation frequency, K is a potential-dependent constant and I (A) is the current corrected for diffusion. The intercept of the graph of $1/i$ *versus* $1/w^{\frac{1}{2}}$ gives I, which when measured as a function of potential gives a Tafel plot and β and K^0 can be obtained from the slope and the intercept, respectively:

$$\log I = \log n FACK^0 + \beta \frac{nF}{RT}(E - E_{\frac{1}{2}}) \quad .. \quad .. \quad (2)$$

where F = Faraday constant, A = electrode area and C = concentration. An example of such a series of the extrapolated plots is shown in Fig. 8. Fig. 9 shows an example of a Tafel plot for obtaining the values of β and K^0.

The kinetic parameters obtained are given in Table 2. As can be seen, there is a slight difference in the charge-transfer kinetic parameters at the three electrodes, which follow the order Au > Pt > C in both DMSO and ACN. This difference may be attributed to the nature of the electrode material. On the other hand, the values obtained for ferrocene are slightly higher than those obtained for the other derivatives, which decrease in the sequence ferrocene > ferrocene carboxyaldehyde > acetylferrocene > benzoylferrocene. This variation might be explained on the basis of the bulk of the substituent and the electron-withdrawal inductive effect, which in turn affect the structure of the double layer existing at the electrode - solution interface.

It is of particular interest to note that the charge transfer reaction rate was faster in DMSO than in ACN. This could be attributed to changes in the solvation sphere or the structure of the double layer of the solvent.[12,13] This indicates a higher activation free energy of the reaction in ACN and consequently the reaction proceeds faster in DMSO.

Determination of Ferrocene and its Derivatives

It is obvious from Figs. 1, 2, 4 and 5 that ferrocene and its substituted derivatives show well defined waves in DMSO and ACN. The height of the wave is linearly dependent on the concentration of the electroactive species and this dependence could be used for the determination of ferrocene and its derivatives.

The limit of determination was found to be 2×10^{-6} M in DMSO and 5×10^{-6} M in ACN (the correlation coefficient of the least-squares plots is better than 0.99).

References

1. Gubin, S. P., *Pure Appl. Chem.*, 1970, **23**, 463
2. Neshvad, G., Roberts, R. M. G., and Silver, J., *J. Organomet. Chem.*, 1982, **240**, 265
3. Page, J. A., and Wilkinson, G., *J. Am. Chem. Soc.*, 1952, **74**, 6149.
4. Wilkinson, G., and Pauson, P. L., *J. Am. Chem. Soc.*, 1954, **76**, 1970.
5. Gubin, S P., *Izv. Akad. Nauk SSSR, Ser. Khim*, 1966, 155.
6. Donnell, J. F. O., Ayres, J. T., and Mann, C. K., *Anal. Chem.*, 1965, **37**, 1161.
7. Birmingham, J. M., *Adv. Organomet. Chem.*, 1965, **2**, 365.
8. Weliky, N., and Gould, E. S , *J. Am. Chem. Soc.*, 1957, **79**, 2742.
9. Levich, V. G., "Physicochemical Hydrodynamics," Prentice Hall, Englewood Cliffs, NJ, 1962
10. Bishop, E., and Cofré, P., *Analyst*, 1981, **106**, 316
11. Abeed, F. A., *PhD Thesis*, University of Exeter, 1980.
12. Beigler, T., Gonzalez, E. R., and Parson, R., *Collect. Czech. Chem. Commun.*, 1971, **36**, 414.
13. Corski, W., and Galus, Z., *J Electroanal. Chem.*, 1986, **201**, 203.

Paper A7/259
Received June 24th, 1987
Accepted September 2nd, 1987