

CCA-1129

YU ISSN 0011-1643

547.631

Original Scientific Paper

Ferrocene Compounds. IX*. Voltammetric Studies on the Oxidation of Some Ferrocene Derivatives

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Received July 13, 1978

Oxidation potentials for ferrocene and a series of mono- (II—VII) and bridged diferrocenyl derivatives (VIII—XIV) have been determined by rotating disk electrode voltammetry and cyclic voltammetry using a platinum electrode in acetonitrile solution. The diffusion coefficients of monoferrocenyl derivatives, ranging from $(0.74 \text{ to } 2.38) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, were evaluated. Analysis of the results obtained for bridged diferrocenyl derivatives has shown that their oxidation potentials are sensitive to structural and electronic effects.

INTRODUCTION

It is well known from voltammetric studies that ferrocene and its derivatives show a reversible one electron oxidation wave¹. Ferricinium salts are stable isolable species². Several research groups have attempted to find a correlation between the oxidation potentials and parameters such as the σ -substituents constants^{1,3-9}, spectroscopic transitions¹⁰ and solvolytic rate constants¹¹, using titrimetric, polarographic and chronopotentiometric techniques.

Several papers have been published recently¹²⁻¹⁶ on the effect of bridging groups on electron transfer between two ferrocene moities. The results presented in this paper have been obtained by investigating the effects of several mono- and bridged diferrocenyl derivatives associated with the electron-transfer process using electrochemical methods.

RESULTS AND DISCUSSION

Monoferrocenyl Derivatives

The half-wave potentials, $E_{1/2}$, obtained by rotating disk voltammetry and the diffusion coefficients of ferrocene (I) and its derivatives II—VII are listed in Table I.

All the examined monoferrocenyl derivatives showed one reversible oxidative wave whose half-wave potential was dependent on the electron-donating or withdrawing character of the substituent. Since the values of the half-wave

* Part VIII: M. Laćan and V. Rapić, *Croat. Chem. Acta* 51 (1978) 325.

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TABLE I

Half-Wave Potentials and Diffusion Coefficients of Monoferrocenyl Derivatives^a

Compd.	Formula ^b	Ref ^c	$E_{1/2}$	$i_L/\omega^{1/2} \cdot c$	$D \times 10^5$
			V vs SCE	mA(rev/min) ^{-1/2} mM ⁻¹	cm ² s ⁻¹
I	FcH	—	0.32	3.84	2.38
II	FcCH ₂ CH=CHPh	19	0.49	3.36	1.95
III	FcCOCH=CHPh	20	0.55	3.08	1.71
IV	FcCHPh ₂	21	0.48	2.88	1.55
V	FcCOCH ₂ COCO ₂ Et	22	0.58	2.63	1.35
VI	$\begin{array}{c} \text{FcCOCH}=\text{C}-\text{CO}_2\text{Et} \\ \\ \text{NH} \\ \\ \text{C}_6\text{H}_3(\text{Cl}) \end{array}$	23	0.72	2.32	1.12
VII	$\begin{array}{c} \text{CO}_2\text{Et} \\ \\ \text{N} \\ / \quad \backslash \\ \text{Fc} \quad \text{H} \end{array}$	23	0.60	1.76	0.74

^a $c = 10^{-3}$ mol dm⁻³; CH₃CN — 0.1 mol dm⁻³ Et₄NClO₄; Pt-electrode ($A = 3.14$ mm²)^b Fc = ferrocenyl^c The compounds listed are prepared according to the references given

potentials for compounds II—VII are shifted to more positive potentials, compared with the $E_{1/2}$ of ferrocene, which was found to be + 0.32 V. vs SCE, it can be concluded that all the substituents attached to the ferrocene ring have an electron-withdrawing character. All the compounds studied gave reversible cyclic voltammograms. The criteria for reversible cyclic voltammograms¹⁷ $E_{pa} - E_{pc}$ close to 58 mV, the peak current ratio i_{pc}/i_{pa} equal to 1.0 the current function ($i_{pc}/v^{1/2}c$) constant, were found to be within the limits of experimental error for the compounds I—VII. The current-potentials curves, obtained with a rotating disk platinum electrode, for all seven compounds show one single wave. The dependence of the limiting current on the square root of the rotation speed (in the range of 100—3000 rev/min) was linear at the potentials which correspond to the plateau on the steady-state current-potential curves, indicating that for all substances the current is diffusion controlled in the plateau region. The diffusion coefficients of the various ferrocene compounds were calculated, by incorporating the values of various parameters in the Levich equation, assuming $n = 1$ in each case.

This value was experimentally confirmed for the oxidation of all the investigated substances by controlled potential coulometry.

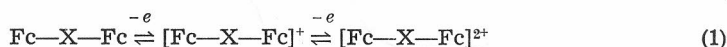
The diffusion coefficients calculated from the Levich equation are tabulated in Table I. The calculated value of the diffusion coefficient for ferrocene (2.38×10^{-5} cm² s⁻¹) obtained with RDE voltammetry is in good agreement with the D -value for ferrocene obtained by the chronopotentiometric technique (2.4×10^{-5} cm² s⁻¹) given by Kuwana et al.¹ The diffusion coefficients shown

in Table I fell in the range $(0.74\text{--}2.38) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The decreasing order of the diffusion coefficients is in agreement with the increasing size and polar effect of substituents. However, it appears that the conclusion of Bacon and Adams¹⁸ that »assumptions about relative D -values should be made with care« is worthy of consideration.

Bridged Diferrocenyl Derivatives


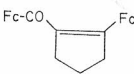
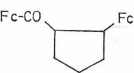
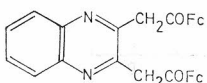
It has been proposed by Watts et al.¹² and Cowan et al.¹⁴⁻¹⁶ that in bridged diferrocenyl derivatives the differences between the first and second half wave potentials (ΔE values) are an indication of the electronic interaction between the two ferrocene moieties. Two types of interaction were proposed — through ligands and through space. The separation of the potentials between two waves depends on the nature of the bridging group. The peak potentials determined by cyclic voltammetry in CH_3CN containing $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$ for compounds VIII—XIV are given in Table II.

The neutral compounds VIII—X undergo two successive reversible one-electron oxidations giving rise to mono- and dication, resp. (eq 1)



(where Fc represents a ferrocenyl unit and X can be one or more bridging groups)

TABLE II
Half-Wave Potentials of Bridged Diferrocenyl Derivatives^a

Compd.	Formula ^b	Ref ^c	$\frac{E_{p1}}{V}$ vs SCE	$\frac{E_{p2}}{V}$ vs SCE	$\frac{\Delta E = E_{p2} - E_{p1}}{V}$	$K_d \times 10^5$
VIII		24	0.39	0.54	0.15	2949
IX		25	0.41	0.65	0.24	8.90
X		25	0.36	0.64	0.28	1.89
XI	$\text{FcCOCH}_2\text{CH}_2\text{COFc}$	26	0.64	—	0	
XII	$\text{FcCOCH}_2\text{CH}_2\text{CH}_2\text{COFc}$	27	0.65	—	0	
XIII	$\text{FcCOCH}_2\text{COCOCH}_2\text{COFc}$	22	0.63	—	0	
XIV		22	0.62	—	0	

^a $c = 10^{-3} \text{ mol dm}^{-3}$; $\text{CH}_3\text{CN} - 0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$; Pt-electrode; sweep rate = 100 mV s^{-1}

^{b, c} See the corresponding footnotes of Table I

The cyclic voltammograms of compounds VIII—X are illustrated in Figure 1. According to the criteria for cyclic voltammograms¹⁷, both charge transfers were close to reversible in all three compounds. Passivization of the electrode was observed during voltammetric measurements of all bridged diferrocenyl derivatives. To obtain constant current function ($i_p/v^{1/2}c$) with sweep rate it was necessary to clean the electrode with sulphuric acid, water and acetone before each measurement. The voltammograms of compounds XI—XIV also showed a reversible behaviour. Exhaustive coulometric oxidation of compounds VIII—XIV resulted in the consumption of 2 F/mol giving rise to pale green solutions of formed dication.

Substances VIII—X represent new mixed-valence compounds derived by one-electron oxidation. Due to the small difference between the first and

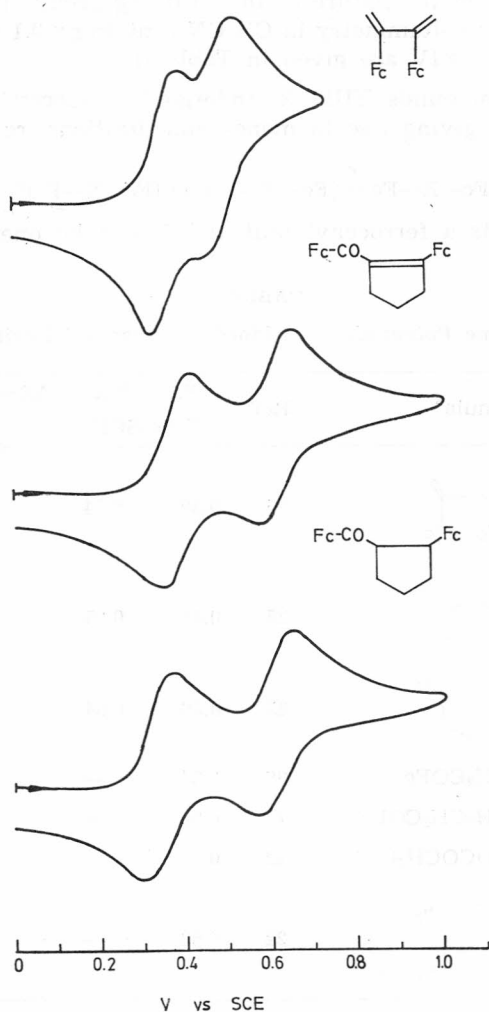
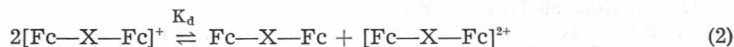


Figure 1. Cyclic voltammograms of some bridged diferrocenyl derivatives; $c = 10^{-3}$ mol dm⁻³; CH₃CN — 0.1 mol dm⁻³ Et₄NClO₄; Pt-electrode; sweep rate = 100 mV s⁻¹.

second peak potentials separate monocation solutions do not exist¹⁶. An equilibrium mixture of three species is formed (eq 2)



The data in Table II show how the changes in relative oxidation peak potentials ($\Delta E = E_{p2} - E_{p1}$) affect the equilibrium constants for the disproportionation reaction (2). ΔE is reduced to zero when the number of C-atoms in the bridging group is greater than 4. Although the number of compounds studied in this paper is too limited to justify general conclusions about the ΔE value and electronic interaction between two ferrocene units, some interesting trends can be noted. It is reasonable to believe that through space interaction between two ferrocene units in IX and X, having rather long bridging groups (3 C-atoms), is relatively unimportant. The increased interaction between two ferrocene moieties in IX and X could be attributed to a ligand inductive effect. However, care must be taken in any interpretation of the ΔE variation because this difference will include the solvation energy of the dication species.

EXPERIMENTAL

Materials

Ferrocene (purum, Fluka) was purified by sublimation at high vacuum, m. p. 173—4 °C. Substances II—XIV were synthesized by procedures given in references¹⁹⁻²⁷ listed in Tables I and II.

Acetonitrile (Koch Light Ltd) was purified by a procedure similar to that previously described²⁸. The supporting electrolyte was tetraethylammonium perchlorate (C. Erba, polarographic grade).

Electrochemistry

Cell, the electrodes and apparatus for cyclic voltammetry, rotating disk voltammetry and coulometry at controlled potential were the same as already described^{29,30}.

Acknowledgement. — This research was supported by grants from the *Councils for Scientific Research, of SR Croatia and SR Bosnia and Herzegovina*. We are very grateful to Miss Dr Z. Ibrišagić for her generous gift of 2,3-diferrocenyl-1,3-butadiene. Acknowledgement is due to Miss M. S. Šuprina and Mrs. J. Brcković for taking IR spectra.

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SAŽETAK

Voltametrijski studij oksidacije nekih ferocenskih derivata

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Primjenom voltametrije s rotirajućom platinskom elektrodom i cikličkom voltametrijom s platinskom elektrodom u acetonitrilnoj otopini određeni su oksidacijski potencijali ferocena i niza mono-(II—VII) i premoštenih diferocencilnih derivata (VIII—XIV). Nađeni difuzioni koeficijenti imaju vrijednosti od $(0.74 \text{ do } 2.38) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Analizom rezultata koji se odnose na premoštene diferocencilne derivate pokazano je da su njihovi oksidacijski potencijali ovisni o strukturnim i elektronskim efektima.

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Prispjelo 12. srpnja 1978.