

BRIDGED FERROCENES—VIII¹

POLAROGRAPHIC HALF-WAVE POTENTIALS OF FERROCENOPHANES AND RELATED COMPOUNDS*

J. E. GORTON, H. L. LENTZNER[†] and W. E. WATTS

School of Physical Sciences, New University of Ulster,
Coleraine, Northern Ireland

(Received in the UK 14 May 1971; Accepted for publication 23 May 1971)

Abstract—Polarographic half-wave potentials have been measured for a series of bridged ferrocenes and non-bridged model compounds. Analysis of the results has shown that the oxidation potentials of ferrocene derivatives are sensitive to structural, conformational, electronic, and possibly field effects.

INTRODUCTION

REVERSIBLE one-electron oxidation of ferrocene to the ferricenium cation is a characteristic reaction of the molecule which may be simply effected chemically, anodically, or photolytically.² The similarity of the oxidation potential of the process to those associated with the oxidation of ferrocyanide anion and hexaquoferrous cation suggested that the electron was removed from a metal orbital. Recent spectroscopic studies^{3,4} have confirmed this view and, although the a_{1g} ($3d_{z^2}$) orbital is the highest filled orbital in ferrocene, have shown that oxidation of ferrocene to the ground state of the ferricenium cation occurs through removal of an electron from the lower lying degenerate e_{2g} level (predominantly $3d_{xy, x^2-y^2}$).

Early qualitative experiments² revealed that the ease of oxidation of ferrocene derivatives was related to the electronic character of the substituent(s) attached to the cyclopentadienyl rings. Electron-donating substituents facilitate oxidation while electron-withdrawing groups have the opposite effect. These observations have since been placed on a quantitative basis. Several groups have investigated the oxidation of ferrocene derivatives by titrimetric,^{5,6} polarographic,^{7,8} and potentiometric techniques⁹⁻¹¹ and have attempted correlation between the oxidation potentials measured by these methods and parameters such as σ -substituent constants,^{5-7,9-11} spectroscopic transitions,⁸ and solvolytic rate constants.¹²

The precise mechanism by which electronic effects are transmitted from one ring in ferrocene to the Fe atom and thence to the other ring has remained enigmatic despite the enormous volume of research which has been devoted to a study of the organic chemistry of the compound. Our interest¹³ in this problem, together with the knowledge accumulated in a study¹⁴ of the unique electronic and conformational properties of bridged ferrocenes, prompted an investigation of the oxidation potentials of a series of these compounds. We also wished to study the steric and structural effects associated with the electron-transfer process and to explore the possibility that the dinuclear ferrocenophanes might serve as model compounds for the synthesis of superconducting polymers.

* Abstracted in part from the Ph.D. thesis of H.L.L., University of Strathclyde (1970)

† Present address: Collège Scientifique Universitaire, Rue de Frères Lumière, Mulhouse, France

DISCUSSION

The polarographic half-wave potentials ($E_{\frac{1}{2}}$)* vs. the saturated calomel electrode (SCE) of the ferrocene derivatives studied are listed in Tables 1 and 2. Following usual practice, $\Delta E_{\frac{1}{2}}$ values are also given relative to the half-wave potential of ferrocene which was found to be +0.34 volts vs. SCE. Thus, a negative $\Delta E_{\frac{1}{2}}$ value indicates that the

TABLE 1. POLAROGRAPHIC HALF-WAVE POTENTIALS OF NON-BRIDGED FERROCENE DERIVATIVES^a

Compound	$E_{\frac{1}{2}}$ ^b volts	$\Delta E_{\frac{1}{2}}$ ^c volts	Lit. $E_{\frac{1}{2}}$ or ($E_{\frac{1}{2}}$) ^d volts
Ferrocene	0.34 (0.01)	—	0.31 ^{8, 24} ; (0.34 ^{9b})
Acetylferrocene	0.62 (0.01)	+0.28	0.56 ⁸ ; (0.57 ^{9a})
Benzoylferrocene	0.61 (0.02)	+0.27	(0.57 ^{9a})
Methoxycarbonylferrocene	0.61 (0.01)	+0.27	0.56 ⁸
1,1'-Dimethylferrocene	0.23 (0.01)	-0.11	(0.24 ^{9b})
1,1'-Diethylferrocene	0.25 (0.01)	-0.09	(0.22 ^{9b})
1,1'-Diphenylferrocene	0.37 (0.01)	+0.03	(0.37 ^{9b})
1-Acetyl-1'-ethylferrocene	0.66 (0.01)	+0.32	
Diferrocenylmethane (14; R = R' = H)	0.30 (0.02)	-0.04	0.19 ^e
	0.40 (0.02)	+0.06	0.31 ^e
2,2-Diferrocenylpropane (14; R = R' = Me)	0.28 (0.02)	-0.06	
	0.44 (0.02)	+0.10	

^a In 90% EtOH aq. vs. SCE

^b Reproducibility limits are given in brackets (Experimental)

^c Relative to the half-wave potential of ferrocene

^d Chronopotentiometric quarter-wave potentials vs. SCE

^e Formal oxidation potentials determined by potentiometric titration (ref. 6b).

compound is more readily oxidized than ferrocene while the reverse is true for a positive value. In order that the values obtained could be compared with those from related studies, we also measured the half-wave potentials (vs. SCE) of a representative collection of non-bridged ferrocenes which had already been investigated by other groups. The correspondence between these measurements is shown by the values listed in Table 1. Finally in this connection, the internal consistency of the results reported was verified by repeated measurements on several samples over the period of the study. In all cases, reproducible results were obtained. In the following discussion, the various types of bridged ferrocene are considered in turn. The half-wave potentials of these compounds are given in Table 2.

* The half-wave potential ($E_{\frac{1}{2}}$) is related to the standard potential (E^0) of the oxidation-reduction system by the expression:¹⁵

$$E_{\frac{1}{2}} = E^0 - (RT/2nF) \log (D/D')$$

The diffusion constants for the reduced and oxidized species (D and D' respectively) are usually not greatly different such that $E_{\frac{1}{2}} \approx E^0$.

[*m*]Ferrocenophanes. Alkyl-substituted ferrocenes are more readily oxidized than ferrocene (Table 1) and this also holds true for the alkyl-bridged compounds (Table 2).

TABLE 2. POLAROGRAPHIC HALF-WAVE POTENTIALS OF BRIDGED FERROCENE DERIVATIVES^a

Compound ^b	$E_{\frac{1}{2}}^c$ volts	$\Delta E_{\frac{1}{2}}^d$ volts
1 ($m=2$)	0.18 (0.02)	-0.16
1 ($m=3$)	0.27 (0.01)	-0.07
1 ($m=4$)	0.26 (0.01)	-0.08
1 ($m=5$)	0.23 (0.01)	-0.11
3 ($m=3$)	0.59 (0.02)	+0.25
3 ($m=4$)	0.61 (0.02)	+0.27
3 ($m=5$)	0.66 (0.01)	+0.32
4	0.56 (0.01)	+0.22
5	0.61 (0.01)	+0.27
6	0.29 (0.01)	-0.05
7	0.21 (0.02)	-0.13
8	0.23 (0.01)	-0.11
9	0.30 (0.02)	-0.04
10 (R=H)	0.43 (0.01)	+0.09
10 (R=Me) ^e	0.43 (0.01)	+0.09
10 (R=Ph) ^e	0.44 (0.01)	+0.10
11 (R=R'=H)	0.25 (0.01)	-0.09
	0.44 (0.02)	+0.10
11 (R=Me, R'=H)	0.23 (0.02)	-0.11
	0.43 (0.02)	+0.09
11 (R=R'=Me)	0.16 (0.02)	-0.18
	0.46 (0.02)	+0.12

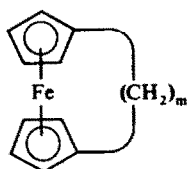
^a In 90% EtOH aq. vs. SCE

^b Formulae are given in the text

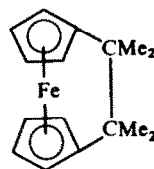
^c Reproducibility limits are given in brackets (Experimental)

^d Relative to the half-wave potential of ferrocene (+0.34 volts)

^e Both *meso* and racemic forms give identical values



1

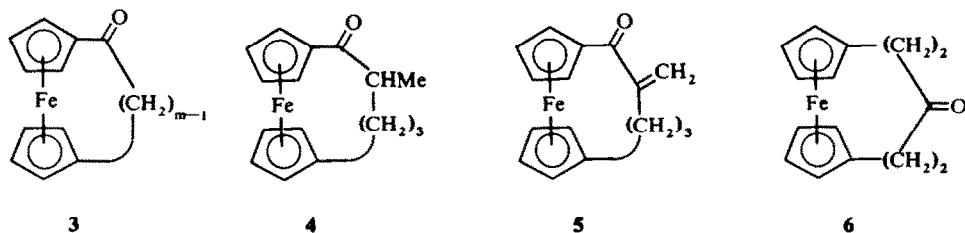


2

The half-wave potentials of [3]-, [4]- and [5]ferrocenophane (**1**; $m=3, 4$ and 5 respectively) are similar in magnitude and the mean value ($E_4=0.25$ volts) is identical with that of a non-bridged model, 1,1'-diethylferrocene. For these three ferrocenophanes, a trend towards an increase in potential as the bridge length is shortened borders on significance. If real, this may perhaps be related to a conformational effect which permits greater hyperconjugative donation of electron density to the cyclopentadienyl orbitals from the methylene groups at the termini of the 5-carbon bridge. The geometrical requirements for hyperconjugative interaction are well documented.¹⁶ These results support the earlier conclusion^{9a} that the electrode reaction is free of steric effects. Thus, although steric shielding of the Fe atom by the bridge should be most effective in the case of the flexible [5]ferrocenophane molecule, a corresponding decrease in the ease of oxidation is not observed.

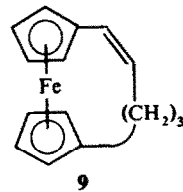
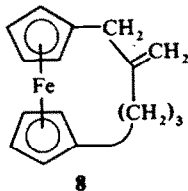
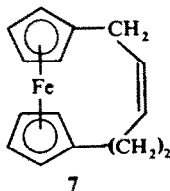
The finding that the half-wave potential of [2]ferrocenophane (**1**; $m=2$) is appreciably lower than those of its homologues must be treated with some reserve. Of all the compounds studied, this derivative alone failed to undergo smooth reversal of oxidation (Experimental). Decomposition was observed to occur during the redox process and consecutive scans using the same solution resulted in progressive diminution of the wave height. Clearly, the corresponding ferricenium cation is unstable under the reaction conditions. However, since reproducible E_4 values were obtained from several independent estimations, it is not unreasonable to infer that one-electron oxidation of this compound is remarkably facile.

It is tempting to attribute this situation to an electronic reorganization of the ferrocene system occasioned by the ring-tilt distortion imposed on the molecule.¹ The cyclopentadienyl rings in the tetramethyl analogue (**2**) are displaced by *ca.* 23° from parallel planes in the crystal¹⁷ and it is unlikely that the geometry of the ferrocene residue in the parent compound (**1**; $m=2$) would differ appreciably. Ballhausen and Dahl have theorized¹⁸ that ring-tilt distortion of this nature would produce a corresponding redistribution of the six metal non-bonding electrons to hybrid orbitals oriented in the direction of the sandwich opening. Since it has been established (Introduction) that oxidation of ferrocene occurs by removal of an electron from the essentially non-bonding e_{2g} orbitals (predominantly $3d_{xy}, x^2-y^2$), ring-tilt induced re-ordering of the non-bonding metal levels should be associated with a corresponding change in the oxidation potential of the molecule. Further, although there is no evidence for the operation of steric effects in the oxidation of *undistorted* ferrocene derivatives (*vide supra*), it might be argued that ring-tilting would expose the electron density at the metal atom such that electron transfer to the electrode could proceed with less steric interference from the attached cyclopentadienyl ligands.



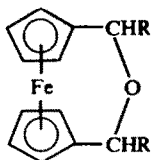
[*m*]Ferrocenophanones. Spectroscopic studies^{14b,c} have shown previously that the degree of resonance interaction between the carbonyl groups of the bridged ketones (3) and the adjacent cyclopentadienyl ring is controlled by the length of the bridging chain. In the case of [5]ferrocenophan-1-one (3; $m=5$), the molecule is free to adopt a conformation in which these groups are coplanar and in which resonance interaction consequently is maximized. It is unsurprising, therefore, that the half-wave potential of this bridged ketone is identical with that of a non-bridged model, 1-acetyl-1'-ethylferrocene, in which the conformational freedom of the acetyl group is unrestricted. For the homologous ketones (3; $m=3$ and 4), the shorter bridges do not permit full conjugation of the carbonyl groups (cf. crystal structure of the former¹⁹) which less effectively withdraw electron density from the ferrocene system. Accordingly, the half-wave potentials of these ketones are lower than that of the [5]-homologue.

Introduction of a Me substituent at the carbon atom adjacent to the carbonyl group in the [5]-ketone (3; $m=5$) has a surprisingly large effect upon the oxidation potential of the molecule. The half-wave potential of ketone 4 is significantly lower than that of the parent ketone and it must be inferred that the steric requirements of the Me group destabilise the molecular conformation in which the carbonyl group and cyclopentadienyl ring are coplanar. A similar, though less pronounced, effect is observed for the $\alpha\beta$ -unsaturated ketone 5. The carbonyl group in this compound cannot fully conjugate simultaneously with the double bond and the cyclopentadienyl ring and, with two sources of electron density to draw upon, interaction with the ferrocene system is attenuated.

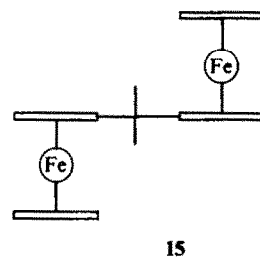
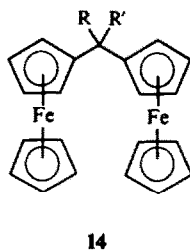
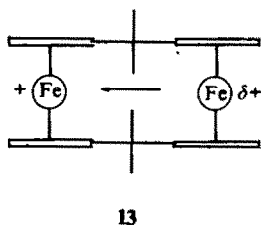
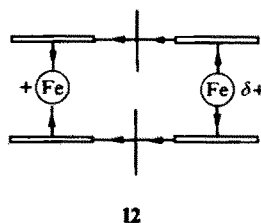
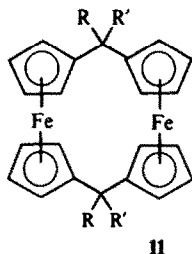


The half-wave potential of [5]ferrocenophan-3-one (6) is only slightly higher than that of [5]ferrocenophane (1; $m=5$) itself. Thus, although the carbonyl group is constrained by the molecular geometry to an environment close to the Fe atom there is no indication of important direct orbital interaction (e.g. between the Fe e_{2g} and carbonyl π^* orbitals). The modest influence observed may be due to a field effect.

[5]Ferrocenophanenes. Both bridged alkenes (7 and 8) exhibit half-wave potentials essentially equal to that of [5]ferrocenophane (1; $m=5$) itself, in harmony with the conclusion from spectroscopic studies^{14c} that the double bonds in these molecules are electronically isolated. In the [5]ferrocenophan-1-ene molecule (9), however, conjugation of the double bond with the ferrocene system leads to the expected increase in half-wave potential over that of the saturated analogue (1; $m=5$).



2-Oxa[3]ferrocenophanes. Substitution of an ether oxygen atom for the central methylene group in the [3]ferrocenophane (**1**; $m=3$) bridge leads to a marked increase in the half-wave potential which is clearly related to an inductive (or field) effect associated with the electronegative oxygen atom. The potentials of the *meso* and racemic forms of the bridged ethers²⁰ (**10**; R = Me and Ph) are indistinguishable from that of the parent compound (**10**; R = H).



[1.1]Ferrocenophanes. Investigation of the oxidation potentials of these dinuclear ferrocenophanes (**11**) was of particular interest since the Fe atoms in the molecule are held in close proximity to each other*. In such a situation, metal-metal electron transfer between a neutral and an oxidized ferrocene residue can be envisaged and, in this connection, it was thought that these molecules might serve as models for polymers with unusual electrical properties. It has been suggested, for example, that an oxidized polyferrocenyl backbone might satisfy one of the requirements for a superconducting polymer.²² Further, a band observed in the near-IR spectrum of the ferrocenylferricenium cation has recently been attributed²³ to an electronic transition from the neutral to the oxidized ferrocene residue.

As indicated in Table 2, the electrode reaction of the [1.1]ferrocenophanes (**11**; R = R' = H and Me; R = Me, R' = H) appears to involve two consecutive one-electron oxidation steps to give presumably the corresponding mono- and then di-ferricenium cations. The results also show that it is appreciably more difficult to remove the second electron than the first, indicating an electronic interaction between the ferrocene and ferricenium units in the mono-cation. Two types of interaction can be envisaged, operating either through the carbon skeleton of the ligands (cf. **12**) or *via* a direct metal-metal interaction or field effect (cf. **13**).

* The Fe-Fe distance for the dimethyl compound (**11**; R = Me, R' = H) was found to be 4.6 Å in the crystal.²¹

In order to assess the relative importance of these effects, polarographic oxidation of the non-annular analogues (**14**; R=R'=H and Me; R=Me, R'=H) was also carried out. Again a two-step oxidation process was noted⁶ although the waves in the polarogram of 1,1-deferrocenyethane (**14**; R = Me, R' = H) were insufficiently resolved to permit calculation of the individual half-wave potentials. The voltage difference between the first and second potentials of these compounds (Table 1) was found to be approximately half that found for the corresponding [1.1]ferrocenophanes [e.g. E_2 (second) — E_1 (first) for **11** (R = R' = H) = 0.19 volts and for **14** (R = R' = H) = 0.10 volts]. Assuming that, for steric reasons, the diferrocenylalkanes (**14**) will prefer a conformation in which the Fe atoms are pseudo-*trans* (cf. **15**), it follows that a substantial part of the effect which raises the second potential of the [1.1]ferrocenophanes (**11**) must be attributed to a direct electrostatic field interaction (cf. **13**).

EXPERIMENTAL

Method. The polarograms were obtained using a Heathkit Polarography Module (Model EVA 19-2) incorporating a saturated calomel reference electrode and a rotating platinum test electrode. The electrodes were cleaned with nitric acid and anodized for a few minutes immediately before use. Measurements were made in a thermostatted cell ($20 \pm 1^\circ$) for 90% ethanol aq. solutions containing sodium perchlorate (10^{-2} M) and perchloric acid (10^{-3} M) as supporting electrolyte and the substrate (2×10^{-4} M). Polarograms were obtained by scanning through a range of increasing potential to the point where a plateau in the wave was achieved. The potential was then allowed to drop and the scan reversed. Symmetry in the curve thus produced was taken as an indication of the reversibility of the redox reaction. Scans were repeated at least twice to check reproducibility limits which are given as bracketed values in the Tables. The E_1 values were estimated in the usual manner from the E vs. $\log\{I/(I-I_d)\}$ plots.¹⁵

Materials. Ethanol, sodium perchlorate, and perchloric acid of Analar grade and ferrocene derivatives of analytical purity were used. The methods of preparation of the ferrocenophane compounds have been described in earlier parts of this series.¹⁴

Acknowledgements—The authors thank Miss E. S. Bolton for technical assistance, the Science Research Council for a post-doctoral fellowship (to J.E.G.) and the University of Strathclyde for a research studentship (to H.L.L.).

REFERENCES

- ¹ Part VII; H. L. Lentzner and W. E. Watts, *Tetrahedron* **27**, 4343 (1971)
- ² See M. Rosenblum, *Chemistry of the Iron Group Metalloenes* Part 1. Interscience, New York (1965)
- ³ D. W. Turner in *Physical Methods in Advanced Inorganic Chemistry*; ed. H. A. O. Hill and P. Day; p. 102. Interscience, New York (1968)
- ⁴ R. Prins, *Chem. Commun.* 280 (1970)
- ⁵ J. G. Mason and M. Rosenblum, *J. Am. Chem. Soc.* **82**, 4206 (1960)
- ⁶ ^a S. P. Gubin and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.* **143**, 1351 (1962)
^b E. G. Perevalova, S. P. Gubin, S. A. Smirnova and A. N. Nesmeyanov, *Ibid.* **147**, 384 (1962)
- ⁷ J. Tirouflet, E. Laviron, R. Dabard and J. Komenda, *Bull. Soc. Chim. France* 857 (1963)
- ⁸ H. Henning and O. Gürtler, *J. Organometal. Chem.* **11**, 307 (1968)
- ⁹ ^a T. Kuwana, D. E. Bublitz and G. L. K. Hoh, *J. Am. Chem. Soc.* **82**, 5811 (1960)
^b G. L. K. Hoh, W. E. McEwan and J. Kleinberg, *Ibid.* **83**, 3949 (1961)
- ¹⁰ ^a W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn and A. P. Sanders, *Ibid.* **86**, 1376 (1964)
^b W. F. Little, C. N. Reilley, J. D. Johnson and A. P. Sanders, *Ibid.* **86**, 1382 (1964)
- ¹¹ D. W. Hall and C. D. Russell, *Ibid.* **89**, 2316 (1967)
- ¹² D. W. Hall, E. A. Hill and J. H. Richards, *Ibid.* **90**, 4972 (1968)
- ¹³ H. L. Lentzner and W. E. Watts, *Chem. Commun.* 906 (1970)

- ¹⁴ ^aT. H. Barr and W. E. Watts, *Tetrahedron* **24**, 3219 (1968)
^b Idem, *Ibid.* **24**, 6111 (1968)
^c Idem, *J. Organometal. Chem.* **15**, 177 (1968)
^d Idem, *Tetrahedron* **25**, 861 (1969)
^e T. H. Barr, E. S. Bolton, H. L. Lentzner and W. E. Watts, *Ibid.* **25**, 5245 (1969)
^f T. H. Barr, H. L. Lentzner and W. E. Watts, *Ibid.* **25**, 6001 (1969)
- ¹⁵ G. W. Ewing, *Instrumental Methods of Chemical Analysis*; 2nd edn., p. 195 *et seq.* McGraw-Hill, New York (1960); H. H. Willard, L. L. Merritt and J. A. Dean, *Instrumental Methods of Analysis*; 4th edn., p. 672 *et seq.* van Nostrand, London (1965)
- ¹⁶ M. J. S. Dewar, *Hyperconjugation*; p. 133. Ronald Press, New York (1962) and e.g. F. R. Jensen and B. E. Smart, *J. Am. Chem. Soc.* **91**, 5686, 5688 (1969)
- ¹⁷ M. B. Laing and K. N. Trueblood, *Acta Cryst.* **19**, 373 (1965)
- ¹⁸ C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.* **15**, 1333 (1961)
- ¹⁹ N. D. Jones, R. E. Marsh and J. H. Richards, *Acta Cryst.* **19**, 330 (1965)
- ²⁰ P. L. Pauson, M. A. Sandhu and W. E. Watts, *J. Chem. Soc. (C)* 251 (1966)
- ²¹ J. S. McKechnie, B. Bersted, I. C. Paul and W. E. Watts, *J. Organometal. Chem.* **8**, P29 (1967)
- ²² See W. A. Little, *Phys. Rev. (A)* **134**, 1416 (1964); R. S. Schneider, *J. Polymer Sci. (C)* **29**, 27 (1970)
- ²³ D. O. Cowan and F. Kaufman, *J. Am. Chem. Soc.* **92**, 219 (1970)
- ²⁴ J. A. Page and G. Wilkinson, *Ibid.* **74**, 6149 (1952)