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ELECTROCHEMICAL REDUCTION OF *sym*- AND *unsym*-BENZOFERROLES. THE GENERATION OF STABLE RADICAL ANION AND DIANION SPECIES

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Summary

Voltammetric investigations on *sym*- and *unsym*-benzoferroles showed both are reduced in two reversible one-electron steps. While *sym*-benzoferrole undergoes the two reduction processes at the same potential giving a stable dianion, the reduction potentials for *unsym*-benzoferrole are separated yielding a stable radical anion while the dianion undergoes a relatively fast decomposition. Interpretation of this behavior is made by a comparison with ferrole itself and a correlation of electrochemical, spectroscopic and MO calculations.

Introduction

Although iron polyolefin-carbonyl derivatives have been the subject of extensive investigations in the past [1,2] very few reports have appeared in the literature regarding their electrochemical reduction [3—6]. Moreover most of these have been concerned with iron tricarbonyl derivatives. Some ferroles have been included in the extensive investigation by Dessy [3b,3c] but no detailed study has been reported. Also no reports of stable reduction products have been published. In this paper, we wish to report our electrochemical studies on the isomeric couple *sym*- and *unsym*-benzoferrole and the generation of very stable anions as primary reduction products.

Results and discussion

The polarographic reduction of *unsym*-benzoferrole (U) in THF at 25°C consists of two one-electron reduction waves ($E_{1/2}$ = —0.89 and —1.30 V), diffu-

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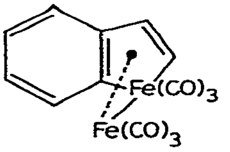
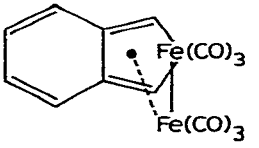
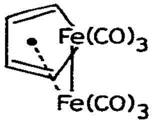
sion controlled ($I_d = 2.7$) *, and electrode reversible ($E_{3/4} - E_{1/4} = 56$ mV). These data are confirmed by differential pulse polarography and cyclic voltammetric (c.v.) measurements. In the c.v. experiments while the first reduction wave (Fig. 1) shows complete reversibility **, the second reduction wave displays the coupled anodic peak only at scan rates greater than 200 mV/s (rate constant for the following reaction 1.0 s^{-1}).



unsym-Benzoferrole (U)



sym-Benzoferrole (S)



Ferrole (F)

Under the same conditions *sym*-benzoferrole shows one two-electron reduction wave ($E_{1/2} = -1.14$ V) diffusion controlled ($I_d = 4.8$) but with $E_{3/4} - E_{1/4} = 65$ mV. Cyclic voltammetric studies (Fig. 2) indicate a reversible couple at the same potential with $E_p^c - E_p^a = 70$ mV. The discrepancy between current and potential data concerning the number of electrons involved in the process could be explained by a small difference between the $E_{1/2}$'s of the two one-electron transfers. In fact in acetonitrile, where $\Delta E_{1/2}$ for U is lower by different solvation and ion-pairing energies (250 mV instead of 410) S displays a two electron process with $E_{3/4} - E_{1/4} = 28$ mV and $E_p^c - E_p^a = 30$ mV. Further support for this proposal comes from coulometric data. U is reduced at -1.1 V passing one electron per molecule of U and at -1.5 V passing two electrons per molecule in contrast, S at -1.3 V requires two electrons per molecule of depolarizer. The reduced solutions are brown and quite stable but very air-sensitive. When these separate solutions are examined by polarography they indicate that the first contains $U^{\dot{-}}$, the second contains decomposition products from U^{2-} and the third contains species S^{2-} as the voltammetric data of the depolarizers predicted. EPR of the two-electron reduction products show no signal for S but two lines for U ($g = 2.04$ and 2.01 at $t = 140$ K) the first one appearing at a g value close to that reported [5] for $Fe(CO)_3^-$ while the second one shows some hydrogen coupling. This suggests that U^{2-} dissociates into $Fe(CO)_3^-$ and $Fe(CO)_3(C_8H_6):^-$. EPR of the one-electron reduction products gives one signal split into five lines.

Although line broadening did not allow a very accurate analysis of the spectra, the unpaired electron appears to be coupled with four equivalent or almost equivalent protons ($g = 2.00$, $a_H = 1.2$ G for $U^{\dot{-}}$; $g = 1.99$, $a_H = 1.6$ G for $S^{\dot{-}}$, $t = 220$ K ***).

In order to help understand the very different stability of the dianions, we examined the electrochemical behavior of ferrole (F). The electronic spectra of F and U display a peak at 406 nm, absent in S (additional broad bands are

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* I_d = polarographic diffusion constant = $i/Cm^{2/3}t^{1/6}$ in μA (mM/l)$^{-1}$ (mg/s)$^{2/3}$ s$^{-1/6}$.

** Peak potential separations are independent of sweep rate in the range 20 to 200 mV/sec.

*** At this temperature we got the best conditions for resolving the hyperfine structure.

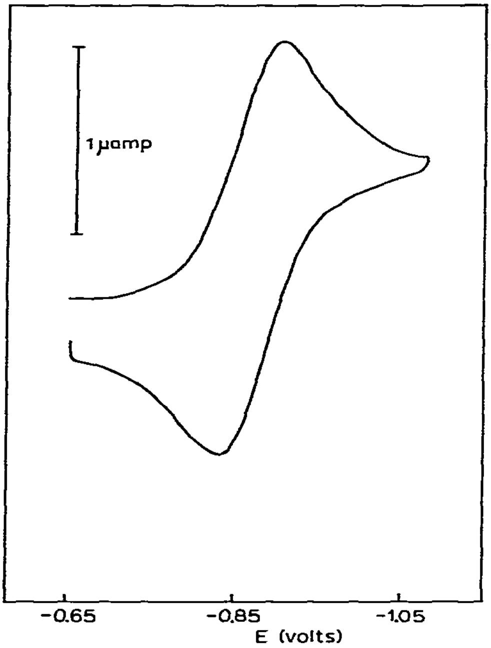

Fig. 1. Cyclic voltammogram of *unsym*-benzoferrole (U) in a THF/0.2 *M* TBAP solution at a Pt disc electrode at 500 mV/sec.

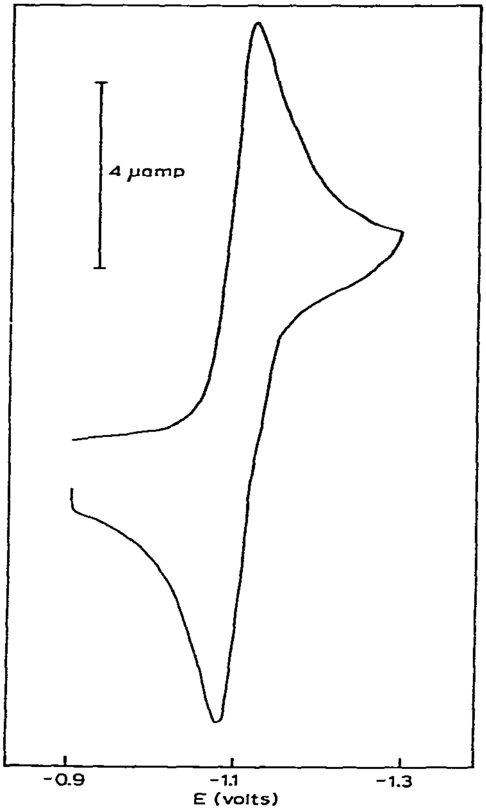

Fig. 2. Cyclic voltammogram of *sym*-benzoferrole (S) in a THF/0.2 *M* TBAP solution at a Pt disc electrode at 500 mV/sec.

present in the spectra of U and S at 470 and 430 nm respectively) and F is reduced in THF at about — 1.30 V, i.e. the same potential as for the second reduction wave of U *. Furthermore c.v. studies (Fig. 3) indicate that although the first reduction wave is one electron, diffusion controlled and electrode reversible, it does not show any coupled anodic peak at scan rates lower than 5 V/s and exhaustive electrolysis passing one electron per molecule of F gives a brown solution with a single EPR line.

The reduction potentials as well as the relative stabilities of reduced U, S and F can be qualitatively explained using the basic molecular orbital scheme proposed by Hoffmann et al. [7,8,11]. For F, the highest filled molecular orbital is a mixture of metal—metal bond of symmetry $1a_1$ and the lowest antibonding orbital of butadiene b_2. The $1a_1$ is considerably stabilized by enjoying added π-bonding with C(1) and C(4) of the butadienyl as shown below. Moreover, C(2) and C(3) bond to the other iron atom. This interaction as pointed out by

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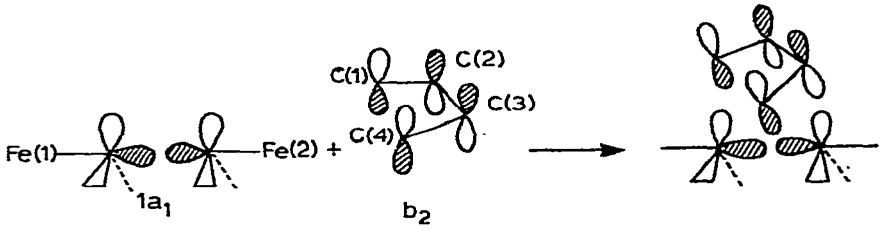
* $E_{1/2}$ value obtained from c.v. at high scan rates.



Hoffmann implies considerable occupation of the lowest antibonding orbital of the butadienyl moiety. Any perturbation of the C_4H_4 ligand which reduces the accepting ability of the lowest π^* will destabilize the ferrole structure. Accordingly, it follows that reduction to the radical anion can be pictured as mainly adding a full electron to the C_4H_4 lowest π^* orbital with concomitant destabilization of the ferrole complex.

In the case of S, *o*-xylylene has two low energy antibonding orbitals of symmetry b_2 and hence we would expect the molecular orbital scheme as shown in Fig. 4. The two antibonding a' orbitals may be essentially degenerate. The two electron reduction of S suggests an ECE type process in which the chemical

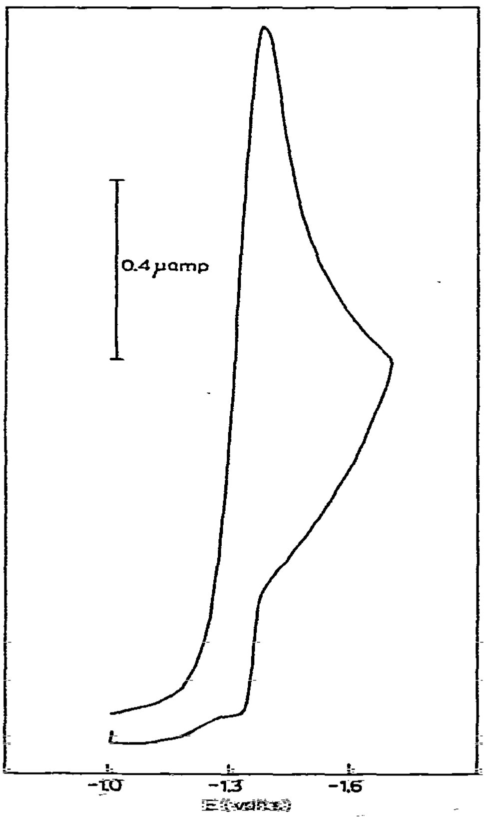


Fig. 3. Cyclic voltammogram of ferrole (F) in a THF/0.2 *M* TBAP solution at a Pt disc electrode at 500 mV/sec.

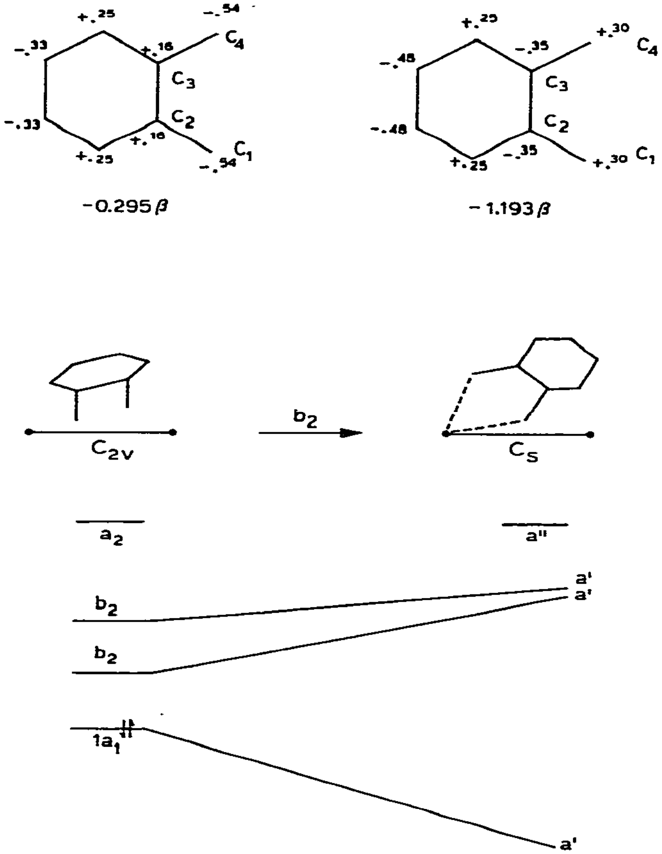


Fig. 4. LUMO's and coefficients for *o*-xylylene.

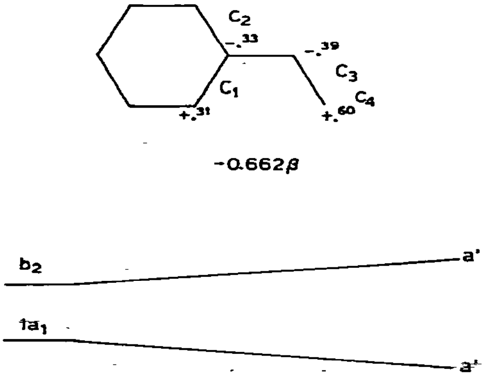


Fig. 5. LUMO and coefficients for *o*-styrylene.

step represents a bond reorganization process. The fact that the electrons are delocalized over a much larger ligand may explain the much increased stability over F anion.

In the case of U, the lowest antibonding orbital of b_2 symmetry is not expected to mix as well with the $1a_1$ orbital because of the smaller interaction of C(1) and C(4) with iron atom Fe(1). The result is a smaller splitting of bonding and antibonding a' and hence a lower reduction potential (Fig. 5). Once again delocalization of the extra electron over the large organic ligand is expected to provide added stability over the F anion.

In conclusion, stable anions of diene-$Fe_2(CO)_6$ complexes can be produced with the appropriate diene organic ligand. The main requirement of the organic ligand is that it has a low energy antibonding orbital of b_2 symmetry and be more delocalized than the butadienyl system.

Experimental

Chemicals and reagents

The complexes have been prepared according to the literature [9,10]. Tetrabutylammonium perchlorate (TBAP) was obtained from Eastman Chemical Co., recrystallized from chloroform/ether and dried in vacuum. Reagent grade tetrahydrofuran (THF) was refluxed for several hours over sodium-potassium alloy under argon atmosphere and distilled directly into the electrochemical cell. All solutions contained 0.2 *M* TBAP as supporting electrolyte. Argon carefully deoxygenated by passage over reduced copper at 450°C was used.

Apparatus and procedure

All experiments were carried out in a liquid jacketed cell at 25°C. Ag/AgCl, NaCl std. aqueous electrode, separated from the test solution by 0.2 *M* TBAP in THF sandwiched between two fritted disks was used as a reference electrode. The working electrode was either a dropping or a hanging drop mercury electrode (platinum electrodes were unsuitable owing to easy passivation). The counter electrode was a mercury pool; in coulometric experiments it was used as a working electrode and the counter electrode was a platinum gauze connected to the solution by an appropriate salt bridge.

The electrochemical apparatus was composed of a PAR Model 173 potentiostat with Model 179 digital coulometer, coupled with a Model 175 universal programmer for polarography and cyclic voltammetry; a PAR Model 174 polarographic analyzer was used in differential pulse polarography. The compensation of ohmic drop was achieved by positive feedback. Voltammograms were recorded by a Hewlett-Packard 7004B x-y recorder or a Tektronix 7313 scope provided with Polaroid Camera attachment. EPR measurements were performed with a x-band Brucker ER 200 D spectrometer equipped with a variable-temperature system.

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11 For complete discussion of symmetry terms see ref. 7 and 8.