

EFFECT OF LIGAND STRUCTURAL CHANGES ON THE REVERSIBLE REDUCTION OF ARENE-IRONCYCLOPENTADIENYL CATIONS

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SUMMARY

The polarographic reduction of the arene-ironcyclopentadienyl compounds (arene = benzene, naphthalene, fluorene, diphenyl, phenanthrene) was investigated on the dropping mercury electrode. The first step of the reduction was found to involve a one-electron reversible reduction resulting in an uncharged formally univalent iron complex. The cyclohexadienyl complex is believed to be a reduction product of the second step.

A study of the structural changes of the ligand shows that the effects of substituents in the π -C₅H₅ and π -C₆H₆ rings on the reaction center—iron atom—are of the same nature and magnitude. Exact correlations between $E_{\frac{1}{2}}$ and σ_p^0 constants indicate that of the total polar effect of a substituent in the aromatic ring the inductive component alone is effectively transferred by a substituted aromatic ring in the direction of the metal atom.

The electrochemical behaviour of ferrocene and some other sandwich-like π -complexes (cobaltocene, dibenzenechromium) has been investigated in some detail. In their oxidized forms they usually form reversible oxidation-reduction systems. On passing from the reduced to the oxidized form the electron changes occur on the molecular orbital entailing a main contribution from the metal orbitals. With ferrocene and dibenzenechromium as examples, systematic investigations of the effects of structural variations (introduction of substituents in the ligands) on the oxidation-reduction properties of the metal were conducted¹⁻³.

A detailed study is under way at present on mixed sandwich-like compounds containing two different π -ligands. A great many such compounds were available as soon as the π -C₅H₅-ligand exchange reaction in ferrocene with benzene, leading to the arene-ironcyclopentadienyl complexes was discovered⁴. This procedure along with the subsequent transformations of substituted arene-ironcyclopentadienyl cations⁵ have made available numerous derivatives containing substituents in the benzene as well as the cyclopentadienyl rings⁵. The large number of structurally similar iron complexes made it possible to compare the effects of the same structural changes in the ligand on the oxidation-reduction properties of the iron atom in ferrocene and arene-ironcyclopentadienyl complexes. Polarographic studies were carried out in aprotic solvents using a dropping mercury electrode.

TABLE I
POLAROGRAPHIC CHARACTERISTICS OF $[\pi\text{-C}_5\text{H}_5\text{Fe}\pi\text{-Ar}]^+\text{A}$
(CH_3CN , $0.1\text{ N } (\text{C}_4\text{H}_9)_4\text{NBF}_6$, $c=2\cdot 10^{-3}$ mole \cdot l $^{-1}$, SCE, 25°)

Ar	$[\pi\text{-C}_5\text{H}_5\text{Fe}\pi\text{-Ar}]\text{BF}_4$				$[\pi\text{-C}_6\text{H}_6\text{Fe}\pi\text{-C}_5\text{H}_5\text{X}]\text{PF}_6$				$[\pi\text{-C}_5\text{H}_5\text{Fe}\pi\text{-CH}_3\text{C}_6\text{H}_4\text{X-p}]\text{PF}_6$			
	$-E_1$ (V)	i_d (μA)	$-E_1$ of noncoord. Ar	X	$-E_1$ (V)	i_d (μA)	X	$-E_1$ (V)	i_d (μA)	X	$-E_1$ (V)	i_d (μA)
(I) Benzene	1.45	4.50	3.4 ^a	(VII) -COCH ₃	1.14	3.80	(XIII) -CN	1.09	3.0		1.09	3.0
	2.39	4.90		(VIII) -Cl	2.00	3.10		1.87	5.40		1.87	5.40
(II) Fluorene	1.40	4.50	^b	(IX) -H	1.25	5.60	(XIV) -Cl	1.30	4.30		1.30	4.30
	2.23	3.20		(X) -OCH ₃	2.30	4.60		2.10	5.60		2.10	5.60
(III) Diphenyl	1.30	4.10	2.70	(XI) -C ₂ H ₅	1.41	5.60	(XV) -F	1.33	5.0		1.33	5.0
	2.22	3.50		(XII) -piperidyl ^c	2.39	5.60		2.36	6.4		2.36	6.4
(IV) Phenanthrene	1.23	4.80	2.50		1.46	5.10	(XVI) -SCH ₃	1.39	4.0		1.39	4.0
	1.80	1.40			2.42	10.9		2.25	4.30		2.25	4.30
(V) Naphthalene	1.07	4.60	2.55		1.48	5.40	(XVII) -NHCOCH ₃	1.44	2.90		1.44	2.90
	1.75	1.40			2.45	7.50		1.68	1.80		1.68	1.80
(VI) Mesitylene ^a	1.55	5.50	—		1.61	5.20	(XVIII) -H	1.46	5.0		1.46	5.0
							(XIX) -OCH ₃	2.44	8.0		2.44	8.0
							(XX) -CH ₃	1.46	5.60		1.46	5.60
								2.55	4.20		2.55	4.20
								1.50	4.60		1.50	4.60
								2.55	6.20		2.55	6.20

^a Anion PF₆⁻. ^b Waves are not observed up to the discharge of the supporting electrolyte. ^c Anion B(C₆H₅)₄⁻.

RESULTS AND DISCUSSION

Characteristics of the reduction waves observed

All the arene-ironcyclopentadienyl compounds investigated exhibit two cathodic waves on the polarograms at potentials from +0.50 to -2.8 V (CH₃CN, 0.1 N (C₄H₉)₄NBF₄) (Fig. 1). Results are summarized in Table 1.

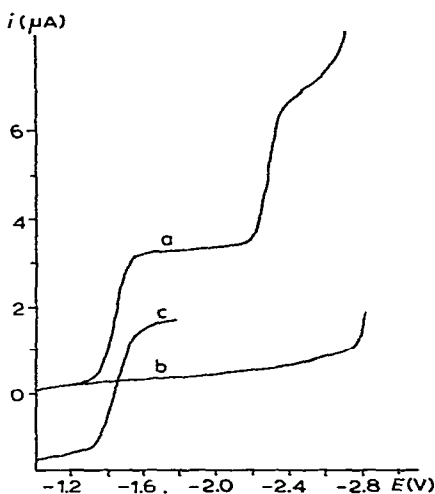
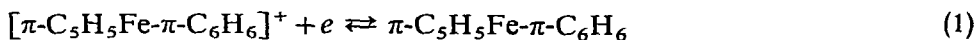


Fig. 1. Polarograms of $[\pi\text{-C}_5\text{H}_5\text{Fe-}\pi\text{-C}_6\text{H}_6]\text{BF}_4$ (CH₃CN, 0.1 N (C₄H₉)₄NBF₄). (a) $c=1\cdot 10^{-3}$ M; (b) curve of supporting electrolyte; (c) curve taken with the Kalousek's commutator method ($E_{\text{auxil.}} = -1.70$ V, $f=25$ Hz).

First wave. The first wave has the character of a diffusion wave: its i_{lim} is proportional to the depolarizer concentration (within the range, $8\text{--}0.2\cdot 10^{-3}$ mole \cdot l⁻¹) and to the square root of the mercury height above the capillary (\sqrt{H}); its temperature coefficient is 1.16%/1°. The wave is a one-electron wave—its height is comparable with the height of the one-electron wave of dibenzenechromium iodide measured under analogous conditions. The slope of $\log [i/(i_d - i)] - E$ is 80 mV indicating the reversibility of the electrochemical process (see also ref. 6). The wave preserves its characteristics in other solvents—aprotic (DMF) and proton-releasing (CH₃CN/H₂O, 1/1). The addition of an equimolar amount or an excess of phenol as a proton donor again makes no change in the wave characteristics. Hence a proton does not participate in the electrochemical reaction and the first wave corresponds to the one-electron reduction of the complex:



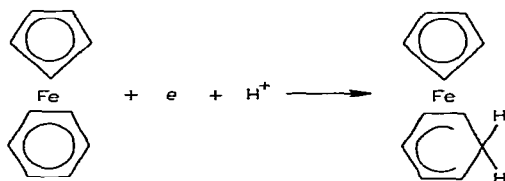
According to eqn. (1) the primary reduction product is an uncharged complex of the formally univalent iron which should oxidize at the reduction potential of the initial complex. Our measurements with a Kalousek commutator method (Fig. 1) (auxiliary voltage, 1.70 V; frequency, 10 and 25 Hz) carried out for a series of complexes showed that the primary product of the electrochemical reduction does indeed oxidize at the reduction potential of the initial complex. This is convincing evidence of the reversibility of the electrochemical reduction.

The life-time of the primary reduction product, however, is probably not very long as can be seen from the chemical reduction of compound I. Polarograms of solutions taken after the reduction of the complex with strong reducing agents (Na/Hg, sodium naphthalinide), which are commonly employed in chemical models of electrochemical reduction, show no oxidation waves from +0.50 to -2.0 V. Chemical reduction of the arene-ironcyclopentadienyl complexes with metal hydrides is known to produce cyclohexadienyl complexes⁷.

We found that $\pi\text{-C}_5\text{H}_5\text{FeC}_6\text{H}_7$ displays one irreversible anodic oxidation wave in the polarogram at -0.01 V. All these results indicate that the primary electrochemical reduction product differs from the final products of chemical reduction with metal hydrides and other reducing agents.

Second wave. For the majority of compounds investigated the second wave is of the same height as the first. It is irreversible and appears at more negative potentials. As in the case of the first wave, the limiting current of the second wave is proportional to the depolarizer concentration and \sqrt{H} . However, the height of this wave is somewhat reduced with increasing temperature (0.6%/1° in the range, 25-40°). Unlike the first wave, the addition of phenol as a proton donor more than doubles the limiting current of the second wave, *i.e.*, protons influence the electrochemical reaction.

These results indicate that the primary product of the first reduction step is an uncharged complex (see eqn. (1)). According to Vlcek⁸, this transition metal complex of a lower oxidation state may have a real, although short, life. Alternatively, it can rapidly decompose or participate in chemical reaction in solution. In the first case, the second wave may correspond to a further reduction of the entire complex or of the coordinated ligand alone. In the latter case it refers to the reduction of compounds that result from the primary reduction product, and this probably does not take place, as can be seen from Table 1, the benzene and cyclopentadienyl ring substituents clearly effect the potential of the second reduction step. Hence, at this stage both these ligands are present in the complex. It may thus be assumed that the second wave appears when the coordinated arene ligand of the uncharged product of the first reduction step is reduced giving rise to a cyclohexadienyl complex, analogous to the reduction by metal hydrides:



Thus, the polarographic study of an arene-ironcyclopentadienyl complex in aprotic solvents makes it possible to divide an overall process of reduction by metal hydrides into two individual steps, the first being a one-electron step and reversible. This stimulated the investigation and interpretation of the structural effects on the potential values of the first wave.

An investigation of the same structural effects on the second step of the reduction is unfortunately impossible owing to its irreversibility and rather uncertain nature.

Localization of the electron changes

The reduction potential of electrochemical reversible processes is known to have a thermodynamic value corresponding to the energy of the lowest vacant molecular orbital accepting an electron during the reduction.

To set forth the localization of the electron changes in the given case means in fact an estimation of the relative contribution from metal and ligand atomic orbitals (AO) into the molecular orbital (MO) where such changes occur during the reduction. According to Vlcek² this may be solved using the differences between the reduction potentials of two structurally similar non-coordinated ligands and those of their complexes (compounds I-V) and using estimated mixing coefficients of the metal and ligand AO's in the lowest vacant MO of the complex. In the present case this value was found to be 0.20; *i.e.*, ligand orbitals contribute only about 20%. Hence, the electron changes during the reduction usually occur on the metal atom. Thus the oxidation-reduction properties of the complexes investigated are not different from those of the other sandwich-like π -complexes. Furthermore, the effect of the ligand structural changes on the potential values confirms that the electron changes occur on the metal atom.

The results obtained make it possible to suggest that the lowest vacant orbital of arene-cyclopentadienyl complexes has a much lower energy than that of the ferrocene molecule whose polarographic reduction is impossible down to the most negative potentials.

Reduction of different arene complexes

The first wave does not change with exchange of one arene ligand for another, but on passing from compound I to V the reduction potentials shift to more positive values in the following order: (Ar=) benzene < fluorene < diphenyl < phenanthrene < naphthalene. A comparison with the tendency to reduction for the respective non-coordinated arenes (benzene < fluorene < diphenyl < phenanthrene \approx naphthalene) shows that the potential changes of compounds I-V follow those of the non-coordinated ligands (see Table 1).

The electron changes in aromatic hydrocarbons during their reduction are known to occur on the antibonding π^* -orbital whose energy decreases from benzene to naphthalene in the same series. Hence, in the complexes the probability of electron transfer from metal to the antibonding arene orbitals should increase in the same sequence. Thus, an effective positive charge at the metal atom increases along these series enhancing the tendency of these complexes to reduction.

It should be noted that similar structural changes in a ligand invoke the same potential shifts in the reversible reduction of the arene-cyclopentadienyl and dicyclopentadienyl complexes. For example, on passing from $(\pi\text{-C}_5\text{H}_5)_2\text{CoClO}_4$ to $(\pi\text{-indenyl})_2\text{CoClO}_4$ the reduction potential shifts by 0.56 V (0.28 V per ring) to positive values⁹. Such a potential difference is rather close to that ($E_{\frac{1}{2}} = 0.38$ V) of compounds I and II (see Table 1).

Substituent effects in $\pi\text{-C}_5\text{H}_5$ and $\pi\text{-C}_6\text{H}_6$ ligands

The introduction of substituents into $\pi\text{-C}_5\text{H}_5$ or $\pi\text{-C}_6\text{H}_6$ rings does not change the character of the first wave of reduction, while $E_{\frac{1}{2}}$ values change considerably with the nature of a substituent. Complexing is hindered by electron-releasing substi-

tents and facilitated by electron-attracting ones. In both π -C₅H₅- and C₆H₆-rings the effect of the methoxy group is intermediate between that of hydrogen and methyl, *i.e.*, it displays a weak electron-releasing action. Such an order of reaction of the electron-releasing substituents was found in the reaction series where direct polar conjugation between substituent and the reaction center does not take place. As in other π -complexes, the additivity rule is obeyed for methyl group effects: the introduction of each following methyl group (compounds VI, IX, XVIII, XX) results in an approximately 0.05 V potential shift to the negative side. Since the first reduction step for all these series follows the same mechanism and substituents make very small structural changes while displaying essentially different electronic effects, an accurate correlation can be drawn between the structures of the complexes investigated and the potentials of their reversible reduction*. Furthermore the potential differs for the strongest electron-attracting and electron-releasing substituents ($\Delta E_{\frac{1}{2}}$ (VII–XII)=0.47 V; $\Delta E_{\frac{1}{2}}$ (XIII–XX)=0.41 V) by several dozen times to a mean square error of experiment. The substituent effects in the electrochemical reaction under study (see eqn. (1)) on a reaction center (iron atom) were estimated quantitatively from the $E_{\frac{1}{2}}$ values obtained. Systematic correlation analysis with different constants showed that both for compounds VII–XII and XIII–XX the most accurate correlation is of $E_{\frac{1}{2}}$ values with σ_p^0 constants of the corresponding substituents (Fig. 2). The effect of substituents in the π -C₅H₅-ring is described by the equation:

$$E_{\frac{1}{2}} = -1.39 + 0.520 \sigma_p^0, \quad r = 0.997$$

and for the π -C₆H₆-ring by

$$E_{\frac{1}{2}} = -1.42 + 0.515 \sigma_p^0, \quad r = 0.995.$$

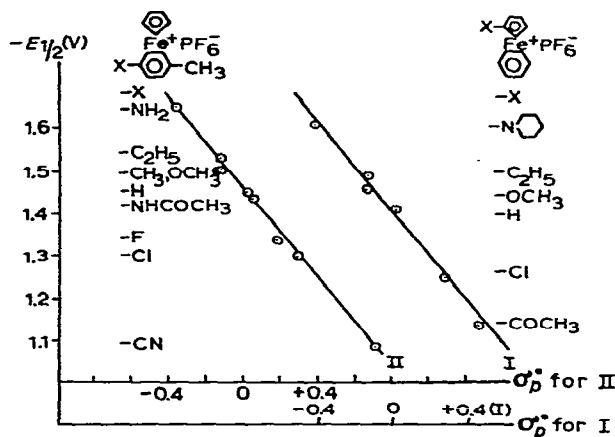


Fig. 2. $E_{\frac{1}{2}}$ of the substituted arene-cyclopentadienyl compounds vs. σ_p^0 constants. (I) [π -C₅H₄XFe- π -C₆H₆]PF₆; (II) [π -C₅H₅Fe- π -CH₃C₆H₄X- p]PF₆.

It can be seen from these data that the effects of substituents in the arene and cyclopentadienyl rings on the common reaction center (iron atom) are similar not

* The nature of the anion in the complex may also affect the value of potential (compare compounds I and IX). Hence all potentials were compared only for compounds having the same anion.

only in character but also in magnitude. Moreover, this effect is paralleled by that of the C_5H_5 -ring substituents on the formal oxidation-reduction potentials (E_r^0) of some mono- and heteroannular disubstituted ferrocenes¹. On the other hand, for these three types of compounds, the sensitivity of the reaction center to the electronic effects of the substituents is practically the same, as can be seen by comparing ρ -values: 0.52 and 0.515 V for the π - C_5H_5 and arene rings of the complexes investigated and 0.50 V for the mono- and disubstituted ferrocenes.

General relationships of the transmission of electronic effects to the metal atom and another ring in the π -complexes have been explored for a number of reaction series¹. From the total polar effect of the substituent, the aromatic ring was found to transmit (in a direction perpendicular to its plane) only an inductive component to the metal atom or to another ring. A good correlation between the $E_{\frac{1}{2}}$ values of arene-cyclopentadienyl complexes and the constants, σ_p^0 , of the substituents in π - C_5H_5 - and π - C_6H_6 -rings means that in the systems investigated and in the other transition metal- π -complexes, the nature of substituent effects is analogous.

Finally it should be pointed out that the accurate linear correlation between $E_{\frac{1}{2}}$ and σ_p^0 also demonstrates the validity of the mechanism suggested for reduction and for localization of the electron changes on the metal atom.

EXPERIMENTAL

Polarographic measurements were carried out on an electronic polarograph PE-312. A dropping mercury electrode provided with a forced dropping system was employed as cathode ($t=0.35$ sec, $m=1.53$ mg·sec⁻¹).

A saturated aqueous calomel electrode was used as anode and reference electrode. Potential measurements were performed with an accuracy of 0.01 V.

All the compounds investigated were prepared and purified by the procedures described^{4,5,10}.

The solvent—acetonitrile (CH_3CN), was first distilled on a rectifying column in a mixture with benzene (100 ml of C_6H_6 /1000 ml of CH_3CN). Pure CH_3CN distilled at 81.5° and was again distilled over P_2O_5 , $LiAlH_4$ and P_2O_5 . The purified CH_3CN shows no waves in the region, +0.5 to -2.8 V. The residual current does not exceed 0.6 μ A at -2.6 V.

The supporting electrolyte, $(C_4H_9)_4NBF_4$, was prepared by the reaction of $(C_4H_9)_4NOH$ with HBF_4 ¹¹ and, unlike the widely used $(C_4H_9)_4NClO_4$ does not absorb water.

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