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REDOX PROPERTIES OF CYCLOPENTADIENYLMETAL COMPOUNDS
I. FERROCENE, RUTHENOCENE, OSMOCENE

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SUMMARY

Potentiometric ($K_2Cr_2O_7$, $CH_3COOH + 0.066\ M\ HClO_4$) and polarographic [$0.1\ M\ (C_4H_9)_4NBF_4$ (Bu_4NBF_4), CH_3CN] oxidations of ferrocene, ruthenocene and osmocene, as well as of ferrocenylruthenocenyl- and ferrocenylosmocenylmethanes, have been investigated at the dropping mercury (DME) and Pt-rotating disc (Pt-electrode) electrodes. It was found that at DME the oxidation of all three metallocenes proceeds reversibly as a one-electron process with the ease of oxidation decreasing in the order: osmocene > ruthenocene > ferrocene. At the Pt-electrode the oxidations of ruthenocene and osmocene are irreversible and, in case of ruthenocene, proceeds as a one step two-electron process, while that of osmocene occurs in two consecutive one-electron steps. The potentiometric oxidation of osmocene on the other hand is a reversible two-electron process.

For ruthenocene and its derivatives a correlation analysis between the half-wave potentials ($E_{\frac{1}{2}}$) and different σ sets has been carried out. With DME ($n=1$), the linear dependence between $E_{\frac{1}{2}}$ and σ_p^0 could be expressed by the relationship: $E_{\frac{1}{2}} = 0.42\ \sigma_p^0 + 0.37$ V; $r = 0.998$, suggesting that for ruthenocene derivatives, as for those of ferrocene and the arenecyclopentadienyl cation, the electronic effects of substituents are transmitted to the reaction centre, *i.e.*, the ruthenium atom, through a mainly inductive mechanism.

INTRODUCTION

Redox reactions, with the metal playing the role of a reaction centre, are specific for metallocenes. In the majority of cases such reactions are reversible and the metallocenium cation may be reduced back to the metallocene. These redox reactions have been studied in the greatest detail for ferrocene and its derivatives. Correlational analysis linking the redox potentials with σ constants estimated for a variety of substituents enabled conclusions regarding the relative electronic effects of these substituents on the ferrocene nucleus to be reached[1].

Ferrocene analogues such as ruthenocene and osmocene have been studied in less detail. Thus Page and Wilkinson[2] first investigated the polarographic behaviour of ruthenocene at the dropping mercury electrode (90% ethanol, $0.1\ M\ NaClO_4+$

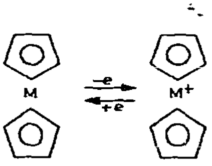
0.01 M $HClO_4$) and showed that ruthenocene reduces more readily than ferrocene (relative values of $E_{\frac{1}{2}}$ are +0.26 and +0.31 V respectively). Tiroflet *et al.*[3] reported the polarographic one-electron oxidation of osmocene (DME, 50% ethanol 0.5 M $HClO_4$, E −0.07 V). Chronopotentiometric oxidation of all three metallocenes, carried out in acetonitrile at Pt-electrode with 0.2 M $LiClO_4$ as supporting electrolyte, has also been reported[4,5]. Under these conditions the oxidation of ruthenocene proceeds as an irreversible, two-electron process while that of osmocene consists of two successive irreversible one-electron stages. However, no systematic study of the electrochemical behaviour of all three metallocenes in an aprotic medium, aimed at elucidating the influence of the metal upon the oxidation process, has been yet conducted. In particular, the results available give no clear evidence as to how the case of cleavage of the first electron from the neutral metallocene changes in the series Fe, Ru and Os. For this reason we have conducted a comparative study of the behaviour of ferrocene, ruthenocene and osmocene under widely varied (but identical for all three metallocenes) conditions. As in other reaction series, it was important to establish that the transmission of electronic effects in substituted ferrocenes[1] and in arenecyclopentadienyliron cations[6] are specifically related to the π-bonding of the cyclopentadienyl ligand-metal atom.

For this reason, in the present work the redox properties of ruthenocene and of a series of its derivatives were investigated* using polarography on the dropping mercury (DME) and Pt rotating disc (Pt-electrode) electrodes in acetonitrile with 0.1 M Bu_4NBF_4 as supporting medium, and potentiometric oxidative titrations as experimental techniques.

RESULTS

1. *Oxidation of ferrocene, ruthenocene and osmocene at the DME*

Ferrocene, ruthenocene and osmocene oxidize easily at DME (0.1 M Bu_4NBF_4, CH_3CN). The results obtained are listed in Table 1. Polarograms of all three metallocenes (Fig. 1a) show one diffusive wave of the same height corresponding to the reversible one-electron transfer process.



(M = Fe, Ru, Os)

The oxidation reversibility of all three metallocenes was established through the Kalousek switch (Fig. 1b), and from the slope of the log $i/(i_d - i) - E$ plot (66 mV), which under the conditions used in this work is characteristic of a reversible one-electron process. All the metallocenes investigated showed no reduction waves up to the discharge range of the supporting electrolyte (−2.8 V).

The compounds (IV)–(VI) (Table 1) exhibit two waves corresponding to the consecutive oxidation of the metallocene nuclei separated by the bridging group.

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* Syntheses of the rutheconene derivatives used in this work was made by the method developed by two of the present authors and Prof. A. N. Nesmeyanov[7].

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF FERROCENE, RUTHENOCENE AND OSMOCENE AND THEIR DERIVATIVES
(0.1 M Bu_4NBF_4, CH_3CN, SCE, 25±0.1°)

Compound		DME (1×10^{-3} M)		n^a	Pt-electrode (1×10^{-3} M)		n^a
		$E_{\frac{1}{2}}$(V)	i(μA)		$E_{\frac{1}{2}}$(V)	i(μA)	
(I)	$C_5H_5FeC_5H_5$	0.42	2.80	1	0.48	5.7	1
(II)	$C_5H_5RuC_5H_5$	0.36	2.50	1	0.78	12.6	2
(III)	$C_5H_5OsC_5H_5$	0.16	2.50	1	0.75	8.0	1
					1.37	6.8	1
(IV)	$C_5H_5FeC_5H_4CH_2C_5H_4RuC_5H_5$	0.34	2.10	1	0.40	3.4	1
		0.50	2.10	1	0.88	7.2	2
(V)	$C_5H_5FeC_5H_4COC_5H_4RuC_5H_5$				0.57	2.7	1
					1.05	4.2	2
(VI)	$C_5H_5FeC_5H_4CH_2C_5H_4OsC_5H_5$	0.14	2.20	1	0.41	4.1	1
		0.49	2.20	1	0.93	4.0	1
(VII)	$C_5H_5Fe(p\text{-}FC_6H_4)C_5H_4$	0.47	2.40				
(VIII)	$C_5H_5Ru(p\text{-}FC_6H_4)C_5H_4$	0.41	2.40				
(IX)	$C_5H_5Os(m\text{-}FC_6H_4)C_5H_4$	0.21	2.30				

[a] Number of electrons.

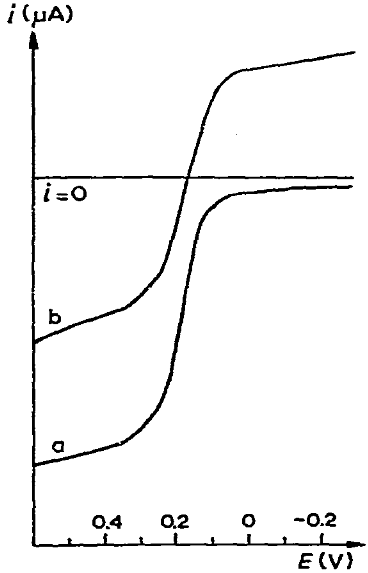

Fig. 1. (a) Polarogram of osmocene at DME (CH_3CN, 0.1 M Bu_4NBF_4, 1×10^{-3} M, SCE); (b) Curve taken with Kalousek switch. E_{aux} 0.5 V, commutation frequency 25 Hz.

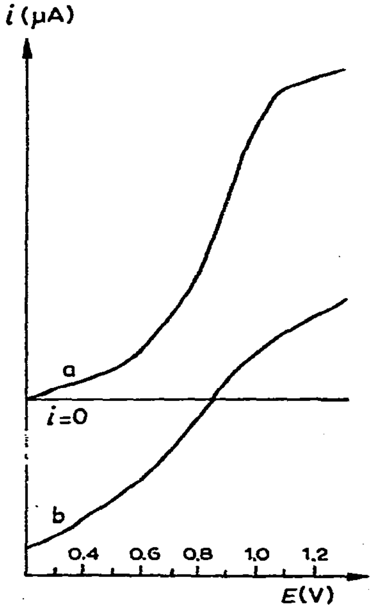

Fig. 2. (a) Polarogram of the first oxidation wave of osmocene on Pt-electrode (0.1 M Bu_4NBF_4, CH_3CN, 1×10^{-3} M; (b) Curve taken with Kalousek switch E_{aux} + 1.2 V, commutation frequency 25 Hz.

Thus, in the case of compound (IV) essentially, the one electron oxidation of the ruthenocenyl nucleus is observed ($E_{\frac{1}{2}}$ +0.34 V), which is somewhat facilitated (with respect to free ruthenocene, $E_{\frac{1}{2}}$ +0.36 V) by the electron releasing effect of the non-oxidized ferrocene nucleus. The second wave, relating to the oxidation of the ferrocenyl nucleus ($E_{\frac{1}{2}}$ +0.50 V), is hindered with respect to that of unsubstituted ferrocene ($E_{\frac{1}{2}}$ +0.42 V) through the electron attractive effect of the oxidized ruthenocenyl nucleus. Similar dependences are observed for compound (VI).

2. *Oxidation of ferrocene, ruthenocene and osmocene at the Pt-electrode*

In a similar fashion to oxidation at the DME, use of rotating disc Pt-electrodes leads to the oxidation of ferrocene through a reversible one-electron process at a potential rather close to that observed for oxidation at DME (Table 1). Unlike ferrocene, however, the polarogram for ruthenocene shows a wave characteristic for a two-electron oxidation process, and yields a limiting current for the observed wave which, on the basis of equal concentrations, is double that of ferrocene. When ferrocene is bonded via some bridging group with a ruthenocene nucleus (compounds (IV) and (V)), the polarogram shows two waves corresponding to the oxidation of both nuclei. In such cases the limiting current for the ruthenocene wave is again twice that for the ferrocenyl nucleus. It follows, therefore, that the difference in wave heights observed during the oxidations of ferrocene and ruthenocene may be attributed to differences in the number of electrons participating in the oxidation processes rather than to different diffusion factors. The doubly charged ruthenicenium cation is an oxidation product of ruthenocene.*

The polarogram for osmocene exhibits two one-electron oxidation waves. The oxidation product in this case is a doubly charged cation similar to that prepared earlier by Fischer *et al.*[9]. It should be noted that oxidation of ruthenocene and osmocene at the Pt-electrode is less reversible (Fig. 2b), and occurs at more positive (with respect to DME) potentials**. The process of reversibility was again investigated by a Kalousek switch, but unlike ferrocene a clear picture regarding the behaviour of ruthenocene and osmocene could not be obtained. It was also observed that the slope of the log $i(i_d-i)-E$ plot for osmocene far exceeds the value expected for a one-electron reversible process.

The polarogram for ferrocenylruthenocenylmethane (IV), in addition to the wave corresponding to the reversible oxidation of the ferrocenyl nucleus ($E_{\frac{1}{2}}$ +0.40 V, $E_{\frac{1}{2}}$(ferrocene) +0.48 V), also exhibits a wave corresponding to a two-electron irreversible oxidation of ruthenocenyl. The half-wave potential for this oxidation (+0.88 V) differs from that for the oxidation of unsubstituted ruthenocene (+0.78 V) because of the electron-attractive effect of the oxidized ferrocenyl nucleus. The same dependencies have also been observed during the oxidation of ferrocenyl osmocenylmethane (VI):

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* In a previous paper we have shown[8] that the oxidation of ruthenocene by $FeCl_3$ results in a doubly charged ruthenocenium cation in the form of salt $[(C_5H_5)_2RuCl]^+[FeCl_4]^-$. Analogous salts are formed in the oxidation of ruthenocene with excess of other oxidizing agents, *e.g.*, bromine and quinone in the presence of BF_3 or HCl.

** The half-wave potentials for all three metallocenes both at DME and Pt-electrodes (Table1) differ considerably, and this allows the quantitative estimation of these compounds when present as mixtures in solution.

in addition to a wave corresponding to the oxidation of the ferrocenyl nucleus ($E_{\frac{1}{2}}$ +0.41 V), there also appears a wave corresponding to a one-electron oxidation of the osmocenyl nucleus ($E_{\frac{1}{2}}$ +0.93 V) which is probably irreversible and whose half-wave potential differs from that of the first wave observed in the oxidation of free osmocene (+0.75 V).

3. *Potentiometric oxidation of ferrocene, ruthenocene and osmocene*

The ferrocene/ferricenium cation system is a classical example of a highly reversible one-electron redox pair. The ferrocene titration curve (Fig. 3a) is entirely symmetric, the index potential being 28.6 mV. Unlike the ferrocene system under the same conditions, however, the establishment of equilibrium between the oxidized and reduced forms of ruthenocene is much slower, the oxidation process being probably irreversible. This makes it impossible to determine a standard redox potential for this system.

From potentiometric titration and polarographic data at DME and Pt-electrodes, it may be shown that the presence of equimolar quantities of ruthenocene does not interfere in the ferrocene titration curve (polarographic wave) and does not affect the value of the redox (half-wave) potential.

Potentiometric titration data for the oxidation of osmocene reveal a characteristic titration curve (with a well defined "jump" (Fig. 3b) obeying the Nernst equation (at $n=2$). The curve is symmetrical, the index potential being 14.3 mV. This indicates that this process is a typical two-electron reversible oxidation. The formal redox potential of the system osmocene/osmicenium dication (E_{f_0}) is equal to −0.324 V. Unlike the case of ruthenocene, the presence of equimolar quantities of osmocene does affect both the shape of titration curve and the formal redox potential of ferrocene (Fig. 3c). Moreover ferrocene has a similar effect upon the respective characteristics of the osmocene titration. The results obtained show that in the mutual presence of osmocene and ferrocene in solution, the addition of an oxidizing agent leads to an electron exchange not only between the oxidized and reduced forms of the same

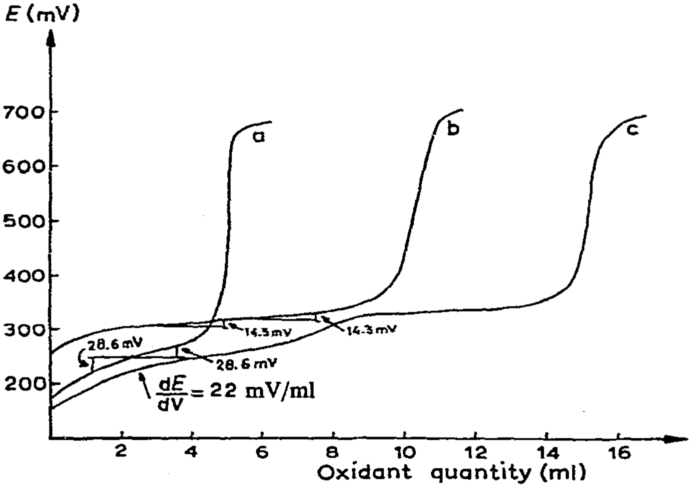
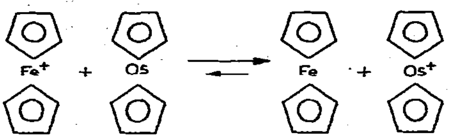


Fig. 3. Titration curve of (a) ferrocene; (b) osmocene; (c) equimolar quantities of ferrocene and osmocene.

metallocene, but also between those of different metallocenes. Similar conclusions may be drawn from the data arising from polarographic analysis. Thus, upon addition of equimolar amounts of osmocene to a solution of ferricenium picrate the anode-cathodic wave* of the ferricenium cation ($E_{\frac{1}{2}}$ + 0.37 V) observed at DME becomes predominantly anodic, while the anodic osmocene oxidation wave (0.13 V) is completely changed to that for osmicenium cation reduction. Hence, with respect to osmocene the ferricenium cation behaves as an oxidant. The equilibrium is rapidly established and shifts



predominantly to the right side. The data for the potentiometric oxidation of ferrocenylmetallocenylmethanes are in a good agreement with those for the oxidation of the free metallocenes. Thus, the shape of the titration curve for ferrocenylruthenocenylmethane (Fig. 4a) is not very different from those of ferrocene and diferrocenylmethane (Fig. 4b). What difference there is is consistent with the fact that the titration of ferrocenylruthenocenylmethane requires half the oxidant quantity required for diferrocenylmethane. Moreover, the value of E_{f_0} of the ferrocenyl nucleus of this compound (−0.222 V) differs from that for methylferrocene (−0.198 V) because of the electron attractive effect of the ruthenocenyl substituent. This E_{f_0} value has been used for the determination of an inductive aromatic constant for the ruthenocenyl substituent[10]. Potentiometric oxidation of ferrocenylosmocenylmethane is similar to that of a mixture of the respective free metallocenes, although the titration curve has a potential "jump" (Fig. 4c) at a point corresponding to the complete oxidation of the

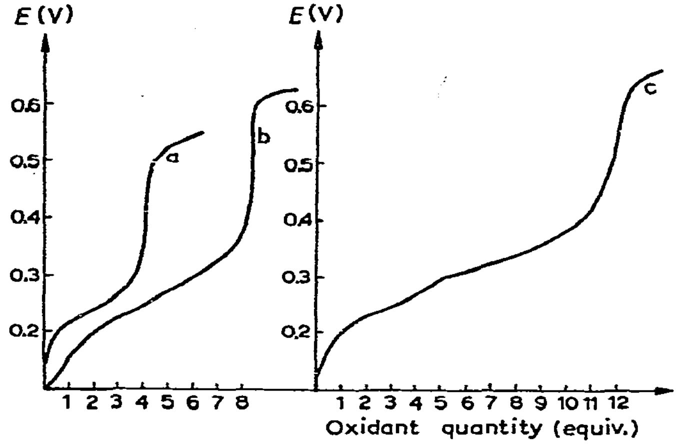


Fig. 4. Curve of the potentiometric titration of; (a) ferrocenylruthenocenylmethane, (b) diferrocenylmethane, and (c) ferrocenylosmocenylmethane.

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* For ferricenium salts cathodic waves are not observed: in these cases the observed waves are always anode-cathodic as a result of the conversion of a part of the ferricenium salt to ferrocene.

ferrocenyl and osmocenyl nuclei. The analytical form of the titration curve is distorted however, and cannot be used for the determination of the oxidation potentials of either the ferrocenyl or osmocenyl nuclei in this compound. The distortion of this titration curve is probably due to an electron exchange between the oxidized form of one metallocene and the reduced form of the other metallocene in a manner similar to that observed for a mixture of the respective free compounds.

4. *Oxidation of substituted ruthenocenes*

The results obtained show that the introduction of substituents into the ruthenocene cyclopentadienyl ring does not change the shape of the wave at either the DME or Pt-electrode, but that the value of the oxidation potential is somewhat changed (Table 2). The difference between the half-wave potentials for the first and last substituents listed in the Table are 0.26 for DME and 0.36 V for the two-electron oxidation occurring at the Pt-electrode.

TABLE 2

THE POLAROGRAPHIC CHARACTERISTICS OF SUBSTITUTED RUTHENOCENES (CH_3CN, 0.1 M Bu_4NBF_4, SCE, 25±0.1°)

Compound $C_5H_5RuC_5H_4X$	DME (1×10^{-3} M)		Pt-electrode (1×10^{-3} M)	
X=	$E_{\frac{1}{2}}$ (V)	i(μA)	$E_{\frac{1}{2}}$ (V)	i(μA)
OCH_3	0.31	2.80	0.65	9.3
C_2H_5	0.32	2.90	0.66	10.1
H	0.36	2.50	0.78	13.0
C_6H_5	0.37	2.80	0.75	12.9
$OCOCH_3$	0.39	2.70	0.84	11.4
$COOCH_3$	0.57	2.50	0.99	12.9
$COCH_3$	0.57	2.50	1.01	9.4
CN	[a]		1.05	9.2

[a] For strong electron-attractive substituents such as the CN-group, the $E_{\frac{1}{2}}$ shift towards positive values was so large that an oxidation wave at DME could not be observed due to the coincident of its limiting current with the anodic current corresponding to mercury dissolution.

DISCUSSION

Despite the fact that the electrochemical redox potentials of the iron group metallocenes have been discussed in a number of other studies[2-5], this paper presents for the first time data relating to the one-electron reversible oxidation of all three metallocenes under the same strictly maintained conditions. Under such conditions the ferrocene/ferricenium cation system has been shown to possess such ideal electrochemical reversibility that neither the nature of the one-electron oxidation process nor the redox potential are changed under any variation of the experimental conditions. Ferrocene analogues, on the other hand, are not so indifferent to changes in the experimental conditions, and undergo reversible one-electron oxidations only under certain conditions. Even such a negligible change of the experimental conditions as a replacement of one electrode (Hg) by another (Pt) is sufficient to change the mechanism of the electrochemical reaction, the processes becoming irreversible and the number of electrons involved in the oxidation process changing. Probably the large metal–carbon distances and the more diffuse nature of the d-atomic orbitals of the heavier elements with respect to those for iron result in the readier polarization of the respective metallocene in the vicinity of the electrode. Moreover, with increasing atomic number the stability of the half-filled d^5 configuration characteristic of the single charged metallocene cations decreases. As a result in ruthenocene and osmocene the doubly charged 16-electron cation with a formal metal valence equal to +4 becomes stable. In support of this viewpoint it should be noted that for the ordinary inorganic complexes of these metals the +4 oxidation states are also more stable, and hence for the iron group metallocenes the most stable oxidation states are those most similar to the expected oxidation states of the respective "free" metal ions.

Substituent effects

The introduction of substituents into the ruthenocene cyclopentadienyl ring considerably changes the half-wave potentials for both one- and two-electron oxidations (Table 2). Electron-releasing substituents facilitate oxidation whereas electron-withdrawing substituents have the reverse effect. The oxidations of all the substituted ruthenocenes investigated in this study follow the same mechanism, the structural changes resulting from the introduction of substituents being negligible while the substituents themselves produce a variety of different electronic effects. Thus the conditions should be such as to allow an accurate correlation between the structures of compounds studied and their oxidation potentials. Moreover, the variation of $E_{\frac{1}{2}}$ ($\Delta E_{\frac{1}{2}}$ values are 0.26 and 0.40 V for DME and Pt-electrode respectively) is well outside the experimental error for such measurements.

The measured half-wave potentials have been used for the quantitative estimation of the substituents effects by assuming that in these electrochemical reactions the ruthenium atom behaves as the reaction center. A correlational analysis has been

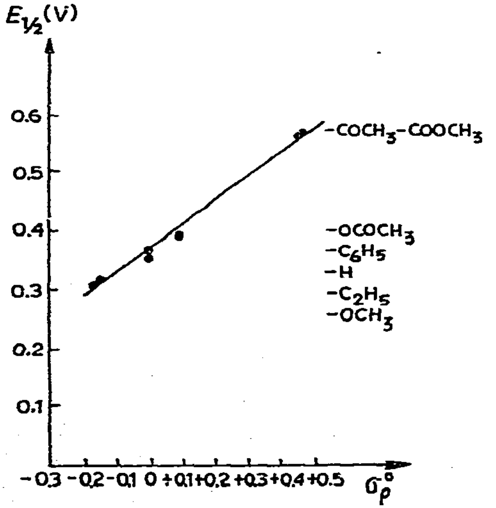
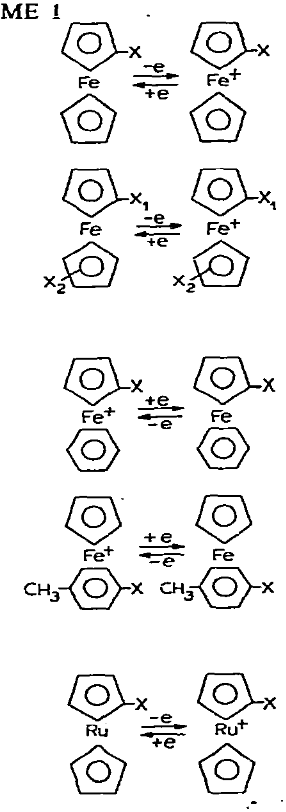


Fig. 5. Correlation of $E_{\frac{1}{2}}$ of ruthenocene derivatives with σ_p^0 (DME).

carried out between the $E_{\frac{1}{2}}$ values for the one-electron oxidation of substituted ruthenocenes (DME) and the corresponding σ values. The best linear dependence between $E_{\frac{1}{2}}$ and σ_p^0 values for the respective substituents* could be expressed by the equation $E_{\frac{1}{2}}=0.42\ \sigma_p^0+0.37$ V; $r=0.998$ (Fig. 5).

These data suggest that the substituents participate in conjugation with the cyclopentadienyl ring and, as commonly accepted, they affect the effective charges at both the π- and σ-ring orbitals. The reaction centre, *i.e.*, the ruthenium atom, on the other hand, is sensitive only to such changes of charge as occur at the σ-rather than the π-ring orbitals. The analogous behaviour of the substituent effects in the mono- and heteroannular disubstituted ferrocenes[1,11] and arenecylopentadienyliron complex cations with substituents in both the arenic and cyclopentadienyl rings[6] (Scheme 1) has been commented upon earlier.

SCHEME 1



$E_{\mathrm{Fc}}=0.53\ \sigma_p^0-0.272$ V; $r=0.992$

$E_{\frac{1}{2}}=0.520\ \sigma_p^0-1.39$ V; $r=0.997$

$E_{\frac{1}{2}}=0.515\ \sigma_p^0-1.42$ V; $r=0.995$

$E_{\frac{1}{2}}=0.42\ \sigma_p^0+0.37$ V; $r=0.998$

Thus, in all these cases irrespective of the nature of the ligand or of the metal the same predominantly inductive substituent effects always occur. In addition, the metal atom reaction centre sensibility is practically the same for all the reaction series in-

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* For two-electron oxidation of derivatives at the Pt-electrode the half-wave potentials could be correlated equally well with σ_p^0 and σ_p constants expressed by the equations: $E_{\frac{1}{2}}=0.49\ \sigma_p^0+0.76$ V; $r=0.982$ and $E_{\frac{1}{2}}=0.46\,\sigma_p+0.76$ V; $r=0.998$. The irreversibility of the oxidation and the large error in the $E_{\frac{1}{2}}$ measurements at the Pt-electrode (with respect to DME) prevented a choice between these two alternative expressions.

vestigated, and is thus independent of either the character of the ligand or the nature of the metal.

There are thus sufficient grounds to assume that the specific effects discussed above are common to all systems with metal–aromatic ring π-bonding. Such effects agree well with the suggestion made by one of the present authors and associates[12] that the aromatic ring σ-orbitals make a significant contribution to bond formation at the transition metal atom.

Localization of electron changes

It is commonly accepted that in the course of reversible redox reactions the electron is removed from the highest occupied orbital of the oxidized complex, and is added to the lowest vacant orbital of the reduced compound. For complexes with bulky organic ligands capable of existing as individual compounds, the possibility that localization of the electron charge occurs during the course of redox reactions is quite feasible. For this reason it is important to determine the relative contributions made by the ligand MO and metal AO to the molecular orbital of the complex in order to establish the source of the electron changes which occur during a redox reaction.

The basic principles which allow the determination of the electron charge localization in the complex have already been discussed[13]. The ferricenium cation is the primary product of the electrochemical oxidation of ferrocene. X-ray diffraction studies have shown that the ferricenium cation in $[(C_5H_5)_2Fe]^+I_3$ has an undistorted, sandwich, ferrocene-like structure[14]. In particular, according to Taube[15], an exlusively high electron exchange rate in the ferrocene/ferricenium cation system provides evidence that no essential changes occur in the character of the metal–ligand bond during the electron exchange process between the reduced and oxidized forms, and that the primary product of the electrochemical reaction possesses a positive charge concentrated at the metal atom. This latter effect is most convincingly demonstrated by the strictly additive effects of substituents in different rings of a ferrocene molecule on the redox potentials. Moreover, for the equilibria presented in Scheme 1, the metal atom is the only possible reaction centre which can be equally sensitive to the effects of substituents in the two different ligands. Furthermore, it has been mentioned above that the most stable oxidized forms of the metallocenes studied in this work are those in which the metal has a formal valency equal to that of the correspondingly most stable "free" ions. Finally, localization of the electron changes in the redox reactions of the iron group metallocenes has been demonstrated using the Vlček method[16].

A comparison of the potential difference between the reversible one-electron oxidations of the cyclopentadienyl "anion" (−0.34 V) and that of its *p*- and *m*-fluorophenyl derivatives (−0.20 and −0.19 V respectively)* with that of the reversible oxidations of the respective iron, ruthenium and osmium complexes enabled the combination coefficients for the metal AO and ligand MO's to be determined for the molecular orbital of the complex responsible for the electron changes occurring during the redox processes. This value was found to be equal to 0.20, indicating that the contribution of the molecular orbitals of the ligand to that of the complex is about 20%. Hence in the redox reactions involving the metallocenes discussed above the electronic changes occur at the metal atom. This conclusion is in good agreement with

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* Measured at the Pt-rotating electrode (0.1 *M* Bu_4NBF_4, DMF), using the lithium salts of the anions.

the majority of quantum-mechanical calculations made for these which have shown that for all the iron group metallocenes the highest occupied molecular orbital responsible for the electronic changes observed during the course of redox reactions is a virtually unchanged non-bonding d_{z^2} orbital.

Ionization potentials of the iron group metallocenes

Recently, it has been demonstrated that reversible redox potentials may be used for estimating molecular ionization potentials (*IP*)[18]. Since the ferrocene/ferricenium cation system possesses uniquely "ideal" electrochemical properties, the limitations to the method do not apply in this case and a fairly precise estimation may be made of the ionization potential of ferrocene. Using the formulae cited in ref. 18 and employing the known solvation energy of the ferricenium cation (55 kcal/mole)[19] and solvation energy for the ferrocene by acetone (13.5 kcal/mole)[20] yields a value for the ionization potential of ferrocene of 7.28 eV. This value is in excellent agreement with the data obtained by other methods*. Similarly, using the reversible redox potentials at DME the corresponding values for ruthenocene and osmocene have also been calculated as 7.22 and 7.02 eV respectively, again in good agreement with previously reported values.[22,23]

It should be noted that in the calculation of the ionization potentials of ruthenocene and osmocene the reasonable assumption was made that the difference of solvation energies for the oxidized and reduced forms of these metallocenes would be the same as in the cases of ferrocene.

Energies of the highest occupied orbitals and the reactivity of ferrocene, ruthenocene, osmocene

The results quoted above show that the relative energy of the molecular orbital associated with redox reactions (which is essentially the same as the metal atomic orbital) decreases in the series: ferrocene > ruthenocene > osmocene. In other words, the ease of removal of the first electron in the metallocenes investigated increases with increasing atomic weight of the metal. It is commonly accepted that in the same series the heavier metals have higher Pauling electronegativities than their lighter analogues[24], and for this reason it might be expected that during interaction with the same type of electron-releasing ligands charge transfer should be greater from the ligands to the heavier elements than to their lighter analogues. As a result the effective positive ligand and negative metal charges associated with the metallocenes should increase with decreasing atomic number of the metal.

Such a conclusion is in good agreement with the change of reactivity observed in the series: ferrocene, ruthenocene, osmocene. In particular, ruthenocene and hilic aromatic substitution reactions[25,26]. In the most extensively used mechanism of electrophilic substitution, formation of a so-called "*d*-complex" between the electrophilic agent and the metal of the metallocene[26,27] is usually assumed to be the rate-determining step in the process. It is obvious that the ease of "*d*-complex" formation should parallel that of electron fission in the above series of metallocenes. However, in these studies we have

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* For example, electron impact measurements give a value of 7.15 eV for the ionization potential of ferrocene, and it is this value which is most often quoted in the literature[21].

observed that metallocenes exhibit a reduced tendency toward entering electrophilic substitution and oxidation reactions. This indicates that either "*d*-complex" formation is not the rate-determining process in these reactions or that some other "common" mechanism of electrophilic aromatic substitution occurs in which the electrophilic agent attacks the five-membered ring. Indeed, as shown experimentally, the electron density of the carbon rings decreases in the series: ferrocene > ruthenocene > osmocene and parallels the metallocene activity in electrophilic substitution reactions.

EXPERIMENTAL

Polarograms were obtained using PE-312 and LP-60a polarographs. The dropping mercury electrode had the following characteristic: m 1.53 mg/sec, t 0.37 sec. Two disc Pt-electrodes were used with surfaces 7 and 1.8 mm^2 and rotation rates 1100 and 920 rotations/min respectively.

A saturated calomel electrode was used as a comparison electrode, and the reversibility of the process was established by means of a Kalousek switch. Measurements were conducted in a cell thermostatted at $25 \pm 0.1°$, the half-wave potentials being measured to accuracies of 0.01 and 0.03 eV at DME and Pt-electrodes respectively.

Ferrocenylosmocenylketone (1) was prepared by the reaction of ferrocenoyl chloride with osmocene in the presence of aluminium chloride. Yield of (I) 5%, m.p. 232° (decompn.) Carbonyl group absorption band at 1628 cm^{-1}.

Ferrocenylosmocenylmethane (II) was obtained using the method described for the preparation of ferrocenylruthenocenylmethane[10]. Yield of (II) 70%, m.p. 152–153°.

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