

REDOX PROPERTIES OF CYCLOPENTADIENYLMETAL COMPOUNDS II*. COBALTOCENE, NICKELOCENE AND RELATED COMPOUNDS

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(Received February 18th, 1971)

SUMMARY

The polarographic behaviour of cobalticinium cation, nickelocene and some of its derivatives at the dropping mercury (DME) and platinum electrodes has been investigated in acetonitrile.

The cobalticinium cation has been found to reduce to cobaltocene after addition of an electron, while nickelocene oxidized to the nickelicinium cation. Using a Pt-rotating electrode the latter ion underwent further oxidation yielding a doubly charged $(C_5H_5)_2Ni^{2+}$ cation. All these processes have been shown to be reversible. At negative potentials cobaltocene and nickelocene undergo irreversible reduction to π -cyclopentadienyl- π -cyclopentadienecobalt and π -cyclopentadienyl- π -cyclopentenylnickel respectively. The effect of proton donors on the processes has been studied. Localization of the electronic changes in the complexes investigated during the course of redox reactions is discussed. The halfwave potentials obtained allow the ionization potentials (*IP*) corresponding to the removal of the first electron from cobaltocene and nickelocene to be calculated.

It has been shown that under polarographic conditions π -cyclopentadienyl-(triphenylphosphine)nickel chloride undergoes disproportionation to nickelocene and a nickel chloride/triphenylphosphine complex.

INTRODUCTION

In a previous communication¹ the redox properties of the iron group metallocenes (ferrocene, ruthenocene, osmocene) have been discussed. Although electrochemical studies of redox reactions involving these compounds had been undertaken earlier in some detail, it was shown that a further investigation of their redox properties using equivalent conditions (aprotic solvent, large potential region) could yield useful information. Thus, the ionization potentials estimated from redox potentials determined under such conditions have been shown to be in a good agreement with values obtained by other techniques.

In the present paper the redox properties of some dicyclopentadienyl com-

* For Part I see ref. 1.

pounds of cobalt and nickel—which are neighbours of iron in the Group VIII of the Periodic Table—are discussed. Nickelocene is known to oxidize readily to a singly charged nickelicenium cation², the latter having also been isolated in the form of its salts with bulky complex anions. On treatment with reducing agents these salts were easily converted back to nickelocene³. The polarographic oxidation of nickelocene has also been studied earlier in aqueous ethanol with NaClO_4 ³ and 0.5 M HClO_4 ⁴ as supporting electrolytes. The results obtained indicated that under these conditions³ the process is not completely reversible electrochemically. At the time that this work was reported nickelocene had not been further oxidized to its doubly charged cation (either chemically^{3,5} or electrochemically^{3,4}). Recently, however, Wilson *et al.*⁶ have observed nickelocene oxidation in acetonitrile at low temperature on a Pt-electrode using a method involving cyclic voltammetry. In addition the picrate of the doubly charged nickelicenium cation has also been obtained⁷. Previous to the work described in this paper, nickelocene had not been reduced electrochemically although it had been reported as reacting with some reducing agents (sodium amalgam, alkaline metals, metal hydrides, hydrogen in the presence of Raney nickel) being transformed to π -cyclopentadienyl- π -cyclopentenylnickel⁸.

Cobaltocene is exceptionally sensitive to the action of oxidants^{3,9} and may be readily oxidized even with such untypical soft oxidants as ferrous and cobalt chlorides¹⁰. On the other hand, it causes the evolution of hydrogen from oxygen free water^{10,11} and for this reason the stable cobalticenium cation is usually employed for electrochemical studies. Reversible polarographic reduction of cobalticenium cation to cobaltocene has been studied in detail in protic solvents^{9,12-14}, and a study has also been made of the reduction of the cobalticenium cation in an aprotic medium^{14,22}.

After chemical reduction to cobalticenium cation converts to π -cyclopentadienyl- π -cyclopentadienecobalt^{8,15}. Electrochemically, cobalticenium cations have been reduced only to cobaltocene⁹⁻¹⁴ and although Vlček¹² made an attempt to reveal the second stage of the reduction of cobalticenium cation it is now considered that the conditions used in this work could not possibly reveal the second reduction stage since this would have been beyond the discharge region of the supporting electrolyte.

In the present work the redox properties of cobaltocene, nickelocene and related compounds have been studied in detail by a polarographic method in aprotic and protic media using DME and Pt-electrodes in the potential region from +2.0 to -2.8 V (SCE).

EXPERIMENTAL

Polarograms were recorded on a Perkin-Elmer 312 polarograph. The dropping mercury electrode had the following characteristics: m 1.53 mg/sec, t 0.37 sec, while the 1.8 mm^2 Pt-disc electrode rotated at a rate of 920 cycles per min. A saturated calomel electrode was used as reference electrode. Measurements were conducted in a thermostatted cell at $25 \pm 0.1^\circ$. On DME and Pt-electrodes the half-wave potentials were measured to an accuracy of 0.01 and 0.03 V respectively. Reversibility was established by means of a Kalousek switch.

Acetonitrile was distilled at 81.5° over P_2O_5 and LiAlH_4 and then over P_2O_5 and KMnO_4 . Purified CH_3CN showed no polarographic waves in the region +2.0

to -2.8 V (SCE). $(C_4H_9)_4NBF_4$ which was used as a supporting electrolyte, was prepared as previously described¹⁶. Nickelocene was also obtained by a previously described procedure¹⁷ (m.p. $173-174^\circ$). Cobalticenium perbromide was synthesized as described in ref. 18, $(tert-C_4H_9C_5H_4)_2Ni$ was obtained by the method of ref. 19, $C_5H_5NiP(C_6H_5)_3Cl$ was obtained by the method of ref. 20 [m.p. $138-139^\circ$ (decompn.)], and $NiCl_2 \cdot 2 P(C_6H_5)_3$ was obtained using the procedure of ref. 21 (decompn. at $247-249^\circ$).

RESULTS AND DISCUSSION

The polarographic characteristic of the compounds investigated are shown in Table 1.

TABLE 1

THE POLAROGRAPHIC CHARACTERISTICS OF THE COBALTICENIUM CATION, NICKELOCENE AND RELATED COMPOUNDS

($0.1 M Bu_4NBF_4$, CH_3CN , SCE, $25 \pm 0.1^\circ$, $1 \times 10^{-3} M$)

Compound	DME				Pt-Electrode			
	$E_{\frac{1}{2}}'$ (V)	i_1 (μA)	$E_{\frac{1}{2}}''$ (V)	i_2 (μA)	$E_{\frac{1}{2}}'$ (V)	i_1 (μA)	$E_{\frac{1}{2}}''$ (V)	i_2 (μA)
$(C_5H_5)_2CoBr_3$	-0.98^a	2.1	-1.92^b	2.8				
$(C_5H_5)_2Ni$	$+0.01^a$	2.6	-1.74^b	3.6	$+0.01^a$	3.0	$+0.75^a$	2.9
$(t-Bu_2)(C_5H_4)_2Ni$	-0.11^a	2.2	-1.86^b	3.2				
$(C_5H_5)_2Fe$	$+0.42^a$	2.8			0.48^a	5.7		

^a Anodic wave. ^b Cathodic wave.

1. The system cobaltocene/cobalticenium cation

Cobalticenium salts are characterized by a well expressed polarographic wave in the region of ca. -1 V on reduction at the DME in acetonitrile (Fig. 1). Wave analysis indicated that the limiting current was of a diffusive character, the height corresponding to a one-electron reduction, and with the process being reversible electrochemically. Thus, in an aprotic medium similar to that used for the system ferrocene/ferricenium cation, the system cobaltocene/cobalticenium cation is a highly reversible redox pair whose potential does not change as the nature of the solvent is changed²².

2. The oxidation of nickelocene

At the DME in acetonitrile the polarograms of nickelocene exhibit an anodic wave at a potential of ca. 0 V (referenced to a saturated calomel electrode (SCE)) (Fig. 2). The limiting current of this wave is of a diffuse character: plots of i_{lim} vs. concentration and \sqrt{H} were linear, with a low value for the temperature coefficient ($0.36\%/1^\circ$). In the concentration region $8-0.5 \times 10^{-3} M$ the $E_{\frac{1}{2}}$ value is independent of the concentration. The slope of the $\log i/(i_a - i)$ vs. E plot (78 mV) in logarithmic coordinates and measurements on a Kalousek switch indicate the reversible nature of the oxidation process. Evidence for the participation of one electron in the oxidation process was obtained from a comparison of the limiting currents of the polarographic

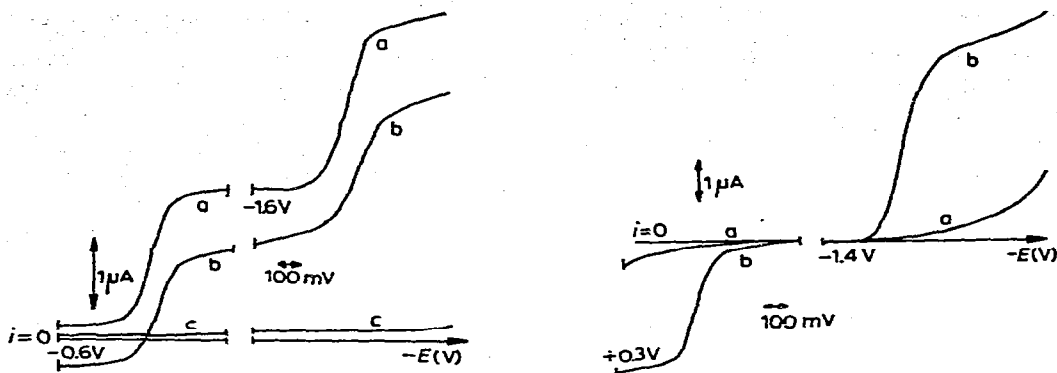


Fig. 1. Polarogram of (a) $(C_5H_5)_2CoBr_3$ ($1 \times 10^{-3} M$); (b) curve taken with a Kalousek switch, E_{auxil} 1.2 V (1st wave) and $-2.4 V$ (2nd wave), f_{comm} 25 Hz; (c) curve of supporting electrolyte [$0.1 M (C_4H_9)_4NBF_4, CH_3CN$].

Fig. 2. Polarogram of nickelocene on DME; (a) curve of supporting solution [$0.1 M (C_4H_9)_4NBF_4, CH_3CN$]; (b) $(C_5H_5)_2Ni$ ($1 \times 10^{-3} M$).

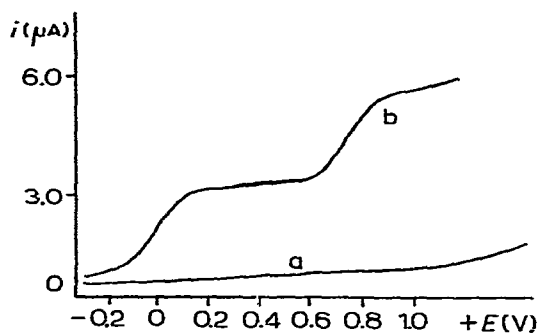


Fig. 3. Polarogram of nickelocene on Pt rotating electrode; (a) curve of supporting solution [$0.1 M (C_4H_9)_4NBF_4, CH_3CN$]; (b) $(C_5H_5)_2Ni$ ($1 \times 10^{-3} M$).

waves for nickelocene and ferrocene at similar concentrations (Table 1).

Changing the solvent from one of an aprotic to an ethanol/benzene solution had no influence on the characteristics of polarographic waves corresponding to the oxidation of nickelocene. The results obtained therefore clearly indicate that the nickelocene/uni-charged nickelicenium cation system, in a similar fashion to those of ferrocene and cobaltocene, corresponds to a highly reversible redox pair.

At rotating Pt-electrodes in acetonitrile nickelocene shows two one-electronic, reversible oxidation waves (Fig. 3). As expected for reversible processes the half-wave potential $E_{1/2}$ for the first nickelocene oxidation stage is independent of the nature of the electrode material. In agreement with other studies⁶ the second oxidation stage of nickelocene may be assumed to be related to the reversible transformation of the uni-charged nickelicenium cation into a doubly-charged entity. It should be pointed out that the life-time of this latter cation on the surface of the electrode is

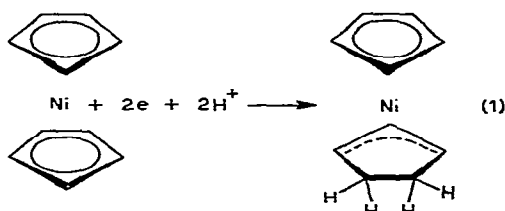
sufficient to allow measurements of the reversibility of the process through the use of a Kalousek switch.

3. The reduction of nickelocene and cobaltocene

When nickelocene is reduced at the DME the cathodic wave appears at negative potentials (Fig. 2).

The wave is of a diffusive character with a linear dependence of the limiting current upon concentration and \sqrt{H} , and with a low value for the temperature coefficient ($0.5\%/1^\circ$). The slope of the $\log i/(i_d - i)$ vs. E (130 mV) and measurements by means of a Kalousek switch, support the irreversible character of reduction process. The cathodic wave of nickelocene is higher than the corresponding oxidation wave, although it is somewhat below the value to be expected for a two-electron reduction. On addition of phenol, the character of cathodic wave remains unchanged but the value of the limiting current increases. The ratio of the heights of the cathodic and anodic waves approaches a value of two (1.8). In a proton-donating medium (ethanol/benzene 1/1) the cathodic wave is well defined, and in this case the ratio of the wave heights is even closer to two.

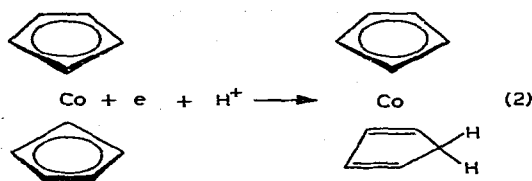
From this it follows that the cathodic wave of nickelocene corresponds to addition of two electrons. Furthermore, protons derived from the solvent participate in an electrode reaction, the entire process being irreversible. The most probable reduction product of nickelocene can only be the π -cyclopentadienyl- π -cyclopentenyl-nickel system:



Such a product has been obtained in the reduction of nickelocene with sodium amalgam^{8*}.

The reduction of the cobaltocenium cation produces not only a reversible first stage but also a second wave at a potential close to -1.9 V (Fig. 1). The characteristics of this latter wave corresponds to a one-electron irreversible diffusion process. In addition, as with nickelocene, the addition of a proton donor affects the value of the limiting current for this wave. Thus, the second cathodic wave of the cobaltocenium cation is probably caused by the addition of an electron and a proton to the cobaltocene initially formed in the process, the π -cyclopentadienyl- π -cyclopentadienecobalt system being the most probable reduction product:

* Polarograms of the reduction product of $(C_5H_5)_2Ni$ with sodium amalgam in alcohol⁸ and of the electrolysis product of $(C_5H_5)_2Ni$ at the potential of the limiting current of cathodic wave (-2.2 V) completely coincide. The π -cyclopentadienyl- π -cyclopentenylnickel system generated by these processes oxidizes at $+0.2$ V.



This latter compound has been found as the final product of the reduction of the cobalticenium cation by alkaline metal hydrides^{8,15}. Thus, it has been shown that this reduction proceeds as two steps, the first being associated with a one-electron reversible process. Similar dependences during the reduction of arenecyclopentadienyl-iron cations have been observed earlier²³.

Localization of electronic changes

It is commonly accepted that in going from an activated depolarizator to a primary product of the electrode reaction the electronic changes which take place during the reduction process occur at the lowest vacant orbital. In the transition metal π -complexes the ligand molecular orbitals and metal atomic orbitals usually make different contributions to the common molecular orbital of the complex, the latter being responsible for the electronic changes which occur during the course of an electrochemical reaction. Depending upon a relative contribution of the metal and ligand orbitals, two possible sites for the electronic changes occurring in such complexes may be distinguished: (a) at the metal orbitals, or (b) at the orbitals of π -bonded ligands. A discussion of the methods usually employed in solving the problem of distinguishing the sites of electronic changes during the course of redox reactions of π -complexes has been reported in²⁴.

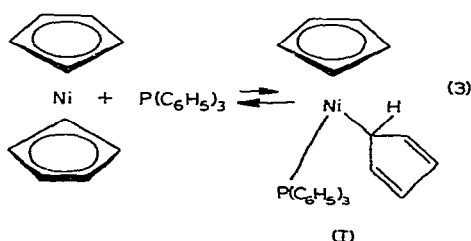
It has been shown that redox reactions of transition metal π -complexes in which electronic changes occur at the metal atom are characterized by the following features. Such reactions are usually one-electron processes, highly reversible electrochemically, and a change in the nature of the solvent and addition of proton donors leaves the characteristics of the polarographic wave unchanged. The reversible oxidation wave of nickelocene and the first reversible reduction stage of the cobalticenium cation both meet all of these requirements. Hence in these cases the electronic changes involved in the processes occur at the metal atom during the course of redox reactions. Furthermore the introduction of two tert-butyl groups into the nickelocene molecule (Table 1) changes the $E_{\frac{1}{2}}$ value of the first oxidation stage by 0.12 V. This result is in good agreement with the value (E 118 mV) estimated from the additive scheme, using the redox potentials of ferrocene and mono-tert-butylferrocene. Since in the last case the electronic changes are localized at the metal atom, the above mentioned good agreement of the tert-butyl substituent effect also argues in favour of the assumed localization of the electronic change at the metal atom.

If the electrochemical reactions of π -complexes proceed irreversibly via solvent proton participation then it may be assumed that in such reactions the electronic changes are localized at the π -bonded carbocyclic ligand orbitals²⁴. From this it follows that in the irreversible reductions discussed above the electronic changes are localized at the cyclopentadienyl ligand orbitals. It is probable that at sufficiently

negative potentials the molecules of nickelocene and cobaltocene undergo such changes under the influence of the electrode field, and assume an electronic configuration with partially occupied five-membered ring orbitals and a closed metal electron shell. Transition into the final products of electrochemical reaction, through the addition of electrons and protons to the ligand, completely stabilizes the molecule due to the formation of a complex with a closed metal electron shell.

Disproportionation of some mono- π -cyclopentadienylnickel complexes

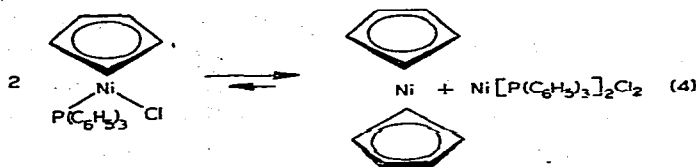
In the previous section the two types of electronic change localization during the course of redox reactions of transition metal complexes was discussed. A third type of localization of electronic change is possible however, involving the localization of electrons in the antibonding orbital of the σ -bond formed between the transition metal and the ligand. This third type of electronic change localization was not discussed in the previous section since in the cobalt and nickel dicyclopentadienyl complexes studied in this work the ligands and metal atoms are linked solely by π -bonds. However, some workers have suggested that nickelocene is capable of conversion to its σ -form in the presence of *n*-donor ligands²⁰:



Thus, it has been assumed that in the presence of excess $P(C_6H_5)_3$ the equilibrium (3) is shifted towards the formation of the σ -cyclopentadienyl complex (I) having a closed metal electron shell.

In an earlier paper²⁵, the transition metal-cyclopentadienyl σ -ligand bond has been shown to be polarographically active and to reduce rather easily. If compound (I) actually forms from nickelocene in large quantities in the presence of triphenylphosphine, it might be expected that polarographic analysis should reveal the reduction of the Ni-cyclopentadienyl σ -bond. However, as shown by the data in Table 2, the presence of triphenylphosphine in the solution does not affect either the anodic or cathodic waves of nickelocene. Moreover, no new waves were observed in the polarograms corresponding to the reduction of the nickel-cyclopentadienyl σ -bond. The presence of excess triphenylphosphine has therefore no effect upon the system, and under the experimental conditions employed in this work the polarographic method does not reveal any shift of equilibrium (3) to the right hand side of this equation.

Indeed, it has been found that under the experimental conditions employed a pure sample of π -cyclopentadienyl(triphenylphosphine)nickel chloride disproportionates almost quantitatively to nickelocene and a (triphenylphosphine)nickel dichloride complex, *viz.*,



This is shown by the data recorded in Table 2 where the observed polarogram indicates that nickelocene and a $\text{NiCl}_2 \cdot 2 \text{P}(\text{C}_6\text{H}_5)_3$ complex occur simultaneously in the solution at the concentrations employed, in agreement with the predictions of eqn. (4).

These experiments indicate therefore that under the conditions described no π -cyclopentadienyl complex with a nickel-ligand σ -bond exists in these solutions at a sufficient concentration to allow their polarographic determination.

TABLE 2

POLAROGRAPHIC CHARACTERISTICS OF SOME NICKELOCENE DERIVATIVES
(0.1 M Bu_4NBF_4 , CH_3CN , SCE, DME, $25 \pm 0.1^\circ$)

Compound	Concentration (M)	$E'_{\frac{1}{2}}$ (V)	i_1 (μA)	$E''_{\frac{1}{2}}$ (V)	i_2 (μA)	$E'''_{\frac{1}{2}}$ (V)	i_3 (μA)	$E''''_{\frac{1}{2}}$ (V)	i_4 (μA)
$(\text{C}_5\text{H}_5)_2\text{Ni} \cdot \text{P}(\text{C}_6\text{H}_5)_3$	1×10^{-3}	+0.24 ^a	0.9	+0.01 ^a	2.6			-1.78 ^b	3.7
$\text{C}_5\text{H}_5\text{Ni} \cdot \text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$	2×10^{-3}	+0.24 ^a	0.9	0.00 ^a	2.2	-1.03 ^b	1.9	-1.79 ^b	2.6
$\text{NiCl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{P}$	1×10^{-3}	+0.32 ^a	0.8			-1.03 ^b	2.2		

^a Anodic wave. ^b Cathodic wave. ^c In addition to this wave an anodic wave with $E_{\frac{1}{2}}$ 0.13 V and a cathodic wave with $E_{\frac{1}{2}}$ 0.34 V were also observed.

Ionization potentials

Recently²⁶ the possibility of using reversible redox potentials for estimating the ionization potential (IP) has been confirmed experimentally, and the formulae enabling such calculations have been used to determine the IP 's of ferrocene, ruthenocene and osmocene¹. The obtained ionization potentials of these compounds were found to be in good agreement with values deduced by other methods. In the present work the ionization potentials of cobaltocene and nickelocene (corresponding to the removal of the first electron) were determined as 5.88 and 6.86 eV respectively, from a similar use of reversible redox potentials.

These values are in good agreement with other published data²⁷.

It should be pointed out that in estimating the ionization potentials of cobaltocene and nickelocene it was assumed that the difference between the solvation energies for the oxidized and reduced forms of these compounds was the same as in the case of ferrocene.

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