Journal of Organometallic Chemistry, 365 (1989) 269–284
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09482

Study of redox reactions of bis(arene)chromium complexes by use of the rotating disk and the rotating ring-disk electrodes

V *. Cathodic processes involving nitriles; cyano derivatives of benzene and dibenzenechromium

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(Received September 19th, 1988)

Abstract

The cathodic reduction in DMSO solutions of six aromatic nitriles of the benzene, and eight dibenzenechromium cyano derivatives have been studied by use of the rotating disk and rotating ring-disk electrodes. A substantial change in the character of the polarization curves of π-complexes in comparison with the same cathodic reduction curves of the benzene series is observed. This change manifests itself in the disappearance of the one-electron waves in the I,E-curves and the emergence of two-electron waves. The stepwise addition of two electrons (EEC-mechanism) for free aromatic nitriles, whose anion radicals (ARs) can be reduced, is replaced by the ECE-mechanism in the nitrile complexes: the reversible transfer of the first electron is followed by the chemical decomposition reaction of anion-radicals whose products are reduced at the potential that AR is formed. The reversibility of the addition of the first electron to the free and the complexed nitriles allows their reactivity to be compared directly under cathodic conditions.

Introduction

The problem of the reactivity of bis(arene)chromium complexes has two important aspects: (1) the study of the influence of substituents in arene ligands on the reactivity of the complex; (2) the change in the arene reactivity due to its coordination with the chromium atom.

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* For part IV see ref. 1.

The ability of the chromium π-complexes to participate in redox reactions, which can be examined with high accuracy by use of electrochemical techniques may help to elucidate the reactivity of bis(arene)chromium complexes.

The general reaction for any dibenzenechromium derivatives is a reversible one-electron oxidation of their neutral forms containing chromium(0), to cationic forms containing chromium(+ 1) (eq. 1).

$$\mathrm{Arene_2Cr} \underset{+e}{\overset{-e}{\rightleftarrows}} \mathrm{Arene_2Cr^+} \qquad (1)$$

The universality and the reversibility of the process as well as the unchanged nature of the reaction centre (chromium atom) on a wide range of compound makes this reaction convenient in solving problems concerning the transmission of the substituent electron effects on the reactivity of the chromium π-complexes in reactions involving the metal atom. An approach to solving the problem has been opened [1,2].

The nature and the strength of the influence of the substituents in one ring on the reaction centre of another can be determined by studying the cathodic reduction processes of the bis(arene)chromium bearing an electro-active group (carbonyl, ester, cyano-groups, halogen atoms, substituents with a double carbon–carbon bonds, etc.). It is obvious that in this case it is necessary to compare the behaviour of a series of complexes of varying composition but containing the same reaction centre. However, such electrochemical reactions have seldom been used for the study we had in mind. The problems we were confronted with were the difficulty in synthesizing a set of the desired compounds, complicated by having to interpret the results of the investigation of the electroreduction processes of complexes containing electrochemically active substituents. The interpretation further is complicated by the fact that the cathodic processes are multi-step processes, thus several electrons and protons take part in the total reaction, in addition some of the reaction stages are irreversible. Despite the irreversibility, it is the comparison of the behaviour of the free and the π-coordinated arenes in the cathodic processes, that allows us to study the effect of coordination with the chromium atom on the reactivity of the arenes. Eight pairs of free arene-bis(arene)chromium complexes containing different reducing groups have been studied previously [3–5].

The synthesis of the nitrile complexes, $(C_6H_5CN)Cr(C_6H_5X)$, ($X = H$, CH_3, OCH_3, CN, F, Cl, CF_3, $COCH_3$) [6–9] and the study of the cathodic processes involving the cyano groups as the reaction centre have allowed us to realize both approaches for the investigation of reactivity in the framework of this paper.

The kinetics and the mechanisms of the cathodic processes are to a large extent, determined by the nature of the group undergoing the reduction and the general structure of the molecule, whereas the processes themselves can proceed differently, depending on the conditions used. In this regard special attention is given to the establishment of the kinetic parameters and reaction mechanism for the cathodic reduction of the free nitriles and their complexes as a necessary step in the solution of the reactivity problems.

The pathways for multi-step reactions and their mechanism can be determined only after the intermediates and end products which are formed during the process have been detected and identified. For this purpose, we used the rotating ring-disk electrode (RRDE) technique [10–13], especially designed for solving such problems. An outline of the method is as follows: the electrochemically active moieties which are formed during the electrode reaction on the rotating disk are carried by a liquid flow to the concentric ring electrode from which their anodic or cathodic polarization curves are recorded. The polarization curves can furnish extensive information about the nature and properties of the intermediates and end products from the disk electrode.

That the chromium(0) π-complexes are oxidized according to reaction (1) makes the use of RRDE effective in recording the reduction products of the initial compounds, whilst a correlation of half-wave potentials of the π-complex oxidations and the σ constant values of the substituents [1,2] permits their identification. RRDE enables detection of other products of the cathodic reduction of aromatic nitriles and their chromium π-complexes, in particular, CN^- anions formed by cathodic elimination of the cyano group. The ability of all the bis(arene)chromium complexes to be oxidized into cations according to reaction 1 leads to another useful feature: the height of the corresponding one-electron anodic wave on the disk electrode can serve as the reference for determining the number of electrons participating in the cathodic reduction process of the electrochemically active grouping. The advantage of the RRDE method is that the presence of radical ion intermediates, their stabilities and further conversions undergone, can be determined. Thus, a qualitative and quantitative comparison of the reactivities is possible not only of the initial compounds but also those of the intermediates that appear during their conversion, thus affording a comprehensive picture of the change in reactivity due to coordination of arene with the metal atom. Our approach is also suitable for the cyano-substituted benzenes and their chromium π-complexes.

Experimental

To obtain comparable data, all the measurements were made under identical conditions. Amalgamated gold was used as the disk and ring material. Dimethylsulfoxide, purified and dried, was the solvent. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte, and the aqueous normal calomel electrode was the reference electrode.

Results

Electrochemical reduction of aromatic nitriles

The cathodic reduction processes of aromatic nitriles in aprotic solvents have been widely studied by use of various electrochemical and ESR techniques [14–21]. In the present work RRDE was used to study the cathodic behaviour in DMSO solutions of six aromatic nitriles containing one, two or four cyano groups per molecule. The data on the half-wave potentials at the disk electrode of the cathodic waves, $E_{1/2}$, of the compound studied, are listed in Table 1, as is information on the cathodic reaction products recorded at the ring electrode (disk electrode potential was maintained in the limiting current region of the first (A) or second (B) wave). The data obtained are in good agreement with the literature.

The cathodic reduction processes of the aromatic nitriles examined by us are characterized by the presence of one or two waves on the polarization curve (Fig. 1).

Table 1

Parameters of electrochemical reduction of aromatic nitriles (RRDE in DMSO)

Entry	Compound	Cathodic A wave			Cathodic B wave		
		$-E^{D}_{1/2}$ (V)	n_A [b]	Reaction products recorded on the ring	$-E^{D}_{1/2}$ (V)	n_B [b]	Reaction products recorded on the ring
1	C_6H_5CN	2.25	1	$[C_6H_5CN]^{\cdot -}$	–	–	–
2	p-$CH_3C_6H_4CN$	2.40	1	$[p\text{-}CH_3C_6H_4CN]^{\cdot -}$	–	–	–
3	m-$C_6H_4(CN)_2$	1.74	1	$[m\text{-}C_6H_4(CN)_2]_2^{2-}$ or CN^-	–	–	–
4	o-$C_6H_4(CN)_2$	1.62	1	$[o\text{-}C_6H_4(CN)_2]^{\cdot -}$	2.55 [a]	2	$[C_6H_5CN]^{\cdot -}$, CN
5	p-$C_6H_4(CN)_2$	1.62	1	$[p\text{-}C_6H_4(CN)_2]^{\cdot -}$	2.40 [a]	2	$[C_6H_5CN]^{\cdot -}$, CN^-
6	1,2,4,5-$C_6H_2(CN)_4$	0.66	1	$[1,2,4,5\text{-}C_6H_2(CN)_4]^{\cdot -}$	1.61	1	$[1,2,4,5\text{-}C_6H_2(CN)_4]^{2-}$

[a] Irreversible wave. [b] n_A and n_B are numbers of added electrons.

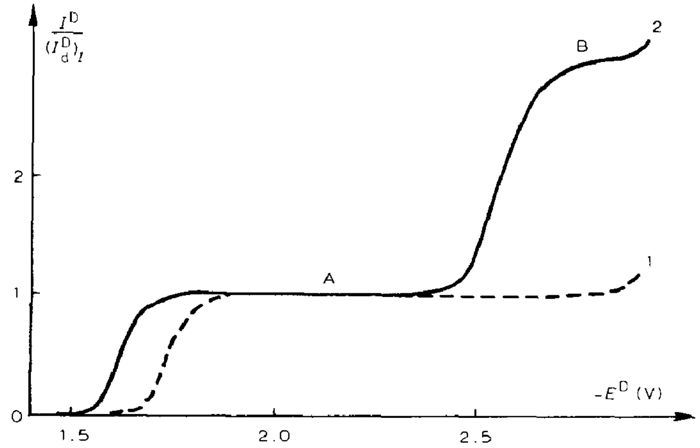

Fig. 1. Polarization curves of the electroreduction of *m*-dicyanobenzene (1) and *o*-dicyanobenzene (2) on the rotating disk electrode made of amalgamated gold in DMSO solution containing 0.1 *M* $(C_4H_9)_4NBF_4$ (the current strength values are compared to the value of the diffusion limiting current of the one-electron process).

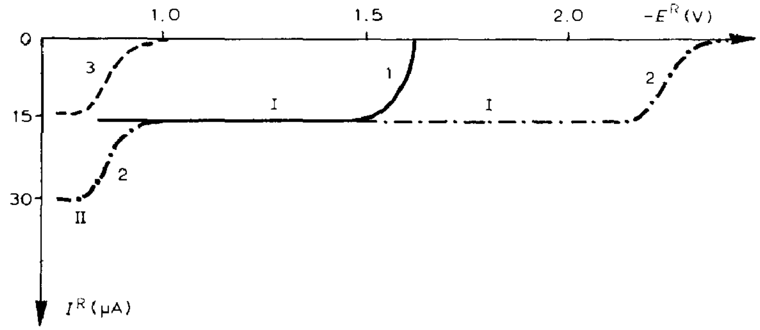

Fig. 2. Polarization curves of the anodic oxidation at the ring electrode (made of amalgamated gold) of the products of the cathodic reduction of *o*-dicyanobenzene at the disk at potentials $E^D = -2.0$ V (1) and $E^D = -2.75$ V (2) and *m*-dicyanobenzene at $E^D = -2.0$ V (3) ($c = 4 \times 10^{-4}$ *M*, $m = 2400$ rpm).

The first (A wave) corresponds to the reversible transfer of one electron and the AR* formation of the initial compounds.

$$Ar(CN)_x \underset{-e}{\overset{+e}{\rightleftharpoons}} [Ar(CN)_x]^{\overline{\cdot}} \quad (\text{where } x = 1, 2, 4) \tag{2}$$

The ARs of the aromatic nitriles listed in Table 1 are fairly stable with except that of *m*-dicyanobenzene (recorded at the ring in quantitative yield). The anodic waves I in Fig. 2 correspond to the oxidation processes of ARs at the ring electrode, for which the half-wave potentials, $E^R_{1/2}$, are shifted towards positive values by ~ 0.06 V in comparison with $E_{1/2}$ of the cathodic reaction, in accord with the theory of reversible processes.

The reactivity of the ARs of the aromatic nitriles depends on the number and the mutual arrangement of the cyano groups in the molecule. The ARs of benzonitrile

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* AR = anion radical.

and *p*-tolunitrile do not undergo further electrochemical reduction below those potentials at which supporting electrolyte discharge begins, and disappear as a result of the slow homogeneous chemical reactions. The ARs of *m*-dicyanobenzene are also not reduced at the electrode: they are unstable and are not detected by RRDE. Instead of the oxidation waves of the ARs at the ring, an oxidation wave due to their chemical conversion products (100% current yield) whose half-wave potential, $E^{R}_{1/2}$ -0.86 V, is shifted by almost 0.9 V with respect to the $E_{1/2}$ of the cathodic reduction process of the initial *m*-dicyanobenzene is observed. Although the nature of the reaction product was not concentrated on two assumptions can be made. (i) The dimerization product of the ARs initially formed [15] is detected at the ring electrode. This product can have different structures, including a head-to-tail dimer. (ii) The species detected at the ring could be the CN^- anions which formed from the elimination of one cyano group of the primary ARs or the dimer product by reaction 3.

$$[m\text{-}C_6H_4(CN)_2]^{\overline{\cdot}} \rightarrow [C_6H_4CN]^{\cdot} + CN^- \qquad (3)$$

There are strong grounds in favour of this assumption. Firstly, the process of cyano group elimination from the ARs of the analogous compound, *m*-fluorobenzonitrile, has been observed previously [16]. Secondly, $E_{1/2}$ -0.86 V, consistent with previous data [22] corresponds to the half-wave potential at which mercury oxidizes, in DMSO solution in the presence of NaCN* ($E_{1/2}(-0.9 \pm 0.1)$ V).

$$Hg + CN^- \underset{+e}{\overset{-e}{\rightleftarrows}} \tfrac{1}{2}Hg_2(CN)_2 \qquad (4)$$

The limiting diffusion current of this process is dependent on the cyanide anion concentration, and the resulting anodic wave detected at the amalgamated gold ring electrode can be used to identify and provide a quantitative analysis of these species. The free radicals prepared according to eq. 3 can be stabilized in various ways, such as dimerization. Because chemical reactions take place after the stage of the reversible electron addition to the *m*-dicyanobenzene molecule, the overall process of the cathodic reduction of this compound is irreversible.

In contrast to the above-mentioned ARs, the anion radical products of the one-electron reduction of 1,2,4,5-tetracyanobenzene, namely, the *ortho*- and *para*-isomers of dicyanobenzene are capable of undergoing further electrochemical reactions at higher negative electrode potentials. Thus the tetracyanobenzene ARs are reversibly reduced to the stable dianions detected at the ring (100% yield) [23]. The ARs of the *ortho*- and *para*-isomers of dicyanobenzene attach two electrons and one proton and are thus irreversibly reduced by eliminating one cyano group.

$$[C_6H_4(CN)_2]^{\overline{\cdot}} \xrightarrow[\text{(BH, proton donor)}]{+2e+BH} [C_6H_5CN]^{\overline{\cdot}} + CN^- + B^- \qquad (5)$$

The products of this reaction were quantitatively detected at the ring electrode (curve 1 in Fig. 2). The oxidation of the benzonitrile ARs is attributed to wave I ($E_{1/2} = -2.25$ V), the CN^- anions to wave II ($E_{1/2}$ -0.86 V).

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* The potential at which mercury is oxidised in the presence of CN^- depends on the solubility product of the salt formed and varies slightly with changes in the water content in the solvent and in the temperature.

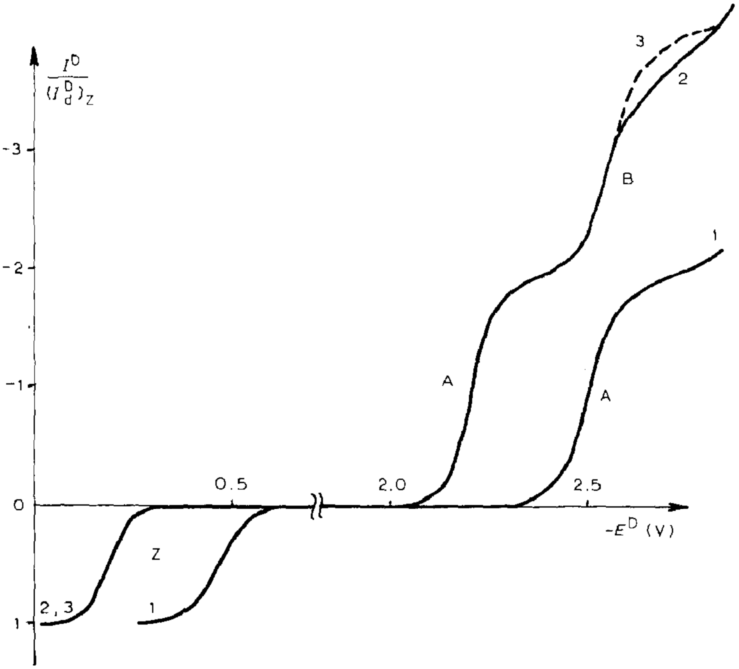

Fig. 3. Polarization curves of the anodic oxidation (Z waves) and cathodic reduction (waves A and B) at the disk electrode of $(C_6H_5CN)Cr(C_6H_5OCH_3)$ (1) and $(C_6H_5CN)_2Cr$ (2, 3) under aprotic conditions (1, 2), in the presence of water or phenol (3) (the current strength values are compared to the value of limiting current of the one-electron anodic wave).

The oxidation half-wave potentials of the tetracyanobenzene dianions and benzonitrile ARs at the ring electrode are approximately the same as the reduction half-wave potentials of the initial compounds. Thus we used a special technique involving the shielding effect of the ring by the disk electrode in RRDE in order to isolate the anodic process and to record the oxidation waves of the relevant products undistorted by the cathodic reaction [23,24]. The methods for identifying the products of electroreduction of *ortho-* and *para*-dicyanobenzene and 1,2,4,5-tetracyanobenzene as well as the questions connected with the intrinsic reaction mechanism including the nature of the elementary act of cathodic reduction are discussed elsewhere [21–24].

Cathodic reduction of bis(benzonitrile)chromium and the mononitriles of the dibenzenechromium $(C_6H_5CN)Cr(C_6H_5X)$ *series with electrochemically inactive substituents* $(X = H, CH_3, OCH_3)$

The polarization curves of all the nitriles of the dibenzenechromium series (Table 2) produced at the rotating disk electrode are characterized by the presence of anodic and cathodic branches. The first (Z wave in Fig. 3) corresponds to the one-electron reversible reaction 1. The cathodic branch of the polarization curves of the electroreduction involves one (mononitrile with $X = H$, CH_3, OCH_3) or two (bis(benzonitrile)chromium) waves. The first wave (A) is two-electronic in all cases, which follows unambiguosly from the comparison of its height with that of the Z wave and from its slope being close to 0.06 V. The B wave of the cathodic reduction

Table 2

Electrochemical redox parameters for nitriles of the dibenzenechromium series of the type $(C_6H_5CN)Cr(C_6H_5X)$ (RRDE in DMSO)

X	Anodic oxidation	Cathodic reduction								Reaction products detected at the ring electrode
	Z wave	A wave		B wave		C wave		D wave		
	$-E_{1/2}$ (V)	$-E_{1/2}$ (V)	n_A	$-E_{1/2}$ (V)	n_B	$-E_{1/2}$ (V)	n_C	$-E_{1/2}$ (V)	n_D	
H	0.50	2.56	2							CN^-, $(C_6H_6)_2Cr$
CH_3	0.53	2.58	2							CN^-, $(C_6H_5CH_3)Cr(C_6H_6)$
OCH_3	0.47	2.56	2							CN^-, $(C_6H_5OCH_3)Cr(C_6H_6)$
CN	0.18	2.21	2							CN^-, $(C_6H_5CN)Cr(C_6H_6)$
				2.56	2 [a]					CN^-, $(C_6H_6)_2Cr$
F	0.30	2.43	2							$(C_6H_5CN)Cr(C_6H_6)$
				2.56	2					CN^-, $(C_6H_6)_2Cr$
Cl	0.31	2.32	2							$(C_6H_5CN)Cr(C_6H_6)$
				2.56	2					CN^-, $(C_6H_6)_2Cr$
CF_3	0.22	2.30	5							$(C_6H_5CN)Cr(C_6H_5CH_3)$ CN^-, $(C_6H_6)Cr(C_6H_5CF_3)$
$COCH_3$ [b]	0.32	2.01	1.1							$[(C_6H_5CN)Cr(C_6H_5COCH_3)]^-$
				2.30	0.4					CN^-, unidentified complexes
						2.52	1			
								2.73	1	

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[a] In solutions with proton-donor additives. [b] The values n were obtained for $m = 2490$ rpm.

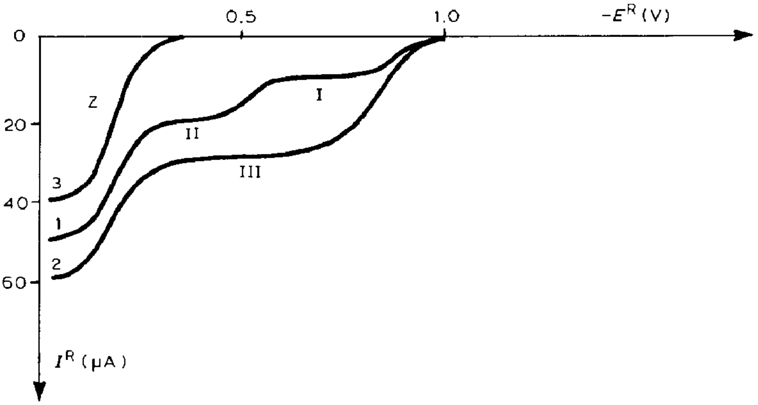

Fig. 4. Polarization curves of the anodic oxidation at the ring electrode of the cathodic reduction products of $(C_6H_5CN)_2Cr$ at the disk potentials of $E^D = -2.4$ V (1) and -2.75 V (2). Curve 3 was measured at disk open circuit ($I^D = 0$) ($c = 1 \times 10^{-3}$ M, $m = 2400$ rpm).

of bis(benzonitrile)chromium involves two parts having different slopes, which probably correspond to the presence of bimolecular chemical reactions involving the intermediate products of the cathodic process. The limiting current of this wave is not reached before the onset of the supporting electrolyte discharge, and the formal n_B value proved to be less than two. The addition of proton donors to the DMSO solution, such as small amounts of water or phenol, improves the shape of the B wave and leads to the appearance of the limiting diffusion current with $n_B = 2$.

RRDE permitted us to detect and identify the stable end-products of the reduction of the cyano-substituted chromium π-complexes. However, in neither case were their ARs detected, although the appropriate ring electrode measurements were carried out at disk electrode potential values corresponding to the entire reduction range of complexed nitriles and not only in the limiting diffusion current region.

The polarization curves of the anodic oxidation (at the ring electrode) of the cathodic reduction products of bis(benzonitrile)chromium at the disk electrode at E^D values corresponding to the limiting currents of A wave (curve 1) and B wave (curve 2) are represented in Fig. 4.

Curve 3 was recorded at the ring, at open circuit disk potential ($I^D = 0$), corresponding to oxidation of the initial complex (Z wave) is also given in the figure for comparison. From the figure, it follows that in the A wave, two products are formed which correspond to equally high waves I ($E^{I}_{1/2}$ -0.86 V) and II ($E^{II}_{1/2}$ -0.5 V). The current yield of the both products is 100%, based upon the assumption that both anodic reactions include one electron transfer. Once the disk circuit is closed the height of the Z wave begins to decrease, because the flow of the initial substance to the ring becomes smaller owing to its cathodic reduction at the disk. This decrease in Z wave is equal to the height of either wave I or II. Hence, both waves must be related to the oxidation of the new chromium complex, the electrode reaction product (when there is no π-complex decomposition, the sum of the heights of the oxidation waves for all the chromium-containing compounds at the ring according to reaction 1 must be constant and equal to the Z wave height in the absence of the disk current - curve 3 in Fig. 4). In accord with the earlier obtained data [1], the value $E^{II}_{1/2}$ -0.5 V corresponds to the oxidation of benzene(benzonitrile)chromium to its cation. On the other hand, the value $E^{I}_{1/2}$ is typical of mercury cyanide formation, (reaction 4). Thus, CN^- anions and the complex, $(C_6H_6)Cr(C_6H_5CN)$, are present at the ring electrode at E^D -2.4 V. This implies that an irreversible elimination of one cyanogroup takes place in the A wave.

$$(C_6H_5CN)_2Cr \xrightarrow{+2e+BH} (C_6H_5CN)Cr(C_6H_6) + CN^- + B^- \qquad (6)$$

The nature of the complex obtained is also supported by the closeness of $E^{B}_{1/2}$ value of the cathodic B wave to the $E_{1/2}$ value for benzene(benzonitrile)chromium.

At E^D -2.75 V (B wave), waves III and Z are recorded at the ring, and wave II is absent. The value of $E^{III}_{1/2}$ differs slightly from the $E^{I}_{1/2}$ value, but it is almost 3 times higher than that of wave I in curve 1. This effect is related to the simultaneous occurrence of two anodic reactions at the ring which take place at similar $E_{1/2}$ values: the oxidation of dibenzenechromium ($E_{1/2}$ -0.8V), and the formation of $Hg_2(CN)_2$ as a result of elimination of two cyano groups from the initial bis(benzonitrile)chromium. Thus, the total process (eq. 7) takes place at B wave potentials for the reduction of bis(benzonitrile)chromium. The B wave characterizes the elimination reaction of the second cyano group from the intermediate benzene(benzonitrile)chromium.

$$(C_6H_5CN)_2Cr \xrightarrow{+4e+2BH} (C_6H_6)_2Cr + 2CN^- + 2B^- \qquad (7)$$

The reduction products of complexed nitriles with substituents X = H, CH_3, OCH_3, detected at the ring electrode, are the same as those cited above: CN^- anions and $(C_6H_6)_2Cr$, $(C_6H_5CH_3)Cr(C_6H_6)$, $(C_6H_5OCH_3)Cr(C_6H_6)$ complexes, respectively. The above compounds are oxidized at the ring at the same potentials at which reaction 4 occurs, and are recorded in the form of summed wave similar to wave III in the case of bis(benzonitrile)chromium.

Thus, the cathodic reduction of all the cited π-complexes in the aprotic medium involves the transfer of two electrons per CN^- group and hence its elimination.

Complexes $(C_6H_5CN)Cr(C_6H_5X)$ with electrochemically active substituents (X = Cl, F, CF_3, $COCH_3$)

Two two-electronic waves, one corresponding to the elimination of the halogen atom and the other to the elimination of the cyano group, are seen in the polarization curves of the reduction of the complexes with X = Cl and F. This follows from the analysis of the reaction products at the ring electrode. So, in the region of the first cathodic wave potentials at the disk, the wave with $E_{1/2}$ -0.5 V corresponding to the oxidation of complex $(C_6H_5CN)Cr(C_6H_6)$ (100% yield) was recorded at the ring, whilst the waves with $E_{1/2}$ -0.6 V typical of the complexes $(C_6H_6)Cr(C_6H_5Cl)$ and $(C_6H_6)Cr(C_6H_5F)$ were not observed ($E_{1/2}$ values are found from the correlation equations [1,2]).

In the region of the limiting currents of the second cathodic waves, the anodic wave at the ring with $E_{1/2}$ -0.5 V vanishes, but a wave corresponding to the simultaneous oxidation of dibenzenechromium and mercury in the presence of CN anions then appears.

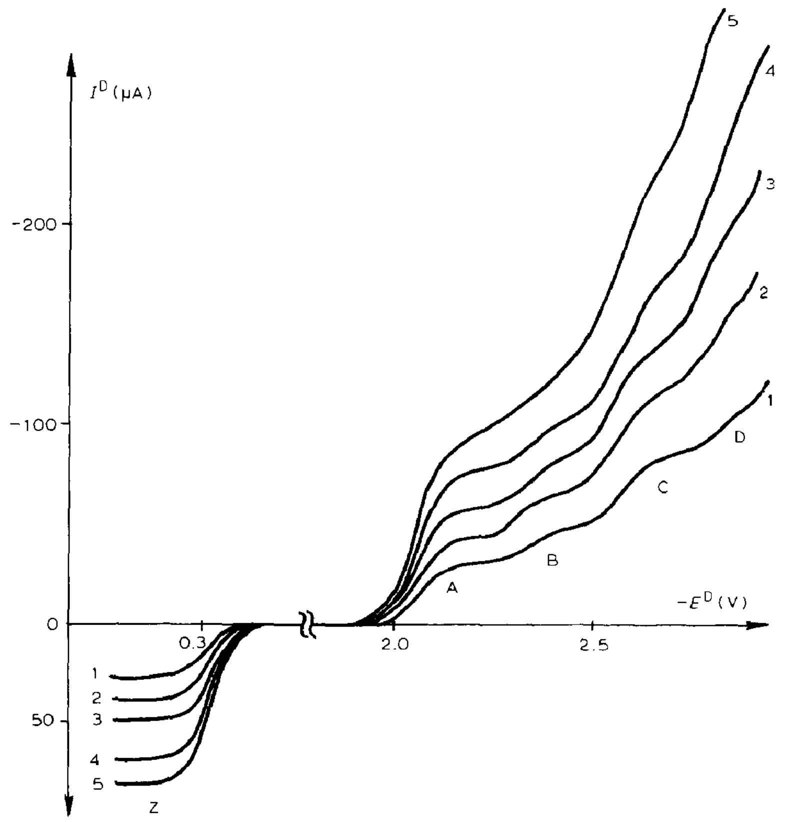

Fig. 5. Polarization curves of the cathodic reduction at the disk electrode of $(C_6H_5CN)Cr(C_6H_5COCH_3)$ ($c = 1.6 \times 10^{-3}$ M) at electrode rotation speed, m (rpm): 1, 390; 2, 900; 3, 1400; 4, 2400; 5, 3350.

When X = CF_3, the kinetic limiting current is followed by a small drop in the polarization curve. The formal number of electrons participating in the process represented by the curve maximum is about 5. In fact, a six-electron conversion of the trifluoromethyl group to methyl is realized. This is facilitated by the presence of strongly accepting CN group in the molecule. A rise in the potential leads to a parallel elimination of the CN anions ($n = 2$) which hinders the defluorination reaction and causes partial inhibition of the overall process.

A wave with $E_{1/2}$ -0.52 V at the ring electrode corresponding to the oxidation of products of these two parallel processes, toluene(benzonitrile)chromium and benzene(trifluoromethylbenzene)chromium is observed.

The most complicated pattern is realized with the reduction of the complex $(C_6H_5CN)Cr(C_6H_5COCH_3)$. The polarization curves of its reduction show four cathodic waves A,B,C,D, (Fig. 5), none of which is a two-electron wave. This is the most distinguishing feature of the behaviour of the acetophenone(benzonitrile)chromium, compared with those of all the other π-complexes containing a cyano group. The height of the A wave over the whole range of the rotation speed of electrode m (390–3350 rpm) exceeds the height of the stringent one-electron wave by 10–15%, its slope is close to 0.06 V. The limiting current of B wave corresponds $n_B \approx 0.4$, the n_C value drops from 1.5 to 1 with a rise in m. In contrast the n_D value rises from 0.7 to 1. In the first approximation, the numbers of electrons (m 2400 rpm), formally participating in the cathodic process, are in the following ratio $n_A/n_B/n_C/n_D = 1.1/0.4/1/1$, respectively.

The waves A and B are fairly close to the reduction waves of bis(acetophenone) chromium on the basis of their characteristics ($E_{1/2}$, n), and are rather typical of the reduction of the aromatic carbonyl compounds containing a group with mobile hydrogen atoms [25,26].

It is possible to relate the small height of B wave in the aprotic solvent to the chemical interaction between the dianion, the primary product of the two-electron cathodic reaction, and the initial compound thus leading to the occurrence of the so-called latent limiting current. RRDE permits the detection of ARs of the initial compound at the ring electrode in the range of potentials of the A wave. The low current yield of these species (Q 12%) points to their unstability. It is possible that one of the AR conversion products is a species capable of being reduced at the disk, causing the slight rise in the height of the cathodic A wave.

The waves C and D also resemble the carbonyl compound reduction waves. The CN anions and unidentified chromium complexes ($E_{1/2}$ -0.53 to -0.57 V) were detected at the ring over the whole range of potentials for the reduction of the initial reagent.

Discussion

The coordination of free arene with the chromium atom in the π-complex does not lead to a loss of ligand aromaticity. The behaviour of the free arenes and their complexes in similar reactions should resemble each other, and any differences to some extent would be quantitative. This holds for the cathodic reduction reactions of aromatic carbonyl compounds, the esters of cinnamic acid and the corresponding bis(arene)chromium complexes; their behaviour is consistent with such a supposition [4]. Thus, in the case of the electroreduction of benzalacetophenone and that of its chromium complex, the mechanisms of the various processes are identical and the rates of dimerization of the ARs (the primary reaction products) are very close to each other [3].

However, the situation changes when we deal with the cathodic reduction of nitriles. As has been mentioned above, all the π-complexes containing the CN group investigated in this work, with the exception of acetophenone(benzonitrile)chromium, have polarization characteristics substantially different from those of the uncoordinated aromatic nitriles. The principal difference is found in the absence of one-electron waves and anion radicals when the complexes are reduced and the appearance of two-electron waves corresponding to the elimination of the cyano group. Thus, at least at first glance, the routes and outcome of the electroreduction of free aromatic nitriles and their chromium π-complexes are different.

The question arises of whether the elimination of the cyano group from the π-complex involves the formation of intermediate ARs or not. The fact that no ARs were detected at the ring does not provide an unambiguous answer to this question, because the AR lifespan is probably too short to detect them. Nevertheless, data obtained to confirm the existence of a multi-step two-electron elimination of the CN group; the first step, that of the transfer of the first electron leading to AR formation as in the cathodic reduction of the free aromatic nitriles, is reversible. This is indicated by the slope of the two-electron wave, close to 0.06 V, which is characteristic for a potential-determining step of an overall irreversible process involving the reversible transfer of one electron *.

This conclusion was also confirmed by applying a special test thus enabling the reversible and irreversible processes in DMSO solutions to be distinguished, but only if carried out at fairly high negative potentials [27]. The test is based on the principle that the addition of even small amounts of tetramethylammonium ions to the DMSO solution containing tetrabutylammonium ions induces a sharp acceleration of the irreversible electron transfer processes as a result of the change in the double electric layer structure, but does not influence the rate of the reversible reaction.

The test shows the $E_{1/2}$ of the second irreversible B wave of *ortho*-dicyanobenzene reduction to shift towards positive values by 0.11 V after the addition of aqueous 5×10^{-4} M tetramethylammonium salt to the solution. The $E_{1/2}$ of the reversible A wave of o-$(CN)_2C_6H_4$ turns out to be insensitive to the addition of $(CH_3)_4N^+$, as in the case of $E_{1/2}$ of two-electron waves of the complex reduction. The conclusion on the stepwise process of the cyano-group elimination and the intermediate π-complex AR formation is in agreement with the data obtained in the course of investigation of bis(benzonitrile)chromium reduction with metallic sodium in dimethoxyethane solution at $-70\,^\circ$C. The unstable ARs of the complex were detected by ESR [28].

Thus, in spite of the irreversibility of the elimination at the cathode, the $E_{1/2}$ value was determined mainly by the reversible stage of AR formation. Likely, the same conclusion is probably also valid for the case when the process starts with elimination of the halogen ions during the reduction of compounds containing halogen ($X = Cl$, F, CF_3).

We have previously observed a linear correlation (eq. 8) [4,5] involving the half-wave potential values for the reversible one-electron reduction processes of π-complexes $E_{1/2}^{\text{red.(C)}}$ and of free arenes $E_{1/2}^{\text{red.(A)}}$, and that of the π-complex oxidation $E_{1/2}^{\text{ox.(C)}}$.

$$\Delta E_{1/2}^{\text{red.(CA)}} = E_{1/2}^{\text{red.(C)}} - E_{1/2}^{\text{red.(A)}} = a + \alpha E_{1/2}^{\text{ox.(C)}} \tag{8}$$

It appears reasonable that this correlation is consistent with the data for the pair of compounds $(C_6H_5CN)_2Cr$–C_6H_5CN although the irreversible process of the complex reduction involves two electrons and only one electron participates in the reduction of the free benzonitrile.

The instability of the π-complex ARs can principally be associated with the participation of these species in further electrochemical reactions with the subsequent (or simultaneous) elimination of the cyano group (the EEC mechanism). Such a reaction pathway is however unlikely. It follows from Table 1 that the ARs of the aromatic nitriles are not reduced, up to supporting electrolyte discharge potentials or the $E_{1/2}$ of their reduction is shifted towards the negative values by about 0.8–0.95 V as compared with $E_{1/2}$ of their formation. There are no grounds to suppose that the rate of the cathodic reduction of π-complex ARs exceeds that of the free arene ARs by many orders of magnitude due to which electrochemical

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* The AR chemical conversion stages that take place after the transfer of the first electron also exerts a small influence on the $E_{1/2}$ value, but under our conditions it is negligible.

reduction of the complex ARs becomes possible at potentials of their synthesis. The most likely reason for the instability of ARs is their chemical decomposition (ECE-mechanism) along one of two possible pathways: (1) elimination of the cyano group from the ARs, as observed in the case of *meta*-fluorobenzonitrile ARs [16], followed by the addition of the second electron to the free radical; (2) disproportionation of the ARs with partial regeneration of the initial complex which again participates in the electrode reaction by forming products of its two-electron reduction and eliminate the cyano group.

Thus, from the above the first stage of the cathodic reduction of the free aromatic nitriles and their chromium complexes is the same – a reversible transfer of one electron. The difference in the behaviour of the nitriles of the two classes is due to the dramatic destabilization of the ARs for coordinated compounds, which leads to a significant decrease in the lifespan of those moieties by several orders of magnitude as comparison with the ARs of free nitriles. Thus, the benzonitrile ARs under aprotic conditions are stable over a long period of time [14,17], whereas the lifespan of π-complex ARs is less than 10^{-3} s, which represents the limit of sensitivity of RRDE. On the other hand, the rate of AR chemical decomposition should be comparatively moderate since extremely high rates for this reaction lead to a break-down in the reversibility of the preceding stage of electron transfer [29], contradicting experimental evidence.

The similarity of the first stages of the electroreduction of the nitriles of the dibenzenechromium series $(C_6H_5CN)Cr(C_6H_5X)$ served as the basis for achieving a correlation between the $E_{1/2}$ of the A wave of the cathodic reduction of those compounds and the σ substituent constants.

It has been found that as in the case of the reversible oxidation of the bisarenechromium complexes to their cations ($n = 1$) [1,2], the $E_{1/2}$ values for the two-electron cathodic waves of the substituted nitriles, where X = H, CH_3, OCH_3, CN, F, Cl, CF_3 are correlated by the *meta*-substituent constants (σ_m, σ_m^0, σ_m^+) (Table 3). The best correlation was observed when σ_m^+ constants were used.

$$E_{1/2}^{\text{red.}} = -2.566 + 0.553\sigma_m^+$$

(correlation coefficient, $r = 0.972$) (9)

In this case a satisfactory correlation was also obtained by using the σ_p^0 constants.

On the whole, the transmission of substituent effects in molecules of different dibenzenechromium compounds made earlier on the basis of the reversible anodic

Table 3

Parameters of the correlation equation $E_{1/2}^{\text{red.(C)}} = \rho_\pi\sigma + b$

Substituent constant [a]	Number of points	ρ_π [b]	$-b$	S_{ρ_π}	S_b	r
σ_m	7	0.567	2.558	0.066	0.023	0.968
σ_m^0	7	0.561	2.562	0.069	0.023	0.964
σ_m^-	7	0.553	2.566	0.060	0.021	0.972
σ_p^0	7	0.440	2.511	0.057	0.020	0.961

[a] σ Constant values are taken from ref. 30, 31. [b] ρ Values can be obtained from formula: $\rho = \rho\pi/(0.058/n)$, where $n = 1$ (the number of electrons participating in the potential determining stage).

reaction 1 examinations [1,2] are supported by results obtained from studies on irreversible cathodic eliminations.

We recently found that there is an analogous linear dependence between the ^{19}F chemical shifts and the *meta*-substituent constants (σ_m^+, σ_m^n) in the complexes $(C_6H_5F)Cr(C_6H_5X)$ [32].

Thus, the electronic influence of substituents in the arene ligand is transmitted to the chromium atom, or through the chromium atom to the reaction centre, or the indicator fluorine atom localized in another ligand by a predominantly inductive mechanism.

The observed destabilization of the dibenzenechromium nitrile ARs as compared to the ARs of the aromatic nitriles and, on the other hand, the similar stabilities of the ARs of carbonyl compounds of the aromatic series and their chromium complexes, is probably due to the diversity of the spin density distributions. The spin density in the ARs of free benzonitrile is located mainly in the *para*- and *ortho*-positions of the benzene ring and to a smaller extent at the cyano group, while in the ARs of carbonyl derivatives of benzene, a significant portion of it is located at the carbonyl carbon atom [33]. Naturally, the changes in the benzene ring induced by the coordination with the chromium atom, in the case of nitriles, lead to a more substantial change in the stability of the AR than in the case of the carbonyl derivatives.

It is of interest that the correlation (eq. 9) satisfies seven of the eight chromium containing π-complexes studied, including halogen-containing ($X = Cl$, F, CF_3) compounds, while the A waves in the above-mentioned cases conform to the dehalogenation process. Only $E_{1/2}$ -2.03 V ($n = 1$) for π-complex with $X = COCH_3$ does not fit the correlation of eq. 9. The deviation of the experimental $E_{1/2}$ value from the calculated according to eq. 9 is ≈ 0.35 V. This is apparently due to an electronic structure of the corresponding ARs that is very different from that of the ARs of other substituted nitriles. Owing to their great stability, the ARs of (benzonitrile)(acetophenone)chromium can be detected at the ring electrode.

Though the mechanism of (benzonitrile)(acetophenone)chromium electroreduction has not been studied comprehensively in this work there are some considerations of relevance. The overall process consists in the addition of four electrons and, in all probability, in eliminating the cyano group and converting the carbonyl group to the hydroxy group. Transfer of the reaction centre then probably occurs; the reaction starts with the reduction of the carbonyl group (waves A and B), the elimination of CN anion from the reduced species (dianion) results in the formation of (benzene)(acetophenone)chromium which is again subjected to electrochemical reduction to give the waves C and D. Such reactions are accomplished, for example, by electroreduction of unsaturated aldehydes and ketones [34,35]: ARs capable of dimerizing emerge during the one-electron process, but after the second electron is transferred, the process progresses to a hydrogenation of unsaturated carbon–carbon bonds, with the carbonyl group in this case being regenerated.

Thus, we have shown that it is possible to establish the identity and difference in the electroduction for free aromatic nitriles and their chromium-containing complexes, as well as to obtain information concerning the problem of reactivity of the dibenzenechromium derivatives. The problem was to a large extent solved by use of the rotating ring-disk electrode technique.

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