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THE STUDY OF REDOX REACTIONS OF BISARENECHROMIUM COMPLEXES BY THE ROTATING DISK AND THE ROTATING RING DISK ELECTRODE TECHNIQUES

III *. CATHODIC REDUCTION OF CHROMIUM(0) π-COMPLEXES AND THE CORRESPONDING ARENES IN DIMETHYL SULFOXIDE SOLUTIONS

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Summary

The rotating disk (RDE) and the rotating ring-disk (RRDE) electrode techniques have been employed to study the cathodic behavior of eight bisarenechromium complexes and seven corresponding arenes in DMSO solutions. In the first electrochemical step of the process reversible addition of one electron results in anion-radicals, whose formation has been demonstrated for certain arenes and chromium π-complexes by oxidation of these particles on the ring electrode.

Substituents on different ligands of bisarenechromium complexes were found to exert pronounced mutual influences. The role of the chromium atom in transfer of electronic effects from one ligand to another is discussed.

It was found that a linear correlation exists between the variations in the free energy of the equilibrium "initial compound $\overset{e}{\rightleftharpoons}$ anion-radical" (due to coordination of free arene with chromium which is displayed as a shift of the cathodic process half-wave potential $\Delta E^{\text{CL}}_{1/2}$) and the half-wave potential of the oxidation of the corresponding Cr^0 π-complex to a cation $E^{\text{X}}_{1/2}$

$$\Delta E^{\text{CL}}_{1/2} = a + \alpha E^{\text{X}}_{1/2}$$

At $E^{\text{X}}_{1/2} < -0.3$ V, complex formation slows down the cathodic process and at $E^{\text{X}}_{1/2} > -0.3$ V the process is facilitated.

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* For part II see ref. 2.

TABLE 1

COMPARISON OF THE CHARACTERISTICS OF THE ELECTROCHEMICAL REDUCTION OF ARENES AND BISARENECHROMIUM COMPLEXES

System	No.	Compound	$E^{L}_{1/2}$, $E^{C}_{1/2}$ (V)	$\Delta E^{CL}_{1/2}$ (V)	$\log(K_C/K_L)$	$E^{X}_{1/2}$ (V) [1]
A	I	C_6H_5CHO	−1,84			
	II	$C_6H_6CrC_6H_5CHO$	−2,15	−0,31	−5,3	−0,55
	III	$(C_6H_5CHO)_2Cr$	−1,84	0,0	0	−0,31
B	IV	$C_6H_5CH{=}CHCOOC_2H_5$	−1,80			
	V	$(C_6H_5CH{=}CHCOOC_2H_5)_2Cr$	−1,88	−0,08	−1,4	−0,59
C	VI	$C_6H_5CH{=}CHCOC_6H_5$	−1,41			
	VII	$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr$	−1,46	−0,05	−0,9	−0,535
D	VIII	$o\text{-}C_6H_4(COOC_2H_5)_2$	−1,92			
	IX	$[o\text{-}C_6H_4(COOC_2H_5)_2]_2Cr$	−1,91	0,01	0,2	−0,24 [b]
E	X	C_6H_5CN	−2,25			
	XI	$(C_6H_5CN)_2Cr$	−2,22 [a]	0,03	0,5	−0,175
F	XII	$C_6H_5COCH_3$	−1,98			
	XIII	$(C_6H_5COCH_3)_2Cr$	−2,02	−0,04	−0,7	−0,42
G	XIV	$C_6H_5C_6H_5$	−2,61			
	XV	$(\eta^6\text{-}C_6H_5C_6H_5)_2Cr$	−2,71	−0,10	−1,7	−0,70

[a] The true value of $E^{C}_{1/2}$ of the one-electron step lies in the range $-2.17\ V \geqslant E^{C}_{1/2} \geqslant -2.22\ V$. [b] Obtained in the present study.

In order to take part in electrode reactions, an arene must contain electrochemically active groups. In π-complexes of arenes with metal atoms this property is retained, though the reactivity may change substantially depending on such factors as the type of the complex, the nature of the metal and the arene or the structure of other ligands. For instance, the rate of cathodic reduction of acetophenone increases by several orders of magnitude in an acetophenonechromium tricarbonyl complex [3]. On the contrary, when benzalacetophenone is bound in bis(benzalacetophenone)chromium the rate of electrochemical reduction is slower than in the free strate by approximately an order of magnitude [2].

In order to reveal the general nature of the effect of coordination with chromium atom on the arene reactivity, we have investigated the cathodic reduction of some bisarenechromium complexes containing various electroactive groups (CHO, $CH{=}CHCOOC_2H_5$, CN, etc.) and the corresponding free arenes (benzaldehyde, ethylcinnamate, benzonitrile, etc.). The fifteen compounds studied (Table 1) corresponded to seven bisarenechromium complex-free arene systems.

A correct solution of the problem requires that two conditions be fulfilled, i.e. within each system the reaction centre and the mechanism of the cathodic reaction should be the same for the free arene and the bisarenechromium complex. Data available on the ESR spectra of anion radicals (AR) formed by bisarene [4] and related [5] chromium π-complexes, as well as quantum chemical calculations of the systems resulting from an electron transfer to d^6-configuration π-complexes [6], indicate that in the AR of bisarenechromium complexes the unpaired electron occupies a lower vacant MO, which can largely be regarded as a π^*-orbital of the ligand [5,6]. In other words, coordination of an arene with chromium does not alter the reaction centre. The results of electrochemical investigations [2] agree with this viewpoint. From this work we also concluded that the first step of the cathodic reduction of benzalacetophenone and bis(benzalacetophenone)chromium follows the same mechanism [2]. As it will be shown below, this conclusion may be extended to the other systems studied in the present work.

In the single-electron reduction of aromatic compounds and their π-complexes with chromium, therefore, the reaction centres are similar and the potential-determining stages identical. Accordingly, changes in reactivity between a free arene and its complex with regard to this reaction reflect the effect of coordination with chromium on the properties of the arene. The quite a broad range of systems studied allows us to pay special attention to the relationship between the changes in reactivity due to complex formation and the structure of the arene.

Results

The total process of cathodic reduction in DMSO of the compounds investigated involves the addition of 2—4 electrons, and there are several waves on the polarization curves obtained using a rotating amalgamated gold disk electrode [2]. In the present study we consider only the first wave.

It was found that for most compounds listed in Table 1 this wave corresponds to a reversible transfer of one electron resulting in formation of anion-radicals (AR):

$$\text{Arene} + e^- \overset{K_L}{\rightleftharpoons} [\text{Arene}]^{\overset{-}{\cdot}} \qquad (1)$$

$$\text{Arene}_2\text{Cr} + e^- \overset{K_C}{\rightleftharpoons} [\text{Arene}_2\text{Cr}]^{\overset{-}{\cdot}} \qquad (2)$$

This conclusion was inferred from the following facts:

1. The heights of the first cathodic waves on the polarization curves of bisarenechromium complexes coincide with those of single-electron waves of anodic oxidation of the same compounds to the corresponding cations * (compounds II, III, V, VII, IX)

$$\text{Arene}_2\text{Cr} \rightleftharpoons [\text{Arene}_2\text{Cr}]^+ + e^- \qquad (3)$$

2. The slope coefficients of the first cathodic waves (0.056—0.065 V) correspond to a reversible single-electron process (compounds I—X, XII).

3. In the reduction of I—VIII and XII studied by the rotating ring-disk electrode technique [7—9], AR of free arenes and bisarenechromium complexes were observed directly **.

The possibility of using these criteria and the rotating ring-disk electrode technique to establish the reversibility of the stage at which the first electron adds to the initial molecule was discussed in more detail in our previous paper [2].

Electrochemical reduction of bis(benzonitrile)chromium in DMSO, characterized by a two-electron wave on the polarization curve, follows a somewhat different pattern. This may be due to either too small a difference in the half-wave potentials ($\Delta E_{1/2} < 0.15$ V) of two subsequent single-electron steps or the formation of an electroactive product via a rapid chemical conversion of AR (ECE mechanism) (for instance, disproportionation with partial regeneration of the initial reagent). It may also be assumed that in the case of bis(benzonitrile)-chromium the first step in the cathodic process also consists of the reversible transfer of one electron to the molecule under reduction and determines the half-wave potential of the total process.

The results on the electroreduction of bis(acetophenone)chromium (XIII), biphenyl (XIV) and bis(biphenyl)chromium (XV) obtained in the present study are largely confined to determination of the $E_{1/2}$ values of the first cathodic waves. No special attention was paid to the questions of reversibility of these waves and the number of electrons added. By analogy with the reduction of chromium complexes containing formyl groups (II, III) it seems more than likely that the reduction of XIII also involves reversible transfer of one electron. On the other hand, it appears that the number of electrons taking part in electroreduction of XV is greater than one.

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[*] We have used an oxidized form of complex IX, i.e. the $[C_6H_4(COOC_2H_5)_2]_2CrI$ salt. In this case the height of the cathodic wave of the reduction of the cation to a neutral compound in a back reaction in eq. 3 is the reference for the single-electron process.

[**] Cathodic reduction of benzonitrile [10] and biphenyl [11] in aprotic media was also reported to give AR.

Consequently, for most systems studied (A, B, C, D, F) reactions 1 and 2 are reversible. This conclusion, it seems, may be extended to the system E as well. As for the system G, there is no conclusive evidence so far which would enable us to be certain about the similarity of the mechanisms of reduction of XIV and XV. However, nothing suggests that the system G differs in any fundamental way from the six others studied. Hence our belief that in this case, too, a comparison of cathodic behavior of free arene and its chromium complex is correct enough.

The AR resulting from reactions 1 and 2 are unstable and disappear in the course of chemical interactions. For AR of aromatic compounds which contain unsaturated carbon—carbon bonds, carbonyl, and some other functional groups, these reactions usually involve dimerization of the AR [12]. The same was reported for bis(benzalacetophenone)chromium [2] and seems plausible for the AR of some other compounds we have studied. This process, as observed previously [2], affects the half-wave potential of reduction of the starting substances. However, the AR dimerization rate constant for a free arene is close to that for its complex with chromium. Therefore, the half-wave potential difference for the complex and the free arene, $\Delta E_{1/2}^{CL} = E_{1/2}^{C} - E_{1/2}^{L}$,* measured in solutions with the same concentration of the depolarizer at a constant rotation speed of the disk electrode prove virtually undistorted by dimerization. For this reason the $\Delta E_{1/2}^{CL}$ values may be used for characterizing the change in reactivity (the free energy of redox equilibriums) when passing from reactions 2 to reactions 1.

Table 1 presents the half-wave potentials of the first waves of the reduction of free arenes ($E_{1/2}^{L}$) and their chromium complexes ($E_{1/2}^{C}$), the differences between these values ($\Delta E_{1/2}^{CL}$), and logarithms of the ratios between the equilibrium constants of reactions 2 (K_C) and 1 (K_L).

Discussion

Analysis of the data in Table 1 suggests the following conclusions.

The formation of bisarenechromium π-complexes usually shifts the half-wave potential of reduction of the arene. The absolute value of this shift and its sign differ depending on two factors, namely, the arene—chromium coordination and the nature of the ligands. This is particularly evident when one compares the half-wave potentials of reduction of benzaldehyde (I), benzene(benzaldehyde)chromium (II) and bis(benzaldehyde)chromium (III) (system A).

With complex II, which contains one formyl group, reduction is much more difficult than in the case of free benzaldehyde. Slowing-down of the process corresponds to a decrease of K_C by five orders of magnitude as compared with K_L ($\Delta E_{1/2}^{CL} = -0.31$ V). This effect far exceeds that caused by the introduction of such a strong electron donor as the diethylamino group into the *para*-position of benzaldehyde. The difference in half-wave potentials for *p*-diethylaminobenzaldehyde and benzaldehyde is $\Delta E_{1/2} = -0.16$ V [13]. Therefore, the chromium-

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* Here and below index "C" refers to the values for bisarenechromium complexes and index "L" to these for free arene (ligand).

benzene fragment acts as a very strong donor with respect to benzaldehyde and increases the electron density in its aromatic ring and on the carbon atom of the carbonyl group. It should be noted that the electron-donating character of the C_6H_6Cr fragment was reported earlier [14,15].

An essentially different picture is observed when comparing II to the symmetric complex III which contains formyl groups in both ligands. In this case $E^{C}_{1/2}$ is approximately equal to $E^{L}_{1/2}$ ($\Delta E^{CL}_{1/2} \approx 0$). In other words, the second formyl group compensates almost completely the increase in the electron density at the reaction center observed in the case of reduction of complex II.

In the reduction of symmetrical π-complexes with substituents in the benzene ring possessing a less electron-withdrawing character than the formyl group (i.e. systems B, C, F and G) $\Delta E^{CL}_{1/2} < 0$ and the equilibrium constants of the corresponding reactions drop by 0.7—1.7 orders of magnitude with respect to K_L. Hence, in this case the chromium-arene fragment * again acts as an electron donor to the group being reduced, although this effect is weakened substantially by the presence of an electron-withdrawing substituent in the ligand.

The strongest electron-withdrawing effect is exerted by the nitrile group. Bis(benzonitrile)chromium (IX, System E) is reduced more readily than free benzonitrile (VIII): $\Delta E^{CL}_{1/2} > 0$, $\log(K_C/K_L) = 0.5$. The bisarenechromium complex is also reduced faster than free arene in the case of bis(diethylphthalate)-chromium (System D) whose molecule contains four electron-withdrawing ester groups.

Thus, coordination with a C_6H_6Cr-fragment causes a drastic fall in the electron affinity of the ligand being reduced. On the other hand, the presence of a strongly electron-withdrawing group on the benzene ligand either somewhat facilitates the reduction of the complex as compared with that of free arene (systems D, E) or has no effect at all (compound III). Complexes containing electron-withdrawing substituents of average strength are generally reduced with greater difficulty than the corresponding free arenes. All these facts indicate that coordination with chromium by itself increases electron density on the arene, whereas electron-withdrawing groups in the complex act in the opposite direction and somewhat compensates (or even exceeds) the former effect. An increase in electron density on the benzene ring π^*-orbitals follows the dative bond mechanism which, according to quantum chemical calculations [16—20] dominates in dibenzenechromium type complexes. The interaction of antibonding e_2 π-orbitals of the ligand with the $d_{x^2-y^2}$, d_{xy} atomic orbitals of chromium is also responsible for the weakened aromaticity of the coordinated benzene [20] thus, in turn, decreasing the electron affinity.

The strong dependence of the reactivity of the coordinated arene on the nature of the second ligand is a remarkable property of bisarenechromium complexes. Substitution of a hydrogen atom in II by a formyl group (III) shifts $E^{C}_{1/2}$ by 0.31 V towards positive values. Assuming, by analogy with reaction 3 [1], that the values of $E^{C}_{1/2}$ for cathodic reduction of bisarenechromium com-

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[*] According to literature data [2,4] it is assumed that delocalization of the unpaired electron in the complex AR involves only one ligand.

plexes (reaction 2) correlate with the constants for *meta*-substituents and using the value $\sigma^{\circ}_{m} = 0.46$ reported [1] for the CHO group, it is possible to evaluate to a first approximation the reaction polarographic constant for the cathodic process 2 as $\rho_{\pi} \approx 0.67$. This value is twice as high as $\rho_{\pi} = 0.33$ for the cathodic reduction of free substituted benzaldehydes in aqueous alkaline solutions [21]. In view of the fact that the electronic effect of the substituent is transferred to the reaction center of the benzaldehyde molecule largely by conjugation, which takes no part in electron transfer in bisarenechromium complexes [1], the above result at first seems strange. It appears that the high sensitivity of the cathodic reaction to the nature of the substituents in the second ligand is due to the presence of a Cr atom donating electron density to the ligand. Introduction of a substituent into the ligand has a strong effect on the electron density at the chromium atom and on the dative component of the metal—ligand bond. This is evidenced by the high sensitivity of reaction 3 to the nature of these substituents ($\rho_{\pi} = 0.51$ *).

As long as the chromium atom and the substituents on the coordinated arene exert a mutual influence, the electronic effect of a substituent is transferred from one ligand to the other via the chromium atom. The participation of the Cr atom in this process leads to a drastic increase in the influence of the substituent on the reaction center. The system works like an amplifier in radioelectronics.

If the above ideas are true, one should expect there to be a correlation between the changes in reactivity with respect to the cathodic reaction when passing from a free arene to its π-complex with chromium ($\Delta E^{\mathrm{CL}}_{1/2}$ and $\log(K_{\mathrm{C}}/K_{\mathrm{L}})$) and the half-wave potentials $E^{\mathrm{X}}_{1/2}$ (Table 1) corresponding to the anodic reaction 3. The latter values may be used as characterizing the capacity of the chromium atom to donate electron density to the ligands. Such a correlation was indeed observed: for all the arene-symmetric chromium π-complex pairs studied $\Delta E^{\mathrm{CL}}_{1/2}$ is a linear function of $E^{\mathrm{X}}_{1/2}$ (Fig. 1).

$$\Delta E^{\mathrm{CL}}_{1/2} = a + \alpha E^{\mathrm{X}}_{1/2} \tag{4}$$

where $a = (0.072 \pm 0.007)$ V, $\alpha = 0.25 \pm 0.015$. The correlation factor $r = 0.991$.

In accordance with the principle of linearity of free energies, therefore, a change in the free energy of an arene due to its coordination in a symmetric bisarenechromium complex is a linear function of the free energy of equilibrium in the neutral complex-cation system (reaction 3). Since $\Delta E^{\mathrm{CL}}_{1/2} = 0.058 \log(K_{\mathrm{C}}/K_{\mathrm{L}})$ and $E^{\mathrm{X}}_{1/2}$ depends linearly on the constants of the *meta*-substituents (σ_{m}, σ°_{m}, σ^{+}_{m}) [1], eq. 4 may be written as

$$\Delta E^{\mathrm{CL}}_{1/2} = b + \beta\Sigma\sigma \tag{5}$$

and

$$\log(K_{\mathrm{C}}/K_{\mathrm{L}}) = g + \gamma\Sigma\sigma \tag{6}$$

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[*] The correlation between $E^{\mathrm{X}}_{1/2}$ and the substituent constants σ°_{m} is taken into account. A symbol m was used in ref. 1 instead of ρ_{π}.

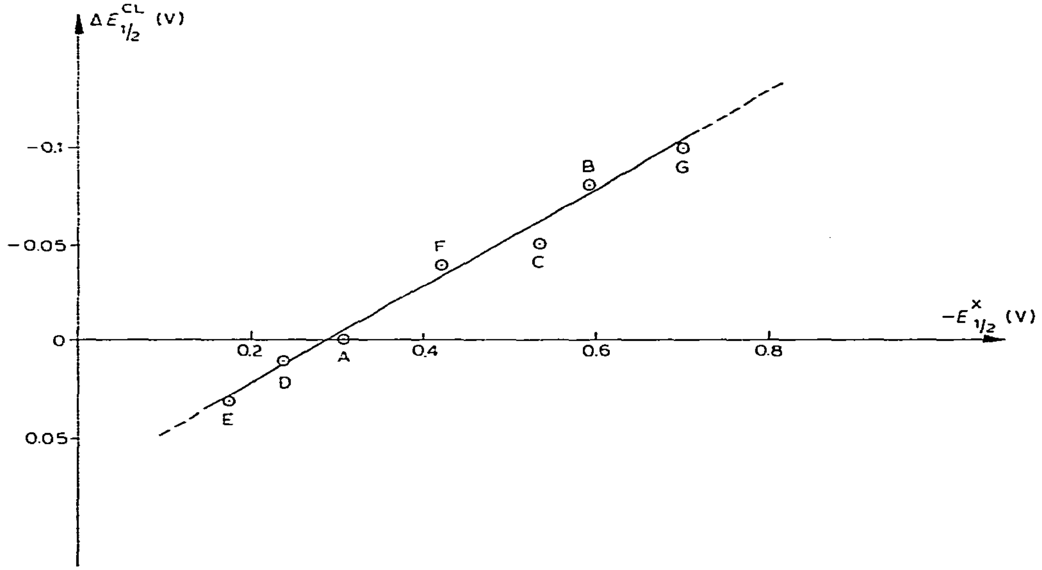

Fig. 1. Correlation between $\Delta E^{CL}_{1/2}$ and $E^{X}_{1/2}$. Points are labelled with letters corresponding to those of the bisarenechromium complex-free arene systems in Table 1.

where $\sigma = \sigma_m$, σ^o_m and σ^+_m. Using the parameters of the correlation equations for $E^X_{1/2}$ obtained previously [1], it is possible to find the constants in eq. 5 and 6, which are the same for all the above-mentioned sets of *meta*-substituent constants; $b \approx -0.125$ V, $\beta = 0.13$ V, $g \approx -2.17$ and $\gamma = 2.2$. Equations 5 and 6 are particular cases of eq. 4 because no universal substituent constants are available for groups with unsaturated carbon—carbon bonds ($CH{=}CHCOOC_2H_5$, $CH{=}CHCOC_6H_5$, etc.) and some others (e.g. ester substituents $COOC_2H_5$ in *ortho*-positions to each other in diethylphthalate).

Interestingly, eq. 4 and 5, as well as the curve corresponding to eq. 4 (Fig. 1), are inferred from the data on similar one-electron cathodic reduction processes of compounds containing different electrochemically active groups (CHO, $COCH_3$, $CH{=}CHCOOC_2H_5$, $CH{=}CHCOC_6H_5$, $(COOC_2H_5)_2$, CN, C_6H_5) rather than the same group as is the case for Hammet's dependence. Common for all the systems studied is a change in free energy resulting from coordination of the arene with chromium. There is no correlation for the cathodic process half-wave potentials $E^C_{1/2}$, which in this case vary in a broad range from −1.46 for compound VII to −2.71 V for compound XV, and correlation is hence sought for differences $\Delta E^{CL}_{1/2}$ obtained for compounds with identical electroactive groups.

Ascribing an index "H" to the values characterizing the benzene-dibenzenechromium system and an index "X" to those referring to the substituted arene-bisarenechromium complex system and taking into account that $b = (\Delta E^{CL}_{1/2})_H$ and $g = \log(K_C/K_L)_H$, eq. 5 and 6 may be written as

$$(\Delta E^{CL}_{1/2})_X - (\Delta E^{CL}_{1/2})_H = \Delta(\Delta E^{CL}_{1/2}) = \beta\Sigma\sigma \quad (7)$$

and

$$\log(K_C/K_L)_X - \log(K_C/K_L)_H = \Delta \log(K_C/K_L) = \gamma\Sigma\sigma \tag{8}$$

Thus, the difference in the change of free energy due to the transition of a substituted arene into a bisarenechromium complex and the similar value for the benzene-dibenzenechromium system is directly proportional to the sum of substituent constants (σ_m, σ_m^o, σ_m^+) in the complex.

The correlation equations written as eq. 7 and 8 demonstrate both the similarity with Hammet's equation and the great difference between them as regards the physical meaning.

We can draw some conclusions from the above linear dependences.

First, they confirm that the potential-determining stages of the electrochemical reduction of all the substances listed in Table 1 are identical.

Second, the role of chromium in transferring the electronic effects of substituents from one aromatic ligand to the other is clearly demonstrated.

Third, the support is given to the postulate formulated in the introduction to this paper, namely that the difference in reactivity with respect to the cathodic process, between a free arene and its bisarenechromium complex, is determined solely by the effect of coordination with chromium on the properties of the arene.

Fourth, the change in cathodic reactivity of the arene due to coordination with chromium shows a correlation with donor-acceptor properties of the ligand substituents. The overall effect of coordination is a sum of two components corresponding to the terms in the right-hand parts of eq. 5 and 6. One of them (b, g) is constant and does not depend on the nature of the substituents, the other ($\beta\Sigma\sigma$, $\gamma\Sigma\sigma$) reflects the contribution of the substituents to the change of free energy arising from the transition of the arene into its chromium complex. Electron-withdrawing substituents decrease the absolute value of $\Delta E_{1/2}^{CL}$ more if their total electron-withdrawing effect is greater. If the latter reaches such a value that the half-wave potential of oxidation of the bisarenechromium complex into a cation, $E_{1/2}^X$, becomes more positive than -0.3 V, the coordination effect changes sign: the difference $\Delta E_{1/2}^{CL}$ becomes positive and the relevant bisarenechromium complexes are reduced more easily than the free arenes.

Finally, proceeding from the calculated $E_{1/2}^L = -3.3$ V for benzene [22] and the value $b = -0.125$ V, one can estimate the hypothetical half-wave potential of dibenzenechromium reduction as $E_{1/2}^C = -3.42$ V.

The results obtained in this study provide experimental support for the conclusion that electronic density in dibenzenechromium is shifted to the ligands so that the Cr atom bears a positive charge. The conclusion has been made on the basis of quantum chemical calculations [16,19] and X-ray electron spectroscopy data [23,24]. Our results are also in agreement with those concerning cathodic reduction of benzene(benzophenone)chromium [25] and electrooxidation of a binuclear complex $C_6H_6CrC_6H_5$-$C_6H_5CrC_6H_6$ [26] and indicate that the $C_6H_6CrC_6H_5$ fragment is of electron-donating nature, the phenyl group being electron-withdrawing [27]. Likewise, there is a qualitative agreement between our findings and the redox properties of acetophenonechromium tricarbonyl. While oxidizing to the corresponding cation at essentially more positive potentials than bisarenechromium complexes, this compound is reduced much more easily than free acetophenone ($\Delta E_{1/2}^{CL} = 0.5$ V) [3,28,29].

Experimental

All the measurements were performed in an inert atmosphere (N_2) with amalgamated gold rotating electrodes in solutions of purified DMSO containing 0.3 M $(C_4H_9)_4NBF_4$. An aqueous normal calomel electrode was used as a reference electrode. The methods of purifying the solvent and tetrabutylammonium fluoroborate, amalgamating the electrode, carrying out measurements with the rotating disk electrode are described in ref. 1; the method for the rotating ring-disk electrode is described in part II [2].

The bisarenechromium complexes were synthesized by standard procedures by metallation of dibenzenechromium (II, V, VII [30], III [31]) or from chromium vapour and arenes (XI [32], XIII [33], IX [34]).

References

1 L.P. Yur'eva, S.M. Peregudova, L.N. Nekrasov, A.P. Korotkov, N.N. Zaitseva, N.V. Zakurin and A.Yu. Vasil'kov, J. Organometal. Chem., 219 (1981) 43.
2 L.N. Nekrasov, L.P. Yur'eva and S.M. Peregudova, J. Organometal. Chem., 238 (1982) 185.
3 V.S. Khandkarova and S.P. Gubin, J. Organometal. Chem., 22 (1970) 149.
4 Ch. Elschenbroich, J. Heck and F. Stohler, VII Internat. Conf. Organometal. Chem., Sept. 12—16, 1977, Kyoto, Japan: Abstr. 4C 36.
5 Ch. Elschenbroich, F. Gerson and F. Stohler, J. Amer. Chem. Soc., 95 (1973) 6956.
6 D.W. Clack and K.D. Warren, J. Organometal. Chem., 152 (1978) C60.
7 A.N. Frumkin and L.N. Nekrasov, Dokl. Akad. Nauk SSSR, 126 (1959) 115.
8 W.J. Albery and M.L. Hitchman, Ring-Disc Electrodes, Clarendon Press, Oxford, 1971.
9 L.N. Nekrasov, in Itogi Nauki i Tekhniki, Ser. Elektrokhimiya, Vol. 17, Moscow, 1981, p. 148.
10 Ph. Rieger, I. Bernal, W. Reinmuth and G. Fraenkel, J. Amer. Chem. Soc., 85 (1963) 683.
11 R. Pointeau and J. Favede, V Intern. Symp. Free Radicals, Uppsala, 1961, 52-1.
12 M.M. Baizer (Ed.), Organic Electrochemistry. An Introduction and a Guide, Marcel Dekker, New York, 1973.
13 L.N. Nekrasov, L.N. Vykhodtseva, A.P. Korotkov and L.P. Yur'eva, Elektrokhimiya, 13 (1977) 735.
14 A. Agarwall, M.J. McGlinchey and T.-S. Tan, J. Organometal. Chem., 141 (1977) 85.
15 H. Brunner and H. Koch, Chem. Ber., 115 (1982) 65.
16 E.M. Shustorovich and M.E. Dyatkina, Dokl. Akad. Nauk SSSR, 128 (1959) 1234.
17 D.W. Clack and K.D. Warren, Inorg. Chim. Acta, 30 (1978) 251.
18 D.W. Clack and W. Smith, Inorg. Chim. Acta, 20 (1976) 93.
19 J. Weber, M. Geoffroy, A. Goursot and E. Penigault, J. Amer. Chem. Soc., 100 (1978) 3995.
20 D.W. Clack and K.D. Warren, J. Organometal. Chem., 162 (1978) 83.
21 P. Zuman, Substituent Effects in Organic Polarography, Plenum Press, New York, 1967.
22 V.G. Mairanovskii, I.E. Valashek and G.I. Samokhvalov, Elektrokhimiya, 3 (1967) 611.
23 H. Binder and Ch. Elschenbroich, Angew. Chem. Int. Ed., 12 (1973) 659.
24 F. Kinomura, T. Tamura, I. Watanabe, Y. Yokoyama and S. Ikeda, Bull. Chem. Soc. Japan, 49 (1976) 3544.
25 S. Valcher and G. Casalbore, Electroanal. Chem., 50 (1974) 359.
26 Ch. Elschenbroich and J. Heck, Angew. Chem. Int. Ed., 16 (1977) 479.
27 A.A. Vlček, Z. Anorg. Allgem. Chem., 304 (1960) 109.
28 S.P. Gubin and L.I. Denisovich in Itogi Nauki i Tekhniki, Ser. Elektrokhimiya, Vol. 13, Moscow, 1978, p. 94.
29 M.K. Kloyd, J.A. McCleverty, J.A. Connor and E.M. Jones, J. Chem. Soc., Dalton, (1973) 1768.
30 A.N. Nesmeyanov, L.P. Yur'eva and N.N. Zaitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 922.
31 A.N. Nesmeyanov, L.P. Yur'eva, S.N. Levchenko and N.N. Zaitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2865.
32 A.N. Nesmeyanov, V.A. Sergeev, N.V. Zakurin, A.Yu. Vasil'kov, A.S. Kogan, L.P. Yur'eva, N.N.

Zaitseva and I.A. Uralets, J. Organometal. Chem., 217 (1981) 195.
33 G.A. Domrachev, Yu.A. Shevelev and V.D. Zinov'ev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 227.
34 Yu.A. Shevelev, V.K. Cherkasov, V.D. Zinov'ev and G.A. Domrachev, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 1936.