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

II *. ELECTROCHEMICAL REDUCTION OF BENZALACETOPHENONE AND BIS(BENZALACETOPHENONE)CHROMIUM

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Summary

The processes of electrochemical reduction of free benzalacetophenone and its symmetrical π-complex with chromium in DMSO show two ($e^- + e^-$) and three ($e^- + e^- + 2e^-$), respectively, cathodic waves on the polarization curves. π-Coordination with the chromium atom exerts little influence on the mechanism of the process in the region of the first cathodic wave potentials. In both cases reversible transfer of one electron is followed by dimerization of the primary products of the electrode reaction, i.e. anion-radicals (AR). AR and the products of their dimerization were detected directly by the rotating ring-disk electrode technique. The reactivity of bis(benzalacetophenone)chromium in the reaction

$$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr + e^- \overset{K_C}{\rightleftharpoons} [(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr]^{\bar{\cdot}}$$

is approximately an order of magnitude lower than that of free benzalacetophenone in a similar reaction:

$$C_6H_5CH{=}CHCOC_6H_5 + e^- \overset{K_L}{\rightleftharpoons} [C_6H_5CH{=}CHCOC_6H_5]^{\bar{\cdot}}$$

Accordingly, the half-wave potential of the former reaction is shifted towards a more negative value and the equilibrium constant decreases: $\log(K_C/K_L) = -0.9 \pm 0.3$.

The effect of coordination on the kinetics of AR dimerization is noticeably less. The rate constant of complex AR dimerization, $k_d^C = (1.5 \pm 0.7) \times 10^4$

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* For part I see ref. 1.

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l mol^{-1} s^{-1}, differs only slightly from that for free benzalacetophenone AR, $k_d^L = (2.1 \pm 0.2) \times 10^4$ l mol^{-1} s^{-1}, which is indirect evidence for the weak participation of the orbitals of chromium and the second ligand in delocalization of the unpaired electron in the π-complex AR. This makes it possible, in the first approximation, to neglect the contribution of AR dimerization to the value of $\Delta E_{1/2}^{CL}$ (the shift of the half-wave potential of the complex with respect to that of free arene) and to use $\Delta E_{1/2}^{CL}$ as a measure of the effect of coordination on the reactivity of arene in their reduction to AR.

Little is known about the reduction of bisarenechromium complexes. Unsubstituted dibenzenechromium cannot be reduced, neither chemically (K, DME, —80°C) [2,3] nor electrochemically [4]. Introduction of electron-withdrawing substituents increases the electron affinity of the dibenzenechromium molecule. For instance, electrochemical reduction at high negative potentials has been reported for benzene(biphenyl)chromium [5]. π-Complexes of chromium with aromatic ketones $(RCOC_6H_5)_2Cr$ ($R = C_6H_5$, p-$CF_3C_6H_4$, C_5H_4N) are reduced by potassium in dimethoxyethane to form the corresponding anion-radicals [6]. Exhaustive reduction leads to dianion-radicals which at temperatures as low as —80°C readily decompose into the metal and the free ketyls. The electrochemical reduction of benzene(benzophenone)chromium has been studied most comprehensively [7].

In order to compare the behavior of a bisarenechromium complex and the free arene in the course of cathodic reaction we have investigated the electrochemical reduction of bis(benzalacetophenone)chromium $(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr$ and benzalacetophenone $C_6H_5CH{=}CHCOC_6H_5$. Such a comparison provides information on the effect of coordination with chromium on the properties of the aromatic ligand.

The measurements were carried out using the rotating disk (RDE) and rotating ring-disk electrode (RRDE) techniques, on amalgamated gold electrodes in DMSO solutions containing tetrabutylammonium borofluoride as the supporting electrolyte.

Results

The compounds under study contain one or two carbonyl groups conjugated with a double carbon—carbon bond, which promotes various chemical interactions (protonation, disproportionation, dimerization, etc.) involving the initial species as well as intermediates of their cathodic reduction. This circumstance complicates the overall electrode process and makes polarization characteristics markedly dependent on experimental conditions. Therefore, electrochemical measurements in this case should be made under conditions which minimize the effect of secondary chemical interactions so that the polarization curves obtained are relatively simple and can be rather easily interpreted.

As is well known, polarization curves may be simplified by performing the experiments in aprotic solvents. This, in particular, was the reason for using DMSO in our study. The clearest picture is obtained at low concentrations of the solute studied ($c \leqslant 10^{-3}\,M$) at a high electrode rotation speed ($m > 50$ s^{-1}).

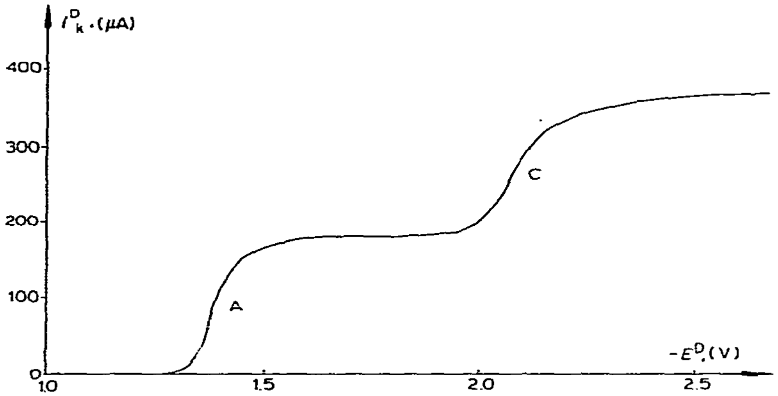

Fig. 1. Polarization curve of cathodic reduction of benzalacetophenone ($c = 2 \times 10^{-3}$ M) on a rotating disk electrode at $m = 84$ s^{-1}.

Under such conditions the effects of the chemical steps of the process on its polarization characteristics (half-wave potentials $E_{1/2}$, the shape, number and height ratio of the waves on the polarization curve) is either completely eliminated or becomes insignificant.

In this fashion we have measured the polarization curves of the reduction of benzalacetophenone and the oxidation and reduction of bis(benzalacetophenone)chromium (Figs. 1 and 2, respectively). The half-wave potentials $E_{1/2}$, the numbers of electrons taking part in the reaction n and the slope coefficients b

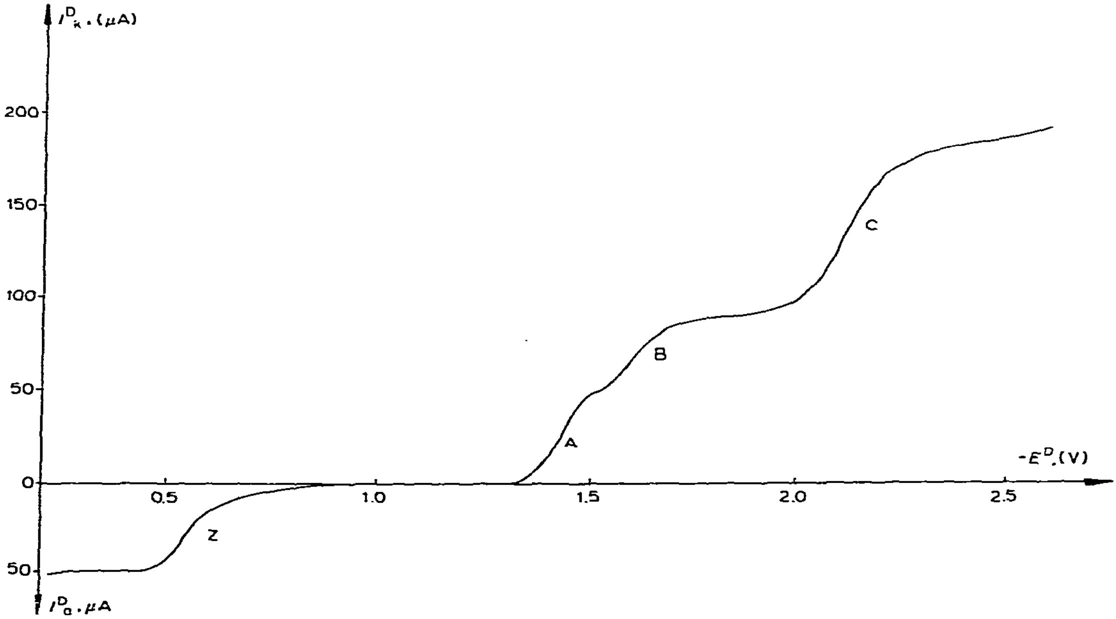

Fig. 2. Polarization curve of anodic oxidation (I^D_a) and cathodic reduction (I^D_c) of bis(benzalacetophenone)-chromium ($c = 9.4 \times 10^{-4}$ M) on a rotating disk electrode at $m = 84$ s^{-1}.

TABLE 1

KINETIC PARAMETERS OF THE PROCESSES STUDIED AND THE LOGARITHM OF THE RATIO BETWEEN THE EQUILIBRIUM CONSTANTS OF REACTIONS (1b) AND (1a)

Compound	Wave					
	A			B		
	$-E_{1/2}$ (V)	n	b (V)	$-E_{1/2}$ (V)	n	b (V)
$C_6H_5CH{=}CHCOC_6H_5$	1.41	1	0.06	No wave		
$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr$	1.46	1	0.06	1.62	1	0.09

for each wave on the curves are presented in Table 1. For reversible processes $b = 2.3\,RT/nF$, for irreversible ones $b = 2.3\,RT/\alpha nF$, where R, T, F and α are the gas constant, absolute temperature, the Faraday number and the transfer coefficient, respectively, and $0 < \alpha < 1$. The table contains also the diffusion coefficients D for the compounds studied in solutions of the composition used. They were calculated according to the formula for the limiting diffusion current density i_d on a rotating disk electrode,

$$i_d = 0.62\,nFD^{2/3}\omega^{1/2}\,\nu^{-1/6}c$$

where $\omega = 2\pi m$ is the angular rotation speed, m is the number of rotations of the electrode per second, ν is the kinematic viscosity of the solution (for DMSO solutions $\nu = 1.8 \times 10^{-2}$ cm^2 s^{-1}) and c is the concentration of the solute.

Considering the polarization curves in Figs. 1 and 2, for both compounds the waves A correspond to reversible addition of one electron to the initial molecule with formation of AR:

$$C_6H_5CH{=}CHCOC_6H_5 + e^- \rightleftharpoons [C_6H_5CH{=}CHCOC_6H_5]^{\overline{\cdot}} \qquad (1a)$$

$$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr + e^- \rightleftharpoons [(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr]^{\overline{\cdot}} \qquad (1b)$$

Wave B in Fig. 2 appears to arise due to addition of an electron to the second ligand of the bisarenechromium AR. This step may result in the formation of biradicals similar to those reported in the chemical reduction of chromium π-complexes containing aromatic ketones as ligands [6]:

$$[(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr]^{\overline{\cdot}} + e^- \rightarrow [(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)^{\overline{\cdot}}]_2Cr \qquad (2)$$

The waves C correspond to further reduction of the radical particles formed in reactions 1a and 2. The free arene AR are reduced via the addition of one electron and the bianion-radicals of the complex via the addition of two electrons. Since the formation of multiply charged anions is unlikely, reactions 3 apparently involve protons supplied by proton-donating components in the solution (e.g. water) or by the molecules of the starting material.

$$[C_6H_5CH{=}CHCOC_6H_5]^{\overline{\cdot}} + e^- \xrightarrow{+x\mathrm{BH}} [(C_6H_5CHCHCOC_6H_5)(H)_x]^{(2-x)^-} \qquad (3a)$$

$x = 0, 1, 2$

C			Z			D (cm^2 s^{-1})	k_d (l mol^{-1} s^{-1})	log K_C/K_L
$-E_{1/2}$ (V)	n	b (V)	$-E_{1/2}$ (V)	n	b (V)			
2.0	1	$\geqslant$0.1	No wave			2.3 $\times 10^{-6}$	(2.1 ± 0.2) $\times 10^4$	−(0.9 ± 0.3)
2.1	2	$\geqslant$0.1	0.54	1	0.06	1.1 $\times 10^{-6}$	(1.5 ± 0.7) $\times 10^4$	

$$[(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)^{\bar{\cdot}}]_2Cr + 2e^- \xrightarrow{+yBH} [(\eta^6\text{-}C_6H_5CHCHCOC_6H_5)_2(H)_yCr]^{(4-y)-} \quad (3b)$$

$y = 0, 1, 2, 3, 4$

The one-electron anodic wave Z (Fig. 2) characterizes the oxidation of a neutral bisarenechromium complex to a cation

$$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr \rightleftharpoons (\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr^+ + e^- \quad (4)$$

The height of this wave may be used as a reference to determine the number of electrons participating in various steps of the cathodic reduction of the complex. The anodic process was discussed in detail in our previous paper [1].

Waves A and Z correspond to reversible electron transfer processes, while waves B and C are irreversible, which follows from the values of the slope coefficient b given in Table 1.

The problem of the reversibility of waves A can be studied in more detail with rotating ring-disk electrode measurements [8—10]. This technique permits the detection and quantitative estimation (by means of the ring electrode) of electrochemically active intermediates and final products of the electrode reaction proceeding on the disk. When potentials corresponding to the limiting current area of waves A on the cathodic curves of both compounds were applied to the disk, the waves of the anodic oxidation of AR resulting from reaction 1 were observed on the ring electrode. The reversibility of these waves and their continuous transformation into the cathodic reduction curves of the initial compounds confirm that the species oxidized on the ring are indeed the primary AR of benzalacetophenone and bis(benzalacetophenone)chromium [11]. Under the above-mentioned experimental conditions (high m and low c) the current efficiency of AR on the disk Q_{AR}, amounts to 100%, which corresponds to complete reversibility of the electrode process. At higher concentrations of the depolarizer and at lower electrode rotation speed, the AR yield decreases and the polarization curve on the ring electrode becomes more complex. For instance, Fig. 3 presents the polarization curve for the oxidation on the ring of the products of the one-electron reduction of bisarenechromium complex on the disk. There are three waves on the curve, the first one (I) corre-

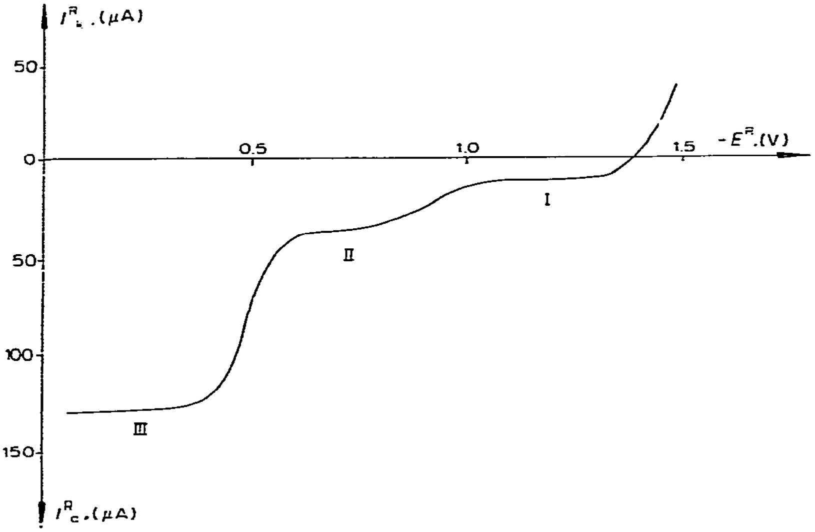

Fig. 3. Polarization curve of anodic oxidation on a ring electrode of cathodic reduction products of bis(benzalacetophenone)chromium ($c = 2 \times 10^{-3}\,M$) on the disk at $E^D = -1.55$ V, $I_c^D = 115$ μA and $m = 34\ \mathrm{s}^{-1}$.

sponding to oxidation of AR, the second (II) to oxidation of products of their conversion and the third (III) having no direct relevance to the cathodic process products but, like wave Z on the disk (Fig. 2), reflecting the formation of cations according to reaction 4. At open circuit disk potential ($I^D = 0$) the ring waves I and II disappear while the wave III does not. Whatever the conditions, the overall current efficiency of the products oxidized at potentials of waves I and II on the ring is 100%. With increasing c at m = const the yield of AR decreases while that of the second product grows. It is evident therefore, that AR disappear and the new product emerges due to a second-order reaction [11], most probably dimerization of AR:

$$2\,[C_6H_5CH{=}CHCOC_6H_5]^{\dot{-}} \xrightarrow{k_d^L} [C_6H_5CHCHCOC_6H_5]_2^{2-} \qquad (5a)$$

$$2\,[(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr]^{\dot{-}} \xrightarrow{k_d^C} [(\eta^6\text{-}C_6H_5CHCHCOC_6H_5)_2Cr]_2^{2-} \qquad (5b)$$

In this case oxidation at wave II potentials on the ring involves the dimeric carbanions $[C_6H_5CHCHCOC_6H_5]_2^{2-}$ and $[(\eta^6\text{-}C_6H_5CHCHCOC_6H_5)_2Cr]_2^{2-}$ or their monoprotonated forms.

To obtain unambiguous evidence for the radical dimerization of AR we have determined $E_{1/2}$ of waves A on the disk electrode as a function of log c and log ω. According to theory [12,13], the half-wave potential (when reversible electron transfer is followed by dimerization) is a function of the dimerization rate constant k_d, the concentration of the substance being reduced c and the angular rotation speed of the electrode ω

$$E_{1/2} = E_0 - \frac{2.3RT}{3nF}\log\frac{3}{1.61^2}\left(\frac{D}{\nu}\right)^{1/3} + \frac{2.3RT}{3nF}\log\frac{k_d c}{\omega} \qquad (6)$$

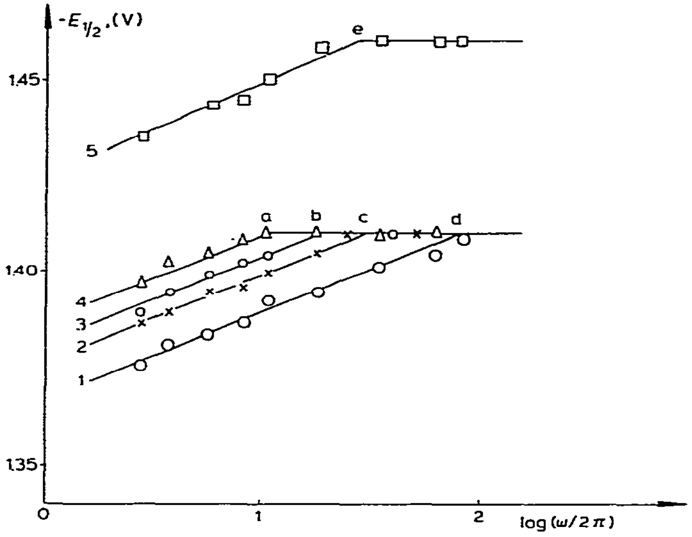

Fig. 4. Half-wave potentials of cathodic reduction of benzalacetophenone (1—4) and bis(benzalacetophenone)chromium (5) on a disk electrode vs. logarithm of the electrode rotation rate $m = \omega/2\pi$ s^{-1} at concentrations of the compounds being reduced: 2×10^{-3} *M* (1); 8×10^{-4} *M* (2); 4×10^{-4} *M* (3); 2×10^{-4} *M* (4); 5.4×10^{-4} *M* (5).

where E_0 is the standard redox potential of the system.

We found that in a certain range of c and ω $E_{1/2}$ depends lineary on their logarithms (Fig. 4). The experimental values of the derivatives $\partial E_{1/2}/\partial \log \omega = -0.023\,V$, $\partial E_{1/2}/\partial \log c = 0.021$ V (benzalacetophenone) and $\partial E_{1/2}/\partial \log \omega = -0.021\,V$ (bis(benzalacetophenone)chromium) proved to be close to the theoretically predicted ones, $2.3RT/3nF = \pm 0.02$ V. Accordingly, the waves A of the reduction of the free arene and its chromium complex correspond to reversible transfer of one electron with the subsequent dimerization of AR. In general, therefore, the waves A are quasi-reversible. However, Fig. 4 indicates that starting from a certain critical value of the electrode rotation speed (points a, b, c, d, e) which decreases with decreasing concentration of the depolarizer, the half-wave potential no longer depends on ω and c any more (horizontal sections of the curves in Fig. 4). This means that under such conditions the rate of AR removal from the solution near the electrode is high enough for their dimerization not to affect the kinetics of the total electrode reaction, which thus becomes completely reversible.

Discussion

The half-wave potentials of compounds taking part in similar electrochemical reactions involving the same mechanism are often used as a measure of the reactivities of the compounds in question. As it has been shown, the mechanisms of the one-electron reduction of benzalacetophenone and bis(benzalacetophenone)chromium are virtually identical. Thus, the effect of coordination on the reactivity of the arene may be revealed by comparing the half-wave potentials of the waves of the π-complex ($E^{\mathrm{C}}_{1/2}$) and free benzalacetophenone ($E^{\mathrm{L}}_{1/2}$). Here and below the indices C and L denote the values referring to the π-complex and free arene (ligand), respectively.

A change in the reactivity of the arene with respect to electroreduction as a result of coordination with chromium is characterized by the difference in half-wave potentials $\Delta E_{1/2}^{\mathrm{CL}} = E_{1/2}^{\mathrm{C}} - E_{1/2}^{\mathrm{L}}$. This approach, however, is valid only under certain conditions and the possibility of using $E_{1/2}^{\mathrm{C}}$, $E_{1/2}^{\mathrm{L}}$ and their difference requires, as well as the physical meaning of these values, comment.

As is well-known, for a reversible electrode reaction

$$E_{1/2} \approx E_0 = \frac{RT}{nF} \ln K \tag{7}$$

where K is the equilibrium constant of the reaction. Accordingly,

$$\Delta E_{1/2}^{\mathrm{CL}} \approx \frac{RT}{nF} \ln \frac{K_{\mathrm{C}}}{K_{\mathrm{L}}} \tag{8}$$

$\Delta E_{1/2}^{\mathrm{CL}}$ describes directly changes in the equilibrium constants of reactions 1 under the effect of coordination, provided they are not complicated by the subsequent dimerization of AR. Such conditions exist in the area of horizontal sections of the curves in Fig. 4, where $E_{1/2}^{\mathrm{C}}$ and $E_{1/2}^{\mathrm{L}}$ do not depend on ω and c. For the compounds studied in this paper $\Delta E_{1/2}^{\mathrm{CL}} = (-0.052 \pm 0.017)$ V, which corresponds to $\log(K_{\mathrm{C}}/K_{\mathrm{L}}) = -0.9 \pm 0.3$. Thus, the equilibrium constant of reaction 1 decreases approximately by an order of magnitude when passing from benzalacetophenone to its π-complex with chromium, i.e. coordination results in a decrease of the reactivity of the initial arene in the cathodic reaction.

The results obtained when the process is completely reversible (horizontal sections of the curves in Fig. 4) are interpreted most easily. It is not always possible, however, to obtain these conditions, since with increasing rate constant of AR dimerisation k_{d} the required conditions may involve unrealistic values of ω and c. Therefore, a correct comparison of $E_{1/2}^{\mathrm{C}}$ and $E_{1/2}^{\mathrm{L}}$ requires a detailed kinetic investigation which may raise certain difficulties. In general, it is more convenient to use a simpler approach based on determining $\Delta E_{1/2}^{\mathrm{CL}}$ in the area of quasi-reversibility (tilted sections on the curves 1—5, Fig. 4), where, as mentioned above, the half-wave potentials are described by eq. 6. In order to eliminate the influence of concentration and rotation speed on $\Delta E_{1/2}^{\mathrm{CL}}$, the measurements should be taken at c = const and ω = const. Since the AR dimerization rate constants for reduction of the free arene and its complex may be different, this would affect the value of $\Delta E_{1/2}^{\mathrm{CL}}$: at c = const, ω = const, $n = 1$

$$\Delta E_{1/2}^{\mathrm{CL}} \approx \frac{2.3RT}{F} \log \frac{K_{\mathrm{C}}}{K_{\mathrm{L}}} + \frac{2.3RT}{3F} \log \frac{k_{\mathrm{d}}^{\mathrm{C}}}{k_{\mathrm{d}}^{\mathrm{L}}} \tag{9}$$

Equation 9 indicates that $\Delta E_{1/2}^{\mathrm{CL}}$ describes the total effect of changes in the reactivity of the reagent in the course of electrochemical reduction and that of AR in the course of dimerization; a change in k_{d} by an order of magnitude will cause an additional shift of $\Delta E_{1/2}^{\mathrm{CL}}$ by 0.02 V. For this reason the use of $\Delta E_{1/2}^{\mathrm{CL}}$ for determining $\log(K_{\mathrm{C}}/K_{\mathrm{L}})$ requires separation of the two effects and evaluation of the second term in eq. 9.

Our kinetic studies have made it possible to calculate by using eq. 6 the rate constants of AR dimerization, k_d^C and k_d^L (Table 1). The average values of k_d differ by a factor of only 1.5, i.e. the second term in the right-hand part of eq. 9 is equal to 0.003 V (from 0.000 to 0.008 V, considering data scatter), which falls into the limits of experimental error in $E_{1/2}$ measurements.

Three conclusions can be drawn from this result.

1. The low value of the correction factor related to a change in k_d when passing from free arene to the chromium π-complex makes it possible to neglect the second term in eq. 9 and assume that the experimental values of $\Delta E_{1/2}^{CL}$ determined at constant c and ω according to eq. 8 describe mainly the change in reactivity of the arene due to its coordination to the metal. It seems reasonable that with other free arene—bisarenechromium complex pairs whose reduction follows a pattern similar to that of benzalacetophenone and bis(benzalacetophenone)chromium the contribution of dimerization to the value of $\Delta E_{1/2}^{CL}$ will also be small.
2. Coordination of benzalacetophenone with chromium slows down noticeably cathodic reduction of the arene to anion-radicals (reaction 1) but affects the AR reactivity in dimerization much less (reaction 5).
3. The similar values of k_d^C and k_d^L provide indirect evidence for the slight participation of Cr orbitals in delocalization of the unpaired electron in the π-complex AR. Indeed, different distributions of spin density in free arene and in the ligand of the complex would have resulted in a considerable difference between the rate constants of AR dimerization. For the same reason it seems most likely that delocalization of the unpaired electron is largely confined to one of the ligands in the π-complex.

These conclusions were drawn from studying the kinetics of electroreduction of benzalacetophenone and bis(benzalacetophenone)chromium in the potential area of the first cathodic waves on the polarization curves (waves A in Figs. 1 and 2). Information may also be obtained from the kinetic behavior of these compounds over the entire range of their reduction potentials. We shall consider only two questions here.

The first one bears on the effect of coordination on the rate of electron addition to the reduced reaction center (waves C in Figs. 1 and 2). As is seen from Table 1, coordination with chromium slows down not only reaction 1 but also reaction 3. Accordingly, $E_{1/2}$ of wave C of the complex is shifted by 0.1 V towards negative values as compared to that of benzalacetophenone.

The second question refers to transfer of the electronic effect of substituents from one ligand of the complex to the other. The fact that the addition of the first (reaction 1b) and the second (reaction 2) electrons to the bis(benzalacetophenone)chromium molecule takes place at different potentials (waves A and B on the polarization curve in Fig. 2, $E_{1/2}^B - E_{1/2}^A \approx -0.16$ V) points to a considerable mutual influence of the ligands in the starting compound. However, reduction of the bianion-radical (reaction 3b) involves simultaneous addition of two electrons. Provided there is no protonation before the electrochemical step, this simultaneous transfer of two electrons shows that negative charges on the ligands of the bisarenechromium complex substantially weaken the mutual influence of the ligands.

Experimental

The polarization measurements of cathodic reduction were carried out with an amalgamated gold rotating disk electrode in purified DMSO solutions containing 0.3 M $(C_4H_9)_4NBF_4$.

The intermediate cathodic reaction products, i.e. AR and dimeric carbanions, were detected by the rotating ring-disk electrode (RRDE) technique developed by Frumkin and Nekrasov [8]. Such an electrode is an integral mechanical system consisting of two independent concentrical electrodes, a disk and a ring lying in the same plane and isolated from each other by a thin teflon interlayer. The geometrical dimensions of the electrode: disk radius $r_1 = 0.25$ cm, the ring internal radius $r_2 = 0.0275$ cm, the ring external radius $r_3 = 0.0375$ cm. An important parameter of a RRDE is its collection efficiency factor N which characterizes the fraction of the stable product synthesized on the disk and reaching the ring electrode. For the RRDE used in this study $N = 0.38$.

The measuring system consisted of two independent electric circuits each involving a potentiostat, a working electrode (an amalgamated gold disk or ring), a counter (Pt) and a reference (aqueous normal calomel) electrodes. The polarization curves were registered on a two-coordinate recorder. To avoid interaction between the two potentiostats, one of them was not earthed.

The experiments were performed as follows. After the solution in the electrochemical cell was bubbled through with nitrogen to remove oxygen from the system, a potential corresponding to the limiting diffusion current of cathodic reaction 1a or 1b (waves A) was applied to the rotating disk electrode. Then on the ring electrode the anodic polarization curve was measured corresponding to oxidation of AR, brought to the ring by a convection flow, and of the products of their conversion. The efficiency Q_i of AR and dimeric carbanions, and the total yield of these particles were determined at several rotation speeds of the electrode and calculated according to the formula

$$Q_\mathrm{i}(\%) = \frac{(I_\mathrm{d}^\mathrm{R})_i}{NI^\mathrm{D}} \times 100$$

where I^D is the cathodic current on the disk electrode and $(I_\mathrm{d}^\mathrm{R})_i$ is the limiting current of anodic waves I, II or of their sum on the ring electrode.

The techniques for amalgamating the electrodes, purifying the solvent and tetrabutylammonium fluoroborate were described previously [1], as was the synthesis of bis(benzalacetophenone)chromium [14].

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 Ch. Elschenbroich, F. Gerson and J. Heinzer, Z. Naturforsch., B27 (1972) 312.
3 Ch. Elschenbroich and F. Gerson, J. Amer. Chem. Soc., 97 (1975) 3556.
4 U. Koelle, W. Holzinger and J. Müller, Z. Naturforsch., B34 (1979) 759.
5 R.E. Dessy, R.B. King and M. Waldrop, J. Amer. Chem. Soc., 88 (1966) 5115.
6 Ch. Elschenbroich, J. Heck and F. Stohler, VII Intern. Conf. Organometal. Chem., Sept. 12—16, 1977, Kyoto, Japan, Abstr. 4C 36.
7 S. Valcher and G. Casalbore, Electroanal. Chem., 50 (1974) 359.
8 A.N. Frumkin and L.N. Nekrasov, Dokl. Akad. Nauk SSSR, 126 (1959) 115.

9 A. Frumkin, L. Nekrasov, B. Levich and Yu. Ivanov, J. Electroanalyt. Chem., 1 (1959/60) 84.
10 W.J. Albery and M.L. Hitchman, Ring-Disc Electrodes, Clarendon Press, Oxford, 1971.
11 L.N. Nekrasov, Intermediates in electrochemical reactions, Faraday Discussions, No. 56, London, 1974, p. 308.
12 Z. Galus and R.N. Adams, J. Electroanalyt. Chem., 4 (1962) 248.
13 L. Nadjo and J.M. Saviant, J. Electroanalyt. Chem., 44 (1973) 327.
14 A.N. Nesmeyanov, L.P. Yur'eva and N.N. Zaitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 922.