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Electrochemistry of diarenechromium complexes

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Abstract. The results of studies on the anodic oxidation and cathodic reduction of diarenechromium complexes are surveyed. The mechanisms of the multistage reactions involving the electrochemical reduction of the complexes are examined. Two aspects of their reactivity are analysed — the nature of the transmission of the electronic effect of substituents in the ligands to the reaction centre and the change in the properties of aromatic compounds as a result of the formation of a complex with a chromium atom. The bibliography includes 133 references.

I. Introduction

A characteristic property of transition metal π-complexes is their ability to enter into oxidation and reduction reactions. Such compounds can exist as neutral molecules and as ions. This is mainly associated with the possible occurrence of different oxidation states of the central metal atom, while the nature of the organic ligands remain unchanged. If the latter are also capable of undergoing oxidation–reduction reactions, the range of redox reactions involving π-complexes is significantly expanded.

The knowledge of the characteristic features of redox processes makes it possible to predict the reactivity of organometallic compounds in different chemical reactions. Electrochemical methods proved to be most effective in the study of redox processes. The high accuracy of the measurement of electrical quantities and the sensitivity of the electrochemical process characteristics to changes in the electronic structure of the molecules ensure a rigorous quantitative level of the investigation.

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The problem of the reactivity of transition metal π-complexes of a particular type includes two important tasks: the study of the influence of the nature of organic ligands and of their substituents on the reactivity of the complexes and the determination of the nature of the change in the properties of the organic molecule as a result of its coordination to the metal atom. In relation to redox processes, the first task can be carried out by finding the standard potentials E_0 as a function of the nature and number of substituents in the ligands of the complex. In practice, instead of thermodynamic quantities E_0, use is usually made of the half-wave potentials $E_{1/2}$ of reversible electrochemical reduction or oxidation reactions of the corresponding complexes. The quantities $E_{1/2}$ are determined from polarisation measurements. Different types of polarography, voltammetry at rotating electrodes, cyclic voltammetry, and other methods are used for this purpose. The values of $E_{1/2}$ quoted in the literature do not as a rule include a correction for the interfacial potential jump at the liquid/liquid boundary, arising at the point of contact between solutions of different compositions. The lack of reliable information about the interfacial potential jumps hinders the comparison of the results obtained for the same system in different solvents. The occurrence of interfacial potential jumps as well as the possible differences in the capacities for solvation of the components of the oxidation–reduction system as a function of the nature of the solvent lead to different values of $E_{1/2}$ measured in different solvents relative to the same reference electrode. However, the above effects are not important if all the measurements for the test series of compounds are carried out in the same solvent under identical experimental conditions.

One of the most important problems in the chemistry of transition metal π-complexes is that of the influence of the coordination of the organic molecule to the transition metal atom on the properties of the former. In order to discover the general features of the effect of complex formation on the reactivity of the 'ligand', a comparative study of the electrochemical behaviour of a group of non-coordinated organic compounds and their π-complexes is carried out.

Among transition metal π-complexes, diarenechromium complexes occupy a special place. The discovery of dibenzenechromium and the determination of its sandwich structure[1,2] played an extremely important role in the establishment and development of modern organometallic chemistry. The characteristic features of the structure of complexes of the dibenzenechromium series, namely the presence of ligands of only one type, their aromatic nature, their ability to exist in a non-coordinated state, the formally zero valence of the

central metal atom in the uncharged complexes, as well as the reversibility of the electron transfer stages in the $Arene_2Cr^{+/0}$ and $Arene_2Cr^{0/-}$ systems render diarenechromium complexes exceptionally convenient for the solution of general problems of the reactivity of transition metal π-complexes.

A wide variety of redox processes, occurring both with retention of the sandwich structure and leading to its disruption, are characteristic of diarenechromium complexes:

$$2Arene + Cr^{3+} \overset{-\bar{e}}{\longleftarrow} Arene_2Cr^{2+} \overset{-\bar{e}}{\rightleftarrows} Arene_2Cr^{+} \overset{-\bar{e}}{\underset{+\bar{e}}{\rightleftarrows}} \rightleftarrows Arene_2Cr \overset{+\bar{e}}{\underset{-\bar{e}}{\rightleftarrows}} Arene_2Cr^{-} \overset{+n\bar{e}}{\longrightarrow} \text{products.} \quad (1)$$

Neutral complexes and singly charged paramagnetic cations are stable while the doubly charged cations and the radical-anions are unstable. Their formation in the course of the reaction has been demonstrated by electrochemical methods and EPR.

Chromium complexes are the only ones among the diarene π-complexes of Group VIA metal complexes whose electrochemistry has been investigated in fair detail. The electrochemical behaviour of molybdenum and tungsten analogues has been hardly studied.

The first electrochemical investigations of diarenechromium complexes[3-15] were performed soon after the synthesis of dibenzenechromium by Fischer.[1] In these investigations, a study was made, in relation to dibenzenechromium and its simplest derivatives containing alkyl and aryl groups in the benzene ligand, of redox processes in the $Arene_2Cr^{+/0}$ systems by polarography at the mercury dropping electrode (MDE). Electrochemical reduction reactions of neutral complexes were initially described for only two examples.[15,16] As the methods of synthesis developed, the range of available diarenechromium complexes expanded. This created preconditions for a systematic study of the reactivity of a large series of complexes of this type both in anodic oxidation and in cathodic reduction reactions. The range of electrochemical methods also expanded. Together with polarography at the MDE, cyclic voltammetry (CVA), the rotating disc electrode (RDE) method, and the rotating ring-disc electrode (RRDE) method came to be widely used.

The study of the polarisation characteristics of the oxidation–reduction processes with participation of chromium π-complexes led to the formulation of the characteristic features of the electrode reactions. The mechanism of the transmission of electronic effects of substituents in the complex molecule was established with the aid of correlation analysis. The nature of the changes in the properties of aromatic compounds in the complex formation process was discovered on the basis of comparative data on the reactivity of arenes and their chromium complexes in cathodic reduction reactions. The use of modern electrochemical experimental methods (CVA, RRDE) made it possible to determine the mechanisms of multistage electrochemical reduction reactions, to identify the unstable reaction intermediates, and to investigate their reactions.

A brief description of studies on the electrochemistry of diarenechromium complexes can be found in a number of publications.[17-26] The aim of the present review was to consider as fully as possible the results of studies over the last 10–15 years and also to discuss the characteristics of the electrochemical processes and the conclusions reached on their basis, which are important for the chemistry of transition metal π-complexes.

II. Electrochemical oxidation and reduction processes in the $Arene_2Cr^{+/0}$ and $Arene_2Cr^{2+/+}$ systems

The reversibility of the one-electron transfer stage

$$Arene_2Cr \overset{-\bar{e}}{\underset{+\bar{e}}{\rightleftarrows}} Arene_2Cr^{+} \quad (2)$$

in protic[3-9,11-13] and aprotic[10,14,27-30] media is characteristic of all the diarenechromium complexes known at the present time. This confirms data obtained by the polarographic, CVA, RDE, and RRDE methods, according to which the half-wave potentials $E_{1/2}^{+/0}$ for the oxidation of the neutral form of the complex and the reduction of the corresponding cation are the same, while the slope of the polarisation curves is 0.06 V, which is close to the theoretical value for a reversible one-electron process. The same value is quoted in most studies for the difference between the potentials of the cathodic (pc) and anodic (pa) peaks on the cyclic voltammogram:

$$\Delta E_p = E_{pa} - E_{pc}$$

for a peak height ratio close to unity:[31] $i_{pc}/i_{pa} \simeq 1$. The polarisation characteristics of the processes, including the values of $E_{1/2}$, are unaffected by the nature of the material of the electrode and the composition and concentration of the supporting electrolyte. The limiting currents on the polarisation curves are diffusional in character.

The data encountered in certain studies which are formally inconsistent with the reversibility of the process, for example the difference between the potentials of the cathodic and anodic peaks on the cyclic voltammograms exceeding appreciably the value for a reversible reaction,[32,33] are in all probability a result of the inadequate accuracy of the experiment and the occurrence of ohmic potential drops in the solution, which has been confirmed convincingly[31] by the comparison of the values of ΔE_p measured with compensation for the ohmic potential drops (ΔE_p = 0.06 V) and without such compensation (ΔE_p = 0.12–0.14 V).

The reversibility of the electrode reactions observed with the aid of the experimental methods mentioned above is a consequence of the high standard exchange current density i_{00} in the test systems or, what amounts to the same thing, the high heterogeneous rate constants for the electron transfer stage at the equilibrium potentials k_s. In such cases, the kinetics of the overall process are wholly determined by the kinetics of the mass transfer stages, while the electrode potentials at each point on the polarisation curve are determined, in conformity with the thermodynamic Nernst formula for the electrode potential, by the logarithm of the ratio of the concentrations (activities) of the oxidised and reduced form of the electrochemically active substance at the electrode. The kinetic parameters of the electron transfer state (i_{00}, k_s, and the transfer coefficients α and β for the cathodic and anodic reactions respectively) can be determined directly using methods making it possible to remove the diffusional limitations and to investigate the kinetics. Thus, according to Gennett et al.,[34] the values of k_s for the bis(biphenyl)chromium$^{+/0}$ system, obtained in the course of impedance measurements by alternating current polarography in seven different solvents, are in the range from 0.3 (benzonitrile) to 4 cm s^{-1} (acetonitrile). Such values correspond to standard exchange current densities into the range 30–400 A cm^{-2} and characterise a very high reversibility of the reaction. The transfer coefficient α for this system proved to be 0.5±0.03.

The results of measurements of the rate constants for homogeneous electron exchange in solutions in hexane and benzene between the oxidised and reduced forms of methyl-substituted dibenzenechromium derivatives ($k_{ex} \sim 3 \times 10^8$ litre mol^{-1} s^{-1}), found by the ^1H NMR and EPR methods, as well as the low activation energies (E_a = 8.6 kJ mol^{-1}) characteristic of

diffusion-controlled reactions are consistent with the data presented above.[35] Similar data have been obtained for other derivatives of dibenzenechromium in dimethyl sulphoxide (DMSO).[28]

A high exchange current density is one of the conditions necessary to permit the use of a particular oxidation-reduction couple as a reference system for the measurement of electrode potentials. This feature as well as the fulfillment of a number of other conditions (closeness of the particles to the spherical shape and their large radius, low ionic charge, stability of both forms of the redox systems and their solubility in different solvents, and the constancy of the geometry of the ligands after electron transfer[36]) enabled the IUPAC Commission on Electrochemistry to recommend the bis(biphenyl)chromium$^{+/0}$ system together with the ferrocene/ferrocenium system for use as a reference electrode (as a portable electrode or as an internal standard) in electrochemical measurements in non-aqueous solvents.[37] Special studies[37,38] have shown that the potential difference between the two systems specified above in 22 organic solvents is virtually constant and the deviation from the average value of 1.124 V is ± 12 mV for an error of the measurements of ± 4 mV. This result indicates the virtually complete absence of effects due to the specific solvation of the cations and an insignificant change in the electrostatic component on passing from one solvent to another. The bis(biphenyl)chromium$^{+/0}$ couple proved to be the best reference system in non-aqueous media. It became possible to compare correctly the parameters of electrode reactions investigated in different organic solvents by potentiometric, voltammetric, and polarographic methods. A table representing a compilation of the half-wave potentials for the electrochemical reduction processes of a large number of metal cations, measured relative to the reference electrode under consideration, in 38 organic solvents has been published.[43] The use of bis(biphenyl)-chromium for similar purposes in aqueous solutions is not indicated in view of the instability of its cationic form, the insolubility of the neutral complex, and the pronounced adsorption phenomena.[39]

The data obtained from electrochemical measurements on the entropies of the electrochemical reduction reactions of bis-(biphenyl)chromium[40] and dibenzenechromium[34] cations in a number of solvents provide information about the temperature variation of the corresponding standard redox potentials. It has been established that the entropies of these reactions decrease linearly with increase in the acceptor number of the solvent.[40]

The change in the charge on the diarenechromium complexes in the course of the one-electron transfer process is accompanied by only a small reorganisation of the inner sphere of this species. Thus, on passing from the reduced to the oxidised form of dibenzene-chromium, the chromium–carbon bond length changes[41,42] by only 0.012 Å, whilst the free energy of the inner-sphere reorganisation ΔG_{is}^{+} is ~ 0.8 kJ mol^{-1}, which is at least 20 times lower than the free energy of the reorganisation of the outer sphere (the solvent). This enabled the authors[34] to use dibenzenechromium as one of the model objects for testing the theory of solvent reorganisation, constituting the basis of modern approaches to the treatment of the elementary electron transfer step in homogeneous oxidation–reduction and electrochemical reactions in condensed systems.[44,45]

Dibenzenechromium and its substituted derivatives are interesting objects for the study of the adsorption of organic cations at the interface. The low solubility of the salts of diarenechromium complexes in water is one of the main causes of the strong adsorption of the cations on the electrodes in aqueous media.[4] The appearance of adsorption waves (Brdicka waves) on the polarograms obtained in aqueous solutions of the iodides of certain alkyl-substituted dibenzenechromium derivatives is associated with this phenomenon.[7–9]

The adsorption of dibenzenechromium and bis(biphenyl)-chromium cations at the aqueous solutions/mercury and solution/air interfaces has been investigated[46,47] by the methods of electrocapillary curves and the maximum air pressure in the bubble. The adsorbability of these species is due to a number of factors: their positive charge, the squeezing effect at the interface owing to the breakdown of the structure of water, the interaction of the π-electrons of the aromatic system with the electrode surface, and the presence of the unpaired electron. The nature of the supporting electrolyte anion also exerts a strong influence on the adsorption. Comparison of the adsorption properties of dibenzenechromium, bis(biphenyl)chromium, and tetraethyl-ammonium cations established that the presence of the unpaired electron and of the π-electron system in the radical-cations of the π-complexes promotes their adsorption on mercury in the absence of the specific interaction of the supporting electrolyte anions with the electrode surface (for sulphate anions), but diminishes the adsorbability somewhat if such interaction does occur (for iodide anions). The appearance of adsorption peaks on the cyclic voltam-mograms of dibenzenechromium, bis(biphenyl)chromium, and dinaphthalenechromium, obtained at a platinum electrode in solutions in tetrahydrofuran (THF), has been noted.[48,49]

The existence of limiting diffusion currents on the electro-chemical reduction or electrochemical oxidation polarisation curves for chromium π-complexes, measured with the aid of the mercury dropping electrode or the rotating disc electrode, makes it possible to determine the diffusion coefficients of these com-pounds. The corresponding data for a series of derivatives of dibenzenechromium in several solvents have been published.[34,39,50]

Diarenechromium complexes are some of the most readily oxidisable transition metal π-complexes. Unsubstituted dibenz-enechromium is oxidised at high negative potentials. The measured value of $E_{1/2}$ (relative to the saturated calomel electrode) depends on the solvent: -0.71 V (DMF), -0.77 V (AN), -0.795 V (BN), -0.93 V (FA),[34] and -0.76 V (DMSO).[29] (The designations of the solvents are indicated in the footnote to Table 1.) Dibenzenemolybdenum is oxidised with somewhat greater difficulty than dibenzenechromium: $\Delta E_{1/2}$ is 0.1 V.[4] There are no literature data on the electrochemical oxidation of dibenzenetungsten.

Comparison[51] of the behaviour of dibenzenechromium, dibenzenevanadium, and cyclopentadienyl(cycloheptatrienyl)-chromium in the electrochemical oxidation reaction showed that the 18-electron dibenzenechromium is oxidised more readily than the 17-electron vanadium complex (the potentials $E_{1/2}$ in DME are -0.72 and -0.35 V respectively) and an asymmetric chromium complex with different ligands ($C_5H_5+C_7H_7$): for the latter, $E_{1/2}^{+/0} = -0.61$ V.

The half-wave potential is strongly influenced by the substituents in the arene ligand. Depending on the nature of the substituents and the number in the complex molecule, the values of $E_{1/2}^{+/0}$ vary from -1 to $+0.4$ V.

The half-wave potentials for the reversible redox transitions $+/0$ and $2+/+$ in the diarenechromium π-complexes are presented in Table 1.

The introduction of alkyl substituents into the dibenzene-chromium molecule shifts $E_{1/2}$ into the region of negative values.[4,6–9,12,27,53] On the other hand, the introduction of phenyl substituents hinders oxidation.[10] The principle of additivity then holds. For example, the shift of $E_{1/2}$ due to the introduction of one alkyl group is the same for the methyl and ethyl groups and amounts to 0.03 V. The validity of the principle of additivity has been indicated also in other studies.[29,31,62] The shift of $E_{1/2}$ after the introduction of one formyl group is 0.27 V, while the shift after the introduction of the cyano-group is 0.3 V (compounds **1**, **44**, **45**, **49**, **56**).† The maintenance of the principle of additivity as the phenyl groups accumulate in the dibenzene-chromium molecule is illustrated in Fig. 1. In a number of

†Here and henceforth the numbers of the compounds in Table 1 are quoted in the text.

Table 1. The potentials $E_{1/2}$ for the $Arene_2Cr^{0/+}$ and $Arene_2Cr^{2+/+}$ redox processes.

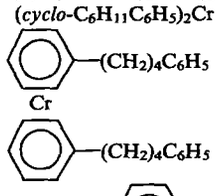
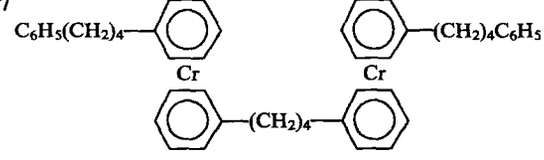
No.	Compound	$-E_{1/2}^{+/0}$/V ($-E_{1/2}^{2+/+}$)/V	Solvent	Supporting electrolyte	Method (electrode)	Ref.
1	$(C_6H_6)_2Cr$	0.97	H_2O	0.5 M LiCl	MDE	6
		0.835	C_2H_5OH	0.5 M LiCl	MDE	5
		0.807[a]	$CH_3OH:C_6H_6=4:1$	0.3 M NaOH	MDE	4
		0.81[a]	$CH_3OH:C_6H_6=4:1$	0.5 M LiCl	MDE	3
		1.04	FA	0.2 M $NaClO_4$	MDE	10
		0.81	DMF	0.2 M $NaClO_4$	MDE	10
		0.80	DMF	0.1 M NEt_4ClO_4	MDE	27
		0.81	DMF	0.1 M NEt_4ClO_4	(Pt)	52
		0.82	DMF	0.1 M NEt_4ClO_4	(Pt)	53
		1.3[b]	DME	0.1 M NBu_4ClO_4	MDE	14
		0.685	DME	0.1 M NBu_4ClO_4	CVA (CG)	54, 55
		0.72	DME	0.1 M NBu_4ClO_4	CVA (CG)	51
		(−1.14)	DME (−45 °C)	0.1 M NBu_4ClO_4	CVA (CG)	51
		(−0.94)[c]	THF (−80 °C)	0.05 M NBu_4PF_6	CVA (Pt)	48
		0.746	DMSO	0.1 M NBu_4ClO_4	CVA (Pt)	28
		0.76	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
		0.770	AN	0.1 M NBu_4PF_6	MDE, CVA (Hg)	34
		0.710	DMF	0.1 M NBu_4PF_6	MDE, CVA (Hg)	34
		0.930	FA	0.1 M NBu_4PF_6	MDE, CVA (Hg)	34
		0.795	BN	0.1 M NBu_4PF_6	MDE, CVA (Hg)	34
		0.80	CH_2Cl_2	0.1 M NBu_4PF_6	CVA (Pt)	56
2	$(CH_3C_6H_5)_2Cr$	0.885[a]	$CH_3OH:C_6H_6$ = 4:1	0.3 M NaOH	MDE	4
		0.775	$C_2H_5OH:C_6H_6$ = 7:3	0.5 M LiCl	MDE	12
		0.89	DMF	NEt_4ClO_4	(Pt)	53
		0.85	DMF	0.1 M NEt_4ClO_4	MDE	27
		1.04	H_2O	0.5 M LiCl	MDE	6
		0.82	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
3	$[1,2\text{-}(CH_3)_2C_6H_4]_2Cr$	1.06	H_2O	0.5 M LiCl	MDE	7
		0.93	DMF	0.1 M NEt_4ClO_4	MDE	27
		0.73	DME	NBu_4ClO_4	CVA (CG)	57
4	$[1,3\text{-}(CH_3)_2C_6H_4]_2Cr$	1.06	H_2O	0.5 M LiCl	MDE	7
		0.92	DMF	0.1 M NEt_4ClO_4	MDE	27
		0.88	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
		0.77	DME	0.1 M NBu_4ClO_4	CVA (CG)	58
5	$[1,4\text{-}(CH_3)_2C_6H_4]_2Cr$	1.06	H_2O	0.5 M LiCl	MDE	7
6	$[1,2,4\text{-}(CH_3)_3C_6H_3]_2Cr$	1.008[a]	$CH_3OH:C_6H_6$ = 4:1	0.3 M NaOH	MDE	4
		0.916	DMSO	0.1 M NBu_4ClO_4	CVA (Pt)	28
7	$[1,3,5\text{-}(CH_3)_3C_6H_3]_2Cr$	1.06	H_2O	0.5 M LiCl	MDE	6
		1.00[a]	$CH_3OH:C_6H_6$ = 4:1	0.3 M NaOH	MDE	4
		0.97	DMF	0.1 M NEt_4ClO_4	MDE	27, 53
		0.94	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
8	$[(CH_3)_6C_6]_2Cr$	1.12	H_2O	0.5 M LiCl	MDE	7
		1.63[d]	THF	NBu_4PF_6	CVA (Pt)	59
		(0.16)[d]	THF	NBu_4PF_6	CVA (Pt)	59
		0.94	DME	NBu_4ClO_4	CVA (CG)	51
		(−0.45)	DME (−45 °C)	NBu_4ClO_4	CVA (CG)	51
9	$(C_2H_5C_6H_5)Cr(C_6H_6)$	0.83	DMF	0.1 M NEt_4ClO_4	MDE	27
10	$(C_2H_5C_6H_5)_2Cr$	1.05	H_2O	0.5 M LiCl	MDE	8
		0.86	DMF	0.1 M NEt_4ClO_4	MDE	27
		0.81	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
11	$[(C_2H_5)_2C_6H_4]Cr(C_6H_5C_2H_5)$	0.89	DMF	0.1 M NEt_4ClO_4	MDE	27
12	$[(C_2H_5)_2C_6H_4]_2Cr$	0.92	DMF	0.1 M NEt_4ClO_4	MDE	27
13	$(iso\text{-}C_3H_7C_6H_5)_2Cr$	0.96	H_2O	0.5 M LiCl	MDE	6
		1.05	H_2O	0.5 M LiCl	MDE	9
14	$[1,3\text{-}(iso\text{-}C_3H_7)_2C_6H_4]_2Cr$	1.02	H_2O	0.5 M LiCl	MDE	9
15	$(cyclo\text{-}C_6H_{11}C_6H_5)_2Cr$	0.90	H_2O	0.5 M LiCl	MDE	6
16		0.82	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
17		0.82	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29

Table 1 (contd).

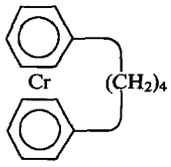
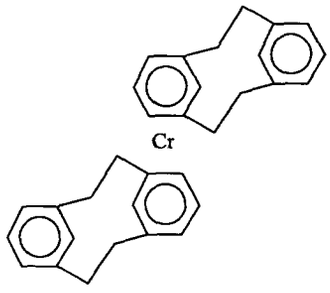
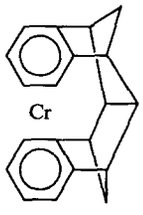
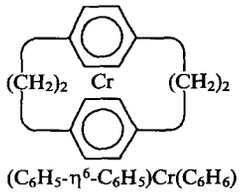
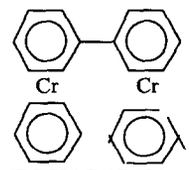
No.	Compound	$-E^{+/0}_{1/2}$/V ($-E^{2+/+}_{1/2}$)/V	Solvent	Supporting electrolyte	Method (electrode)	Ref.
18		0.79	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
19		0.82	DME	0.1 M NBu_4ClO_4	CVA (CG)	58
20		0.73	DME	0.1 M NBu_4ClO_4	CVA (CG)	57
21		0.74 (−1.24)	DME DME (−45 °C)	0.1 M NBu_4ClO_4	CVA (CG)	51
22	$(C_6H_5\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	0.87	H_2O	0.5 M LiCl	MDE	7
		0.78(5)	C_2H_5OH	0.5 M LiCl	MDE	5
		1.3[b]	DME	0.1 M NBu_4ClO_4	MDE	15
23	$(C_6H_5\text{-}\eta^6\text{-}C_6H_5)_2Cr$	0.669[e]	H_2O	1 M KCl	MDE	39
		0.66	H_2O	0.5 M LiCl	MDE	6
		0.72	C_2H_5OH	0.5 M LiCl	MDE	5
		0.697	$C_2H_5OH:C_6H_6 = 4:1$	0.1 M LiCl	MDE	11
		1.340[f]	THF	0.1 M NBu_4BF_4	CVA (Pt)	60
		1.10[b]	DMF	0.1 M NEt_4ClO_4	CVA (CG)	30
		0.74	DMF	0.1 M NEt_4ClO_4	(Pt)	53
		0.750	DMF	0.5 M $NaClO_4$	CVA (Pt)	10
		0.89	FA	0.5 M $NaClO_4$	CVA (Pt)	10
		0.645	DMSO	0.1 M NBu_4ClO_4	CVA (Pt)	28
		0.66	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
24	$(4\text{-}FC_6H_4\text{-}\eta^6\text{-}C_6H_5)Cr(\eta^6\text{-}C_6H_5C_6H_5)$	0.686	$C_2H_5OH:C_6H_6 = 4:1$	0.1 M LiCl	MDE	11
25	$(4\text{-}ClC_6H_4\text{-}\eta^6\text{-}C_6H_5)Cr(\eta^6\text{-}C_6H_5C_6H_5)$	0.679	$C_2H_5OH:C_6H_6 = 4:1$	0.1 M LiCl	MDE	11
26	$(4\text{-}BrC_6H_4\text{-}\eta^6\text{-}C_6H_5)Cr(\eta^6\text{-}C_6H_5C_6H_5)$	0.672	$C_2H_5OH:C_6H_6 = 4:1$	0.1 M LiCl	MDE	11
27	$[(C_6H_5)_3\text{-}\eta^6\text{-}C_6H_3]_2Cr$	0.53	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	24, 61, 62
28	$[(C_6H_5)_6\text{-}\eta^6\text{-}C_6]_2Cr$	0.28	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	24, 61, 62
29		0.82[e] 0.37	AN	0.1 M NEt_4BF_4	CVA	63
30	$(FC_6H_5)Cr(C_6H_6)$	0.57	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
31	$(FC_6H_5)_2Cr$	0.367	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
32	$(ClC_6H_5)_2Cr$	0.336	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
33	$[1,4\text{-}(CH_3)_2\text{-}2\text{-}ClC_6H_3]_2Cr$	0.516	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
34	$(IC_6H_5)_2Cr$	0.34	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62

Table 1 (contd).

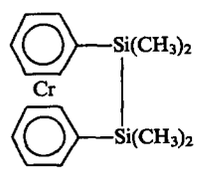
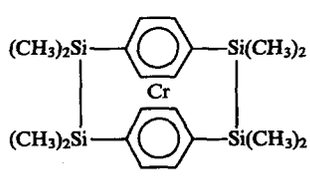
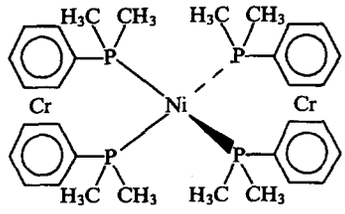
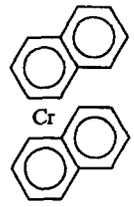
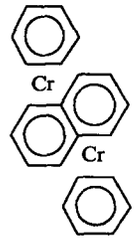
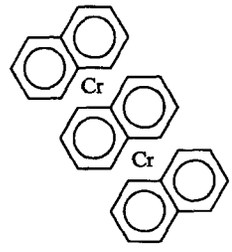
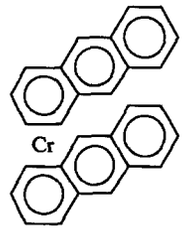
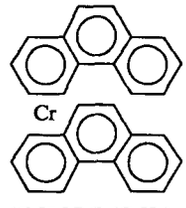
No.	Compound	$-E^{+/0}_{1/2}$/V $(-E^{2+/+}_{1/2})$/V	Solvent	Supporting electrolyte	Method (electrode)	Ref.
35	$(CF_3C_6H_5)_2Cr$	0.24	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
		0.190	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
36	$[1,3\text{-}(CF_3)_2C_6H_4]_2Cr$	−0.385	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
37	$[1,4\text{-}(CF_3)_2C_6H_4]_2Cr$	−0.337	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
38	$(1,2\text{-}CF_3C_6H_4Cl)_2Cr$	−0.165	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
39	$(1,4\text{-}CF_3C_6H_4Cl)_2Cr$	−0.125	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
40	$(CH_3OC_6H_5)_2Cr$	0.767	AN	0.1 M NBu_4ClO_4	CVA (Pt)	32
41	$[(CH_3)_2NC_6H_5]Cr(C_6H_6)$	0.958	AN	0.1 M NBu_4ClO_4	CVA (CG)	31
42	$[(CH_3)_2NC_6H_5]_2Cr$	1.075	AN	0.1 M NBu_4ClO_4	CVA (CG)	31
43	$[(CH_3)_2NC_6H_5]Cr(C_6H_5COOCH_3)$	0.743	AN	0.1 M NBu_4ClO_4	CVA (CG)	31
44	$(HCOC_6H_5)Cr(C_6H_6)$	0.51	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
45	$(HCOC_6H_5)_2Cr$	0.27	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
46	$(CH_3COC_6H_5)Cr(C_6H_6)$	0.616	AN	0.1 M NBu_4ClO_4	CVA (CG)	31
47	$(CH_3COC_6H_5)_2Cr$	0.429	AN	0.1 M NBu_4ClO_4	CVA (CG)	31
		0.38	DMSO	NBu_4BF_4	RDE (Hg/Au)	29
48	$(C_6H_5CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	0.59	DMF	0.1 M NEt_4ClO_4	MDE	16, 53
49	$(NCC_6H_5)Cr(C_6H_6)$	0.46	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
50	$(NCC_6H_5)Cr(C_6H_5CH_3)$	0.49	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
51	$(NCC_6H_5)Cr(C_6H_5OCH_3)$	0.43	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
52	$(NCC_6H_5)Cr(C_6H_5COCH_3)$	0.28	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
53	$(NCC_6H_5)Cr(C_6H_5F)$	0.26	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
54	$(NCC_6H_5)Cr(C_6H_5Cl)$	0.27	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
55	$(NCC_6H_5)Cr(C_6H_5CF_3)$	0.18	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
56	$(NCC_6H_5)_2Cr$	0.14	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	62
57	$(CH_3OCOC_6H_5)Cr(C_6H_6)$	0.615	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
58	$(CH_3OCOC_6H_5)_2Cr$	0.407	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
59	$(C_2H_5OCOC_6H_5)Cr(C_6H_6)$	0.617	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
60	$(C_2H_5OCOC_6H_5)_2Cr$	0.421	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
		0.65	H_2O	0.1 M KCl	CVA (Pt)	64
61	$[1,2\text{-}(CH_3OCO)_2C_6H_4]Cr(C_6H_6)$	0.464	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
62	$[1,2\text{-}(CH_3OCO)_2C_6H_4]_2Cr$	0.157	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
63	$[1,2\text{-}(C_2H_5OCO)_2C_6H_4]_2Cr$	0.20	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	65
64	$[1,3\text{-}(CH_3OCO)_2C_6H_4]Cr(C_6H_6)$	0.409	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
65	$[1,3\text{-}(CH_3OCO)_2C_6H_4]_2Cr$	0.064	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
66	$[1,4\text{-}(CH_3OCO)_2C_6H_4]Cr(C_6H_6)$	0.407	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
67	$[1,4\text{-}(CH_3OCO)_2C_6H_4]_2Cr$	0.049	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
68	$(CH_3OCOCH_2C_6H_5)Cr(C_6H_6)$	0.782	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
69	$(CH_3OCOCH_2C_6H_5)_2Cr$	0.751	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
70	$(C_2H_5OCOCH_2C_6H_5)Cr(C_6H_6)$	0.797	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
71	$(C_2H_5OCOCH_2C_6H_5)_2Cr$	0.759	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
		0.70	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
72	$(CH_3OCOCH_2CH_2C_6H_5)Cr(C_6H_6)$	0.826	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
73	$(CH_3OCOCH_2CH_2C_6H_5)_2Cr$	0.837	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
74	$(C_2H_5OCOCH_2CH_2C_6H_5)Cr(C_6H_6)$	0.834	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
75	$(C_2H_5OCOCH_2CH_2C_6H_5)_2Cr$	0.840	AN	0.1 M NBu_4ClO_4	CVA (Pt)	31
		0.80	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
76	$(C_2H_5OCOCH=CHC_6H_5)_2Cr$	0.55	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
77	$(C_6H_5COCH=CH\text{-}\eta^6\text{-}C_6H_5)_2Cr$	0.50	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	29
78	$(C_6H_5C\equiv C\text{-}\eta^6\text{-}C_6H_5)_2Cr$	0.68	DMSO	0.1 M NBu_4BF_4	RDE (Hg/Au)	61, 62
79	$[(C_6H_5)_3Si\text{-}\eta^6\text{-}C_6H_5]_2Cr$	0.55	DME	0.1 M NEt_3ClO_4	CVA (CG)	66
80		0.69	DME	0.1 M NBu_4ClO_4	CVA (Pt)	67
81		0.66	DME	0.1 M NBu_4ClO_4	CVA (Pt)	67
82	$[(CH_3)_2PC_6H_5]Cr(C_6H_6)$	0.62	DME	0.1 M NBu_4ClO_4	CVA (CG)	68
83	$[(CH_3)_2PC_6H_5]_2Cr$	0.57	DME	0.1 M NBu_4ClO_4	CVA (CG)	68

Table 1 (contd).

No.	Compound		$-E_{1/2}^{+/0}$/V ($-E_{1/2}^{2+/+}$)/V	Solvent	Supporting electrolyte	Method (electrode)	Ref.
84			0.70	DME	0.1 M NBu_4ClO_4	CVA (CG)	68
85			1.190[d] (−0.196)[d] 1.84[d]	THF THF EDA	NBu_4PF_6 NBu_4PF_6 NBu_4PF_6	CVA (Pt) CVA (Pt) CVA (Pt)	49 49 49
86			0.80[d] (−0.38)[d]	THF THF	NBu_4PF_6 NBu_4PF_6	CVA (Pt) CVA (Pt)	49 49
87			2.04[d]	EDA	NBu_4PF_6	CVA (Pt)	49
88			1.4[b]	DME	0.1 M NBu_4ClO_4	MDE	15
89			0.651 (−0.82)	DMF DMF	0.1 M NBu_4ClO_4 0.1 M NBu_4ClO_4	CVA (Pt) CVA (Pt)	69 69
90	$(C_5H_5N)Cr(C_6H_6)$		0.560	DME	0.1 M NBu_4ClO_4	CVA (CG)	55
91	$(C_5H_5N)_2Cr$		0.445	DME	0.1 M NBu_4ClO_4	CVA (CG)	55
92	$(C_5H_5As)_2Cr$		0.51	DME	0.1 M NBu_4ClO_4	CVA (CG)	54
93	$(C_5H_5BR)_2Cr$	$R=CH_3$	−0.45	CH_2Cl_2	NBu_4PF_6	CVA (Pt)	70
94	$(C_5H_5BR)_2Cr$	$R=C_6H_5$	−0.53	CH_2Cl_2	NBu_4PF_6	CVA (Pt)	70

Note. The half-wave potentials $E_{1/2}$ were determined either directly from the polarisation curves (MDE, RDE) or were found as half the sum of the potentials of the cathodic (E_{pc}) and anodic (E_{pa}) peaks on the cyclic voltammograms. Unless stipulated otherwise, the electrode potentials listed in Table 1 and in the other tables and also quoted in the text were measured relative to the potential of the aqueous saturated calomel electrode. In the remaining cases, the reference electrode employed is indicated. The table also presents the experimental conditions (the method of measurement, the material of the electrode, the solvent, and the composition of the supporting electrolyte), the most important of which is the nature of the solvent when the process is reversible. The following abbreviations have been adopted in the table and in the text: CG = carbon glass, AN = acetonitrile, BN = benzonitrile, DMSO = dimethylsulphoxide, DMF = dimethylformamide, DME = dimethoxyethane, THF = tetrahydrofuran, FA = formamide, EDA = ethylenediamine.

Reference electrodes: [a] calomel electrode, 0.5 M LiCl, $CH_3-C_6H_6$; [b] $Ag/AgClO_4$; [c] Ag/AgCl/4 M aqueous LiCl; [d] $Ag/AgNO_3$; [e] Ag/AgCl; [f] $Ag/AgBF_4$.

Indeed, the kinetic stabilisation of the cation $Arene_2Cr^{2+}$ is achieved either with the aid of peripheral substitution in a dibenzenechromium molecule or as a result of a decrease in the experimental temperature. Thus, in the oxidation of bis(hexamethylbenzene)chromium in THF[59] and dimethoxyethane[51] at 20 °C and a reduced temperature, it was possible to observe two pairs of reversible peaks corresponding to two one-electron transitions. It was established by low-temperature cyclic voltammetry at a platinum electrode that dibenzenechromium and bis(biphenyl)chromium are also oxidised reversibly in dry THF to doubly charged cations, which are stable in terms of the time scale of the voltamperometric measurements below −80° and −60 °C respectively.[48,95] The anodic oxidation of the cation ({η^{12}-[2.2]paracyclophane}chromium)$^+$ **21** is reversible even at room temperature.[51]

The presence of cathodic peaks due to the electrochemical reduction of the cations $Arene_2Cr^{2+}$ on the cyclic voltammograms constitutes direct proof of the formation of these species during the anodic process. According to Elschenbroich et al.,[51] the lifetime of the doubly charged dibenzenechromium, bis(hexamethylbenzene)chromium, and {η^{12}-[2.2]paracyclophane}chromium cations in dimethoxyethane at −40 °C is several seconds, minutes, and hours respectively.

There are grounds for the assumption that the first stage of the anodic oxidation of the singly charged cations $Arene_2Cr^+$ [reaction (3)] consists as a rule of reversible electron transfer, preceding the chemical reaction with participation of doubly charged species, and determines to a large extent the half-wave potential for the overall irreversible process. We may note that the half-wave potential for the irreversible oxidation of $Arene_2Cr^+$ as well as for the reversible process (2) depends on the nature of the substituent in the arene ligand. Thus, in the presence of two electron-accepting substituents[31] COOR or COR in the dibenzenechromium molecule, the half-wave potential is 1.25 V, while in the presence of two electron-donating groups $N(CH_3)_2$ it amounts to 0.8 V.

During the electrochemical oxidation process, an electron is removed from the HOMO of the complex. In order to solve the problem of the nature of the frontier orbitals in transition metal π-complexes, Vlcek[5] proposed a method based on the comparison of the differences between the half-wave potentials for the reversible oxidation (or reduction) of two structurally similar complexes and the corresponding non-coordinated ligands. The relative contribution of the ligand MO and of the metal AO to the overall MO of the complex was estimated for the dibenzenechromium–bis(biphenyl)chromium system. The highest molecular orbital of the complex, in which electronic changes take place in the course of the electrochemical oxidation process, is a MO localised predominantly on the chromium atom[5,17] (the contribution of the ligand MO does not exceed 15%). Similar conclusions were reached in the study of diarene chromium complexes by quantum-chemical[82–85] and photo-electron spectroscopic (PES)[86,87] methods and also by the EPR of paramagnetic cationic complexes.[88]

The universality and reversibility of the one-electron oxidation of neutral diarenechromium complexes to the cationic form makes this reaction exceptionally convenient for the solution of problems associated with the transmission of the electronic effect of substituents in the dibenzenechromium molecule to the reaction centre (the chromium atom). The reversibility of the process rules out the influence on $E_{1/2}^{+/0}$ of heterogeneous factors associated with the specific features of the electrochemical process — the structure of the electrical double layer, adsorption, etc. For this reason, the value of $E_{1/2}$, which is close to the thermodynamic standard potential E_0, reflects objectively the influence of substituents on the reactivity of the complexes in redox reactions and can serve as its measure.

Table 3. Parameters of the correlation between $E_{1/2}^{+/0}$ and the substituent constants.[61,62]

Substituent constant	No. of points	ρ_π/V	$-b_1$/V	$-\rho$	r	S_{ρ_π}	S_{b_1}
σ_m^0	19	0.513	0.749	8.9	0.992	0.018	0.012
σ_m^+	20	0.520	0.760	9.0	0.990	0.017	0.011
σ_m	25	0.541	0.748	9.3	0.986	0.019	0.012
σ_p^0	17	0.396	0.635	6.8	0.964	0.028	0.019
σ_p	25	0.350	0.602	6.0	0.920	0.031	0.021
σ_I	23	0.456	0.717	7.9	0.814	0.071	0.047
σ_R	21	0.341	0.463	5.9	0.570	0.113	0.042

Note. b_1 and ρ_π are the parameters of the correlation equation; $\rho = \rho_\pi/0.058$; S_{ρ_π} and S_{b_1} are the standard deviations; r is the correlation coefficient; the constants σ were taken from Gordon and Ford[93] and Kochi and Hammond.[94]

In order to estimate quantitatively the electronic influence of substituents in the electrochemical oxidation of diarenechromium complexes, the correlations between $E_{1/2}^{+/0}$ and different σ constants of the substituents were analysed systematically in a number of studies[29,61,62] (Table 3). According to the Hammett–Zuman equation,[89] we have

$$E_{1/2} = b_1 + \rho_\pi \sum \sigma \,, \qquad (4)$$

where ρ_π is the polarographic reaction constant, b_1 the half-wave potential for the oxidation of dibenzenechromium, and $\Sigma\sigma$ the sum of the substituent constants. When the σ constants corresponding to only the resonance (σ_R) or the inductive (σ_I) mechanisms of the transmission of the influence of substituents are used, a linear relation is not obtained. The best correlation is observed between $E_{1/2}^{+/0}$ and the σ constants to which the main contribution comes from the inductive component: σ_m, σ_m^+, and σ_m^0.

The reversible oxidation of diarenechromium complexes is characterised by high absolute values of ρ, which indicates a high sensitivity of the dibenzenechromium system to the electronic influence of the substituents. High values of ρ are also observed in the series of oxidation–reduction reactions of ferrocene.[90] They are in general characteristic of reactions involving ions.[91] Compared with ferrocene, dibenzenechromium is a less conducting system. This can be inferred from the half-wave potential shift $\Delta E_{1/2}$ after the introduction of the same substituent (for example, CF_3) into the dibenzenechromium and ferrocene molecules. It amounts to 0.26 V in the first case[32,62] and 0.32 V in the second.[92]

The excellent correlation between $E_{1/2}^{+/0}$ and the σ constants of the *meta*-substituents led to the conclusion that the electronic influence of the substituents in the arene ligand on the reaction centre (the chromium atom) is transmitted predominantly via an inductive mechanism; the conjugation in the arene ligand exists only to the extent that this effect is reflected in the constants of the *meta*-substituent.[29,61,62]

The results of other studies carried out with a significantly smaller number of objects are on the whole similar. For example, a linear correlation between $E_{1/2}^{+/0}$ and the σ_m constants has been observed:[28]

$$E_{1/2}^{+/0} = -0.78 + 0.32 \sum \sigma_m \,. \qquad (5)$$

Two correlation equations have been obtained by Treichel et al.:[32]

$$E_{1/2}^{+/0} = -0.801 + 0.637\sigma_m \,, \quad r = 0.986 \,; \qquad (6)$$

$$E_{1/2}^{+/0} = -0.530 + 0.413\sigma_p \,, \quad r = 0.976 \,. \qquad (7)$$

The similarity of the correlation coefficients precluded an ambiguous choice between these equations. It is noteworthy that the experimental data obtained in the above study[32] by cyclic

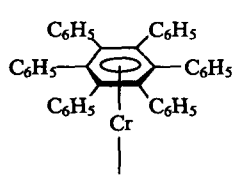
voltammetry are not quite correct. The potentials of the anodic and cathodic peaks are strongly distorted by the ohmic potential drops in solution, indicated by the difference between the potentials of the anodic and cathodic peaks, which exceeds the theoretical value (0.059 V) by a factor of 1.5–5. The deviation of the value of $E_{1/2}^{+/0}$ for dibenzenechromium from the correlation (7) is also striking: the experimental value is $E_{1/2}^{+/0} = -0.716$ V, while the value obtained from Eqn. (7) is $E_{1/2}^{+/0} = -0.530$ V.

The conclusion that the transmission of the electronic influence of substituents to the chromium atom is inductive was also reached in a study[53] where a correlation was observed between $E_{1/2}^{+/0}$ and the Taft substituent constants for six diarenechromium complexes.

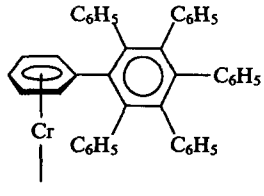
The results of the electrochemical study of the electronic effects in the diarenechromium π-complexes agree with data obtained by other physical methods. A correlation between the first ionisation potentials in the gas phase (IP_1) and the constants σ_m^0 has been established by photoelectron spectroscopy.[87] A correlation has been found between the chemical shift of fluorine and the constants σ_m^+ and σ_m^n (r = 0.958 and 0.952 respectively) with the aid of ^{19}F NMR for a series of heteroannularly disubstituted dibenzenechromium derivatives $(XC_6H_5)Cr(C_6H_5F)$.[96] Hence it follows that the electronic effects of the substituents at one of the arene ligands are exerted across the chromium atom on the indicator fluorine atom in the other ligand also predominantly via an inductive mechanism.

The correlation Eqn. (4) was used to confirm the structure of bis(iodobenzene)chromium.[97] The experimental value $E_{1/2}^{+/0} = -0.38$ V proved to be close to the value −0.40 V calculated by Eqn. (4).

An analogous approach was used to establish the structure of bis(hexaphenylbenzene)chromium obtained by the cyclotrimerisation of diphenylacetylene in the reaction with atomic chromium.[98] The observed[62] half-wave potential for the oxidation of the complex is −0.32 V, which confirms structure A assuming the additive influence of the phenyl ring on the oxidation potential (Fig. 1). If the alternative structure B is obtained, the half-wave potential for the oxidation of the complex would be close to $E_{1/2}^{+/0}$ for bis(biphenyl)chromium (−0.72 V).



A



B

The half-wave potentials $E_{1/2}^{+/0}$ for dibenzenechromium derivatives in DMSO have been compared[62] with the ionisation potentials IP_1 of the same complexes in the gas phase. A satisfactory correlation, described by the equation

$$E_{1/2}^{+/0} = -4.08(\pm 0.16) + 0.62(\pm 0.03)IP_1\,, \quad r = 0.990, \qquad (8)$$

was observed. The coefficient of IP_1 in the equation differs from unity and reflects the contribution of the solvation effects to the energetics of the oxidation reaction in solution in DMSO. The ionisation potentials of various diarenechromium complexes can be calculated using this equation with a fairly high degree of accuracy, which is important, because the experimental determination of the ionisation potentials is difficult compared with the determination of $E_{1/2}^{+/0}$. The existence of a correlation between $E_{1/2}^{+/0}$ and IP_1 shows that the photoelectron processes in the gas phase and the electrochemical oxidation in solution take place with participation of the same molecular orbitals localised predominantly on the chromium atom.

The parallel variation of the redox potentials of a number of sandwich chromium complexes (including three diarene complexes) and the potentials IP_1 of the same compounds in the gas phase was noted previously.[28]

A linear correlation has been observed[51] between the electrochemical potential $E_{1/2}(C_{12}H_{12}M^{+/0})$ for the dibenzene and cyclopentadienylcycloheptatrienyl complexes of chromium and vanadium and their IP_1 obtained from the photoelectron spectra:

$$IP_1 = 6.20 + 0.99E_{1/2}^{+/0}\,, \quad r = 0.995\,. \qquad (9)$$

The half-wave potentials $E_{1/2}$ vary in parallel with the appearance potentials of the molecular ions obtained from the mass spectra.[99]

It has been shown[100, 101] that the standard redox potentials of a series of sandwich complexes of transition metals, including diarenechromium and diarenemolybdenum complexes, are linearly correlated with the gas-phase ionisation potentials of the corresponding metals.

III. Cathodic reduction of diarenechromium(0) complexes

Data on the electrochemical reduction of more than 30 diarenechromium complexes have now been published (Table 4).

The main difference between the cathodic reduction reactions and the processes examined in the previous section consists in the fact that they occur with participation of a molecular orbital the main contribution to which comes from the π orbital of the aromatic ligand. This conclusion is justified by the results of quantum-chemical calculations[85, 102–106] carried out in different years for dibenzenechromium and dinaphthalenechromium molecules and has been confirmed by numerous experimental data. In particular, this is indicated by the similarity of the polarisation characteristics of the electrochemical reduction of free arenes and the corresponding diarenechromium complexes, including the similarity of the half-wave potentials $E_{1/2}$ for the electrochemical reduction of arenes ($E_{1/2}^{A}$) and the complexes ($E_{1/2}^{C}$)‡ (Table 5).

The application of Vlcek's methods[5, 17–19] makes it possible to estimate the contribution of the lowest unoccupied molecular orbitals (LUMO) of the arene ligands in the complex, the results showing that it is the dominant contribution (~90%). This is also indicated by the parallel variation of $E_{1/2}^{A}$ and $E_{1/2}^{C}$ for symmetrical complexes (Table 5). Thus, depending on the nature and number of the substituents in the benzene ring, $E_{1/2}^{A}$ shifts towards positive values in the sequence $C_6H_5 < CF_3 < (C_6H_5)_3 < CN < COCH_3 < (COOC_2H_5)_2 < CHO < CH{=}CHCOOC_2H_5 < CH{=}CHCOC_6H_5$. The ease of the reduction of $Arene_2Cr$ increases in the same sequence. Only the CHO and $CH{=}CHCOOC_2H_5$ groups are an exception. They change places on passing from the arene to the complex.

The electron affinity is determined by the donor–acceptor properties of the substituents in the arene ring and also, and to an even greater degree, by the extent of the conjugated system. Among the compounds investigated,[50, 65, 107] benzylideneacetophenone and its complex are reduced more readily than the others, since this arene contains the most extensive conjugation system, although, judging from the value of $E_{1/2}^{+/0}$, the substituent $CH = CHCOC_6H_5$ is a moderately strong electron acceptor. A different picture is observed in the anodic oxidation of zerovalent chromium complexes where the electronic changes are localised not on the ligand π-orbitals but on the atomic orbitals of the metal.[62] In terms of their ability to hinder the oxidation of the complex, the above substituents can be arranged in the following sequence: $C_6H_5 < CH{=}CHCOOC_2H_5 < (C_6H_5)_3 < CH{=}CHCOC_6H_5 < COCH_3 < CHO < CF_3 < (COOC_2H_5)_2 < CN$, i.e. in this case the increase in the electron-accepting capacity of the substituent, characterised by the σ constant of the *meta*-substituents, is decisive.

‡Here and henceforth the superscripts A and C denote quantities referring to the free arenes and the chromium complexes respectively.

Table 4. The half-wave potentials $E_{1/2}$ for the cathodic reduction of diarenechromium(0) complexes.

No.	Compound	$-E^{C}_{1/2}$/V	Solvent	Supporting electrolyte	Method (electrode)	Ref.
1	$(C_6H_5\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	3.3[a]	DME	NBu_4ClO_4	MDE	15
2	$(C_6H_5\text{-}\eta^6\text{-}C_6H_5)_2Cr$	2.60	DMSO	NBu_4BF_4	RRDE (Hg/Au)	24, 61
3	$[(C_6H_5)_3\text{-}\eta^6\text{-}C_6H_3]_2Cr$	2.37	DMSO	NBu_4BF_4	RRDE (Hg/Au)	61
4	$(CF_3C_6H_5)_2Cr$	2.46	DMSO	NBu_4BF_4	RRDE (Hg/Au)	24, 61
5	$(HCOC_6H_5)Cr(C_6H_6)$	2.11	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
6	$(HCOC_6H_5)_2Cr$	1.80	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
7	$(C_2H_5OCOCH=CH\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.84	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
8	$(C_6H_5COCH=CH\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.42	DMSO	NBu_4BF_4	RRDE (Hg/Au)	50
9	$(CH_3COC_6H_5)_2Cr$	1.98	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
10	$(C_6H_5CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	1.91	DMF	NBu_4ClO_4	MDE	16
		1.92	DMF	NBu_4ClO_4	CVA (Pt)	108
11	$(C_6H_5CO\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.75	DMF	NBu_4ClO_4	CVA (Pt)	108
12	$(4\text{-}CH_3C_6H_4CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	1.97	DMF	NBu_4ClO_4	CVA (Pt)	108
13	$(4\text{-}CH_3C_6H_4CO\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.77	DMF	NBu_4ClO_4	CVA (Pt)	108
14	$(4\text{-}FC_6H_4CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	1.93	DMF	NBu_4ClO_4	CVA (Pt)	108
15	$(4\text{-}FC_6H_4CO\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.73	DMF	NBu_4ClO_4	CVA (Pt)	108
16	$(4\text{-}CF_3C_6H_4CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	1.65	DMF	NBu_4ClO_4	CVA (Pt)	108
17	$(4\text{-}CF_3C_6H_4CO\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.51	DMF	NBu_4ClO_4	CVA (Pt)	108
18	$(4\text{-}NC_5H_4CO\text{-}\eta^6\text{-}C_6H_5)Cr(C_6H_6)$	1.61	DMF	NBu_4ClO_4	CVA (Pt)	108
19	$(4\text{-}NC_5H_4CO\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.45	DMF	NBu_4ClO_4	CVA (Pt)	108
20	$[1,2\text{-}(C_2H_5OCO)_2C_6H_4]_2Cr$	1.87	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
21	$(NCC_6H_5)Cr(C_6H_6)$	2.52	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
22	$(NCC_6H_5)Cr(C_6H_5CH_3)$	2.54	DMSO	NBu_5BF_4	RRDE (Hg/Au)	109
23	$(NCC_6H_5)Cr(C_6H_5OCH_3)$	2.52	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
24	$(NCC_6H_5)Cr(C_6H_5F)$	2.39	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
25	$(NCC_6H_5)Cr(C_6H_5Cl)$	2.28	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
26	$(NCC_6H_5)Cr(C_6H_5CF_3)$	2.26	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
27	$(NCC_6H_5)Cr(C_6H_5COCH_3)$	1.97	DMSO	NBu_4BF_4	RRDE (Hg/Au)	109
28	$(NCC_6H_5)_2Cr$	2.18	DMSO	NBu_4BF_4	RRDE (Hg/Au)	65
29	$[(C_6H_5)_3Si\text{-}\eta^6\text{-}C_6H_5]_2Cr$	2.813	DME (−50 °C)	NEt_4ClO_4	CVA (CG)	66
30	$(\eta^6\text{-}C_{10}H_8)_2Cr$	3.126[b]	THF	NBu_4PF_6	CVA (Pt)	49
		1.84[b]	EDA	NBu_4PF_6	CVA (Pt)	49
31	$(C_6H_6)Cr(\mu\text{-}\eta^6,\eta^6\text{-}C_{10}H_8)Cr(C_6H_6)$	1.10[b]	THF	NBu_4PF_6	CVA (Pt)	49
32	$[(\mu\text{-}\eta^6,\eta^6\text{-}C_{10}H_8)Cr]_n$	2.04[b]	EDA	NBu_4PF_6	CVA (Pt)	49
33	$(C_{14}H_{10})_2Cr$	2.235	DMF	NBu_4ClO_4	CVA (CG)	69
34	$(C_5H_5As)_2Cr$	1.36	DME	NBu_4ClO_4	CVA (CG)	54
35	$(CH_3BC_5H_5)_2Cr$	1.26	CH_2Cl_2	NBu_4PF_6	CVA (Pt)	70
36	$(C_6H_5\text{-}\eta^6\text{-}BC_5H_5)_2Cr$	1.01	CH_2Cl_2	NBu_4PF_6	CVA (Pt)	70

Reference electrodes: [a] 1×10^{-3} M $Ag/AgClO_4$; [b] $Ag/AgNO_3$.

The agreement between the reaction constants ρ in the Hammett equation for the electrochemical reduction of the noncoordinated ketones $4\text{-}XC_6H_4COC_6H_5$ and their asymmetric complexes $(4\text{-}XC_6H_4COC_6H_5)Cr(C_6H_6)$ and the symmetrical complexes $(4\text{-}XC_6H_4COC_6H_5)_2Cr$ [108] as well as the small difference between the rate constants for the dimerisation of the radical-anions of benzylideneacetophenone and bis(benzylidene-acetophenone)-chromium can serve as additional arguments in support of the conclusion that the electronic changes in the course of the electrochemical reduction of the complexes are localised on the π-orbitals of the ligand.[50]

The structure of the radical-anions formed on electrochemical reduction or by chemical generation also confirms this conclusion. According to EPR data, the unpaired electron in the radical-anions of ketones,[108] trimethylsilyl-substituted derivatives of dibenzenechromium[110] and dibenzonitrilechromium,[111] as well as unsubstituted dibenzenechromium[112] and the isoelectronic cyclopentadienyl(cycloheptatrienyl)chromium[106] is localised on the molecular orbital the main contribution to which comes from the ligand π-orbital.

The involvement in the cathodic reduction of the zerovalent chromium π-complexes of the LUMO which has predominantly the character of the ligand π-orbital makes it possible to estimate the changes in the reactivity of the arenes due to the formation of complexes with the chromium atom by comparing the characteristic features of the electrochemical reduction of the chromium π-complexes and the corresponding arenes containing identical electrochemically active groups. This approach is characteristic of the majority of studies (in general not very numerous) of the cathodic reactions of diarenechromium(0) complexes.

Another feature of the electrochemical reduction reactions of diarenechromium complexes distinguishing them from the reversible reaction (2) is the greater complexity of the cathodic processes. The overall processes are as a rule irreversible, consist of many stages, and are characterised by the involvement of several electrons and protons, possible retardation of the electron transfer stages, and the presence of stages involving chemical reactions of the intermediates.

The choice of the potentials $E^{C}_{1/2}$ and $E^{A}_{1/2}$ as the reactivity criteria makes it necessary to justify the comparability of these quantities for complexes of different structure and also for pairs of complex–arene compounds with isotypical electroactive groups. This presupposes in its turn that the preliminary kinetic study of the mechanisms of the electrochemical reduction of the test compounds is carried out and the potential determining stage of the overall process is discovered under identical conditions. This problem, which is of independent interest also for electrochemical

Table 5. Comparative characteristics of the electrochemical reduction of arenes and diarenechromium complexes.[24, 61, 65, 107]

System	Compound	$-E^{A}_{1/2}$/V $-E^{C}_{1/2}$/V	$-\Delta E^{CA}_{1/2}$/V	$-\lg\frac{K^C}{K^A}$	$-E^{+/0}_{1/2}$/V
I	$C_6H_5C_6H_5$	2.50	0.10	1.7	0.66
	$(C_6H_5\text{-}\eta^6\text{-}C_6H_5)_2Cr$	2.60			
II	$C_2H_5OCOCH=CHC_6H_5$	1.76	0.08	1.4	0.55
	$(C_2H_5OCOCH=CHC_6H_5)_2Cr$	1.84			
III	$(C_6H_5)_3C_6H_3$	2.29	0.08	1.4	0.53
	$[(C_6H_5)_3\text{-}\eta^6\text{-}C_6H_3]_2Cr$	2.37			
IV	$C_6H_5COCH=CHC_6H_5$	1.37	0.05	0.9	0.50
	$(C_6H_5COCH=CH\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.42			
V	$CH_3COC_6H_5$	1.94	0.04	0.7	0.38
	$(CH_3COC_6H_5)_2Cr$	1.98			
VI	$HCOC_6H_5$	1.80	0.31	5.3	0.51
	$(HCOC_6H_5)Cr(C_6H_6)$	2.11	0	0	0.27
	$(HCOC_6H_5)_2Cr$	1.80			
VII	$CF_3C_6H_5$	2.46	0	0	0.24
	$(CF_3C_6H_5)_2Cr$	2.46			
VIII	$1,2\text{-}(C_2H_5OCO)_2C_6H_4$	1.88	−0.01	−0.2	0.20
	$[1,2\text{-}(C_2H_5OCO)_2C_6H_4]_2Cr$	1.87			
IX	NCC_6H_5	2.21	0.31	5.3	0.46
	$(NCC_6H_5)Cr(C_6H_6)$	2.52	−0.03	−0.5	0.14
	$(NCC_6H_5)_2Cr$	2.18			

kinetics, has been examined in greatest detail in several studies[50, 61, 65, 107, 109] of the mechanisms of the electrochemical reduction of 17 diarenechromium complexes with different substituents in DMSO.

The complexity of the kinetics of the multistage electrode processes necessitates the use of methods which yield, together with the usual polarisation characteristics, information about the appearance during the reaction of unstable intermediates (including free-radical or radical-ion intermediates), their nature, and properties.

In the study of the electrochemical reduction of chromium π-complexes, such methods were cyclic voltammetry at normal and reduced (cryoelectrochemical measurements) temperatures, EPR with electrochemical or chemical generation of paramagnetic species, and the method of a rotating ring-disc electrode.

The method of a rotation ring-disc electrode (RRDE), proposed by Frumkin and Nekrasov[113, 114] and representing a definite alternative to cyclic voltammetry, is based on the use of a single mechanical system consisting of two concentric electrodes—a disc and a ring—located in a single plane and separated by a thin insulating layer. The electrochemical reaction investigated is carried out at the disc electrode and the resulting unstable intermediate or stable final product of the reaction passes to the layer of solution near the electrode and is supplied by the convective stream of liquid to the ring, with the aid of which it can be detected in terms of its oxidation or reduction current. The comprehensive and in certain respects also unique possibilities of the method have led to its wide scale employment in electro-chemical kinetics, including studies on the electrochemistry of organic compounds.[115–118]

The existence of the reaction involving electrochemical oxidation to the cation, which is universal for the diarenechromium(0) complexes [reaction (2)], makes these compounds convenient objects for the study of their cathodic behaviour by the RRDE method. This reaction makes it possible to detect at the ring electrode all the intermediates of the cathodic process. The yield of the corresponding products can be inferred from the anodic limiting current at the ring and the dependence of the yield of the products on the rate of rotation of the electrode yields information about their stability in further reactions. The values of $E^{C}_{1/2}$ for the wave observed at the ring help to identify the species detected.

The first complex whose cathodic reduction was achieved proved to be benzene(biphenyl)chromium.[15] At the present time, the cathodic reduction reactions have been investigated for a wide range of diarenechromium complexes containing the COR, CN, C=C, C_6H_5, and other groups as substituents (Table 4).

Like benzene, unsubstituted dibenzenechromium has an extremely low electron affinity. The report of the direct electrochemical reduction of benzene to the radical-anion did not appear[119] until 1988 ($E_{1/2}$ = −3.38 V). Despite repeated attempts,[4, 56, 101] dibenzenechromium has not yet been reduced at the electrode, although it has been possible to obtain[112] its radical-anions chemically by treatment with potassium in dimethoxyethane in the presence of a crown-ether at −70 °C.

Compared with dibenzenechromium, its asymmetric analogue cyclopentadienyl(cycloheptatrienyl)chromium has a higher electron affinity:[51] it is reduced at carbon glass, the potential of the cathodic peak being E_{pc} = −2.90 V (DME, −35 °C). Ferrocene, which is isoelectronic with dibenzenechromium, is also reduced[120] at the cathode ($E_{1/2}$ = −2.93 V, DMF, −30 °C).

The introduction into the benzene or dibenzenechromium molecule of groups reducing the electron density in the benzene ring and increasing the extent of the conjugation chain ensures the electrochemical reduction of these compounds in the range of electrochemical potentials accessible to measurements.

The electrochemical reduction reactions of the majority of complexes investigated are usually characterised, like those of the non-coordinated arenes, by the presence of several waves on the polarisation curves corresponding to different macroscopic reaction stages. In the literature, attention is concentrated on the first cathodic waves, while the nature of the subsequent waves has been studied in less detail.

In the analysis of the characteristics of the cathodic process, the test compounds can be usefully divided into several groups. Each of these groups includes a series of π-complexes–corresponding arene systems. The formal criteria of the assignment of substances to a particular group are the number of added electrons n in the range of potentials of the first cathodic wave and the presence or absence of similarity in other process characteristics in this range of potentials in the electrochemical reduction of the π-complex and the arene in aprotic media.

Table 6. Parameters of the electrochemical reduction and oxidation of diarenechromium complexes and of the reduction of the corresponding arenes at an amalgamated gold rotating disc electrode in DMSO.[50,61,65]

Compound	Reduction									Oxidation		
	A wave			*B* wave			*C* wave			*Z* wave		
	$-E_{1/2}$/V	*n*	*b*/V	$-E_{1/2}$/V	*n*	*b*/V	$-E_{1/2}$/V	*n*	*b*/V	$-E^{+/0}_{1/2}$/V	*n*	*b*/V
$C_6H_5COCH=CHC_6H_5$	1.41	1	0.060				2.00	1	0.10			
$(C_6H_5COCH=CH\text{-}\eta^6\text{-}C_6H_5)_2Cr$	1.46	1	0.060	1.62	1	0.090	2.10	2	0.10	0.535	1	0.060
$C_2H_5OCOCH=CHC_6H_5$[a]	1.80	1	0.060				2.28	1	0.10			
$(C_2H_5OCOCH=CHC_6H_5)_2Cr$	1.88	1	0.070	2.09	1	0.100	2.82	1	0.10	0.59	1	0.060
$HCOC_6H_5$	1.84	1	0.060				2.30	1	0.08			
$(HCOC_6H_5)Cr(C_6H_6)$	2.15	1	0.060				2.56	1	0.08	0.55	1	0.058
$(HCOC_6H_5)_2Cr$	1.84	1	0.060	2.24	1	0.080	2.69	1	0.10	0.31	1	0.058

[a] Data of Nekrasov and Korotkov.[121]

The mechanisms of the reduction of the π-complexes combined in one group are identical or similar. Different mechanisms of the cathodic processes correspond to different groups of complexes, which constitutes in essence but not formally the basis of the adopted classification. The mechanism of the electrochemical reduction of arenes is in some cases fully identical with that for the π-complexes of the given group (carbonyl compounds, activated olefins), whilst in others, together with the general similarity, there is also an appreciable difference between them (nitriles).

The first group includes aldehydes, ketones, esters, and their vinylogues of the benzene and dibenzenechromium series. The similarity of the electrochemical behaviour under the conditions of the cathodic reaction is characteristic of compounds of this group.[16,50,65,108] In particular, it is manifested by the presence on the polarisation curves of one-electron reduction waves for both the free arenes and their chromium complexes and also by the similarity of the polarisation characteristics of each component of the Arene–$Arene_2Cr$ system (Table 6). In many instances, it has been possible with the aid of the RRDE method,[50,65] cyclic voltammetry, and EPR[108] to observe directly the formation of one-electron transfer products—radical-anions capable of dimerising.

Such similarity was first established[16] on the basis of classical polarographic data, potentiodynamic measurements, coulometry, and preparative electrolysis at a controlled potential and subsequent analysis of the reaction products when the electrochemical reduction reactions of aromatic carbonyl compounds and benzene(benzophenone)chromium were compared in DMF and aqueous alcoholic solutions of different acidity. The polarogram for the reduction of benzene(benzophenone)-chromium in DMF shows two one electron-waves with the potentials $E_{1/2}$ = −1.91 and −2.01 V. The first cathodic wave corresponds to the formation of the radical-anion, while the product of the two electron transfer is a dianion, which is unstable and is rapidly protonated to the alkoxide ion. The latter decomposes slowly in its turn in the bulk of the solution with rupture of the C–C bond and the formation of dibenzene-chromium. It follows from the comparison of the half-wave potentials for the reduction of benzene(benzophenone)chromium ($E_{1/2}$ = −1.91 V) and of the free benzophenone ($E_{1/2}$ = −1.72 V) that the coordination of the benzophenone molecule to the π-C_6H_6Cr fragment hinders the reduction reaction. Comparison of the values of $E_{1/2}$ for a series of ketones C_6H_5COX, where X = CH_3, $C_6H_6CrC_6H_5$, H, or C_6H_5, led the authors to the conclusion that dibenzenechromium resembles the methyl group as a substituent. The Taft substituent constant σ_T for the $C_6H_6CrC_6H_5$ group, found by interpolation, proved to be 0.19.

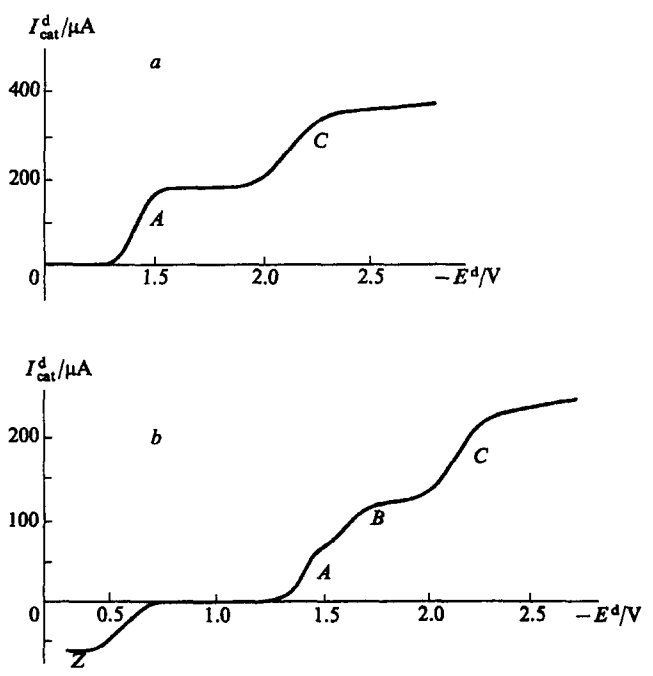


Figure 2. Polarisation curves at the rotating disc electrode in solutions of benzylideneacetophenone ($c = 2\times10^{-3}$ M) (*a*) and bis(benzylidene-acetophenone)chromium ($c = 9.4\times10^{-4}$ M) (*b*) in DMSO in the presence of 0.1 M $N(C_4H_9)_4BF_4$ (ω = 528 s^{-1}).

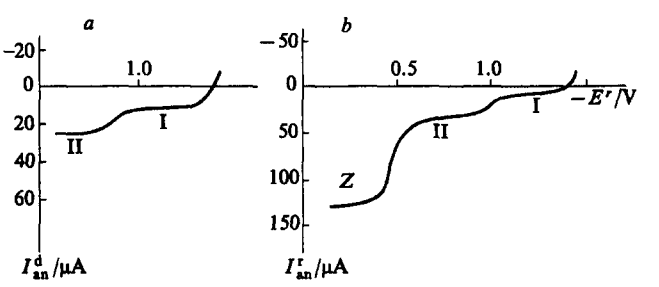


Figure 3. Polarisation curves for the anodic oxidation at the ring electrode of the products of the electrochemical reduction at the disc electrode of benzylideneacetophenone ($c = 4\times10^{-4}$ M) (*a*) and bis(benzylidene-acetophenone)chromium ($c = 2\times10^{-3}$ M) (*b*); E^d = −1.51 V, ω = 214 s^{-1}.

The polarisation characteristics ($E_{1/2}$, the slope b, the number of electrons n participating in the reaction) of all the electrochemical reduction waves (A, B, C) of a series of chromium π-complexes and the non-coordinated arenes, belonging to the first group of compounds, obtained with the aid of an amalgamated gold rotating disc electrode in solutions in DMSO with tributylammonium tetrafluoroborate ($TBABF_4$) as the supporting electrolyte, are presented in Table 6, which also contains analogous data on the Z waves for the electrochemical oxidation of the same complexes.

The kinetics and mechanisms of the electrochemical reduction of benzylideneacetophenone and bis(benzylideneacetophenone)-chromium have been investigated in greatest detail.[50] The polarisation curves for these compounds are presented in Fig. 2, while the corresponding quantitative characteristics are in Table 6. The A waves for the electrochemical reduction of both substances correspond to the reversible addition of one electron and the formation of radical-anions, detected by the RRDE method (I waves in Fig. 3):

$$C_6H_5CH=CHCOC_6H_5 \underset{-\bar{e}}{\overset{+\bar{e}}{\rightleftarrows}} C_6H_5CH=CHCOC_6H_5]^{\cdot -},$$

$$(C_6H_5CH=CHCOC_6H_5)_2Cr \underset{-\bar{e}}{\overset{+\bar{e}}{\rightleftarrows}}$$

$$\leftrightarrows (C_6H_5CH=CHCOC_6H_5)_2Cr]^{\cdot -} .$$

The cathodic B wave for the reduction of the complex can be related to the addition of an electron to the second ligand of the complex radial-anion. This wave is absent from the polarisation curve for the free arene. The C waves correspond to further reduction reactions of the radical species, and the Z waves (Figs. 2*b* and 3*b*) correspond to the electrochemical oxidation of the initial complex. The radical-anions derived from both compounds are unstable and enter into a dimerisation reaction, whose products are also detected at the ring electrode (II waves in Fig. 3).

Thus in the region of the potentials of the A waves, a two-stage reaction takes place: the reversible one-electron transfer stage is followed by the bimolecular chemical dimerisation reaction, which exerts a definite effect on the parameters of the electrode process (EC mechanism), as a consequence of which the A waves acquire a quasi-reversible character.[122]

The potentials $E^A_{1/2}$ and $E^C_{1/2}$, measured by the rotating electrode method under the conditions of the operation of the above electrochemical reduction mechanism, are[123,124] functions of the angular rate of rotation of the electrode ω, the depolariser concentration c, and the dimerisation constant of the radical species k_d:

$$E_{1/2} = E_0 + \frac{2.3RT}{3F}\lg 0.864\left(\frac{\nu}{D}\right)^{1/3} + \frac{2.3RT}{3F}\lg\frac{k_d c}{\omega} , \qquad (10)$$

where F is the Faraday constant, D the diffusion coefficient of the reactant, and ν the kinematic viscosity of the solution.

The experimental[50] dependences of $E^A_{1/2}$ and $E^C_{1/2}$ on $\lg\omega$ at different concentrations c are presented in Fig. 4. They consist of two linear sections—inclined and horizontal. The first reflects the influence of the dimerisation reaction on the half-wave potential. The rates obtained experimentally, $\Delta E^A_{1/2}/\Delta\lg\omega = -0.023$ V, $\Delta E^A_{1/2}/\Delta\lg c = -0.021$ V (for benzylideneacetophenone) and $\Delta E^C_{1/2}/\Delta\lg\omega = -0.021$ V [for bis(benzylideneacetophenone)-chromium] proved to be similar to the values predicted by theory for radical dimerisation ($2.3RT/3F = \pm 0.019$ V). For low concentrations c and high values of ω, the potentials $E^A_{1/2}$ and $E^C_{1/2}$ are independent of further increase in the rate of rotation of the electrode (the horizontal section of the curves in Fig. 4), since the rapid removal of the radical-anions from the layer near the electrode prevents the influence of their dimerisation on the electrode process, which becomes fully reversible under the given conditions. The radical-anions are then detected at the ring electrode with 100% yield, while the II oxidation waves for the dimers are absent. The rate constants for the dimerisation of the benzylideneacetophenone and bis(benzylideneaceto-phenone)-chromium radical-anions were calculated by Eqn. (10) from the experimental data obtained by the rotating disc electrode method:

$$k^A_d = (2.1 \pm 0.2) \times 10^4 \text{ litre mol}^{-1}\text{ s}^{-1},$$

$$k^C_d = (1.5 \pm 0.7) \times 10^4 \text{ litre mol}^{-1}\text{ s}^{-1} .$$

Similar values of k^A_d and k^C_d were also determined by an independent procedure using the RRDE method and a semiempirical calibration curve[125] relating the yield of the radical-anions at the ring electrode to the dimerisation rate constant:

$$k^A_d = (1.5 \pm 0.3) \times 10^4 \text{litre mol}^{-1}\text{ s}^{-1},$$

$$k^C_d = (1.2 \pm 0.5) \times 10^4 \text{ litre mol}^{-1}\text{ s}^{-1} .$$

The small difference between the rate constants for the dimerisation of the radical-anions of the π-complex and the free arene is striking.

A similar EC mechanism of the electrochemical reduction reactions is characteristic also of other classes of substances of the benzene and dibenzenechromium series forming part of the first group of compounds, including those listed in Table 6.

The mechanism is modified somewhat and simplified for benzophenone derivatives. Because of the high stability of the radical-anion of benzophenone itself and apparently also the radical-anions of the π-complexes containing benzophenone and its substituted derivatives as ligands,[108] the chemical stage of the reaction which follows electron transfer, does not occur in the layer near the electrode even when the solution is gently stirred.[126] The only potential-determining stage of the process is the reversible addition of an electron, a situation similar to that observed for the electrochemical reduction of benzylideneacetophenone and its chromium complex at comparatively high rates of rotation of the disc electrode.

The second group of compounds comprises mainly aromatic and complex nitriles (Table 7). An important feature of these substances is that nitriles of the dibenzenechromium series behave

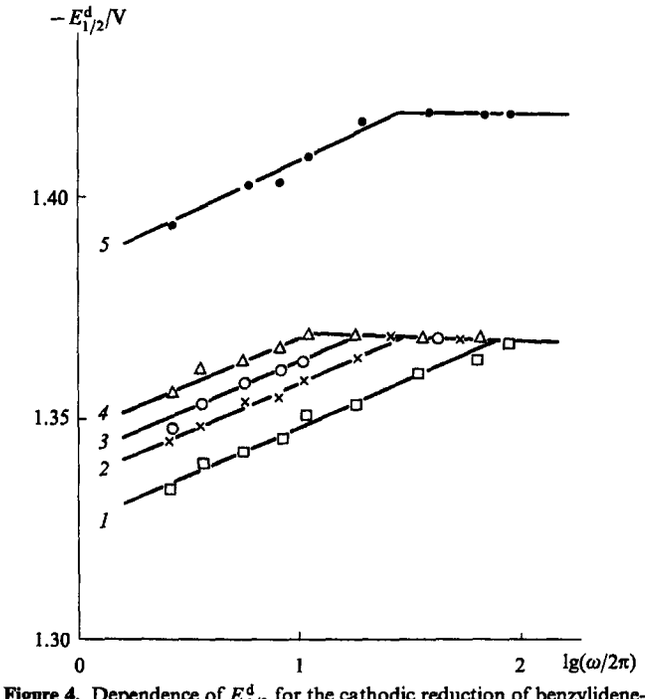


Figure 4. Dependence of $E^d_{1/2}$ for the cathodic reduction of benzylideneacetophenone (lines *1*–*4*) and bis(benzylideneacetophenone)chromium (line *5*) at a rotating disc electrode in solutions in DMSO on the logarithm of the angular rate of rotation of the disc electrode at different molar concentrations of the reactants: (*1*) 2×10^{-3}; (*2*) 8×10^{-4}; (*3*) 4×10^{-4}; (*4*) 2×10^{-4}; (*5*) 5.4×10^{-4}.

Table 7. Characteristics of the electrochemical reduction reactions of nitrile derivatives of benzene and dibenzenechromium.[109]

N	Compound	Cathodic wave *A*			Cathodic wave *B*		
		$-E_{1/2}$, V	*n*	Reaction products detected at ring electrode	$-E_{1/2}$, V	*n*	Reaction products detected at ring electrode
1	C_6H_5CN	2.25	1	$[C_6H_5CN]^{\cdot-}$			
2	1,4-$CH_3C_6H_4CN$	2.40	1	$[1,4\text{-}CH_3C_6H_4CN]^{\cdot-}$			
3	1,3-$C_6H_4(CN)_2$	1.74	1	$[1,3\text{-}C_6H_4(CN)_2]_2^{2-}$			
4	1,2-$C_6H_4(CN)_2$	1.62	1	$[1,2\text{-}C_6H_4(CN)_2]^{\cdot-}$	2.55	2	$[C_6H_5CN]^{\cdot-}$, CN^-
5	1,4-$C_6H_4(CN)_2$	1.62	1	$[1,4\text{-}C_6H_4(CN)_2]^{\cdot-}$	2.40	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	$[1,2,4,5\text{-}C_6H_2(CN)_4]^{2-}$
7	$(NCC_6H_5)Cr(C_6H_5CH_3)$	2.58	2	CN^-, $(C_6H_6)Cr(C_6H_5CH_3)$			
8	$(NCC_6H_5)Cr(C_6H_6)$	2.56	2	CN^-, $(C_6H_6)_2Cr$			
9	$(NCC_6H_5)Cr(C_6H_5OCH_3)$	2.56	2	CN^-, $(C_6H_6)Cr(C_6H_5OCH_3)$			
10	$(NCC_6H_5)_2Cr$	2.22	2	CN^-, $(C_6H_6)Cr(C_6H_5CN)$	2.56	2	CN^-, $(C_6H_6)_2Cr$
11	$(NCC_6H_5)Cr(C_6H_5F)$	2.43	2	$(NCC_6H_5)Cr(C_6H_6)$	2.56	2	CN^-, $(C_6H_6)_2Cr$
12	$(NCC_6H_5)Cr(C_6H_5Cl)$	2.32	2	$(NCC_6H_5)Cr(C_6H_6)$, Cl^-	2.56	2	CN^-, $(C_6H_6)_2Cr$
13	$(NCC_6H_5)Cr(C_6H_5CF_3)$	2.30	6	$(NCC_6H_5)Cr(C_6H_5CF_3)$, $(C_6H_6)Cr(C_6H_5CF_3)$, CN^-			
14	$(NCC_6H_5)Cr(C_6H_5COCH_3)$	2.01	1	$[(NCC_6H_5)Cr(C_6H_5COCH_3)]^{\cdot-}$	2.30	0.4	CN^-, unidentified complexes

differently from the nitriles of the aromatic series under the conditions of cathodic reduction in aprotic media (DMSO, THF).[109] The main difference consists in the absence of reversible one-electron waves from the polarisation curves for the electrochemical reduction of complexes **7–13**§ and their appearance in the reduction of the non-coordinated compounds **1–6**. Instead of the one-electron waves, the polarisation curves for the complex nitriles show one (mononitrile) or two (dinitrile) irreversible two-electron waves. A characteristic feature of the π-complexes, assigned to the second group of compounds, is the occurrence of a rapid chemical reaction with participation of the intermediate products of the one-electron transfer, leading to the elimination of the cyano-group or halogen atoms if the latter form part of the molecule.

In view of the uncertainty in the pathways leading to the reduction of nitriles of different structure, direct comparison of the characteristic features of the reduction of benzonitrile and its π-complexes, necessary for the quantitative comparison of the reactivities, proves insufficient to obtain objective information about the similarities and differences between the mechanisms of the electrochemical reduction of the two types of compounds. The approach based on a comparison of the electrochemical properties of complexes of the type $(NCC_6H_5)Cr(C_6H_5X)$ in a series of cyanobenzenes is more effective. For this reason, Table 7 includes, together with the characteristics of the electrochemical reduction of the π-complexes and free benzonitrile, also the analogous data for the isomers of dicyanobenzene and tetra-cyanobenzene.

In the range of potentials of the *A* wave for the electrochemical reduction of benzonitriles, stable radical-anions can be detected in quantitative yields by the RRDE method. An exception is *m*-dicyanobenzene, whose radical-anions are unstable. The reactivity of the radical-anions depends on the molecular structure. The radical-anions derived from mononitriles and 1,3-dicyanobenzene are not reduced at the electrode in the range of potentials accessible to measurements. A shift of the potential towards negative values by almost 1 V compared with $E^A_{1/2}$ for the formation of the radical-anions (*B* waves) is necessary for the electrochemical reduction of the radical-anions of the *ortho*- and *para*-isomers of dicyanobenzene and 1,2,4,5-tetracyanobenzene.

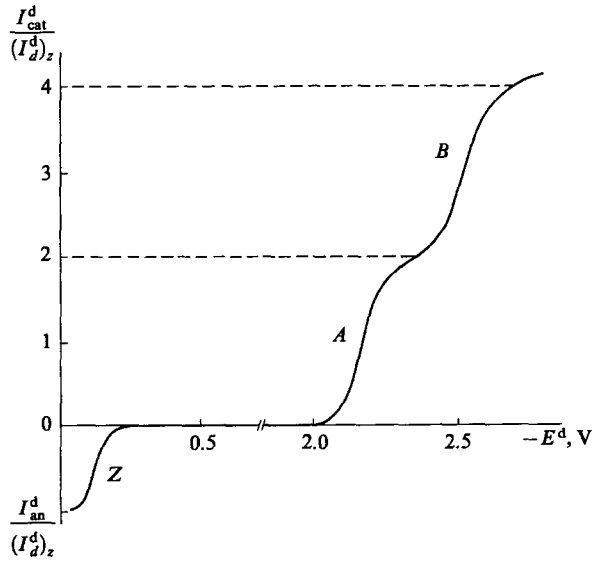


Figure 5. Normalised polarisation curve for the anodic oxidation and cathodic reduction of dibenzonitrilechromium at a rotating disc electrode in DMSO.

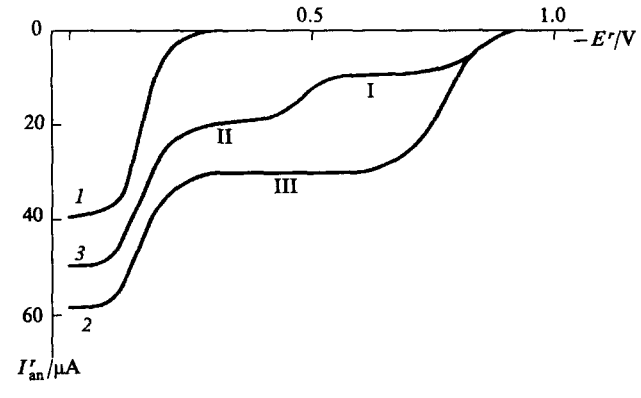


Figure 6. Polarisation curves for the electrochemical oxidation at the ring electrode of the product of the electrochemical reduction of dibenzonitrilechromium at the rotating disc electrode in DMSO at $E^d = -2.4$ V (line *1*) and -2.75 V (line *2*) and for the open circuit of the disc electrode ($I^d = 0$) (line *3*) ($\omega = 250$ s^{-1}). I–III numbers of the waves.

§ Here and henceforth the numbers of compounds in Table 7 are quoted in the text.

The electrochemical reduction of the radical-anions of 1,2- and 1,4-dicyanobenzenes leads to the elimination of one CN group and further reduction of the resulting benzonitrile and its radical-anion.

$$[C_6H_4(CN)_2]^{\cdot-} \xrightarrow[-CN^-,-B^-]{+\bar{e}+BH} C_6H_5CN \overset{+\bar{e}}{\rightleftarrows} [C_6H_5CN]^{\cdot-}$$

The irreversible two-electron *B* wave on the polarisation curves for the reduction of these compounds corresponds to this process. The increase in the number of cyano-groups in the molecule to four is responsible for the reversibility of the electrochemical reduction of the radical-anions of tetracyanobenzene to the dianions, which can be detected with 100% yield.[127]

A completely different picture is observed in the electrochemical reduction of the π-complex nitriles. With the exception of the complex $(NCC_6H_5)Cr(C_6H_5COCH_3)$, whose characteristics in the region of the potentials of the *A* and *B* waves permitted its assignment to the first group of substances, the radical-anions of the complex nitriles could not be detected in any instance by the RRDE method at room temperature, although the formation of the radical-anions of dibenzonitrilechromium as a result of chemical reduction with metallic potassium in dimethoxyethane at −70 °C has been demonstrated by the EPR method.[111] The two-electron *A* waves correspond to the elimination reaction of the CN group (compounds **7**–**10**), the stable products of which, namely the CN^- anion and the complexes $(C_6H_6)Cr(C_6H_5X)$ (X = H, CH_3, OCH_3, CN), can be detected at the amalgamated gold ring electrode.¶ In this respect, the nitriles of the dibenzenechromium series exhibit a greater similarity to the *ortho*- and *para*-isomers of dicyanobenzene than to benzonitrile.

Figure. 5 presents the polarisation curve for the electrochemical oxidation and reduction of the complex $(NCC_6H_5)_2Cr$ at the rotating disc electrode in solution in DMSO normalised with respect to the limiting current of the one-electron anodic oxidation of the complex to the cation (*Z* wave). Each of the cathodic waves (*A* and *B*) is of the two-electron type. Fig. 6 presents voltammograms of the anodic oxidation at the ring electrode of the products of the cathodic reduction of dibenzonitrilechromium at disc potentials E^d corresponding to the limiting currents of the *A* wave (curve *1*) and the *B* wave (curve *2*). In the region of the *A* wave, two products are formed, to which correspond two waves of equal height — the I wave ($E^{I}_{1/2} = -0.82$ V) and the II wave ($E^{II}_{1/2} = -0.46$ V). The current yields for each are 100%. The potentials $E^{I}_{1/2}$ and $E^{II}_{1/2}$ are characteristic of processes involving the formation of mercury cyanide and the oxidation of the complex $(C_6H_6)Cr(C_6H_5CN)$ to the cation respectively. Thus the following reaction takes place in the region of the potential of the *A* wave:

$$(NCC_6H_5)_2Cr \xrightarrow[-CN^-,-B^-]{+2\bar{e}+BH} (C_6H_6)Cr(C_6H_5CN)\,.$$

At the potentials of the *B* wave, a single III wave is observed at the ring electrode, its height exceeding by a factor of 3 that of the I wave on curve *1*. This finding is associated with the simultaneous occurrence of two anodic reactions with similar potentials $E_{1/2}$ — the oxidation of dibenzenechromium ($E^{+/0}_{1/2} = -0.76$ V) and the formation of $Hg_2(CN)_2$ as a result of the elimination of two cyano-groups from this initial complex. Consequently the following overall process takes place in the range of potentials of the *B* wave:

$$(NCC_6H_5)_2Cr \xrightarrow[-2CN^-,-2B^-]{+4\bar{e}+2BH} (C_6H_6)_2Cr\,,$$

and the *B* wave itself characterises the elimination of the second cyano-group from the intermediate product — benzene(benzonitrile)chromium.

¶ The detection of the CN^- anions is based on the appearance in their presence in the layer near the ring electrode of the mercury oxidation wave with formation of mercury cyanide $Hg_2(CN)_2$ ($E_{1/2} = -0.82$ V).

Analysis of the reaction products by the RRDE method (Table 7) shows that, in the electrochemical reduction of the complex nitriles $(NCC_6H_5)Cr(C_6H_5X)$, where X = F, Cl, CF_3, the elimination of the CN group (*B* wave) is preceded by the elimination of the halogen (*A* wave).

An extremely important factor is the closeness of the slopes of the *A* wave for all the compounds included in Table 7 to 0.06 V regardless of the number of added electrons *n* and the reversible (aromatic nitriles) or irreversible (π-complexes) nature of the wave. This means that the electrochemical reduction of complex nitriles includes a chemical reaction between two electron transfer stages (ECE mechanism) and that the potential determining stage in the overall irreversible process is the reversible addition of the first electron to the initial molecule, which leads to the formation of unstable radical-anions.

The different behaviour at the cathode of free aromatic nitriles and their chromium complexes is due to the marked destabilisation of the radical-anions in the case of coordinated compounds, which diminishes the lifetime of these species compared with the radical-anions of the type $(XC_6H_4CN)^{\cdot-}$ by several orders of magnitude. The instability of the radical-anions of the complex nitriles is not related to their direct reduction at the electrode and is determined by their chemical decomposition via one of two possible pathways: the elimination of the cyano-group (halogen atom) from the radical-anion (a first-order reaction) with subsequent addition of a second electron to the free radical formed or disproportionation of the radical-anion (a second-order reaction) with partial regeneration of the initial complex, which again enters into the electrode reaction, and the formation of a dianion from which the cyano-group is eliminated in the form of the cyanide anion.

The mechanism of the process including the stage involving the reversible transfer of the first electron and the elimination of fluorine atoms operates[61] also in the reduction of trifluoromethylbenzene and its symmetrical chromium complex $(CF_3C_6H_5)_2Cr$. On the polarisation curve for the electrochemical reduction of this complex, it is possible to observe at low depolariser concentrations and for slow rotation of the electrode two waves corresponding to the addition of two (*A* wave) and four (*B* wave) electrons with subsequent formation of the complexes $(CF_3C_6H_5)Cr(C_6H_5CHF_2)$ and $(CF_3C_6H_5)Cr(C_6H_5CH_3)$.

The influence of proton-donating additives (benzoic acid, malonic ester, phenol, water) on the electrochemical reduction of complex nitriles has been investigated.[61] In the presence of additives, the elimination of the cyano-group is replaced by its partial or complete hydrogenation. In the presence of ammonium ions, which are reduced at the electrode more readily than the complex nitriles, the latter limiting current effect occurs[128, 129] — a decrease in the height of the two-electron cathodic waves for the electrochemical reduction of the nitriles to the one-electron level without change in $E_{1/2}$ and in the composition of the products of the cathodic reaction.[61] The cause of this phenomenon is either the interaction of the NH_4^+ ions as proton donor with the intermediate product of the electrochemical reduction of the nitriles (latent limiting current of the second kind) or the replacement of the electrochemical stage involving the addition of a second electron to the initial nitrile molecule by the stage in which the radical-anion is reduced chemically by the ammonium amalgam formed in the course of the reaction (latent limiting current of the first kind).

The third group of compounds includes aromatic hydrocarbons — phenylbenzenes and condensed systems as well as their chromium complexes. The electrochemical reduction reactions of the π-complexes containing naphthalene,[49] phenanthrene,[69] and biphenyl[48] as ligands were investigated by cyclic voltammetry, while the pairs of compounds[24, 61] $(C_6H_5)_2$–$[(C_6H_5)_2]_2Cr$ and $(C_6H_5)_3C_6H_3$–$[(C_6H_5)_3C_6H_3]_2Cr$ were studied by the RRDE method.

The first stage in the electrochemical reduction of aromatic hydrocarbons is known to be the reversible addition of an electron. The radical-anions formed are in many instances fairly stable and can be detected by various methods. Their destruction is attributed to the protonation reaction and subsequent transfer of a second electron either from the electrode or from a second radical-anion to the free radical.[130] The final products of the electrochemical reduction of aromatic hydrocarbons are partly hydrogenated compounds. There is every reason to assume that a similar mechanism, including a radical-anion protonation stage, operates also in the reduction of the corresponding π-complexes. The reversibility of the first electrochemical stage is indicated[61] by the slope of the cathodic wave $b \simeq 0.06$ V and the detection of the radical-anions of diphenanthrenechromium[69] and (naphthalene)-dibenzenedichromium.[49] The stability of the radical-anions of the non-coordinated phenylbenzenes appreciably exceeds that of the radical-anions of their π-complexes. Thus radical-anions have been detected in 50 and 100% yields by the RRDE method at the ring electrode at room temperature in the region of the first one-electron waves for the electrochemical reduction of biphenyl and a mixture of triphenylbenzene isomers respectively. In the electrochemical reduction of the corresponding complexes under the same conditions, the first cathodic waves in DMSO are characterised by $n = 4$ (biphenyl) and $n = 2$ (triphenylbenzene) and the radical-anions cannot be detected. The radical-anions of the π-complexes of condensed hydrocarbons are more stable, as a result of which the electrochemical reduction of diphenanthrene-chromium ($n = 1$) proves to be reversible.

There are incomplete literature data on the quasi-reversible one-electron cathodic reduction reactions of di(arsabenzene)-chromium[54] at 25 °C and bis(triphenylsilylbenzene)chromium[66] at −50 °C. The peaks due to the anodic oxidation of the radical-anions of both complexes were detected by cyclic voltammetry, which provides grounds for extending the conclusion that the first electron addition stage is reversible also to these compounds. As in the anodic oxidation reaction, di(arsabenzene)chromium behaves anomalously, being reduced at the cathode ($E^{C}_{1/2} = -1.36$ V) significantly more readily than free arsa-benzene ($E^{A}_{1/2} = -2.08$ V).

Thus, despite the irreversibility of many processes and the significant differences in the nature of the chemical stages of the reaction (dimerisation or protonation of the radical-anion, elimination of electroactive groups), the principal potential determining stage common to all the compounds of the benzene and dibenzenechromium series examined is the reversible addition of the first electron to the depolariser molecule.

IV. Characteristic features of the change in the reactivity of arenes under the influence of coordination to a chromium atom in one-electron transfer reactions

The establishment of the reversibility of the first electron addition stage in the electrochemical reduction reactions of free arenes and diarenechromium complexes is important from the standpoint of the possibility of using irreversible or quasi-reversible cathodic processes in the study of the reactivities of these compounds. On the one hand, there is a prospect of obtaining quantitative data concerning the influence of substituents in complexes, containing identical electrochemically active groups, on the ease of their reduction. In combination with correlation analysis, this makes it possible to assess the nature of the transmission of the electronic effects of substituents in one of the ligands to the reaction centre in the second ligand. Thus the potentials $E^{C}_{1/2}$ for the electro-chemical reduction of the heteroannularly substituted complex nitriles (compounds **7**–**13** in Table 7) are satisfactorily correlated[109] with the sets of substituent constants $\sigma^0_p, \sigma^0_m, \sigma_m$, and σ^+_m ($r = 0.961-0.972$). This indicates the predominantly inductive mechanism of the transmission of electronic effects in the molecule of the complex and agrees with conclusions reached as a result of the study of the reversible anodic oxidation reactions of the diarenechromium(0) complexes[29,61,62] and the ^{19}F NMR spectra.[96]

On the other hand, a basis appears for a quantitative comparison of the reactivities of the free and metal-coordinated arenes in similar electrochemical reduction reactions. A necessary precondition for the solution of this problem is the identity, noted above, of the reaction centres in the arenes and their π-complexes in cathodic reduction. We may note that the identical type of the main potential determining one-electron stage in the electrochemical reduction of the classes of compounds examined justifies the comparison of the potentials $E^{C}_{1/2}$ and $E^{A}_{1/2}$ of the first cathodic waves regardless of the total number of added electrons, which need not necessarily be identical in reactions involving an arene and its π-complex (electrochemical reduction of aromatic and complex nitriles).

For fully reversible processes, the half-wave potential difference $\Delta E^{CA}_{1/2}$ serves as a measure of the change in the reactivity of the arene as a result of its coordination to a chromium atom:

$$\Delta E^{CA}_{1/2} = E^{C}_{1/2} - E^{A}_{1/2} \simeq E^{C}_{0} - E^{A}_{0} = \frac{2.3RT}{F} \lg \frac{K^{C}}{K^{A}} , \qquad (11)$$

where K^{C} and K^{A} are the equilibrium constants of the corresponding redox processes. The quantity $\Delta E^{CA}_{1/2}$ characterises the overall effect of the change in the reactivities of the reactant in the electrochemical reduction reaction and of the radical-anion in the subsequent chemical reaction. Thus when the rotating disc electrode method is used in the case of the dimerisation of the radical-anions, the potentials $E^{C}_{1/2}$ and $E^{A}_{1/2}$ are defined by Eqn. (10) and their difference for $c = \text{const}$ and $\omega = \text{const}$ is defined by the equation

$$\Delta E^{CA}_{1/2} = \frac{2.3RT}{F} \lg \frac{K^{C}}{K^{A}} + \frac{2.3RT}{3F} \lg \frac{k^{C}_{d}}{k^{A}_{d}} + \frac{2.3RT}{9F} \lg \frac{D^{A}}{D^{C}} . \qquad (12)$$

Estimation of the contributions of the second and third terms on the right-hand side of the equation to $\Delta E^{CA}_{1/2}$ showed[50] that, at least for the first group of compounds, these terms can be neglected to a first approximation and the experimental quantity

$$\Delta E^{CA}_{1/2} \simeq \frac{2.3RT}{F} \lg \frac{K^{C}}{K^{A}} ,$$

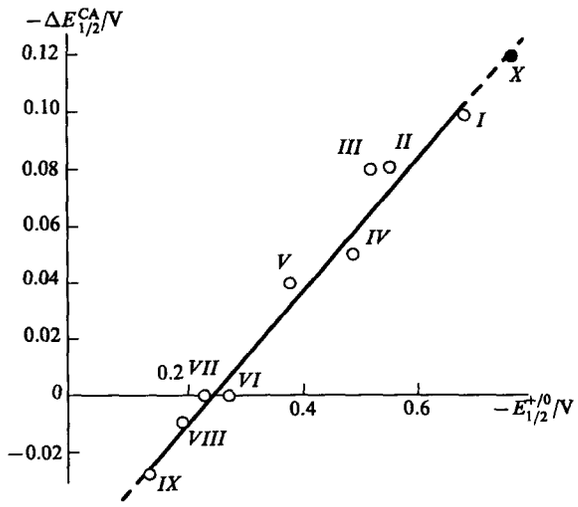


Figure 7. Correlation between $\Delta E^{CA}_{1/2}$ and $E^{+/0}_{1/2}$. The numbering of the points corresponds to the numbering of the Arene–$Arene_2Cr$ systems in Table 5; X = calculated value of $\Delta E^{CA}_{1/2}$ for the C_6H_6–$(C_6H_6)_2Cr$ system.

characterises virtually only the change in the reactivity of the arene in the electrochemical reduction reaction as a result of its coordination to the metal atom.

The quantities $\Delta E_{1/2}^{CA}$ and $\lg(K^C/K^A)$ for a series of systems are presented in Table 5. Analysis of the data in the table permits the conclusion that the formation of π-complexes leads as a rule to a shift of the half-wave potential. The most marked difference is observed on passing from the free arene XC_6H_5 to the asymmetric complex $(XC_6H_5)Cr(C_6H_6)$, in which the arene (benzaldehyde, benzonitrile) is coordinated to the benzenechromium fragment. The value $\Delta E_{1/2}^{CA} = -0.31$ V corresponds to a decrease in the equilibrium constant of the electrochemical reduction reaction of the complex K^C by five orders of magnitude compared with K^A for the arene. Thus the fragment π-C_6H_6Cr plays the role of a very powerful donor relative to the arene, inducing an increase in electron density in the aromatic ring. On formation of symmetrical complexes $(XC_6H_5)_2Cr$, the difference $\Delta E_{1/2}^{CA}$ is significantly smaller and, depending on the nature of the substituent X and also on the number of substituents in the ligands, changes both in absolute magnitude and in sign. These results are fully consistent with data[108] for the Arene–(Arene)Cr(C_6H_6)–$Arene)_2Cr$ system.

It has been established in a study of the characteristics of the cathodic processes for nine pairs of Arene–$Arene_2Cr$ compounds (Table 5)[65, 107] that there is a linear relation between the half-wave potential difference for the electrochemical reduction reactions involving each pair of substances $\Delta E_{1/2}^{CA}$ and the half-wave potential $E_{1/2}^{+/0}$ for the reversible anodic oxidation of the neutral form of the π-complex to the singly charged cation (Fig. 7):

$$\Delta E_{1/2}^{CA} = a' + \alpha' E_{1/2}^{+/0}, \quad (13)$$

where $a' = 0.072 \pm 0.007$ V, $\alpha' = 0.25 \pm 0.015$, and $r = 0.991$.

Since $\Delta E_{1/2}^{CA}$ is defined by Eqn. (11) and $E_{1/2}^{+/0}$ is a linear function[24, 61, 62] of the constants of the *meta*-substituents (σ_m, σ_m^0, σ_m^+), Eqn. (13) can be transformed into

$$\Delta E_{1/2}^{CA} = b' + \beta' \sum \sigma, \quad (14)$$

$$\lg \frac{K^C}{K^A} = g' + \gamma' \sum \sigma, \quad (15)$$

where $b' \simeq -0.125$ V, $\beta' = 0.13$, $g' \simeq -2.17$, $\gamma' = 2.2$, and $\sum\sigma$ is the sum of the Hammett constants of the *meta*-substituents.

Eqns. (13)–(15) correspond to the principle of linear free energy relationships and relate the change in the free energy as a result of the coordination of the arene to the metal atom involving the formation of a symmetrical π-complex to the free energy of the redox reaction (2) or other reactions involving the complexes, the logarithms of the equilibrium constants (rate constants) of which are correlated with the constants of the *meta*-substituents in the aromatic ring.

The unusual feature of Eqns. (13)–(15) and the significant difference between them and the Hammett correlation equations consist in the fact that the quantities $\Delta E_{1/2}^{CA}$ characterise pairs of compounds differing from one another in the nature of the reaction centre—in the electrochemically active group. The existence under these conditions of the linear relations (13)–(15) shows that the correlation equations obtained are based on a cause common to all the Arene–$Arene_2Cr$ systems investigated—the transition of the free arene to the state in which it is coordinated to chromium atom, i.e. on complex formation. In relation to this process, the electroactive groups play the role of substituents in the arene and do not participate directly in the process but do influence the distribution of electron density in the molecule. The electrochemical cathodic reduction reaction is in essence an indicator reaction, which makes it possible to determine the free energy change on transition of the arene to the state where it is coordinated to a chromium atom.

It follows from Eqns. (14) and (15) that the overall effect of the coordination of the arene to chromium consists of two components. The first component, characterised by the first term (b', g') is constant for all the symmetrical diarene-chromium complexes investigated and is responsible for the retardation of the cathodic reaction relative to the electrochemical reduction of the free arene. The second component (the $\beta' \sum\sigma$ and $\gamma' \sum\sigma$ terms) is variable and is determined by the nature and number of substituents in the arene ligands. Substituents with electron-accepting properties compensate to some extent for the inhibition of the reaction induced by the constant component of the coordination effect. In the presence of electron-accepting substituents, which give rise to $E_{1/2}^{+/0} > -0.3$ V, the overall effect of complex formation changes sign and the π-complex is reduced more readily than the corresponding free arene.

The relations obtained make it possible to calculate the potentials $E_{1/2}^C$ and hence also E_0^C for the electrochemical reduction reactions of symmetrical chromium π-complexes, provided that the corresponding values for the free arenes are known. This is of special interest in those cases where the cathodic process does not occur in the range of potentials accessible to measurements. Thus, according to Eqn. (14) the half-wave potential for the electrochemical reduction of dibenzene-chromium should be displaced approximately by 0.125 V towards negative values compared with $E_{1/2}^A$ for benzene. Since the potential for the $C_6H_6^{0/-}$ redox transition found experimentally[119] in solution in dimethoxyethane at −90 °C proved to be −3.38 V, the potential $E_{1/2}^C$ for dibenzene-chromium under these conditions should be about −3.5 V, i.e. should be in the range of potentials of the reduction of the solvent or the supporting electrolyte. This has been confirmed by Gavrilov et al.,[48] who were unable to observe the peak due to the electrochemical reduction of dibenzenechromium before the onset of the reduction of the supporting electrolyte under the conditions of the electrochemical reduction of benzene.

The available experimental data permit certain conclusions concerning the influence of coordination to chromium on the stability of the radical-anions—the intermediates in the electrochemical reduction of arenes and their complexes. In the case of compounds of the first group, the coordination of the arene to the metal has comparatively little effect on the stability of the radical-anions, especially in the presence of a double bond in the side chain [benzylideneacetophenone–bis(benzylideneaceto-phenone)-chromium, ethyl cinnamate–bis(ethyl cinnamate)-chromium]. The stability of the radical-anions falls somewhat as a result of the acceleration of the dimerisation reaction in the sequence $[C_6H_5CHO] > [(C_6H_5CHO)Cr(C_6H_6)] > [(C_6H_5CHO)_2Cr]$, which can be inferred from the decrease in the yield of the radical-anions at the ring electrode. The radical-anions of the complexes in the second group (nitriles) are appreciably less stable than the radical-anions of benzonitrile. They rapidly eliminate CN^- anions and are converted into neutral radicals, which are reduced at the electrode.

Table 8.

Compound	G/V
$(C_6H_6)_2Cr$	2.7
$(CF_3C_6H_5)_2Cr$	2.2
$(NCC_6H_5)_2Cr$	2.0
$(C_6H_5$-η^6-$C_6H_5)_2Cr$	1.9
$[(C_6H_5)_3$-η^6-$C_6H_3]_2Cr$	1.8
$[1,2$-$(C_2H_5OCO)_2C_6H_4]_2Cr$	1.7
$(CH_3COC_6H_5)_2Cr$	1.6
$(HCOC_6H_5)_2Cr$	1.5
$(C_2H_5OCOCH=CHC_6H_5)_2Cr$	1.3
$(C_6H_5COCH=CH$-η^6-$C_6H_5)_2Cr$	0.9

The difference in the behaviour of the radical-anions of the π-complexes belonging to the first and second groups of compounds is apparently due to the different nature of the distribution of the electron density.[131,132] In the radical-anions of free benzonitrile, the spin density is localised predominantly in the *para* and *ortho*-positions in the benzene ring and to a lesser extent on the cyano-group. On the other hand, in the presence of carbonyl groups (C=O, CH=CH−C=O), in the benzene ring, an appreciable proportion of the spin density in the radical-anion is on a carbon atom in the side chain. Naturally, the changes in electron density in the benzene ring induced by the coordination to chromium lead in the case of nitriles to a more significant changes in the stability of the radical-anions than in the case of carbonyl and vinyl derivatives.

Yet another aspect of the problem of the reactivity of the diarenechromium complexes is associated with the concept of the electrochemical gap G defined as the difference between the half-wave potentials for the anodic oxidation and cathodic reduction reactions of the complex.[133] The potentials $E_{1/2}$ characterise the relative energies of the frontier orbitals, while G characterises the difference between the energies of the HOMO and LUMO (energy gap).

Compounds of the benzene series are characterised by a wide electrochemical gap. Thus $G > 6$ V for benzene. The complex formation reaction between benzene and chromium leads to a marked narrowing of the gap (to 2.7 V) due to the fact that the HOMO of the complex is localised on the metal and lies appreciably above the HOMO of benzene, whereas the LUMO of the complex and the arene are of the same type and their energies are similar (see Table 8).

As mentioned above, in the diarenechromium complexes, the HOMO is influenced primarily by the electronegativity of the substituents in the ligands, whereas for the LUMO the conjugation effects are of greatest importance. The different character of the influence of substituents on the $E_{1/2}$ for the electrochemical oxidation and reduction processes, established in a number of studies,[24,29,61,62,65] alters the electrochemical gap. The gap is widest in dibenzenechromium and its derivatives containing substituents with a weak mesomeric effect (CN, CF_3) and is narrowest in complexes whose ligands have a long conjugation chain (ethyl cinnamate, benzylideneacetophenone).

The above analysis of studies on the chemistry of diarenechromium complexes demonstrates the interest in these compounds by chemists concerned with different disciplines. This is due to the characteristic features of the structure and chemical properties of dibenzenechromium and its derivatives and also the possibility of using them as convenient model compounds for the elucidation of general problems of the reactivity of transition metal π-complexes. Studies on these lines, to a large extent based on the investigation of the reversible electron transfer reaction in neutral complex/single charged cation systems, are most numerous and are of direct interest for organoelement chemistry and the chemistry of coordination compounds. The above reaction has also proved useful in the solution of certain problems of theoretical electrochemistry (a test of the theory of the reorganisation of the solvent, the creation of new reference electrodes suitable for the comparison of the results of electrochemical measurements in non-aqueous media of different nature). During the last 25 years, undoubted progress has been achieved also in the study of the kinetics and mechanisms of multistage cathodic processes with participation of diarenechromium(0) complexes.

However, one should note that at the present time the literature contains virtually no published study of preparative electrochemistry—not only on the synthesis of chromium complexes but also on the introduction of functional groups into the latter, although the results of the investigation of the kinetics of redox processes open the way in principle to the electrosynthesis of new compounds of the given class.

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