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Study of redox reactions of bis(arene)chromium complexes by the rotating disk electrode technique

IV *. Electrochemical oxidation and ionization potentials of bis(arene)chromium complexes

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Abstract

The reversible electrochemical oxidation of a series of bis(arene)chromium complexes has been studied by use of the rotating disk electrode technique in aprotic solvent (DMSO). The half-wave potentials $E_{1/2}$ show an excellent correlation with the *meta*-substituent constants. The $E_{1/2}$ values were found to correlate well with the vertical ionization potentials (IP) of the same complexes in the gas phase determined from their He(I) photoelectronic spectra.

One of the characteristic features of transition metal π-complexes is their capability to participate in reactions involving a single electron transfer. Both the oxidation reaction of the bis(arene)chromium complexes by electrochemical techniques and comparison of the half-wave potential values ($E_{1/2}$) with those of their vertical ionization potentials in the gas phase (IP) offer valuable information on the mechanism of substituent-effect transmission in a molecule as well as on the behaviour and energy of the highest occupied molecular orbital (HOMO).

We recently applied the rotating disk electrode (RDE) technique (in DMSO) to the study of the reaction of reversible one-electron oxidation of 20 dibenzenechromium derivatives containing various substituents [2].

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

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* For Part III see ref. 1.

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It has been shown that $E_{1/2}$ values for this process correlate well with various sets of σ constants for *meta*-substituents. The results of the investigation of reaction 1 by the method of cyclic voltammetry in non-aqueous solvents such as DMSO, acetonitrile (AN) and dimethylformamide (DMFA) were published simultaneously [3–7]. The electrochemical oxidation of bis(phenanthrene)chromium in DMFA [7] and of bis(mesitylene)chromium in THF [8] to double-charged $Arene_2Cr^{2+}$ cations has also been reported. Photoelectronic spectra (PES) of dibenzenechromium and its alkyl-, halogen- and other substituted derivatives have been examined previously [9–11]. A linear relationship between $E_{1/2}$ of reaction 1 for a number of sandwich chromium complexes (including three bisarene complexes) and *IP* of the same complexes was found [3]. The standard redox potential values for transition metal sandwich complexes (including dibenzenechromium and bisarene complexes of Mo, Fe, and Ru) were shown to correlate linearly with the gas phase ionization potentials of the respective metals [12].

The present paper is an extension of a previous report [2] and is devoted to the study of the anodic oxidation reactions of a series of symmetrical and unsymmetrical bis(arene)chromium complexes of cyano-, halogen-, phenyl- and phenylethynyl-substituted benzenes. The latter were obtained by us recently [13–18], but had not yet been investigated electrochemically. We have also recorded the photoelectronic spectra of some of the above complexes and compared the first ionization potentials

Table 1

$E_{1/2}$ values for bis(arene)chromium complexes in DMSO and IP_1 values in the gas phase

Compound		$-E_{1/2}$ (V) (NCE)	IP_1 (eV)
$[1,3,5\text{-}(CH_3)_3C_6H_3]_2Cr$	(I)	0.98 [2]	5.01
			5.01 [10]
			4.97 [11]
$(CH_3C_6H_5)_2Cr$	(II)	0.86 [2]	5.24 [9]
			5.31 [11]
$(C_6H_6)_2Cr$	(III)	0.80 [2]	5.40
			5.40 [9]
$(C_6H_5C{\equiv}CC_6H_5)_2Cr$	(IV)	0.72	
$(C_6H_6)Cr(C_6H_5F)$	(V)	0.61	
$[(C_6H_5)_3C_6H_3]_2Cr$ [a]	(VI)	0.57	
$(CH_3C_6H_5)Cr(C_6H_5CN)$	(VII)	0.53	5.73
$(C_6H_6)Cr(C_6H_5CN)$	(VIII)	0.50	5.85
$(CH_3OC_6H_5)Cr(C_6H_5CN)$	(IX)	0.47	5.75
$(FC_6H_5)_2Cr$	(X)	0.425 [2]	5.91 [11]
$(ClC_6H_5)_2Cr$	(XI)	0.385 [2]	5.90 [11]
$(IC_6H_5)_2Cr$	(XII)	0.38	
$[(C_6H_5)_6C_6]_2Cr$ [b]	(XIII)	0.32	
$(CH_3COC_6H_5)Cr(C_6H_5CN)$	(XIV)	0.32	
$(ClC_6H_5)Cr(C_6H_5CN)$	(XV)	0.31	6.09
$(FC_6H_5)Cr(C_6H_5CN)$	(XVI)	0.30	6.14
$(CF_3C_6H_5)_2Cr$	(XVII)	0.28	
$(CF_3C_6H_5)Cr(C_6H_5CN)$	(XVIII)	0.22	6.21
$(CNC_6H_5)_2Cr$	(XIX)	0.175 [2]	6.41

[a] Mixture of isomeric complexes bearing the ligands 1,2,4- and 1,3,5-triphenylbenzene. [b] $E_{1/2}$ for bis(hexaphenylbenzene)chromium were not included in the correlation with the σ constants.

(IP_1) in the gas phase with the half-wave potentials $E_{1/2}$ of anodic oxidation of the same complexes.

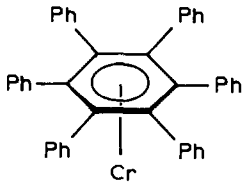
Results and discussion

The half-wave potential values for the reversible one-electron oxidation of a series of bis(arene)chromium complexes are listed in Table 1. For comparison, we have included in the table the $E_{1/2}$ values for dibenzenechromium and a number of symmetrically substituted complexes from ref. [2].

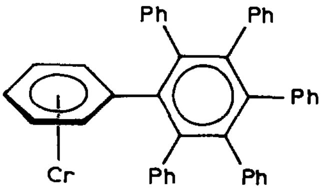
The values of the first ionization potentials of the bis(arene)chromium complexes IP_1 were determined by us from their spectra, or were taken from the literature.

Some of the data collected in Table 1 require special comments. For example, comparison of $E_{1/2}$ value for anisol(benzonitrile)chromium (IX) with that of benzene(benzonitrile)chromium (VII), reveals that the methoxy group has a weak electron-withdrawing ability, which shifts $E_{1/2}$ by 30 mV towards positive values. The same methoxy group effect was observed when analyzing the anodic oxidation of bis(anisol)chromium in DMSO [2,3]. At the same time, when the reaction is carried out in acetonitrile, the methoxy group, according to ref. [4], is a donor of average strength. From the PES data (Table 1), it can be seen that this group is also a donor. One may presume that the weakening of the electron-donor ability of the methoxy group in DMSO is due to the ability of the sulfur atom of the DMSO molecule to coordinate with the lone electron pair of the methoxy group oxygen atom [19].

The effect of the substituents on the half-wave potentials strictly obeys the additivity principle, described previously [2]. Deviation from additivity was observed in the case of bis(hexaphenylbenzene)chromium (XIII). This complex resulted from cyclotrimerization of diphenylacetylene during reaction with chromium [16], and probably has structure **A** in which the chromium atom is coordinated to the central benzene ring.



(A)



(B)

Structure **B**, with the chromium atom coordinated to one of the peripheral rings is less likely, owing to steric hindrance, since the hexaphenylbenzene molecule is not planar and has a propellar structure so that the side phenyl rings partly screen each other [20]. The $E^{\text{exp}}_{1/2}$ value of -0.32 V found experimentally for bis(hexaphenylbenzene)chromium and that calculated according to the additivity rule for structure **A**, $E^{\text{calc}}_{1/2}$ -0.2 V, as well as the comparison of these values with that of $E_{1/2}$ for bis(biphenyl)chromium (-0.7 V [2]) confirms structure **A**. Apparently, the chromium atom in isomeric triphenylbenzene complexes is also coordinated to the central benzene ring.

On the basis of the recent data presented in Table 1, as well as the values of $E_{1/2}$

Table 2

Parameters of the correlation equation (2) for various sets of substituent constants

Substituent constant	Number of points	ρ_π (V)	$-b$ (V)	$-\rho$	r	S_{ρ_π}	S_b
σ_m°	19	0.513	0.789	8.9	0.992	0.016	0.012
σ_m	25	0.541	0.788	9.3	0.986	0.019	0.012
σ_p°	17	0.396	0.675	6.8	0.964	0.028	0.019
σ_p	25	0.350	0.642	6.0	0.920	0.031	0.021

reported in ref. 2, we made a repeat correlation analysis of $E_{1/2}$ using various sets of *meta*-substituent constants *.

$$E_{1/2} = \rho_\pi \Sigma\sigma + b \tag{2}$$

In this equation 'b' represents the half-wave potential of the oxidation of dibenzenechromium, ρ_π the polarographic constant, $\Sigma\sigma$ the sum of the substituent constants for the above-mentioned series. The correlation equation parameters ρ_π, b; the reaction constant $\rho = -\rho_\pi/0.058$; the mean deviations S_{ρ_π} and S_b, and the correlation coefficients r are listed in Table 2.

The results of the correlation analysis are in full agreement with the conclusions in ref. 2, although the values for the parameters of the correlation equation 2 changed only slightly.

From Table 2 it can be seen that there is a good correlation when *meta*-substituent constants are used, the best results being obtained for σ_m° constants. Thus, a study of electrochemical oxidation of the new group of dibenzenechromium derivatives confirms the conclusion made earlier [2] that substituent electronic effects in the arene ligand of the dibenzenechromium molecule are transmitted to the reaction centre at the chromium atom mainly by an inductive mechanism. The resonance effects in the benzene rings are weakened as a result of their coordination with the chromium atom.

The high correlation coefficients permits the use of the $E_{1/2}$ value to determine the values of the substituent constants.

The correlation between the half-wave potentials of the oxidation of bis(arene)chromium complexes and the σ_m substituent constants has been indicated elsewhere [3,4]. However, no correlation coefficient was given in ref. 3, while in ref. 4 the electrochemical experiment was not carried out thoroughly as there is a significant discrepancy (in some cases as high as 0.3 V) in the anodic and cathodic peak potentials in the cyclic voltammograms. A striking contrast between the results of the redox investigation of the benzene chromium complexes and those of the condensed aromatic hydrocarbons [6] was observed. Values of $E_{1/2}$ are independent of the nature of the ligand and are equal to the dibenzenechromium oxidation half-wave potential [6]. Unfortunately, the complexes prepared in the above work by the Fischer–Hafner method have not been fully characterized, whereas the condensed hydrocarbons are known to undergo hydrogenation during this synthesis [23,24]. For this reason, the results obtained are somewhat dubious. According to

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* σ-values were taken from ref. 21, those for $C_6H_5C{\equiv}C$ group from ref. 22.

ref. 7, bis(phenanthrene)chromium prepared from phenanthrene and chromium vapour is oxidized to the corresponding cation at a considerably more positive potential ($E_{1/2}$ −0.65 V, DMFA, SCE) than in the case of unsubstituted dibenzenechromium ($E_{1/2}$ −0.8 V).

Table 1 shows the parallelism between the variation of $E_{1/2}$ in DMSO for dibenzenechromium oxidation and the variation of the first ionization potentials of the same compounds in the gas phase (with the exception of the methoxy group, as was mentioned above). The linear correlation between those values is described by the following correlation equation:

$$E_{1/2} = +0.62(\pm 0.03)IP_1 - 4.08(\pm 0.16) \qquad (3)$$

(Correlation coefficient $r = 0.990$)

The slope of the regression line, which is considerably less than unity, mirrors a significant contribution from the solvation effect to the energetics of the oxidation reaction in solution.

Thus, on the basis of eq. 3, the not readily accessible ionization potentials can be calculated from the electrochemical data for different bis(arene)chromium complexes.

The first ionization potential corresponds to the removal of the electron from the highest occupied molecular orbital of the a_{1g}-type [9] localized predominantly on the $3d_{z^2}$-chromium atomic orbital (according to ESR data on dibenzenechromium(I) cation [25] and quantum chemical calculations [26]). The correlation between $E_{1/2}$ and IP_1 indicates that the photoionization process in the gas phase and the electrochemical oxidation in DMSO involves the same molecular orbital.

Experimental

The polarization measurements were carried out with an amalgamated gold rotating disk electrode in DMSO. Tetrabutylammonium fluoroborate $(C_4H_9)_4NBF_4$ (0.1 M) was used as supporting electrolyte, NCE as the reference electrode. The apparatus, electrochemical techniques and reagent purifications have been described previously [2]. He(I) photoelectron spectra recorded with an ES 3201 spectrometer equipped with a heated sample inlet. The energy resolution was 40 meV, the PE spectra were calibrated against the $^2P_{3/2}$ and $^2P_{1/2}$ Xe lines. The ionization error was ±0.02 eV.

The synthesis of unsymmetrical V, VII–IX, XIV–XVI and XVIII (Table 1) was carried out by co-condensation of chromium and arenes vapours [13–15]. Complexes IV, VI and XIII were prepared by reaction of chromium with phenyl- or diphenylacetylene, respectively [16,17]. Bis(iodobenzene)chromium (XII) was prepared in the form of iodide of the corresponding cation by treating the metallation product of the reaction, dibenzenechromium with the tetramethylethylene diamine complex of butyllithium [18], with iodine.

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