Journal of Organometallic Chemistry, 219 (1981) 43—51
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE STUDY OF REDOX REACTIONS OF BISARENECHROMIUM COMPLEXES BY THE ROTATING DISK ELECTRODE TECHNIQUE

I. OXIDATION OF BISARENECHROMIUM(0) COMPLEXES AND REDUCTION OF BISARENECHROMIUM(I) CATIONS

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(Received April 7th, 1981)

Summary

The redox properties of twenty bisarenechromium complexes have been studied by the rotating disk electrode technique in an aprotic solvent (DMSO). The half-wave potentials, $E_{1/2}$, have been found to correlate well with the *meta*-substituent constants. The conclusion is drawn that the electronic effects of substituents are mainly transferred to the reaction centre (the metal atom) by the inductive mechanism. The conjugation of substituents with the coordinated ring is weaker in bisarenechromium complexes than in ferrocene derivatives.

Electrochemical methods have been widely applied to study redox reactions of transition metal π-complexes. Knowledge of the reactivity of the compound as a function of the substituent provides the possibility of estimating the nature of substituent electronic effects on the reaction centre (the metal atom). This approach has proved fruitful in the chemistry of ferrocene [1—3] and arenecyclopentadienyliron cations [4]. At the same time, electrochemical redox reactions of bisarenechromium compounds have only been studied insufficiently, mostly with alkyl- and arylsubstituted dibenzenechromium compounds [5—11]. The development of synthetic techniques based on metallation of dibenzenechromium and on interactions of aromatic compounds with atomic chromium has provided synthetic routes to dibenzenechromium derivatives containing various substituents and made it possible to study their electrochemical behaviour in detail.

In this work, we have applied the rotating disk electrode technique to study a number of bisarenechromium derivatives containing alkyl, phenyl, carbonyl, methoxy and cyano groups, halogen atoms, and groups with double bonds con-

0022-328X/81/0000—0000/$02.75

jugated with the carbonyl or carbethoxy functions in aprotic media. The relation between the nature of the substituent and the reactivity of the bisarenechromium compound in reversible redox reactions of the type

$$\text{Arene}_2\text{Cr} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{Arene}_2\text{Cr}^+ \qquad (1)$$

has been studied. The half-wave potentials, $E_{1/2}$, for reaction 1 determined from polarization measurements with a rotating disk electrode were taken as measure of the reactivity.

Results and discussion

The twenty bisarenechormium complexes studied in this work are listed in Table 1. All the compounds except for benzene(benzaldehyde)chromium (XIV) and bis(η^6-1,4-diphenylbutane)-μ-(η^6, η^6-1,4-diphenylbutane)dichromium (VI) contain the same substituents in both arene ligands. For compounds I to VIII, XI and XII which are in their oxidized forms, cathode reduction has been studied. Both oxidized and reduced forms of unsubstituted dibenzenechromium (IX) and bis(anisole)chromium (X) have been studied to obtain their cathodic and anodic polarization curves. The other compounds, which are uncharged complexes of zerovalent chromium, have been subjected to disk electrode anodic oxidation.

The redox reactions involving a change of the chromium atom charge proceed by transfer of one electron (or two electrons on the case of the binuclear complex VI). The evidence for the reversibility of these processes is as follows.

TABLE 1

THE COMPOUNDS STUDIED AND THEIR HALF-WAVE POTENTIALS, $E_{1/2}$, IN REDOX REACTION 1 (DMSO, 0.1 M Bu_4NBF_4, $C = 2 \times 10^{-3}$ M, N.C.E.)

	Compound	$-E_{1/2}$(V)
I	$[1,3,5\text{-}(CH_3)_3C_6H_3]_2CrI$	0.98
II	$[1,3\text{-}(CH_3)_2C_6H_4]_2CrI$	0.92
III	$(CH_3C_6H_5)_2CrI$	0.86
IV	$(C_2H_5C_6H_5)_2CrI$	0.86
V	$[\eta^6\text{-}C_6H_5(CH_2)_4C_6H_5]_2CrI$	0.86
VI	$[\eta^6\text{-}C_6H_5(CH_2)_4C_6H_5]_2\text{-}\mu[\eta^6\text{-}C_6H_5(CH_2)_4C_6H_5\text{-}\eta^6]$ Cr_2I_2	0.86
VII	$(C_6H_5CH_2CH_2COOC_2H_5)_2CrI$	0.84
VIII	$[\eta^6\text{-}C_6H_5(CH_2)_4C_6H_5\text{-}\eta^6]$ CrI	0.83
IX	$(C_6H_6)_2Cr$ [a]	0.80
X	$(CH_3OC_6H_5)_2Cr$ [a]	0.79
XI	$(C_6H_5CH_2COOC_2H_5)_2CrI$	0.74
XII	$(\eta^6\text{-}C_6H_5C_6H_5)_2CrI$	0.70
XIII	$(C_6H_5CH{=}CHCOOC_2H_5)_2Cr$	0.59
XIV	$(HCOC_6H_5)Cr(C_6H_6)$	0.55
XV	$(\eta^6\text{-}C_6H_5CH{=}CHCOC_6H_5)_2Cr$	0.535
XVI	$(FC_6H_5)_2Cr$	0.425
XVII	$(CH_3COC_6H_5)_2Cr$	0.42
XVIII	$(ClC_6H_5)_2Cr$	0.385
XIX	$(HCOC_6H_5)_2Cr$	0.31
XX	$(NCC_6H_5)_2Cr$	0.175

[a] Both neutral and cationic forms of the compounds were studied.

(a) The half-wave potentials determined from the anodic and cathodic polarization curves measured with a disk electrode for the bisarenechromium(0)/bisarenechromium(I) iodide systems coincide.

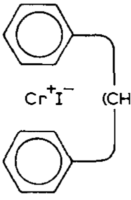
(b) The $E_{1/2}$ value for a given compound is independent of the electrode material (platinum, amalgamated gold).

(c) Most polarization curves have slopes of 0.056 to 0.065 V (0.029 V for VI) which compare well with the theoretical value of $2.3RT/nF$ calculated from the Nernst thermodynamic formula. Judging from the slope value (0.07 V) a slight deviation from reversibility may be suspected only for VII and XI, which contain ester groups in the alkyl side chains.

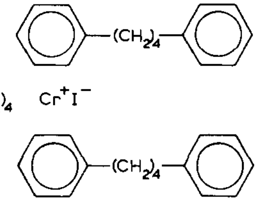
The half-wave potential values for all the compounds studied are in the range −0.17 to −1.0 V (these values are listed in Table 1).

As is seen from Table 1, the electron-donating alkyl substituents facilitate the oxidation and shift the potentials to the negative values. The methoxy group has a very weak electron-withdrawing action. The phenyl group, halogen atoms and substituents containing multiple C=O, C≡N, C=C—C=O bonds hinder the oxidation.

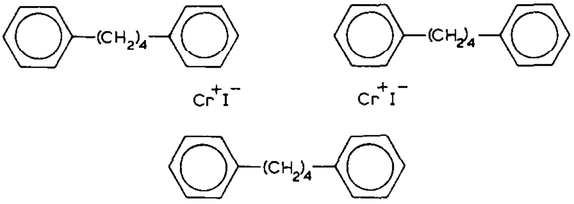
Compounds XIII, XI and VII may serve as examples demonstrating decrease of the electron-withdrawing action of the carbethoxy substituent upon the introduction of a vinyl group or one or two methylene units, respectively, between this substituent and the dibenzenechromium nucleus. The methyl, ethyl and δ-phenylbutyl groups show the same electron donating ability (III, IV and V, respectively). The bridging tetramethylene group in VIII has a weaker electron-donating action than that of open-chain substituents (IV and V). As expected, the binuclear complex VI undergoes one-step two-electron reduction characterized by the same half-wave potential as the reduction of the corresponding mononuclear complex V.



(VIII)



(V)



(VI)

The additive nature of the substituent effects on the $E_{1/2}$ values of alkyl-substituted dibenzenechromium compounds [7] found earlier is confirmed by the present results: the introduction of each aldehyde group into dibenzenechromium causes a 0.25 V potential shift to positive values. The $\Delta E_{1/2}$ increment per methyl group is −0.03 V.

In order to quantitatively describe the substituent effects in the electrochemical redox reactions of bisarenechromium complexes, we have carried out a detailed correlation analysis of the $E_{1/2}$ values using various sets of σ values (Table 2) according to the equation

$$E_{1/2} = (m\sigma + b) \tag{2}$$

The parameters m and b, the correlation coefficient r, and the standard devia-

TABLE 2

SUBSTITUENT CONSTANTS [12] USED IN CORRELATION ANALYSIS

Substituent	σ_m	σ_m^n	σ_m^0	σ_m^+	σ_p	σ_p^0	σ_I
H	0	0	0	0	0	0	0
CH_3	−0.069	−0.069	−0.07	−0.065	−0.170	−0.15	−0.05
C_2H_5	−0.07	−0.072		−0.064	−0.151		−0.05
$CH_2CH_2COOC_2H_5$	−0.027 [a]						
$CH_2COOC_2H_5$				−0.01 [c]			
OCH_3	0.115	0.076	0.06 [b]	0.047	−0.268	−0.16 [b]	0.26
C_6H_5	0.06			0.109	−0.01		0.1
F	0.337	0.337	0.35	0.352	0.062	0.17	0.52
Cl	0.373	0.373	0.35	0.399	0.227	0.27	0.47
$COCH_3$	0.376	0.376	0.34	(0.36) [d]	0.502	0.40 [b]	0.28
CHO	0.355	(0.48) [d]	(0.46) [d]	(0.46) [d]	0.22		0.31
CN	0.56	0.613	0.62	0.562	0.660	0.63 [b]	0.56

[a] The σ_m value for CH_2CH_2COOH [13] is used. [b] The σ values for nonaqueous solutions are taken from ref. 14. [c] The σ_m^+ constant is from ref. 15. [d] The σ values are determined from the corresponding correlation equations in this work.

TABLE 3

PARAMETERS OF CORRELATIONS OF $E_{1/2}$ VALUES WITH SUBSTITUENT CONSTANTS

Substituent constant	Number of points	m	b	ρ	r	S_m	S_b
σ_m	14	0.544	—0.787	—9.9	0.982	0.029	0.015
σ_m^n	10	0.508	—0.792	—8.7	0.994	0.018	0.010
σ_m^0	9	0.51	—0.787	—8.8	0.994	0.020	0.012
σ_m^+	11	0.529	—0.797	—9.1	0.997	0.014	0.007
σ_p	13	0.366	—0.648	—6.3	0.912	0.050	0.031
σ_p^0	9	0.354	—0.645	—6.1	0.867	0.072	0.048
σ_I	13	0.493	—0.804	—8.5	0.910	0.06	0.038

tions S_m and S_b are given in Table 3. This Table also includes the reaction constant, ρ, values determined from the relation

$$\rho = -mnF/2.3RT = -m/0.058$$

The correlation equations found were applied to determine certain constant values for the formyl and acetyl substituents absent in the handbooks. The σ values thus calculated are given in parentheses in Table 2. The correlation analysis showed that none of the sets of *para*-substituent constants correspond to the redox potentials of dibenzenechromium compounds. On the contrary, with the *meta*-substituent constants, a good or a satisfactory correlation is always observed. This is, in particular, true of the Hammett constants, σ_{meta} ($r = 0.982$) (Fig. 1). A more detailed analysis, however, reveals certain deviations from the general pattern. The methoxy group stands out strongly. In addition, complexes containing various numbers of substituents of the same type (alkyl or formyl groups) have their $E_{1/2}$ potentials on two straight lines with different slopes. These lines intersect at the point corresponding to unsubstituted dibenzenechromium (dashed lines in Fig. 1).

An excellent correlation was obtained for other *meta*-substituent constants, the "normal" Van Bekkum, Verkade and Webster constants (σ_m^n), the Taft constants (σ_m^0), and the electrophilic constants (σ_m^+) (Table 3). The fact that these three sets show good correlations is explained by the corresponding values falling close together for most substituents, except for the methoxy group which is characterized by a strong M-effect. Considerable variations in the methoxy group constants from one set to another provide the possibility of using the deviation of the experimental bis(anisole)chromium half-wave potential values from the corresponding straight correlation lines ($\Delta E'_{1/2} = -0.79 - E_{1/2}^{\text{calcd}}$) as an additional criterion for the choice of the substituent constant set yielding the best-fit correlation. As follows from Table 4, the set of the electrophilic constants σ_m^+ ($\Delta E'_{1/2} = -0.04$ V) should be preferred.

The straight line in the plot of $E_{1/2}$ vs. σ_m^+ (Fig. 2) shows not only the highest correlation coefficient but also the smallest standard deviations S_m and S_b. Besides, the coefficient b for that line practically coincides with the $E_{1/2}$ value for unsubstituted dibenzenechromium.

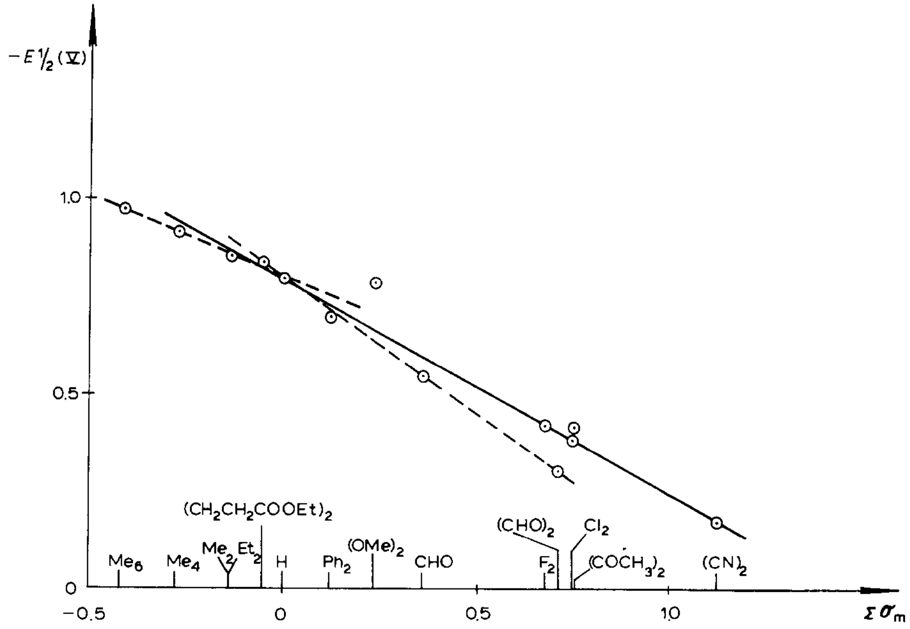


Fig. 1. Correlation between $E_{1/2}$ and Hammett σ_{meta} constant values.

The fact that the $E_{1/2}$ values correlate with the *meta*-substituent constants and do not correlate with the constants of *para*-substituents is of principal importance. It shows that the inductive mechanism plays the major part in the transfer of the substituent electronic effects to the metal atom.

As mentioned, an excellent correlation is observed with two similar, in their physical nature, sets of constants, σ_m^0 and σ_m^n. Hence, the conclusion may be drawn that, first, the electronic effects of the substituents are transferred from the arene ligand to the chromium by the inductive mechanism. Second, the transfer of substituent electronic effects within the ligand coordinated to the metal is also governed by the inductive mechanism; the conjugation between the substituent and the arene ligand only occurs to the extent reflected in the *meta*-substituent constants. With certain substituents such as OCH_3 and, possibly, NR_2, the conjugation effects are seemingly somewhat stronger than for other groups. For that reason, the substituent constant σ_m^+ describes the behavi-

TABLE 4

THE $\Delta E'_{1/2}$ VALUES FOR BIS(ANISOLE)CHROMIUM OBTAINED USING VARIOUS SETS OF *meta*-SUBSTITUENT CONSTANTS

σ	$-\Delta E'_{1/2}$(V)
σ_m	0.13
σ_m^n	0.08
σ_m^0	0.06
σ_m^+	0.04

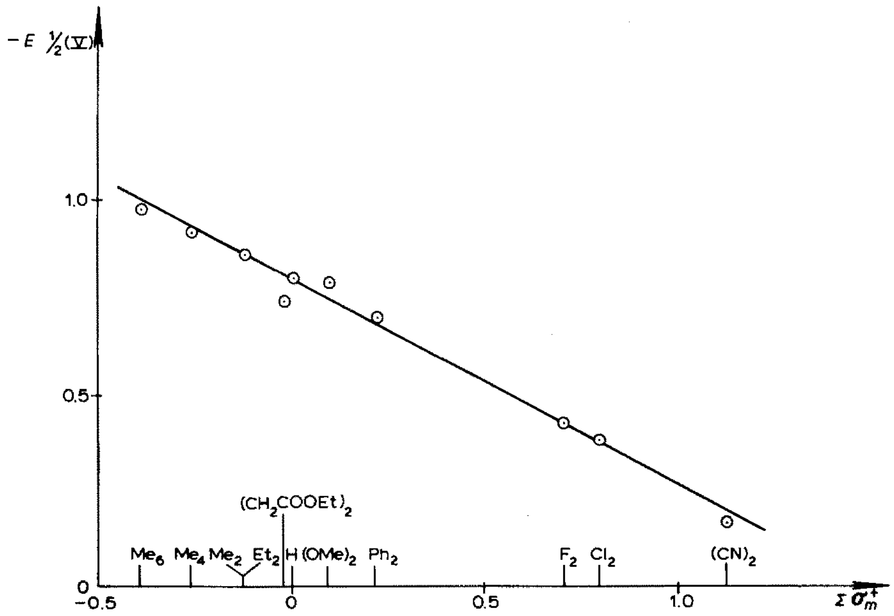


Fig. 2. Correlation between $E_{1/2}$ and electrophilic σ_{meta}^{+} constant values.

our of the methoxy group in bis(anisole)chromium better than other constant sets do. Previously [16], the correlation of the $E_{1/2}$ values with the Hammett constants σ_{meta} had been predicted from qualitative considerations of the stability of bisarenechromium compounds towards oxidation with atmospheric oxygen.

It is of interest to compare the type of the transfer of electronic effects in various metal π-complexes. According to the literature data, the electronic effects of ferrocenes [3], arenecyclopentadienyliron cations [4], ruthenocenes [17] on the $E_{1/2}$ potentials show the best correlations with the σ_p^0 constants. That means that the electronic effects are transferred across the metal—ligand bonds in these complexes by the inductive mechanism, while conjugation between the aromatic ring and the substituent does occur. At the same time, dibenzenechromium compounds are characterized by a far weaker conjugation between the substituents and the arene ring compared with other complexes.

The characteristic behaviour of bisarenechromium complexes, which manifests itself in a drastic weakening of resonance effects in the arene ligand, has been discussed earlier [18] in works on the ^{13}C NMR spectra of these compounds [18,19]. According to quantum chemical calculations [20], dibenzenechromium shows the strongest decrease in C—C bond order because of decrease in the aromatic character of the arene upon coordination to the metal. The difference between dibenzenechromium and other metal π-complexes is probably caused by the difference in the nature of the metal to ligand bonding. In metal cyclopentadienyl complexes, the interaction between the bonding ring π-orbitals and the metal d_{xz} and d_{yz} levels predominates, which causes ligand to metal transfer of electronic density and decrease of the C—C bond order [20]. With benzene complexes, the major reason for the decrease of the C—C bond order is an interaction between the ligand antibonding π-orbitals and metal $d_{x^2-y^2}$ and d_{xy} levels. This results in transfer of electrons from the metal to the ligand π^*-orbitals.

Like the redox reactions in the ferrocene series [3], the reversible redox reaction of bisarenechromium complexes is characterized by a high absolute value of the reaction constant ρ (Table 3) and, consequently, by the high sensitivity to substituent electronic effects.

Experimental

The electrochemical measurements were carried out with platinum and amalgamated gold rotating disk electrodes (RDE) of 2.5 mm radius. The gold electrode surface was amalgamated by electrochemical deposition of mercury from saturated aqueous $Hg_2(NO_3)_2$ for 3 min at 1.5 mA. The rate of electrode rotation varied in the range 175 to 8000 rpm. The electrochemical cell used had a central compartment of 20 ml in volume in which RDE was placed and a side compartment for a platinum counter electrode separated from the main compartment by a porous glass diaphragm. The operating compartment was linked to a reference electrode (N.C.E.) with the Luggin capillary. The electrochemical experiments were run under an inert atmosphere (N_2) at 21—22°C. The polarization curves were taken with a P-5827M potentiostat and registered on a two-coordinate recorder. Current measurements were read from a M-254 volt-ammeter. The potentials were measured to an accuracy of 5 mV. The solvent, DMSO, was purified by freezing out and repeated distillation (the second distillation over CaH_2) in a nitrogen flow under vacuum (b.p. 40—43°C/1 mm Hg). The solvent thus purified contained not more than 0.1 weight % water.

Tetrabutylammonium fluoroboride ($TBABF_4$) was used as supporting electrolyte. It was recrystallized three times from water/methanol (1/1) and dried under vacuum at 70°C over P_2O_5.

The compounds studied were synthesized by standard procedures by metallation of dibenzenechromium (XIII, XIV, XV [21]), XIX [22]), or from chromium vapour and arenes (V, VI, VIII [23], VII, XI [24], X, XVI, XVIII [18]).

Acknowledgement

The authors wish to express their thanks to B.G. Gribov, B.I. Kozyrkin, G.A. Domrachev and Yu. A. Shevelev for gifts of some bisarenechromium compounds.

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