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An Electrochemical Study of Chromium(0) Complexes of Arenes which have Electronegative Substituent Groups

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Using cyclic voltammetry, $E_{1/2}$ *values were determined for the process* $Cr(arene)_2 \rightleftharpoons [Cr(arene)_2]^+ + e$ *(arene =* C_6H_5R*, for R = H,* CF_3*, Cl, F,* OCH_3*; p- and m-*$C_6H_4(CF_3)_2$*, o- and p-*$C_6H_4(CF_3)Cl$*; 1,4*$(CH_3)_2$*-2-*ClC_6H_3*) in acetonitrile. Compounds with electron withdrawing groups on the arene ligands have higher* $E_{1/2}$ *values indicating that they are more difficult to oxidize. This is in accord with a simple model in which withdrawal of electron density from the metal to the ligands stabilizes the HOMO, a primarily metal orbital, in these systems. Possible correlations between* $E_{1/2}$ *and the Hammett substituent constants,* σ_m *and* σ_p *for the substituent groups on the ligands, are investigated.*

Introduction

Many bis(arene)chromium complexes have now been synthesized by the metal atom reactor route [1]. This includes complexes having electronegative substituent groups (halide or trifluoromethyl groups) on the arene ligand. Such complexes cannot be made in the traditional Fischer–Hafner synthesis [2] because the ligands are not compatible with reaction conditions.

The most striking feature of this group of compounds is their stability in air. In contrast to bis(benzene)chromium which is extremely air sensitive, these compounds are often air stable. For example, it is reported that the compound $Cr(m\text{-}C_6H_4(CF_3)_2)_2$ can be boiled at 200 °C in air with only slow decomposition [1d]. This air stability must be a consequence of kinetics since reactions of virtually all organometallic compounds with oxygen are thermodynamically favored because of the high heats of formation of metal oxides.

There is precedent that electron donating or withdrawing substituent groups on hydrocarbon ligand can also influence the thermodynamics of oxidative processes for hydrocarbon–metal complexes. Substituent groups have a notable effect on the oxidation potentials of $Fe(C_5H_4R)_2$ [3, 4] in the redox couple:

$$Fe(C_5H_4R)_2 \rightleftharpoons [Fe(C_5H_4R)_2]^+ + e.$$

Electron donating groups decrease the potential for this oxidation while electron withdrawing groups increase the potential. This result is easily rationalized qualitatively. Oxidation required removal of an electron from an orbital in the complex which is primarily metal in character. The ease of electron loss should be related to the stabilization of this metal orbital which will depend on the extent of donation of electron density to the metal center by the ligand groups. This, in turn, is influenced by donor or acceptor abilities of substituent groups on the ligands.

Attempts were made to correlate oxidation potential data on substituted ferrocenes with substituent group parameters. The best fit [4] for these data arose using an algebraic combination of Hammett σ_m and σ_p values.

Less study has been accorded the bis(arene)chromium redox couples:

$$Cr(arene)_2 \rightleftharpoons [Cr(arene)_2]^+ + e.$$

Electron donating methyl groups on a coordinated benzene ring are known to lower the oxidation potential somewhat. This effect is cumulative, a larger number of methyl groups causing the oxidation potentials to fall at progressively lower values [5].

With the availability of additional bis(arene)chromium(0) complexes it seemed desirable to look further at the electrochemistry of these complexes. Our interest was abetted by the unusual air stability of those complexes having CF_3 and other electro-

TABLE I. Cyclic Voltammetric Data[a] in Acetonitrile for Bis(arene)chromium Complexes.

Compound	½ $[E_{p,a} + E_{p,c}]$[b]	$[E_{p,a} - E_{p,c}]$[b]	Scan Rate[c]
$Cr(C_6H_5OCH_3)_2$	−0.767	0.134	200
$[Cr(C_6H_5OCH_3)_2]B(C_6H_5)_4$	−0.753	0.130	50
$Cr(C_6H_6)_2$[d]	−0.716	0.144	200
$Cr(1,4\text{-}(CH_3)_2\text{-}2\text{-}ClC_6H_3)_2$	−0.516	0.092	200
$Cr(C_6H_5F)_2$	−0.367	0.073	50
$Cr(C_6H_5Cl)_2$	−0.336	0.092	100
$Cr(C_6H_5CF_3)_2$	−0.190	0.220	200
$(Cr(p\text{-}CF_3C_6H_4Cl)_2$	+0.125	0.130	200
$Cr(o\text{-}CF_3C_6H_4Cl)_2$	+0.165	0.110	200
$Cr(m\text{-}C_6H_4(CF_3)_2)_2$	+0.385	0.130	200
$Cr(p\text{-}C_6H_4(CF_3)_2)_2$	+0.337	0.295	200

[a] Concentration of compound approximately 5×10^{-3} *M*; $[Bu_4N][ClO_4]$ (0.1 *M*) used as supporting electrolyte. [b] Reported in volts *vs.* saturated calomel electrode (aqueous KCl). [c] Scan rate measured in mV/sec. [d] The difference between this number and the literature values [5] arises due to the different solvents employed.

negative arene ring substituent groups. We report the results of this study below.

Experimental

The compounds used in this study were prepared utilizing the metal atom reactor, as described in the literature [1d, 6]. Samples of the pure compounds were stored in sealed glass ampoules under argon prior to use.

Electrochemical measurements were made in acetonitrile at 25 °C using a three-electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (aqueous KCl) reference electrode [7]. Voltage and current functions were controlled using a Princeton Applied Research Electrochemistry System, Model 170, incorporating compensation for internal resistive potential drop. Tetrabutylammonium perchlorate (~0.1 *M*) was employed as the supporting electrolyte and substrate concentrations were ~5×10^{-3} *M*. Solutions of the complexes were prepared under nitrogen in the solvent which had been previously deaerated. The electrochemical cell was also purged with nitrogen prior to use.

Sweep rates were varied from 50 to 200 mV/sec. The peak separations, $|E_{p,a} - E_{p,c}|$, generally exceeded 59 mV and varied as a function of scan rate. The ratios between the anodic and cathodic peak currents, $i_{p,a}/i_{p,c}$, were unity. The electron transfer process was interpreted to be quasi-reversible, *i.e.*, moderately slow electron transfer relative to the rate of the potential change [8]. Data from these experiments are presented in Table I.

Results and Discussion

The following compounds were included in this electrochemical study: $Cr(C_6H_5R)_2$ (R = H, CF_3, Cl, F, OCH_3), $Cr(C_6H_4(CF_3)_2)_2$ (*m*- and *p*-isomers), $Cr(CF_3C_6H_4Cl)_2$ (*o*- and *p*-isomers), and $Cr(1,4\text{-}(CH_3)_2\text{-}2\text{-}ClC_6H_3)_2$; also included was $[Cr(C_6H_5OCH_3)_2]BPh_4$. Each of the chromium(0) complexes was prepared using metal atom reactor techniques; and the chromium(1) complex, $[Cr(C_6H_5OCH_3)_2]BPh_4$, was obtained from $Cr(C_6H_5OCH_3)_2$ by oxidation followed by metathesis. Excepting $Cr(C_6H_6)_2$, $Cr(C_6H_5OCH_3)_2$ and $Cr(1,4\text{-}(CH_3)_2\text{-}2\text{-}ClC_6H_3)_2$, the complexes are quite air stable. It is noted that the arene ring substituent groups vary from strongly electron withdrawing (CF_3) to moderately good electron donating (OCH_3) *vs* hydrogen.

Each of the compounds exhibited a well-behaved electrochemical oxidation in range from −0.8 V to +0.4 V (Table II). On the basis of the behavior for previously reported bis(arene)chromium(0) systems, these processes were defined as one electron oxidations. This assumption was supported by cyclic voltammetry on $Cr(C_6H_4OCH_3)_2$ and $[Cr(C_6H_4OCH_3)_2]^+$ which gave identical current-voltage traces.

There was no evidence for degradation or further reaction of the reactants or products of these redox couples, or for the formation of other electroactive species; neither was there evidence for further oxidation or reduction processes within the range of the applied potential. The ratio between the anodic and cathodic peak currents, $i_{p,a}/i_{p,c}$, in all cases, was unity. The value of ½$(E_{p,a} + E_{p,c})$ was independent of

TABLE II. Data Used for Correlations between $E_{1/2}$ Values and Hammett σ_m and σ_p Parameters.[a]

Substituent	$E_{1/2}$	$\Sigma\sigma_m$[b,c]	$\Sigma\sigma_p$[b,c]
OMe	−0.767	+0.230	−0.536
H	−0.716	0	0
1,4(CH$_3$)$_2$-2-Cl	−0.516	0.470	−0.226
F	−0.367	0.674	+0.124
Cl	−0.336	0.764	0.454
CF$_3$	−0.190	0.860	1.080
p-Cl,CF$_3$	+0.125	1.61	1.534
o-Cl,CF$_3$	+0.165	1.61	1.534
m-(CF$_3$)$_2$	+0.387	1.72	2.160
p-(CF$_3$)$_2$	+0.337	1.72	2.160

[a] From ref. 9. [b] Sum of σ values: *e.g.*, for Cr[C$_6$H$_4$-(CF$_3$)$_2$]$_2$, $\Sigma\sigma_m = 4\ \sigma_m = 4(0.43) = 1.72$. [c] Least squares fit: $E_{1/2} = 0.637\ \sigma_m - 0.801$, with correlation coefficient $r = 0.987$. [d] Least squares fit: $E_{1/2} = 0.413\sigma_p - 0.530$, $r = 0.976$.

scan rate. The peak separation, $|E_{p,a} - E_{p,c}|$, was greater than 59 mV and increased as the scan rate was increased. The electrochemical processes appear to be quasi-reversible; *i.e.*, they are processes for which there is moderately slow electron transfer compared to the rate of potential change [8].

It is seen from the data in Table I that the potentials necessary for oxidation of these bis(arene)-chromium complexes varied widely, from −0.767 V for Cr(C$_6$H$_5$OCH$_3$)$_2$ to +0.385 V *vs* SCE for Cr(*m*-C$_6$H$_4$(CF$_3$)$_2$)$_2$. The general trend, from lower to higher $E_{1/2}$ values, depending on the ability of the substituent groups to withdraw electron density, was expected in view of the earlier studies on ferrocenes [3, 4]. However the magnitude of this variation, over a 1.15 V range, was striking. In the previous studies on substituted ferrocenes the variation of oxidation potential was limited to a narrower range, this being a consequence of the limited selection of substituent groups chosen. The specific inclusion of the CF$_3$ group in our work substantially extended the range of $E_{1/2}$ values. No previous data is available on the effect of a CF$_3$ group in the oxidation of any hydrocarbon complex.

It seemed desirable to determine what sort of correlation might exist between the $E_{1/2}$ data measured for this series of bis(arene)chromium(0) complexes and the parameters associated with aryl ring substituents. While a correlation was expected its exact nature was uncertain since excepting the ferrocene work there is no real precedent concerning effectiveness of transmission of substituent group effects across the metal–hydrocarbon bond.

Correlations were sought between $E_{1/2}$ values and a number of substituent group parameters. Data and results for two of these attempts, using the Hammett parameters σ_p and σ_m [9], are given in Table II and the results are portrayed graphically in Fig. 1. In each case a satisfactory linear correlation was found to exist. The derived (least squares) relationships were:

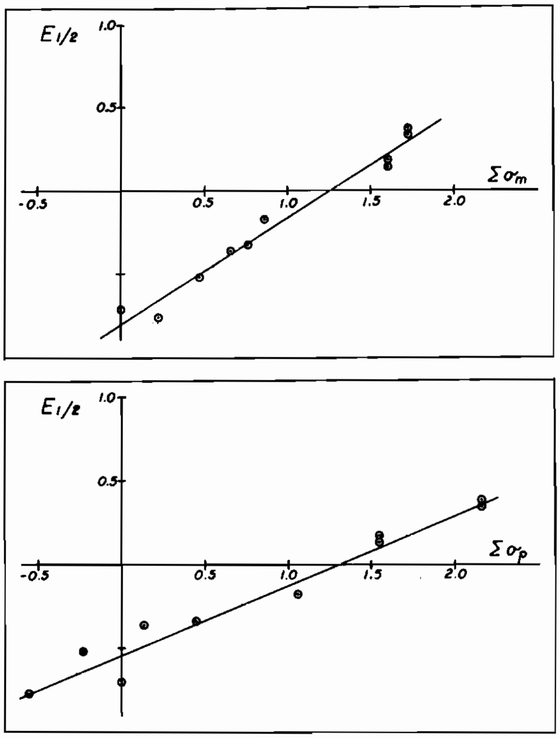

Fig. 1. Top: $E_{1/2}$ *vs.* $\Sigma\sigma_m$; Bottom: $E_{1/2}$ *vs* $\Sigma\sigma_p$.

$$E_{1/2} = 0.637\ \sigma_m - 0.801; r = 0.987$$
$$E_{1/2} = 0.413\ \sigma_p - 0.530; r = 0.976$$

where r is the correlation coefficient [10].

The extent of the correlations of $E_{1/2}$ with σ_m and σ_p is judged to be essentially the same based on the values of the correlation coefficients. This appears to be enigmatic since these two parameters are intended to denote quite different characteristics; σ_m is essentially an inductive parameter while σ_p is intended to incorporate both inductive and resonance contributions. Our approach to this situation is not to try to choose one parameter over the other; indeed there appears to be no basis for making such a choice. Rather, we offer the comment that it is probably impossible to match these data perfectly with any known set of parameters. The general satisfactory data fit for $E_{1/2}$ with both σ_m and σ_p implies a fact that we already know, that the ease of oxidation is proportional to the extent of negative charge buildup at the metal site, *i.e.*, it is proportional to the HOMO energy, which is in turn proportional to the donor ability of the ligand [11]. However, there are subtleties defining the HOMO energies in these complexes which cannot be assessed accurately. We saw this before when we looked at oxidations of various isomeric complexes $[Mn(CO)_{6-n}(CNCH_3)_n]^+$ (n = 3, 4) [12]; there we were able to qualitatively explain these differences since the theory was simpler. In the system at hand, however, the uncertainties of describing the metal–arene bond (especially in complexes of low symmetry) mitigates against a further analysis of the problem.

It is possible that additional data could lead to the focusing of attention on one or the other parameters. If further work is to follow, a choice of substituent groups with widely varying parameters is desired; especially needed are groups which are capable of diverse resonance interactions. Groups which only act inductively will add little, though they will probably improve the correlation. We note in passing that there is an excellent correlation between the literature $E_{1/2}$ data and σ_m for the bis(methylbenzene) chromium complexes; for these systems we find $E_{1/2} = 0.6569\ \sigma_m - 0.7881$, with $r = 0.994$.

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