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ELECTROCHEMICAL AND ESR KINETICS STUDIES OF ELECTRON TRANSFER IN THE SYSTEM BIS(η^6-ARENE)CHROMIUM(0)/BIS(η^6-ARENE)CHROMIUM(I)

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Summary

The self-exchange rates and activation parameters in the (η^6-arene)$_2$Cr^0/(η^6-arene)$_2$Cr^I systems (where arene = toluene, benzene, methoxylbenzene, biphenyl, ethylbenzoate and chlorobenzene) have been measured by the ESR line broadening technique in DMSO solvent. The one-electron reduction was investigated by cyclic voltammetry for the series of substituted complexes of (η^6-arene)$_2$Cr^I. A linear correlation was obtained between the measured $E_{1/2}$ values and the sum of Hammett parameters, $\Sigma\sigma_m$. For a series of solvents, a linear relationship between log k (the exchange rate constant of (biph)$_2$Cr$^{0/+1}$) and $\left(\frac{1}{n^2}-\frac{1}{D_s}\right)$ where n^2 and D_s are the optical and static dielectric constants of the solvent medium, respectively, has been observed. This linearity is predicted by Marcus treatment for outer-sphere electron transfer process. A correlation of the oxidation stability of sandwich compounds with their gas-phase ionization potentials is evident from a linear relationship between the oxidation half-potentials $E_{1/2}$ (or sum of Hammett $\Sigma\sigma_m$ values) and the gas-phase ionization potentials.

Introduction

Electron exchange between various sandwich compounds and the corresponding cation has been investigated by several groups [1,2]. Typical of this class is the reaction between ferrocene and ferricinium ion [2—4].

Among those methods for measuring the rates of exchange reactions, the ESR method has been applied to electron transfer reactions between aromatic hydrocarbons and their anion or cation radicals [5,6]. The ESR line broadening method cannot be applied to the ferrocene systems because of the short relaxation time characteristic of the ferricinium cation [7] so further corroboration of results seems unlikely.

The isoelectronic and isostructural bis(η^6-arene)chromium(0) complexes (abbreviated Ar_2Cr) and the corresponding chromium(I) cation (abbreviated Ar_2Cr^I) can be studied by ESR line broadening. Their molecular orbital bonding schemes are well known [8]. Polarograms of cation and neutral species yield similar $E_{1/2}$ values, indicating the reversibility of the reduction-oxidation couple [9]. Methyl derivatives, like bis(toluene)chromium, have more negative reduction potentials, whereas phenyl derivatives like bis(biphenyl)chromium, have more positive reduction potentials [10]. A good correlation is obtained between the reduction potential and localization of the highest occupied molecular orbital (HOMO) predicted by substituent effects [11]. Therefore, a correlation with exchange rates would be interesting. The core sandwich structure remains essentially the same throughout the series of derivatives [12], so the free energy change related to electronic reorganization and inner sphere contributions can be eliminated for theoretical treatment. The fact that one of the reactants is neutral allows further simplification in theoretical calculations of the exchange rate, since coulombic interactions are absent. Finally, the electron exchange would necessarily be simple, because the reaction of the ligand, ion transfer, or atom-transfer are unlikely.

For these reasons, the electron exchange between Ar_2Cr^0 and Ar_2Cr^I was studied by ESR linewidth measurements. The effects of substituents upon the exchange rate were studied, and the effect of solvent variation on the exchange rate was determined in relation to the predictions of the Marcus theory [13].

Experimental section

Materials and syntheses

The (η^6-arene)$_2$chromium(0) complexes which were synthesized by metal-ligand condensation techniques [14b,15] contain functional groups (i.e. CH_3, H, $COOC_2H_5$). The compounds prepared by Friedel-Crafts syntheses [16] contain H and Ph. Bis(chlorobenzene)chromium, $(C_6H_5Cl)_2Br$, bis(methoxybenzene)chromium, $(C_6H_5OCH_3)_2Cr$, and bis(1,3,5-trimethylbenzene)chromium $[(C_6H_3(CH_3)_3]_2Cr$, were kindly provided by K.L. Klabunde, Kansas State University.

As an example of the vapor syntheses of chromarenes, $(C_6H_5CH_3)_2Cr$, was prepared by the following procedure. In a liter flask (—196°C), chromium vapor was produced by electrical heating (8 V, 60 A) in a close-wound, conical tungsten basket at a pressure of $<10^{-4}$ Torr. In typical experiment, toluene (8 ml) was condensed with chromium vapor (600 mg) over 1 h. The reaction flask was allowed to warm to room temperature and the excess unreacted toluene was removed in a vacuum. A cold finger was placed in the flask and the product sublimed at 70°C in a vacuum. The black solid was removed from the cold finger and stored in the argon-filled dry box.

These compounds were identified by mass and NMR spectra. Mass spectral data: *m/e* 276, $C_{12}H_{10}Cl_2Cr$ (5.8), 360, $C_{24}H_{20}Cr$ (4.6), 208, $C_{12}H_{12}Cr$ (63.6), 236, $C_{14}H_{16}Cr$ (60.2), 268, $C_{14}H_{16}O_2Cr$ (22.1), 352, $C_{18}H_{20}O_4Cr$ (20.2), 292, $C_{18}H_{24}Cr$ (100).

The bis(η^6-arene)chromium(I) cations were obtained by oxidizing these chromium(0) compounds in the air in the presence of water, giving the hydroxide of bis(η^6-arene)chromium(i). By adding sodium tetraphenylborate or potassium iodide to these aqueous solutions, the precipitate of yellow tetraphenylborate or iodide salt of bis(η^6-arene)chromium(I) was collected, filtered, washed with water, then ether, and dried in a vacuum at room temperature. The purity of the compounds was verified by IR, UV-visible spectra and microanalyses. The IR bands in the 300—500 cm^{-1} region are characteristic of diarene sandwich compounds [17]. The functional groups, $-CH_3$ -Ph, -H, $-OCH_3$, $-COOC_2H_5$, -Cl were confirmed by IR. Among these Cr^I complexes, $(C_6H_5OCH_3)_2CrBPh_4$ is easily oxidized and had to be stored in an argon-filled dry-box.

All the solvents used for ESR or cyclic voltammetry measurements were purified by standard techniques [18].

Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was prepared by mixing tetrabutylammonium hydroxide and ammonium hexafluorophosphate in acetone, followed by precipitation by the addition of water and the precipitate was recrystallized three times from 95% ethanol. Tetrabutylammonium perchlorate (Bu_4NClO_4) was obtained from G.F. Smith Chemical Co. and recrystallized three times from 95% ethanol.

ESR kinetics measurements

ESR spectra were recorded by use of a Varian E-4 ESR spectrophotometer with a variable temperature controller. The exchange solutions were prepared in the argon-filled dry-box by preparing a solution of the complex cation (typically 10^{-4} *M*) with varying concentrations of zerovalent complex and a constant cation concentration. Samples were added, in the dry-box, to a 3 mm ESR tube by means of a glass syringe and the tubes were sealed on a standard vacuum line. The rates of the rapid electron-transfer reactions were determined from the increase in line widths after the adding of known amounts of zerovalent complexes. The slow exchange limits were used for all cases in DMSO and other solvents. The calculation of the rate constants were made according to the procedures described elsewhere [5b].

ESR spectra simulation

The ESR spectra were simulated by using the computer program ESRSIM [19]. The *g* values of the chromium electron, the hyperfine coupling constants of the hydrogen and chromium, and the line widths were adjusted to obtain the best fit to the observed spectra.

Good agreement within experimental uncertainty between the calculated concentration and the concentration obtained from ESR spectra was obtained.

Cyclic voltammetry

The standard reduction potentials of all of the Cr^0/Cr^I couples were measured by cyclic voltammetry with a PAR 174 polarograph, coupled to a Hewlett-Packard Model 7045A fast X-Y recorder.

Two-compartment glass cells (solution, ca. 10 ml) were employed for the electrochemical measurements. Contact of the solution with the aqueous saturated calomel reference electrode (SCE) was through a glass frit of very fine grade. The solution was deaerated by a stream of dry nitrogen before the potential was scanned. The experiments were carried out in DMSO ($\sim 10^{-3}$ *M*) at room temperature with 0.1 *M* tetrabutylammonium perchlorate as the supporting electrolyte, by using a platinum "flag" working electrode [20]. Although the separation of cathodic and anodic peaks (Table 3) was larger than the theoretical separation of 57 mV, the unit ratio of the peak current, i_c/i_a, gives evidence for reversible one-electron processes.

Oxidation potentials of the three couples $(C_6H_6)_2Cr^0/(C_6H_6)_2Cr^+$, $(C_6H_5CH_3)_2Cr^0/(C_6H_5CH_3)_2Cr^+$, and $[C_6H_3(CH_3)_3]_2Cr^0/[C_6H_3(CH_3)_3]_2{}^+Cr$ were measured in dichloromethane ($\sim 10^{-3}$ *M* solution) at room temperature with 0.1 *M* tetrabutylammonium hexafluorophosphate against SCE. The scanning voltage was 100 mV/s and the current range 100 μA.

Other measurements

Infrared spectra were obtained by means of a Perkin-Elmer 457 spectrophotometer in KBr pellets at room temperature.

Mass spectra were recorded by use of Finnigan 4000 mass spectrometer (70 eV) with an Incos data system.

NMR spectra were obtained by use of a Varian T-60 or a Bruker WM 250 spectrometer. UV-visible spectra were recorded by use of a Cary model 14 spectrophotometer.

Results and discussion

ESR measurement

Data indicating a monotonic decrease in the intensity (or increase in the linewidth) of the ESR spectrum of the bis(arene)chromium cation with the addition of the respective zerovalent complex have been obtained. An example (Fig. 1) shows the effect on the spectra of $[(C_6H_5Cl)_2Cr]BPh_4$ (5.4×10^{-4} *M* in DMSO) of the addition of $(C_6H_5Cl)_2Cr$ to give concentration of 0, 10^{-2}, 10^{-1} *M*, respectively, at 22°C.

The representative spectra of six solutions of $(C_6H_5Cl_3)_2Cr^0/(C_6H_5Cl_3)_2Cr^+$ in

TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS IN THE Ar_2Cr^0/Ar_2Cr^+ ELECTRON TRANSFER REACTION IN DMSO

No.	Arene	$k \times 10^{-7}$ (M^{-1} sec^{-1}) [a]	E_a (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol) [b]	$\Delta S^{\neq}$ (eu) [b]
1	$C_6H_5CH_3$ [c]	3.33 ± 0.41	4.6 ± 0.6	4.0 ± 0.8	—10.5 ± 3.0
2	C_6H_6 [d]	5.99 ± 0.73	4.0 ± 0.3	3.4 ± 0.5	—12.2 ± 2.4
3	$C_6H_5OCH_3$ [c]	7.73 ± 0.56	3.6 ± 0.4	3.0 ± 0.6	—12.3 ± 2.5
4	$C_6H_5C_6H_5$ [d]	23.2 ± 3.1	2.6 ± 0.4	2.0 ± 0.6	—13.4 ± 2.8
5	$C6H_5COOC_2H_5$ [c]	31.5 ± 5.2	2.3 ± 0.3	1.7 ± 0.5	—13.9 ± 2.6
6	C_6H_5Cl [c]	20.0 ± 2.1	2.9 ± 0.2	2.3 ± 0.4	—12.8 ± 2.2

[a] At 22°C. [b] Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated from $k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT}\right)$.

[c] Tetraphenylborate salt of bis(η^6-arene)chromium(I). [d] Iodide salt of bis(η^6-arene)chromium(I).

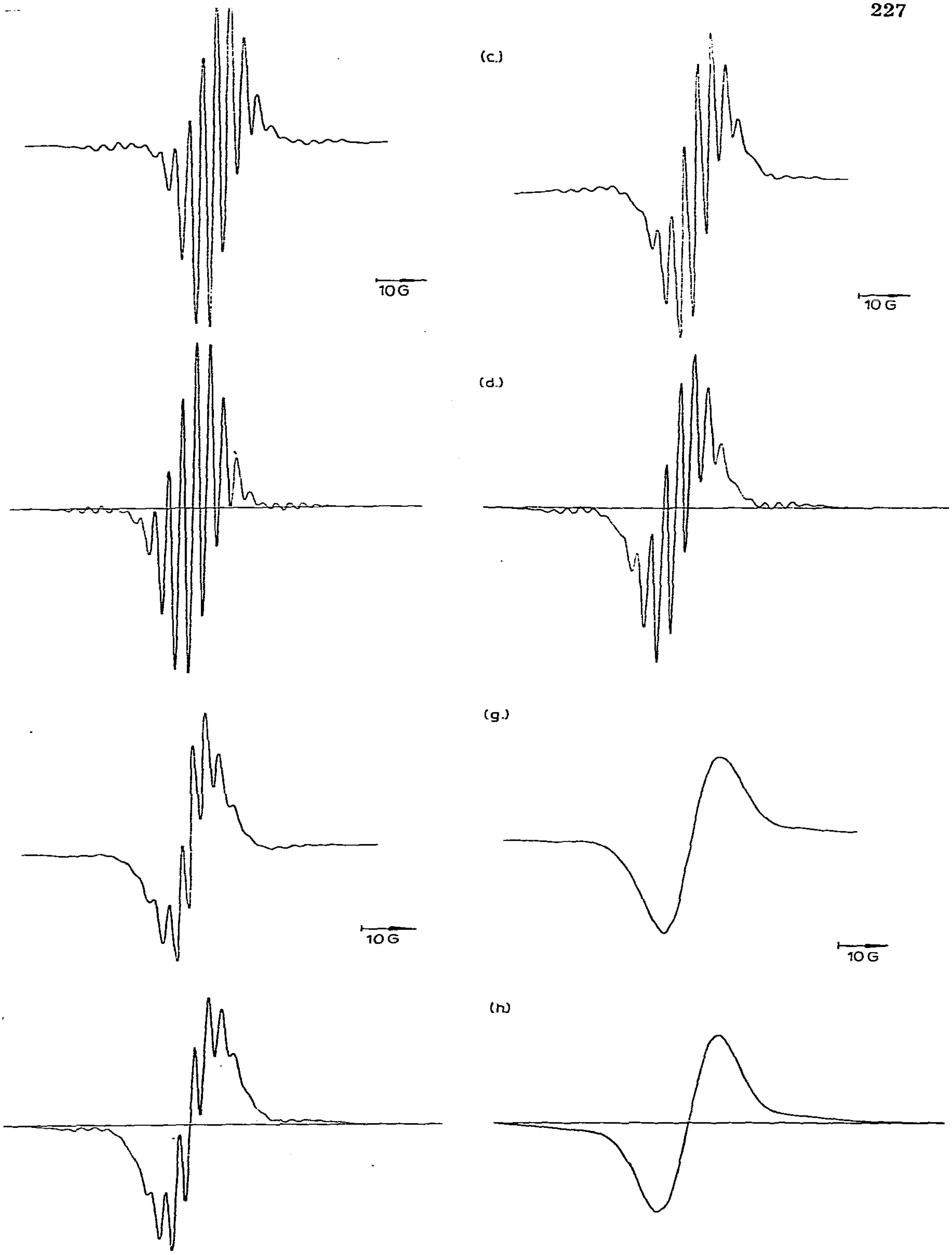

Fig. 1. ESR spectra of 5.4 × 10^{-4} *M* $(C_6H_5Cl)_2Cr^+$ in DMSO (a) No added $(C_6H_5Cl)_2Cr^0$ (22°C). (b) Computer simulation. (c) Added ~4 × 10^{-2} *M* $(C_6H_5Cl)_2Cr^0$ (22°C). (d) Computer simulation. (e) Added ~8 × 10^{-2} *M* $(C_6H_5Cl)_2Cr^0$ (22°C). (f) Computer simulation. (g) Added ~2 × 10^{-1} *M* $(C_6H_5Cl)_2Cr^0$ (22°C). (h) Computer simulation.

DMSO at 22°C and varying concentration of $(C_6H_5Cl)Cr^0$ were examined for broadening of the hyperfine components. It was observed that the broadening of the hyperfine components was a linear function of concentration, and allowed the calculation of the exchange rate constant, $k = 7.7_3 \times 10^7\ M^{-1}\ sec^{-1}$. The results for the several $(arene)_2Cr/(arene)_2Cr^+$ are given in Table 1. The activation energies were obtained from plots of log k vs. $1/T$.

Errors of 10—20% are introduced in these rate constants from the concentration and line-width determination due to both the intrinsic lack of precision in area measurements and the changing line shape at these concentrations. The effects of solvent variation on the exchange rate of bis(biphenyl)$Cr^{0/+}$ are listed in Table 2.

Redox potentials

One-electron reduction potentials of bis(η^6-arene)chromium cations were measured in DMSO by cyclic voltammetry. Typical cyclic voltammograms are shown in Fig. 2. The separation of the peak potential and the height of peaks is close to (Table 3) unity.

All the half-wave potentials, ($E_{1/2}$) Ar_2Cr^0/Ar_2Cr^+, for the complexes are given in Table 3.

The observed variation in the $E_{1/2}$ for the complexes shows that the inductive effect of substituents on the arene system is transmitted to the chromium atom. The Cr^I oxidation state is destabilized by increasing the electron-withdrawing strength of the substituents (more positive potentials) and stabilized by the increasing electron-donating strength of substituents (more negative potentials).

The Hammett's parameters $\Sigma\sigma_m$ for substituents are listed together with the $E_{1/2}$ values in Table 3.

The sum of the $\Sigma\sigma m$ values for the substituents in the complexes were plotted against the $E_{1/2}$ values. The straight line obeys the following equation

TABLE 2

SOLVENT EFFECTS ON RATE CONSTANTS AND ACTIVATION PARAMETERS IN THE SYSTEM $(biph)_2Cr/(biph)_2CrI$

Solvent	$k \times 10^{-8}$ (M^{-1} sec^{-1}) [a]	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (eu)	$\frac{1}{n^2} - \frac{1}{D_s}$ [b]
Benzene/methanol = 9/1 (v/v)	6.08 ± 0.70	1.7 ± 0.4	—12.6 ± 2.1	~0.29
BZN [c]	3.76 ± 0.24	2.1 ± 0.5	—12.3 ± 2.3	0.388
DMSO [d]	2.33 ± 0.21	2.0 ± 0.6	—13.4 ± 2.8	0.438
DMF [e]	2.14 ± 0.54	2.5 ± 0.6	—12.0 ± 2.4	0.462
Benzene/methanol = 1/4 (v/v)	1.62 ± 0.28	3.1 ± 0.5	—10.5 ± 2.7	0.501
PC [f]	1.49 ± 0.31	3.3 ± 0.4	—10.0 ± 2.9	0.481
Benzene/methanol= 1/7 (v/v)	1.21 ± 0.12	3.2 ± 0.5	—10.7 ± 2.6	0.515

[a] 22°C. [b] n^2 and D_s optical and static dielectric constant. [c] Benzonitrile. [d] Dimethylsulfoxide. [e] *N,N*-Dimethylformamide. [f] Propylene carbonate.

TABLE 3

CYCLIC VOLTAMMETRY OF Cr^I COMPLEXES IN DMSO/0.1 *M* Bu_4NClO_4 AT 25°C

Compound	$-E_{1/2}$ [a] (V vs. SCE)	ΔE_p (mV) [b]	$\frac{i_c}{i_a}$ [c]	$\Sigma\sigma_m$ [d]
$[C_6H_3(CH_3)_3]_2CrBPh_4$	0.916	90	1.04	−0.42
$(C_6H_5CH_3)_2CrBPh_4$	0.810	78	1.03	−0.14
$(C_6H_6)_2CrI$	0.746	75	1.03	0
$(C_6H_5OCH_3)_2CrBPh_4$	0.728	80	1.06	+0.23
$(C_6H_5C_6H_5)_2CrI$	0.645	68	1.02	+0.44
$(C_6H_5COOC_2H_5)_2BrBPh_4$	0.558	71	1.06	+0.73
$(C_6H_5Cl)_2CrBPh_4$	0.338	73	1.03	+0.74

[a] $E_{1/2}$ values were calculated as the average of the anodic and cathodic peak potential. [b] ΔE_p is the difference in anodic and cathodic peak. [c] Ratio of the peak currents for the cathodic (i_c) and anodic (i_a) waves. [d] The sum of Hammett parameters for different substituents [21].

(slope $\rho = 0.32$).

$$-E_{1/2} = 0.78 - 0.32\ \Sigma\sigma_m$$

The reduction of bis(ethylbenzoate)chromium(I) in DMSO is abnormal (Fig. 3). Two reduction waves were found with a one electron reversible process in about a 1 : 0.6 ratio of height. The first wave appears at $E_{1/2} = -0.355$ V, $\Delta E_p = 73$ mv, $i_c/i_a = 1.03$, the second at −0.558 V.

Electron transfer

In the Marcus theory [13], λ_0 and λ_i are the outer and inner sphere reorganization contributions to the parameter λ and a_1 and a_2 are the radii of the two reactants, r, the distance between the two centers of the reactants in the

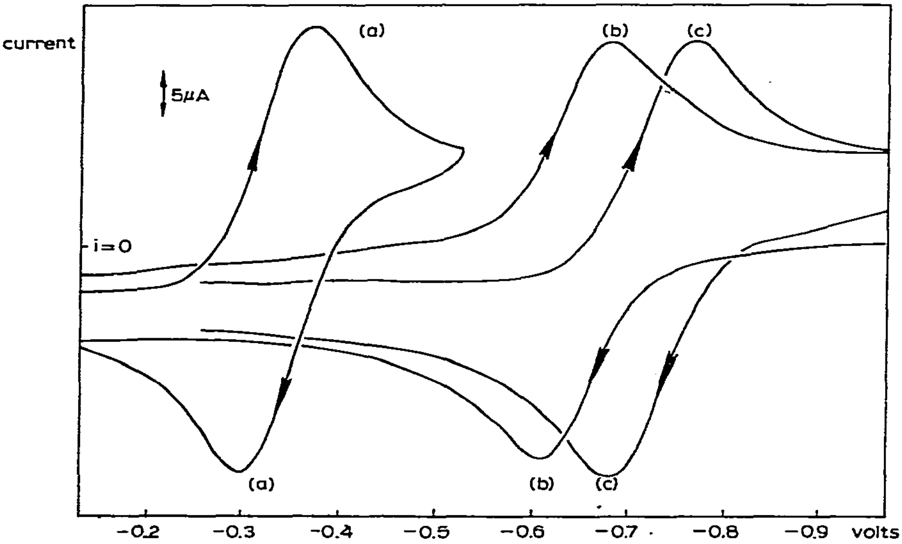

Fig. 2. 100 mV/s cyclic voltammograms of ~10^{-3} *M* (a) $(C_6H_5Cl)_2Cr^+$ (b) $(C_6H_5C_6H_5)_2Cr^+$ (c) $(C_6H_5OCH_3)_2Cr^+$ in DMSO/0.1 *M* Bu_4NClO_4 at Pt electrode vs. SCE (25°C).

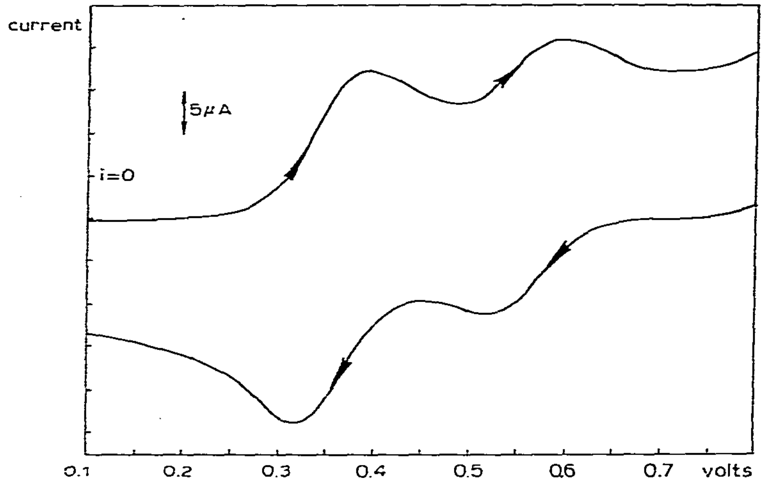

Fig. 3. Cyclic voltammogram of $(C_6H_5COOC_2H_5)_2Cr^+$ ($\sim 10^{-3}$ M) at 25°C in DMSO/0.1 M Bu_4NClO_4. The scan rate was 100 mV/sec at Pt electrode.

activated complex; n and D_s are the refractive index and static dielectric constant, respectively.

For the type of electron-transfer reactions we have studied, the standard free energy of reaction is zero and the work term is small and can be neglected, since one of the reactants is neutral. If it is also assumed that $a_1 = a_2$, $r = a_1 + a_2$, the free energy of activation becomes

$$\Delta G^* = \frac{\lambda}{4} = \frac{\lambda_i}{4} + \frac{\lambda_o}{4} = \frac{\lambda_i}{4} + \frac{\Delta e^2}{8a_1}\left(\frac{1}{n^2} - \frac{1}{D_s}\right)$$

and

$$k = Z \exp\left(\frac{-\Delta G^*}{RT}\right) = Z \exp\left(\frac{-\lambda}{4RT}\right)$$

or

$$\log k = \log Z - \frac{\lambda}{9.2RT}$$

A plot of log k vs. $\left(\frac{1}{n^2} - \frac{1}{D_s}\right)$ should be linear with slope $\frac{-\Delta e^2}{18.42RTa_1}$ an intercept $\log Z - \frac{\lambda_i}{9.2RT}$. In such a graph, the electron exchange for bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) in seven different solvents shows the expected linearity. From the slope, a_1 was calculated to be 6.4 Å. Thus the separation of cation and parent in the activated complex is about 12.8 Å. The head—head and side—side distance of Cr—Cr$^+$ in Cr(biph)$_2^{0/+}$ are 8.0 [22] and 11.6 Å [23], respectively. Thus it seems reasonable to suggest a "side-by-side" positioning of chromarene derivatives in the transition state rather than a "sitting on top" arrangement. This proposal for a "side-by-side" mechanism is also supported by kinetics studies of ferrocenes and carbollyl derivatives [2a]. However, Elschenbroich and Zenneck [1] have investigated the electron exchange in chromarene systems and postulated a "sitting on top" mechanism because there is no significant influence of the degree of methylation on the rate of electron exchange. From the intercept, $\lambda i/4$ was calculated to be 0.6 kcal mole^{-1}. This result implies only a small inner-sphere reorganization contribution to the total free energy of activation from the core sandwich structural rearrangement in the transition state.

The kinetics data for the six "self-exchange" rates for the type of reaction are given by the reaction

$$Cr(C_6H_5X)_2 + Cr(C_6H_5X)_2^+ \rightleftharpoons Cr(C_6H_5X)_2^+ + Cr(C_6H_5X)_2$$

where X = $-CH_3$, $-H$, $-OCH_3$, $-C_6H_5$, $-COOC_2H_5$, $-Cl$. If an outer-sphere mechanism is assumed, the cross reaction is given by the reaction:

The rate constant k_{ij} can be expressed as

$$k_{ij} = (k_{ii}k_{jj}K_{ij}f_{ij})^{1/2}$$

where k_{ii} and k_{jj} are the self-exchange rate constants for each chromarene (Ar_2Cr) and $(Ar_2Cr)^+$, corresponding to the process shown above, K_{ij} is the one-electron equilibrium constant obtained by the relevant ΔE^0 value for the cross reaction, f_{ij} is given by the expression

$$\log f_{ij} = (\log K_{ij})^2/4 \log(k_{ii}k_{jj}/Z^2)$$

where Z is the collision frequency (10^{11} M^{-1} sec^{-1}).

Good estimates of K_{ij} can be obtained from $\Delta E_{1/2}$ values of various reactant couples. The cross-reaction rate constants k_{ij} can be calculated by using the five self-exchange rate constants (Table 1) together with the known equilibrium constants (Table 4).

The effect of solvent and substituents on rates are demonstrated in plots of $T\Delta S^{\neq}$ against $\Delta H^{\neq}$. These effects lead to the result that they will generally give rise to a fairly exact compensation between $\Delta H^{\neq}$ and $T\Delta S^{\neq}$. This compensation effect [24] is found and the plots of $\Delta H^{\neq}$ vs. $T\Delta S^{\neq}$ are good straight lines.

Replacement of electron-withdrawing group substituents in the arene ring may lead to a higher positive charge building up the metal and retard the one-

TABLE 4

CROSS-REACTION CONSTANTS k_{ij} FOR ELECTRON TRANSFER REACTION

Reaction	$k \times 10^{-8}$ (M^{-1} sec^{-1})	Reaction	$k \times 10^{-8}$ (M^{-1} sec^{-1})
11	0.33	34	6.21
12	1.49	35	28.8
13	2.34	41	0.026
14	15.6	42	0.14
15	59.8	43	0.24
21	0.12	44	2.33
22	0.60	45	13.3
23	0.97	51	0.003
24	7.45	52	0.018
25	29.2	53	0.036
31	0.093	54	0.43
32	0.48	55	3.15
33	0.77		

electron oxidation to Ar_2Cr^+. If the changes in the lowest ionization potentials for neutral sandwich complexes of chromium are related to a change in electron density about the Cr^0 center, it is reasonable to assume that the same variation in electron density should be reflected in $E_{1/2}$ for oxidation of neutral chromium sandwich complexes. A plot of $E_{1/2}$ of $Cr^{I/0}$ correlates well with the gas-phase ionization potentials of chromium aromatic sandwich complexes. The trend of the air stability of the chromium compounds is $17e^- > 16e^- > 18e^-$. The $E_{1/2}$ values and ionization potential values for sandwich complexes are collected in Table 5.

The increase in electron density on the central metal is due to the electron-donating methyl substitution which causes a general decrease in the ionization energy also observed in the Mo [25], Nb [26], and Fe [27] complexes, whereas in $Fe(ClCp)_2$ the electron-withdrawing group produces the opposite effect. An electron withdrawing group has a kinetic stabilizing effect: CF_3 and F are the best substituents [14]. Hao and McGlinchey [28] showed that ^1H and ^{13}C NMR chemical shifts for a series of unsymmetrical bis(η^6-arene)chromium derivatives could be correlated with $\Sigma\sigma_m$ and the oxidative stability of the complexes. We

TABLE 5

ELECTROCHEMICAL PARAMETERS AND IONIZATION POTENTIALS FOR THE CHROMIUM SANDWICH COMPOUNDS

Compound [e]	No. of e^-	$-E_{1/2}$ [a]	IP (eV) [d]
$Cr(mes)_2$	18	0.982 [b]	5.01
$Cr(tol)_2$	18	0.867 [b]	5.24
$Cr(bz)_2$	18	0.813 [b]	5.40
Cr(cp)(cht)	18	0.65 [c]	5.59
$Cr(cp)_2$	16	0.61 [c]	5.7
Cr(bz)(cp)	17	0.19 [c]	6.20

[a] Measure in CH_2Cl_2/0.1 M Bu_4NPF_6 at Pt electrode of cyclic voltammetry at 25°C. [b] This work. [c] Ref. 30. [d] Ref. 31. [e] bz = benzene, tol = toluene, mes = mesitylene, cp = cyclopentadienyl, cht = cycloheptatrienyl.

TABLE 6

SUMMARY OF IONIZATION POTENTIALS [a] AND $\Sigma\sigma_m$ OF METAL SANDWICH COMPOUNDS

Compound	IP (eV)	$\Sigma\sigma_m$	Compound	IP (eV)	$\Sigma\sigma_m$
$Cr(mes)_2$	5.01	0.42	$Nb(mes)_2$	5.18 [b]	−0.42
$Cr(tol)_2$	5.24	0.14	$Nb(tol)_2$	5.49 [b]	−0.14
$Cr(bz)_2$	5.40	0	$Nb(bz)_2$	5.57 [b]	−0
$Mo(mes)_2$	5.13	0.42	$(CH_3Cp)_2Fe$	6.88	−0.14
$Mo(tol)_2$	5.32	0.14	$(Cp)_2Fe$	6.72	−0
$Mo(bz)_2$	5.52	0	$(ClCp)_2Fe$	7.03	0.74

[a] Ref. 27. [b] Ref. 26.

have tried to correct for this substituent effect on the air stability of sandwich complexes, by using the sum of the Hammett σ_m parameters of substituents vs. gas-phase ionization potentials: straight lines are found. The ionization potentials are listed in Table 6.

The generalized MO scheme [8] is given for 17 e^- and 18 e^- complexes such $(bz)_2Cr^+$ and $(bz)_2Cr^0$. J.C. Green and M.L.H. Green [26,29] assigned the photoelectron spectra of such $(\eta^6\text{-arene})_2M$ (M = Ti, Nb, Cr, Mo, W) species in terms of the MO model. The highest occupied orbital, a_{1g}, is essentially non-bonding and explains why it may contain 0, 1 and 2 electrons with little effect on thermal stability.

The a_{1g} (metal d orbital) ionization energies increase for the compounds $(mes)_2M$, $(tol)_2M$ and $(bz)_2M$ (M = Cr, Mo, Nb). The plots of $\Sigma\sigma_m$ vs. IP are parallel lines similar to those of substituted ferrocene compounds and reflects the chemical similarity.

In conclusion, it appears that the electron exchange reactions proceed by the outer sphere mechanism and probably by the side to side transition state. Substituent effects and solvent effects on the reactions correlate well with the Marcus theory and supported by electrochemical results, ionization potentials, and Hammett σ_m parameters point to electron densities about chromium being affected by inductive effects and account for variations in exchange rates [*].

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[*] For the self-exchange reaction studied here, the experimental rate constants are considerably below the calculated diffusion-controlled limit ($K_D \approx 10^{10}\ M^{-1}\ sec^{-1}$). It is not necessary to make corrections for diffusional effect [24].

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