Polarographic Reduction Potentials and Substituent Group Electronic Effects for a Series of Tris(1,3-diketonato)chromium(III) Chelates in Dimethyl Sulfoxide and in Dioxane–Water

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A series of 20 tris(1,3-diketonato)chromium(III) chelates was prepared and studied polarographically in dimethyl sulfoxide and in 85% dioxane–15% H_2O. In DMSO two or three one-electron waves are observed. The first wave is assigned to the Cr(III) → Cr(II) reduction. This reduction is reversible in DMSO based on the slope of E_{dme} *vs.* log $i/(i_d - i)$ and on the results of the cyclic voltammetric current–potential curves. In general, only one wave is observed in 85% dioxane and it is significantly less reversible than in DMSO. The $E_{1/2}$ of the first wave varies from −0.4 to −1.8 V *vs.* sce, depending upon the substituents on the chelate rings. The effect of the substituent groups on $E_{1/2}$ is additive and is determined by the nature of its electron polarizing ability. A strong correlation exists between $E_{1/2}$ and the sum of the Hammett polar substituent constants, $\Sigma\sigma_x$. A slope of nearly 1.0 is obtained for a plot of $E_{1/2}$ *vs.* $\Sigma\sigma_x$ when σ_{para} is used for R_1 and R_3 groups and σ_{meta} is used for R_2 groups. This result implies that $E_{1/2}$ differences within the series are due to differences in the electron density at the oxygens. In terms of ligand field theory, the $E_{1/2}$ differences are presumed to be due to changes in the spherical, repulsive portion of the ligand potential field.

Introduction

The polarographic investigation of Cr(1,3-diketonato)$_3$ chelates is of interest from several points of view. (1) Since the only known derivative of 1,3-propanedione is tris(1,3-propanedionato)chromium(III), assessing the electronic effect of the simplest 1,3-diketonate chelate ring necessarily involves a study of Cr(III) chelates. (2) The inertness of Cr(III) compounds leaves no doubt that the species being reduced is the intact molecular complex. (3) The degree of reversibility of the Cr(III) → Cr(II) reduction can be expected to be solvent dependent, thereby allowing one to test the importance of reversibility on the measured $E_{1/2}$ values. (4) Since the spectral properties of Cr(1,3-diketonato)$_3$ chelates are well studied, comparisons between spectral and polarographic results can in theory be made.

In the present investigation 20 tris(1,3-diketonato)chromium(III) chelates were prepared and studied polarographically in dimethyl sulfoxide and in 85% dioxane–15% H_2O. The generalized formula for the chelates studied is shown below
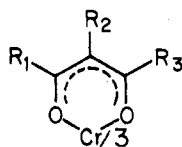
where R_1 and R_3 = H, CH_3, t-C_4H_9, C_6H_5, or CF_3 and R_2 = H, CH_3, C_2H_5, or n-C_4H_9.

Experimental Section

Synthesis. The chromium(III) chelates were prepared by established methods[1,2] and purified chromatographically on an alumina column. The ligands substituted in the 2 position were prepared by combining 0.33 mol of the parent ligand, 0.1 mol of the appropriate alkyl iodide, 0.6 mol of K_2CO_3 (heated at 100° overnight), and 30 ml of acetone in a 100 ml round-bottomed flask. This mixture was refluxed with stirring for 12 hr. After cooling, the reaction mixture was poured into 300 ml of H_2O. The crude product was extracted into ether and the ether evaporated at room temperature. For 2-Et-DBM and 2-Bu-DBM, the solid products were recrystallized from ether. For all other products, liquids resulted which were chelated directly without further purification.

Polarographic Measurements. The polarographic apparatus has been described previously.[3] Cyclic voltammetric current *vs.* potential curves were obtained using a platinum electrode at a scan rate of 0.025 V/sec. All solutions were 1.0×10^{-3} M with respect to Cr(III) and 0.1 M with respect to the supporting electrolyte, [(Et)$_4$N]ClO$_4$. Purification of the dioxane and [(Et)$_4$N]ClO$_4$ has been described previously.[3] Reagent grade dimethyl sulfoxide was used without further purification. All solutions were degassed with solvent presaturated N_2 for 30 min and N_2 was directed over the surface of the solution during polarographic runs.

Results

The chromium chelates reported in Tables I and II were studied polarographically in dimethyl sulfoxide and/or 85% dioxane–15% water. In all cases [(C$_2$H$_5$)$_4$N]ClO$_4$ was the supporting electrolyte. The interpretation of the polarographic waves is complicated somewhat by the periodic premature release of a drop from the dropping mercury electrode. When this happens a decrease in the current results which requires several succeeding drops to be restored to its proper value. This phenomenon is observed on the rising portion of the wave and on the diffusion-controlled plateau. The cause appears to be a function of the compound since it is observed in both solvent systems. Although it is annoying, the waves are readily interpretable and the results are reproducible.

In DMSO multiple waves are observed in all but one case. The values of the diffusion currents for these waves suggest a series of one-electron reductions. For the compounds 4, 6, and 9, three waves with similar diffusion currents are observed. Only the first wave will be discussed in detail. The process associated with this wave is assigned to the Cr(1,3-diketonato)$_3$ + e⁻ → Cr(1,3-diketonato)$_3$⁻ reduction. For representative complexes, the slope of E_{dme} *vs.* log $i/(i_d - i)$ for this wave is very nearly the theoretical value for 59.15 mV for a reversible one-electron reduction. Cyclic voltammetric results confirmed that the reduction is reversible. Interestingly, for Cr(DBM)$_3$ the cyclic results showed that all three of the waves are reversible in DMSO (Figure 1). An indication that the second and third one-electron waves are closely related to the first for all complexes is that the separation (in volts) between the waves is very nearly constant. With the exception of Cr(HFA)$_3$ and Cr(TFBzac)$_3$, the separation between waves one and two is 0.46 ± 0.04 V. For compounds in which three waves are observed, the separation between the first and third is 0.76 ± 0.01 V. Thus, although the half-wave potentials vary considerably from compound to compound, the separation between the waves is nearly

(1) J. P. Collman, E. T. Kettleman, W. S. Hart, and N. A. Moore, *Inorg. Syn.*, 8, 141, 144 (1966).

(2) R. Charles, *Inorg. Syn.*, 8, 138 (1966).

(3) R. F. Handy and R. L. Lintvedt, *Inorg. Chim. Acta*, submitted for publication.

Table I. Nomenclature, Abbreviation, and Analytical Data for the Tris(1,3-diketonato)chromium(III) Chelates Studied

| | | | | Analysis | | | |
| | | | | Calcd | | Found | |
No.	Abbr	Systematic name	Mp, deg	C	H	C	H
1.	Cr(PDO)$_3$	Tris(1,3-propanedionato)chromium(III)[a]	181				
2.	Cr(BDO)$_3$	Tris(1,3-butanedionato)chromium(III)[a]	171				
3.	Cr(t-C$_4$H$_9$PDO)$_3$	Tris(4,4-dimethyl-1,3-pentandionato)chromium(III)[a]	116 trans[b] 135 cis	58.2	7.6	58.6	7.9
4.	Cr(C$_6$H$_5$PDO)$_3$	Tris(1-phenyl-1,3-propanedionato)chromium(III)[a]	194 trans[b] 197 cis	65.7	4.3	65.7 66.4	4.8 4.6
5.	Cr(Acac)$_3$	Tris(2,4-pentanedionato)chromium(III)[a]	216				
6.	Cr(TFA)$_3$	Tris(1,1,1-trifluoro-2,4-pentandionato)chromium(III)[a]	156 trans[b] 112 cis				
7.	Cr(HFA)$_3$	Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-chromium(III)[a]	84				
8.	Cr(BZac)$_3$	Tris(1-phenyl-1,3-butanedionato)chromium(III)[a]	235				
9.	Cr(DBM)$_3$	Tris(1,3-diphenyl-1,3-propanedionato)chromium-(III)[a]	330				
10.	Cr(TFBzac)$_3$	Tris(1,1,1-trifluoro-4-phenyl-2,4-butanedionato)-chromium(III)[a]	170	51.7	2.6	52.7	2.9
11.	Cr(TFDMH)$_3$	Tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)-chromium(III)	56				
12.	Cr(3-Me-Acac)$_3$	Tris(3-methyl-2,4-pentanedionato)chromium(III)	100 subl	55.2	6.91	55.4	7.10
13.	Cr(3-Et-Acac)$_3$	Tris(3-ethyl-2,4-pentanedionato)chromium(III)	153	58.2	7.62	58.1	7.78
14.	Cr(3-Bu-Acac)$_3$	Tris(3-n-butyl-2,4-pentanedionato)chromium(III)	136	62.7	8.70	62.6	8.91
15.	Cr(2-Me-Bzac)$_3$	Tris(1-phenyl-2-methyl-1,3-butanedionato)-chromium(III)	117	68.6	5.72	68.1	5.70
16.	Cr(2-Et-Bzac)$_3$	Tris(1-phenyl-2-ethyl-1,3-butanedionato)-chromium(III)	75	69.8	6.30	69.5	6.29
17.	Cr(2-Bu-Bzac)$_3$	Tris(1-phenyl-2-n-butyl-1,3-butanedionato)-chromium(III)	101	71.7	7.25	70.8	7.03
18.	Cr(2-Me-DBM)$_3$	Tris(1,3-diphenyl-2-methyl-1,3-propanedionato)-chromium(III)	268	75.5	5.11	75.7	5.96
19.	Cr(2-Et-DBM)$_3$	Tris(1,3-diphenyl-2-ethyl-1,3-propanedionato)-chromium(III)	251	76.0	5.59	74.9	5.60
20.	Cr(2-Bu-DBM)$_3$	Tris(1,3-diphenyl-2-n-butyl-1,3-propanedionato)-chromium(III)	221	76.9	6.41	76.7	6.14

[a] Prepared and characterized in a previous investigation of spectral properties; A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, **10**, 478 (1971).
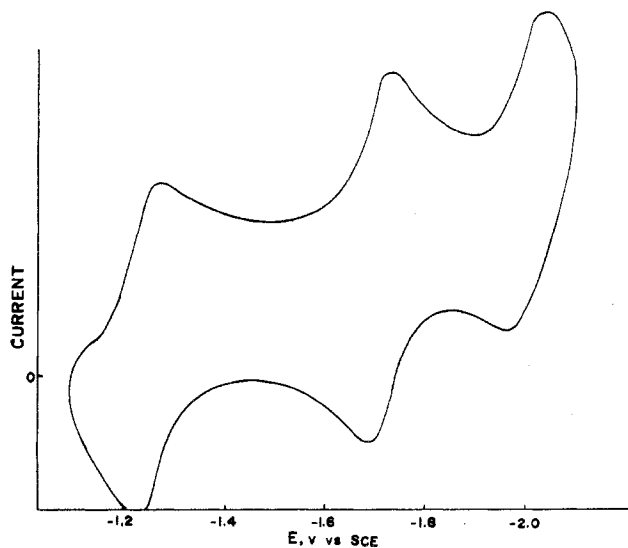[b] The trans isomer is assigned as the first band eluted from an alumina chromatography column.

Figure 1. Cyclic voltommetric current vs. potential curve for the reduction of Cr(DBM)$_3$ in DMSO.

Figure 2. Plot of $E_{1/2}$ (V) vs. the sum of the Hammett σ constants, $\Sigma\sigma_x$, for the substituents R$_1$, R$_2$, and R$_3$. For R$_1$ and R$_3$, σ_x is the para position value. For R$_2$, σ_x is the meta position value.

constant. As expected, the $E_{1/2}$ for the first wave is a function of the polar substituent constant, σ_x. This relationship is shown in Figure 2.

The reductions in 85% dioxane–15% H$_2$O are significantly different from those in DMSO in that generally only one wave is observed, and based on E_{dme} vs. log $i/(i_d - i)$ plots the reductions are more irreversible than in DMSO. These differences are presumed due to the large amounts of water in the solvent system. The fact that multiple waves are not ob-
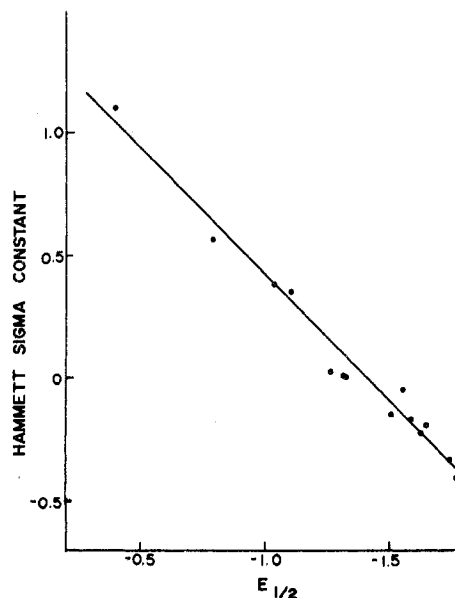
served in 85% dioxane suggests that there is chemical decomposition of the reduction product. Under such conditions the reduction would, of course, be irreversible. For this reason, arguments dealing with substituent group electronic effects may be strictly valid only for results obtained in DMSO. In most instances, however, the $E_{1/2}$ values in the

Table II. Polarographic Results in DMSO and 85% Dioxane–15% H_2O and the Sum of the Hammett Polar Substituent Constants

No.	Compd	R_1	R_2	R_3	$E_{1/2}$ (V) vs. sce	i_d, μ^a	Slope, mV^a	$E_{1/2}$ (V) vs. sce	i_d, μ^a	Slope, mV^a	$\Sigma\alpha_x{}^b$
					DMSO			**85% dioxane–15% H_2O**			
1.	Cr(PDO)$_3$	H	H	H	−1.32	1.63					0.00
					−1.82	1.30					
2.	Cr(BDO)$_3$	CH$_3$	H	H	−1.58	1.72					−0.17
					−2.00	1.78					
3.	Cr(t-C$_4$H$_9$PDO)$_3$	t-C$_4$H$_9$	H	H	−1.64	1.48					−0.20
					−2.04	1.49					
4.	Cr(C$_6$H$_5$PDO)$_3$	C$_6$H$_5$	H	H	−1.31	1.12		−1.38	0.82	55	+0.01
					−1.82	1.12					
					−2.14	0.82					
5.	Cr(Acac)$_3$	CH$_3$	H	CH$_3$	−1.73	1.19	58	−1.67	1.04	63	−0.34
					−2.16	1.27					
6.	Cr(TFA)$_3$	CF$_3$	H	CH$_3$	−1.04	1.38		−1.11	0.90	71	+0.38
					−1.54	0.78					
					−1.87	1.12					
7.	Cr(HFA)$_3$	CF$_3$	H	CF$_3$	−0.40	1.16		−0.39	0.30	69	+1.10
					−1.48	1.17					
8.	Cr(Bzac)$_3$	C$_6$H$_5$	H	CH$_3$	−1.50	1.04	60	−1.53	0.95	58	−0.16
					−1.95	1.56					
9.	Cr(DBM)$_3$	C$_6$H$_5$	H	C$_6$H$_5$	−1.26	0.71	58	−1.40	0.75	75	+0.02
					−1.72	0.89		−1.65	3.57		
					−2.03	0.89					
10.	Cr(TFBzac)$_3$	C$_6$H$_5$	H	CF$_3$	−0.79	1.14		−0.97	0.76	54	+0.56
					−1.34	1.17					
					−1.78	1.36					
11.	Cr(TFDMH)$_3$	t-C$_4$H$_9$	H	CF$_3$	−1.10	1.20					+0.35
12.	Cr(3-Me-Acac)$_3$	CH$_3$	CH$_3$	CH$_3$				−1.76	0.77		−0.41
13.	Cr(3-Et-Acac)$_3$	CH$_3$	C$_2$H$_5$	CH$_3$				−1.78	0.93		−0.38
14.	Cr(3-Bu-Acac)$_3$	CH$_3$	n-C$_3$H$_7$	CH$_3$				−1.84			−0.39
15.	Cr(2-Me-Bzac)$_3$	C$_6$H$_5$	CH$_3$	CH$_3$				−1.62	4.64	101	−0.23
16.	Cr(2-Et-Bzac)$_3$	C$_6$H$_5$	C$_2$H$_5$	CH$_3$				−1.63	3.00	86	−0.20
17.	Cr(2-Bu-Bzac)$_3$	C$_6$H$_5$	n-C$_3$H$_7$	CH$_3$				−1.65	2.62	92	−0.21
18.	Cr(2-Me-DBM)$_3$	C$_6$H$_5$	CH$_3$	C$_6$H$_5$				−1.55	3.48	63	−0.05
19.	Cr(2-Et-DBM)$_3$	C$_6$H$_5$	C$_2$H$_5$	C$_6$H$_5$				−1.56	3.68	70	−0.02
20.	Cr(2-Bu-DBM)$_3$	C$_6$H$_5$	n-C$_3$H$_7$	C$_6$H$_5$				−1.58	3.64	63	−0.03

^{a} Slope of E_{dme} vs. log $i/(i_d - i)$. ^{b} H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953). σ_{meta} values are used for R_2; σ_{para} values are used for R_1 and R_3.

two solvent systems are quite similar and comparisons can be made.

For solubility reasons, the entire series of chelates substituted on the central carbons of the chelate rings were studied only in 85% dioxane. The results show that substitution in the 2 position has only a small effect on the reduction potential when compared to the parent compound.

Discussion

The polarographic results for the Cr(1,3-diketonato)$_3$ chelates are explicable on the basis of substituent group electronic effects. The most convincing proof of this is the additivity of the substituent group effect on $E_{1/2}$. The effect of C$_6$H$_5$, CH$_3$, CF$_3$, and t-C$_4$H$_9$ on the $E_{1/2}$ can be assessed relative to H by using Cr(1,3-propandionato)$_3$ as the reference. Once the effect of several groups is determined in this manner they may be recombined in different ways to give empirically calculated $E_{1/2}$ values which can be compared to experimental results. Some experimental and calculated results are shown in Table III. The excellent agreement between calculated and experimental $E_{1/2}$ values proves that the effects are additive.

The additivity of the substituent effect allows one to devise a scale analogous to the Hammett σ functions. A comparison of the polarographically derived scale and the corresponding Hammett meta and para σ values is given in Table IV. In general, the polarographic values agree well with σ_p. It is interesting to note that a plot of Δ/R vs. σ_p gives a line whose slope is very nearly equal to one. Since the correlation between Δ/R and σ_p is so strong and the 1,3 substituents are

Table III. Evaluation of Substituent Group Electronic Effects^a

A. Effect of R on $E_{1/2}$ Relative to H (in DMSO)

R$_1$	R$_2$	R$_3$	$E_{1/2}$, V	$\Delta =$ [$E_{1/2} - E_{1/2}$Cr-(PDO)$_3$], V	Shift per R group, Δ/R, V per R
H	H	H	−1.32	0	0
CH$_3$	H	CH$_3$	−1.73	−0.41	−0.21
CF$_3$	H	CF$_3$	−0.40	0.92	0.46
C$_6$H$_5$	H	C$_6$H$_5$	−1.26	0.06	0.03
t-C$_4$H$_9$	H	H	−1.64	−0.32	−0.32

B. Comparison of Calculated and Observed $E_{1/2}$

R$_1$	R$_2$	R$_3$	Calcd $E_{1/2}$, V^b	Obsd $E_{1/2}$, V	Diff, V
CH$_3$	H	H	−1.53	−1.58	−0.05
C$_6$H$_5$	H	H	−1.29	−1.31	−0.02
CH$_3$	H	C$_6$H$_5$	−1.50	−1.50	0.00
CH$_3$	H	CF$_3$	−1.07	−1.04	0.03
C$_6$H$_5$	H	CF$_3$	−0.83	−0.79	0.04
t-C$_4$H$_9$	H	CF$_3$	−1.18	−1.10	0.08
					Av ±0.04

^{a} A comparison between empirically calculated and experimental $E_{1/2}$ values. ^{b} Calculated $E_{1/2} = E_{1/2}$Cr(PDO)$_3$ + Δ/R_1 + Δ/R_3.

ortho and para to the oxygens, it appears that the major electronic effects are being experienced at the oxygens rather than at the metal position itself. Previous arguments have been advanced for using σ_m to correlate $E_{1/2}$ and substituent constants since the 1,3 substituents are meta to the metal posi-

Table IV. Polarographically Determined Substituent Electronic Effects and Hammett σ Values

R	Δ/R	$\sigma_p{}^a$	$\sigma_m{}^a$
H	0	0	0
CH_3	−0.21	−0.17	−0.07
$t\text{-}C_4H_9$	−0.32	−0.20	−0.12
C_6H_5	0.03	0.01	0.22
CF_3	0.46	0.55	0.42

a See, for example, H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953).

tion.[4,5] In terms of understanding electronic polarization about the chelate rings, the results reported herein dictate the use of a para position substituent constant. Patterson and Holm[5] have correlated $\Sigma\sigma_m$ vs. $E_{1/2}$ for a series of Ru-(1,3-diketonates)$_3$ which undergoes a reversible one-electron reduction. It is interesting to note that their correlation is greatly improved if σ_p values are used for the 1,3 substituents rather than σ_m values. The improvement is largely due to the fact that phenyls appear to have very weak interactions similar to H. Thus, they act more as para substituents than as meta substituents. Differences between σ_m and σ_p for other groups are much less pronounced.

Additional support for this reasoning is obtained by inspection of the 2-substituted methyl derivatives (compounds no. 12, 15, and 18). In these chelates the central methyl group is meta to the oxygens and para to the metal. If the major thrust of this methyl group is on the oxygens, the $E_{1/2}$ values would be expected to be 0.07 V more negative than the H-substituted parent since $\sigma_m = -0.07$. If, on the other hand, the methyl is primarily affecting the electron density of the metal itself, the $E_{1/2}$ would be expected to be 0.17 V more negative than the parent compounds since $\sigma_p = 0.17$ V. In the cases of Cr(Acac)$_3$-Cr(3-Me-Acac)$_3$ and Cr(Bzac)$_3$-Cr(2-Me-Bzac)$_3$ the methyl group causes $E_{1/2}$ to be 0.09 V more negative than the parent chelate which is in good agreement with $\sigma_m = -0.07$. For Cr(DBM)$_3$-Cr(2-Me-DBM)$_3$ the difference is −0.15 V, which is close to the σ_p value of −0.17. Thus, the situation for the central carbon is not unambiguous, but in the less complex chelates its electronic effect appears adequately described by σ_m.

It has been pointed out in previous papers[3,4] that in order to correlate $E_{1/2}$ of Cu(1,3-diketonates)$_2$ to $\Sigma\sigma_x$ the chelates must be similarly substituted, *i.e.*, all aliphatic, all aromatic, or all mixed aliphatic–aromatic substituents. Correlations between these classes of Cu(II) chelates are not straightforward. The same is not true, however, for the Cr(III) and Ru(III)[5] 1,3-diketonates. For these chelates which exhibit reversible reductions strong correlations between $\Sigma\sigma_x$ and $E_{1/2}$ exist regardless of the nature of the substituent group. The other obvious difference between the Cu(II) reductions and Cr(III) or Ru(III) reductions is the orientation of the diketonates about the metal. It is likely that the electrode can interact much more directly with the chelated Cu(II) than with chelated M(III). Regardless of the details, it is apparent that mechanistic considerations are important in determining the nature of the ligand's influence on reduction potentials.

(4) R. L. Lintvedt, H. D. Russell, and H. F. Holtzclaw, Jr., *Inorg. Chem.*, 5, 1603 (1966).
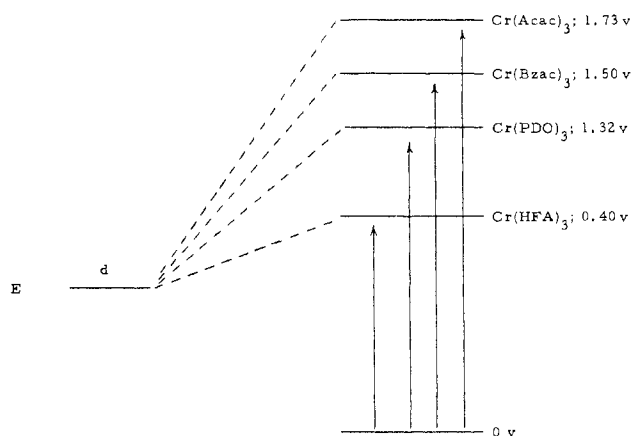(5) G. H. Patterson and R. H. Holm, *Inorg. Chem.*, 11, 2285 (1972).

Figure 3. Schematic representation of the influence of the spherical ligand field potential on $E_{1/2}$. The zero-point energy is taken as the electrode with zero applied potential.

The ligand field spectral properties of Cr(1,3-diketonato)$_3$ chelates have been quite well studied[6,7] and it is, therefore, of interest to see if a correlation exists between spectral and polarographic results. Inspection of the usual ligand field parameters of $10Dq$, B, and C[7] shows that no apparent relationship exists between these parameters and $E_{1/2}$. Certainly reduction potential differences are in no way accounted for by differences in $10Dq$. At this point it appears that the determining factor is just the energy of the metal acceptor orbital relative to the electrode and this this energy is greatly influenced by the nature of the ligand. Since the d–d spectral properties are quite similar from one chelate to the next, the ligand field splitting of the metal orbitals is about the same for all chelates.[7] However, the destabilizing repulsive effect (or spherical ligand field potential) of the ligands is a reasonable way to account for $E_{1/2}$ differences. This is shown schematically in Figure 3. On this basis, it is understandable that chelates with the strongest electron-withdrawing ligands reduce most positively, since the magnitude of the potential field is a function of the charge on the oxygens. The transition arrows in Figure 3 represent the $E_{1/2}$ values for four representative chelates.

(6) L. S. Forster, *Transition Metal Chem.*, 5, 1 (1969).
(7) A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, 10, 478 (1971).