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Steric Effects on Activation Energy for the Electrochemical Oxidation of Organocobaloximes

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Heterogeneous electron transfer rate constants were determined as a function of electrode potential for one-electron oxidation in acetonitrile (AN) at 0 °C of a series of organocobaloximes [R–Co(DH)$_2$L] bearing widely different organic groups. Reaction entropies were determined by voltammetric half-wave potential ($E^r_{1/2}$) measurements in a non-isothermal cell. The electron transfer coefficients and reorganization parameters were calculated following the Marcus theory. The reaction free energies relative to a reference couple ΔG° are linearly correlated with the polar Taft constant of the organic substituent R.

The steric effects on ΔG° are shown by the correlation of $E^r_{1/2}$ with the Co–C bond distance.

Assuming constancy of double layer effects along the series in the given solution composition, the trends of the apparent rate constants k_{app} were considered in order to evaluate the effects of the nature of the organic ligand on the activation energy $\Delta G^{\neq}$ of the electron transfer. The steric effects on $\Delta G^{\neq}$ are pointed out i.a. by consideration of the relationship between $\Delta G^{\neq}$ and ΔG°.

Introduction

One electron transfer as a preliminary step in the reductive and oxidative cleavage of the cobalt–carbon bond in organometallic chelates was reported in previous studies of chemical [1, 3–5] and electrochemical [2] behaviour of models of Vit. B12 group coenzymes. Chelates of general formula [R–Co(chel)L], where R is an organic group, (alkyl, cycloalkyl, aryl), L is a donor ligand* and (chel) encompasses a variety of chelating agents such as tetradentate bis-dimethylglyoximato dianion or Schiff base chelating agent, with N_2 or N_2O_4 donor atom set [1], undergo both one-electron reduction and oxidation:

$$[\text{R–Co(chel)L}] \pm e^- \rightleftharpoons [\text{R–Co(chel)L}]^{\mp} \quad (1)$$

The electrochemical process gives rise to relatively unstable radical anions and radical cations respectively [2–4, 4–11].

The organic group in the product of the oxidative electron transfer is easily subject to nucleophilic displacement giving rise to an E.C.E. process [2d, 3a]. In suitable experimental conditions (when the subsequent homogeneous chemical reaction is slow) the simple electron transfer can be studied independent from any following chemical reaction [4]. In this case a redox couple is formed by the organometallic complex and the cation radical, which is kinetically stable with respect to changes in the coordination shell at least in the time scale of the electron transfer process, and the kinetic data for the simple electron transfer can be obtained.

The influence of the nature of the organic group R as an axial ligand with planar macrocyclic or pseudomacrocyclic chelating agents on the polarographic half-wave potentials was pointed out in several studies [2, 4, 7]. Correlation with Taft constant σ* was generally observed.

On the other hand, steric effects on chemical one electron oxidations of organometallic compounds were only recently investigated in homoleptic alkytin, lead and mercury compounds [12] and the determination of the rate constants of one electron oxidation of some methyl and ethyl derivatives of two cobalt macrocycles was included in a more general study of the mechanism of oxidative cleavage of organometallic compounds [16].

The assessment and distinction of steric from electronic effects of the organic substituent in organocobalt models of Vit. B12 group coenzymes appears to be relevant in connection with enzymatic reactions involving cobalt–carbon bond formation and cleavage.

In the present paper we report the thermodynamic and kinetic parameters for the heterogeneous one-electron oxidation at Pt electrode in a series of organo-bis-dimethylglyoximato cobalt(III) chelates (organocobaloximes) [R–Co(DH)$_2$H$_2$O] in AN.

The organic groups R include primary, secondary and cyclic alkyls and substituted benzyls and cover

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*The preferred coordination number of the cobalt chelates is typically 6 (occasionally 5) for Co(III), 5 for Co(II) and either 5 or 4 for Co(I). In donor solvents, solvent molecules can be coordinated to one or both axial positions free of more strongly bonded, or covalently bonded ligands.

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TABLE I. Summary of Electrochemical and Thermodynamic Data for Reaction $[R{-}Co(DH)_2H_2O] - e^- \rightleftharpoons [R{-}Co(DH)_2H_2O]^+$.

N	R[a]	$E^r_{1/2}$ V vs. SCE ±0.003	$E_p^a - E_p^c$ mV	ΔG° Kcal mol^{-1} ±0.07	ΔS° Cal mol^{-1} K^{-1} ±1.5	σ	E_s	d^b(Co–C) Å
1	CH_3	+0.785	58	18.12	–4	0	0	1.998
2	C_2H_5	+0.753	54	17.38	–4	–0.10	–0.07	2.035
3	n-C_3H_7	+0.750	55	17.31	–5	–0.12	–0.36	
4	n-C_4H_9	+0.751	60	17.34	–4	–0.13	–0.39	
5	i-C_4H_9	+0.754	59	17.41		–0.13	–0.93	
6	neopentyl	+0.732	63	16.90		–0.17	–1.74	2.060
7	$CN(CH_2)_3$	+0.810		18.70		–0.30		
8	CF_3CH_2	+0.902	62	20.82		+0.92		2.010
9	i-C_3H_7	+0.708	60	16.34	–8	–0.19	–0.47	2.085
10	3-pentyl	+0.677	61	15.63	–10	–0.23	–1.98	
11	c-C_5H_9	+0.720	60	16.62		–0.20		
12	$C_6H_5CH_2$	+0.758	54	17.50		+0.22		
13	p-$CH_3C_6H_4CH_2$	+0.740	60	17.08		+0.17		
14	p-$ClC_6H_4CH_2$	+0.780	56	18.01		+0.28		
15	p-$NO_2C_6H_4CH_2$	+0.833	62	19.23				
16	C_6H_5	+0.861	56	19.88		+0.60		

[a] Organic group in organocobaloxime. [b] See reference [27].

different steric requirements and electronic effects (see Table I).

Using the present and literature data we wish to show that the consideration of trends of: (a) the thermodynamic driving force as reflected by the half-wave potential; (b) the electron transfer rate constants of reaction 2; (c) the transfer coefficient and the reorganization term as calculated following the Marcus treatment, together allow us to point out the consequences of changes in steric requirements of R on the energetics of electron transfer:

$$[R{-}Co(DH)_2H_2O] - e^- \rightleftharpoons [R{-}Co(DH)_2H_2O]^+ \quad (2)$$

Experimental

Materials

AN (RPE Carlo Erba) was dried with 4-Å molecular sieves. Tetraethylammoniumperchlorate (TEAP), (Carlo Erba) was dried *in vacuo*. The complexes studied were prepared according to the methods already reported [17]. All electrochemical measurements were carried out in AN containing 1.2×10^{-3} mol dm^{-3} cobalt(III) complex and 0.1 mol dm^{-3} TEAP as the supporting electrolyte. The solutions were freshly prepared in the electrochemical cell, deaerated with pure, dry nitrogen. During all the experiments the cell was protected from light to avoid the decomposition of the compounds.

Apparatus

An Amel Model 471 multipolarograph equipped with a Model 460 stand was used to record current–potential curves in both D.C. and A.C. experiments. All measurements were carried out in a three-electrode system in a cell protected in a Faraday's cage. A Tacussel EDI rotating platinum disk electrode (RPDE) of radius r = 1 mm was used as working electrode. Precise control of rotation speed was ensured by an independent servo-control electronic amplifier. The platinum surface was cleaned in hot nitric acid [18] for several minutes, followed by repeated washings in distilled water. Before the beginning of the experiment the Pt electrode was treated with a repetitive cyclic scan from –0.2 to +0.2 V *vs.* NaCl-saturated calomel electrode (SCE) for several minutes at low scanning rate and rotation speed. Using this procedure we obtained reproducible data. A platinum-wire microelectrode was used as the working electrode in linear sweep voltammetry and in A.C. experiments. A NaCl-SCE was used as the reference electrode separated by a salt bridge containing the same electrolyte in AN as the examined solution. The counter electrode consisted of a platinum-wire. Cyclic voltammetry was carried out with an operational amplifier-based three-electrode electronic polarograph, Amel Model 448, equipped with positive feed-back compensation.

Evaluation of Electron Transfer Rate Constants

The electron transfer rate constants were obtained from the voltammetric curves recorded with the RPDE following the procedure described in [19] and using the eqn. 3 proposed in [20]:

$$\frac{i_L}{nFAck} = \frac{(i_L - i)}{i} - \frac{(i_L - i_r)}{i_r} \quad (3)$$

where i_L is the limiting current of the voltammetric wave, i_r is the current calculated for the hypothetical reversible process at the same potential were the current i is measured, and k is the heterogeneous rate constant at the same potential; n is the number of electrons involved, F is the Faraday constant, A the electrode area and c the concentration of the electroactive species in the bulk of the solution.

A typical voltammetric wave is shown in Fig. 1(a); an example of the treatment of the experimental data for the same wave is shown in Fig. 1(b).

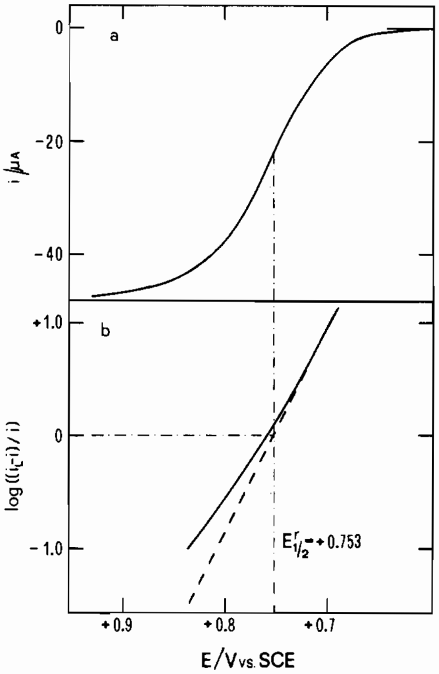

Fig. 1. a) Typical anodic wave recorded in a AN solution containing $[C_2H_5-Co(DH)_2H_2O]$ (1.26×10^{-3} mol dm^{-3}) and TEAP (0.1 mol dm^{-3}) at 0 ℃. b) Semilogarithmic analysis using the method proposed by Koryta.

For all the complexes examined the voltammetric waves were recorded at rotation rates of 2500 to 3500 rpm and potential sweep rate of 5 mV s^{-1}. The values of the reversible half-wave potentials were obtained by extrapolation of the $\log[i_L - i/i]$ *vs.* E plot with the theoretical reversible slope of 54 mV obtained at a potential sweep rate of 1 mV s^{-1} and a small rotation speed rate.

The $E^r_{1/2}$ values obtained with this procedure were reproducible within 3 mV.

The $E^r_{1/2}$ values obtained from RPDE voltammetry agreed with the mean of the cathodic (E_p^c) and anodic (E_p^a) peak potentials measured with cyclic voltammetry, and with the values obtained with A.C. fundamental harmonic voltammetry, within a range of 5 mV.

Assuming that the ratio of the diffusion coefficients of the terms of the redox couple in eqn. 2 is very near to unity, the $E^r_{1/2}$ values can be regarded as standard redox potentials of the corresponding couples E°.

Evaluation of Reaction Entropies

We obtained the $\Delta S^\circ = F(\Delta E^\circ/\Delta T)$ values for the reaction 2 from $E^r_{1/2}$ in a non-isothermal cell [14] using fundamental harmonic A.C. voltammetry in order to evaluate small (± 0.5 mV) shifts of the $E_{1/2}$ values.

The experiments were carried out in the following conditions: the temperature of the cell was varied in the range −25.0 ℃ to + 10.0 ℃ ± 0.1℃ while the salt bridge holding the SCE was maintained at a constant temperature of + 25.0 ℃ ± 0.05 ℃; the D.C. scan rate was 1 mV s^{-1}. The A.C. superimposed signal was 7 mV peak to peak and 50 Hz.

The logarithmic analysis of the fundamental harmonic A.C. wave and its half-width were very close to the theoretical values for a one electron reversible process [22] for all compounds examined at any temperature.

Results

The Electron Transfer Process

One-electron oxidation of organo-bis-dimethylglyoximato cobalt chelates (organocobaloximes) $[R-Co(DH)_2L]$ was investigated in AN [3a, 6], CH_2Cl_2 [3a], dimethylformamide [6–8] and in aqueous solution [4, 5].

Evidence was presented [3, 7] for the cleavage of the Co–R bond following the electron transfer in an E.C.E. process in the presence of typical nucleophyles such as pyridine or Cl^- at room temperature:

$$[R-Co(DH)_2L] - e^- \rightleftharpoons [R-Co(DH)_2L]^+ \tag{4}$$

$$[R-Co(DH)_2L]^+ + nuc^- \longrightarrow R-nuc + [Co(DH)_2L_2] \tag{5}$$

As judged from the characteristics of cyclic voltammograms at low temperature and sufficiently fast potential sweep, or from anodic waves obtained with a rotating disk electrode [6] in AN 0.1 mol dm^{-3} tetraethylammonium fluoroborate, the electrode process was reported as reversible or quasireversible.

The data so far reported show that the rate of the heterogeneous electron transfer is influenced by the nature of the solvent and of the supporting electrolyte, and generally falls within the time scale of cyclic voltammetry.

We have found that at 0 ℃ in AN and TEAP 0.1 mol dm^{-3} the examined complexes yielded cyclic voltammograms typical of simple reversible one-electron oxidation. In fact the peak current ratio $i_{pc}/i_{pa} \simeq 1$ and peak potential difference was $\Delta E_p \simeq$

60 mV (see Fig. 3 and Table I, respectively). The anodic waves obtained with the RPDE at low rotation rate and potential sweep rate of 1 mV s^{-1}, show also the characteristics of simple one-electron reversible or quasi reversible oxidation, *i.e.* $\Delta E/\Delta \log[i_L - i/i] \simeq 54$ mV. No evidence was obtained for absorption phenomena at the Pt electrode by conventional criteria.

All the results confirm that the coupling of the heterogeneous electron transfer with a homogeneous chemical reaction does not interfere with the determination of the thermodynamic and kinetic parameters of the simple electron transfer.

E.T. Rate Constants

Rate constants for the reaction 2 were determined as described above by analysis of the RPDE voltammograms.

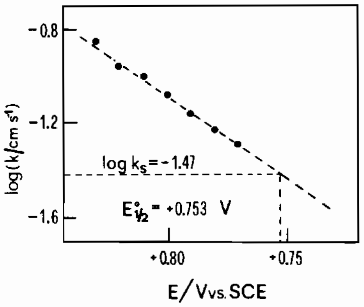

Fig. 2. Dependence of log(k) on the electrode potential for oxidation of $[C_2H_5-Co(DH)_2H_2O]$ in the same conditions as in Fig. 1.

Figure 2 shows a typical set of data obtained for the oxidation of $[C_2H_5Co(DH)_2H_2O]$ as a plot of the log of the observed (apparent) rate constant log k(app) as a function of the electrode potential E.

It is recognized that the observed rate constants and transfer coefficients should be corrected for the diffuse double layer effects [23, 24]. In non-aqueous solvents, and especially for reactions taking place at solid electrodes, the usual correction procedures are difficult owing to a much less extended knowledge of the interphase as compared with the Hg-aqueous solution double-layer [25, 26].

For a given electrode reaction in a series of closely related complexes in the same solution composition, we may assume that the double-layer structure is not significantly different from term to term of the series. It is likely that the difference of contributions of the work terms for different couples will be negligible as compared with the intramolecular reorganization energy.

In other words, in the series of present complexes in the same solution composition we may assume that the double-layer contribution to the free energy barrier for the one electron oxidation is nearly constant and that the difference in the free energy of activation can be explained in terms of differences in intramolecular rearrangement.

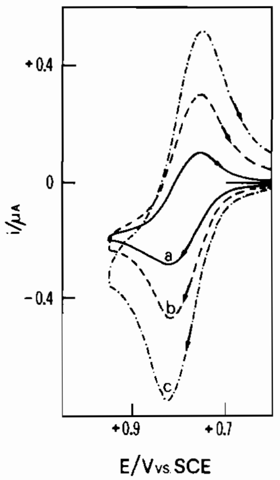

Fig. 3. Cyclic voltammograms for the oxidation of $[C_2H_5-Co(DH)_2H_2O]$ (in the same conditions as in Fig. 1) on Pt electrode at different scan rate: a) 20 mV s^{-1}; b) 50 mV s^{-1}; c) 100 mV s^{-1}.

From the corresponding plots, the standard apparent rate constant (k_s) was obtained for all the terms of the series of organocobaloximes examined.

Apparent transfer coefficients α(app) can be calculated from these plots and eqn. 6:

$$\alpha_{app} = 2.303 \frac{RT}{F} \frac{\partial \log k_{app}}{\partial E} \tag{6}$$

Values of log k_s and α(app) are reported in Table II. From the linear dependence of log k_s on E it can be concluded that no potential dependence of α(app) can be observed within the accessible potential range (about 60 mV for all the complexes examined).

The free energy of activation is related to the rate constant and was calculated with eqn. 7:

$$k = Z \exp(-\Delta G^{\ddagger}/RT) \tag{7}$$

where Z is the heterogeneous collision number at the electrode (about 10^4). From the k_s values the standard free energy of activation for process 2 reported were obtained.

Discussion

Free Energy Relationships

The shift of $E^r_{1/2}$ due to the changes of substituent R spans a range of *ca.* 200 mV (*i.e.* of about 4.5 kcal/mol in terms of ΔG°).

The inspection of the trends of $E^r_{1/2}$ in Table I confirms the marked dependence of the redox behaviour of the present chelates from the nature of

TABLE II. Summary of Kinetic Data for Reaction $[R-Co(DH)_2H_2O] - e^- \rightleftharpoons [R-Co(DH)_2H_2O]^+$.

N	R	log k_s ±0.02	$\Delta G_o^{\neq}$ Kcal mol^{-1} ±0.03	λ Kcal mol^{-1} ±8	α ±0.02
1	CH_3	−1.55	6.90	20	0.53
2	C_2H_5	−1.47	6.81	31	0.46
3	n-C_3H_7	−1.50	6.84	37	0.42
4	n-C_4H_9	−1.52	6.87	51	0.35
5	i-C_4H_9	−1.66	7.04	41	0.39
6	neopentyl	−1.63	7.00	54	0.36
7	$CN(CH_2)_3$	−1.95	7.40	72	0.30
8	CF_3CH_2	−1.97	7.43	129	0.24
9	i-C_3H_7	−1.65	7.03	52	0.35
10	3-pentyl	−1.88	7.33	109	0.25
11	c-C_5H_9	−1.72	7.09	58	0.34
12	$C_6H_5CH_2$	−1.54	6.89	34	0.43
13	p-$CH_3C_6H_4CH_2$	−1.52	6.87	65	0.33
14	p-$ClC_6H_4CH_2$	−1.56	6.92	25	0.47
15	p-$NO_2C_6H_4CH_2$	−1.70	7.09	51	0.37
16	C_6H_5	−1.95	7.43	74	0.30

the covalently bound axial ligand R. A particularly strong thermodynamic influence was found for covalently bonded organic groups R in the [R–Co(salen)], [R–Co(DO)(DOH)pn][ClO_4] chelates [1]. This influence is qualitatively reflected in the linear free energy relationship between the shift of redox potentials for the one-electron reductions toward more cathodic potentials and the increase of the pK of the corresponding hydrocarbon acid RH.

As far as the organocobaloximes are concerned, recent work on $[R-Co(DH)_2H_2O]$ in 1 mol dm^{-3} $HClO_4$ pointed out the relationship of $E^r_{1/2}$ with a) the pK of the corresponding RH and b) with the Taft constant [4, 3].

Our results in AN solution show also, as a general trend, a displacement of the $E^r_{1/2}$ toward more negative potential with increasing value of the Taft constant of the substituent (Fig. 4). It must be noted, however, that it is difficult to recognize a single linear relationship holding for the whole set of data. Apparently the accepted values of the σ^* Taft constant are not able to give a single free energy relationship reflecting the thermodynamic effect of substituents R of different types on the redox potentials. In fact a linear correlation between $E^r_{1/2}$ and σ^* with the slope ($\rho \sim 0.1$) proposed in [4] is obtained if the substituents -C_6H_5 and -CH_2CF_3 are included, while a linear correlation with higher slope is found if only primary or secondary alkyl groups are considered. Moreover the slope of the correlation of the data of secondary alkyl is slightly different from that of the primary alkyls. One can see from the plot of Fig. 4 that substitution at the alpha carbon atom of the organic group R (increasing the bulkiness of the latter) from primary to secondary alkyls increases the ρ value of the linear relationship.

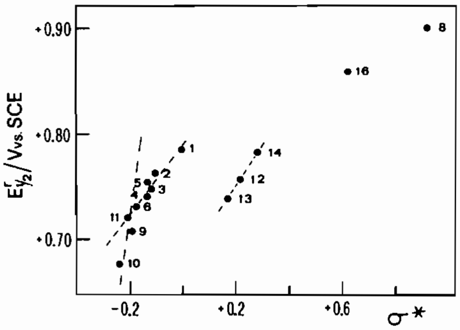

Fig. 4. Taft plot for the $E^r_{1/2}$ for redox couples $[R-Co(DH)_2H_2O]/[R-Co(DH)_2H_2O]^+$ in AN and TEAP 0.1 mol dm^{-3} at 0 °C. The label numbers are refered to Table I.

In agreement with the above result in aqueous $HClO_4$ [4] *p*-substitution in benzyl derivatives results in displacement of $E^r_{1/2}$ which is linearly correlated with σ_p Hammet parameters.

From the above evidence one can conclude that $E^r_{1/2}$ is sensitive to polar effects of alkyl groups, while the more pronounced effect of secondary alkyls as shown by the slope of the linear correlation may be explained by contributions due to molecular distortion. *p*-Substituted benzyl groups influence $E^r_{1/2}$ with a different mechanism, as is shown by the different relationship between $E^r_{1/2}$ and σ^*. The difference in the electronic effects of alkyls and the *p*-substituted benzyls may be attributed to interactions of the aromatic ring with the equatorial ligand. On the other hand, the strongest evidence of the steric effects on the free energy of the heterogeneous one electron oxidation is given by the regular increase of $E^r_{1/2}$ with

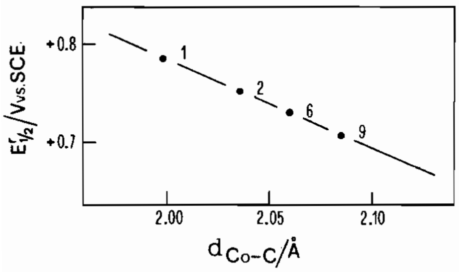

Fig. 5. Plot of $E^r_{1/2}$ *vs.* d(Co–C) for: 1) CH_3; 2) C_2H_5; 6) neopentyl; 9) i-C_3H_7.

increasing Co–C bond distance (Fig. 5). In fact the latter value linearly increases with increasing steric requirement of the organic group R [27].

This trend can be explained by the influence of increasing steric requirements of R on the dependence in energy necessary to change the Co–C bond length on going from the neutral molecule to the radical cation.

Reaction Entropies

The entropies of transition metal ions are known to be strongly dependent upon their charge and the nature of coordinated ligands. Entropy changes are attributed to variations in the structure of the solvent surrounding the ions in aqueous solution, as well as to electrostatic factors, and may represent a significant contribution to the driving force for the E.T. Low E.T. entropies of metal chelates are explained by the influence of increasing stability of the coordination sphere as compared with labile weak complexing unidentate ligands. In fact iron(III–II) couples and ruthenium(III–II) couples like tris(1,10 phenanthroline) ($Fe^{3+/2+}(phen)_3$ $Ru^{3+/2+}(phen)_3$) and tris(2,2'-bipyridine) ($Fe^{3+/2+}(bipy)_3$) show $\Delta S°$ value close to zero. On the other hand cobalt chelates such as $Co(phen)_3{}^{3+/2+}$ or $Co(bipy)_3{}^{3+/2+}$ and planar macrocyclic Co(III)/Co(II) couples have been found to exhibit high $\Delta S°$ values [14]. The stability of both terms of the redox couples of the present chelates in the time scale of the electrochemical techniques allow us to determine approximate values for the reversible E.T. entropies (eqn. 2) from accurate values of $E^r_{1/2}$ at different temperature in a non-isothermal cell (see Experimental). The one electron oxidation is accompanied by a small and negative entropy change (Table I).

Apparently, electrochemical reaction entropies of present organocobaloximes in AN are low, as expected, and rank as those of the above-mentioned iron and ruthenium couples. The lower $\Delta S°$ value for organocobaloximes as compared with $Co(phen)_3{}^{3+/2+}$ and $Co(bipy)_3{}^{3+/2+}$ could be described as being at least partly due to the lower charge of the central metal ion.

On the other hand the generally low value of $\Delta S°$ can be ascribed to the increase shielding of the charge of the central metal ion by the relatively large and stable chelating agent and by the covalently bound organic group [14].

The difference in $\Delta S°$ among the different terms of the series are small when compared with the uncertainty of the experimental data, and cannot be used to draw indications on the possible different effects of R on the E.T. entropy.

It must be noted however that the reaction entropies of organocobaloximes bearing bulky substituents are distinctly higher than those found for non-bulky compounds.

The Activation Free Energy

The kinetic results can be discussed at least qualitatively, assuming that factors which may give a more important contribution to the free energy of activation are related to the geometry and electronic structure differences between the reacting chelate and the chelate in the transition state. Of intramolecular factors contributing to the free energy barrier we consider only the changes in the organic group R along the series, since for all terms the charge and structure of the equatorial part of the coordination sphere are the same. Thus, the heterogeneous reaction rate constants are also influenced by the nature of R.

The rate constants lie in a relatively narrow range between 0.013 and 0.036 cm s^{-1}, similar to the results obtained [16] for structurally different classes of organometallic complexes, including some cobalt macrocycles.

The corresponding range of free energies of activation spans only *ca.* 0.6 kcal/mol.

The absence of strong differences in rate constants and their average values are consistent with an E.T. process occurring with a common outer sphere mechanism in all present cases.

The influence of the alkyl groups on the activation free energy is reflected by the correlation with the steric parameter E_s, which shows a rough linear dependence of $\Delta G^{\neq}$ with E_s for the primary, with the exception of the CH_3 group (See Fig. 6).

A distinction between electronic and steric effects of R can be made by consideration of the plot of

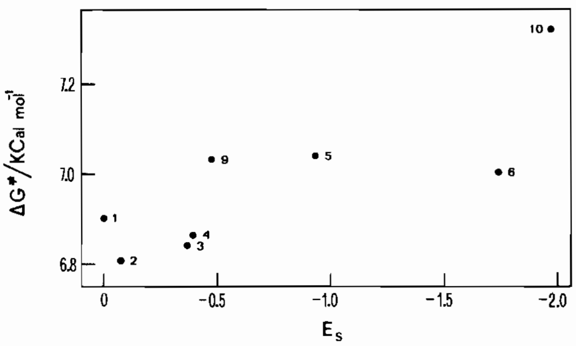

Fig. 6. Plot of $\Delta G^{\neq}$ *vs.* E_s for some compounds.

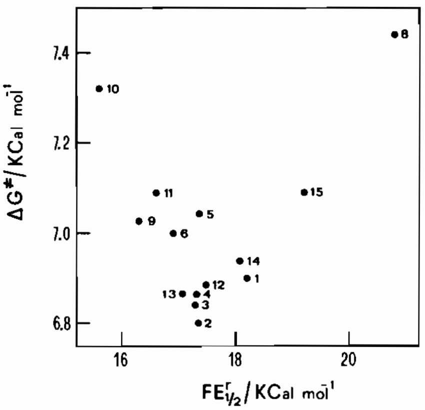

Fig. 7. Plot of $\Delta G^{\neq}$ *vs.* $FE^r_{1/2}$ for some compounds.

$\Delta G_s^{\ddagger}$ *vs.* $FE^r_{1/2}$ (see Fig. 7) the former represents the activation free energy calculated from k_s of the E.T. process at equilibrium potential $E = E^r_{1/2}$, while $E^r_{1/2}$ represents the free energy of redox reaction of the couple $[R{-}Co(DH)_2L]/[RCo(DH)_2L]^+$ relative to the SCE. The free energy of activation shows a roughly linear increase with increasing oxidation potential for the chelates with less bulky R groups. On the other hand the presence of bulky substituents cause strong deviations from linear relationships. Thus we can distinguish the increase of the activation free energy related to the displacement of $E^r_{1/2}$ toward more positive value from that which is related to the bulkiness of the R group.

Following the Marcus treatment [28] a quatitative basis for the understanding of the energetics of the electron transfer is offered also by the 'reorganization' term λ representing the standard free energy of activation when the electrode potential equals the formal potential E° in the absence of double layer effects.

$\Delta G^{\neq}$ is related to λ by the well known free energy relationship [28]

$$\Delta G^{\neq} = \frac{w_r + w_p}{2} + \frac{\lambda}{4} + \frac{F(E - E^\circ)}{2} + \frac{[F(E - E^\circ) + w_p - w_r]^2}{4\lambda} \qquad (8)$$

where F is the Faraday constant, $E - E^\circ$ is the electrode overpotential and w_p and w_r give the reversible electric work necessary to bring reactants (r) or products (p) in their standard states from the bulky of the solution into the configuration relative to the electrode surface required for E.T.

As in the present case $w_r = 0$, eqn. 8 can be written in the form

$$\sqrt{\Delta G^{\neq}} = \frac{\sqrt{\lambda}}{2} + \frac{FE^\circ + w_p}{2\sqrt{\lambda}} - \frac{F}{2\sqrt{\lambda}}\,E \qquad (9)$$

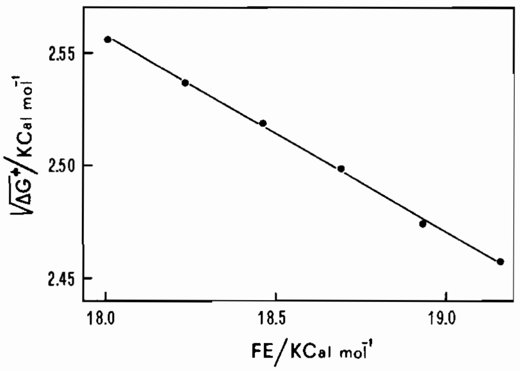

Fig. 8. Plot of $\sqrt{\Delta G^{\neq}}$ *vs.* FE for $[C_2H_5{-}Co(DH)_2H_2O]$.

which shows the linear correlation between $\sqrt{G^{\ddagger}}$ and E under assumption of constant w_D (see Fig. 8).

From the slope of the plot of $\sqrt{G^{\ddagger}}$ *vs.* E the reorganization factor λ was calculated and is reported in Table II. The values span a range of about 100 kcal/mol with most representatives in the range from 30 to 50 kcal/mol. Distinctly higher λ values are obtained either when a strong electron withdrawing power ($-CH_2CH_3$, $-(CH_2)_3CN$) or a big steric requirement of an R group is present (C_5H_{11}, neo-C_5H_{11}, i-C_3H_7).

These variations of λ values with the nature of R groups contrast with the nearly constant values of λ = 41 kcal/mol obtained for the homogeneous oxidation of homoleptic alkyl metals R_nM (M = Sn, Pb, Hg) where steric effects were not evidenced.

In our case higher values of λ apparently reflect both electronic effects and steric distortions on the axial Co–C bond, where bigger changes in the transition from reacting particle and the activation state are localized.

From the Marcus treatment the transfer coefficients are related to the reorganization term λ by eqn. 10:

$$\alpha = 0.5 + \frac{1}{2\lambda}(E - E^\circ) + w_p - w_r + 0.5\lambda_i\langle 1_s\rangle \qquad (10)$$

If we assume that for uncharged particles $w_r = 0$ and for the present series of closely related compounds in a given solution w_p = constant, then α values at the standard potential $E = E^\circ$ would be constant (and < 0.5) except for the last term, where λ_i is the contribution of the inner coordination shell to the reorganization energy term λ and $\langle 1_s\rangle$ is a dimensionless antisymmetric function of the bond force constants of the reactant and of the product in the inner coordination shell [28].

The electrochemical transfer coefficient for the one electron oxidation of the present chelates lies in the range 0.3–0.4. These values are consistent with the results reported for several alkylmetal compounds, including organometallic cobalt chelate [15]. With our results one observes a tendency toward the decrease of the α value with the increase of the steric requirements of the organic substituent. Differences in α values from term to term of the series can also be related to differences in the changes of bond length and angles (*i.e.* changes in molecular distortions) between the reactant and the product.

Conclusions

From the above results it can be concluded that in contrast to the case of solvated metal ions where the dominant contribution to the changes in the activation free energy for the E.T. is given by the changes in solvatation shell, in the case of the present chelates the changes of activation free energy is influenced mostly by the nature of the axial organic substituent. The analysis of this influence leads to the suggestion that the differences in ΔG° and $\Delta G^\ddagger$ can be localized in the molecular axis where the axial ligands are located. Changes in bond distances and angles along this axis appear to be relevant to the thermodynamics and kinetics of the E.T.

We suggest that changes in activation free energy are ruled mainly by the distortions accompanying the changes in electron density distribution from the reagent to the transition state, and thus are sensitive to the steric requirement of the axial organic group.

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