

## THERMODYNAMIC AND KINETIC EFFECTS OF THE ORGANIC GROUP IN THE ELECTROCHEMICAL REDUCTION OF ORGANOCOBALOXIMES \*

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### Summary

The electrochemical reduction of alkylcobaloximes at the dropping mercury electrode involves an initial one electron transfer process to give a radical anion with the cobalt in the  $\text{Co}^{\text{II}}$  formal oxidation state. The Co–C bond cleavage in the radical anion is an homolytic process yielding the  $\text{Co}^{\text{I}}$  cobaloxime and competing with a second electron transfer. The nature of the organic group and of the solvent coordinated in the *trans* position to the Co atom influences the thermodynamics of the electron transfer and the stability of the radical anion. Electronic and steric effects on the thermodynamics of the first electron transfer can be distinguished. These effects have only a small influence on the kinetics of the first electron transfer.

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### Introduction

The organometallic chemistry of cobalt chelates is a subject of continuing interest in view of the key role played by the reactivity of the cobalt–carbon bond in the chemistry and biochemistry of vitamin  $\text{B}_{12}$  group complexes [1,2]. One relevant problem in the understanding of the reactions of vitamin  $\text{B}_{12}$  and methyl- $\text{B}_{12}$  coenzymes is the recognition of factors which influence the mechanism of the cleavage of the Co–C bond.

Important experiments support the current belief that homolytic cleavage is involved in the initial steps of the coenzyme reaction, but the metal centre probably plays an additional role, including a change of its oxidation state [3]. In this context it would be especially useful to know the influence of the nature of the organic group bonded to the cobalt atom on the mechanism of the cleavage, in order to help

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differentiate between the homolytic 5'-deoxyadenosyl-cobalt bond cleavage in the coenzyme and the subsequent cobalt(II)-carbon atom interaction in the coenzyme/substrate reaction.

Electrochemistry has, since the earliest studies on vitamin B<sub>12</sub>, been the most direct source of information on the stability of the different oxidation states of the cobalt atom in different surroundings. Previous work led to the assessment of the relationship between the electron-donating ability of the axial ligands, including the organic groups, as well as of the equatorial chelate, and the relative stability of the formal oxidation state of the metal atom in vitamin B<sub>12</sub> and in model compounds [4-8].

The cleavage of the Co-C bond can also be studied as a reaction coupled with the heterogeneous electron transfer by various electrochemical techniques. Electrochemical oxidative cleavage of cobaloximes with intermediate formation of a relatively unstable alkyl/cobalt(IV) cation/radical chelate [8-14] was recently shown [15] to be influenced not only by electronic but also by steric effects. Electrochemical reductive cleavage was also investigated [6-8,16-20], and a fate suggested for the primary heterogeneous reduction product was proposed [21].

This work is concerned with the mechanism of the electrode process in the electrochemical reduction of organocobaloximes and with the differentiation between the thermodynamic and the kinetic parameters of the reductive heterogeneous electron transfer and of the coupled chemical reaction, as revealed by the influence of the nature of the organic group and of the solvent.

## Results

Electrochemical reduction of organocobaloximes R-Co(DH)<sub>2</sub>H<sub>2</sub>O in aprotic solvents, viz. dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile (AN), at a dropping mercury electrode (DME) takes place in two separate steps. The two processes are evident in both the polarographic and the cyclic voltammetric experiments. In pyridine (Py) or in the presence of a strong donor species, a single step is observed by these techniques. A third peak was apparent in polarography and in cyclic voltammetry (CV) under certain conditions, but it was not investigated in detail.

The separation of the polarographic half-wave potentials ( $E_{1/2}$ ) and voltammetric peak potentials ( $E_p$ ) is dependent on the nature of the solvent and of the organic group. A typical case of reasonably well separated reduction steps is shown in the polarograms and cyclic voltammograms of n-C<sub>4</sub>H<sub>9</sub>Co(DH)<sub>2</sub>H<sub>2</sub>O in DMF (Fig. 1a and Fig. 2a), whereas CH<sub>3</sub>Co(DH)<sub>2</sub>H<sub>2</sub>O gives strongly overlapping reduction waves and voltammetric peaks (Fig. 1b and Fig. 2b).

The most interesting feature is the influence of the nature of the organic group and of the solvent on the characteristics of the first electron transfer in the polarographic and CV experiments. In DMF 0.1 M tetraethylammonium perchlorate (TEAP) solution at DME, two different patterns, (a) and (b), were observed:

*Pattern (a).* With R = C<sub>3</sub>H<sub>7</sub>, iso-C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, iso-C<sub>4</sub>H<sub>9</sub> and C<sub>6</sub>H<sub>5</sub>, the first reduction step is quasi-reversible (qr) and the second is fully reversible.

CV experiments show the increase of  $\Delta E_p$  of the anodic/cathodic peak couple due to the first ET (when both peaks are visible) with increasing scan rate, in agreement with a quasi-reversible behaviour of the ET [22].

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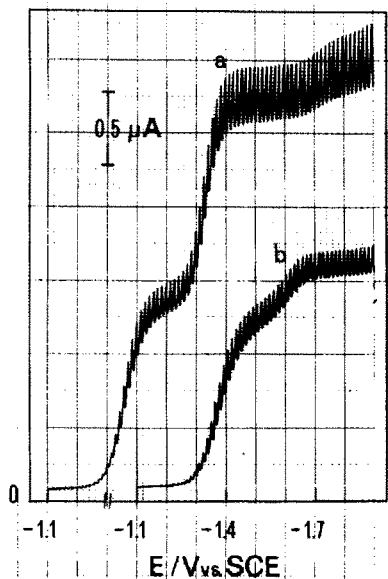


Fig. 1. Polarograms in DMF and TEAP, 0.1 *M* at 0°C for, (a)  $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}$   $1.5 \times 10^{-3}$  *M*, (b)  $\text{CH}_3\text{Co}(\text{DH})_2\text{H}_2\text{O}$   $1.4 \times 10^{-3}$  *M*.

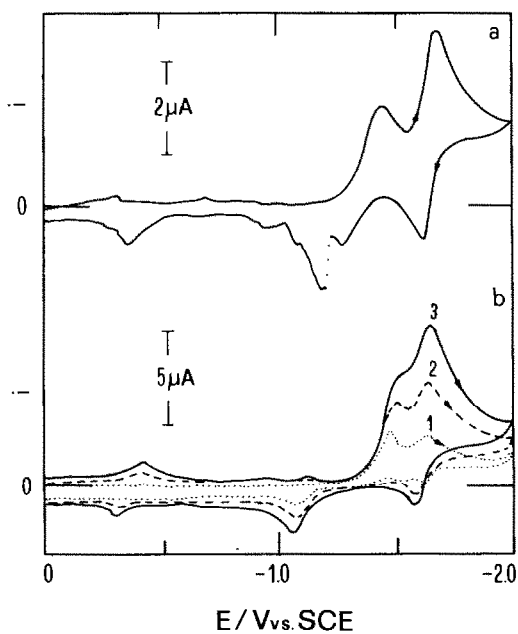
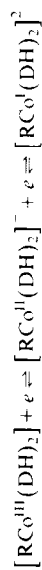


Fig. 2. Cyclic voltammograms in DMF and TEAP, 0.1 *M* at 0°C for, (a)  $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}$   $1.5 \times 10^{-3}$  *M* at  $0.10 \text{ V s}^{-1}$  scan rate; (b)  $\text{CH}_3\text{Co}(\text{DH})_2\text{H}_2\text{O}$   $1.8 \times 10^{-3}$  *M* at (1)  $0.1 \text{ V s}^{-1}$ , (2)  $2.5 \text{ V s}^{-1}$ , (3)  $5.0 \text{ V s}^{-1}$  scan rate.

TABLE I  
SUMMARY OF ELECTROCHEMICAL DATA IN DMF AND TEAP 0.1 M AT 0°C FOR THE REACTION



R	$E_{1/2}$ (V vs. SCE)		$\frac{\Delta E}{\Delta \log i/(id - i)}$ (mV)		$i_d$ ( $\text{cm}^2 \cdot \text{s}^{-1/2} \cdot \mu\text{A}^{1/6}$ )		$n$	$\log k^0$	$\Delta E_p$ (mV)		
	I	II	I	II	I	II			I	II	
1	CH <sub>3</sub>	-1.362	-1.60	83	-	1.115	0.28	0.80	(-3.23)	-	60
2	C <sub>2</sub> H <sub>5</sub>	-1.364	-1.63	54	-	1.028	0.72	-	(-3.20)	-	60
3	n-C <sub>3</sub> H <sub>7</sub>	-1.366	-1.64	54	54	1.057	1.10	-	-2.97	170	60
4	i-C <sub>3</sub> H <sub>7</sub>	-1.318	-1.65	54	54	1.068	1.12	-	-2.64	130	60
5	n-C <sub>4</sub> H <sub>9</sub>	-1.366	-1.64	54	54	1.076	1.11	0.95	-2.85	180	60
6	i-C <sub>4</sub> H <sub>9</sub>	-1.337	-1.63	54	54	1.146	1.10	-	-2.78	150	60
7	C <sub>6</sub> H <sub>5</sub>	-1.240	-1.44	56	54	1.150	1.20	0.98	-2.50	-	60
8	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	-1.180	-1.55	66	-	0.990	0.34	-	-	-	60
9	CF <sub>3</sub> CH <sub>2</sub>	-1.127	-1.36	80	-	1.206	0.90	-	(-2.70)	170	-

The reversibility of the second ET process is shown by the linear plot of  $E$  against  $\log i/(i_d - i)$  (a slope 54 mV (log-plot)) and by the separation,  $\Delta E_p$ , of about 60 mV between the cathodic and the anodic peak potentials, corresponding to a one-electron process. On the other hand the non linear log-plot for the first ET indicates a qr process which is also a one-electron process, as is shown by the ratio of the polarographic diffusion currents  $(i_d)_{II}/(i_d)_I$  (Table 1) and by the ratio of the cathodic peak currents  $(i_{pc})_{II}/(i_{pc})_I$  in cyclic voltammetry (Table 2), both ratios being unity for all the above complexes.

*Pattern (b).* With  $R = CH_3, C_2H_5, C_6H_5CH_2, CF_3CH_2$  the reduction still takes place in two steps, the first being qr and the second fully reversible, on the same criteria as above, but  $(i_d)_{II}/(i_d)_I < 1$  in polarography (Fig. 1b), and  $(i_{pc})_{II}/(i_{pc})_I$  increases as the scan rate increases (Fig. 2b).

As far as the reoxidation process in CV is concerned, no anodic peak is observed for the first couple, within a range of about 200 mV positive with respect to the cathodic peak, even at the fastest scan rates which could be used under our conditions. The value of the ratio  $(i_p)_{II}/(i_p)_I$  is thus clearly different from that for group (a) (Table 2). Furthermore, in the series of complexes falling into category (a) the anodic sweep recorded by reversing the scan immediately after the potential of the first ET, as well as the anodic sweep recorded after pre-electrolysis at the potential of the first ET show the anodic peaks characteristic of the  $Co^I-Co^{II}$  and  $Co^{II}-Co^{III}$  oxidations steps of the  $[Co(DH)_2(H_2O)_2]^+$  under the same conditions. Moreover the anodic peak currents of both processes decrease with increasing scan rate.

All the above evidence points to a chemical reaction following the first ET and withdrawing the primary reduction product to the second ET. The chemical reaction apparently involves the rupture of the Co-C bond and formation of a  $Co^I$  species. Conclusive proof of this is provided by a controlled potential reduction, which shows that in the process corresponding to the first ET one Faraday is consumed per mole of complex and the final product is an unstable  $Co^I$  species, as shown by spectral and electrochemical properties of the solution.

Partial formation of the starting material by electrochemical reoxidation could be observed only in DMSO and in the presence of one equivalent of pyridine, as previously described by Gaudemer et al. [21].

Whilst looking for the origin of the differences in the polarographic and voltammetric behaviour between the two groups of organocobaloximes, as described above,

TABLE 2

LIST OF RATIOS BETWEEN  $(i_{pc})_{II}$  AND  $(i_{pc})_I$  FOR SOME  $[RCo(DH)_2H_2O]$  IN DMF AND TEAP 0.1 M AT 0°C

Scan rate (V s <sup>-1</sup> )	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	n-C <sub>3</sub> H <sub>7</sub>	i-C <sub>3</sub> H <sub>7</sub>	n-C <sub>4</sub> H <sub>9</sub>	i-C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>
0.2	0.3	0.5	1	1	1	1	1	0.3
0.4	0.4	0.7	1	1	1	1	1	0.6
1	0.5	0.8	1	1	1	1	1	0.7
2.5	0.6	0.9	1	1	1	1	-	0.7
5.0	0.7	0.9	1	1	1	1	-	0.8
10.0	0.8	0.9	1	1	1	1	-	0.8

we investigated the kinetics of the first ET process. The experimental observations were complicated by the proximity of the potentials for the two ET processes, I and II, which lead to the overlap of the CV peaks at higher scan rates and thus prevents use of a wider range of scan rates in cyclic voltammetry. Furthermore in the reverse anodic scan new peaks appear, apparently due to decomposition products of the primary product of the ET. At higher scan rates these anodic peaks overlap with the anodic peak of the first redox couple. Even so, the kinetics of the first ET can be studied when the polarographic waves (or the anodic/cathodic peak couple in CV) do not overlap too seriously.

The rate of the first quasi-reversible ET was determined from the analysis of the  $i$  vs.  $t$  curves during a drop life in the rising portion of the polarographic wave using Ayabe's method [23], and the results are shown in Table 1.

The standard rate constants of the first ET lie in the relatively narrow range  $3 \times 10^{-3}$  to  $6 \times 10^{-4} \text{ s}^{-1}$ , and do not reflect the difference in the polarographic and voltammetric behaviour of the first ET between the  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{C}_6\text{H}_5\text{CH}_2$  derivatives on the one hand and the  $\text{C}_3$  and  $\text{C}_4$  alkyl or  $\text{C}_6\text{H}_5$  derivatives on the other.

In view of the fast decomposition of the primary reduction product it is possible that the electrode process for the former group of compounds is not controlled solely by the ET step, since the chemical reaction following this step could be fast enough to be involved. Thus the values of the standard rate constants of the first ET for these compounds could be influenced by the coupled chemical reaction.

#### *Solvent effects*

The nature of the solvent markedly influences the potential at which the first electrode process takes place (Fig. 3). The trends of half wave potentials of the two processes I and II in various aprotic solvents are reported in Table 3 for two representative complexes, viz.  $\text{CH}_3\text{-Co}(\text{DH})_2\text{S}$  and  $\text{C}_3\text{H}_7\text{-Co}(\text{DH})_2\text{S}$ , where S is the solvent molecule, assumed to be coordinated in the *trans* position to the cobalt atom. The  $E_{1/2}$  values show the same trend for both compounds. Unexpectedly, the redox potential is shifted towards more negative values with decreasing donicity of the solvent, except for pyridine; in this case a strong cathodic displacement of  $E_{1/2}$  leads to the merging of the two one-electron processes in a single two-electron wave (Fig. 4).

The polarographic data for some pyridinato complexes of organo-cobaloximes are shown in Table 4. The effect of a strongly donating ligand in *trans* position to the organic group is also shown by the even more negative value of the two electron reduction of the tributylphosphine derivative  $\text{CH}_3\text{Co}(\text{DH})_2\text{PBu}_3$ . The nature of the solvent also influences the ratio of the limiting polarographic currents of the two successive ET processes  $(i_d)_{II}/(i_d)_I$ .

In AN and DMSO the two electrode processes overlap too seriously to allow them to be investigated separately, (Fig. 3), but it can be seen that even in these solvents the ratios of the polarographic limiting currents of the two electrode processes for  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  derivatives provide evidence for the decomposition of the primary reduction product. The ratio  $(i_d)_{II}/(i_d)_I$  for solutions of the same concentration and in the same experimental conditions decreases in the order  $\text{AN} > \text{DMF} > \text{DMSO}$ .

When DMF is used as the aprotic solvent the widest separation of the potentials

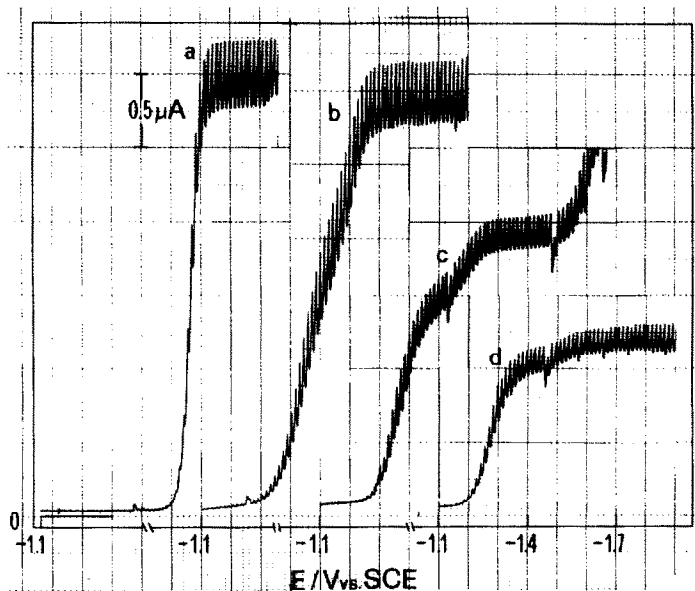


Fig. 3. Polarograms for  $\text{CH}_3\text{Co}(\text{DH})_2\text{H}_2\text{O}$  in different solvents, TEAP 0.1 M;  $c$  values ( $\times 10^{-3}$ ) at  $0^\circ\text{C}$ . (a) Py, 1.84 M (b) AN, 1.71 M (c) DMF, 1.60 M (d) DMSO, 1.71 M.

TABLE 3

VALUES OF  $(E_{1/2})\text{I}$  AND  $(E_{1/2})\text{II}$  IN VARIOUS DONOR SOLVENTS

Solvent	AN	DMF	DMSO	Py
R = $\text{C}_3\text{H}_7$ I	-1.47	-1.36	-1.35	
II	-1.66	-1.64	-1.64	-1.67
$(i_d)\text{II}/(i_d)\text{I}$	1	1	1	1
R = $\text{CH}_3$ I	-1.44	-1.36	-1.28	
II	-1.60	-1.64	-1.54	-1.61
$(i_d)\text{II}/(i_d)\text{I}$	1	0.3	0.1	1
DN <sup>a</sup>	14	26.6	29.3	33.1

<sup>a</sup> Gutmann's donor number.

TABLE 4

POLAROGRAPHIC DATA FOR SOME COMPLEXES IN Py AND TEAP 0.1 M AT  $0^\circ\text{C}$

R	$E_{1/2}$ (V vs. SCE)	$\Delta E$ $\Delta \log i/(i_d - i)$ (mV)	$i_d$ ( $\text{cm}^2/3t^{1/6}$ )
$\text{CH}_3$	-1.613	28	2.52
$\text{CH}_3^a$	-1.763	66	2.49
$\text{C}_2\text{H}_5$	-1.634	38	2.43
n- $\text{C}_3\text{H}_7$	-1.669	37	2.41
i- $\text{C}_3\text{H}_7$	-1.621	44	2.45
$\text{C}_6\text{H}_5$	-1.409	29	2.48
$[\text{Co}(\text{DH})_2\text{Py}_2]^+$	I -0.338	I 58	I 1.04
	II -0.130	II 54	II 1.09

<sup>a</sup> Tributylphosphine derivative  $\text{CH}_3\text{Co}(\text{DH})_2\text{PBU}_3$ .

of the first and second electrode processes can be obtained without addition of other coordinating agents. Moreover, as we have seen above, this solvent appears to discriminate strongly between different organic groups bonded to the cobalt atom as far as the rate of the chemical reaction following the ET is concerned.

## Discussion

The electrode processes undergone by organocobaloximes  $\text{RCo}(\text{DH})_2\text{H}_2\text{O}$  in DMF clearly involve successive formation of species in the oxidation state  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{I}}$ , but for the derivatives containing  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$  and  $\text{CF}_3\text{CH}_2$ , the evidence points to a chemical reaction following the first ET process. From CV at low scanning rates it is apparent that this reaction is faster than the second ET process, and also faster than the disproportionation reaction between the  $\text{Co}^{\text{II}}$  species.

A disproportionation reaction was observed with the one electron reduction product of the methyl derivative of the closely related  $\text{Co}^{\text{III}}$  complex for the ligand 1,3-diacetylmonoximeiminodiacetylmonoximateiminopropane  $[\text{CH}_3\text{Co}(\text{DO})(\text{DOH})\text{pn}]^+$  [6,8]. The  $[\text{CH}_3\text{Co}^{\text{II}}(\text{DO})(\text{DOH})\text{pn}]^0$  primary reduction product gives the  $\text{Co}^{\text{III}}$  dimethyl derivative and  $[\text{Co}^{\text{I}}(\text{DO})(\text{DOH})\text{pn}]^-$ .

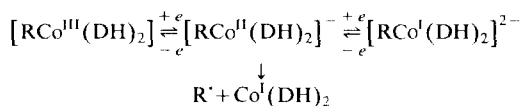
The reaction of the primary reduction product for all the examined compounds, including the derivatives containing  $\text{R} = \text{C}_3\text{H}_7, \text{iso-C}_3\text{H}_7, \text{n-C}_4\text{H}_9, \text{iso-C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$ , is revealed by the CPR at the potential of the first ET, which gives a  $\text{Co}^{\text{I}}$  species with consumption of one electron per molecule, as proved by the presence of the  $\text{Co}^{\text{I}}\text{-Co}^{\text{II}}$  and  $\text{Co}^{\text{II}}\text{-Co}^{\text{III}}$  anodic peaks in CV of the solution reduced with one equivalent per mole of the organocobaloxime.

The behaviour of the two groups of complexes examined differs in the rate of cleavage of the  $\text{Co-C}$  bond: in the first set, the  $\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2, \text{CF}_3\text{CH}_2$  derivatives, the chemical reaction occurs within the electrode reaction layer, while in the second set, the  $\text{C}_3$  and  $\text{C}_4$  alkyl and  $\text{C}_6\text{H}_5$  derivatives, the reaction is slow compared with the time scale of the polarographic and CV experiments. In both cases the primary reduction product is the  $[\text{R-Co}(\text{DH})_2\text{S}]^-$  radical anion, and its most probable fate is the cleavage of the  $\text{Co-C}$  bond, as depicted in Scheme 1.

Using DMSO containing one equivalent of pyridine Gaudemer was able to reisolate the starting compound from the reduction of some alkyl and benzylcobaloximes. We were able to reproduce his results (with somewhat lower yields) under the same experimental conditions but not with DMF or DMSO as solvent or in the absence of pyridine. Apparently the reversible trapping of the organic group by the equatorial ligand, which Gaudemer assumes in order to explain the reversible displacement of the organic group from the cobalt atom, is related to the presence of the pyridine, which is coordinated in the *trans* position to the metal atom.

The reactions of the primary reduction products containing the organic group bonded to a cobalt atom in the  $\text{Co}^{\text{II}}$  oxidation state reveal the tendency for release of

SCHEME 1. The *trans*-axial ligand is not included in the formula.





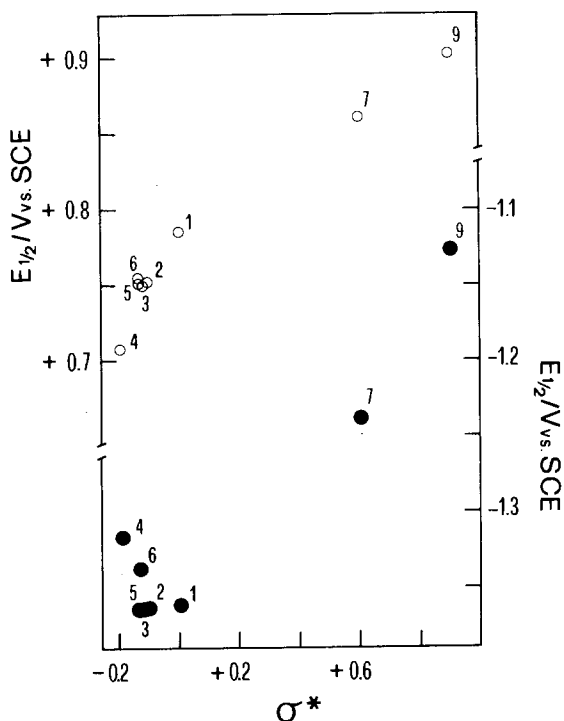


Fig. 4. ● Dependence of  $E_{1/2}$  for  $[\text{RCo}(\text{DH})_2\text{H}_2\text{O}]^+ e \rightarrow [\text{RCo}(\text{DH})_2\text{H}_2\text{O}]^-$  on  $\sigma^*$  in DMF and TEAP, 0.1  $M$  at  $0^\circ\text{C}$ . ○ Dependence of  $E_{1/2}$  for  $[\text{RCo}(\text{DH})_2\text{H}_2\text{O}]^- e \rightarrow [\text{RCo}(\text{DH})_2\text{H}_2\text{O}]^+$  on  $\sigma^*$  [16] in AN and TEAP, 0.1  $M$  at  $0^\circ\text{C}$ . The label numbers correspond to Table 1.

the organic radical by transfer to any suitable nearby radical trapping center. The thermodynamic and kinetic influence of the nature of the organic group can be recognized in the shifts of  $E_{1/2}$ . A direct electronic effect is clearly seen from the displacement of the reduction potentials of the process toward less negative potentials for the derivatives containing the electron-withdrawing organic groups  $\text{C}_6\text{H}_5$  and  $\text{CF}_3\text{CH}_2$  (Fig. 4). Some shifts of the reduction potentials, in the same direction from the value for the methyl-substituted cobaloxime are also observed in the case of the higher and branched alkyl derivatives.

The deviations from an approximately linear relationship with Taft's  $\sigma^*$  constant can be ascribed to the influence of steric strain on the electronic structure around the cobalt atom (Fig. 4). The displacement of the reduction potentials toward values more positive than expected from the  $\sigma$  constant indicates that the steric strain lowers the free energy of the process.

The reduction potentials for the second electrode process appear to be irregularly distributed within a narrow range and no trend can be recognized.

The above trends of half-wave potentials of ET can now be compared with those revealed by our previous work on the electrochemical oxidation of cobaloximes [15]. These trends for the half-wave potentials of the oxidation and reduction are compared schematically in Fig. 4. A direct electronic effect, of, for example,  $\text{CF}_3\text{CH}_2$  or  $\text{C}_6\text{H}_5$  is revealed by the shift in the same direction of the half-wave potentials for both oxidation and reduction. In fact, an increase in the withdrawing power of the

organic group leads to an increase in the free energy of oxidation, while that of reduction decreases.

A small but distinct deviation from this trend is evident for the higher and branched alkyl derivatives: the free energies for the reduction process are displaced in the opposite direction compared with those for the oxidation process. If the origin of this deviation lies in structural differences in the substituted cobaloximes induced by structural differences in the organic group, it could be inferred that both the oxidation and the reduction are apparently facilitated, for thermodynamic reasons, by increase in the steric strain. The influence of the nature of the organic group on the kinetics of the first ET is rather small. An increase is observed upon increasing the electron withdrawing power of the organic group and on going from methylcobaloxime to the branched and higher alkyl derivatives.

Comparison of the features of the standard rate constants for the one electron reduction with those reported previously for one electron oxidation [15], reveals that the activation energies for the reductive ET increase and those for the oxidative ET are lower for branched alkyl substituted cobaloximes than for normal alkyl derivatives.

The final point to be discussed concerns the solvent effect. The influence of the solvent is apparent in the thermodynamics of the first reduction step and in the kinetics of the chemical reaction following the first ET. Except for pyridine, decreasing donicity of the solvent (which is assumed to be coordinated to the cobalt atom in the axial position *trans* to the organic group) shifts the  $E_{1/2}$  towards more negative values. This trend is opposite to that observed for electrochemical one-electron oxidation of organocobalt chelates of tetradentate Schiff's bases [15], and shows that the effect of the solvent cannot be explained in the present case in terms of its electron donor power.

The shift of  $E_{1/2}$  is stronger for the first ET. This changes the separation between the potentials of the two successive one electron processes. This effect is most marked in pyridine, where all the examined cobaloximes undergo a single two electron reduction process which also involves the Co-C bond cleavage. The separation of the two ET processes and the rate of decomposition of the primary reduction product both increase within the sequence AN < DMF < DMSO.

In conclusion, the electrode process involves the homolytic cleavage of the Co-C bond in the radical anion formed by the first ET. The nature of the organic group influences the reduction potentials, the ET rate, and the cleavage rate of the Co-C bond. Electronic and steric effects on the reduction potentials can be observed, and distinguished from one another, but steric effects on the ET rate are only slight for the present compounds. The nature of the solvent mainly influences the  $E_{1/2}$  and the stability of the radical anion.

Thus, reductive cleavage of the Co-C bond in the organocobaloximes is dominated by the potential of the first one electron transfer and by the rate of the homolytic cleavage of the Co-C bond in the radical anion. Both factors are influenced by the nature of the axial ligands, the organic group, and the coordinating solvent.

## Experimental

### Materials

DMF, AN, DMSO, and Py (RPE-Carlo Erba) were dried over 4-Å molecular

sieves, and TEAP (RPE-Carlo Erba) was dried in vacuo. The complexes studied were prepared as previously described [24].

All the electrochemical measurements were carried out in the solvent containing about  $1.5 \times 10^{-3} M$  complex and  $0.1 M$  (TEAP) as the supporting electrolyte. All the solutions were freshly prepared in the electrochemical cell, deaerated with pure dry nitrogen, and protected from light to avoid photodecomposition.

#### Apparatus

The instrumentation for polarographic measures was as previously described [15]. For CPR measurements an Amel multipurpose unit 563 connected with an Amel 557/SU potentiostat and equipped with a model 460 stand was used. Instantaneous polarographic currents were measured using an operational amplifier-based three electrode electronic polarograph Amel Model 448. The recorder was a Nicolet digital oscilloscope 2090-IIIA connected by an IEEE-488 GPIB interface to an Apple II Europlus 48K computer. Currents were evaluated after correcting by comparison with a calibration curve prepared using standard resistances instead of the cell. All data were collected and mathematically treated with this system. For CV measurements we used an Amel potentiostat Model 551 equipped with positive feed-back compensation connected with an Amel function generator Model 568, and all data were recorded by the Nicolet-Apple system as described before.

All measurements were performed in a three electrode system; the counter electrode was a platinum wire while the reference electrode was a SCE electrode saturated with NaCl and separated by a salt bridge containing  $0.1 M$  TEAP in the

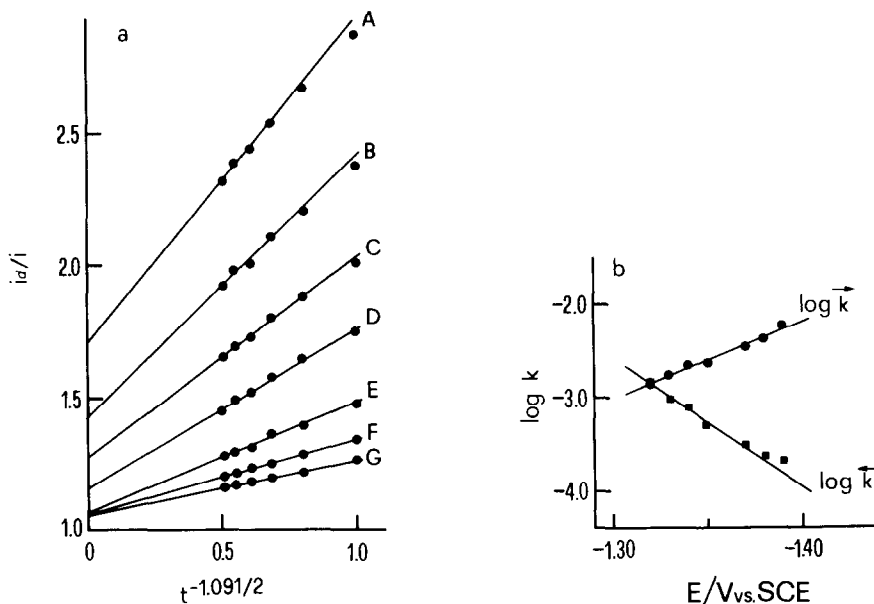


Fig. 5. (a) Treatment of experimental data for  $[C_4H_9Co(DH)_2H_2O]$  in DMF and TEAP,  $0.1 M$ , obtained from  $i$  vs.  $t$  curves in the rising portion of the polarographic waves at the following potentials: (A)  $-1.32$ ; (B)  $-1.33$ ; (C)  $-1.34$ ; (D)  $-1.35$ ; (E)  $-1.37$ ; (F)  $-1.38$ ; (G)  $-1.39$  V vs. SCE. (b) Dependence of  $\log \bar{k}$  and  $\log \bar{k}$  on the electrode potential.

same solvent as in the solution examined. For polarography and instantaneous polarographic currents the working electrode was a Smoler's DME electrode with  $m$   $0.395 \text{ mg sec}^{-1}$  when the height,  $h$ , of the mercury column was 56.5 cm. For CV measurements we used a Long Last Sessile Electrode (LLSE Amel Model 498) with a drop-life longer than 300 sec in solution, with  $m$   $0.009 \text{ mg sec}^{-1}$  at  $h$  65 cm, making measurements only during the last portion of the drop life when the variation of its area could be considered practically zero.

#### *Evaluation of electron rate constants*

The electron transfer rate constants for the first ET of compounds examined was determined by analysis of instantaneous polarographic currents using the method proposed by Ayabe [23]. This method is convenient for use with the greater number of experimental data which can be readily collected by the digital recording devices and on-line treatment. An example of processing of experimental data is shown in Fig. 5.

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