Journal of Organometallic Chemistry, 222 (1981) 311—321
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CONTROLLED-POTENTIAL ELECTROLYSIS OF ALKYLCOBALOMIXES: STABILITY OF THE COBALT—CARBON BOND IN THE REDUCED SPECIES

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(Received July 21st, 1981)

Summary

Bis(dimethylglyoximato)cobalt complexes (cobaloximes) of various types (denoted by R-Co(DMG)$_2$-L, where R = Cl or alkyl group and L = pyridine) have been used in studies of electrocatalytic reductions of organic compounds involving an alkylcobalt intermediate. Voltammetry and polarography were used to establish the electrochemical characteristics of many alkyl cobaloximes, and two reduction steps were observed:

$$\text{R-Co}^{III}(\text{DMG})_2/\text{R-Co}^{II}(\text{DMG})_2 \text{ and } \text{R-Co}^{II}(\text{DMG})_2/\text{R-Co}^{I}(\text{DMG})_2,$$

as previously described. Cyclic voltammetry confirmed that the cobalt—carbon bond is broken during the reduction of the alkylcobalt compounds.

Coulometric reduction of alkylcobaloximes gave characteristic waves of the dealkylated products. However, after reoxidation, good yields (60 to 95%) of the starting material were recovered. In the case of the optically active cobalt compounds (+)-2-octylcobaloxime and (—)-2-octylcobaloxime, complete retention of configuration was observed. Reversible trapping of the R groups by the equatorial ligand is proposed to account for the results.

In the course of our studies concerning the electrocatalytical activity of bis-(dimethylglyoximato)cobalt complexes (cobaloximes) we have found it necessary to reinvestigate the electrochemical behaviour of these compounds in dimethylsulfoxide solution, and in particular to study the stability of alkylcobalt complexes having the cobalt ion in different oxidation states.

0022-328X/81/0000—0000/$02.50

The electrochemical properties of alkylcobalt complexes have previously been studied [1,4] thoroughly by various groups and it is generally agreed that the complexes decompose during the electrochemical reduction at a controlled potential by the following route:

$$\begin{tikzcd}
R[Co^{III}] \arrow[r, "e^-"] & R[Co^{II}]^- \arrow[r, "e^-"] \arrow[d] & R[Co^{I}]^{2-} \arrow[d] \\
& R^- + [Co^{II}] \arrow[r] & R^- + [Co^{I}]^-
\end{tikzcd}$$

where [Co] denotes the non-alkylated cobaloxime and R[Co] the alkylcobaloxime. This behaviour was assumed to be general for complexes of the type concerned, but Costa observed that the cobaloximes deserved further investigations [2].

Voltammetric and polarographic studies in dimethylsulfoxide have been complemented by electrolysis at controlled potentials followed by reoxidation. After careful reisolation, the products have been analyzed by visible and NMR spectroscopy. We report below extensive data for the electrolysis of alkylcobaloximes at controlled potentials both on mercury and platinum electrodes. Our results show that in the case of cobaloximes the behaviour of alkylcobalt complexes is more complicated than was previously assumed, mainly on the basis of electrochemical measurements.

Experimental part

Electrochemical studies were carried out in DMSO dried over activated alumina and stored over molecular sieves. The supporting electrolyte was 0.1 *M* tetraethylammonium perchlorate (TEAP) from Carlo-Erba recrystallized twice from MeOH. The reference electrode was an aqueous calomel electrode (SCE) isolated in a separate compartment containing the supporting electrolyte in DMSO. Electrochemical measurements and reisolation were carried out in the total absence of light under an inert atmosphere.

Alkylcobaloximes were prepared and purified by known methods. After electrolysis and reoxidation, either electrochemically or by air or oxygen bubbling, the cobaloximes were extracted with ethyl acetate or chloroform, and each extract was washed three times with an equal volume of water to remove supporting electrolyte and DMSO. One equivalent of pyridine was added to prevent decomposition of alkylcobaloximes.

NMR spectra were recorded in $CDCl_3$ with TMS as internal reference.

Results

1. Voltammetry and polarography of alkylcobaloximes

Alkylcobaloximes exhibit two monoelectronic waves both at a rotating platinum electrode and at a dropping mercury electrode. Typical polarograms and voltammograms are shown in Fig. 1 and 2. These waves have been assigned to the following reactions:

$R[Co^{III}] + e^- \rightarrow R[Co^{II}]^-$ and $R[Co^{II}]^- + e^- \rightarrow R[Co^{I}]^{2-}$

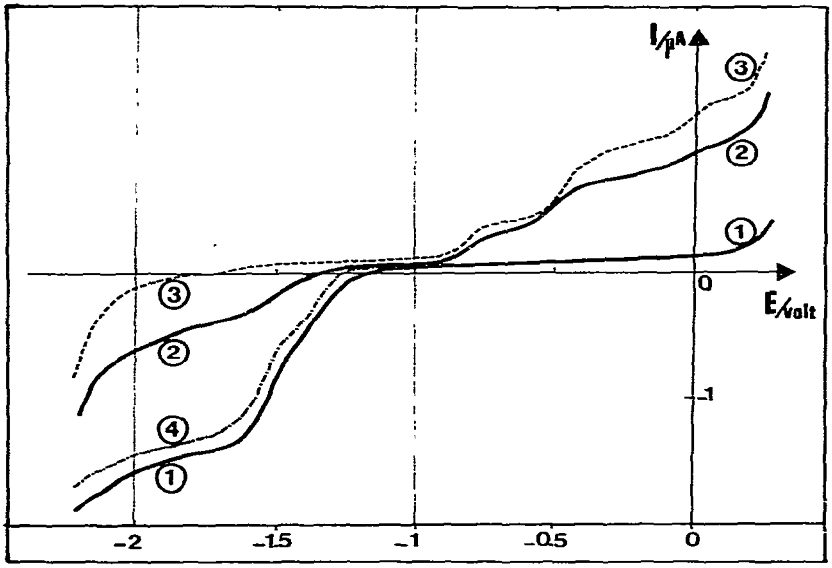


Fig. 1. Evolution of the polarograms of 1.33 10^{-3} M n-heptylcobaloxime during the course of electrolysis at E = —2.1 V on a mercury pool in DMSO: (1) before electrolysis; (2) and (3) during electrolysis; (4) after reoxidation of the reduction products.

Reduction potentials in DMSO are listed in Table 1. Logarithmic analysis of the curves shows that the two waves are almost reversible when R = alkyl (**1** to **9**). When R = benzyl (**10** to **12**) or substituted-alkyl (**13** to **15**) the first wave tends to be irreversible.

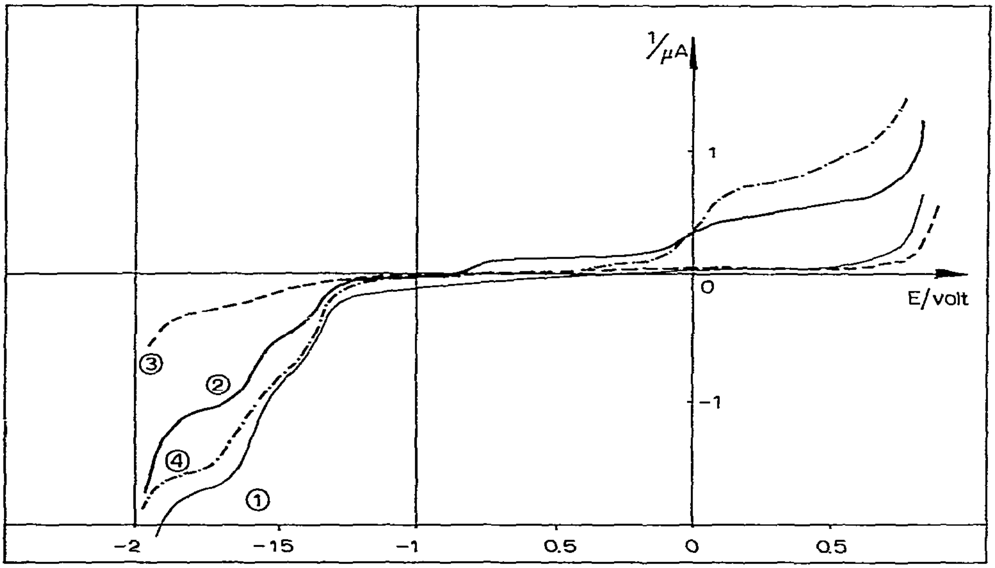
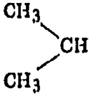
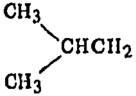
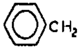
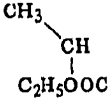


Fig. 2. Evolution of voltammograms of 3.2 10^{-4} M ethylpyridinato cobaloxime at a rotating platinum electrode (ω = 500 rpm) during the course of the coulometric reduction on platinum at E = —1.7 V; (1) before electrolysis; (2) during and (3) at the end of electrolysis; (4) after reoxidation at E = +0.25 V.

TABLE 1

REDUCTION OF ALKYLCOBALOXIMES IN DMSO + 0.1 *M* Et_4NClO_4 [a]

No.	R	Pt				DME			
		$E^1_{1/2}$	P_1	$E^2_{1/2}$	P_2	$E^1_{1/2}$	P_1	$E^2_{1/2}$	P_2
1	CH_3	−1.40	0.070	−1.55	0.065	−1.28	0.066	−1.46	0.060
2	CH_3CH_2	−1.47	0.070	−1.64	0.060	−1.32	0.061	−1.52	0.060
3		−1.37	0.070	−1.63	0.060	−1.32	0.107	−1.57	0.070
4	$CH_3(CH_2)_3$	—	—	—	—	−1.34	0.077	−1.55	0.070
5		−1.35	0.090	−1.61	0.090				
6	$Br(CH_2)_5$	−1.40	0.090	−1.60	0.100				
7	$CH_2{=}CH(CH_2)_4$	−1.34	0.060	−1.54	0.055	−1.38	0.060	−1.58	0.060
8	$CH_3(CH_2)_6$	−1.45	0.090	−1.60	0.060				
9	$CH_3(CH_2)_5CHCH_3$	−1.35	0.064	−1.51	0.069				
10		−1.28	0.108	−1.55	0.076	−1.13	0.082	−1.33	0.075
11		−1.30	0.090	−1.55	0.060				
12		−1.05	0.075	−1.30	0.055				
13		−1.15	0.100	−1.40	0.065				
14	$CH_3OOCH_2CH_2$	−1.10	0.120	−1.25	0.095				
15	CH_3CHCN	—	—	—	—	−1.21	0.087	−1.38	0.075

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[a] Half-wave potentials (V/aqueous ECS). Slopes (P_1 and P_2) of $E = f \log (I_d - I)/I$. Rotating platinum electrode (Pt) (ω = 500 rpm) and dropping mercury electrode (DME).

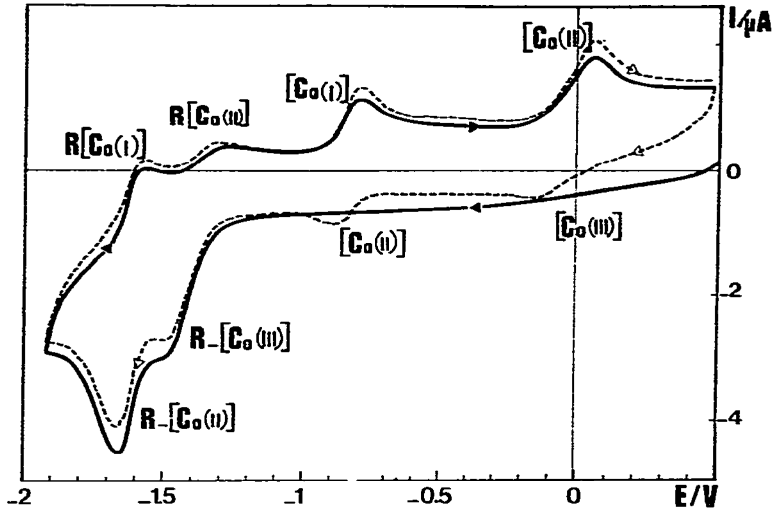


Fig. 3. Cyclic voltammetry (potential scan: 0.2 V s^{-1}) of 4.3 10^{-4} *M* ethylcobaloxime in DMSO + 0.1 *M* Et_4NClO_4 at a platinum electrode; ——— 1st scan; — — — 2nd scan.

Half-wave potentials for alkylcobalt complexes **1** to **9** are almost independent of the nature of the R group. However, as observed by Hohokabe [3], less negative reduction potentials are observed for alkylcobaloximes in which the formal R^- carbanions can be stabilized by electron-withdrawing groups (Table 1: **10** to **15**). Larger effects were observed by Costa [4] with alkylcobalt-salen, for which the half-wave potentials depend markedly on the nature of the R group.

2. *Cyclic voltammetry at a platinum electrode*

Cyclic voltammograms for ethylcobaloxime (**2**) are shown in Fig. 3. The first scanning towards reduction potential shows characteristic peaks corresponding to the two waves observed in linear voltammetry. Scanning the potentials back towards positive values first shows reoxidation of alkylcobalt(I) and alkylcobalt(II) formed at the electrode, confirming the quasi-reversibility of the process (Table 2). Then two peaks at −0.83 V and −0.0 V, corresponding to the reoxidation of non-alkylated cobalt(I) and cobalt(II), are observed.

3. *Quantitative coulometric reduction of alkylcobaloximes*

We carried out the electrolysis of various alkylcobaloximes on both mercury and platinum electrodes, and attempted to reisolate the products after reoxidation. The products were analysed by NMR and visible spectroscopy.

Since the two potentials:

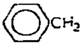
$$E_{1/2}(\mathrm{R[Co^{III}]/R[Co^{II}]^-}) \text{ and } E_{1/2}(\mathrm{R[Co^{II}]^-/R[Co^{I}]^{2-}})$$

are very close to each other we assume that electrolysis of alkylcobalt complex directly yields $\mathrm{R[Co^{I}]^{2-}}$, and that it is impossible to obtain quantitative yields of products corresponding to the +II oxidation state of cobalt.

a) Reduction of alkylcobaloxime at a platinum electrode. The values of the

TABLE 2

CYCLIC VOLTAMMETRY OF SOME ALKYLCOBALOXIMES AT A PLATINUM ELECTRODE [a]

	R	Ep_a	Ep_c	ΔEp
$R[Co^{III}]/R[Co^{II}]^-$	CH_3CH_2 (2)	—1.28	—1.48	0.20
	$Br(CH_2)_5$ (6)	—1.32	—1.47	0.15
	$CH_2{=}CH(CH_2)_4$ (7)	—1.38	—1.54	0.16
	$CH_3(CH_2)_6$ (8)	—1.28	—1.52	0.24
	$CH_3(CH_2)_5CHCH_3$ (9)	—1.30	—1.41	0.11
	 (10)	—1.18	—1.30	0.12
$R[Co^{II}]^-/R[Co^I]^{2-}$	CH_3CH_2 (2)	—1.56	—1.65	0.19
	$Br(CH_2)_5$ (6)	—1.53	—1.63	0.10
	$CH_2{=}CH(CH_2)_4$ (7)	—1.66	—1.74	0.08
	$CH_3(CH_2)_6$ (8)	—1.80	—1.72	0.08
	$CH_3(CH_2)_5CHCH_3$ (9)	—1.55	—1.60	0.05
	 (10)	—1.35	—1.58	0.23

[a] Potential sweep: 0.2 V s^{-1}; Ep_a and Ep_c = anodic and cathodic peaks.

electrolysis potentials, Faraday consumptions, and yields of some purified products reclaimed after reoxidation are listed in Table 3. In Fig. 2 are shown the voltammetric curves of ethylcobaloxime (2) in the course of controlled potential electrolysis (—1.7 V) at platinum electrode. During the electrolysis two waves appear at potentials corresponding to dealkylated cobalt(II) and cobalt(I). At the end of the electrolysis only one wave at 0.0 V is still present, the height of which is half of that expected. Reoxidation of the solution leads to waves corresponding to the starting material (in 90% yield) with no reduction waves corresponding to the dealkylated cobalt observed during the electrolysis.

b) Reduction of alkylcobaloximes on a mercury pool electrode. Polarographic curves obtained at different steps of the controlled potential reduction (—2.1 V) of heptyl cobaloxime (8) at a mercury pool electrode are shown in Fig. 1 and typical values and yields of reclaimed products are listed in Table 3. Under these conditions, formation of $R[Co^{II}]^-$ is detected during electrolysis by its oxidation wave at —1.3 V as observed in Fig. 2. The dealkylated cobalt complex is formed, characterized by its reoxidation waves at —0.8 V and 0.0 V. These two waves are still present at the end of the reduction; a third wave at —0.5 V is also observed, but could not be assigned. The diffusion limiting current at the end of the electrolysis is equal to that observed before the reduction. Reoxidation of the solution leads to the observation of the waves of the starting material with no trace of reduction waves at —0.8 V, —0.5 V and 0.0 V. All the reductions showed complete disappearance of the starting material and required 2 Faradays per mol of cobalt complex.

After reoxidation, the product exhibits an electrochemical behaviour which is identical to that of the starting material, but in most cases the products could be reisolated in good yields (65 to 90%) and were analyzed by NMR and visible

TABLE 3

COULOMETRIC REDUCTION OF SOME ALKYLCOBALOXIMES AT PLATINUM AND AT MERCURY POOL ELECTRODES

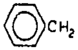
R	Pt				Hg			
	C_R[Co^{III}] (mol l^{-1})	Electr. potential (V)	*Q* (cb)	Yield (%)	C_R[Co^{III}] (mol l^{-1})	Electr. Potential (V)	*Q* (cb)	Yield (%)
CH_3	5,44 X 10^{-4}	−1,8	70,9	67,5	3,58 X 10^{-4}	−1,7	50,4	73,0
CH_3CH_2	2,60 X 10^{-4}	−1,7	35,1	70,0	4,60 X 10^{-4}	−1,8	53,3	60,0
$CH_3(CH_2)_3$					2,87 X 10^{-4}	−2,0	38,8	70,0
$CH_3(CH_2)_6$	3,15 X 10^{-4}	−1,8	38,3	63,0	2,83 X 10^{-4}	−1,8	35,5	65,0
 (10)	3,64 X 10^{-4}	−1,6	42,1	60,0	3,60 X 10^{-4}	−2,0	52,1	75,0

TABLE 4

CONTROLLED POTENTIAL REDUCTION AND REOXIDATION OF OPTICALLY ACTIVE ALKYLCOBALOXIME

Before electrolysis	α_{546}	After electrolysis and reoxidation reclaimed product	α_{546}	Yield (%)
(+)octylcobaloxime	+53.3	(+)octylcobaloxime	+55	85
(—)octylcobaloxime	—59	(—)octylcobaloxime	—53	68

spectroscopy. They were found to be identical to the starting products except in one case (6 in Table 1); in this case, 45% of a cobalt complex different from the starting product was recovered. This complex is assumed to be an alkyldicobalt complex [Co]$(CH_2)_5$[Co].

c) Reduction of alkylcobaloximes with isomerizable R groups. To obtain more information about the mechanisms of these reductions and reoxidations, and to see whether the Co—C bond is cleaved by reduction and reoxidation, we studied the electrolysis of optically-active 2-octylcobaloxime (9). The recovered 2-octylcobaloxime was found to be optically active and to have retained its configuration (Table 4).

Reduction of 5-hexenylcobaloxime (7) followed by reoxidation gave unchanged 7 in 90% yield. The 5-hexenyl radical cyclises to give cyclopentylmethyl radical with a rate constant of 10^5 s^{-1} [7], but no traces of cyclopentylmethylcobaloxime could be detected by NMR spectroscopy (^1H and ^{13}C).

d) Reduction of alkylcobaloxime R[Co] in the presence of alkyl halides R'X (X = Cl, Br). Attempts to trap the dealkylated cobaloxime(I) have been made using alkyl halides with a different alkyl group. Excess of an alkyl halide was added at the end of electrolysis. In all cases, except methylcobaloxime (1), organocobalt complexes were recovered in good yield and proved to be mixtures of R[Co] and R'[Co], with the former predominating. The results are listed in Table 5.

TABLE 5

RATIO OF ALKYLCOBALOXIME R[Co] AND R'[Co] OBTAINED BY ELECTROCHEMICAL REDUCTION OF R[Co^{III}] AND ADDITION OF R'X AT THE END OF THE ELECTROLYSIS [a]

	R[Co^{III}] $\times 10^{-4}$ (mol)	R'X $\times 10^{-3}$ (mol)	E (V)	%R[Co]	%R'[Co]	R_T (%)
R = $CH_3(CH_2)_6$ R' = CH_3CH_2	5.7	8	—2.2	70	30	80
R = CH_3CH_2 R' = $CH_3(CH_2)_5$	7.4	7.9	—2	69	31	70
R = CH_3CH_2 R' = CH_3	7.6	8.5	—2	87	13	75
R = CH_3 R' = CH_3CH_2	7.3	6.6	—2	100	not detected	85

[a] E = reduction potential of R[Co^{III}]; % R[Co] and % R'[Co]: ratio of alkylcobaloximes R[Co^{III}] and R'[Co^{III}] obtained after recovery and NMR analysis: R_T = total yield of the process (referred to the initial amount of R[Co^{III}].

Discussion

As we pointed out at the beginning of this paper, it is widely accepted that the cobalt—carbon bond undergoes dissociation during the reduction of organocobalt complexes. This was clearly demonstrated by Costa et al. [4,8] for alkylcobalt-salen and cobalt-BAE, and they proposed that the stability of Co—C bond decreased in the order:

$C_6H_5 > CH_3 > C_2H_5$

Benzene was recovered in 80% yield after electrolysis of phenylcobalt-salen and this is reasonable evidence for the rupture of Co—C bond in this case. The voltammetric curves of the reoxidized solution in this case show typical waves of dealkylated cobalt complex. In the case of cobaloximes, Schauzer [1] concluded that there was complete reduction of organocobalt complexes leading to cobalt(0) followed by decomposition of the product. Brockway and al. [9] came to the same conclusion for Co-salen compounds containing perfluoroalkyl groups.

Rupture of the Co—C bond was also suggested during the electrolysis of alkylporphyrins [10], although reoxidation of the products was not studied. Our results outlined above lead us to consider different possibilities. Voltammetric and polarographic measurements provide evidence for the rupture of the Co—C bond, in the form of waves which seem characteristic of dealkylated complexes and formation of R′[Co] complexes when R′X is added to the solution after electrolysis.

On the other hand, the recovery of quantitative yields of complexes after reoxidation and purification, and the complete retention of configuration for the optically active compounds contradict simple rupture of the cobalt—carbon bond. A reasonable assumption is that after reduction R group is still bonded to the cobalt complex. Such a species should exhibit the electrochemical properties of $R[Co^{II}]^{\overline{\cdot}}$ or $R[Co^{I}]^{2-}$ and would be reisolated as the starting product after reoxidation. Since this is only observed on mercury (Fig. 1), and with a diffusion current corresponding to 30% of the total product, not more than this percentage of alkylated cobalt complex should be recovered. Thus we must propose another scheme of reaction which accounts for all the results. Several pathways depending on the oxidation states of the cobalt, can be envisaged for the rupture of the cobalt—carbon bond:

$R[Co^{II}]^{\overline{\cdot}} \rightarrow R^- + [Co^{II}]^{\cdot}$

$R[Co^{II}]^{\overline{\cdot}} \rightarrow R^{\cdot} + [Co^{I}]^-$

$R[Co^{I}]^{2-} \rightarrow R^- + [Co^{I}]^-$

In contrast to Schrauzer's results [1], none of our experiments indicate $[Co^0]$ formation.

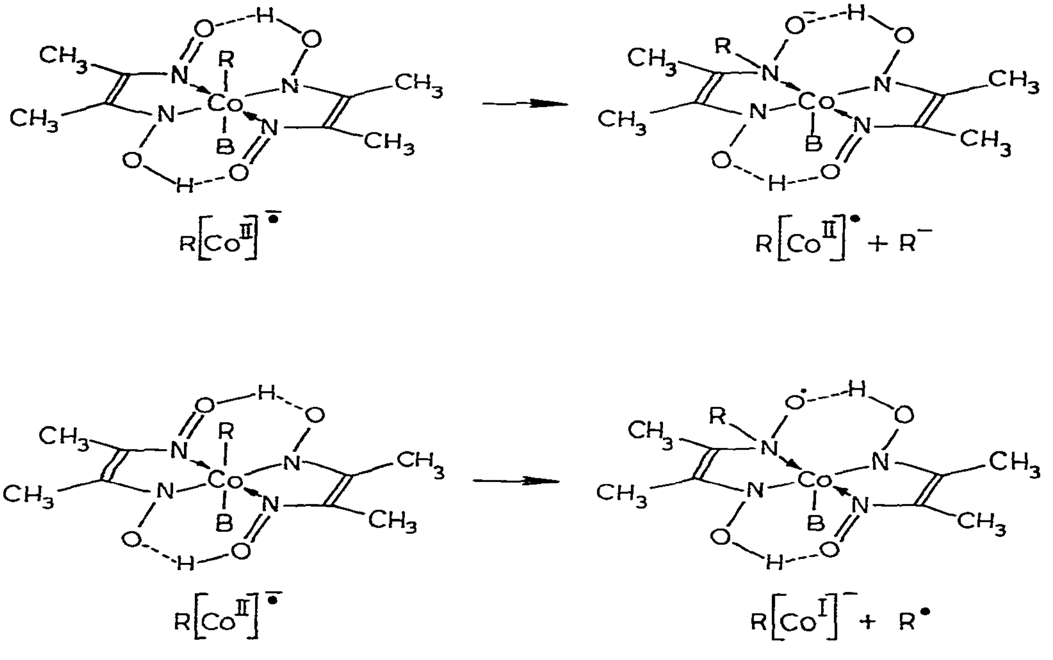
As we have previously shown [11] $R[Co^{II}]^{\overline{\cdot}}$ can be formed directly or through the antidisproportionation reaction:

$R[Co^{I}]^{2-} + R[Co^{III}] \rightarrow 2\ R[Co^{II}]^{\overline{\cdot}}$

Studies using the rotating ring-disk platinum electrode show that the stability

SCHEME 1

PROPOSED SCHEME OF ALKYL TRANSFER IN REDUCED ALKYLCOBALOXIME $R[Co^{II}]^{-}$



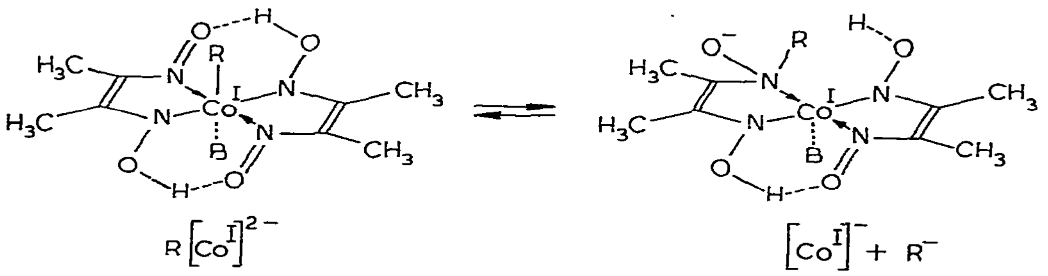
of this species is strongly dependent on the nature of R.

But while these reaction schemes are consistent with the rupture of cobalt—carbon bond, they do not account for the reversible formation of the starting material. So we must assume that during the process the R group is transferred to an "appropriate position" on the equatorial ligand by a mechanism still to be defined. This alkyl transfer that occurs with the reduced alkylcobaloxime is reversible (Schemes 1 and 2).

Examples of alkylation of equatorial ligands have been reported in the literature. Alkylation of tetraphenylporphyrin has been proposed by Lexa et al. [12] in the electrolysis of butyl bromide catalyzed by cobalt(II) porphyrin. These authors noted that the visible spectrum of the porphyrin is modified during the process toward a spectrum associated with less aromaticity in the por-

SCHEME 2

PROPOSED SCHEME OF ALKYL TRANSFER IN REDUCED ALKYLCOBALOXIME $R[Co^{I}]^{2-}$



phyrin ring: their explanation implies alkylation of the ring, although they did not isolate any alkylated product at the end of the reaction. A metal-to-ligand alkyl transfer was also proposed by Callot and Shaeffer [13] who showed that in cobalt and rhodium porphyrins the alkyl group can be reversibly transferred from the metal to a nitrogen atom of the ligand.

We are now carrying out electrochemical reduction and ESR measurements in order to obtain some evidence for the participation of the postulated intermediates

Acknowledgments

We thank professor B. Trémillon and Professor M.D. Johnson for fruitful discussions and Dr. J. Deniau for providing the optically active cobaloximes.

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