Reaction of Electrogenerated $[Co^{I}(salen)]$ † with t-Butyl Bromide and t-Butyl Chloride

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The compound $[Co^{I}(salen)]^-$ [salen = *NN'*-ethylenebis(salicylideneiminate)] electrogenerated in the presence of Bu^tX (X = Cl or Br) yields $[Co^{II}(salen)]$ and organic products. With Bu^tBr the reaction takes place in two steps, the rates of which have been determined. The first step leads to rapid disappearance of $[Co^{I}(salen)]^-$ by a second-order reaction and has been studied by cyclic voltammetry. The second step is the slower regeneration of $[Co^{II}(salen)]$. When $[Co^{II}(salen)]$ is reduced to $[Co^{I}(salen)]^-$ in the presence of Bu^tBr an overall electrocatalytic process ensues which has been studied by controlled-potential reduction and polarography. All evidence is consistent with the formation of an unstable organometallic intermediate which decomposes into $[Co^{II}(salen)]$. 2-Methylpropene and hydrogen are the main products arising from the butyl radical.

THE reaction of square-planar cobalt(I) chelates with alkyl halides is one of the more general routes to the preparation of cobalt(III) alkyl complexes.[1] The oxidation state I is made accessible by suitable chelating agents such as the quadridentate Schiff bases derived from salicylaldehyde,[2] acetylacetone,[3] diacetyl monoxime,[4] or the bis(bidentate chelate) systems such as bis(diacetyl dioxime).[5,‡]

The same reaction was employed to prepare alkyl derivatives of cobalt chelates of biological interest such as cobalt porphyrins [6] and cobalamin.[7]

Two mechanisms were originally considered for the reaction of cobalt(I) chelates with alkyl halides.[8] The S_N2 displacement, equation (1), and a free-radical mechanism, equations (2) and (3). The former was

$$[Co^{I}(chelate)]^- + R{-}X \longrightarrow [CoR(chelate)] + X^- \quad (1)$$

$$[Co^{I}(chelate)]^- + R{-}X \xrightarrow{k} [Co^{II}(chelate)] + R^\bullet + X^- \quad (2)$$

$$[Co^{II}(chelate)] + R^\bullet \xrightarrow{\text{fast}} [CoR(chelate)] \quad (3)$$

generally preferred on the basis of relative-rate data for a variety of alkyl halides and from a comparison of the sensitivity of the reaction to the nature of the leaving group and of the alkyl group with that of classical S_N2 reactions.

The instability of secondary-alkyl cobalamines and the failure to obtain the tertiary-alkyl–cobalt complexes was attributed to steric hindrance.[8] The reaction of cobaloximes(I) with tertiary alkyl halides, which also fails to give the organometallic derivative as a stable product,[8] may be explained, in principle, either by steric hindrance or by the instability of the Co–C bond.

On the other hand, a comparison of the rate constants of the reaction of vitamin B_{12s} and of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)-cobalt(I) with CH_3I, which is about four orders of magnitude higher in the latter case, led Endicott and co-workers [9] to suggest that in this particular case the reaction takes place by a radical mechanism generating Co^{II}, $CH_3^\bullet$, and I^-.

The nature and mechanism of the formation and cleavage of the Co–C bond in the model chelates are key points for understanding the reaction mechanism of the B_{12} coenzyme.[1a,7] The main aspects are the formal oxidation state of the cobalt atom involved, the charge transferred from the equatorial and from the *trans* axial ligand to the Co–C bond through the metal atom, and the stereochemistry. Previous proposals for cobalt(I) derivatives of corrins as active forms of the B_{12} coenzyme were based on the particular reactivity of cobalt(I) species in displacement or electron-transfer reactions [10] but there is now substantial evidence for the reversible formation of cobalt(II) species (vitamin B_{12r}) and organic radicals.[11]

Following previous studies on the reaction of electrogenerated cobalt(I) chelates with organic halides,[12] we show in this paper that the reaction of *NN'*-ethylenebis(salicylideneiminato)cobaltate(I), $[Co^{I}(salen)]^-$, electrochemically generated from $[Co^{II}(salen)]$, with t-butyl bromide does not afford the organocobalt derivative but gives an unstable intermediate which in turn decomposes regenerating $[Co^{II}(salen)]$, and also yields 2-methylpropene and hydrogen. The overall electrochemical reaction results in the electrocatalytical one-electron reduction of the organic halide at much less cathodic potentials than the uncatalyzed highly irreversible two-electron reduction.

While this work was in progress other studies were reported on the reaction of electrogenerated $[Ni^{I}(salen)]^-$ and $[Co^{I}(bipy)_3]^+$ (bipy = 2,2'-bipyridyl) complexes with organic halides for which the formation of organometallic intermediates is also proposed.[13,14]

EXPERIMENTAL

Materials.—The compound $[Co^{II}(salen)]$ was prepared by published procedures. Dimethyl formamide (dmf) (Erba) was dried with 4 Å molecular sieves. t-Butyl bromide and Bu^tCl were purified by successive distillations. The salt $[NBu_4][ClO_4]$ was not used as supporting electrolyte because of the competing reaction of $[NBu_4]^+$ with $[Co^{I}(salen)]^-$.[12] Anhydrous $Li[ClO_4]$ (Fluka) was dried at 50 °C

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† *NN'*-Ethylenebis(salicylideneiminato)cobaltate(I).

‡ Diacetyl = butane-2,3-dione.

in vacuo. Na[ClO$_4$] (Erba) was recrystallized and dried by the same procedure.

Apparatus and Methods.—Polarographic measurements were made on an Amel model 471 multipolarograph equipped with a model 460 stand. A model 694 universal cell was used. The characteristics of the dropping mercury electrode (d.m.e.) made from a 45° bent glass capillary in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}) at 25 °C were: flow rate = 1.15 mg s^{-1}, drop time = 3 s, and height of the mercury level 63.5 cm. A Metrohm saturated calomel electrode (s.c.e.) filled with a saturated aqueous solution of NaCl was used as a reference electrode, separated by a salt bridge containing the same electrolyte as the examined solution. A platinum wire was used as counter electrode.

Controlled-potential electrolysis was performed with the AMEL model 557/SU potentiostat as previously described.[15]

The cyclic-voltammetric apparatus and the method used for the calculation of pseudo-first-order rate constants for [Co^{I}(salen)]$^-$ disappearance have already been described.[12] The observed rate constant ($k_{obs.}''$) of the rate-determining step for the electrocatalytic process, *i.e.* the regeneration of [Co^{II}(salen)] under pseudo-first-order conditions, was evaluated from the parameter $i_l/i_d = \Psi(X)$ where i_l/i_d is the polarographic instantaneous limiting current divided by the instantaneous diffusion current, at dropping times t = 5—8 s, and $\Psi(X)$ is a function of $X = k_{obs.}''\,t$, tabulated by Koutecky.[16]

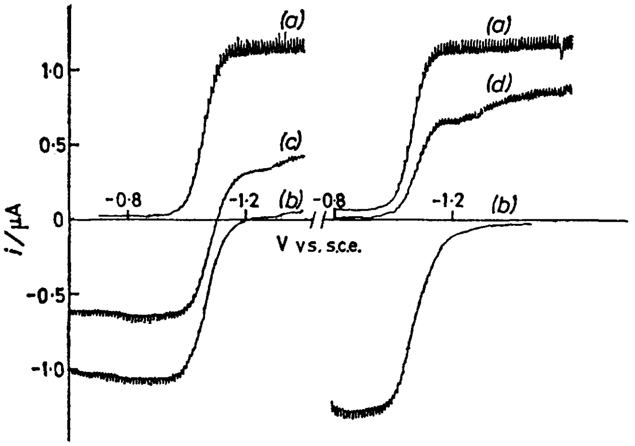

FIGURE 1 Polarograms of [Co^{II}(salen)] (2.8 mmol dm^{-3}) solutions in dmf–Li[ClO$_4$] (0.2 mol dm^{-3}): (*a*) at 0 °C; (*b*) after exhaustive electrochemical reduction at −1.5 V *vs.* s.c.e.; (*c*) solution (*b*) after addition of an equimolar amount of Bu^{t}Cl after 44 min; (*d*) after addition of equimolar amount of Bu^{t}Br

The products from controlled-potential electrocatalytic reduction were identified by gas–solid chromatography (g.s.c.) and their retention times compared with authentic samples. Chromatographic analyses of 2-methylpropene were carried out with 2 m columns of silica gel, and of hydrogen with 2 m columns of no. 5A molecular sieves. A Carlo Erba G.T. gas chromatograph was used.

The Reaction between Electrogenerated [Co^{I}(salen)]$^-$ *and* Bu^{t}X (X = Cl *or* Br).—By controlled-potential reduction of a red solution of [Co^{II}(salen)] (*ca.* 2 mmol dm^{-3}) and Li[ClO$_4$] (0.2 mol dm^{-3}) at 0 °C a green solution of [Co^{I}(salen)]$^-$ is obtained.[12] The polarogram shows the anodic wave due to [Co^{I}(salen)]$^-$ reoxidation with unchanged half-wave potential $E_{\frac{1}{2}}$ = −1.06 *vs.* s.c.e. relative to the cathodic wave due to [Co^{II}(salen)] reduction in the parent solution (Figure 1).

Addition of an equimolecular amount of Bu^{t}Br leads to the formation of Br$^-$ in a 1 : 1 stoicheiometric ratio [from polarographic anodic double wave at $(E_{\frac{1}{2}})_1$ + 0.2 and $(E_{\frac{1}{2}})_2$ −0.28 V *vs.* s.c.e.], loss of [Co^{I}(salen)]$^-$ (absence of any anodic current at = 1.06 V *vs.* s.c.e.), and partial formation of [Co^{II}(salen)] [cathodic wave with $E_{\frac{1}{2}}$ −1.06 V, Figure 1(*d*)]. The $E_{\frac{1}{2}}$ of the [Co^{II}(salen)]$\longleftrightarrow$[Co^{I}(salen)]$^-$ redox process is displaced towards positive values by increasing the Bu^{t}Br concentration in agreement with a chemical reaction involving the product of the heterogeneous electron transfer. The formation of a stoicheiometric amount of [Co^{II}(salen)] ensues slowly. The same reaction with Bu^{t}Cl instead of Bu^{t}Br leads to a change from the anodic wave of [Co^{I}(salen)]$^-$ to a mixed anodic–cathodic wave showing the presence of both [Co^{II}(salen)] and [Co^{I}(salen)]$^-$ [Figure 1(*c*)]. The reaction with Bu^{t}Cl also affords eventually stoicheiometric formation of [Co^{II}(salen)] and of halide ion (Table 1), but more slowly than with Bu^{t}Br.

TABLE 1

Stoicheiometric data for reactions (5)—(7)

[Co^{I}(salen)]$^-$ [a] mmol	t-Butyl halide	[Bu^{t}X] / [Co^{I}(salen)$^-$]	Amount [b] of Br$^-$ mmol
0.056	Bu^{t}Br	1	0.060
0.037	Bu^{t}Br	19	0.040
0.058	Bu^{t}Cl	20	0.053

[a] Electrogenerated. [b] Determined from anodic wave current.

In both cases at the end of the reaction the halide ions and [Co^{II}(salen)] are the only electrochemically active species present.

In a typical run the overall reaction under pseudo-first-order conditions between electrogenerated [Co^{I}(salen)]$^-$ (2.6 × 10^{-3} mol dm^{-3}) and Bu^{t}Cl (4.5 × 10^{-3} mol dm^{-3}) in dmf–Li[ClO$_4$] (0.2 mol dm^{-3}) at 25 °C took place with a rate constant $k_{obs.} = 1 \times 10^{-3}$ s^{-1} {calculated from the increase of [Co^{II}(salen)] concentration followed from the increase of cathodic diffusion current of the [Co^{II}(salen)] cathodic wave, against time}. The first step of the reaction with Bu^{t}Br was studied by cyclic voltammetry. Solutions of [Co^{II}(salen)] alone in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}) at 0 °C show the reversible one-electron redox process with anodic ($i_p{}^a$) and cathodic ($i_p{}^c$) peak currents with $i_p{}^a/i_p{}^c = 1$ and $E_p{}^c$ − 1.194 V *vs.* s.c.e. with ΔE_p = 83 mV. After addition of Bu^{t}Br the reverse (anodic) peak current for [Co^{I}(salen)]$^-$ reoxidation decreases with increasing Bu^{t}Br concentration and with decreasing the potential scan rate (see Figure 2). On the other hand, the forward cathodic peak current does not increase (Figure 2) showing that while the reaction with the alkyl halide is fast {[Co^{I}(salen)]$^-$ reoxidation peak smaller or absent} the regeneration of the cobalt(II) complex by the homogeneous chemical reaction does not influence the cathodic peak current. At a single potential sweep rate, $i_p{}^c/i_p{}^a$ is a linear function of the rate of the chemical reaction involving [Co^{I}(salen)]$^-$ and was used to calculate the rate constant of disappearance of the latter, as the first step of the reaction with Bu^{t}Br. Under pseudo-first-order conditions, $k_{obs.}'$ was determined following the Nicholson treatment (Table 2).

Controlled-potential Reduction of [Co^{II}(salen)] *in the Presence of an Excess of* Bu^{t}Br.—When the controlled-potential reduction of [Co^{II}(salen)] (*ca.* 2 mmol dm^{-3}) in dmf–Na[ClO$_4$] (0.2 mol dm^{-3}) is carried out at −1.3 V in the presence of an excess of Bu^{t}Br (*ca.* 0.04 mol dm^{-3}) with an electrolysis rate of the order of 0.5 × 10^{-5} mmol s^{-1} cm^{-2} the solution is not discoloured and the polarograms show a practically unchanged [Co^{II}(salen)]$\longrightarrow$[Co^{I}(salen)]$^-$ reduction wave between −1.2 and −1.3 V until an excess of Bu^{t}Br is present.

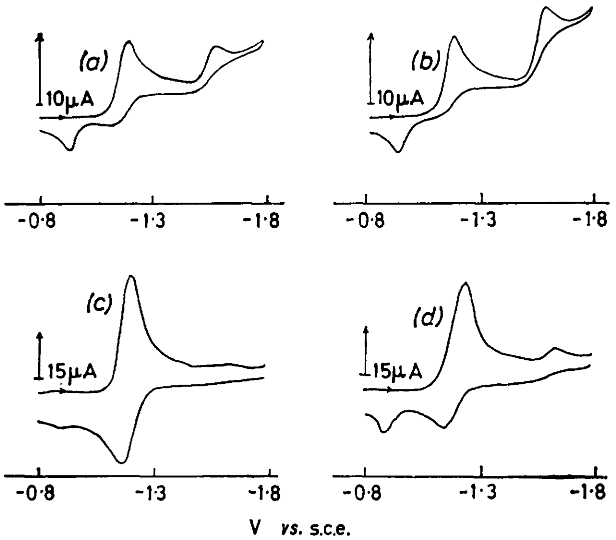

FIGURE 2 Cyclic-voltammetric experiments on [Co^{II}(salen)] (1.69 mmol dm^{-3}) in the presence of Bu^{t}Br in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}). Concentration of Bu^{t}Br: (a) and (c), 8.9 × 10^{-3}; (b) and (d), 40.05 × 10^{-3} mol dm^{-3}. Scanning rate: (a) and (b), 1; (c) and (d), 40 V s^{-1}

At the same time the anodic double wave due to oxidation of Br$^-$ develops. The height of this wave is found to be proportional to the quantity of electricity passed during the electrolysis in agreement with the equation: Bu^{t}Br + e$^-$ $\longrightarrow$ Br$^-$ + products (Table 3). The main products were found to be 2-methylpropene and hydrogen.

TABLE 2

Rate constant for the first step of the reaction of [Co^{I}(salen)]$^-$ (0.31 × 10^{-3} mol dm^{-3}) with Bu^{t}Br *

10^3[Bu^{t}Br] / mol dm^{-3}	$k_{obs.}$ / s^{-1}	10^{-2}k / dm^3 mol^{-1} s^{-1}
4.4	4.82	1.09
8.9	9.84	1.11
13.3	14.90	1.12
17.8	18.34	1.03

* Estimated from cyclic-voltammetric peak current ratio at 6 V s^{-1} from −0.8 to −1.35 V vs. s.c.e. (τ = 0.023 8 s).

TABLE 3

Coulometric data for the catalyzed reduction of Bu^{t}Br in the presence of [Co^{II}(salen)] in dmf–Na[ClO$_4$] (0.1 mol dm^{-3})

Amount of [Co^{II}(salen)] / mmol	Bu^{t}Br / [Co^{II}(salen)]	E * / V	Charge / C	Yield of Br$^-$ / mol per 10^5 C	Products
0.038	16.3	−1.3	12	0.81	C_4H_8, H_2
0.036	17.0	−1.3	25	0.88	
0.020	6.5	−1.6	12	0.90	C_4H_8
0.036	5.0	−1.6	16	0.94	
0.033	18.0	−1.7	21	0.90	

* Controlled potential of reduction in V vs. s.c.e.

Electrocatalytic Character of Polarographic Reduction of [Co^{II}(salen)] *in the Presence of an Excess of* Bu^{t}Br.—In the presence of an excess of Bu^{t}Br at 25 °C the mean polarographic limiting current ($\bar{i}_l$) of the [Co^{II}(salen)]$\longrightarrow$[Co^{I}(salen)]$^-$ reduction wave exceeds the value of the mean diffusion current ($\bar{i}_d$) for the [Co^{II}(salen)] reduction at the same concentration, and increases with increasing Bu^{t}Br concentration (Figure 3).

The catalytic process is also revealed by the slope of the log–log plot of the instantaneous polarographic current during the life of a drop on the d.m.e. which was found to be in the range 0.45–0.55 (Figure 4).

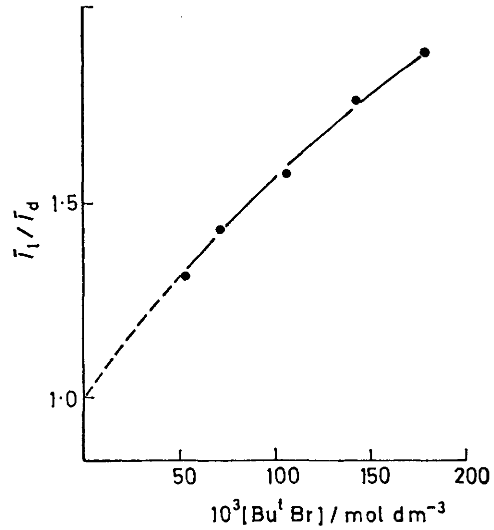

FIGURE 3 Plot of $\bar{i}_l/\bar{i}_d$ against [Bu^{t}Br] for solutions of [Co^{II}(salen)] (1.72 mmol dm^{-3}) in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}) at 25 °C

The rate constant of the catalytic process was not determined from the ratio $\bar{i}_l/\bar{i}_d$ at 25 °C because of the slow solvolysis of Bu^{t}Br competing with the reaction with [Co^{I}(salen)]$^-$. At 0 °C the solvolysis is not appreciable but the regeneration of [Co^{II}(salen)] is also slow and $\bar{i}_l/\bar{i}_d$ is close to unity. Thus the ratio of instantaneous currents i_l/i_d was used to calculate the pseudo-first-order rate constant $k_{obs.}''$ of the reaction regenerating [Co^{II}(salen)], following the treatment of Koutecky.[16] The plot of k_{obs}'' vs. Bu^{t}Br concentration is linear and the intercept is very nearly zero (Figure 5).

The characteristics of both the instantaneous and of the mean polarographic current of [Co^{II}(salen)] in the presence of an excess of Bu^{t}Cl show that the regeneration of [Co^{II}(salen)] is too slow to give rise to appreciable electrocatalysis on the time scale of the polarographic experiment.

The Electroreduction of Bu^{t}Br *by* [Co^{II}(salen)] *at Potentials more Cathodic than ca.* −1.4 V *vs. s.c.e.*—While the mean limiting current for the reduction of [Co^{II}(salen)] in the presence of an excess of Bu^{t}Cl is constant and diffusion controlled along the plateau of the polarographic wave, a second cathodic wave with limiting current increasing with potential is registered from a solution containing an excess of Bu^{t}Br (Figure 6). The log i — log t plot for the second wave (Figure 4) has a slope of 0.88.

The second (polarographic) cathodic wave corresponds to the cathodic peak which occurs at *ca.* -1.59 V *vs.* s.c.e. on triangular-wave voltammetry of the same solutions (Figure 2). The height of the second cathodic peak increases with decreasing potential scan rate and with increasing Bu^{t}Br concentration, *i.e.* by increasing the extent of the chemical reaction consuming [Co^I(salen)]$^-$ at the electrode. This cathodic peak shows no anodic counterpart in the same potential range even at the highest accessible sweep rates and can be connected with the anodic peak at -0.9 V *vs.* s.c.e. This electrode process is being studied in more detail and the results of the electrochemical investigations will be published elsewhere.

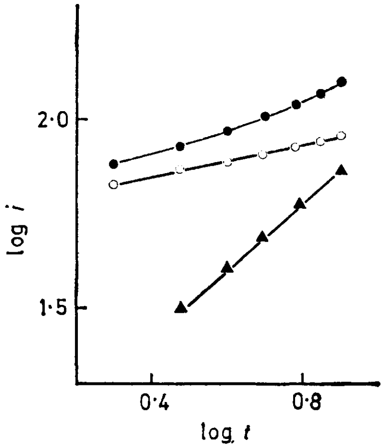

FIGURE 4 Plot of log i against log t for a solution of [Co^{II}(salen)] (1.69 mmol dm^{-3}) in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}) at 0 °C; alone at $E = -1.3$ V *vs.* s.c.e. (○), in the presence of Bu^{t}Br (44.5 mmol dm^{-3}) at $E = -1.3$ (●), and -1.6 V *vs.* s.c.e. (▲)

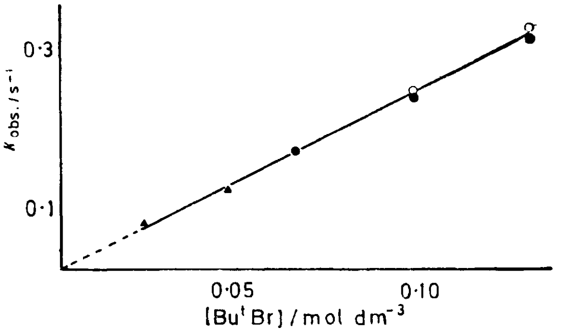

FIGURE 5 Plot of $k_{obs.}''$ against [Bu^{t}Br] for the reaction regenerating [Co^{II}(salen)] [2.39 × 10^{-3} (●), 1.26 × 10^{-3} (○), and 1.16 × 10^{-3} mol dm^{-3} (▲)]

RESULTS AND DISCUSSION

Addition of Bu^{t}Br to electrogenerated [Co^I(salen)]$^-$ results in the rapid disappearance of cobalt(I) species but only slow regeneration of [Co^{II}(salen)]. Under the same reaction conditions the addition of Bu^{t}Cl to [Co^I(salen)]$^-$ is followed by the slow oxidation of [Co^I(salen)]$^-$ to [Co^{II}(salen)] by the organic halide. In both cases at the end of the overall reaction the stoicheiometry of equation (4) holds. The rate constant of the overall reaction with Bu^{t}Cl under pseudo-first-order conditions is $k_{obs.} = 1 \times 10^{-3}$ s^{-1}. It can be shown that the reaction of electrogenerated [Co^I(salen)]$^-$ with Bu^{t}Br takes place in two steps: the first, as revealed by cyclic voltammetry which allows us to follow the fast chemical reaction coupled with the electron transfer, is the consumption of electrogenerated [Co^I(salen)]$^-$ in the presence of an excess of Bu^{t}Br. The second step of the reaction can be studied by polarography, where the time scale of the electrochemical experiment is slower than that used in cyclic voltammetry. In fact, the conventional polarographic wave due to the reduction of [Co^{II}(salen)] acquires an electrocatalytic character in the presence of an excess of Bu^{t}Br showing the slower regeneration of [Co^{II}(salen)] following the rapid reaction of [Co^I(salen)]$^-$ with Bu^{t}Br. The rate of the first step of the reaction is found to depend on the Bu^{t}Br concentration and the second-order rate constant $k = 1.09 \times 10^3$ dm^3 mol^{-1} s^{-1} is obtained. The regeneration of [Co^{II}(salen)], as followed by controlled-potential reduction of [Co^{II}(salen)] in the presence of an excess of Bu^{t}Br, gives rise to electrocatalytic

$$[\mathrm{Co^I(salen)}]^- + \mathrm{Bu^tX} \longrightarrow [\mathrm{Co^{II}(salen)}] + \mathrm{X^-} + \text{products from } \mathrm{Bu^t} \quad (4)$$

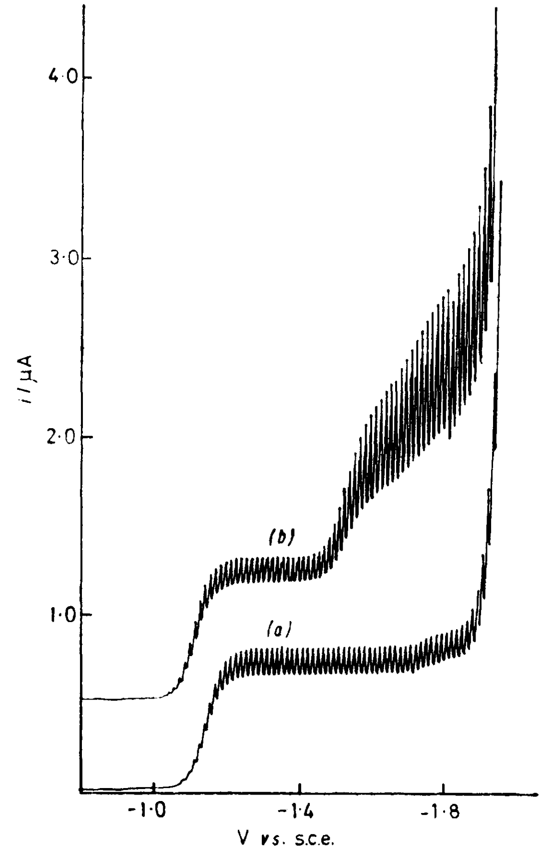

FIGURE 6 Polarograms of [Co^{II}(salen)] (8.9 mmol dm^{-3}) solutions in dmf–Na[ClO$_4$] (0.1 mol dm^{-3}) in the presence of (*a*) Bu^{t}Cl (31.8 × 10^{-3} mol dm^{-3}) and (*b*) Bu^{t}Br (9.0 × 10^{-3} mol dm^{-3})

reduction of $\mathrm{Bu^tBr}$ and formation of 2-methylpropene and hydrogen. The pseudo-first-order rate constant of the second step of the overall reaction [equations (5)—(7)] is calculated from the characteristics of the electrocatalytic instantaneous current and found to be linearly related with $\mathrm{Bu^tBr}$ concentration, with an intercept close to zero.

All the above evidence is consistent with a mechanism involving the formation of an organometallic intermediate whose instability gives rise to the catalytic cycle shown below. Reaction (6) is first order both in $[\mathrm{Co^I(salen)^-}]$ and in $[\mathrm{Bu^tBr}]$.

$$[\mathrm{Co^{II}(salen)}] + \mathrm{e} \xrightarrow{k_s} [\mathrm{Co^I(salen)}]^- \qquad (5)$$

$$[\mathrm{Co^I(salen)}]^- + \mathrm{Bu^tBr} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{CoBu^t(Br)(salen)}]^- \qquad (6)$$

$$[\mathrm{CoBu^t(Br)(salen)}]^- \xrightarrow{k_2} [\mathrm{Co^{II}(salen)}] + \mathrm{C_4H_8} + \tfrac{1}{2}\mathrm{H_2} + \mathrm{Br^-} \qquad (7)$$

The reaction follows the rate law (8) with $k_{\mathrm{obs.}}' = k_1[\mathrm{Bu^tBr}]$.

$$-\,\mathrm{d}[\mathrm{Co^I(salen)^-}]/\mathrm{d}t = k_1[\mathrm{Co^I(salen)^-}][\mathrm{Bu^tBr}] \qquad (8)$$

On the other hand, the second step regenerating the $[\mathrm{Co^{II}(salen)}]$ takes place by a slower reaction. The observed rate constant $k_{\mathrm{obs.}}''$ for the regeneration of cobalt(II) should be expressed by equation (9) where

$$k_{\mathrm{obs.}}'' = k_2K[\mathrm{Bu^tBr}]/(1 + K[\mathrm{Bu^tBr}]) \qquad (9)$$

$K = k_1/k_{-1}$. The observed linear relationship between $k_{\mathrm{obs.}}''$ and $[\mathrm{Bu^tBr}]$ concentration may be explained if $K[\mathrm{Bu^tBr}] \ll 1$.

The formation of an intermediate organometallic derivative was also proposed in the reaction of electrogenerated $[\mathrm{Co^I(bipy)_3}]^+$ and acrylonitrile or allyl chloride. In the latter case the instability of the π-bonded mixed complex results in the regeneration of $[\mathrm{Co^{II}(bipy)_2}]^{2+}$ and a catalytic cycle ensues.[14]

In the case of $[\mathrm{Co^{II}(salen)}]$–$\mathrm{Bu^tBr}$ reduction it is possible to distinguish kinetically the two steps of the catalytic cycle, which also apparently arises from the instability of the intermediate.

However, $\mathrm{Bu^tCl}$ is also reduced by $[\mathrm{Co^I(salen)}]^-$ with regeneration of $[\mathrm{Co^{II}(salen)}]$ but the reaction does not give rise to a catalytic current for $[\mathrm{Co^{II}(salen)}]$ reduction owing to the slowness of the reaction on the time scale of the polarographic experiment. The formation of an intermediate, if it occurs, does not take place in the reaction layer at the electrode and therefore cannot be observed.

Comparison with the rate constants of other $[\mathrm{Co^I(salen)}]$ reactions with alkyl bromides shows that the rate constants are in the order $\mathrm{Bu^t} > \mathrm{Pr^n} > \mathrm{Et}$.[8]

The presence of two, kinetically distinct, steps for the reaction of $[\mathrm{Co^I(salen)}]^-$ with $\mathrm{Bu^tBr}$ shows that the transition state leading to the formation of the Co–C bond from cobalt(I) chelate and RX may be different to that leading to the reverse reaction. In fact the reverse of the reaction taking place between (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(II) and alkyl radicals leads to a stable Co–C bond while the reaction of the corresponding cobalt(I) chelate with RX fails to give the organometallic product.[17]

Thus, the stability of the Co–C bond is not necessarily correlated with the rate of reaction between cobalt(I) chelates and alkyl halides. This can explain the lack of correlation between the rate of reaction of vitamin $\mathrm{B_{12s}}$ and cobaloximes(I) with secondary organic halides (which are of the same order of magnitude) and the stability of the organometallic derivatives.[8] In fact the secondary alkyl derivatives of vitamin $\mathrm{B_{12s}}$ are unstable, although they can be obtained from cobaloximes(I).

The formation of 2-methylpropene and hydrogen suggests that the decomposition of the intermediate may include a C–H bond breaking. The decomposition of the t-butyl radical may take place within the co-ordination sphere of the cobalt atom.

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REFERENCES

[1] (*a*) D. Dodd and M. D. Johnson, *Organometallic Chem. Rev.*, 1973, **52**, 1; (*b*) D. G. Brown, *Progr. Inorg. Chem.*, 1973, **18**, 177.

[2] G. Costa, G. Mestroni, and G. Pallizer, *J. Organometallic Chem.*, 1968, **11**, 333.

[3] G. Costa and G. Mestroni, *J. Organometallic Chem.*, 1968, **11**, 325.

[4] G. Costa, G. Mestroni, and E. de Savorgnani, *Inorg. Chim. Acta*, 1969, **3**, 323.

[5] G. N. Schrauzer, R. J. Windgassen, and J. Kohule, *Chem. Ber.*, 1965, **98**, 3324.

[6] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnoch, *J. Chem. Soc.* (*A*), 1968, 881.

[7] J. M. Pratt, ' Inorganic Chemistry of Vitamin $\mathrm{B_{12}}$,' Academic Press, London, 1972, p. 224.

[8] G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, 1969, **91**, 3341.

[9] D. P. Rillema, J. F. Endicott, and E. Papaconstantinon, *Inorg. Chem.*, 1971, **10**, 1739.

[10] G. N. Schrauzer and J. W. Siebert, *J. Amer. Chem. Soc.*, 1970, **92**, 1022.

[11] T. H. Finlay, J. Valinsky, K. Sato, and R. H. Abeles, *J. Biol. Chem.*, 1972, **247**, 4197.

[12] G. Costa, A. Puxeddu, and E. Reisenhofer, *J.C.S. Dalton*, 1973, 2034.

[13] C. Gosden, K. P. Nealy, and D. Pletcher, *J.C.S. Dalton*, 1978, 972.

[14] S. Margel and F. C. Anson, *J. Electrochem. Soc.*, 1978, **125**, 1232.

[15] J. Hanzlik, A. Puxeddu, and G. Costa, *J.C.S. Dalton*, 1977, 542.

[16] J. Koutecky, *Coll. Czech. Chem. Comm.*, 1953, **18**, 311.

[17] M. Perrèe-Fauvet and A. Gaudemer, *J. Organometallic Chem.*, 1976, **120**, 439.