Reactions of Cobalt(I) Complexes with Ammonium and Sulphonium Ions and Organic Halides

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Kinetic measurements are reported for the dealkylation reactions of ammonium and sulphonium compounds and organic halides with cobalt(I) complexes of a series of tetradentate Schiff's bases. The reaction was followed by polarography and cyclic voltammetry. The kinetics conformed to a second order rate law and pseudo-first order plots were obtained in the presence of an excess of substrate. The plot of $E_{\frac{1}{2}}$ values *vs.* log k'' for the reaction with PhBr and EtBr and $[Me_2SC_6H_4Me]^+$ shows a linear free energy relationship suggesting a simple S_N2 displacement reaction and confirming that the nucleophilicity of cobalt(I) species is influenced by the nature of the chelating ligands.

THE chemistry of cobalt complexes formed by planar tetradentate chelating agents with delocalised electronic structure is of great interest in view of the possible mechanistic relationships with the biochemical reactions of vitamin B_{12}.[1-3]

Reaction of cobalt(I) model complexes with organic halides leads to organometallic derivatives.[4-6] Feasible biochemical pathways to coenzyme B_{12} involving formation of the cobalt(I) complex vitamin B_{12S} have been suggested, based on the reduction of aquocobalamin by dithiols[7] and on the reaction of the cobalt(I) deriva-

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[1] G. Costa, *Pure Appl. Chem.*, 1972, **30**, 335.

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[3] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta*, 1970, **4**, 41 and references therein.

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

[5] G. Costa, G. Mestroni, and G. Pellizer, *J. Organometallic Chem.*, 1968, **11**, 333.

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

[7] F. M. Huennekens, 'Biological Oxidations,' ed. T. P. Singer, Interscience, New York, 1968, p. 439.

tive with *S*-adenosylmethionine or other sulphonium salts.[8]

In the particular case of the formation of methylcobalamin, in the vitamin B_{12} dependent methionine biosynthesis, the methyl donor was shown to be a nitrogen compound, *viz.* 5-methyltetrahydrofolate[9] though *S*-adenosylmethionine is required in catalytic amounts.

The transfer of an organic group from a sulphonium salt to a model complex was previously reported but the corresponding reaction from an *N*-alkyl nitrogen compound to vitamin B_{12S} or to reduced cobaloximes was unsuccessful[10] until we recently reported[11] that cobalt(I) chelates react in dimethylformamide (DMF) with alkylammonium salts leading to cleavage of a C–Co bond.

It is of considerable importance to gain knowledge of the reaction of a series of cobalt(I) nucleophiles toward potential organic-group donors.

Previous studies[12-14] showed that cobalt(I) complexes can be quantitatively generated by reversible electrochemical reduction of $[Co^{II}(chel)]^0$ * in DMF at a mercury electrode, while the reaction of the cobalt(I) species with a suitable substrate can be easily followed quantitatively from the decrease of cobalt(I) concentration measured by conventional polarography or triangular sweep voltammetry.

The present paper deals with the kinetics of these transalkylation reactions and points out linear free-energy relationships between rate constants and redox potentials providing experimental support for the S_N2 reaction mechanism and enlarging the chemical basis for the understanding of the enzyme catalysed transmethylation.

EXPERIMENTAL

All measurements were performed in anhydrous DMF, at 0 °C and in the dark owing to the photolability of the organometallic derivatives. The supporting electrolyte was 0·2M $LiClO_4$. Effects arising from the association of the Li^+ with $[Co^I(chel)]^-$ ions in DMF were indeed observed. The following strong displacements of the $E_{\frac{1}{2}}$ values for the cobalt(II)–cobalt(I) couple by varying the gegenion were measured:

$[Co^{II}(salen)]^0 \longleftrightarrow [Co^I(salen)]^-$: $E_{\frac{1}{2}} = -1{\cdot}23$ V *vs.* S.C.E. (Bu_4NClO_4 0·2M), −1·24 (Et_4NClO_4 0·2M), −1·18 ($KClO_4$ 0·2M), −1·06 ($LiClO_4$ 0·2M).

$[Co^{II}(bae)]^0 \longleftrightarrow [Co^I(bae)]^-$: $E_{\frac{1}{2}} = -1{\cdot}73$ (Bu_4NClO_4 0·2M), −1·76 (Et_4NClO_4 0·2M), −1·67 ($KClO_4$ 0·2M), −1·50 ($LiClO_4$ 0·2M), −1·45 [$Mg(ClO_4)_2$ −0·1M].

Despite this Li^+ was used throughout the work instead of cation containing alkyl groups as the latter (*e.g.* Bu_4N^+) behave as competing electrophiles.

Apparatus and Methods.—The basic equipment has been described.[15]

The reactions were studied under pseudo-first-order conditions with the alkyl-donor reactant in a large excess. The cobalt(I) complex was obtained by exhaustive controlled potential reduction of the $[Co^{II}(chel)]^0$ complex. The weighed amount of solid alkylammonium salt was then added under nitrogen and the decrease of the $[Co^I(chel)]^-$ in the reaction solution was followed by recording the anodic diffusion current of the $[Co^I(chel)]^-$ against time.

The reactions of $[Co^I(chel)]^-$ with $[Me_2SC_6H_4Me]^+ClO_4^-$ and with organic halides were so rapid that the use of cyclic triangular wave voltammetry was required to generate the cobalt(I) species in the presence of the large excess of substrate. The concentration of the starting $[Co^I(chel)]^-$-complex was kept constant. The upper limit was $0{\cdot}3 \times 10^{-3}$M to avoid complication due to absorption at the electrode.

In the absence of substrate the ratio of the anodic peak current (i_{ap}) to the cathodic peak current (i_{cp}) in the cyclic polarogram was one showing that the cobalt(I) species is stable in the time scale of the experiment.

In the presence of the substrate the cobalt(I) species electrochemically generated in the cathodic scan of the cyclic polarogram is consumed by the rapid reaction with the substrate and the ratio of i_{ap}/i_{cp} decreases to below one. The i_{ap}/i_{cp} ratio is a function of the rate of the chemical reaction involving the cobalt(I) chelate, and of the time τ from the half wave potential to the switching potential. The rate constant k_{obs} were obtained from cyclic polarograms by the Nicholson's procedure.[16,17]

Materials.—The complexes were prepared following the procedures reported previously.[3] Dimethylformamide was purified over potassium carbonate and then distilled under reduced pressure before use. Other reagents were of analytical grade.

RESULTS

When a solution of the cobalt(II) chelate is reduced in DMF all the complex is obtained as cobalt(I) species with consumption of almost exactly one Faraday per mole and the cobalt(II) cathodic polarographic wave is substituted by the corresponding anodic wave of the cobalt(I) species.

In the absence of competing electrophiles (*e.g.* H_2O) † the

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* Where chel stands for one of the following chelating ligands bae: *NN'*-ethylene(acetylacetonedi-iminato); mesal: *NN'*-ethylenebis(α,α'-dimethylsalicylidineiminato); salen: *NN'*-ethylenebis(salicylideneiminato); saloph: *NN'-o*-phenylenebis-(salicylideneiminato).

† In the presence of traces of H_2O a catalytic process takes place due to the reactions

$$[Co^{II}(chel)]^0 + e \longrightarrow [Co^I(chel)]^-$$
$$[Co^I(chel)]^- + H_2O \longrightarrow [Co^{II}(chel)]^0 + \tfrac{1}{2}H_2 + OH^-$$

When all the H_2O present is reacted the complex is eventually obtained in the cobalt(I) state.

[8] H. A. O. Hill, ' Corrinoids,' in ' Inorganic Biochemistry,' ed. by G. Eichorn, Elsevier, Amsterdam, 1972, and references therein.

[9] R. L. Blakey, ' The Biochemistry of Folic Acid and Related Pteridines,' eds. A. Neuberger and L. Tatum, North Holland, Amsterdam and London, 1969.

[10] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1967, **89**, 3607.

[11] G. Costa, A. Puxeddu, and E. Reisenhofer, *Tetrahedron Letters*, 1972, 2167.

[12] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.*, 1970, 2870.

[13] G. Costa, A. Puxeddu, and E. Reisenhofer, *Chem. Comm.*, 1971, 993.

[14] G. Costa, A. Puxeddu, and E. Reisenhofer, *Experientia Suppl.*, 1971, **18**, 235.

[15] G. Costa, A. Puxeddu, and E. Reisenhofer, *J.C.S. Dalton*, 1972, 1519.

[16] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[17] R. S. Nicholson, *Analyt. Chem.*, 1965, **37**, 1406.

cobalt(I) species react in the dark with organic group donor substrates as follows:

$$(a)\ [\mathrm{Co^{I}(chel)}]^- + \mathrm{R'NR_3} \begin{cases} \longrightarrow [\mathrm{Co^{II}(chel)}]^0 + \mathrm{NR_3} + \mathrm{R'} \\ \longrightarrow [\mathrm{RCo^{III}(chel)}]^0 + \mathrm{NR_3} \end{cases}$$

$$(b)\ [\mathrm{Co^{I}(chel)}]^- + [\mathrm{Me_2SC_6H_4Me}]^+ \longrightarrow [\mathrm{MeCo^{III}(chel)}]^0 + \mathrm{MeSC_6H_4Me}$$

$$(c)\ [\mathrm{Co^{I}(chel)}]^- + \mathrm{RX} \longrightarrow [\mathrm{RCo^{III}(chel)}]^0 + \mathrm{X}^-$$

Reactions with Alkylammonium Salts.—When $[\mathrm{Co^{I}(salen)}]^-$ (2×10^{-3}M) is electrochemically generated from $[\mathrm{Co^{II}(salen)}]^0$ at $-1{\cdot}2$ V *vs.* S.C.E. and then treated with a 20 fold excess of ammonium salt $[\mathrm{R'NR_3}]^+$ (R′ = Me, Et, PhCH$_2$, Ph; R = Me, Et) in DMF (0·2M-LiClO$_4$) at 0 °C in the dark, the consumption of the cobalt(I) species can be followed by the decrease of the anodic wave corresponding to the oxidation cobalt(I) ⟶ cobalt(II) at the electrode.

In the same time two cathodic waves develop due to the $[\mathrm{Co^{II}(salen)}]^0$ ($E_{\frac{1}{2}} = -1{\cdot}05$ V *vs.* S.C.E.) and $[\mathrm{R'Co^{III}(salen)}]^0$ (R′ = Me: $E_{\frac{1}{2}} = -1{\cdot}4$ V; R′ = Ph: $E_{\frac{1}{2}} = -1{\cdot}6$ V *vs.* S.C.E.) formed by the reactions in the bulk of the solution:

$$[\mathrm{Co^{I}(salen)}]^- + [\mathrm{R'NR_3}]^+ \longrightarrow [\mathrm{Co^{II}(salen)}]^0 + \mathrm{NR_3} + \mathrm{R'}\cdot \quad (1)$$

$$[\mathrm{Co^{I}(salen)}]^- + [\mathrm{R'NR_3}]^+ \longrightarrow [\mathrm{R'Co^{III}(salen)}]^0 + \mathrm{NR_3} \quad (2)$$

(R′ = Me, Ph; R = Me).

When the $[\mathrm{Co^{I}(salen)}]^-$ is electrochemically generated in the presence of a 20-fold excess of ammonium compounds the formation of $[\mathrm{R'Co^{III}(salen)}]^0$ is almost quantitative. Furthermore the yield in the organometallic derivative appears to be sensitive to the nature of the organic group R′ (Ph > Me).

When $[\mathrm{Co^{I}(bae)}]^-$ is electrochemically generated from $[\mathrm{Co^{II}(bae)}]^0$ (at $-1{\cdot}65$ V *vs.* S.C.E.) and then treated with $[\mathrm{NEt_4}]^+$, quantitative formation of $[\mathrm{Co^{II}(bae)}]^0$ takes place:

$$[\mathrm{Co^{I}(bae)}]^- + [\mathrm{NEt_4}]^+ \longrightarrow [\mathrm{Co^{II}(bae)}]^0 + \mathrm{NEt_3} + \mathrm{Et}\cdot$$

Accordingly the polarogram of the reaction solution shows only the cathodic wave of $[\mathrm{Co^{II}(bae)}]^0$. The NR$_3$ was recovered and identified as NEt$_4$I after reaction with EtI in dichloroethane and the ethylene–ethane mixture formed from the ethyl radical was identified by g.l.c.

When the $[\mathrm{Co^{I}(bae)}]^-$ is electrochemically generated in the presence of an excess of ammonium compounds, a catalytic reduction process takes place until the ammonium ion is consumed:

$$[\mathrm{Co^{II}(bae)}]^0 \xrightarrow[-1\cdot6\ \mathrm{v}]{\mathrm{C.P.R.}} [\mathrm{Co^{I}(bae)}]^- \xrightarrow{\mathrm{NR_4}^+} [\mathrm{Co^{II}(bae)}]^0 + \mathrm{NR_3} + \mathrm{R}\cdot$$

Catalytic reduction was observed with $[\mathrm{Co^{I}(bae)}]^-$ in the presence of substrates such as $[\mathrm{NMe_4}]^+$, methylpyridinium, methylpiperidinium, methylpyrrolidinium, $[\mathrm{NEt_4}]^+$, $[\mathrm{PhNMe_3}]^+$ perchlorates giving CH$_4$, CH$_2$=CH$_2$, C$_6$H$_6$ as final dealkylation products.

The reactions of $[\mathrm{Co^{I}(chel)}]^-$ with $[\mathrm{R'NR_3}]^+$ are too slow to be followed by cyclic voltammetry. The voltammogram of the chelate solution in the presence of an excess of ammonium salt clearly shows the cathodic peak due to the reduction of the $[\mathrm{Co^{II}(chel)}]^0$ species and the anodic peak of the $[\mathrm{Co^{I}(chel)}]^-$ reoxidation. The characteristics of the peak ($i_{\mathrm{ap}}/i_{\mathrm{cp}} = 1$; $\Delta E_{\frac{1}{2}} = 60$—100 mV) are consistent with a reversible, fast electron transfer. These data are independent from the sweep rate between 0·0015 and 40 V s^{-1} showing that the reaction of $[\mathrm{Co^{I}(chel)}]^-$ with the ammonium ions are too slow to influence the electrode process characteristics.

The kinetics of a simple reaction leading only to the cobalt(II) species *i.e.*

$$[\mathrm{Co^{I}(bae)}]^- + [\mathrm{NEt_4}]^+ \longrightarrow [\mathrm{Co^{II}(bae)}]^0 + \mathrm{NEt_3} + \mathrm{Et}\cdot$$

was followed from the decrease of the diffusion current of the electrochemically generated $[\mathrm{Co^{I}(bae)}]^-$, after addition of the ammonium salt.

The second order rate expression $\dfrac{1}{C^\circ_{\mathrm{A}} - C^\circ_{\mathrm{B}}} \ln \dfrac{C_{\mathrm{A}}}{C_{\mathrm{B}}} = kt$ + constant was obeyed, with $k'' = 1 \times 10^{-1}$ mol^{-1} s^{-1}.

The observed rates $-\,\mathrm{d}[\mathrm{cobalt(I)}]^-/\mathrm{d}t$ for the reaction of $[\mathrm{Co^{I}(salen)}]^-$ with $[\mathrm{NMe_4}]^+$ and $[\mathrm{PhNMe_3}]^+$ are not very different but the kinetics are more complicated owing the competing reactions (1) and (2).

Reactions with Sulphonium Salts.—When $[\mathrm{Co^{II}(salen)}]^0$ (1×10^{-3}M) in DMF is reduced at controlled potential at $-1{\cdot}2$ V *vs.* S.C.E. in the presence of something less than the stoichiometric amount of the $[\mathrm{Me_2SC_6H_4Me}]^+\mathrm{ClO_4}^-$ (to avoid the presence of unreacted sulphonium ion in the reaction solution), the organometallic $[\mathrm{MeCo^{III}(salen)}]^0$ is formed with consumption of 1 Faraday. The characteristic green colour of $[\mathrm{Co^{I}(salen)}]^-$ was never observed. This indicates that the $[\mathrm{Co^{I}(salen)}]^-$ which is formed by electrochemical reduction immediately reacts with the substrate $[\mathrm{Me_2SC_6H_4Me}]^+$.

The polarogram at the end of the experiment shows both the waves due to the small excess amount of $[\mathrm{Co^{II}(salen)}]^0$ ($E_{\frac{1}{2}} = -1{\cdot}05$ V *vs.* S.C.E.) and to the product $[\mathrm{MeCO^{III}}$-$\mathrm{(salen)}]^0$ ($E_{\frac{1}{2}} = -1{\cdot}50$ V *vs.* S.C.E.) (see Figure 1). From the diffusion currents of both waves the amounts of $[\mathrm{Co^{II}(salen)}]^0$ and $[\mathrm{MeCo^{III}(salen)}]^0$ species were found in agreement with the coulometric measurement.

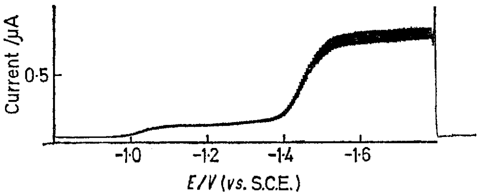

FIGURE 1 Polarogram after controlled potential reduction at $-1{\cdot}2$ V *vs.* S.C.E. of $[\mathrm{Co^{II}(salen)}]^0$ in the presence of $[\mathrm{Me_2SC_6H_4Me}]^+$

The reaction of the cobalt(I) species with the substrate can be followed by triangular potential sweep voltammetry and the k_{obs} can be calculated as described in the Experimental section. The reaction follows the rate law

$$k_{\mathrm{obs}} = k_{\mathrm{chel}}[\mathrm{Me_2SC_6H_4Me}]^+$$

when $[\mathrm{Co^{II}(salen)}]^0$ is kept constant. The k_{chel} values for the reaction of a number of chelating agent towards $[\mathrm{Me_2SC_6H_4Me}]^+$ are $[\mathrm{Co^{II}(mesal)}]^0$ ($0{\cdot}2 \times 10^{-3}$M) $2{\cdot}3 \times 10^4$, $[\mathrm{Co^{II}(salen)}]^0$ ($0{\cdot}2 \times 10^{-3}$M) $1{\cdot}9 \times 10^3$, $[\mathrm{Co^{II}(saloph)}]^0$ ($0{\cdot}2 \times 10^{-3}$M) $2{\cdot}5 \times 10^2$ mol^{-1} s^{-1}.

A linear free energy relationships was found with the nucleophilicity of the cobalt(I) species as given by the $E_{\frac{1}{2}}$

of the cobalt(II)–cobalt(I) reversible electron transfer (see Figure 2).

Reactions with Organic Halides.—When $[Co^{II}(chel)]^0$ (chel = bae, mesal, salen) is reduced to $[Co^{I}(chel)]^-$ in DMF at the mercury pool electrode in the presence of PhBr as substrate the reaction product is in all cases the corresponding organometallic derivative $[PhCo^{III}(chel)]^0$.

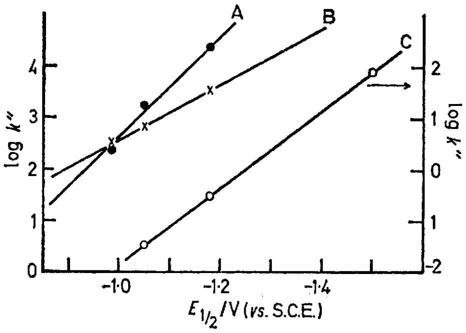

FIGURE 2 Relationship between log k'' for the reactions A, $[Co^{I}(chel)]^- + [Me_2SC_6H_4Me]^+$; B, $[Co^{I}(chel)]^- + EtBr$; and C, $[Co^{I}(chel)]^- + PhBr$; and $E_{\frac{1}{2}}$ for the redox process $[Co^{II}(chel)]^0 \rightleftharpoons [Co^{I}(chel)]^-$

In fact the reaction rate of $[Co^{I}(bae)]^-$ with PhBr is high enough to cause the full development of both the characteristic reversible waves at −1·5 and −1·65 V *vs.* S.C.E.* corresponding to the $[Co^{II}(chel)]^0 \leftrightarrow [Co^{I}(chel)]^-$ and $[RCo^{II}(chel)]^0 \leftrightarrow [RCo^{II}(chel)]^-$ redox steps in the conventional polarogram (sweep rate −0·0015 V s^{-1}) of $[Co^{II}(bae)]^0$ in the presence of PhBr (see Figure 3).

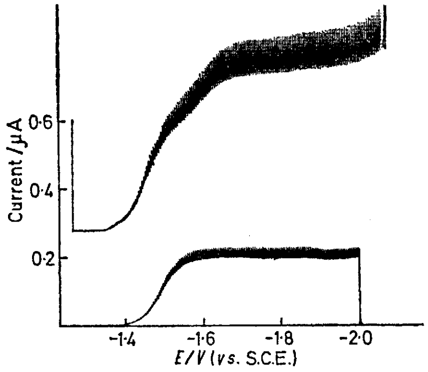

FIGURE 3 Polarogram of $[Co^{II}(bae)]^0$ ($0{\cdot}3 \times 10^{-3}$M) upper curve, alone and lower curve, in the presence of excess of PhBr

When a $[Co^{II}(chel)]^0$ solution (0·15—0·30 × 10^{-3}M in DMF) is examined by triangular potential sweep voltammetry in the presence of a 20—100 fold excess of PhBr, the decrease of the ratio of the anodic to the cathodic peak corresponding to the $[Co^{II}(chel)]^0 \leftrightarrow [Co^{I}(chel)]^-$ redox step as a function of sweep rate (see Figure 4) shows the reaction of the electrochemically generated cobalt(I) species and allows the calculation of the reaction rate. The reaction follows the rate law equation:

$$\frac{d[RCo^{III}(chel)]}{dt} = k''[Co^{I}(chel)]^-[PhBr]$$

which reduces to:

$$k_{obs} = k[_{chel}PhBr]$$

at constant $[Co^{II}(chel)]^0$ concentration.

The dependence of the reaction rates on the $[Co^{I}(chel)]^-$ concentration was not studied owing to the small concentration range accessible without complications due to absorption phenomena.

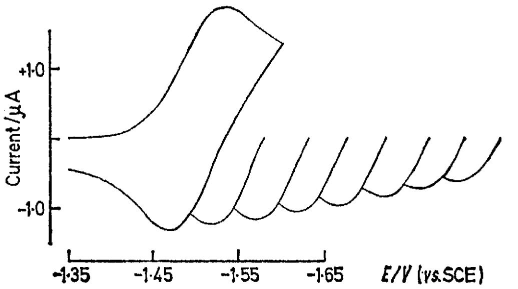

FIGURE 4 Triangular sweep voltammogram from −1·35 to −1·6 V for $[Co^{II}(bae)]^0$ ($0{\cdot}3 \times 10^{-3}$M); with a dropping mercury electrode; voltage sweep rate 1·0 V s^{-1}; at increasing substrate concentrations of PhBr (see Table) the anodic peak currents decrease

The reactivity of $[Co^{I}(bae)]^-$, $[Co^{I}(mesal)]^-$, and $[Co^{I}(salen)]^-$ towards PhBr as substrate and the reactivity of $[Co^{I}(mesal)]^-$, $[Co^{I}(salen)]^-$, and $[Co^{I}(saloph)]^-$ towards EtBr as substrate are reported in the Table.

$[Co^{II}(chel)]^0$	[PhBr]	k_{obs}/s^{-1}	$k''_{chel}/M^{-1}\,s^{-1}$
$[Co^{II}(bae)]^0$	11·4 × 10^{-3}M	0·863	86·5
0·3 × 10^{-3}M	15·2	1·267	83·2
τ = 0·102	19·0	1·550	81·5
	26·8	2·324	86·7
$[Co^{II}(mesal)]^0$	34·5 × 10^{-3}M	0·00794	0·289
0·2 × 10^{-3}M	69·0	0·02182	0·316
τ = 5·04	100·0	0·02877	0·288
	145·0	0·04167	0·287
$[Co^{II}(salen)]^0$	0·200M	0·00545	0·0273
0·25 × 10^{-3}M	0·475	0·0158	0·0334
τ = 5·04	0·850	0·0258	0·0303
	1·240	0·0397	0·0320
	[EtBr]		
$[Co^{II}(mesal)]^0$	5·3 × 10^{-3}M	20·41	3·85 × 10^3
0·2 × 10^{-3}M	8·0	29·60	3·70
τ = 9·8 × 10^{-3}	10·65	38·26	3·59
	13·3	48·98	3·68
$[Co^{II}(salen)]^0$	5·3 × 10^{-3}M	4·00	7·55 × 10^2
0·2 × 10^{-3}M	8·0	6·15	7·69
τ = 3·25	10·65	7·69	7·22
= × 10^{-2}	13·3	10·16	7·63
	15·95	12·31	7·72
$[Co^{II}(saloph)]^0$	8·8 × 10^{-3}M	2·73	3·09 × 10^2
0·2 × 10^{-3}M	14·1	4·39	3·12
τ = 3·3 × 10^{-2}	19·4	5·91	3·04
	24·7	7·73	3·13

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* $E_{\frac{1}{2}}$ Values for the overlapping waves were obtained by the method of I. Ružić, ref. 18.

[18] I. Ružič and M. Branica, *J. Electroanalyt. Chem.*, 1969, **22**, 243.

The effect of the nucleophilicity of the cobalt(I) species is illustrated by the linear free-energy relationship between the half-wave potential ($E_{\frac{1}{2}}$) of the cobalt(I)–cobalt(II) reversible polarographic wave and log k'' (see Figure 2).

DISCUSSION

We have previously shown that the nature of the equatorial chelating agent in a series of cobalt complexes including the present ones, affects the redox potential of the complex. A trend of redox potentials was thus found which is consistent with ground state properties and reactivity [12] and is expressed by the polarographic half-wave potentials of the reversible one electron transfer cobalt(III)–cobalt(II): $E_{\frac{1}{2}}$(I) and cobalt(II)–cobalt(I): $E_{\frac{1}{2}}$(II) of the species $[\mathrm{Co^{III}(chel)L_2}]^+$ and $[\mathrm{Co^{II}(chel)}]^0$ respectively.

When the nucleophilicity n is substituted by the $E_{\frac{1}{2}}$(II) values (in DMF) the free energy relationship of Swain and Scott [19] becomes

$$\log k'' = \log k_0 - sE_{\frac{1}{2}}$$

where the slope s reflects the sensitivity of the substrate to the nature of the attacking nucleophile.

Present results show that the Swain and Scott equation is obeyed for the reaction of cobalt(I) nucleophiles with organic halides and sulphonium compounds.

From the plots of Figure 2, the values $s = 5{\cdot}4$, $7{\cdot}4$, and $9{\cdot}4$ are found for EtBr, PhBr, and $[\mathrm{Me_2SC_6H_4Me}]^+$ respectively. From the plot of $-E_{\frac{1}{2}}$ for the oxidation of several organometallic anions at a platinum electrode *vs.* log k'' for the reaction with alkyl halides as reported by Dessy *et al.*,[20] a slope in a same range as that found in the present work is obtained ($s = 6{\cdot}6$).

The present results concerning the effect of the chelating agent on the reactivity of the attacking nucleophile, together with previous data of Schrauzer and Deutsch [6] on the effect of the nature of the alkyl and of the leaving group, enlarge the knowledge of the bimolecular substitution reaction $[\mathrm{Co^I(chel)}]^- + \mathrm{RX}$ and allows us to extend this mechanism to where the sulphonium compounds act as donors.

The relatively high sensitivity of rate to the nucleophilicity of the cobalt(I) species indicates that the development of carbonium ion character of the alkyl group in the transition state is not far advanced, *i.e.* the C–S and C–Br bond breaking is limited.

Taking into account the average relative rates of reaction of alkyl halides with nucleophiles [21] the magnitude of reaction rate of MeBr can be approximately predicted from that of EtBr. From this value the trend of relative reactivity of MeBr > $[\mathrm{Me_2SC_6H_4Me}]^+$ > $[\mathrm{NMe_4}]^+$ with present nucleophiles can be predicted with the possible exception of $[\mathrm{Co^I(bae)}]^-$.

The reaction of cobalt(I) nucleophiles with alkylammonium compounds exhibits an interesting feature reminiscent of the reaction of low spin cobalt(II) complexes in that two alternative reaction paths are possible:

(*a*) bimolecular nucleophilic displacement (substitution controlled reaction)

$$[\mathrm{Co^I(chel)}]^- + [\mathrm{NR_4}]^+ \longrightarrow [\mathrm{RCo^{III}(chel)}]^0 + \mathrm{NR_3}$$

(*b*) redox process (electron transfer controlled)

$$[\mathrm{Co^I(chel)}]^- + [\mathrm{NR_4}]^+ \longrightarrow [\mathrm{Co^{II}(chel)}]^0 + \dot{\mathrm{N}}\mathrm{R_4}$$
$$\dot{\mathrm{N}}\mathrm{R_4} \longrightarrow \mathrm{NR_3} + \dot{\mathrm{R}}$$

The latter occurs as the sole reaction when chel = bae, while $[\mathrm{Co^I(salen)}]^-$ appears to react by both paths.

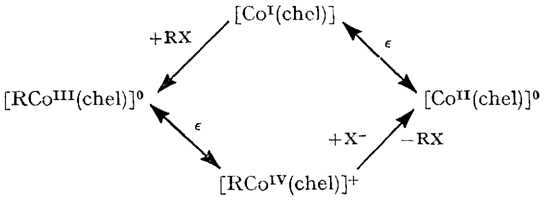
It is interesting to point out that a catalytical reduction of $[\mathrm{NR_4}]^+$ takes place by the mechanism (*b*) in the presence of $[\mathrm{Co^{II}(chel)}]^0$ in the correspondence of the reduction potential of the latter ($-1{\cdot}6$ V *vs.* S.C.E.). The potential is dramatically displaced (*ca.* 1·5 V) towards less cathodic values relative that of $[\mathrm{NR_4}]^+$ reduction at the platinum electrode in hexamethylphosphorictriamide.[22] The formation of $\dot{\mathrm{N}}\mathrm{R_4}$ involves apparently a very different activation energy in the two cases.

The formation of the Co–C bond involving cobalt(I) intermediates is an essential step of the vitamin $\mathrm{B_{12}}$ dependent transalkylation. The formation and cleavage of the Co–C bond can be supposed to involve the cobalt(III) and cobalt(I) formal oxidation states

$$\left[\mathrm{Co^{III}(chel)}\right]^+ \xrightarrow{+2e} \left[\mathrm{Co^{I}(chel)}\right]^- \xrightarrow[-\mathrm{D}^-]{+\mathrm{RD}} \left[\mathrm{RCo^{III}(chel)}\right]^0 \xrightarrow[-\mathrm{RA}]{+\mathrm{A}^-} \left[\mathrm{Co^{I}(chel)}\right]^-$$

where D and A are the donor and acceptor groups in the catalytical transalkylation.

On the other hand the present results can be relevant also in connection with a different mechanism involving cobalt(I) and cobalt(II) oxidation states as in the following scheme:



Both redox processes in the above scheme were pointed out as reversible one electron transfer.[12,15] Both the cobalt(I) and cobalt(IV) species are very reactive and the formation and rupture of the Co–C bond are formulated as oxidative addition and reductive dealkyl-

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ation respectively. Furthermore the chemical oxidation to [RCo^{IV}(chel)]$^+$ was independently reported.[23,24]

The bridging alkyl group involved in the key intermediate can be described as a cation or as a free radical depending on the extent of charge transfer preceding the organic group transfer. Even a homolytic mechanism could be thus invoked as a limiting case. This aspect of the reactivity of cobalt(I) nucleophiles as acceptors and [RCo^{IV}(chel)]$^+$ as donors is currently being studied.

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