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Reactivity of Organocobalt(IV) chelate Complexes toward Nucleophiles: Diversity of Mechanisms

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The chemistry of labile organocobalt(IV) chelate complexes, [RCo(chel)]$^+$ (where chel represents a tetradentate or bis-bidentate equatorial ligand derived from a Schiff base or α-dioxime), generated by one-electron oxidation of the corresponding organocobalt(III) compounds, has been examined in acetonitrile solutions using electrochemical methods. Reactivity patterns and mechanisms have been correlated with the structural features of the complexes. In most cases pyridine reacts rapidly with the organocobalt(IV) complexes to displace the organic ligand, R, by nucleophilic substitution at the α-carbon atom. The results of kinetic measurements suggest that these reactions proceed through S_N2 mechanisms in the case of α-dioximato complexes and S_Ni mechanisms in the case of Schiff base complexes. In certain cases the Co(IV)–carbon bond apparently undergoes rapid unimolecular heterolytic or homolytic dissociation.

Introduction

Recent work in these laboratories [1–3] has shown that oxidized forms of σ-organocobalt chelates* react readily with nucleophiles to undergo substitution at the α-carbon atom. Extending these studies, we have examined the kinetics of reactions of pyridine with such complexes. A diverse pattern of reaction schemes and mechanisms has been identified and found to be related to the nature of the chelating ligand.

Results

Our present studies encompass two series of complexes, namely:

(*a*) *p*-Substituted benzylbis(dimethylglyoximato)cobalt complexes, [p-$XC_6H_4CH_2Co(dmgH)_2$] (designated I), with X = OMe, Me, H, F, Cl, COOEt and NO_2.

(*b*) Ethylcobalt chelate complexes, [EtCo(chel)] (designated II) with various chelating ligands derived from Schiff bases and α-dioximes, notably: chel = acacen, salen, salphen, $(dmgH)_2$ and $(dpgH)_2$†. The behaviour of [MeCo(salen)] also was examined.

Studies were performed using acetonitrile containing 0.1 *M* Et_4NBF_4 as the reaction medium. Electro-oxidation of the corresponding organocobalt(III) chelate compounds at disc platinum microelectrodes, both stationary (cyclic voltammetry, abbreviated CVA) and rotating, was selected as the principal technique. In some cases, controlled potential electrolysis (CPE) also was employed.

In the absence of pyridine all the complexes, except I with X = OMe, yielded cyclic voltamograms characteristic of reversible electron transfer according to eqn. 1, provided that the potential sweep was sufficiently fast and/or the temperature sufficiently low. This behaviour is illustrated in Fig. 1a. Anodic waves, obtained with the rotating disc electrode (RDE) technique, also conformed to single electron reversible oxidation behaviour, *i.e.*, $\partial E/\partial \log [i/(i_l - i)] \cong 60$ mV, i_l being proportional to $\sqrt{\omega}$.

Addition of pyridine resulted in qualitative changes of the voltamograms in all cases but one,

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*In accord with earlier practice [4, 5] these complexes of the general formula [RCo(chel)L]$^+$, where chel is a tetradentate or bis(bidentate) ligand dianion, are designated organocobalt(IV) chelates. In the formulas used to represent these complexes the axial base ligand, L, will generally be omitted and the complexes abbreviated [RCo(chel)]$^+$.

†The abbreviations used are derived from ref. [6], *i.e.*, acacen = bis(acetylacetonato)ethylenediamine, salen = bis(salicylidenato)ethylenediamine, salphen = bis(salicylidenato)-*o*-phenylenediamine, $(dmgH)_2$ = bis(dimethylglyoximate), and $(dpgH)_2$ = bis(diphenylglyoximate).

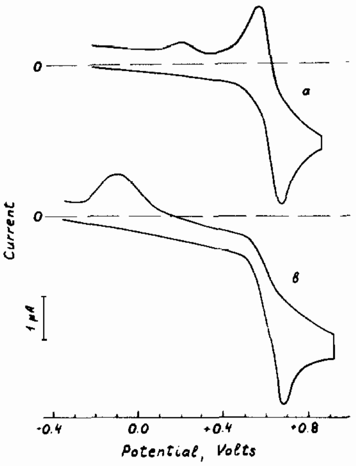

Fig. 1. Cyclic voltamograms for the oxidation of [EtCo(salen)] (0.6 m*M*) at a platinum anode (a) in absence of pyridine; (b) with 12 m*M* pyridine added. (0.1 *M* solution of Et_4NBF_4 in MeCN as supporting electrolyte, 20 °C; potential referred to a calomel electrode with 4 *M* aqueous LiCl. Potential sweep rate 0.1 V/s).

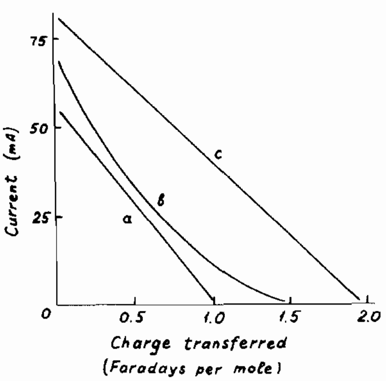

Fig. 2. Controlled potential oxidation of [n-BuCo(salen)] (1.5 m*M*) at a platinum anode: dependence of current on charge transferred (a) in absence of pyridine at −35 °C; (b) in absence of pyridine at 20 °C; (c) in the presence of 6 m*M* pyridine at 20 °C. (0.1 *M* solution of Et_4NBF_4 in MeCN as supporting electrolyte, 20 °C; in all cases a plateau potential was maintained, *vis.* +0.8 V *vs.* a calomel electrode with 4 *M* aqueous LiCl).

namely I with X = OMe which again exhibited exceptional behaviour. For most of the complexes, except II with chel = acacen, these changes (Fig. 1) indicated the development of an ECE process. The results of controlled potential oxidation of these organocobalt(III) chelates in the presence of pyridine, notably the influence of the latter on the number of electrons transferred (Fig. 2) and on the nature of the products [1], supported this conclusion and permitted the stoichiometry of the process corresponding to the steps depicted by eqns. 1–3 (where $E_1 > E_2$) to be established*†.

$$[RCo^{III}(chel)] \underset{E_1}{\overset{-e}{\rightleftharpoons}} [RCo^{IV}(chel)]^+ \qquad (1)$$

$$[RCo^{IV}(chel)]^+ + Py \longrightarrow RPy^+ + [Co^{II}(chel)] \qquad (2)$$

$$[Co^{II}(chel)] \underset{E_2}{\overset{-e}{\rightleftharpoons}} [Co^{III}(chel)]^+ \qquad (3)$$

Thus, the application of electrochemical methods to measure the kinetics of the homogeneous reaction 2, involved in the overall anodic process (eqns. 1–3), seems appropriate. The technique selected by us was voltammetry at RDE. The treatment was based on the solution of the related diffusion-kinetic problem by Feldberg *et al.* [11] with the assumption that the rate of reaction 2 is first order in $[RCo^{IV}(chel)]^+$. Furthermore, since in all cases $(E_1–E_2) > 200$ mV, the homogeneous redox equilibrium corresponding to eqn. 4 was assumed to be shifted completely to the right ($K \sim \infty$).

$$[RCo^{IV}(chel)]^+ + [Co^{II}(chel)] \overset{K}{\rightleftharpoons} [RCo^{III}(chel)] + [Co^{III}(chel)]^+ \qquad (4)$$

The experimental data could be fitted satisfactorily to Feldberg's plot [11], n_{app} *vs.* $(\nu/D)^{1/3}k/\omega$, where $n_{app} \cong i_l/i_d$, over the whole range of the rotation rates employed (23–610 rad/sec) as illustrated by Fig. 3. (The iterative procedure for this fitting process has been described elsewhere [12]). These results provide convincing evidence for our earlier suggestions concerning the electrode processes. Moreover, they permit calculation of the (pseudo-) first order rate constant, k, of the homogeneous reaction 2.

Certain additional information about the mechanism of the homogeneous reactions was obtained from the half-wave potential measurements at RDE performed under special conditions, namely when the

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*In the formulas used to represent the cobalt chelates, complexation of the cobalt with pyridine is omitted for the sake of brevity. However, it is appropriate to note here that the combination of the literature data [7–9] on the coordination equilibria,

$$[RCo^{III}(chel)] + Py \rightleftharpoons [RCo^{III}(chel)Py]$$

and of data obtained by us on the effect of pyridine on the potential of the redox equilibrium corresponding to eqn. 1, indicates that, under the conditions of our experiments, the organocobalt complexes are present and react predominantly as the pyridine adducts, *i.e.* $[RCo^{III}(chel)Py]$ and $[RCo^{IV}(chel)Py]^+$.

†It is recognized (see *e.g.*, [10]) that an ECE process also involves a homogeneous redox equilibrium, in the present case that depicted by eqn. 4.

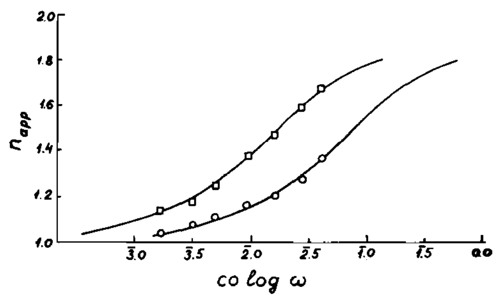


Fig. 3. Fitting of some experimental data obtained at RDE to the theoretical plot calculated [11] for the ECE processes. ○, EtCo(salen); □, $C_6H_5CH_2Co(dmgH)_2$. (Concentrations of the complexes, 0.6 m*M*; concentrations of pyridine, 12 m*M*).

second electron transfer step 3 was not present. This condition could be realized at low temperatures or at sufficiently fast reaction rates. Several complexes, namely $[C_6H_5CH_2Co(dmgH)_2]$, $[EtCo(dmgH)_2]$ and [EtCo(salen)], were examined. In each case the half-wave potential was essentially independent of both the rotation rate and the pyridine concentration. This result demonstrates that these cases involve a simple electron transfer process (eqn. 1), uncomplicated by subsequent chemical reactions. Hence, it may be concluded that if the homogeneous reaction 2 is a multi-step process, the first step is rate-determining.

Values of the (pseudo-) first order rate constant k were obtained for each complex at various concentrations of pyridine to establish the kinetic dependence on the latter. In the case of α-dioximates the reactions were found to obey the second order rate law corresponding to eqn. 5 (although for complexes I with X = H and Me some contribution from a first order path cannot be excluded; see Table I).

$$-d[RCo(chel)^+]/dt = k_{II}[RCo(chel)^+][Py] \qquad (5)$$

On the other hand, the reactions of complexes of Schiff bases (chel = salen or salphen) obeyed first order kinetics, *i.e.*,

$$-d[RCo(chel)^+]/dt = k_I[RCo(chel)^+] \qquad (6)$$

These kinetic dependencies are depicted in Fig. 4 and values of k_I and k_{II} are listed in Table I.

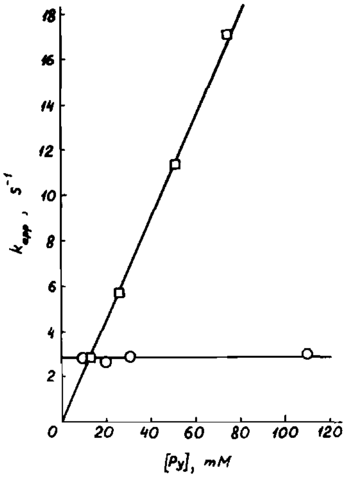


Fig. 4. Reaction kinetics for two complexes of the [EtCo-(chel)]$^+$ series: dependence of (pseudo) rate constant on the pyridine concentration. ○, chel = salphen; □, chel = $(dmgH)_2$. (0.1 *M* solution of Et_4NBF_4 in MeCN as reaction medium, 20 °C).

Somewhat different behaviour was observed for the [RCo(acacen)]$^+$ and [MeCo(salen)]$^+$ complexes. In these cases, while according to the CVA data addi-

TABLE I. Rate Constants for the Reactions between [RCo(chel)]$^+$ Complexes and Pyridine in Acetonitrile Solutions Containing 0.1 *M* Et_4NBF_4 at 20 °C.

Complex	Rate Constant		
	k_I, sec^{-1}	$k_{II} \times 10^{-2}$, M^{-1} sec^{-1}	$E_{1/2}$, V[a]
$[p\text{-}MeC_6H_4CH_2Co(dmgH)_2]^+$	0.39 ± 0.08	0.83 ± 0.07	0.784
$[C_6H_5CH_2Co(dmgH)_2]^+$	0.38 ± 0.17	1.01 ± 0.33	0.800
$[p\text{-}FC_6H_4CH_2Co(dmgH)_2]^+$		2.09 ± 0.68	0.814
$[p\text{-}ClC_6H_4CH_2Co(dmgH)_2]^+$		2.66 ± 0.59	0.830
$[p\text{-}EtOCOC_6H_4CH_2Co(dmgH)_2]^+$		5.83 ± 1.03	0.852
$[p\text{-}O_2NC_6H_4CH_2Co(dmgH)_2]^+$		13.80 ± 4.88	0.885
$[EtCo(dmgH)_2]^+$		2.22 ± 0.58	0.782
$[EtCo(dpgH)_2]^+$		~21	1.070
$[EtCo(salen)]^+$	0.58 ± 0.06		0.695
$[EtCo(salphen)]^+$	2.80 ± 0.26		0.947

[a] Potentials of the reversible processes, $[RCo^{III}(chel)] \underset{}{\overset{-e}{\rightleftharpoons}} [RCo^{IV}(chel)]^+$ according to CVA data: $E_{1/2} = (E_{pa} + E_{pc})/2$ (Supporting electrolyte and temperature are the same as for the kinetic experiments).

tion of pyridine also accelerated the decomposition reactions, the trends of the limiting currents at RDE did not follow the pattern of the ECE process. Instead, a steady continuous decay of the currents was observed. After the controlled potential oxidation of [BuCo(acacen)] in the presence of pyridine, both 1-butene and butane were detected as products.

Finally, CVA data revealed the oxidation of $[p$-MeOC$_6$H$_5$CH$_2$Co^{III}(dmgH)$_2]$ to be irreversible (exhibiting no cathodic peak) even in the absence of pyridine at −35 °C and with sweep rates as high as 100 V/sec. Measurements at RDE also indicated decomposition of the oxidized form to be very fast and apparently independent of the pyridine concentration.

Discussion

We have identified four different types of cleavage of the metal–carbon bond in organocobalt(IV) chelates. (In the classification of reactions the reaction center is assumed to be the α-carbon atom bonded to the metal).

The behaviour of the α-dioximato complexes appears to be the most clear-cut. Thus, the kinetic data for these complexes suggest an S_N2 reaction with pyridine according to eqn. 2. This is supported not only by the first order dependence on pyridine (Fig. 4 and Table I), but also by the dependence of k_{II} on the electronic influences of the ligands R and chel. Thus, the data for the series of complexes $[p$-XC$_6$H$_4$CH$_2$Co(dmgH)$_2]$ yield a good linear correlation of log k_{II} with the Hammett substituent constants σ_p^0, (Fig.5), corresponding to values of +1.33 and 0.9927 for ρ and for the correlation coefficient, respectively. Furthermore, comparison of the data in Table I for [EtCo(dmgH)$_2$] and [EtCo(dpgH)$_2$] indicates that the reaction rates increase with decreasing donor ability of the chelating ligand characterized by the equilibrium potentials of the corresponding redox systems (*i.e.*, of E_1 in eqn. 1 values of which also are listed in Table I).

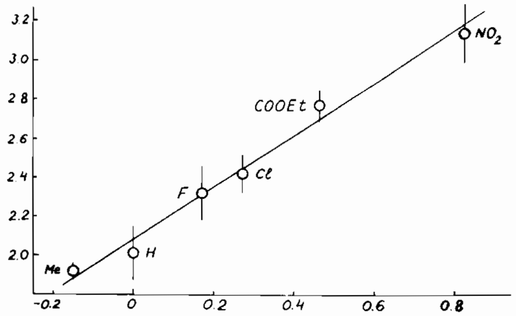
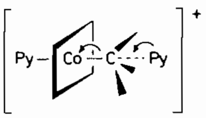


Fig. 5. Correlation of rates of reaction between *p*-substituted benzylbis(dimethylglyoximato)cobalt(IV) ions, $[p$-XC$_6$H$_4$-CH$_2$Co(dmgH)$_2]^+$, and pyridine with the σ_p^0 Hammett constants of the X substituents. (Reaction conditions: 0.1 *M* of Et$_4$NBF$_4$ in MeCN as the medium, 20 °C. The σ_p^0 values cited are from reference [13]).

These results are consistent with a conventional S_N2 mechanism with a moderately polar transition state (III), *i.e.*,



III

It should be noted that the same mechanism has been established in an investigation of the stereochemistry of the reaction of sec-alkylbis(dimethylglyoximato)cobalt(IV) with chloride ion in aqueous solution [2].

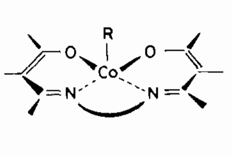
The kinetic behaviour of complexes of Schiff bases was found to be quite different. In the cases of [EtCo(salen)]$^+$ and [EtCo(salphen)]$^+$ the results can be summarized as follows:

(*1*) The reaction rates are first order in the complex and zero order in pyridine.

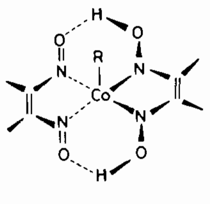
(*2*) The rate constant k_I decreases with increasing donor ability of the chelating ligand.

(*3*) The first step of the reaction is rate-determining.

This behaviour suggests that these reactions proceed through either an S_N1 or S_Ni mechanism (in the latter case, corresponding to the initial transfer of the organic group R within the coordination sphere, *i.e.*, from the metal to the chelating ligand) but does not permit a choice to be made between these alternatives. However, the differences between the kinetic behaviour of the Schiff base complexes on the one hand and of the α-dioximato complexes on the other hand can be explained satisfactorily only by assuming the mechanism to be S_Ni. Since the S_N1 mechanism does not directly involve the chelating ligand, the role of the latter is expected to reflect mainly the electronic influence. Thus, the transition from the S_N2 to the S_N1 mechanism should be favored by a decrease in the donor ability of the ligand, *i.e.*, by an increase in the redox potential, E_1. Such a trend is not supported by the data in Table I. On the other hand, the reactivity of the complexes, in the case of S_Ni reactions proceeding within the coordination sphere with direct participation of the chelating ligand, should depend on the properties of the latter (the nature of the donor atoms coordinated to the cobalt, symmetry of the ligand, its dipole moment, *etc.*). From this point of view opportunities for intra-coordination sphere nucleophilic substitution in complexes of Schiff bases (IV) would appear to be more favorable than in the α-dioximato complexes (V). Thus, in the case of complexes of cobalt(III) with Schiff bases, the enolate oxygen atoms act directly as the nucleophilic reaction centers (*i.e.*, for protonation [14] as well as complexation with metal ions [15]), whereas in the case of α-dioximato ligands the nucleophilic centers are oxygen atoms located outside the coordination sphere of cobalt [16].

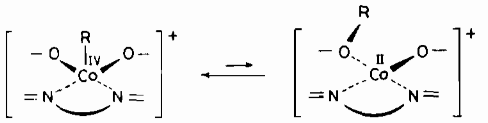


IV



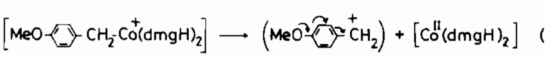
V

For the above reasons, the rate-determining step of the reaction between the Schiff base complexes (chel = salen or salphen) and pyridine is believed to involve transfer of the positively charged organic group (R) within the coordination sphere, *i.e.*, from the metal to an oxygen atom of the coordinated ligand. If this conclusion is valid, the kinetic features of the reaction indicate this step to be reversible with the equilibrium shifted to the left, *i.e.*,



(7)

The extremely high lability of $[p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{-Co(dmgH)}_2]^+$ can be attributed to the electronic influence of the methoxy group which is expected to contribute to the stabilization of the benzyl carbonium ion and thereby render this complex particularly unstable with respect to heterolytic cleavage of the metal–carbon bond, *i.e.*,



(8)

$$[\text{MeO-C}_6\text{H}_4\text{-CH}_2\text{-}\overset{+}{\text{Co}}(\text{dmgH})_2] \longrightarrow (\text{MeO-C}_6\text{H}_4\text{-}\overset{+}{\text{C}}\text{H}_2) + [\overset{\text{II}}{\text{Co}}(\text{dmgH})_2] \quad (8)$$

Finally, the pattern of electron-oxidation of [RCo(acacen)] and [MeCo(salen)] in the presence of pyridine corresponds to an electrode process involving the formation of organic radicals (indistinct stoichiometry, fouling of the anode, formation of $R^{\bullet}$ disproportionation products) according the eqn. 9. Homolytic decomposition of the organocobalt(IV) chelates presumably is favored by the relative stabilization of the products, *i.e.*, of $R^{\bullet}$ and $[\text{Co}^{\text{III}}(\text{chel})\text{L}]$, compared with the products of the competing heterolytic process ('R^+' and $[\text{Co}^{\text{II}}(\text{chel})\text{L}]$). High electron-donating ability of the chelating ligand and of the axial base, as well as high ionization potential of the free radical $R^{\bullet}$, are expected to contribute to such stabilization. These trends are consistent with the experimental data.

$$[\text{RCo}^{\text{IV}}(\text{chel})\text{L}]^+ \begin{array}{l} \nearrow (\text{R}^+) + [\text{Co}^{\text{II}}(\text{chel})\text{L}] \\ \searrow (\text{R}^{\bullet}) + [\text{Co}^{\text{III}}(\text{chel})\text{L}] \end{array} \quad (9)$$

The qualitative correlations that we have found between the structure and reactivity of the organocobalt(IV) chelates are summarized in Table II.

Experimental

Reagents

The starting organocobalt(III) chelate compounds were the axial base-free complexes [RCo(chel)] in the case of [EtCo(acacen)] and [EtCo(salen)] and the aquo-complexes $[\text{RCo(chel)}(\text{H}_2\text{O})]$ in all other cases. These were prepared by appropriate adaptations of the procedures of ref. [19] for chel = $(\text{dmgH})_2$ or $(\text{dpgH})_2$, and of ref. [20] for chel = acacen, salen or salphen. When appropriate, the complexes were characterized polarographically (in the same medium as used in the electro-oxidation experiments, *i.e.*, acetonitrile containing 0.1 *M* Et_4NBF_4) and spectrophotometrically, as well as by elemental and aquametric analysis.

Commerical 'pure' grade pyridine was dried over KOH and distilled through a 30 cm dephlegmator; the fraction boiling within a 0.2 °C range was collected. Commerical 'pure' grade acetonitrile was purified as described elsewhere [21]. Et_4NBF_4 was prepared according to published procedures [22].

Cell and Electrodes

Measurements were performed with a three-electrode thermostatted cylindrical cell, having a non-transparent (metal) jacket and a non-transparent (teflon) cap to protect the solutions from light. The working electrodes were disc platinum electrodes. One of them, a stationary electrode employed for CVA, was fabricated from a 1.5 mm diameter wire soldered into a thick-walled glass tube. The other electrode, used for measurements by the RDE technique, was 0.9 mm in diameter, enclosed in a teflon cylinder mantle of 10 mm diameter. The potential was measured relative to an external calomel electrode with a 4 *M* aqueous solution of LiCl. This electrode, provided with an agar gel bridge, was connected to the main half-element by means of an additional bridge filled with the supporting solution. The auxilliary electrode was fabricated from a thin platinum sheet and had a surface area of 1 cm^2. Openings in the cell cup permitted introduction of the working electrode (at the center), the auxilliary electrode, the electrolytic bridge, a nitrogen inlet tube, and also addition of solutions and reagents.

Instruments

For the experiments with the CVA technique a Universal polarograph GWP 673 (GDR) was

TABLE II. Reaction Patterns of Organocobalt(IV) Chelates $[RCo(chel)]^+$ in the Presence of Pyridine.

$[RCo(chel)]^+$	Donor Atoms in the Chelating Ligand	$E_{1/2}$, V[a]	$R^\cdot$ I, eV[b]	Main Reaction Route	Mechanism of Cleavage of Co(IV)–C Bond
$[EtCo(acacen)]^+$	N_2O_2	0.433	8.38	$R(Co^{IV})^+ \rightarrow (R^\cdot) + Co^{III})^+$	Homolytic
$[MeCo(salen)]^+$	N_2O_2	0.766	9.84	$R(Co^{IV})^+ \rightarrow (R^\cdot) + Co^{III})^+$	Homolytic
$[EtCo(salen)]^+$	N_2O_2	0.695	8.38	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_Ni
$[EtCo(salphen)]^+$	N_2O_2	0.947	8.38	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_Ni
$[EtCo(damgH)_2]^+$	N_4	0.782	8.38	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[EtCo(dpgH)_2]^+$	N_4	1.070	8.38	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}O_2NC_6H_4CH_2Co(dmgH)_2]^+$	N_4	0.885		$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}EtOCOC_6H_4CH_2Co(dmgH)_2]^+$	N_4	0.852		$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}ClC_6H_4CH_2Co(dmgH)_2]^+$	N_4	0.830	7.95	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}FC_6H_4CH_2Co(dmgH)_2]^+$	N_4	0.814	7.78	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[C_6H_5CH_2Co(dmgH)_2]^+$	N_4	0.800	7.76	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}MeC_6H_4CH_2Co(dmgH)_2]^+$	N_4	0.784	7.46	$R(Co^{IV})^+ + Py \rightarrow RPy^+ + (Co^{II})$	S_N2
$[p\text{-}MeOC_6H_4CH_2Co(dmgH)_2]^+$	N_4		6.82	$R(Co^{IV})^+ \rightarrow (R^+) + (Co^{II})$[c]	S_N1 (?)

[a] Potentials of the reversible processes, $[RCo^{III}(chel)] \xrightleftharpoons{-e} [RCo^{IV}(chel)]^+$ derived from CVA data (0.1 *M* solution of Et_4NBF_4 in MeCN as supporting electrolyte, 20 °C): $E_{1/2} = (E_{pa} + E_{pc})/2$. [b] Values of ionization potential derived from electron impact measurements [17, 18]. [c] Extremely rapid decomposition even in the absence of pyridine.

employed, with the positive feedback providing compensation of the potential drop between the tip of the electrolytic bridge and the working electrode.

Measurements at the RDE were performed with a potentiostatic polarograph OH-102 (Hungary) and a step belted asynchronous motor drive for the rotating disc electrode, designed at the Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R. and modified by us for extending the range of the rotation rates to 100–10,000 r.p.m. The rotation rate of the electrode was measured by means of a photoelectronic tachometer.

Experimental Procedure

Freshly prepared supporting solution (0.1 *M* Et_4NBF_4 in acetonitrile) was placed in the main compartment of the cell and flushed with nitrogen, previously saturated with acetonitrile at the same temperature as the cell. To reduce the transfer of water and foreign ions from the reference electrode into the solution under investigation, the end of the reference electrode bridge was initially soaked in a separate portion of the background solution. The cell was then assembled, the additional bridge was filled with the supporting solution, and a batch of the complex under investigation was introduced and dissolved with stirring and bubbling of nitrogen. During the electrochemical measurements an inert atmosphere was maintained in the cell by passing nitrogen over the solution. The solution was further flushed with nitrogen after addition of each new portion of the reagent, *i.e.*, of the pyridine solution. Before recording each curve, the working electrodes were mechanically cleaned by polishing them with fine alumina powder.

The concentration of the organocobalt(III) chelate was generally in the range 0.2 to 2 m*M*, the typical value in kinetic experiments being about 0.5 m*M*. The pyridine concentration was generally varied from 0.75 to 150 m*M*, the kinetic experiments typically spanning the range 7.5 to 75 m*M*. In no case did conversion of the complex through electrolysis, for a series of kinetic measurements at RDE on the same solution, exceed 1% of the initial concentration.

Additional Data and Measurements

To calculate the kinetic constants from the Feldberg plots it is necessary to know the kinematic viscosity of the solution and the diffusion coefficient of the electro-active species. The kinematic viscosity of the supporting electrolyte solution was assumed to be equal to that of pure acetonitrile, *i.e.*, 4.6×10^{-3} *St* at 20 °C (obtained by interpolation of published data [23]). The diffusion coefficients of the $[RCo^{III}(chel)Py]$ complexes were determined experimentally, from the same kinetic experiments, using the formula,

$$D = \left[\frac{i_d/c}{i_d^0/n_o c_o}\right]^{3/2} D_o \qquad (10)$$

derived from the Levich equation. The index 'o' relates to a 'standard' electroactive substance for which purpose, ferrocene was selected ($n_o = 1$; $D_o = 2.4 \times 10^{-5}$ cm^2 sec^{-1} [24]). In addition, experiments with ferrocene made it possible (*i*) to establish the range of rotation rates over which the Levich equation applies and, hence, kinetic experiments could be performed, and (*ii*) to standardize the measurements of potentials and estimate their reproducibility.

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