Electrochemical Generation and Reactivity of Organo-cobalt(IV) and -rhodium(IV) Chelates

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Summary Electro-oxidation of organo-cobalt(III) and -rhodium(III) chelates yields fairly stable species retaining a σ-bonded organic ligand, which behaves as a carbonium ion being readily transferred to nucleophiles.

The +4 oxidation state is not typical for cobalt[1] though it seems to occur in cobalt phthalocyanine dihalides.[2] Formation of transient species containing a metal–carbon bond during oxidation of certain organocobalt chelates [RCo^{III}(chel)] has been suggested on the basis of kinetic data.[3,4] Costa *et al.*[5] showed that some of such cobalt(III) complexes in dimethylformamide were oxidised at a platinum anode in a one-electron process and claimed that the resulting species were unstable. We have investigated the electro-oxidation of organocobalt chelates and their rhodium analogues and have found that the products of electron transfer are of considerable stability in weakly basic (MeCN) or non-solvating (CH_2Cl_2) aprotic media. Thus it is now possible to examine the reactivity and other properties of these unusual complexes involving the formally tetravalent metals, [RM^{IV}(chel)]$^+$.

Cyclic voltammograms of the [RM^{III}(salen)] and [RM^{III}(dmgH)$_2$] complexes, where salen and (dmgH)$_2$ denote the dianions of bis(salicylidene)ethylenediamine and bis(dimethylglyoxime) respectively and R is a primary or secondary alkyl group follow closely the pattern for a reversible electron transfer, at least for fast scans (Table), indicating appreciable stability of the electron-transfer products.† The lifetime of the [$\text{Bu}^{\text{n}}\text{Co}^{\text{IV}}$(salen)]$^+$ species was estimated to be several minutes at 25 °C both in MeCN and CH_2Cl_2. The $\text{Bu}^{\text{n}}\text{Co}^{\text{III}}$(salen) complex was converted into the Co^{IV} complex upon controlled potential electrolysis at a lower temperature in either solvent. Thus, the process carried out came to completion at −35 to −40 °C after 1 F/mol had passed, and the only essential product (detected by cyclic voltammetry) was that of the electron transfer. E.s.r. investigation (in collaboration with K. I. Zamaraev, A. T. Nikitaev, and G. A. Nikitaeva) showed that frozen solutions of the electrolysis products in CH_2Cl_2–toluene gave signals which did not originate from any known paramagnetic chelate of the Co(salen) series but may well be attributed to low-spin cobalt-complexes with axial symmetry.

Table

Cyclic voltammetry data on electro-oxidation of organo-cobalt(III) and -rhodium(III) chelates.[a]

Complex	$E_{\frac{1}{2}}$/V[b]	ΔE_{pac}/mV[c]
[MeCo(dmgH)$_2$(py)]	+0·920	86
[EtCo(dmgH)$_2$(py)]	+0·885	84
[PhCH_2Co(dmgH)$_2$(py) ..	+0·884	90
[MeCo(salen)]	+0·739[d]	74
[EtCo(salen)]	+0·668[d]	60
[Bu^{n}Co(salen)]	+0·668[d]	61
[Pr^{i}Co(salen)]	+0·488	72
[Pr^{n}Co(salen)(py)] ..	+0·662	60
[MeRh(salen)(py)]	+0·838	77
[Pr^{n}Rh(salen)(py)] ..	+0·813	72
[Pr^{i}Rh(salen)(py)]	+0·772	70

[a] Measurements at a platinum electrode with 0·1 M Et_4NBF_4 in MeCN as supporting electrolyte; potential referred to a calomel electrode with 4 M aqueous LiCl. [b] Half-sum of anodic and cathodic peak potentials. [c] Difference between the same potentials. [d] Measurements with rotating disc electrode at 300—6000 r.p.m. indicated the corresponding waves to be diffusion controlled.

Cyclic voltammetry and controlled potential electrolysis provided evidence for splitting of the metal–carbon bond in reactions following the electron transfer. The action of typical nucleophiles (B) such as Cl^- or pyridine results in heterolysis (1) of the M^{IV}–C bond, the overall electrode

$$\text{R(M}^{\text{IV}})^+ + \text{B} \rightarrow \text{RB}^+ + (\text{M}^{\text{II}}) \qquad (1)$$

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† Our first results were reported in ref. 6. Recently we were informed by Professor J. Halpern that he also observed formation of the [RCo^{IV}(dmgH)$_2$]$^+$ species by cyclic voltammetry.

reaction having all the features of the *ECE* mechanism

$$\begin{tikzcd} R(M^{III}) \arrow[r, shift left, "-e"] & R(M^{IV})^+ \arrow[l, shift left, "E_1"] \arrow[d, "B"] & \\ & RB^+ + (M^{II}) \arrow[r, shift left, "-e"] & (M^{III})^+ \arrow[l, shift left, "E_2"] \end{tikzcd} \qquad E_1 > E_2 \tag{2}$$

[reactions (2)].‡ In the presence of pyridine (py), controlled potential oxidation of $[Bu^nCo^{III}(salen)]$ was complete after passage of 2F/mol, with yields of $[Co^{III}(salen)(py)_2]^+$ and the alkylpyridinium salt being almost quantitative, proving that the *ECE* mechanism was operating. Cyclic voltammetry and rotating disc electrode techniques enabled us to establish the following reactivity series of $[RM^{IV}(salen)]^+$ complexes towards pyridine: Me > Et > Pr^n > Bu^n. This series is the same as that for the electrophilic reactivity of n-alkylcobalt(III) chelates,[7] both being typical for S_N2 reactions.

The half-wave potential of the process $R(M^{III}) \overset{-e}{\rightleftharpoons} R\text{-}(M^{IV})^+$ (Table) also depends markedly on R especially in the case of the cobalt complexes. This influence is consistent with the direction of the inductive effect ($E_{\frac{1}{2}}$: Me >Et ≃ Pr^n ≃ Bu^n > Pr^i).

Thus both the ease of formation of the organometallic cations $[RM^{IV}(chel)]^+$ and their reactivity are profoundly dependent on the nature of the σ-bonded organic ligand.§ These results may indicate that during oxidation of the organometal(III) chelates the electron density changes mainly at the metal ion and the organic group R rather than at the chelating ligand. Further, the metal–carbon bonding in organocobalt chelates has been treated[8,9] as a resonance hybrid of three limiting structures, in this case (I)—(III). The reactivity of the species in question

$$\begin{array}{ccc} R^- & R & R^+ \\ & | & \\ (M^{IV})^{2+} & (M^{III})^+ & (M^{II}) \\ \text{(I)} & \text{(II)} & \text{(III)} \end{array}$$

suggests that the structure (III) *i.e.* carbonium ion complex, contributes significantly to the structure.

Since these cobalt chelates are conventional models of vitamin B_{12} our findings may have biochemical implications. We suggest that reversible one-electron oxidation of organocobalt entities and subsequent reactions of the electrophilic products RCo^{IV} should be borne in mind as a tentative pathway when vitamin B_{12}-dependent enzymatic processes involving nucleophilic substrates[7,9] are considered.

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‡ The reactions following electron transfer in the absence of such nucleophiles are more complicated and will be discussed elsewhere.

§ A sharp difference between the anodic behaviour of the organometal chelate $[RCo^{III}(salen)]$ and that of the $[Co^{III}(salen)]^+$ complex is relevant. The latter is oxidized irreversibly (E_P + 1·38 V in MeCN), the voltammogram not being reproducible in following scans.

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