

Transition-metal Complexes of Pyrrole Pigments. XXI. One-electron Oxidation of Water Mediated by a Cobalt(III)-Tetradehydrocorrins Complex[†]

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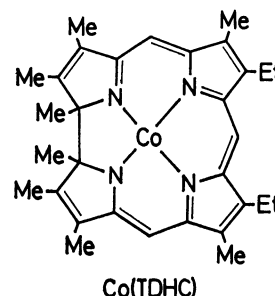
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The cobalt(III) complex of tetradehydrocorrins (TDHC), having pK_{a1} 6.15 and pK_{a2} 11.50 for successive acid-dissociation of axial aqua ligands, undergoes auto-reduction to the cobalt(II) complex in aqueous carbonate solutions. Kinetic analysis of the reaction indicates the following mechanism: a one-electron transfer from the axial hydroxo ligand to the metal site, subsequent homolytic cleavage of the Co–OH bond, and finally scavenging of the resulting hydroxyl radical with the carbonate ion. At relatively low concentrations of the carbonate ion, the scavenging step is rate-determining; while at $[CO_3^{2-}] \geq 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ for $[Co^{III}(TDHC)]$ of 7.62×10^{-5} – $1.27 \times 10^{-5} \text{ mol dm}^{-3}$, the initial bond homolysis becomes rate-determining. Analysis of the kinetic data in reference to relevant electrode potentials indicates that the powerful oxidation ability of $Co^{III}(TDHC)$ is responsible for one-electron oxidation of the hydroxo ligand. Reduction of $Co^{III}(TDHC)$ also takes place in the absence of the carbonate ion, the apparent rate increasing with rise of pH in the range 11–12; deprotonation of the hydroxyl radical, which may prevent the hydroxyl radical and the cobalt(II) species from backward recombination, takes place. The one-electron oxidation of the hydroxo ligand was also significantly accelerated by addition of acetonitrile or *t*-butyl alcohol.

The photosynthetic oxidation of water to dioxygen occurring in the photosystem-II has led to challenges to the discovery of chemical systems capable of oxidizing water. The manganese ion is believed to be an essential component of photosystem-II.¹⁾ Thus, various types of manganese complexes,^{2–5)} mononuclear and binuclear, in homogeneous solutions or as coated on metal surfaces,^{6,7)} have been studied as models of biological water oxidation. Other homogeneous metal complex systems as regards water oxidation include the tris(bipyridine) and tris(phenanthroline) complexes of iron(III),⁸⁾ osmium(III),^{8,9)} and ruthenium(III).¹⁰⁾ Another system of great importance employs heterogeneous noble-metal oxides such as RuO_2 which can mediate, when dispersed in aqueous media, oxidation of water to dioxygen by agents which have appropriate redox potentials such as $Ru(bpy)_3^{3+}$.^{11,12)}

Water can be oxidized most readily by a four-electron transfer process from a thermodynamic viewpoint; one-electron oxidation of water ($E^0 = +2.8 \text{ V vs. SHE}$) or even hydroxide ion ($E^0 = +2.0 \text{ V vs. SHE}$) is much less favorable than the four-electron process ($E^0 = +1.229 \text{ V vs. SHE}$).¹³⁾ The four-electron transfer is not achieved by using ordinary mononuclear metal complexes in homogeneous phase even if the complexes have appropriate redox potentials, since such complexes can, in principle, oxidize water by a one-electron transfer process. However, clarification of the one-electron water-oxidation mechanism seems not only to provide a basis for understanding the mechanism of photosynthetic oxygen evolution reactions but also to offer relevant information for designing more elaborated multi-electron oxidation catalysis in homogeneous phase. No unambiguous demonstration has been presented for the direct one-electron oxidation of water or hydroxide ion, either free or metal-coordinated, with metal complexes, although the auto-reduction of manganese(IV)–hematoporphyrin would involve such a process.³⁾

The present study is based on the finding that a cobalt(II)-tetradehydrocorrins complex undergoes facile reduction to the corresponding cobalt(I) complex in an aprotic solvent with hydroxide ion.¹⁴⁾ In the course of our research on the mechanistic aspects of this and related reactions, we have investigated the reduction behavior of a cobalt(III) complex of tetradehydrocorrins in aqueous media, and demonstrated the one-electron oxidation of water as coordinated to the metal site in the form of the axial hydroxo ligand.



Results

Formation of $Co^{III}(TDHC)$. The cobalt(III) complex of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrins (abbreviated as TDHC), $Co^{III}(TDHC)$, was obtained by oxidation of $[Co^{II}(TDHC)]-ClO_4$ ^{14,15)} in water–methanol (99 : 1 v/v); air-oxidation or chemical oxidation either with hypochlorite or chlorine, oxidation being carried out in acidic media. The apparent first-order rate constant for the air-oxidation at 20 °C was proportional to hydrogen ion concentration ($0.01 \leq [H^+] \leq 0.1 \text{ mol dm}^{-3}$):¹⁶⁾ $k/s^{-1} = 0.29[H^+]$, as in the case of a related AD–didehydrocorrins complex.¹⁷⁾ The initial product, hydrogen peroxide, could not be detected since each peroxide readily oxidizes two more molecules of the cobalt(II) complex.¹⁶⁾ In fact, the oxidation rate was much larger in the presence of varying amounts of hydrogen peroxide than

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in its absence and linearly dependent on $[\text{H}_2\text{O}_2]$: $k/s^{-1} = 2.8 \times 10^{-3} + k'[\text{H}_2\text{O}_2]$ at $[\text{H}^+] = 9.8 \times 10^{-3} \text{ mol dm}^{-3}$ where $k' = 196 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The electronic spectrum of $\text{Co}^{\text{III}}(\text{TDHC})$ was dependent neither on the method of preparation described above nor on the nature of acid employed (hydrochloric, perchloric, or sulfuric acid). This indicates that a simple diaqua ligation takes place at the axial sites of $\text{Co}^{\text{III}}(\text{TDHC})$ in acidic media. The air-oxidation rate of $\text{Co}^{\text{II}}(\text{TDHC})$ was not affected to any detectable extent even in the presence of an equimolar amount of hydrogen cyanide, although the product was the aquacyano derivative, $[(\text{CN})(\text{H}_2\text{O})\text{Co}^{\text{III}}(\text{TDHC})]^+$. This indicates that no cyanide ion is involved in the oxidation of $\text{Co}^{\text{II}}(\text{TDHC})$ and the oxidation product, $[(\text{H}_2\text{O})_2\text{Co}^{\text{III}}(\text{TDHC})]^{2+}$, is subsequently converted into $[(\text{CN})(\text{H}_2\text{O})\text{Co}^{\text{III}}(\text{TDHC})]^+$.

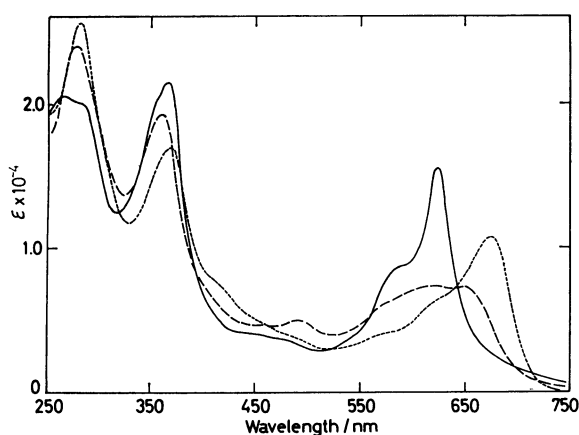
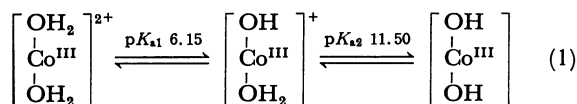


Fig. 1. Electronic absorption spectra of diaqua (—), aquahydroxo (---), and dihydroxo (.....) species of $\text{Co}^{\text{III}}(\text{TDHC})$ in water-methanol (99.2 : 0.8 v/v) at 10 °C.

The spectral feature of $\text{Co}^{\text{III}}(\text{TDHC})$ varies as the axial ligands change from diaqua through cyanoaqua to dicyano in a similar manner as observed for the cobalt(III) complexes of AD-didehydrocorrin and cobinamide.¹⁷⁾ The successive acid dissociation of the two axial aqua ligands (Eq. 1) was confirmed by spectrophotometric titration of $\text{Co}^{\text{III}}(\text{TDHC})$ at 10 °C over a wide pH range: $\text{p}K_{\text{a}1}$ 6.15 and $\text{p}K_{\text{a}2}$ 11.50.¹⁸⁾ The choice of temperature (10 °C) is simply due to the fact that the reaction of the complex takes place at higher temperatures. Figure 1 shows the electronic spectra of the diaqua, aquahydroxo, and dihydroxo species.



Carbonate- and Hydroxide-induced Reduction of $\text{Co}^{\text{III}}(\text{TDHC})$. In aqueous carbonate solutions containing methanol (0.8% by volume) at 38.4 °C, $\text{Co}^{\text{III}}(\text{TDHC})$ underwent facile reduction to $\text{Co}^{\text{II}}(\text{TDHC})$ in quantitative yield. The product was identified by electronic spectroscopy and vapor pressure osmometric molecular weight determination. It was also converted

into $(\text{CN})_2\text{Co}^{\text{III}}(\text{TDHC})$,^{15,19)} which was identified by electronic and NMR spectroscopy. The results preclude any possible modification of the TDHC structure during the course of reduction. When the conversion $\text{Co}(\text{III}) \rightarrow \text{Co}(\text{II})$ was followed spectrophotometrically, clear isosbestic points were observed at 264, 354, 443, and 579 nm. At carbonate concentrations greater than $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ for $[\text{Co}^{\text{III}}(\text{TDHC})]$ of $1.27 \times 10^{-5} - 7.62 \times 10^{-5} \text{ mol dm}^{-3}$, the reduction of $\text{Co}^{\text{III}}(\text{TDHC})$ followed first-order kinetics with respect to $\text{Co}^{\text{III}}(\text{TDHC})$ with the first-order rate constant independent of carbonate concentration; linear first-order plot almost to 100% conversion for any given run and no dependence of the rate constant on initial concentration of the complex. The first-order dependence of the reaction on $\text{Co}^{\text{III}}(\text{TDHC})$ rules out the participation of any equilibria involving a dimer such as the hydroxo-bridged one. The limiting (or leveled-off) rate constant (Fig. 2) depends neither on pH (Table 1) nor on concentration of chloride or perchlorate ion; for added chloride (0.07 mol dm^{-3}) or perchlorate (0.008 mol dm^{-3}) in addition to the carbonate ion, the rate constant remained the

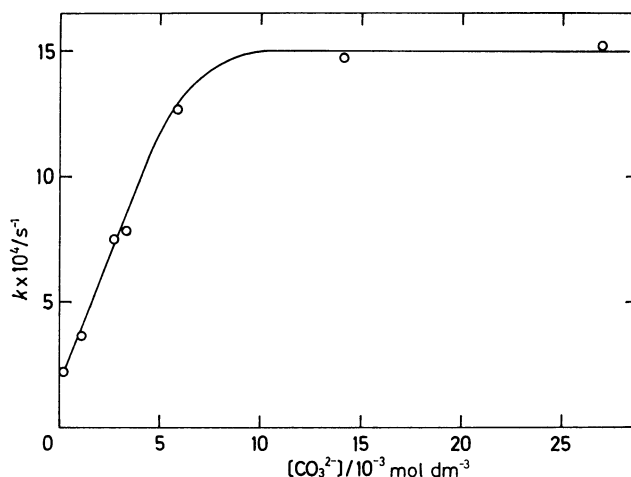


Fig. 2. Correlation of first-order rate constant with carbonate concentration for reduction of $\text{Co}^{\text{III}}(\text{TDHC})$ in water-methanol (99.2 : 0.8 v/v) at 38.4 °C and pH 9.5 ± 0.2 .

TABLE 1. APPARENT FIRST-ORDER RATE CONSTANTS FOR CARBONATE- AND HYDROXIDE- INDUCED REDUCTION OF $\text{Co}^{\text{III}}(\text{TDHC})$ ^{a)}

Effective anion	pH	k/s^{-1}
Carbonate (0.11 mol dm^{-3}) ^{b)}	9.3	1.5×10^{-3}
	9.7	1.5×10^{-3}
	11.0	1.5×10^{-3}
Hydroxide ^{c)}	10.7	2.6×10^{-4}
	11.4	6.1×10^{-4}
	11.7	8.1×10^{-4}
	12.2	1.1×10^{-3}
	13.1	ca. 1×10^{-4}

a) In water containing methanol (0.8% by volume) at 38.4 °C; initial concentration of $\text{Co}^{\text{III}}(\text{TDHC})$, $3.81 \times 10^{-5} \text{ mol dm}^{-3}$. b) Total concentration of carbonate and hydrogencarbonate. c) Carbonate-free sodium hydroxide solution used.

TABLE 2. ACTIVATION PARAMETERS FOR HOMOLYSIS OF Co(III)–OH BOND^{a)}

Entry	Medium (composition) ^{b)}	ΔH^* kcal mol ⁻¹	ΔS^* cal deg ⁻¹ mol ⁻¹	ΔG^* kcal mol ⁻¹
1	H ₂ O–CH ₃ OH (99.2 : 0.8)	23.9	+4.7	22.4
2	H ₂ O–CH ₃ CN–CH ₃ OH (85.5 : 13.7 : 0.8)	21.6	+1.4	21.2
3	H ₂ O–CH ₃ CN–CH ₃ OH (77.3 : 21.9 : 0.8)	18.7	–6.6	20.8
4	H ₂ O– <i>t</i> -C ₄ H ₉ OH–CH ₃ OH (77.3 : 21.9 : 0.8)	18.5	–7.1	20.7

a) At 38.4 °C. Initial concentration of Co^{III}(TDHC), 3.81×10^{-5} mol dm⁻³. Other experimental conditions ([CO₃²⁻], pH, temperature range): entry number 1, (1.5×10^{-2} mol dm⁻³, 9.4, 20.0–47.7 °C); 2, (0.19 mol dm⁻³, 11.4, 20.0–38.4 °C); 3, (0.19 mol dm⁻³, 11.5, 24.5–38.4 °C); 4, (0.19 mol dm⁻³, 11.9, 20.0–38.4 °C). b) Volume percent.

same. The rate constant showed linear dependence on [CO₃²⁻] at lower concentrations of the carbonate ion (Fig. 2). Methanol (0.8% by volume) involved in the reaction medium as a cosolvent could be eliminated or replaced by acetonitrile or *N,N*-dimethylformamide at 0.8% by volume without affecting the limiting rate constant. Phosphate and borate ions in place of carbonate were less effective for promoting the reduction of Co^{III}(TDHC). The activation parameters were obtained at a carbonate concentration in the rate-saturation range (1.5×10^{-2} mol dm⁻³, refer to Fig. 2) for the temperature range 20.0–47.7 °C (Table 2). Another important aspect of the carbonate-induced reduction is the photo-catalysis. Co^{III}(TDHC) (3.81×10^{-5} mol dm⁻³) in 6.5×10^{-2} mol dm⁻³ carbonate was completely reduced to the Co(II) species at 0 °C in 90 min under irradiation with a 100-W high pressure mercury lamp from a distance of 11 cm, while the conversion was less than 10% in the dark in a period of 180 min under otherwise identical conditions.

In the absence of buffer salts, the reduction of Co^{III}(TDHC) did occur with concomitant formation of hydrogen peroxide as detected by iodometry. The apparent first-order rate increased with rise of pH from 10.7 to 12.2 and approached the limiting rate constant

for the carbonate-induced reaction (Table 1). The reaction was also photo-catalyzed in a similar way to that observed for the carbonate-induced reaction. The proton dissociation with pK_{a2} 11.50 resulted in an appreciable reduction in reactivity as seen from the rate constant at pH 13.1.

In the presence of the carbonate ion at rate-saturation level (0.19 mol dm⁻³), the reduction of Co^{III}(TDHC) was facilitated by added organic cosolvents such as acetonitrile and *t*-butyl alcohol (Fig. 3). The activation parameters obtained are summarized in Table 2. The rate-acceleration upon addition of organic cosolvents is brought about by favorable activation enthalpy changes.

Discussion

Formation of Hydroxyl Radical and Its Scavenging. In order to establish the mechanism involved in the reduction of Co^{III}(TDHC) in aqueous carbonate solutions, we must identify the reductant (or species being oxidized), elucidate the electron transfer mechanism, and clarify the specific role of the carbonate ion. As regards the product, Co^{II}(TDHC), the TDHC ligand remains intact, no concomitant oxidation of the macrocyclic ligand taking place. This is in marked contrast to the base-induced reduction of Ni(III)²⁰ and Co(III)²¹ complexes of *N*₄-macrocycles. An outer-sphere oxidation of water is highly unlikely because of the gross mismatch of the reduction potential (+0.59¹⁷) or +0.54 V *vs.* SCE²²) in methanol) of L₂Co^{III}(TDHC) (L being a solvent molecule coordinated at the axial site) and the one-electron oxidation potential of water ($E^0 = +2.8$ V *vs.* SHE). A possibility that the free hydroxyl ion would act as a stoichiometric reductant can also be ruled out since the carbonate-induced reaction rate is independent of the pH in the range 9.3–11.0 (Table 1). Thus, the present oxido-reduction must be an intramolecular process involving the axial hydroxo ligand.²² In view of one-electron transfer stoichiometry and the fact that the carbonate ion, which has no effect on the electronic spectrum of the present complex, is a powerful hydroxyl radical scavenger,^{23–26}) we can formulate the mechanism as follows: a reversible one-electron transfer from an axial hydroxo ligand to Co(III) and subsequent dissociation of the axial bond, followed by scavenging of the resulting

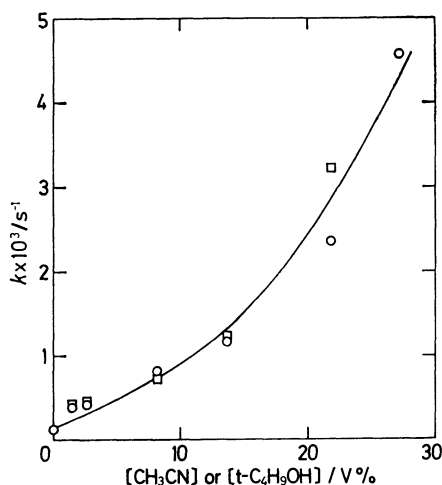
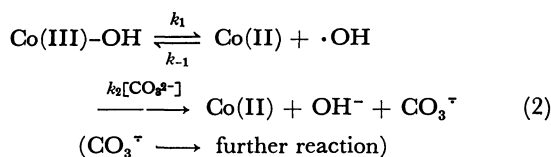


Fig. 3. Correlation of first-order rate constant with content of organic solvents for reduction of Co^{III}(TDHC) in water–acetonitrile (○) and in water–*t*-butyl alcohol (□), both containing 0.19 mol dm⁻³ carbonate and 0.8% (v/v) methanol, at 20.0 °C.

hydroxyl radical with the carbonate ion²⁷⁾ (Eq. 2).



The proposed mechanism involving homolytic cleavage of the Co(III)-OH bond is consistent with the photochemical acceleration as well as the observed dependency of the rate on carbonate concentration (Fig. 2). At relatively low concentrations of carbonate, the $k_2[\text{CO}_3^{2-}]$ process is rate-determining as reflected on the rate which is linearly dependent on the carbonate concentration. As the carbonate concentration is raised to the level where $k_2[\text{CO}_3^{2-}] \gg k_{-1}$, the k_1 process becomes the rate-determining step for which the rate is independent of carbonate concentration. The validity of Eq. 2 should be further examined by kinetic analysis of the data under steady state treatment. A steady state approximation is applied with respect to the hydroxyl radical, the steady state concentration, $[\cdot\text{OH}]_{ss}$, being given by

$$[\cdot\text{OH}]_{ss} = \frac{k_1[\text{Co(III)}]}{k_{-1}[\text{Co(II)}] + k_2[\text{CO}_3^{2-}]} \quad (3)$$

Eq. 3. The rate law for disappearance of Co^{III}(TDHC) is then represented by Eq. 4. A simple first-order

$$\begin{aligned} -\frac{d[\text{Co(III)}]}{dt} &= k_1[\text{Co(III)}] - k_{-1}[\text{Co(II)}][\cdot\text{OH}]_{ss} \\ &= k_2[\text{CO}_3^{2-}][\cdot\text{OH}]_{ss} \\ &= \frac{k_1 k_2 [\text{Co(III)}][\text{CO}_3^{2-}]}{k_{-1}[\text{Co(II)}] + k_2[\text{CO}_3^{2-}]} \quad (4) \end{aligned}$$

kinetics is derived under the conditions $k_2[\text{CO}_3^{2-}] \gg k_{-1}[\text{Co(II)}]$ with first-order rate constant k_1 . Under the other extreme conditions as represented by $k_{-1}[\text{Co(II)}] \gg k_2[\text{CO}_3^{2-}]$, Eq. 4 is simplified to Eq. 5. The kinetic data for runs at carbonate concentrations of 2.3×10^{-4} and 1.7×10^{-3} mol dm⁻³ (the lowest two concentrations employed here) were satisfactorily analyzed by means of Eq. 5 or its integrated form, Eq. 6.²⁸⁾

$$-\frac{d[\text{Co(III)}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{CO}_3^{2-}] \frac{[\text{Co(III)}]}{[\text{Co(II)}]} \quad (5)$$

$$[\text{Co(III)}] - [\text{Co(III)}]_0 \ln[\text{Co(III)}]_0 = \frac{k_1 k_2}{k_{-1}} [\text{CO}_3^{2-}] t \quad (6)$$

Except for the early stage of reaction, a plot of $-d[\text{Co(III)}]/dt$ vs. $[\text{Co(III)}]/[\text{Co(II)}]$ yielded a straight line with the slope $k_1 k_2 [\text{CO}_3^{2-}]/k_{-1}$ (Fig. 4), where k_1 is the limiting rate constant in Fig. 2 (1.5×10^{-3} s⁻¹) (see Experimental). It is reasonable to assume that the highly exothermic k_{-1} process is diffusion-controlled, i. e., $k_{-1} \approx 10^{10}$ dm³ mol⁻¹ s⁻¹. The k_2 values are calculated to be: 6×10^7 and 2×10^7 dm³ mol⁻¹ s⁻¹ for runs at carbonate concentrations of 2.3×10^{-4} and 1.7×10^{-3} mol dm⁻³, respectively. These values are comparable to the rate constant for bimolecular reaction of the hydroxyl radical with the carbonate ion obtained from a pulse-radiolysis study:²⁴⁾ 4.2×10^8 dm³ mol⁻¹ s⁻¹.²⁹⁾ The activation enthalpy as large as 23.9 kcal mol⁻¹ and the positive activation entropy (+4.7 cal deg⁻¹ mol⁻¹) (Table 2) for the k_1 process are consistent

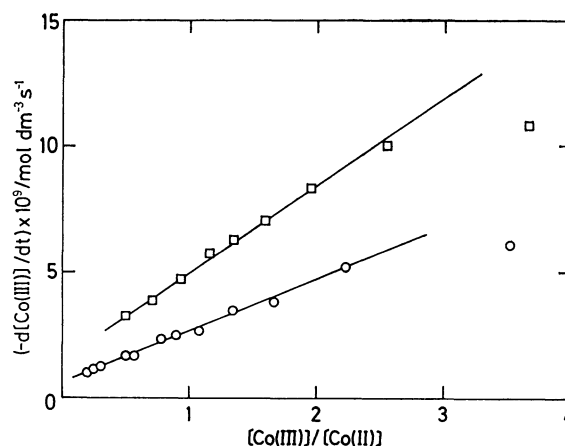
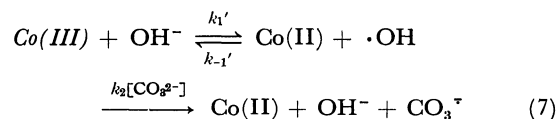


Fig. 4. Analysis of kinetic data (Eq. 5) for reduction of Co^{III}(TDHC) in water-methanol (99.2 : 0.8 v/v) in the presence of 2.3×10^{-4} mol dm⁻³ (O) and 1.7×10^{-3} mol dm⁻³ (□) carbonate at 38.4 °C.

with a highly endothermic unimolecular dissociation process.

Correlation with Electrode Potentials. Judging from the Co(II)/Co(III) redox potential for Co^{II}(TDHC) in methanol (+0.59¹⁷⁾ or 0.54 V vs. SCE²²⁾ and the one-electron oxidation potential of the hydroxide ion in water (+2.0 V vs. SHE),¹³⁾ the standard free energy change for an outer-sphere oxidation of the free hydroxide ion by L₂Co^{III}(TDHC) (L being a solvent molecule) would amount to ca. 27 kcal mol⁻¹ and the process would proceed quite slowly at ordinary temperatures. The intramolecular oxidation of the hydroxyl ligand can be regarded, from a thermodynamic viewpoint, as an oxidation of the coordination-free hydroxide ion by *naked* Co^{III}(TDHC) whose Co(II)/Co(III) potential may be assumed equivalent to that in a non-coordinating solvent; +0.97 V vs. SCE in CH₂Cl₂.¹⁷⁾ The accompanying free energy change would be reduced from 27 kcal mol⁻¹ for an outer-sphere oxidation to ca. 18 kcal mol⁻¹. In the light of such evaluation, the free energy of activation for the bond dissociation (k_1 process), $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, 22.4 kcal mol⁻¹ (Table 2) is reasonable in magnitude. In order to get further insight into the correlation with electrode potential, the kinetic data were analyzed on the basis of simplified reaction scheme; a reversible electron transfer between *naked* Co^{III}(TDHC) (Co(III)) and OH⁻ followed by scavenging of the hydroxyl radical with the carbonate ion as given by Eq. 7.



Under the conditions where scavenging is the rate-determining process, the apparent first-order rate constant is given by $(k_1'/k_{-1}')k_2[\text{CO}_3^{2-}]$; $(k_1'/k_{-1}')k_2$ corresponds to the slope (0.21 dm³ mol⁻¹ s⁻¹) of the linear portion of rate constant vs. $[\text{CO}_3^{2-}]$ profile in Fig. 2. If k_2 is taken for the range of 6×10^7 (calculated as above) through 1×10^9 dm³ mol⁻¹ s⁻¹ (based on pulse radiolysis), the hypothetical equilibrium constant,

(8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyltetrahydrocor-

rinato)cobalt(II) perchlorate, $[\text{Co}^{\text{II}}(\text{TDHC})]\text{ClO}_4$, was prepared according to the procedure of Dolphin *et al.*¹⁵) Found: C, 59.62; H, 5.92; N, 8.91%. Calcd for $\text{C}_{31}\text{H}_{37}\text{ClCoN}_4\text{O}_4$: C, 59.67; H, 5.98; N, 8.98%. Water was deionized and distilled with a Pyrex distilling apparatus. Acetonitrile and *t*-butyl alcohol were fractionally distilled just before use. All the other chemicals were of analytical grade.

Formation of $\text{Co}^{\text{III}}(\text{TDHC})$ and Acid Dissociation of Its Diaqua Complex. Oxidation of a reddish-purple solution of $[\text{Co}^{\text{II}}(\text{TDHC})]\text{ClO}_4$ by three different oxidants (air, hypochlorite, and chlorine) under acidic conditions gave a greenish-blue solution of $\text{Co}^{\text{III}}(\text{TDHC})$ as confirmed by electronic spectroscopy. For air oxidation, the simplest procedure, a methanol solution of $\text{Co}^{\text{II}}(\text{TDHC})$ (1 part) was mixed with water (100 part) containing an appropriate amount of an acid and the mixture was exposed to the air at room temperature. Under anaerobic conditions neither oxidation nor spectral change was detected. For oxidation by hypochlorite or chlorine, a 100- μl sample of a methanol solution of $\text{Co}^{\text{II}}(\text{TDHC})$ ($4.65 \times 10^{-3} \text{ mol dm}^{-3}$) was injected into a deoxygenated 0.01-mol dm^{-3} HCl solution (3 ml) containing 2 μl of aqueous NaOCl solution (10% active chlorine) and 7 μl of saturated aqueous Cl_2 solution, respectively, at room temperature. Oxidation took place almost instantaneously.

A methanol solution of $\text{Co}^{\text{II}}(\text{TDHC})$ ($4.65 \times 10^{-3} \text{ mol dm}^{-3}$, 30 μl) was added to 3 ml of water containing an appropriate amount of hydrochloric acid, and hydrogen peroxide or hydrogen cyanide for specified experiments, at $20.0 \pm 0.1^\circ\text{C}$; the absorbance change at 490 nm then being measured at the same temperature. As regards the preparative scale experiment, 15 mg ($2.4 \times 10^{-5} \text{ mol}$) of $\text{Co}^{\text{II}}(\text{TDHC})$ was oxidized in water (50 ml) containing methanol (0.5 ml) and 1-mol dm^{-3} HCl (0.5 ml). The cobalt complex was extracted into dichloromethane, and the aqueous layer was found to be free of hydrogen peroxide by iodometric analysis. $\text{Co}^{\text{III}}(\text{TDHC})$ was relatively stable only when diluted in acidic aqueous media and quite readily reconverted into the original $\text{Co}(\text{II})$ complex during the course of isolation such as extraction with organic solvents (dichloromethane, benzene, and ether), precipitation from aqueous solution by adding an organic solvent, careful concentration (with partial regeneration of $\text{Co}^{\text{II}}(\text{TDHC})$), and evaporation of aqueous solutions (with complete conversion into $\text{Co}^{\text{II}}(\text{TDHC})$).

Spectra were recorded for a series of solutions of $\text{Co}^{\text{III}}(\text{TDHC})$ ($2.79 \times 10^{-5} \text{ mol dm}^{-3}$) in aqueous buffers at various pH (2.13–13.45) and at 10.0°C . The absorbance at 620 nm ($2.13 \leq \text{pH} \leq 10.22$) or at 670 nm ($8.10 \leq \text{pH} \leq 13.45$) was plotted against pH, and the pK_a values for acid dissociation of the coordinated water molecules were determined graphically. The buffer systems used were as follows: pH 2.13–3.30, HCl; 3.75–5.58, acetate; 6.25–7.75, phosphate; 8.10, borate; 9.25–10.93, carbonate; 10.20–13.45, NaOH.

Kinetic Measurements. Acidic solutions of $\text{Co}^{\text{III}}(\text{TDHC})$ were prepared by mixing 30 μl of a methanol solution of $\text{Co}^{\text{II}}(\text{TDHC})$ ($4.65 \times 10^{-3} \text{ mol dm}^{-3}$) and water (appropriate amount) containing 30 μl of 1-mol dm^{-3} HCl and the resulting solutions were allowed to stand at room temperature for at least 30 min. Acetonitrile or *t*-butyl alcohol (appropriate amount) was added for specified experiments. No inorganic salts were added to the solutions unless otherwise stated because of their possible contribution to scavenging of the hydroxyl radical. The solutions were then placed in a specially designed quartz cell (1-cm path length) set in a spectrophotometer and preequilibrated at desired temperatures under nitrogen atmosphere. The reaction was initiated by injecting an appropriate amount of aqueous Na_2CO_3 – NaHCO_3 (1.0 or 2.0 mol dm^{-3}) or aqueous NaOH (18.8 mol

dm^{-3}). The final solutions were adjusted at a constant volume of 3.66 ml with $3.81 \times 10^{-5} \text{ mol dm}^{-3}$ of $\text{Co}^{\text{III}}(\text{TDHC})$. The course of reaction was followed by monitoring the absorbance change at 490 nm (an absorption maximum for $\text{Co}^{\text{II}}(\text{TDHC})$). The concentrations of carbonate ion were calculated from the known amounts of $([\text{CO}_3^{2-}] + [\text{HCO}_3^-])$ and pH of the solutions measured for every kinetic runs, in reference to the pK_a value of carbonate. The pK_a of carbonate in mixed solvents was independently determined by potentiometric titration: 10.7 in water–acetonitrile (86.3 : 13.7 v/v), and 10.6 in water–*t*-butyl alcohol (86.3 : 13.7 v/v). Analyses of kinetic data according to Eq. 5 were performed by evaluating $[\text{Co}(\text{II})]$ and $[\text{Co}(\text{III})]$ first at an appropriate time interval and then taking the average value for each time interval (Δt): $-d[\text{Co}(\text{III})]/dt = ([\text{Co}(\text{III})]_t - [\text{Co}(\text{III})]_{t+\Delta t})/\Delta t$; $[\text{Co}(\text{III})]/[\text{Co}(\text{II})] = ([\text{Co}(\text{III})]_t + [\text{Co}(\text{III})]_{t+\Delta t})/([\text{Co}(\text{II})]_{t+\Delta t} + [\text{Co}(\text{II})]_t)$. Activation parameters were calculated as follows: $E_a = \Delta H^\ddagger + RT$ (E_a , activation energy from Arrhenius plot), $k_{38.4^\circ\text{C}} = (kT/h) \cdot \exp(-\Delta G^\ddagger/RT)$, and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

Reduction of $\text{Co}^{\text{III}}(\text{TDHC})$ in Carbonate Solutions: Formation of $\text{Co}^{\text{II}}(\text{TDHC})$. A solution of $\text{Co}^{\text{III}}(\text{TDHC})$, prepared from $[\text{Co}^{\text{II}}(\text{TDHC})]\text{ClO}_4$ (29 mg) in water (1 l) containing 1 mol dm^{-3} HCl (10 ml) and methanol (10 ml), was mixed with 110 ml of 1.0 mol dm^{-3} aqueous Na_2CO_3 solution. The mixture was allowed to stand at 40°C for 30 min with occasional swirling, at room temperature for 4 h to complete the $\text{Co}(\text{III}) \rightarrow \text{Co}(\text{II})$ conversion, and then extracted with dichloromethane (100 ml $\times 2$). The extract was washed with a saturated NaClO₄ solution (50 ml), dried (Na_2SO_4), and evaporated to give $[\text{Co}^{\text{II}}(\text{TDHC})]\text{ClO}_4$ (25 mg, 86%). Its electronic spectrum and molecular weight (measured by vapor pressure osmometry for methanol solutions) were identical with those of the authentic sample. The $\text{Co}(\text{II})$ complex thus obtained was dissolved in methanol (10 ml), and potassium cyanide (30 mg) was added. The mixture was allowed to stand at room temperature for 10 h, the solvent was removed *in vacuo*, and the residue was extracted with chloroform. Evaporation of chloroform gave $(\text{CN})_2\text{Co}^{\text{III}}(\text{TDHC})^{15}$ (17 mg, 65% from the initial $\text{Co}(\text{II})$ complex): electronic and NMR spectra were identical with those of the authentic sample. ^1H NMR (CDCl_3): δ 6.91 (s, 2H, C(5)–H and C(15)–H), 6.87 (s, 1H, C(10)–H), 2.86 (q, 4H, CH_2CH_3), 2.45 (s, 12H, CH_3 's on C(3), C(7), C(13), and C(17)), 2.33 (s, 6H, CH_3 's on C(2) and C(18)), 1.34 (t, 6H, CH_2CH_3), and 0.76 (s, 6H, CH_3 's on C(1) and C(9)).

Reduction of $\text{Co}^{\text{III}}(\text{TDHC})$ in the Absence of Carbonate: Detection of Hydrogen Peroxide.

A solution of $\text{Co}^{\text{III}}(\text{TDHC})$, prepared in a manner similar to that described above by air oxidation of $\text{Co}^{\text{II}}(\text{TDHC})$ in acidic aqueous media with or without methanol (1%), was carefully concentrated at temperatures below 30°C . A 10-ml portion of the resulting solution (*ca.* $1 \times 10^{-3} \text{ mol dm}^{-3}$ in $\text{Co}^{\text{III}}(\text{TDHC})$) was mixed anaerobically with an appropriate amount of carbonate-free aqueous NaOH; pH of the solution, 12.3. The mixture was allowed to stand at room temperature for 40 min. The $\text{Co}^{\text{II}}(\text{TDHC})$ complex precipitated from the solution was removed by filtration, and the amount of hydrogen peroxide in the filtrate was determined by iodometric analysis. A solution to be examined was purged with argon for 5 min, and 10% aqueous KI solution (1 ml) and 4 mol dm^{-3} aqueous H_2SO_4 (2 ml) were added. After being bubbled with argon for 5 min, the mixture was titrated with $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous $\text{Na}_2\text{S}_2\text{O}_3$; 30% yield at best on the basis of the $\text{Co}(\text{III})$ complex used. The low yield of hydrogen peroxide was at least due to its further reaction with $\text{Co}^{\text{II}}(\text{TDHC})$ to give unidentified product(s), as independently confirmed by spectrophotometric means.

References

- 1) G. M. Cheniae and I. F. Martin, *Biochim. Biophys. Acta*, **197**, 219 (1970).
- 2) M. Calvin, *Science*, **184**, 375 (1974); S. R. Cooper and M. Calvin, *ibid.*, **185**, 376 (1974); M. Calvin, *Acc. Chem. Res.*, **11**, 369 (1978).
- 3) I. Tabushi and S. Kojo, *Tetrahedron Lett.*, **1974**, 1577.
- 4) L. J. Boucher and C. G. Coe, *Inorg. Chem.*, **14**, 1289 (1975); **15**, 1334 (1976).
- 5) M. M. Morrison and D. T. Sawyer, *J. Am. Chem. Soc.*, **99**, 257 (1977); D. T. Sawyer, M. E. Bodini, L. A. Willis, T. L. Riechel, and K. D. Magers, in "Bioinorganic Chemistry-II," Advances in Chemistry Series 162, ed by K. N. Raymond, American Chemical Society, Washington, D. C. (1977), Chap. 19.
- 6) M. Aizawa, M. Hirano, and S. Suzuki, *Electrochim. Acta*, **24**, 89 (1979).
- 7) Y. Umezawa and T. Yamamura, *J. Electrochem. Soc.*, **126**, 705 (1979).
- 8) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, **1972**, 866.
- 9) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, **1975**, 845.
- 10) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).
- 11) J. Kiwi and M. Grätzel, *Angew. Chem.*, **91**, 659 (1979); K. Kalyanasundaram and M. Grätzel, *ibid.*, **91**, 759 (1979).
- 12) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979).
- 13) D. Dvos, "Electrochemical Data," Elsevier, Amsterdam (1975), pp. 247–261.
- 14) Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, **49**, 683 (1976).
- 15) D. Dolphin, R. L. N. Harris, J. L. Huppertz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc., C*, **1966**, 30.
- 16) Discussion on the mechanism of acid-catalyzed autoxidation of transition-metal complexes: J. J. Pignatello and F. R. Jensen, *J. Am. Chem. Soc.*, **101**, 5929 (1979). Autoxidation of vitamin B₁₂: J. M. Pratt, "Inorganic Chemistry of Vitamin B₁₂," Academic Press, London (1972), pp. 202–204.
- 17) Y. Murakami, Y. Aoyama, and K. Tokunaga, *J. Am. Chem. Soc.*, **102**, 6736 (1980).
- 18) The pK_a values are reasonable for this type of Co(III) complexes: cobinamide, pK_{a1} 6.0 (G. C. Hayward, H. A. O. Hill, J. M. Pratt, N. J. Vanston, and R. J. P. Williams, *J. Chem. Soc.*, **1965**, 6485); AD-didehydrocorrin complex, pK_{a1} 6.2 and pK_{a2} 11.2 (Ref. 17); meso-tetrakis(1-methylpyridinium-4-yl)porphyrin complex, pK_{a1} 6.0 and pK_{a2} 10.0 (R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973)).
- 19) Y. Murakami, Y. Aoyama, and S. Nakanishi, *Chem. Lett.*, **1976**, 857; *Inorg. Nucl. Chem. Lett.*, **12**, 809 (1976).
- 20) E. K. Barefield and M. T. Mocella, *J. Am. Chem. Soc.*, **97**, 4238 (1975).
- 21) J. A. Switzer and J. F. Endicott, *J. Am. Chem. Soc.*, **102**, 1181 (1980).
- 22) An intramolecular reduction of a cobalt(III) complex of TDHC involving axial cyano ligands has been reported without mechanistic analysis: C. M. Elson, A. Hamilton, and A. W. Johnson, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 775.
- 23) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1417 (1965); **61**, 1674 (1965).
- 24) J. L. Weeks and J. Rabani, *J. Phys. Chem.*, **70**, 2100 (1966).
- 25) D. Behar, G. Czapski, and I. Doehovny, *J. Phys. Chem.*, **74**, 2206 (1970).
- 26) J. P. Henry and A. M. Michelson, in "Superoxide and Superoxide Dismutases," ed by A. M. Michelson, J. M. McCord, and I. Fridovich, Academic Press, London (1977), pp. 283–290 and references therein.
- 27) For one-electron auto-reduction of iron(III)-porphyrin with concomitant oxidation of certain potential ligands to radicals: J. D. Gaudio and G. N. La Mar, *J. Am. Chem. Soc.*, **98**, 3014 (1976); G. N. La Mar and J. D. Gaudio, in "Bioinorganic Chemistry-II," Advances in Chemistry Series 162, ed by K. N. Raymond, American Chemical Society, Washington, D. C. (1977), Chap. 12.
- 28) The data shown in Fig. 2 have a non-zero intercept. This may be due to small rate contribution from scavenging of the hydroxyl radical with the hydrogencarbonate ion and from hydroxide-induced process (Table 1). The hydrogencarbonate-induced process is neglected in order to obtain a reasonable estimate of the scavenging rate constant for the hydroxyl radical with carbonate, the scavenging rate constant with hydrogencarbonate being 28 times smaller than that with carbonate.²⁴⁾
- 29) The linear correlations in Fig. 4 are for the range of $[\text{Co(III)}]/[\text{Co(II)}] \leq 2.5$; i.e., $[\text{Co(II)}] \geq 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ($[\text{Co}]_T = 3.81 \times 10^{-5} \text{ mol dm}^{-3}$); $k_{-1}[\text{Co(II)}] \geq (10^{10})(1.0 \times 10^{-5}) = 10^5$. The product of calculated k_2 and [carbonate] is $(6 \times 10^7)(2.3 \times 10^{-4}) = 1.4 \times 10^4$ or $(2 \times 10^7)(1.7 \times 10^{-3}) = 3.4 \times 10^4$. Thus, the assumption, $k_{-1}[\text{Co(II)}] \gg k_2[\text{carbonate}]$, is satisfied for $2.3 \times 10^{-4} \text{ mol dm}^{-3}$ carbonate and to a lesser extent for $1.7 \times 10^{-3} \text{ mol dm}^{-3}$ carbonate. The calculated k_2 values are one- to two-order of magnitude (if corrected for temperature difference) smaller than that from the pulse radiolysis study. Since the experimental conditions are not identical, the difference may not be meaningful, but it could be due to an oversimplification of the k_{-1} process. The radical pair described as $(\text{Co(II)} + \cdot\text{OH})$ in Eq. 2 would be more accurately represented as $\{\text{Co(II)} \cdot \text{OH}\} \rightleftharpoons \text{Co(II)} + \cdot\text{OH}$; an equilibrium between the intimate radical pair within a common solvent cage and the solvent separated radical pair. Recombination of the Co(II) species and $\cdot\text{OH}$ in the cage would be much faster than in the bimolecular encounter process. If the limiting rate constant k_1 is to represent the true homolytic rate constant (i.e., scavenging of the hydroxyl radical derived therefrom takes place with a 100% efficiency) and if the pulse-radiolysis rate for the scavenging step is the same under the present kinetic conditions, $k_{-1} \cong 10^{11} - 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (regarded as the effective recombination rate constant including the contribution from the in-cage process).
- 30) A. Stanienda and G. Biebl, *Z. Phys. Chem. (Frankfurt am Main) [N. F.]*, **52**, 254 (1967).
- 31) M. Conlon, A. W. Johnson, W. R. Overand, D. Rajapaksa, and C. M. Elson, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 2281.
- 32) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York (1966), p. 43.
- 33) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **70**, 761 (1966).