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

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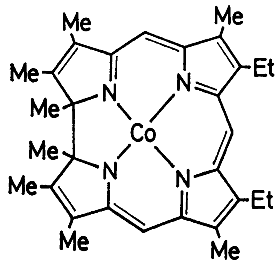
The cobalt(III) complex of tetradehydrocorrin (TDHC), having $\mathrm{p}K_{a1}$ 6.15 and $\mathrm{p}K_{a2}$ 11.50 for successive acid-dissociation of axial aqua ligands, undergoes auto-reduction to the cobalt(II) complex in aqueous carbonate solutions. Kinetic analysis of the reaction indicates the following 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 $[\mathrm{CO_3}^{2-}] \geqq 1.0 \times 10^{-2}$ mol dm^{-3} for $[\mathrm{Co^{III}(TDHC)}]$ of 7.62×10^{-6}—1.27×10^{-5} 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 $\mathrm{Co^{III}(TDHC)}$ is responsible for one-electron oxidation of the hydroxo ligand. Reduction of $\mathrm{Co^{III}(TDHC)}$ 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 $\mathrm{RuO_2}$ which can mediate, when dispersed in aqueous media, oxidation of water to dioxygen by agents which have appropriate redox potentials such as $\mathrm{Ru(bpy)_3}^{3+}$.[11,12)]

Water can be oxidized most readily by a four-electron transfer process from a thermodynamic viewpoint; one-electron oxidation of water ($E^0 = +2.8$ V *vs.* SHE) or even hydroxide ion ($E^0 = +2.0$ V *vs.* SHE) is much less favorable than the four-electron process ($E^0 = +1.229$ 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)-tetradehydrocorrin 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 tetradehydrocorrin 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.



Co(TDHC)

Results

Formation of $Co^{III}(TDHC)$. The cobalt(III) complex of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin (abbreviated as TDHC), $\mathrm{Co^{III}}$(TDHC), was obtained by oxidation of $[\mathrm{Co^{II}(TDHC)}]\mathrm{ClO_4}$[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 ($0.01 \leqq [\mathrm{H^+}] \leqq 0.1$ mol dm^{-3}):[16)] $k/\mathrm{s^{-1}} = 0.29[\mathrm{H^+}]$, as in the case of a related AD–didehydrocorrin 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 $[H_2O_2]$: $k/s^{-1}=2.8\times10^{-3}+k'[H_2O_2]$ at $[H^+]=9.8\times10^{-3}$ mol dm^{-3} where $k'=196$ dm^3 mol^{-1} s^{-1}. The electronic spectrum of Co^{III}(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 Co^{III}(TDHC) in acidic media. The air-oxidation rate of Co^{II}(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, $[(CN)(H_2O)Co^{III}(TDHC)]^+$. This indicates that no cyanide ion is involved in the oxidation of Co^{II}(TDHC) and the oxidation product, $[(H_2O)_2Co^{III}(TDHC)]^{2+}$, is subsequently converted into $[(CN)(H_2O)Co^{III}(TDHC)]^+$.

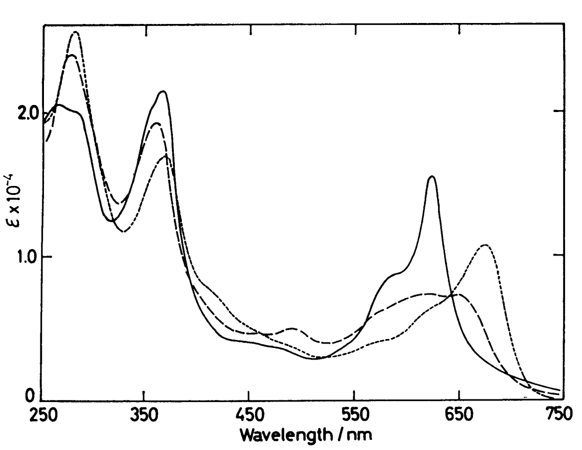
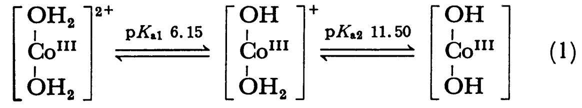


Fig. 1. Electronic absorption spectra of diaqua (——), aquahydroxo (— —), and dihydroxo (······) species of Co^{III}(TDHC) in water–methanol (99.2 : 0.8 v/v) at 10 °C.

The spectral feature of Co^{III}(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 Co^{III}(TDHC) at 10 °C over a wide pH range: pK_{a1} 6.15 and pK_{a2} 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.



$$\begin{bmatrix}OH_2\\Co^{III}\\OH_2\end{bmatrix}^{2+}\xrightleftharpoons{pK_{a1}\ 6.15}\begin{bmatrix}OH\\Co^{III}\\OH_2\end{bmatrix}^{+}\xrightleftharpoons{pK_{a2}\ 11.50}\begin{bmatrix}OH\\Co^{III}\\OH\end{bmatrix}\qquad(1)$$

Carbonate- and Hydroxide-induced Reduction of Co^{III}*(TDHC).* In aqueous carbonate solutions containing methanol (0.8% by volume) at 38.4 °C, Co^{III}(TDHC) underwent facile reduction to Co^{II}(TDHC) in quantitative yield. The product was identified by electronic spectroscopy and vapor pressure osmometric molecular weight determination. It was also converted into $(CN)_2Co^{III}(TDHC)$,[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 Co(III)→Co(II) was followed spectrophotometrically, clear isosbestic points were observed at 264, 354, 443, and 579 nm. At carbonate concentrations greater than 1.0×10^{-2} mol dm^{-3} for $[Co^{III}(TDHC)]$ of 1.27×10^{-5}—7.62×10^{-5} mol dm^{-3}, the reduction of Co^{III}(TDHC) followed first-order kinetics with respect to Co^{III}(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 Co^{III}(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

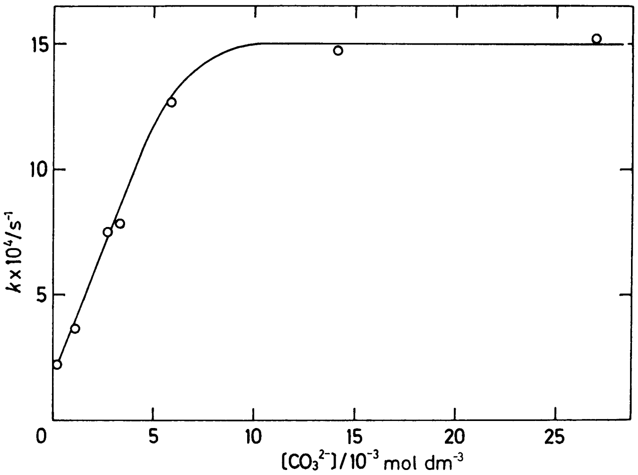


Fig. 2. Correlation of first-order rate constant with carbonate concentration for reduction of Co^{III}(TDHC) in water–methanol (99.2 : 0.8 v/v) at 38.4 °C and pH 9.5±0.2.

Table 1. Apparent first-order rate constants for carbonate- and hydroxide- induced reduction of Co^{III} (TDHC)[a)]

Effective anion	pH	k/s^{-1}
Carbonate (0.11 mol dm^{-3})[b)]	9.3	1.5×10^{-3}
(0.082 mol dm^{-3})[b)]	9.7	1.5×10^{-3}
(0.082 mol dm^{-3})[b)]	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 Co^{III} (TDHC), 3.81×10^{-5} 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)$^{b)}$	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal deg^{-1} mol^{-1}	$\Delta G^{\neq}$ kcal mol^{-1}
1	H_2O–CH_3OH (99.2 : 0.8)	23.9	+4.7	22.4
2	H_2O–CH_3CN–CH_3OH (85.5 : 13.7 : 0.8)	21.6	+1.4	21.2
3	H_2O–CH_3CN–CH_3OH (77.3 : 21.9 : 0.8)	18.7	−6.6	20.8
4	H_2O–t-C_4H_9OH–CH_3OH (77.3 : 21.9 : 0.8)	18.5	−7.1	20.7

a) At 38.4 °C. Initial concentartion of Co^{III} (TDHC), 3.81×10^{-5} mol dm^{-3}. Other experimental conditions ([CO_3^{2-}], 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 [CO_3^{2-}] 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.

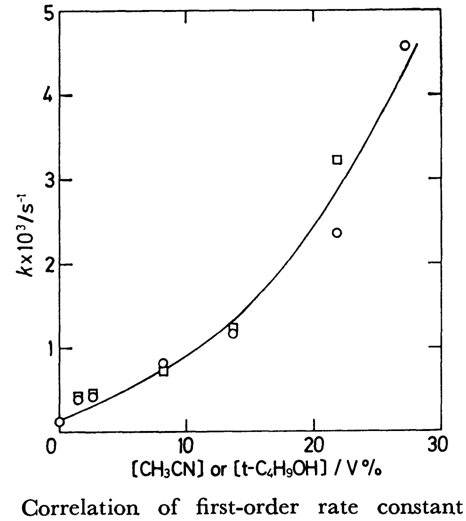


Fig. 3. Correlation of first-order rate constant with content of organic solvents for reduction of Co^{III}-(TDHC) in water–acetonitrile (○) and in water–t-butyl alcohol (□), both containing 0.19 mol dm^{-3} carbonate and 0.8% (v/v) methanol, at 20.0 °C.

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 (+0.59[17] or +0.54 V *vs.* SCE[22] in methanol) of L_2Co^{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 hydroxyl radical with the carbonate ion[27] (Eq. 2).

$$\mathrm{Co(III)\text{-}OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co(II)} + \cdot\mathrm{OH}$$

$$\xrightarrow{k_2[\mathrm{CO_3^{2-}}]} \mathrm{Co(II)} + \mathrm{OH^-} + \mathrm{CO_3^{\cdot-}} \qquad (2)$$

$$(\mathrm{CO_3^{\cdot-}} \longrightarrow \text{further reaction})$$

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 $k_2[\mathrm{CO_3^{2-}}]$ 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 $k_2[\mathrm{CO_3^{2-}}] \gg k_{-1}$, 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, $[\cdot\mathrm{OH}]_{\mathrm{ss}}$, being given by

$$[\cdot\mathrm{OH}]_{\mathrm{ss}} = \frac{k_1[\mathrm{Co(III)}]}{k_{-1}[\mathrm{Co(II)}] + k_2[\mathrm{CO_3^{2-}}]} \qquad (3)$$

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

$$-\frac{\mathrm{d[Co(III)]}}{\mathrm{d}t} = k_1[\mathrm{Co(III)}] - k_{-1}[\mathrm{Co(II)}][\cdot\mathrm{OH}]_{\mathrm{ss}}$$

$$= k_2[\mathrm{CO_3^{2-}}][\cdot\mathrm{OH}]_{\mathrm{ss}}$$

$$= \frac{k_1k_2[\mathrm{Co(III)}][\mathrm{CO_3^{2-}}]}{k_{-1}[\mathrm{Co(II)}] + k_2[\mathrm{CO_3^{2-}}]} \qquad (4)$$

kinetics is derived under the conditions $k_2[\mathrm{CO_3^{2-}}] \gg k_{-1}[\mathrm{Co(II)}]$ with first-order rate constant k_1. Under the other extreme conditions as represented by $k_{-1}[\mathrm{Co(II)}] \gg k_2[\mathrm{CO_3^{2-}}]$, 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]

$$-\frac{\mathrm{d[Co(III)]}}{\mathrm{d}t} = \frac{k_1k_2}{k_{-1}}[\mathrm{CO_3^{2-}}]\frac{[\mathrm{Co(III)}]}{[\mathrm{Co(II)}]} \qquad (5)$$

$$\left[[\mathrm{Co(III)}] - [\mathrm{Co(III)}]_0 \ln[\mathrm{Co(III)}]\right]_0^t = \frac{k_1k_2}{k_{-1}}[\mathrm{CO_3^{2-}}]t \qquad (6)$$

Except for the early stage of reaction, a plot of $-\mathrm{d[Co(III)]}/\mathrm{d}t$ *vs.* [Co(III)]/[Co(II)] yielded a straight line with the slope $k_1k_2[\mathrm{CO_3^{2-}}]/k_{-1}$ (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.*, $k_{-1} \cong 10^{10}$ dm^3 mol^{-1} s^{-1}. The k_2 values are calculated to be: 6×10^7 and 2×10^7 dm^3 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 dm^3 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 with a highly endothermic unimolecular dissociation process.

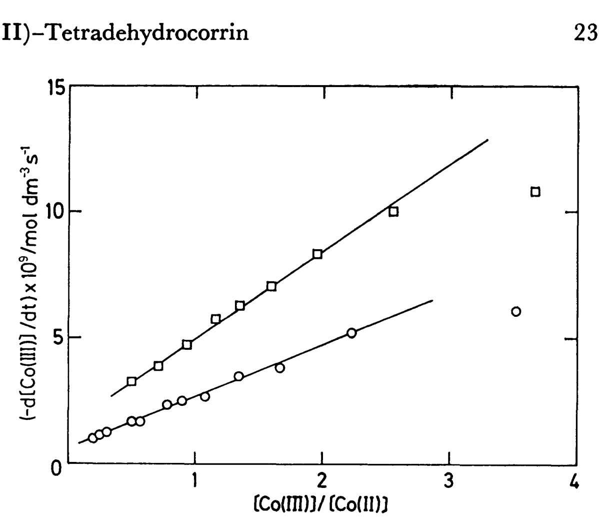


Fig. 4. Analysis of kinetic data (Eq. 5) for reduction of $\mathrm{Co^{III}}$(TDHC) in water–methanol (99.2 : 0.8 v/v) in the presence of 2.3×10^{-4} mol dm^{-3} (○) and 1.7×10^{-3} mol dm^{-3} (□) carbonate at 38.4 °C.

Correlation with Electrode Potentials. Judging from the Co(II)/Co(III) redox potential for $\mathrm{Co^{II}}$(TDHC) in methanol (+0.59[17] or 0.54 V *vs.* SCE[22]) 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 $\mathrm{L_2Co^{III}}$(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 hydroxo ligand can be regarded, from a thermodynamic viewpoint, as an oxidation of the coordination-free hydroxide ion by *naked* $\mathrm{Co^{III}}$(TDHC) whose Co(II)/Co(III) potential may be assumed equivalent to that in a noncoordinating solvent; +0.97 V *vs.* SCE in $\mathrm{CH_2Cl_2}$.[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), $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$, 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* $\mathrm{Co^{III}}$(TDHC) (*Co(III)*) and $\mathrm{OH^-}$ followed by scavenging of the hydroxyl radical with the carbonate ion as given by Eq. 7.

$$\mathit{Co(III)} + \mathrm{OH^-} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{Co(II)} + \cdot\mathrm{OH}$$

$$\xrightarrow{k_2[\mathrm{CO_3^{2-}}]} \mathrm{Co(II)} + \mathrm{OH^-} + \mathrm{CO_3^{\cdot-}} \qquad (7)$$

Under the conditions where scavenging is the rate-determining process, the apparent first-order rate constant is given by $(k_1'/k_{-1}')k_2[\mathrm{CO_3^{2-}}]$; $(k_1'/k_{-1}')k_2$ corresponds to the slope (0.21 dm^3 mol^{-1} s^{-1}) of the linear portion of rate constant *vs.* $[\mathrm{CO_3^{2-}}]$ profile in Fig. 2. If k_2 is taken for the range of 6×10^7 (calculated as above) through 1×10^9 dm^3 mol^{-1} s^{-1} (based on pulse radiolysis), the hypothetical equilibrium constant,

$K=k_1'/k_{-1}'$, would be in the range 3.5×10^{-9}—2.1×10^{-10}. A value of 1.23—1.16 V *vs.* SCE is obtained for $E_{\mathrm{Co(II)/Co(III)}}$ at 38.4 °C ($E_{\mathrm{OH^-/\cdot OH}}=+2.0$ V *vs.* SHE) by means of

$$-RT\ln K=\Delta G^0=F(E_{\mathrm{OH^-/\cdot OH}}-E_{\mathrm{Co(II)/Co(III)}}), \qquad (8)$$

where F and E denote Faraday constant and electrode potential, respectively. The redox potential is consistent with the kinetic parameters based on Eq. 7 and close to the observed one in CH_2Cl_2 (+0.97 V *vs.* SCE). The argument may indicate that the one-electron oxidation of the hydroxide ion can be expected in the light of powerful oxidation capacity of $\mathrm{Co^{III}}$(TDHC). In fact, the Co(II)/Co(III) redox potential of +0.97 V *vs.* SCE seems exceptional for the cobalt complexes of pyrrole pigments; +0.3 V for Co(etioporphyrin) in butyronitrile[30] and −0.26 V for Co(octaalkylcorrole) in CH_2Cl_2.[31]

Effects of Organic Cosolvents. Acetonitrile and *t*-butyl alcohol are known as potential hydroxyl radical scavengers. The scavenging efficiency of such solvents, however, does not seem to be the primary origin for the rate acceleration (Fig. 3) since the presence of sufficient amount of carbonate (0.19 mol dm^{-3}) assures that we are dealing with the rate-determining homolytic k_1 process which is free from the scavenging effect exercised by such organic solvents. Thus, the rate acceleration by organic cosolvents added must be solely due to their medium effects. The solvation status must change along the Co(III)–OH bond homolysis from highly solvated anionic hydroxo ligand at the initial state to the neutral hydroxyl radical which requires less solvation by water. As the content of an organic solvent increases, solvation of the hydroxo ligand becomes less effective with the consequence that the hydroxo ligand is less stabilized on the one hand and the surrounding water molecules get more translational freedom on the other at the ground state of reaction, resulting in the reduction of activation enthalpy with the compensating change in activation entropy. This is what was observed (Table 2). A major contributor to the potential energy to be overcome in the oxidation of both hydroxide ion and hydroxo ligand would be the stabilization of the ground state through solvation of such reactants. Desolvation of both hydroxide ion and hydroxo ligand, even to a small extent, would result in significant enhancement of their oxidation since the hydration energy of the hydroxide ion in water is greater than 100 kcal mol^{-1}.[32]

Reduction of $\mathit{Co^{III}}$(TDHC) without Radical Scavenger. Concerning the reduction of $\mathrm{Co^{III}}$(TDHC) in the pH range 11—12 (Table 1) in the absence of the carbonate ion or other potential anions, the following remarks are given. (1) The reaction is photo-catalyzed in a manner similar to that in the carbonate system; (2) in reference to the mechanism for the carbonate system (Eq. 2), the hydroxide ion can never be regarded as a hydroxyl radical scavenger; and (3) the reaction rate increases with increasing [OH^-], approaching the limiting value for the carbonate-induced reaction. The pH-rate correlation seems to reflect the proton dissociation equilibrium (inactive form$\rightleftharpoons$active form+H^+) with pK_a around 11.5. This can not be referred to the conversion from the aquahydroxo into the dihydroxo form (Eq. 1) with pK_{a2} 11.50 in spite of numerical coincidence, since a sharp rate reduction is observed at pH 13.1 where the dihydroxo species predominates (Table 1). Thus, the reactive species should be the aquahydroxo species whose population becomes smaller while the overall rate constant increases with increasing pH. As an alternative and highly plausible equilibrium, we suggest the proton-dissociation of the hydroxyl radical whose pK_a is 11.8.[24] The hydroxyl radical is a super-oxidant and its most likely fate in the absence of its scavenger would be recombination with the Co(II) complex, *i. e.*, oxidation of the Co(II) species by the hydroxyl radical. This reverse process would not be effective for the anionic conjugate base ($\mathrm{O}^{\bar{\cdot}}$) which is considered to be a far less effective oxidant. Under these circumstances, the dimerization of $\mathrm{O}^{\bar{\cdot}}$ to peroxide, a well characterized reaction,[33] may compete with the backward recombination of the hydroxyl radical with the Co(II) species

$$\mathrm{H_2O\text{-}Co(III)\text{-}OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2O\text{-}Co(II)} + \cdot\mathrm{OH}$$

$$\underset{-\mathrm{OH^-};\ k_{-2}'}{\overset{\mathrm{OH^-};\ k_2'}{\rightleftharpoons}} \mathrm{H_2O\text{-}Co(II)} + \begin{array}[t]{l}\mathrm{O}^{\bar{\cdot}}\\ \llcorner\!\!\longrightarrow \mathrm{H_2O_2}\end{array} + \mathrm{H_2O} \qquad (9)$$

(Eq. 9). This mechanism is consistent with the observed pH-dependence of reaction rate for the pH range 11—12. It involves the deprotonation of the hydroxyl radical and its subsequent reaction, and is thus important for water oxidation since the process requires no additional radical scavengers. It is unfortunate that the accidental coincidence of the pK_a values of the second aqua ligand of the complex and the hydroxyl radical makes a detailed analysis of the kinetic data difficult.

Conclusion

(1) One-electron oxidation of a hydroxo ligand coordinated to $\mathrm{Co^{III}}$(TDHC) does take place in aqueous media. The Co(III)–OH bond undergoes homolytic cleavage to yield the hydroxyl radical first. This is an effective and conventional process for water oxidation. (2) For effective progress of the reaction, there must be some mechanism by which the back recombination of the hydroxyl radical and the Co(II) species can be prevented or depressed. (3) Oxidation of the hydroxide ion and possibly other anions, coordinated or not coordinated to metal complexes, may be accelerated by addition of organic cosolvents to aqueous media *via* a desolvation mechanism.

Experimental

Instruments and Materials. Electronic spectra were obtained with thermostated quartz cells (1-cm path length) set in either a Union Giken SM-401 high sensitive spectrophotometer or a Hitachi 124 spectrophotometer. ^{1}H NMR spectra were taken on a Hitachi R-24B spectrometer with tetramethylsilane as an internal reference. A Hitachi-Perkin Elmer 115 vapor pressure osmometer was used to determine molecular weights. pH-Measurements were carried out with a Beckman Expandomatic SS-2 pH meter equipped with a Metrohm EA-125 combined electrode, calibrated against standard aqueous buffers.

(8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(II) perchlorate, [Co^{II}(TDHC)]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 $C_{31}H_{37}ClCoN_4O_4$: 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 Co^{III}(TDHC) and Acid Dissociation of Its Diaqua Complex. Oxidation of a reddish-purple solution of [Co^{II}(TDHC)]ClO$_4$ by three different oxidants (air, hypochlorite, and chlorine) under acidic conditions gave a greenish-blue solution of Co^{III}(TDHC) as confirmed by electronic spectroscopy. For air oxidation, the simplest procedure, a methanol solution of Co^{II}(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 Co^{II}(TDHC) (4.65×10^{-3} 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 Co^{II}(TDHC) (4.65×10^{-3} mol dm^{-2}, 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±0.1 °C; the absorbance change at 490 nm then being measured at the same temperature. As regards the preparative scale experiment, 15 mg (2.4×10^{-5} mol) of Co^{II}(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. Co^{III}(TDHC) was relatively stable only when diluted in acidic aqueous media and quite readily reconverted into the original Co(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 Co^{II}(TDHC)), and evaporation of aqueous solutions (with complete conversion into Co^{II}(TDHC)).

Spectra were recorded for a series of solutions of Co^{III}(TDHC) (2.79×10^{-5} mol dm^{-3}) in aqueous buffers at various pH (2.13—13.45) and at 10.0 °C. The absorbance at 620 nm ($2.13\leq\mathrm{pH}\leq10.22$) or at 670 nm ($8.10\leq\mathrm{pH}\leq13.45$) 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 Co^{III}(TDHC) were prepared by mixing 30 μl of a methanol solution of Co^{II}(TDHC) (4.65×10^{-3} 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$_2$CO$_3$–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 3.81×10^{-5} mol dm^{-3} of Co^{III}(TDHC). The course of reaction was followed by monitoring the absorbance change at 490 nm (an absorption maximum for Co^{II}(TDHC)). The concentrations of carbonate ion were calculated from the known amounts of ($[CO_3^{2-}]+[HCO_3^-]$) 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 [Co(II)] and [Co(III)] first at an appropriate time interval and then taking the average value for each time interval (Δt): $-\mathrm{d}[\mathrm{Co(III)}]/dt=([\mathrm{Co(III)}]_t-[\mathrm{Co(III)}]_{t+\Delta t})/\Delta t$; $[\mathrm{Co(III)}]/[\mathrm{Co(II)}]=([\mathrm{Co(III)}]_t+[\mathrm{Co(III)}]_{t+\Delta t})/([\mathrm{Co(II)}]_{t+\Delta t}+[\mathrm{Co(II)}]_t)$. Activation parameters were calculated as follows: $E_a=\Delta H^{\neq}+RT$ (E_a, activation energy from Arrhenius plot), $k_{38.4\,^\circ\mathrm{C}}=(\mathbf{k}T/h)\text{-}\exp(-\Delta G^{\neq}/RT)$, and $\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq}$.

Reduction of Co^{III}(TDHC) in Carbonate Solutions: Formation of Co^{II}(TDHC). A solution of Co^{III}(TDHC), prepared from [Co^{II}(TDHC)]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$_2$CO$_3$ 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 Co(III)→Co(II) conversion, and then extracted with dichloromethane (100 ml×2). The extract was washed with a saturated NaClO$_4$ solution (50 ml), dried (Na$_2$SO$_4$), and evaporated to give [Co^{II}(TDHC)]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 Co(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 (CN)$_2$Co^{III}(TDHC)[15] (17 mg, 65% from the initial Co(II) complex): electronic and NMR spectra were identical with those of the authentic sample. ^{1}H 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, $C\underline{H}_2CH_3$), 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, $CH_2C\underline{H}_3$), and 0.76 (s, 6H, CH$_3$'s on C(1) and C(9)).

Reduction of Co^{III}(TDHC) in the Absence of Carbonate: Detection of Hydrogen Peroxide. A solution of Co^{III}(TDHC), prepared in a manner similar to that described above by air oxidation of Co^{II}(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.* 1×10^{-3} mol dm^{-3} in Co^{III}(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 Co^{II}(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$_2$SO$_4$ (2 ml) were added. After being bubbled with argon for 5 min, the mixture was titrated with 5.0×10^{-3} mol dm^{-3} aqueous Na$_2$S$_2$O$_3$; 30% yield at best on the basis of the Co(III) complex used. The low yield of hydrogen peroxide was at least due to its further reaction with Co^{II}(TDHC) to give unidentified product(s), as independently confirmed by spectrophotometric means.

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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 $[\mathrm{Co(III)}]/[\mathrm{Co(II)}] \leqq 2.5$; *i.e.*, $[\mathrm{Co(II)}] \geqq 1.0\times10^{-5}$ mol dm^{-3} ($[\mathrm{Co}]_T = 3.81\times10^{-5}$ mol dm^{-3}); $k_{-1}[\mathrm{Co(II)}] \geqq (10^{10})(1.0\times10^{-5}) = 10^5$. The product of calculated k_2 and [carbonate] is $(6\times10^7)(2.3\times10^{-4}) = 1.4\times10^4$ or $(2\times10^7)(1.7\times10^{-3}) = 3.4\times10^4$. Thus, the assumption, $k_{-1}[\mathrm{Co(II)}] \gg k_2$[carbonate], is satisfied for 2.3×10^{-4} mol dm^{-3} carbonate and to a lesser extent for 1.7×10^{-3} 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 $(\mathrm{Co(II)} + \cdot\mathrm{OH})$ in Eq. 2 would be more accurately represented as $\{\mathrm{Co(II)}\cdot\mathrm{OH}\} \rightleftharpoons \mathrm{Co(II)} + \cdot\mathrm{OH}$; 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 $\cdot$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} dm^3 mol^{-1} s^{-1} (regarded as the effective recombination rate constant including the contribution from the in-cage process).

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