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Disproportionation and Reduction of (tetradehydrocorrinato)cobalt Complexes in Alkaline Aqueous Media[†]

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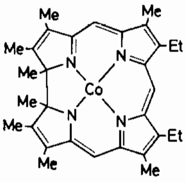
Photosynthetic energy conversion involves, as a key step, the photo-induced charge separation through electron transfer processes affording a pair of oxidant and reductant [1, 2]. We are currently making an alternative approach in place of the photo-induced mechanism; utilization of metal-ion disproportionation ($2M^{n+} \rightleftharpoons M^{(n+1)+} + M^{(n-1)+}$) which also produces a pair of oxidant ($M^{(n+1)+}$) and reductant ($M^{(n-1)+}$) simultaneously. The first unambiguous evidence is reported here for the disproportionation of a cobalt(II) complex of N_4-macrocycle along with further reduction of the resulting cobalt(III) complex. Schrauzer and Windgassen [3] suggested the disproportionation of vitamin B_{12r} and cobaloxime(II) in strongly alkaline media, based on indirect spectral evidence. Fukui and his collaborators [4] also claimed the disproportionation of B_{12r} occurred, on the basis of other observations; a mixture of B_{12r} and methyl iodide in aqueous electrolyte solution at neutral pH was converted to an equimolar mixture of B_{12a} and the methyl-cobalt derivative. However, a thorough kinetic analysis of the related alkylation reactions of B_{12r} led to a quite different conclusion which does not invoke the disproportionation [5]. Similarly, an early proposal made by Schrauzer as regards the disproportionation of cobaloxime(II) [3] has been disproved recently in the light of detailed kinetic analysis of the reaction concerned [6].



Co(TDHC)

Experimental

The Co(II) and Co(III) complexes of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin (TDHC), $[Co(II)(TDHC)]ClO_4$ and $[(OH_2)_2Co(III)(TDHC)]Cl_2$, were prepared as described previously [7]. Electronic spectra were obtained with a Union Giken SM-401 high sensitive spectrophotometer.

Auto-reduction of $(OH)_2Co(III)(TDHC)$ was initiated by injection of an appropriate amount of aqueous NaOH (18.8 *M*) to an aqueous solution of $[(OH_2)_2Co(III)(TDHC)]^{2+}$ [7] containing a small amount of methanol. Auto-reduction of $(OH)_2Co(III)(TDHC)$ derived from disproportionation of Co(II)(TDHC) was initiated by injection of a methanol solution of Co(II)(TDHC) to water containing an appropriate amount of NaOH. In kinetic runs of both auto-reduction reactions, the final solutions were adjusted to contain 0.8% (v/v) methanol and 3.81×10^{-5} *M* of the cobalt complex. Methanol as a co-solvent could be eliminated without affecting the reaction rate. The reduction of the Co(III) complex was followed spectrophotometrically by monitoring the absorbance change at 675 nm [an absorption maximum for $(OH)_2Co(III)(TDHC)$] or 530 nm (an absorption maximum for Co(I)(TDHC)].

Rapid reaction between $(OH)_2Co(III)(TDHC)$ and $HS(CH_2)_2OH$ was measured with a Union Giken RA-401 stopped flow spectrophotometer: equal volumes of a solution of $(OH)_2Co(III)(TDHC)$ (1.69×10^{-4} *M*) in water–methanol (97.4: 2.6 v/v), which contained 7.6×10^{-2} *M* of the hydroxide ion, and an aqueous solution of $HS(CH_2)_2OH$ (an appropriate amount) were rapidly mixed to initiate the reaction.

Activation parameters were calculated by utilizing relations: $E_a = \Delta H^{\ddagger} + RT$ (E_a, activation energy from Arrhenius plot); $k = (kT/h)\exp(-\Delta G^{\ddagger}/RT)$, and $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ at 38.4 °C.

Results and Discussion

In strongly alkaline aqueous media ($[OH^-] \geqq 1$ *M*) containing 1% (v/v) methanol at 3 °C, Co(II)(TDHC) [7–9] underwent instantaneous and complete disproportionation to an equimolar mixture of well-characterized Co(I) (TDHC) [10, 11] and $(OH)_2$-Co(III) (TDHC) (the hydroxo ligands being at the axial sites) [7]. The electronic spectrum of the resulting solution exhibited all of the characteristic features of the Co(I) and Co(III) species and was superimposable on the calculated spectrum for the equimolar mixture of these two complexes (Fig. 1). The disproportionation mixture underwent no further

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TABLE I. Fractions of Co(I), Co(II), and Co(III) Complexes of TDHC in water–methanol (99%:1 v/v at 3 °C.[a]

$[OH^-]/M$	$[Co(I)]/M$	$[Co(III)]/M$	$[Co(II)]/M$	K/M^{-2} [b]
1.03×10^{-1}	2.64×10^{-5}	2.64×10^{-5}	1.10×10^{-5}	546
7.76×10^{-2}	2.51×10^{-5}	2.51×10^{-5}	1.36×10^{-5}	563
5.15×10^{-2}	2.255×10^{-5}	2.255×10^{-5}	1.87×10^{-5}	548

[a] Total concentration of the cobalt species. 6.38×10^{-5} *M*. [b] $K = [Co(III)][Co(I)] \& [Co(II)]^2 [OH^-]^2$.

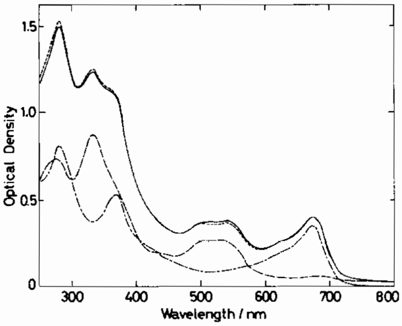

Fig. 1. Electronic absorption spectra of cobalt complexes in water–methanol (99:1 v/v) at 3 °C: ———, Co(II)(TDHC) (6.38×10^{-5} *M*) after disproportionation at $[OH^-] = 1.0$ *M*; –·–, $(OH)_2Co(III)(TDHC)$ (3.19×10^{-5} *M*) at $[OH^-] = 0.2$ *M*; – – –, Co(I)(TDHC) (3.19×10^{-5} *M*) at $[OH^-] = 0.1$ *M*; ------, calculated spectrum for a solution containing $(OH)_2Co(III)(TDHC)$ (3.19×10^{-5} *M*) and Co(I)(TDHC) (3.19×10^{-5} *M*).

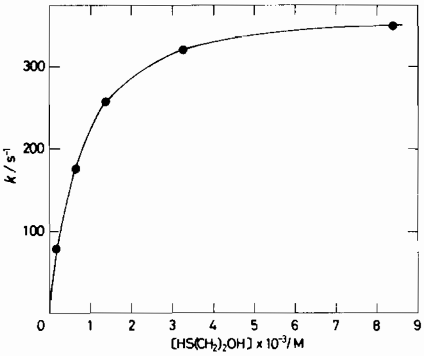

Fig. 2. Correlation of pseudo-first-order rate constant for reduction of $(OH)_2Co(III)(TDHC)$ (8.45×10^{-5} *M*) with concentration of $HS(CH_2)_2OH$ at 1.5 °C in water–methanol (98.7:1.3 v/v) containing 3.8×10^{-2} *M* of the hydroxide ion.

reaction at 3 °C (*vide infra*). At lower concentrations of the hydroxide ion, the disproportionation was incomplete. Analysis of the compositions of Co(I), Co(II), and Co(III) complexes was performed in reference to the absorbance change at 675 nm (Table I), the stoichiometry being established by eqn. (1): 552 M^{-2} as an average value at 3 °C for $K = [(OH)_2Co(III)(TDHC)][Co(I)(TDHC)]/[Co(II)(TDHC)]^2[OH^-]^2$.

$$2Co(II)(TDHC) + 2OH^- \overset{K}{\rightleftharpoons} (OH)_2Co(III)(TDHC) + + Co(I)(TDHC) \qquad (1)$$

The tervalent cobalt complex, $(OH)_2Co(III)(TDHC)$, underwent reduction quite readily to afford Co(I)(TDHC) upon treatment with a thiol. The reduction with excess $HS(CH_2)_2OH$ was investigated in some detail at 1.5 ± 0.4 °C by the stopped flow technique following the absorbance decay at 675 nm for the Co(III) complex: initial concentrations in water–methanol (98.7:1.3 v/v); $(OH)_2Co(III)(TDHC)$ 8.45×10^{-5} *M*, OH^- 3.8×10^{-2} *M*. A correlation between pseudo-first-order rate constant (as regards the cobalt complex) and initial thiol concentration is shown in Fig. 2; a rate constant at the saturation range being *ca.* 350 s^{-1} [2 ms half-life with respect to the Co(III) complex] and an apparent second-order rate constant at lower thiol concentrations *ca.* 5×10^5 M^{-1} s^{-1}. The saturation-type correlation indicates the existence of pre-equilibrium formation of the thiol adduct, followed by intramolecular electron transfer from the thiol to the cobalt species. Such being the case, the rate enhancement along with an increase of thiol concentration is primarily due to the increase in a fraction of the thiol adduct and the reaction rate at saturation level may be referred to the electron transfer process. An alternative mechanism involves a pre-equilibrium ligand dissociation to give penta-coordinate intermediate which may be either re-converted to the original hexa-coordinate species or reduced with the thiol. In the light of the latter mechanism, the saturated rate is referred to the rate-determining ligand dissociation process.

In the absence of any additional reductant, $(OH)_2Co(III)(TDHC)$, either prepared by oxidation of Co(II)(TDHC) or derived from disproportionation of Co(II)(TDHC) as above, was observed to undergo auto-reduction to Co(I)(TDHC) in strongly alkaline

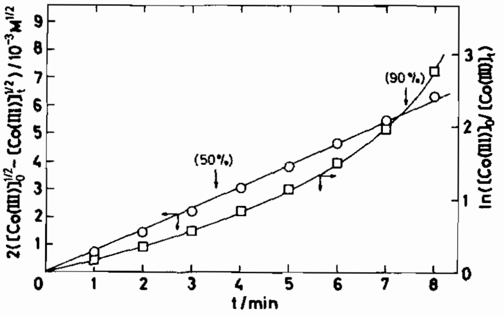

Fig. 3. Analysis of kinetic data for reduction of $(OH)_2Co$(III)(TDHC) in water–methanol (99.2:0.8 v/v) containing 1.2 *M* of the hydroxide ion at 38.4 °C; half-order plot (○) and first-order plot (□). Percentage numerals in parentheses indicate the conversion rates of the cobalt(III) complex.

aqueous media ($[OH^-] \geq 1$ *M*) at higher temperature (20–40 °C). The conversion from Co(III) to Co(I) species exhibited good spectral behavior accompanied with clear isosbestic points at 306, 597 and 703 nm, and followed some complicated kinetics as shown by eqn. (2). Plot of $2([Co(III)]_0^{1/2} - [Co(III)]_t^{1/2})$ *vs.* time (t) at

$$-d[Co(III)]/dt = k[Co(III)]^{1/2}[OH^-]^2 \qquad (2)$$

a fixed hydroxide-ion concentration gave a straight line throughout the run up to almost 100% conversion (Fig. 3), and the slope ($k' = k[OH^-]^2$) was correlated linearly with $[OH^-]^2$ as shown in Fig. 4; Co(III) stands for $(OH)_2Co$(III)(TDHC). Figure 3 also includes the first-order plot, $\ln([Co(III)]_0/[Co(III)]_t)$ vs. t; a serious deviation from linearity being evident. All the rate data in Fig. 4 are satisfactorily placed on a single line irrespective of the methods for formation of the Co(III) complex (oxidation or disproportionation of the Co(II) species); the slope in Fig. 4 providing $k = 6.7 \times 10^{-6}$ $M^{-3/2}$ s^{-1} at 38.4 °C. The temperature dependence (20–38.4 °C) of k allows to evaluate the activation parameters: $\Delta H^{\ddagger}$, 20.0 kcal mol^{-1}; $\Delta S^{\ddagger}$, −18.5 cal deg^{-1} mol^{-1}. The apparent two-electron reduction of $(OH)_2Co$(III)(TDHC) under strongly alkaline conditions seems not to involve the Co(III)–OH bond homolysis in a marked contrast to the kinetic behavior of $[(OH_2)(OH)Co(III)(TDHC)]^+$ [7]: the present reaction rate exhibits strong dependency on the hydroxide-ion concentration (eqn. (2)), and is not influenced by the presence of the carbonate ion, a powerful hydroxyl radical scavenger.

The reaction with which we are presently concerned may bear a closer resemblance to the reductions of the tris(2,2′-bipyridine) and tris(1,10-phenanthroline) complexes of iron(III) [12], osmium(III) [12, 13], and ruthenium(III) [14] to the corresponding bivalent metal complexes. The simplest mechanism in our favor, consistent with the observed kinetics (eqn. (2)), is given by eqns. (3)–(5).

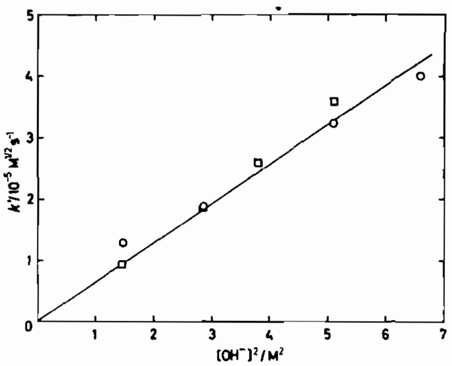

Fig. 4. Correlation of apparent half-order rate constant k′ ($\approx k[OH^-]^2$) with $[OH^-]^2$ for reduction of $(OH)_2Co$(III)(TDHC) in water–methanol (99:1 v/v) at 38.4 °C: Co(III) (TDHC) used; by disproportionation (○), and by direct oxidation of Co(II)(TDHC) (□) [refer to eqn. (2)].

$$[Co(III)]_2 \overset{K_d}{\rightleftharpoons} 2Co(III) \qquad (3)$$

$$Co(III) \overset{OH^-}{\rightleftharpoons} [Co(III){-}OH^- \leftrightarrow Co(I){-}OH^+] \qquad (4)$$

$$[Co(III){-}OH^- \leftrightarrow Co(I){-}OH^+] \xrightarrow{OH^-} Co(I) + H_2O_2 \qquad (5)$$

This mechanism assumes that Co(III)(TDHC) in strongly alkaline media exists practically as a dimer, $[Co(III)]_2$, which is in equilibrium with two molecules of the active monomer (eqn. (3)) so that $[Co(III)] = (\frac{1}{2})K_d[Co(III)]_T^{1/2}$; T stands for total concentration. The assumption of the initial existence of a dimer species is somewhat obligatory in order to explain the half-order kinetic dependence on $[Co(III)]_T$. Furthermore, the dimer formation has many and good precedents in porphyrin and phthalocyanin chemistry [15]. The mode of dimerization would be a simple association [15] or, instead, involve a covalent linkage such as a μ-oxo bridge prominent for ferric porphyrin in alkaline solutions [15].

The monomer is then reduced by successive attack of two molecules of OH^-. The first step (eqn. (4)) is the reversible association of OH– with the Co(III) species, and then the resulting adduct undergoes the rate-determining reaction with the second OH^- in the second step [equation (5)]. Such a rate-determining process is consistent with the observed large negative entropy of activation. Reactions of the iron(III), osmium(III), and ruthenium(III) complexes cited above with the hydroxide ion have been claimed to involve addition of OH^- to the unsaturated ligands.

Reduction of metal complexes with the hydroxide ion (or ideally water) may constitute a half reaction of water splitting into oxygen and hydrogen molecules. The most important finding in the present study is that such a powerful oxidant as $(OH)_2Co$-

(III)(TDHC) can be derived from disproportionation of the corresponding Co(II) complex without retroreaction with its reductant partner Co(I)(TDHC) to the original Co(II) complex in strongly alkaline media. It is interesting to note that an artificial photosynthesis system of wide use in these days involves photoinduced electron transfer from a donor (*e.g.*, a Ru(II) complex) to an acceptor (*e.g.*, dialkylviologen dication). Such a donor-acceptor reaction process is considered to stand as a reference to the present disproportionation reaction. However, a special device is required to avoid the thermal retro-electron transfer [16] between the resulting Ru(III) complex and the viologen cation radical so that the charge separation is effectively performed [17].

References

1 (a) J. Kiwi and M. Grätzel, *Angew. Chem., 91,* 659 (1979);
(b) K. Kalyanasundaram and M. Grätzel, *ibid., 91,* 759 (1979).
2 J.-M. Lehn, J. P. Sauvage and R. Ziessel, *Nouv. J. Chim., 3,* 423 (1979).
3 (a) G. N. Schrauzer and R. J. Windgassen, *Chem. Ber., 99,* 602 (1966);
(b) G. N. Schrauzer, *Acc. Chem. Res., 1,* 97 (1968).
4 R. Yamada, S. Shimizu and S. Fukui, *Biochemistry, 7,* 1713 (1968).
5 H.-U. Blaser and J. Halpern, *J. Am. Chem. Soc., 102,* 1684 (1980).
6 L. I. Simándi, S. Németh and É. Budózáhonyi, *Inorg. Chim. Acta, 45,* L143 (1980).
7 Y. Murakami, Y. Aoyama and T. Tada, *Bull. Chem. Soc. Jpn.,* in press.
8 D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson and I. T. Kay, *J. Chem. Soc. (C),* 30 (1966).
9 Y. Murakami, K. Sakata, Y. Tanaka and T. Matsuo, *Bull. Chem. Soc. Jpn., 48,* 3622 (1975).
10 N. S. Hush and I. S. Woolsey, *J. Am. Chem. Soc., 94,* 4107 (1972).
11 Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Jpn., 49,* 683 (1976).
12 G. Nord and O. J. Wernberg, *J. Chem. Soc., Dalton Trans.,* 866 (1972).
13 G. Nord and O. J. Wernberg, *J. Chem. Soc., Dalton Trans.,* 845 (1975).
14 C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A., 72,* 2858 (1975).
15 P. Hambright, in 'Porphyrins and Metalloporphyrins', K. M. Smith, Ed., Elsevier Scientific Publishing Co., Amsterdam (1975) pp. 265–268.
16 R. C. Young, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc., 98,* 286 (1976).
17 P.-A. Brugger and M. Grätzel, *J. Am. Chem. Soc., 102,* 2461 (1980).