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Electrochemical Carbon-Skeleton Rearrangements as Catalyzed by Cyano-Coordinated Hydrophobic Vitamin B_{12}

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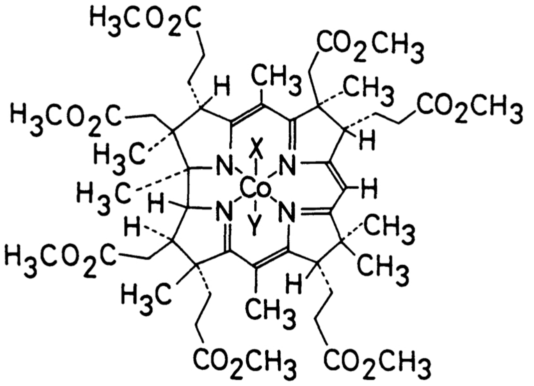
Electrochemical carbon-skeleton rearrangements catalyzed by heptamethyl cobyrinate perchlorate proceeded more efficiently upon coordination of the cyanide ion to the central cobalt atom, and such enhanced catalysis was originated from facilitated formation of an anionic intermediate.

We have prepared hydrophobic vitamin B_{12} derivatives in order to simulate various functions of vitamin B_{12} exerted in the hydrophobic reaction sites of enzymes concerned1) and investigated their catalytic reactions.2) We have previously demonstrated for the first time that the carbon-skeleton rearrangements, which are characteristic reactions mediated by vitamin B_{12}-dependent enzymes, were catalyzed by a vitamin B_{12} model under electrochemical conditions.3) We have also postulated that the electrochemical carbon-skeleton rearrangements proceed through the formation of anionic intermediates. Meanwhile, Schrauzer et al. reported that coordination of the cyanide ion to methylcobalamin or methylcobaloxime at the cobalt atom resulted in an increase in electron density at the metal atom and favored reduction of the methyl group to give the corresponding carbanion upon photolysis.4,5) Therefore, the cyano-coordinated hydrophobic vitamin B_{12} is expected to enhance the formation of anionic intermediates during the electrolysis. In this regard, we investigated here the cyanide-coordination effect on the electrochemical carbon-skeleton rearrangements as catalyzed by a hydrophobic vitamin B_{12}.

The redox behavior of heptamethyl cobyrinate perchlorate, [Cob(II)7C_1ester]ClO_4, has been clarified previously,6) but those of heptamethyl cyanoaquacobyrinate



[Cob(II)7C_1ester]ClO_4: X = Y = None

$(CN)_2$Cob(III)7C_1ester: X = Y = CN

[(CN)(H_2O)Cob(III)7C_1ester]ClO_4: X = CN,
Y = H_2O

[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4: X = CH_3,
Y = H_2O

perchlorate, [(CN)(H_2O)Cob(III)7C_1ester]ClO_4, and heptamethyl dicyanocobyrinate, $(CN)_2$Cob(III)7C_1ester, have not been examined yet. Thus, the redox behaviors of these hydrophobic vitamin B_{12}'s having one and two cyano groups were investigated in this study. Cyclic voltammograms of [(CN)(H_2O)Cob(III)7C_1ester]ClO_4 and $(CN)_2$-Cob(III)7C_1ester in N,N-dimethylformamide (DMF) are shown in Fig. 1. The cyclic voltammogram of [Cob(II)7C_1ester]ClO_4 showed two simple redox couples assigned to Co(III)/Co(II) and Co(II)/Co(I),6) but those for the cyano-coordinated complexes are rather complicated (Fig. 1). In order to identify the complex species formed during each redox cycle, the controlled-potential electrolyses were performed. We assigned observed redox peaks as indicated in Fig. 1. These redox behaviors are similar to those observed for cyanocobalamin and dicyanocobalamin reported by Lexa et al.7,8) The Co(II)/Co(I) redox potential for [Cob(II)7C_1ester]ClO_4 is -0.61 V vs. SCE,6) but the reduction potential forming the Co^I species was shifted by ca. 1 V to the cathodic side in the presence of the cyanide ion. The Co(III)/Co(II) redox couple originated from the cyano-free species was not observed in the voltammogram of $(CN)_2$Cob(III)7C_1ester (Fig. 1B).

The controlled-potential electrolysis of 1-bromo-2-cyano-2-ethoxycarbonylpropane in DMF was carried out in the presence of three different hydrophobic vitamin B_{12}'s, [Cob(II)7C_1ester]ClO_4, [(CN)(H_2O)Cob(III)7C_1ester]ClO_4, and $(CN)_2$Cob(III)-7C_1ester, in a manner identical with that previously reported.3) The following findings were based on the product analyses given in Table 1. (i) The electrolysis catalyzed by [(CN)(H_2O)Cob(III)7C_1ester]ClO_4 with one cyano group went to completion in a short period of time, and the ratio of rearrangement products, (B + C)/A in Table 1, was large as compared with the ratio for the reaction catalyzed by [Cob(II)7C_1ester]ClO_4. (ii) The (B + C)/A ratio was further advanced by employing $(CN)_2$Cob(III)7C_1ester with two cyano groups as a catalyst. However, a longer period of time was required to complete the electrolysis. (iii) Under all the con-

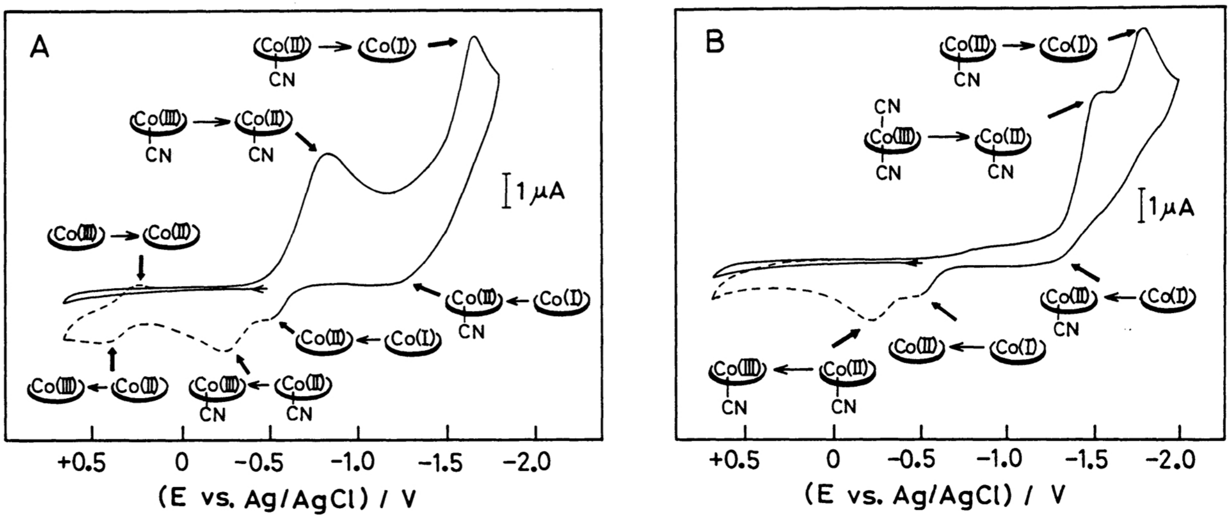
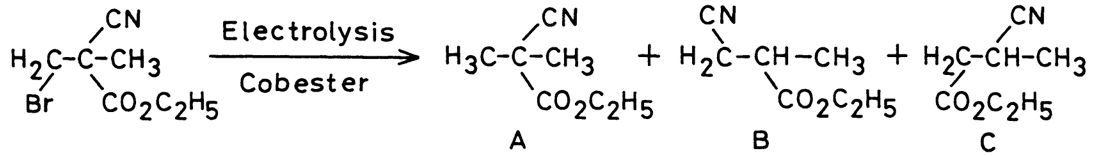


Fig. 1. Cyclic voltammograms of hydrophobic vitamin B_{12}'s in DMF containing 5.0×10^{-2} mol dm^{-3} tetra-n-butylammonium perchlorate at 20 ± 2 °C, sweep rate at 100 mV s^{-1}: A, [(CN)(H_2O)Cob(III)7C_1ester]ClO_4 (7.0×10^{-4} mol dm^{-3}); B, $(CN)_2$Cob-(III)7C_1ester (7.0×10^{-4} mol dm^{-3}).



(1)

Table 1. Product analyses for controlled-potential (-2.0 V vs. SCE) electrolysis of 1-bromo-2-cyano-2-ethoxycarbonylpropane catalyzed by hydrophobic vitamin B_{12}'s[a)]

Catalyst	Electrolysis conditions		Yield/%[c)]		Product ratio
	Charge[b)]	Period	A	B + C	(B + C)/A
	F mol^{-1}	h			
Complex 1[d)]	2.0	8	28—32	62—67	2.2
Complex 2[e)]	2.0	3	18—20	78—80	4.2
Complex 3[f)]	2.0	8	13—17	74—77	5.0

a) Electrolysis was carried out in a two-compartment cell equipped with Pt electrodes at 20 ± 2 °C under argon atmosphere in the dark. Starting solutions composed of: catalyst, 2.6 x 10^{-5} mol; 1-bromo-2-cyano-2-ethoxycarbonylpropane, 1.0 g (4.5 x 10^{-3} mol); 30 mL of DMF containing 0.50 mol dm^{-3} tetra-n-butylammonium tetrafluoroborate. b) Electrical charge passed per mol of the substrate. c) Based on an initial amount of the substrate; analyzed by means of GLC; refer to structures in Eq. 1 for A, B, and C. d) $[Cob(II)7C_1ester]ClO_4$. e) $[(CN)(H_2O)Cob(III)\text{-}7C_1ester]ClO_4$. f) $(CN)_2Cob(III)7C_1ester$.

ditions, the ester-migrated product (C) was produced more favorably than the cyano-migrated one (B), B/C = 4/96. Therefore, the cyano group in the products did not come from the catalyst having the cyano group. The similar electrolysis tendency as regards the cyanide effect was observed for other substrates having carboxylic ester and acetyl groups in place of the cyano group.

Since the rearrangement reaction proceeded more readily in the presence of cyanide ions, spectroscopic measurements were carried out as follows in order to clarify the electrolysis catalyzed by the complex with one cyano group. (i) The ligation constant between heptamethyl methylaquacobyrinate perchlorate, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$, and the cyanide ion in DMF was evaluated from the absorbance decrease at 500 nm by a method similar to that described previously;[1)] log K = 5.0 ± 0.1. This value is quite large, so that the alkylated complex formed in the course of electrolysis is expected to be in the cyano-coordinated structure. (ii) The rate constant for the cobalt-carbon bond cleavage in DMF was enhanced upon addition of cyanide ions under anaerobic irradiation conditions: the pseudo-first-order rate constant (k_{obsd}) was 2.4 x 10^{-5} s^{-1} for $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (5.0 x 10^{-6} mol dm^{-3}) without tetra-n-butylammonium cyanide (TBACN); k_{obsd} was 1.7 x 10^{-2} s^{-1} for the same methylated complex at the identical concentration in the presence of TBACN (2.5 x 10^{-5} mol dm^{-3}). Since $(CN)_2Cob(III)7C_1ester$ was obtained after completion of the photolysis in the presence of cyanide ions, the cobalt-carbon bond seems to undergo heterolytic cleavage. (iii) The cobalt-carbon bond cleavage of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ under anaerobic irradiation con-

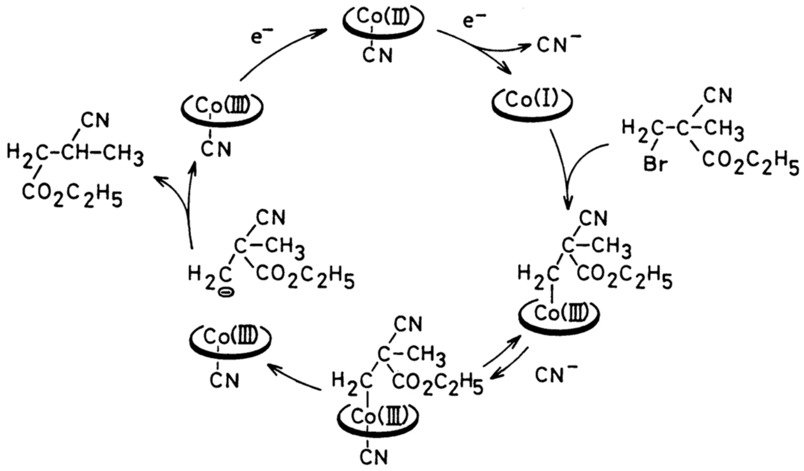


Fig. 2. Schematic representation of reaction cycle catalyzed by $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$.

ditions was examined by the spin-trapping technique with α-phenyl-N-(t-butyl)-nitrone (PBN). ESR signals attributable to the PBN spin adduct were clearly observed without coordination of the cyanide ion, while the signal intensities became weaker upon addition of cyanide ions. As for the Co^{II} species, strong signals were detected for the former case, but there were quite weak signals for the latter case causing the cyano-coordination. This result indicates that the alkylated complex is cleaved predominantly to the Co^{III} complex and the anionic species in the presence of the coordinated cyano group.

The reaction cycle catalyzed by $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ is consistent with the scheme shown in Fig. 2 on the basis of the above measurements. The rearrangement reaction catalyzed by the cyano-coordinated hydrophobic vitamin B_{12} proceeds more readily than that catalyzed by the hydrophobic complex without the cyano group, since formation of the anionic intermediate is facilitated via coordination of the cyanide ion to the central cobalt atom. On the other hand, the electrolysis catalyzed by $(CN)_2Cob(III)7C_1ester$ requires a longer period of time for its completion, since the dicyano complex requires a higher reduction potential for generation of the univalent cobalt species. The present study demonstrates that $[(CN)(H_2O)Cob(III)7C_1ester]ClO_4$ is the most effective catalyst for the electrochemical carbon-skeleton rearrangements.

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