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ELECTROCHEMICAL CARBON-SKELETON REARRANGEMENT AS CATALYZED BY HYDROPHOBIC VITAMIN B_{12} IN NONAQUEOUS MEDIA

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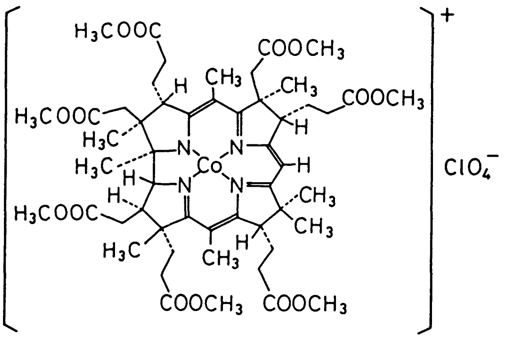
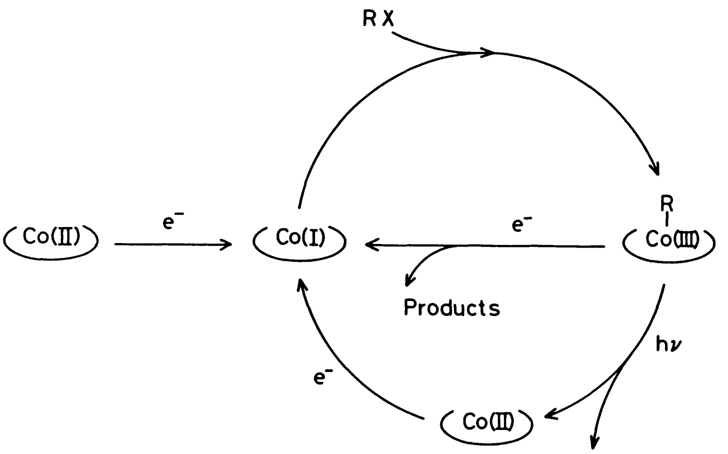
The controlled-potential electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane at -1.50 V vs. SCE as catalyzed by a hydrophobic vitamin B_{12} in DMF proceeded to give 1,2-bis(ethoxycarbonyl)propane as a major product in the presence of acetic acid under argon atmosphere in the dark.

We have previously pointed out that [Cob(II)7C_1ester]ClO_4 is readily reduced to the univalent cobalt species of highly nucleophilic character by electrochemical means in nonaqueous media.1) In the light of our previous study, the catalytic reaction cycles shown in Scheme 1 were established in the present work. In particular, we have successfully carried out the rearrangement reaction by electrochemical means for the first time as catalyzed by [Cob(II)7C_1ester]ClO_4.

An alkylated complex, generated by the reaction between a univalent cobalt complex and an alkyl halide (RX), is generally decomposed by photolysis or electrolysis to afford reduction and/or rearrangement products. In this regard, the redox behavior of heptamethyl methylaquacobyrinate perchlorate, [(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4, was examined in N,N-dimethylformamide (DMF) by menas of cyclic voltammetry (Fig. 1) in order to estimate the reduction potential for decomposition of alkylated complexes. The cyclic voltammogram is similar in appearance to those for methylcobalamin and methylcobinamide reported by Lexa and Savéant2) and Rubinson et al.3) In the course of the initial sweep of cyclic voltammetry (solid line



[Cob(II)7C_1ester]ClO_4



Scheme 1.

in Fig. 1), a single irreversible reduction peak, which is assigned to the one-electron reduction intermediate, was observed at -1.32 V vs. SCE, while a very weak peak (-1.20 V vs. SCE) and a more intense peak (-0.53 V vs. SCE) were observed in the anodic sweep; the latter being attributed to the Co(I)/Co(II) oxidation. The second cathodic sweep, curve 2 in Fig. 1 (broken line), showed two reduction peaks at -0.69 V, assigned to the Co(II)/Co(I) reduction, and at -1.32 V vs. SCE. The $E_{1/2}$ value for Co(II)/Co(I) is -0.61 V vs. SCE and in agreement with that for [Cob(II)7C_1-ester]ClO_4 measured in DMF.[1] The characteristic feature of redox behavior observed in the subsequent repeated cyclic sweeps remained the same. The voltammogram indicates that the methylated complex is decomposed to afford Cob(I)-7C_1ester and the methyl radical in a potential range more cathodic than -1.32 V vs. SCE.

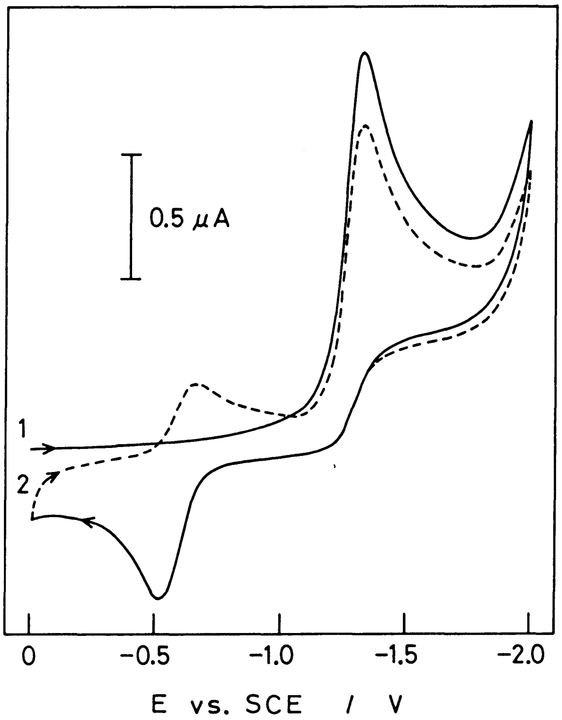
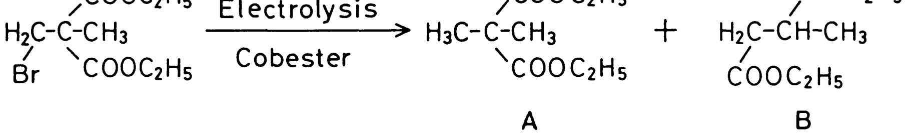


Fig. 1. Cyclic voltammogram of [$(CH_3)(H_2O)$Cob(III)7C_1ester]ClO_4 (6.1×10^{-4} mol dm^{-3}) in DMF containing 5.0×10^{-2} mol dm^{-3} TBAF at 20 ± 2 °C in the dark; sweep rate, 100 mV s^{-1}.

The electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane, which is considered to be a model substrate for methylmalonyl-CoA mutase, was carried out upon addition of [Cob(II)7C_1ester]ClO_4 in a cylindrical-type three-electrode cell which was divided into two internal compartments with a single sheet of microporous polypropylene membrane. A DMF solution of [Cob(II)7C_1ester]ClO_4, 2,2-bis(ethoxycarbonyl)-1-bromopropane, an additive (acetic acid or 2-propanol), and tetrabutylammonium tetrafluoroborate (TBAF; a supporting electrolyte) was subjected to electrolysis at an appropriate controlled-potential under argon atmosphere. Then, the reaction mixture was distilled in vacuo and analyzed for products by menas of GLC. The following findings were obtained on the basis of the product analyses given in Table 1 (refer to Eq. 1). (i) At -1.0 V vs. SCE: products were obtained only when the reaction mixture was irradiated with the visible light, and the major product was the reduced one (A in Eq. 1). (ii) At -1.5 V vs. SCE in the dark: the rearrangement product (B in Eq. 1) was the major one when a certain proton source such as acetic acid or propionic



$$\underset{Br}{H_2C}-C(CH_3)(COOC_2H_5)_2 \xrightarrow[\text{Cobester}]{\text{Electrolysis}} \underset{A}{H_3C-C(CH_3)(COOC_2H_5)_2} + \underset{B}{H_2C(COOC_2H_5)-CH(COOC_2H_5)-CH_3} \qquad (1)$$

Table 1. Product analyses for controlled-potential electrolysis of 2,2-bis-(ethoxycarbonyl)-1-bromopropane as catalyzed by hydrophobic vitamin B_{12}[a)]

Entry	Electrolysis conditions					Yields/%[e)]	
	Potential V vs. SCE	Irradiation[b)]	Additive[c)]	Charge[d)] F mol^{-1}	Period h	A[f)]	B[g)]
1	-1.0	Irradiation	CH_3COOH	0.2	9	9 – 12	Trace
2	-1.5	Irradiation	CH_3COOH	3.0	12	36 – 41	3 – 10
3	-1.5	In the dark	CH_3COOH	3.0	6	16 – 18	40 – 46
4	-1.5	In the dark	C_2H_5COOH	3.0	9	15 – 17	25 – 28
5	-1.5	In the dark	$(CH_3)_2CHOH$	1.0	23	32 – 37	Trace
6	-1.5	In the dark	None	1.0	23	25 – 36	ca. 1

a) Electrolysis was carried out in a two-compartment cell equipped with Pt electrodes at 20 ± 2 °C under argon atmosphere. Starting solutions composed of: [Cob-(II)7C_1ester]ClO_4, 30 mg (2.6 x 10^{-5} mol); 2,2-bis(ethoxycarbonyl)-1-bromopropane, 1.0 g (3.8 x 10^{-3} mol); 30 mL of DMF containing 0.50 mol dm^{-3} TBAF. b) Irradiation with a 300-W tungsten lamp from a distance of 50 cm. c) CH_3COOH, 0.50 g (8.3 x 10^{-3} mol); C_2H_5COOH, 0.61 g (8.3 x 10^{-3} mol); $(CH_3)_2CHOH$, 0.50 g (8.3 x 10^{-3} mol). d) Electrical charge passed per mol of the substrate. e) Based on an initial amount of the substrate; the rest was the unreacted substrate; analyzed by GLC. Recovery of the catalyst: 80-90% at -1.0 V; 60-70% at -1.5 V vs. SCE. f) 2,2-Bis(ethoxycarbonyl)propane. g) 1,2-Bis(ethoxycarbonyl)propane.

acid was added, while the reduction product was largely obtained when 2-propanol was added or without any additive. (iii) At -1.5 V vs. SCE under irradiation with the visible light: the major product was the reduced one even in the presence of acetic acid.

The controlled-potential electrolysis without irradiation was followed by electronic spectroscopy as shown in Fig. 2. When the electrolysis was carried out at -1.0 V vs. SCE, [Cob(II)7C_1ester]ClO_4 was transformed into the corresponding alkylated complex with absorption maxima at 305 and 474 nm (curve B in Fig. 2). On the other hand, absorption maxima were observed at 280, 302, 391, and 474 nm at -1.5 V vs. SCE; indicating the formation of the alkylated complex and Cob(I)7C_1-ester (curve C in Fig. 2). A similar spectral change was observed even in the absence of acetic acid. However, the absorbance intensity originated from Cob(I)-7C_1ester was larger than that observed in the presence of acetic acid. These spectral changes indicate that the alkylated complex is formed at -1.0 V vs. SCE and electrochemically decomposed at -1.5 V vs. SCE.

The reaction without irradiation was also examined by the spin-trapping technique with α-phenyl-N-(t-butyl)nitrone (PBN).[4)] ESR spectra for the PBN spin adducts formed in the course of electrolysis at -1.5 V vs. SCE are shown in Fig. 3. ESR signals attributable to the PBN spin adducts were clearly observed (Fig. 3A), while the signal intensities became much weaker upon addition of acetic acid. The result indicates that the radical species are generated as the electrolysis intermediates at -1.5 V vs. SCE without any proton donor while the proton donor

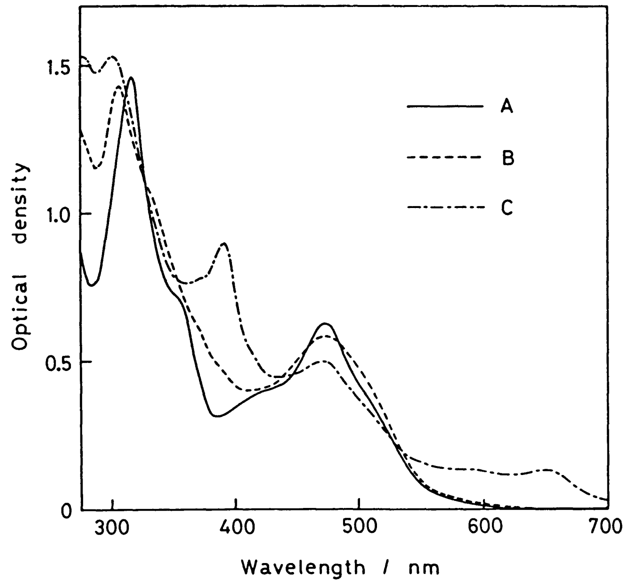


Fig. 2. Electronic spectra observed steadily during electrolysis of a DMF solution containing [Cob(II)7C$_1$ester]ClO$_4$ (5.2 x 10^{-5} mol dm^{-3}), 2,2-bis(ethoxycarbonyl)-1-bromopropane (1.5 x 10^{-2} mol dm^{-3}), TBAF (0.20 mol dm^{-3}), and acetic acid (1.2 x 10^{-2} mol dm^{-3}) at 20.5 ± 0.1 °C: A, before electrolysis; B, at -1.0 V vs. SCE; C, at -1.5 V vs. SCE.

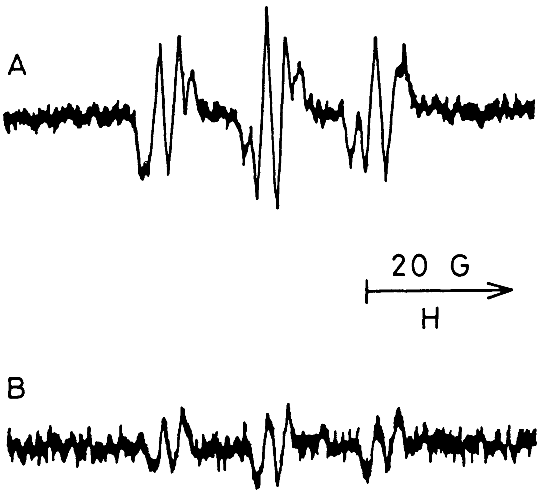


Fig. 3. ESR spectra observed during electrolysis (at -1.5 V vs. SCE) of a DMF solution containing [Cob(II)7C$_1$ester]ClO$_4$ (1.7 x 10^{-3} mol dm^{-3}), 2,2-bis(ethoxycarbonyl)-1-bromopropane (0.25 mol dm^{-3}), PBN (0.10 mol dm^{-3}), and TBAF (0.10 mol dm^{-3}) at room temperature: A, without acetic acid; B, in the presence of acetic acid (0.56 mol dm^{-3}).

(acetic acid) inhibits the formation of such radicals to a large extent.

The present study demonstrates the first example of the rearrangement reaction as catalyzed by a vitamin B$_{12}$ model under electrochemical conditions. The rearrangement product was obtained in 6 h at yields that are 60-70 times as much as a molar quantity of the hydrophobic vitamin B$_{12}$ under the most favorable electrolysis conditions. Even though the identical radical species are produced during the reaction of the present substrate with tributyltin hydride, the ethoxycarbonyl group was not found to migrate to afford the rearrangement product (B).$^{5)}$ Consequently, the rearrangement reaction must proceed via formation of an anionic intermediate to afford product B.

References

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