CHEMISTRY LETTERS, pp. 555-558, 1986.

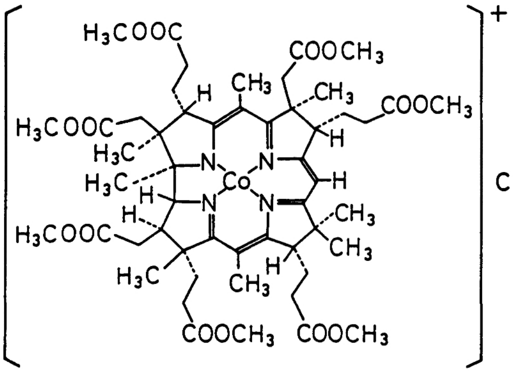
REACTION MECHANISMS FOR ELECTROCHEMICAL CARBON-SKELETON REARRANGEMENT AS CATALYZED BY HYDROPHOBIC VITAMIN B_{12} IN NONAQUEOUS MEDIA[1)]

Yukito MURAKAMI,* Yoshio HISAEDA, Takako TASHIRO, and Yoshihisa MATSUDA
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

Reaction mechanisms for the controlled-potential electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane at -1.0, -1.5, and -2.0 V vs. SCE as catalyzed by a hydrophobic vitamin B_{12} were clarified. The carbon-skeleton rearrangement was postulated to proceed via formation of anionic intermediates.

We have previously reported that the controlled-potential electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane, which is considered to be a model substrate for methylmalonyl-CoA mutase, at -1.5 V vs. SCE was catalyzed by a hydrophobic vitamin B_{12} in N,N-dimethylformamide (DMF) to give 1,2-bis(ethoxycarbonyl)propane (B in Eq. 1) as a major product in the presence of acetic acid under argon atmosphere in the dark.[2)] This reaction is the first example for the carbon-skeleton rearrangement catalyzed by a vitamin B_{12} model under electrochemical conditions. We report here on the electrochemical reaction carried out at -1.8 and -2.0 V vs. SCE by using a combination of a substrate and a catalyst identical with the previous ones. In the light of the present and previous studies, we postulate the reaction mechanisms concerned.

The redox behavior of heptamethylcobyrinate perchlorate, $[Cob(II)7C_1ester]ClO_4$, in DMF containing 2,2-bis(ethoxycarbonyl)-1-bromopropane in a large excess and tetrabutylammonium tetrafluoroborate



$[Cob(II)7C_1ester]ClO_4$

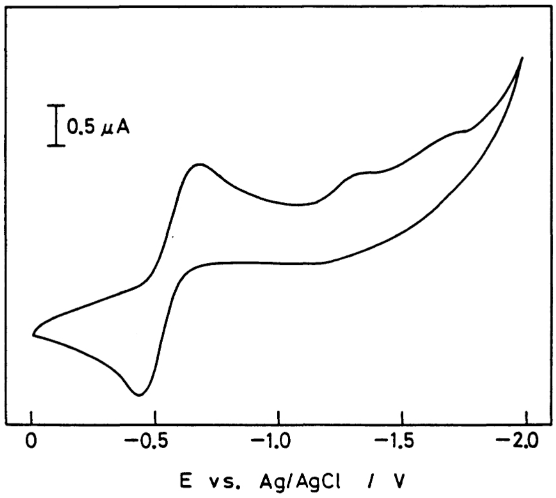
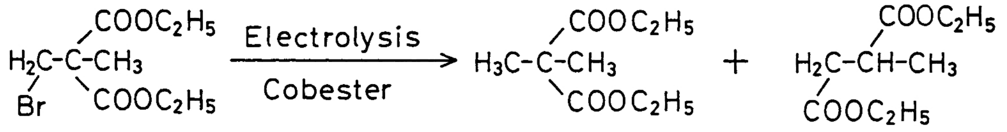


Fig. 1. Cyclic voltammogram of $[Cob(II)7C_1ester]ClO_4$ (7.2×10^{-4} mol dm^{-3}) in DMF containing 0.10 mol dm^{-3} 2,2-bis(ethoxycarbonyl)-1-bromopropane and 0.10 mol dm^{-3} TBAF at 20 ± 2 °C in the dark; sweep rate, 100 mV s^{-1}.



A B

(1)

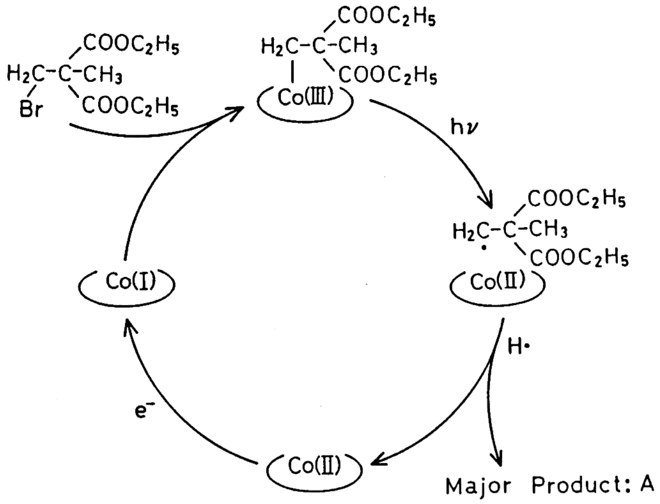
Table 1. Product analyses for controlled-potential electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane as catalyzed by hydrophobic vitamin B_{12} [a)]

Entry	Electrolysis conditions					Yield/% [e)]	
	Potential V vs. SCE	Irradiation [b)]	Additive [c)]	Charge [d)] F mol^{-1}	Period h	A [f)]	B [g)]
1 [h)]	-1.0	Irradiation	CH_3COOH	0.2	9	9 - 12	Trace
2 [h)]	-1.5	In the dark	CH_3COOH	3.0	6	16 - 18	40 - 46
3 [h)]	-1.5	In the dark	None	1.0	23	25 - 36	ca. 1
4	-1.8	In the dark	None	2.0	23	24 - 28	23 - 31
5	-2.0	In the dark	None	2.0	2	11 - 18	76 - 84

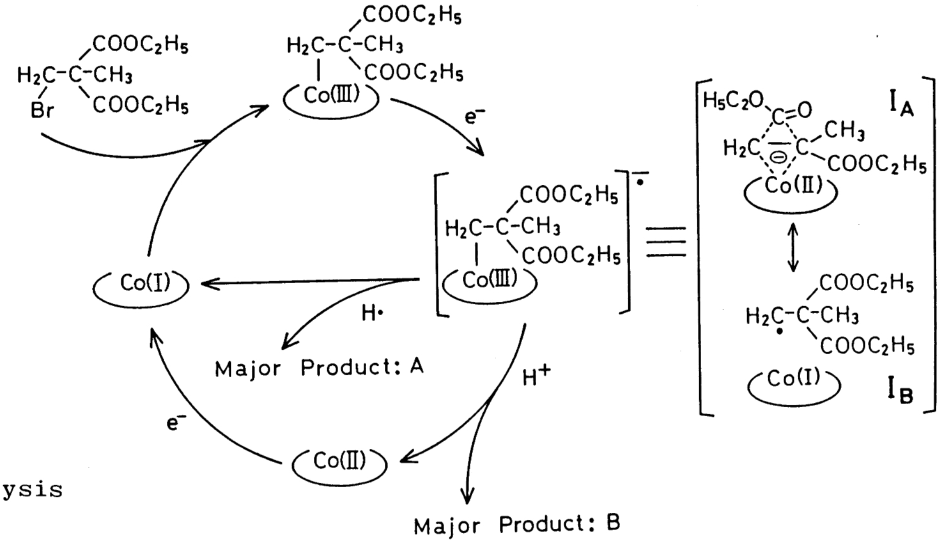
a) Electrolysis was carried out in a two-compartment cell equipped with Pt electrodes at 20 ± 2 °C under argon atmosphere. Starting solutions composed of: [Cob(II)7C_1ester]ClO_4, 30 mg (2.6 x 10^{-5} mol); 2,2-bis(ethoxycarbonyl)-1-bromopropane, 1.0 g (3.8 x 10^{-3} mol); 30 mL of DMF containing 0.50 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). 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; ca. 50% at -1.8 and -2.0 V vs. SCE. f) 2,2-Bis(ethoxycarbonyl)propane. g) 1,2-Bis(ethoxycarbonyl)propane. h) Cited from Ref. 2.

(TBAF) as a supporting electrolyte was examined by means of cyclic voltammetry (Fig. 1). The Co(II)/Co(I) redox couple for [Cob(II)7C_1ester]ClO_4 was observed at -0.56 V vs. Ag/AgCl.[3)] Two irreversible reduction peaks assigned to the one- and two-electron reduction intermediates of an alkylated complex, which is generated by the reaction between the Co^I species and the alkyl halide, were observed at ca. -1.3 V and ca. -1.8 V vs. Ag/AgCl, respectively. This result indicates that mutually different intermediates are generated by the electrolysis at -1.0, -1.5, and -2.0 V vs. SCE.[4)]

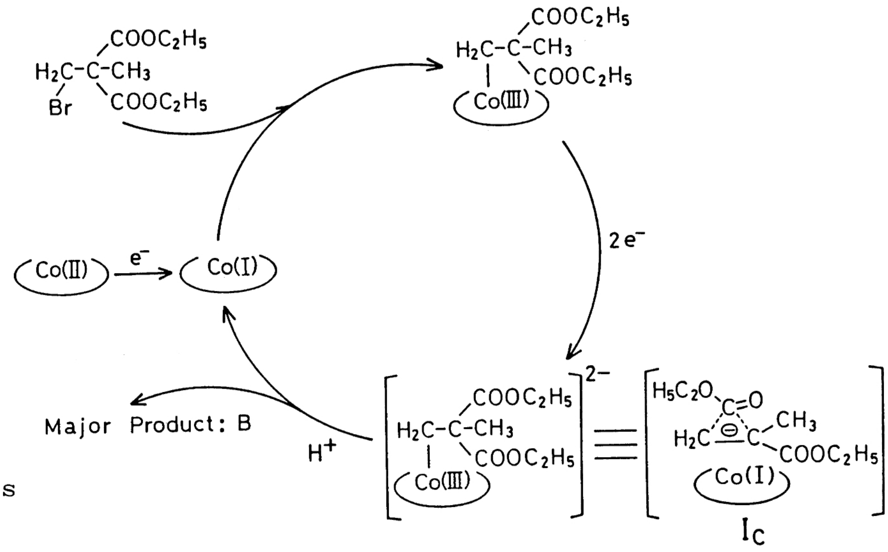
The electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane was carried out upon addition of [Cob(II)7C_1ester]ClO_4 in a manner identical with that previously reported.[2)] The following findings were based on the product analyses given in Table 1 (refer to Eq. 1). (i) At -1.0 V vs. SCE: products were obtained only when the reaction mixture was irradiated with the visible light, and the major product was the reduced one (A). (ii) At -1.5 V vs. SCE: the rearrangement product (B) was the major one when an efficient proton source such as acetic acid was added, while the reduction product (A) was largely obtained without any additive. When CH_3COOD was used as a proton source, the rearrangement product containing one deuterium, $(H_5C_2O_2C)CH_2CD(CH_3)(CO_2C_2H_5)$, was obtained.[5)] (iii) At -2.0 V vs. SCE in the dark:



Scheme 1. Electrolysis at -1.0 V vs. SCE.



Scheme 2. Electrolysis at -1.5 V vs. SCE.



Scheme 3. Electrolysis at -2.0 V vs. SCE.

the rearrangement product (B) was the major one even in the absence of acetic acid.

The reaction mechanisms for controlled-potential electrolysis were investigated by means of electronic spectroscopy and coulometry as well as by the spin-trapping ESR technique. The reaction at -1.0 V vs. SCE proceeded as shown in Scheme 1 on the following basis:2) one electron was consumed for the reaction; electronic spectra indicated the formation of the alkylated complex; ESR signals attributable to a spin adduct, formed with α-phenyl-N-(t-butyl)nitrone (PBN), were clearly observed under irradiation conditions; product A was the major one.

The reaction at -1.5 V vs. SCE was found to proceed as shown in Scheme 2 on the basis of the product analysis and the following results:2) electronic spectra indicated the electrochemical decomposition of the alkylated complex; ESR signals attributable to the PBN adduct were clearly observed, while the signals became much weaker upon addition of acetic acid; the one-electron reduction took place in the light of coulometry. The alkylated complex was reduced to the one-electron reduction intermediate at -1.5 V vs. SCE in the dark. The electronic structure for the intermediate seems to be represented by two canonical forms I_A and I_B (Scheme 2). The proton attack on the β-carbon of the substrate must induce the carbon-skeleton rearrangement, followed by the cobalt—carbon cleavage. On the other hand, the one-electron reduction intermediate is spontaneously decomposed to afford the Co^I chelate and the alkyl radical in the absence of any proton source.

The reaction at -2.0 V vs. SCE must proceed as shown in Scheme 3 on the basis of the product analysis and the following results: the Co^I species was steadily observed by electronic spectroscopy during the electrolysis; the two-electron reduction took place as confirmed by coulometry. The alkylated complex is converted into the two-electron reduction intermediate at a potential more cathodic than -1.8 V vs. SCE in the dark. This intermediate is decomposed to the Co^I chelate and an anionic species, and the rearrangement product is obtained from the latter species.

In conclusion, it became apparent that the rearrangement product derived from 2,2-bis(ethoxycarbonyl)-1-bromopropane is obtained primarily from the anionic intermediates, I_A and I_C, while simple reduction product (A) is mainly produced from the radical species. In particular, the two-electron reduction intermediate (I_C) is more effective in affording the rearrangement product.

References

1) Contribution No. 821 from this Department.
2) Y. Murakami, Y. Hisaeda, T. Tashiro, and Y. Matsuda, Chem. Lett., 1985, 1813.
3) Y. Murakami, Y. Hisaeda, A. Kajihara, and T. Ohno, Bull. Chem. Soc. Jpn., 57, 405 (1984).
4) Both SCE and Ag/AgCl were used as reference electrodes; potentials vs. SCE are more cathodic by 30 mV relative to those vs. Ag/AgCl.
5) After being separated by GLC, the products were analyzed by means of ^{1}H-NMR and mass spectral measurements; isotopic purity of product B, 55—60 %D.

(Received February 14, 1986)