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Redox Behavior of Simple Vitamin B_{12} Model Complexes with Cobalt-Carbon Bonds and Catalytic Carbon-Skeleton Rearrangements

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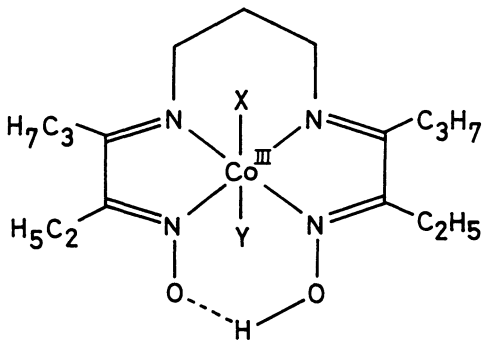
The cobalt complex of 2,10-diethyl-3,9-dipropyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol catalyzed electrolyses of alkyl halides with electron-withdrawing groups at the β-position to afford rearrangement products via oxidation of the corresponding dialkylated complexes as intermediates.

Vitamin B_{12}-dependent enzymes catalyze various isomerization reactions accompanied with carbon-skeleton rearrangements. It is of particular importance to clarify the reaction behavior of vitamin B_{12} in hydrophobic microenvironments in order to simulate catalytic functions of the enzymes concerned. We have been dealing with hydrophobic vitamin B_{12} derivatives, which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B_{12}, and found that electrochemical carbon-skeleton rearrangements were catalyzed efficiently by these complexes.[1] For those cases, the reaction takes place with a catalytic cycle shown in Fig. 1: the Co^{II} complex is electrochemically reduced to the Co^{I} species, and the corresponding alkylated complex is generated by reaction of the super-nucleophilic Co^{I} with a substrate, a substituted alkyl bromide; the alkylated complex is decomposed by photolysis or electrolysis to afford the corresponding products, and the cobalt complex acts as a mediator repeatedly. This finding prompted us to develop a simple model complex, which shows redox behavior analogous



1: X = Y = Br
2: X = CH_3, Y = H_2O
3: X = Y = CH_3

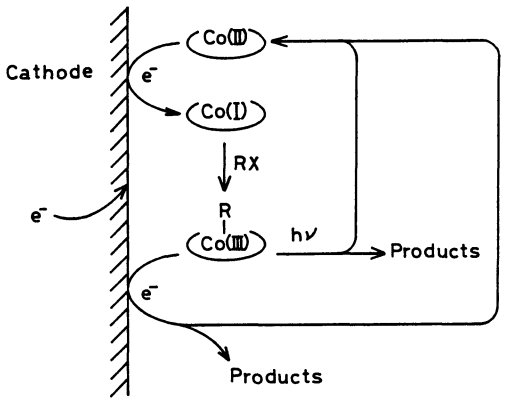


Fig. 1. Schematic representation of electrochemical catalysis.

to that of vitamin B_{12} with respect to the nuclear cobalt and catalyzes the isomerization reaction in a similar manner. In this regard, we have reported previously on the electrochemical carbon-skeleton rearrangement catalyzed by the cobalt complex of 2,10-diethyl-3,9-dipropyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol.[2] The catalytic behavior of this simple complex was found to be different from that of the hydrophobic vitamin B_{12} in the following respects. A base such as imidazole, which is capable of coordinating to the nuclear cobalt, was essential to the reaction catalyzed by the former complex; the cobalt-carbon bond was effectively activated by the trans effect arising from the coordinated axial base. When imidazole was not present, the corresponding dialkylated complex, which is inactive for the electrochemical reduction, was formed in the course of reaction, and consequently the catalytic reaction ceased to proceed. Therefore, we investigated in this work the redox behavior of the same model complex with cobalt-carbon bond(s) and the novel catalytic system for the carbon-skeleton rearrangement via oxidation of the dialkylated complex.

The mono- and di-methylated cobalt complexes (**2** and **3**, respectively) have been prepared and identified previously.[2] The redox behavior of similar cobalt complexes with the cobalt-carbon bond was studied in acetonitrile rather extensively.[3,4] Firstly, we applied cyclic voltammetry to complexes **2** and **3** under argon atmosphere in order to clarify their redox behavior in N,N-dimethylformamide (DMF). As shown in Fig. 2 for the case of complex **2**, a single and irreversible one-electron reduction peak was observed at -1.50 V vs. Ag/AgCl during scanning for the potential range from -1.0 to -2.0 V vs. Ag/AgCl. In the course of scanning for the potential range from -1.0 V vs. Ag/AgCl to the anodic side, there were observed two oxidation peaks; a reversible Co(I)/Co(II) oxidation peak at -0.65 V vs. Ag/AgCl and another irreversible and small oxidation peak at +0.73 V vs. Ag/AgCl, the latter being originated from the one-electron oxidation of the dimethylated complex (**3**). The latter oxidation peak was not observed when the potential was scanned for

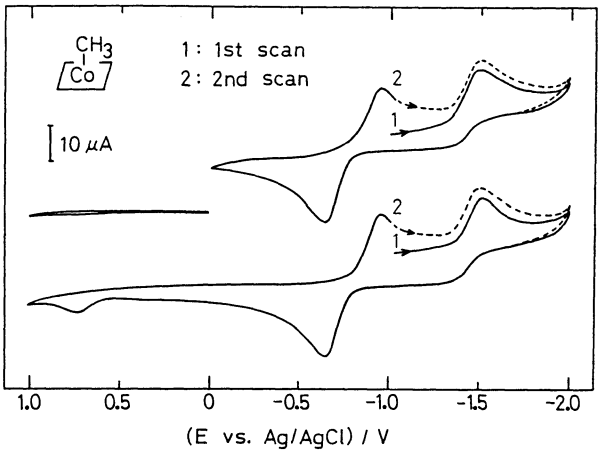


Fig. 2. Cyclic voltammograms of **2** (4.5×10^{-3} mol dm^{-3}) containing 0.10 mol dm^{-3} tetra-n-butylammonium perchlorate in DMF at 20 ± 2 °C in the dark: scan rate, 100 mV s^{-1}.

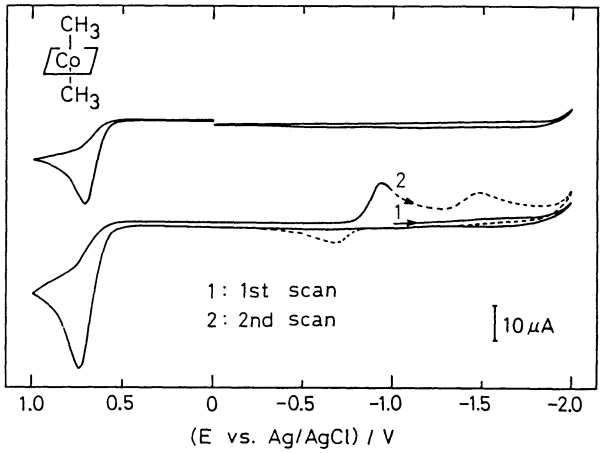
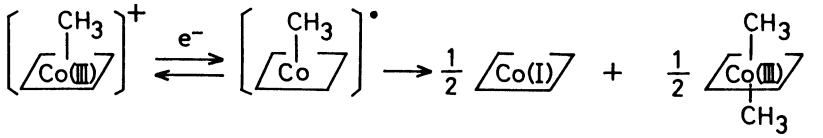


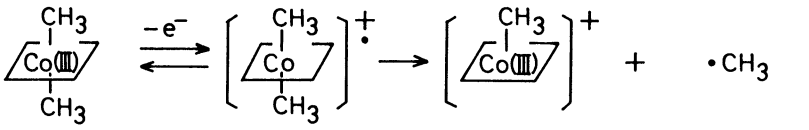
Fig. 3. Cyclic voltammograms of **3** (4.5×10^{-3} mol dm^{-3}) containing 0.10 mol dm^{-3} tetra-n-butylammonium perchlorate in DMF at 20 ± 2 °C in the dark: scan rate, 100 mV s^{-1}.

the range from 0 to +0.10 V vs. Ag/AgCl. After the controlled-potential electrolysis of **2** was completed at -2.0 V vs. Ag/AgCl under anaerobic conditions, the absorption maximum originally observed for **2** at 465 nm was shifted to 410 nm when the sample was exposed to air for elimination of the Co^{I} species; the latter band being due to **3**. This apparently indicates that **2** is disproportionated to **3** and the Co^{I} species by the electrochemical reduction as shown by Eq. 1. This behavior is quite different from that observed for the corresponding hydrophobic vitamin B_{12}.[5] The dimethylated complex is inactive for electrochemical reduction; no peak was observed in the potential range from 0 to -2.0 V vs. Ag/AgCl as shown in Fig. 3. An irreversible oxidation peak was observed at +0.73 V vs. Ag/AgCl. When the potential was sweeped repeatedly between +1.0 and -2.0 V vs. Ag/AgCl, the redox behavior became similar to that of **2**. These facts indicate that **3** is cleaved to afford **2** and the methyl radical by the electrochemical oxidation as shown by Eq. 2.[3]

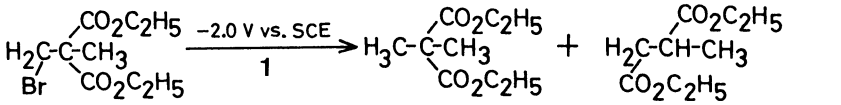
The electrolysis of 2,2-bis(ethoxycarbonyl)-1-bromopropane was carried out upon addition of **1** in a three-electrode cell, which was divided into two internal compartments with a diaphragm, in a manner identical with that previously reported.[1] The catalytic reaction did not proceed efficiently (refer to the data given below Eq. 3), because the dialkylated complex was formed in the course of the reaction. As for the reactions with other substrates such as 2-acetyl-1-bromo-2-ethoxycarbonylpropane and 1-bromo-2-cyano-2-ethoxycarbonylpropane, similar results



(1)

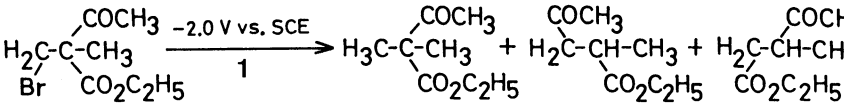


(2)



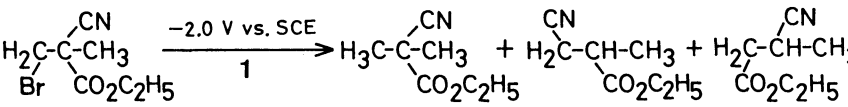
(3)

Divided cell	7-11%	1-2%
Undivided cell	18-20%	53-55%



(4)

Divided cell	1-2%	7-8%	Trace
Undivided cell	3-4%	83-85%	Trace



(5)

Divided cell	1-2%	Trace	8-10%
Undivided cell	10-12%	Trace	58-60%

were obtained; refer to the data shown below Eqs. 4 and 5, respectively. In the light of the redox behavior of the dimethylated complex (**3**), the dialkylated complex must give products, plausibly involving the corresponding isomerization product, by the electrochemical oxidation. Therefore, we removed the diaphragm from the divided cell and the electrolysis was carried out in a single-compartment cell equipped with platinum electrodes at 20 ± 2 °C under argon atmosphere.

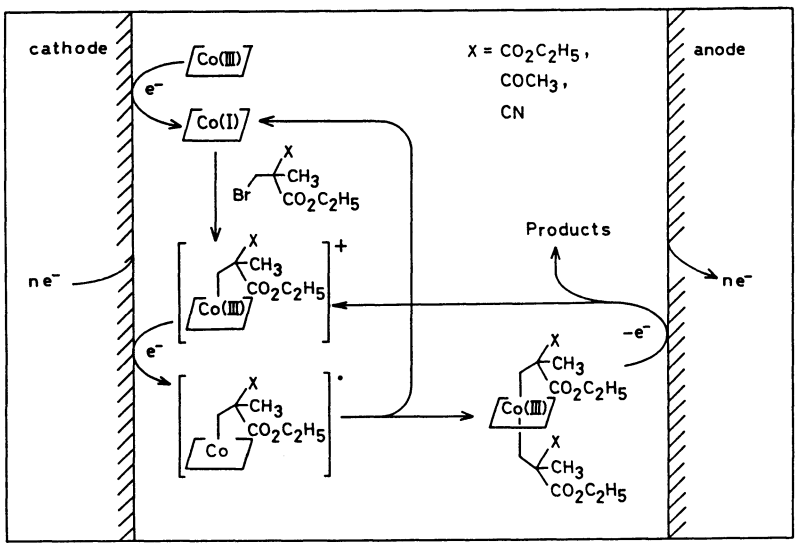


Fig. 4. Schematic representation of electrochemical catalysis in the undivided cell.

A DMF solution of **1** (8.7×10^{-4} mol dm^{-3}), a substrate (0.14 mol dm^{-3}), and tetra-n-butylammonium tetrafluoroborate (0.46 mol dm^{-3}) was subjected to electrolysis at -2.0 V vs. SCE of the cathode in the dark for 8 h. Then, the reaction mixture was distilled in vacuo and analyzed for products by means of GLC; refer to the data given below Eqs. 3—5. These results indicate that the rearrangement reactions proceed efficiently in the undivided cell. The electrolysis plausibly proceeds via the reaction cycle shown in Fig. 4. The tervalent cobalt complex (**1**) is first converted into the univalent cobalt complex by the electrochemical reduction, and the resulting species is subjected to the electrophilic attack by an alkyl bromide to afford the corresponding alkylated complex as the intermediate. This species is subsequently reduced to the one-electron reduction intermediate, which is then disproportionated to the dialkylated complex and the univalent cobalt species. The dialkylated complex is decomposed to give the monoalkylated complex and the products by the electrochemical oxidation on the anode.

In conclusion, the coupled electrochemical redox processes facilitated the carbon-skeleton rearrangement via formation of the dialkylated complex as the oxidizable intermediate.

References

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