Journal of Inorganic Biochemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Inorganic Biochemistry

journal homepage: www.elsevier.com/locate/jinorgbio

Reprint of: Impact of the corrin framework of vitamin B_{12} on the electrochemical carbon-skeleton rearrangement in comparison to an imine/oxime planar ligand; tuning selectivity in 1,2-migration of a functional group by controlling electrolysis potential

Keishiro Tahara[a,b], Ling Pan[a,c], Ryoko Yamaguchi[a], Hisashi Shimakoshi[a], Masaaki Abe[b], Yoshio Hisaeda[a,d,*]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan
[b] Department of Material Science, Graduate School of Material Science, University of Hyogo, 3-2-1, Kouto, Kamigori, Ako 6781297, Japan
[c] Department of Chemistry, Northeast Normal University, Changchun 130024, PR China
[d] Center for Molecular Systems (CMS), Kyushu University, Fukuoka 819-0395, Japan

ARTICLE INFO

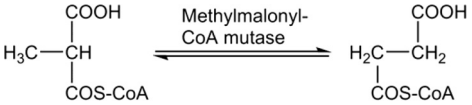
Keywords:
Vitamin B_{12}
Heptamethyl cobyrinate
Electrolysis
Carbon-skeleton rearrangement
1,2-Migration

ABSTRACT

Among the coenzyme B_{12}-dependent enzymes, methylmalonyl-CoA mutase (MMCM) catalyzes the carbon-skeleton rearrangement reaction between *R*-methylmalonyl-CoA and succinyl-CoA. Diethyl 2-bromomethyl-2-phenylmalonate, an alkyl bromide substrate having two different migrating groups (phenyl and carboxylic ester groups) on the *β*-carbon, was applied to the electrolysis mediated by a hydrophobic vitamin B_{12} model complex, heptamethyl cobyrinate perchlorate in this study. The electrolysis of the substrate at − 1.0 V *vs.* Ag-AgCl by light irradiation afforded the simple reduced product (diethyl 2-methyl-2-phenylmalonate) and the phenyl migrated product (diethyl 2-benzyl-2-phenylmalonate), as well as the electrolysis of the substrate at − 1.5 V *vs.* Ag-AgCl in the dark. The electrolysis of the substrate at − 2.0 V *vs.* Ag-AgCl afforded the carboxylic ester migrated product (diethyl phenylsuccinate) as the major product. The selectivity for the migrating group was successfully tuned by controlling the electrolysis potential. We clarified that the cathodic chemistry of the Co(III) alkylated heptamethyl cobyrinate is critical for the selectivity of the migrating group through mechanistic investigations and comparisons to the simple vitamin B_{12} model complex, an imine/oxime-type cobalt complex.

1. Introduction

Biomimetic catalysis is a challenging issue that must be addressed for green and eco-friendly molecular transformations. In particular, enzymatic radical catalysis has attracted increasing attention because several enzymes utilize the high reactivity of free radicals to achieve chemically difficult reactions [1–5]. Certain enzymes utilize the coenzyme B_{12} (adenosylcobalamin) as an organometallic cofactor, whose Co−C bond is homolytically cleaved to form the radical in the active center [6–9]. They catalyze various isomerizations *via* the 1,2-excahnge of a hydrogen atom and a functional group utilizing the high reactivity of the catalytic radical. Among the coenzyme B_{12}-dependent enzymes, methylmalonyl-CoA mutase (MMCM) catalyzes the carbon-skeleton rearrangement reaction between *R*-methylmalonyl-CoA and succinyl-CoA (Eq. (1)). To achieve the MMCM-type 1,2-migration reactions under non-enzymatic conditions or bio-inspired functions, two methods have been adopted for several decades. The first method is the fabrication of the artificial enzymes composed of a functional equivalent of B_{12} (i.e., B_{12} model complexes) and that of an apoenzyme (i.e., micelle, vesicle, protein) [10–12]. The second method is the use of synthetic B_{12} model complexes as catalysts [13–17].



(1)

In the context of the second method, the imine/oxime-type cobalt complexes, such as [Co(III){(DO)(DOH)pn}Br_2] **2** as shown in Fig. 1, have been investigated ((DO)(DOH)pn = 3,7-diazanona-2,7-diene-1-one oximato) [18–21]. They have a square planar monoanionic ligand as a suitable model for the corrin framework. The imine/oxime-type

DOI of original article: http://dx.doi.org/10.1016/j.jinorgbio.2017.07.021
* Corresponding author at: Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan.
E-mail address: yhisatcm@mail.cstm.kyushu-u.ac.jp (Y. Hisaeda).

http://dx.doi.org/10.1016/j.jinorgbio.2017.09.021
Received 8 April 2017; Received in revised form 27 June 2017; Accepted 18 July 2017

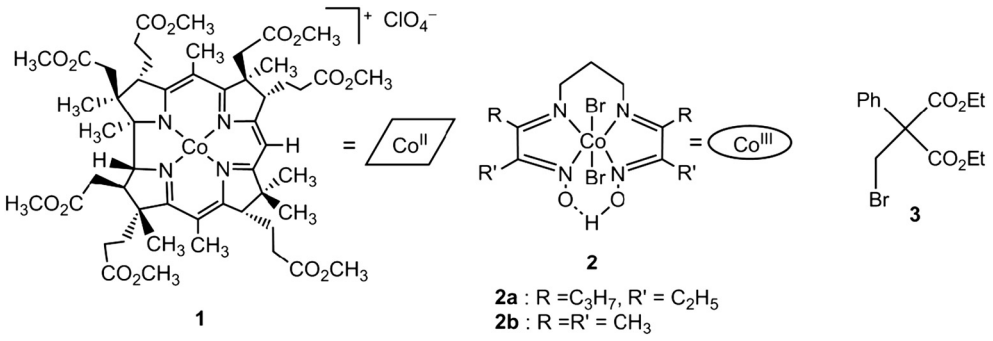
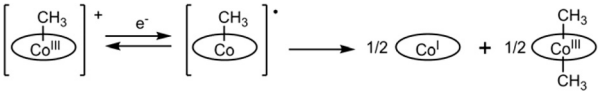


Fig. 1. Structures of catalysts **1** and **2**, and substrate **3**.

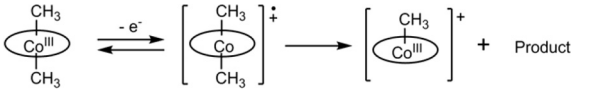
Table 1
Electrochemical reactivity of methylated complexes of **1** and **2**.

Cobalt complex	Monomethylated complex (1st reduction wave)	Dimethylated complex (1st oxidation wave)	Ref.
1	Reduction active (− 1.32 *vs.* SCE in DMF/*n*-Bu_4NBF_4)	No formation of dialkylated complex	[24]
2a	Reduction active (− 1.50 *vs.* Ag/AgCl in DMF/*n*-Bu_4NClO_4)	Oxidation active (+ 0.73 V *vs.* Ag/AgCl in DMF/*n*-Bu_4NClO_4)	[20]

cobalt complex can acquire both the monoalkylated and dialkylated forms. The Co(III) monoalkylated complex is active for electrochemical reduction, resulting in the disproportionation to the Co(I) species and the Co(III) dialkylated complex, while the resulting Co(III) dialkylated complex is active for the electrochemical oxidation, resulting in fragmentation to the Co(III) monoalkylated species, as exemplified by the electrochemical reactivity of the Co(III)-CH_3 and Co(III)-$(CH_3)_2$ complexes of compound **2a** in Eqs. (2) and (3), and Table 1. We demonstrated that compound **2** successfully mediates the 1,2-migration of the carboxylic ester group under electrochemical conditions [20]. In our previous study, to probe the mechanism of the electrochemical carbon-skeleton rearrangements mediated by **2**, we used diethyl 2-bromomethyl-2-phenylmalonate **3** as an alkyl bromide substrate, which has not only two carboxylic ester groups but also a phenyl group on the *β*-carbon (see Table 2) [21]. Given the reported 1,2-phenyl migration in the *β*-phenyl carbon centered radical [22,23], we choose the phenyl group as an additional migrating group because the product contribution could provide mechanistic insights into the 1,2-migration. We clarified that the oxidation process of the Co(III) dialkylated complex is crucial for the 1,2-migration of the carboxylic ester group *via* fragmentation to the Co(III) monoalkylated complex [21].



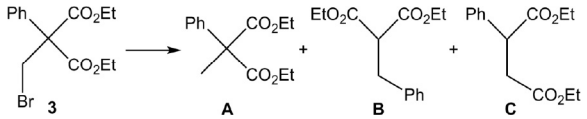
(2)



(3)

Simultaneously, we have been dealing with a hydrophobic B_{12} model complex, heptamethyl cobyrinate perchlorate [Cob(II)7C_1ester]ClO_4 **1**, which has the same corrin framework as the naturally occurring B_{12} [16] as shown in Fig. 1. The B_{12} model complex can have an alkyl group as an axial ligand but cannot have two alkyl groups. The Co(III) monoalkylated complex is active for the electrochemical reduction, resulting in fragmentation to the Co(I) species, as exemplified by the electrochemical reactivity of the Co(III)-CH_3 complex of **1** in Eq. (4) and Table 1 [24]. Interestingly, we demonstrated that compound **1**

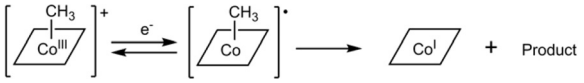
Table 2
Electrolysis of **3** mediated by **1** and **2**.[a]



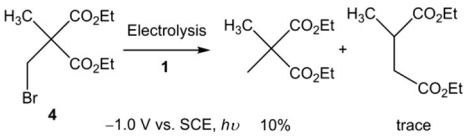
Entry	Catalyst	Potential/V[b]	Charge/F mol^{-1}[c]	Cell type	Conversion/%[d]	Product ratio/%[e]			
						A	B	C	
1[f,g]	**1**	− 1.0	0.15	Divided	10	74	24	2	This work
2[f]	**1**	− 1.5	0.13	Divided	15	81	17	2	This work
3[f]	**1**	− 2.0	2.25	Divided	85	32	5	63	This work
4[h]	**2b**	− 0.90	0.4	Undivided[i]	3	98	2	Trace	Ref. [21]
5[h]	**2b**	− 1.20	1.5	Undivided[i]	10	36	1	62	Ref. [21]
6[h]	**2b**	− 1.20	0.3	Divided	10	83	11	6	Ref. [21]
7[h,j]	**2b**	− 1.20	1.7	Undivided[i]	36	86	8	6	Ref. [21]

[a] Controlled-potential electrolyses were carried out in DMF using a three-electrode cell divided into two internal compartments with a single sheet of a microporous polypropylene membrane. Pt mesh working and Ag-AgCl reference electrodes were set in one side and Pt mesh counter electrode on the other side.
[b] Employed potential (V) *vs.* Ag-AgCl.
[c] Electrical charge passed per mol of **3**.
[d] Conversion was estimated by the recovery of **3**.
[e] Products were analyzed by GC.
[f] Initial concentration: [**1**] = 9.3×10^{-4} M, [**3**] = 0.10 M, [*n*-Bu_4NBF_4] = 0.5 M.
[g] Light irradiation by a 300 W tungsten lamp.
[h] Initial concentration: [**2b**] = 9.3×10^{-4} M, [**3**] = 0.10 M, [*n*-Bu_4NBF_4] = 0.25 M.
[i] In an undivided cell (without a single sheet of a polypropylene membrane).
[j] Use of a Zn counter electrode instead of a Pt mesh counter electrode.

also mediates the 1,2-migration of the carboxylic ester group under electrochemical conditions (Eq. (5)) [25]. For the carbon-skeleton rearrangement reactions, the reduction process of the Co(III) monoalkylated complex is crucial for the 1,2-migration of the carboxylic ester group *via* an anionic intermediate. However, the electrochemical application of carbon-skeleton rearrangements still represents an almost unexplored area because of the few catalyst examples.



(4)



−1.0 V vs. SCE, *hυ*	10%	trace
−1.5 V vs. SCE	30%	trace
−2.0 V vs. SCE	15%	80%

(5)

To expand the scope of the types of migrating functional groups in electrochemical carbon-skeleton rearrangements, substrate **3** was applied to the **1**-mediated electrolysis in this study. In carrying out this study, we have constructed a new method for electrochemically controlling the selectivity for the 1,2-migrating group (phenyl *vs.* carboxylic ester group) with **1**. In addition, the product contribution provided additional mechanistic insights into the **1**-mediated 1,2-migration. Furthermore, by comparing **1** to **2**, we have clarified the impact of the corrin framework of vitamin B_{12} on the carbon-skeleton rearrangement.

2. Experimental

2.1. Materials

All solvents and chemicals used in the syntheses were of reagent grade and used without further purification. For the electrochemical studies, *N,N*-dimethylformamide (DMF) was stirred for one day in the presence of BaO under a nitrogen atmosphere, then distilled under reduced pressure. Heptamethyl cobyrinate perchlorate [Cob(II) $7C_1$ester]ClO_4 **1** was synthesized according to the previously reported methods [16a]. The substrate, diethyl 2-bromomethyl-2-phenylmalonate **3**, and the authentic samples of diethyl 2-methyl-2-phenylmalonate **A** and diethyl phenylsuccinate **C** were synthesized according to a previously reported method [21]. The authentic samples of diethyl 2-benzyl-2-phenylmalonate **B** were purchased from Tokyo Kasei Kogyo (TCI).

2.2. General analyses and measurements

The ESR spectra were obtained using a JEOL JES-ME3 X-band spectrometer equipped with a 100 kHz field modulation unit, and a standard MgO/Mn^{II} sample calibrated with an NMR field. The ^1H NMR spectra were obtained by a Bruker AMX-500 (500 MHz) or a Bruker AC-250P (250 MHz) spectrometer.

All the voltammetric experiments were carried out using an apparatus composed of a Hokuto Denko HA-501 potentiostat/galvanostat and a Hokuto Denko HB-104 function generator. The experiments were performed using a conventional three-electrode system. Platinum wires (0.50 mm diameter) were employed as the counter and working electrodes, and an Ag-AgCl (3.0 M NaCl) electrode as the reference electrode. Nonaqueous DMF solutions containing **1** (7.2×10^{-4}), **3** (1.0×10^{-2} M) and *n*-Bu_4NBF_4 (5.0×10^{-2} M) were deaerated prior to each measurement, and an argon atmosphere was maintained inside the cell throughout each measurement. All measurements were carried out at room temperature. The $E_{1/2}$ value of ferrocene/ferrocenium (Fc/Fc^+) was 0.56 V *vs.* Ag-AgCl with this setup.

The controlled-potential electrolysis of **3** (0.10 M) was carried out in the presence of **1** (9.3×10^{-4} M) in DMF containing *n*-Bu_4NBF_4 (0.50 M) in a cylindrical three-electrode cell with a single sheet of a microporous polypropylene membrane which was divided into two internal compartments under a nitrogen atmosphere. Platinum mesh working counter electrodes and an Ag-AgCl reference electrode were used in this system. The applied potential between the working and reference electrodes during the electrolysis was maintained constant by a Hokuto Denko HA-305 potentiostat/galvanostat, and the reaction was monitored by a Hokuto Denko HF-201 coulomb/ampere-hour meter. The light irradiation was carried out by a 300 W tungsten lamp. After the electrolysis, DMF was removed by evaporation under reduced pressure and 30 mL of $CHCl_3$ was added to the residue. The chloroform layer was washed with water (3 × 40 mL) to completely remove the DMF then dried over Na_2SO_4. The filtrate was then concentrated to dryness. The residue was passed through a silica gel short column eluting with $CHCl_3$ to remove the *n*-Bu_4NPF_6 and **2**, and the products were then analyzed by GC. The GC data were obtained using a Shimadzu GC-4C or GC-9APF apparatus.

3. Results and discussion

3.1. Electrochemical behavior of 1 in the presence of 3

We first investigated the redox behavior of **1** in the presence of the substrate **3** by cyclic voltammetry. As shown in Fig. 2, the redox couple of Co(II)/Co(I) was observed at − 0.61 V *vs.* Ag-AgCl, which is consistent with a previous study of **1** [24]. As the Co(I) species of the B_{12} derivatives is one of the strongest supernucleophiles [26–28], the formed Co(I) species of **1** reacts with **3** to form the corresponding Co(III) alkyl complex by debromination as expressed in Eq. (6) [29]. In addition, two irreversible reduction peaks were observed at − 1.3 and − 1.8 V *vs.* Ag-AgCl as shown in Fig. 2. Because no reduction peaks were observed in the absence of **1** in the range of − 2.0 to 0 V *vs.* Ag-AgCl, the two irreversible reduction peaks at − 1.3 and − 1.8 V *vs.* Ag-AgCl do not originate from the substrate **3** itself. The potentials of the two irreversible peaks in Fig. 2 are comparable to those of the formation of the one-electron-reduced and two-electron-reduced species of another Co(III) alkyl complex resulting from diethyl 2-bromomethylmalonate **4** used in our previous study [24,25]. Thus, the two irreversible peaks at − 1.3 and − 1.8 V *vs.* Ag-AgCl in Fig. 2 are ascribed to the formation of the one-electron-reduced and two-electron-reduced species of the corresponding Co(III) alkyl complex, respectively, as expressed in Eq. (7). The multi-electron process of the monoalkylated complex of **1** is a characteristic feature of the corrin framework, while the one-electron reduction of the monoalkylated complex of **2** results in

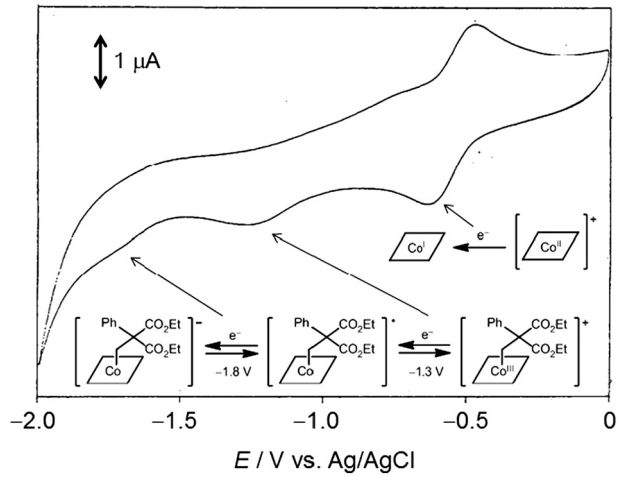
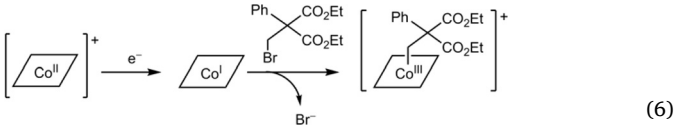
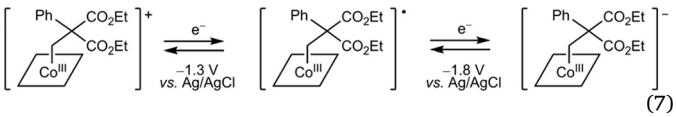


Fig. 2. Cyclic voltammograms of **1** (7.2×10^{-4} M) in the presence of an excess of **3** (1.0×10^{-2} M) and in DMF containing *n*-Bu_4NBF_4 (5.0×10^{-2} M).

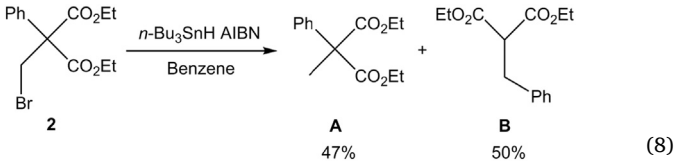
the disproportionation to the Co(I) species and the dialkylated complex (Eq. (8)) [21]. The B_{12} model complex **1** does not form a dialkylated complex because of the steric hindrance of the corrin with the cobalt center during the second alkylation. While the anodic electrochemistry of the dialkylated complex of **2** is critical for the electrolysis of **3**, the cathodic electrochemistry of the monoalkylated complex of **1** is a key process in the electrolysis of **3** as discussed below.



(6)



(7)



(8)

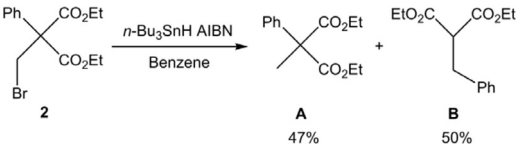
3.2. Controlled-potential electrolysis of 3 mediated by 1

Based on the investigation by cyclic voltammetry, the controlled-potential electrolysis of **3** in the presence of a catalytic amount of **1** was carried out in DMF under several conditions. The products were analyzed by GC as summarized in Table 2. When the electrolysis was carried out at − 1.0 V *vs.* Ag-AgCl along with light irradiation (Entry 1), the phenyl migrated product **B** was obtained in a 24% product ratio, and the simple reduced product **A** was obtained as the major product. When the electrolysis was carried out at − 1.5 V *vs.* Ag-AgCl (Entry 2), the phenyl migrated product **B** was also obtained and the product contribution was not changed. On the other hand, when the electrolysis was carried out at − 2.0 V *vs.* Ag-AgCl (Entry 3), the conversion of **3** was significantly increased. This is probably because the reactivity of the Co(III) alkyl intermediate complex varies at the applied potential. Interestingly, the formation of **B** decreased and the product ratio of the carboxylic ester migrated product **C** was obtained in a 63% product ratio as the major product. It is noticeable that the selectivity for the migrating group (phenyl *vs.* carboxylic ester group) was tuned by controlling the electrolysis potential.

In our previous **2**-mediated electrolysis, the participation of the anodic process during the 1,2-migration of the carboxylic ester group was confirmed by the fact that the selectivity for **C** was enhanced by removing the cell partition (Entry 5 *vs.* Entry 6) and was dependent on the type of the counter (Zn or Pt) electrodes (Entry 5 *vs.* Entry 7) [21]. This enabled the duet redox process between the reduction of the monoalkylated complex and oxidation of the dialkylated complex. On the other hand, during the present **1**-mediated electrolysis, the participation of the anodic process in the 1,2-migration of the carboxylic ester group is ruled out because the electrolysis cell was divided into two internal compartments with a polypropylene membrane.

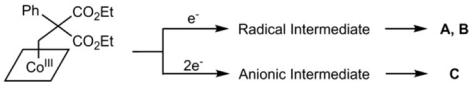
3.3. Mechanistic aspects

To obtain a mechanistic insight into the **1**-mediated electrolysis of **3** at − 1.0 V and − 1.5 V *vs.* Ag-AgCl, the electrolysis in the presence of a spin trap agent, *α*-phenyl *N*-tertiary-butyl nitrone (PBN) (0.83 equivalent *vs.* **3**), was monitored by ESR. When the electrolysis was carried out at − 1.0 V *vs.* Ag-AgCl along with light irradiation, a spin trap adduct was observed in the ESR spectrum ($g = 2.01$, $A_N = 1.37 \times 10^{-3}\,cm^{-1}$, $A_H = 2.7 \times 10^{-4}\,cm^{-1}$) as shown in Fig. S2a. When the electrolysis was carried out at − 1.5 V *vs.* Ag-AgCl, a spin trap adduct was also observed ($g = 2.01$, $A_N = 1.37 \times 10^{-3}\,cm^{-1}$, $A_H = 2.7 \times 10^{-4}\,cm^{-1}$) as shown in Fig. S2b [30]. These results imply the involvement of a radical intermediate for the formations of **A** and **B**. This is consistent with a previous study on the radical-involved reaction of **3** using conventional methods with *n*-Bu_3SnH and AIBN, leading the hydrodebromination of the *β*-carbon of the alkyl bromide **3** as well as the 1,2-phenyl migration in the *β*-phenyl carbon centered radical, as expressed in Eq. (9). The present selectivity for **B** in DMF was about 27–35% lower than the previous one in benzene in a former study because DMF is a good hydrogen radical donor [31]. The radical intermediate in the present study results from the photolysis or the one-electron reduction of the monoalkylated complex of **1**. This is consistent with the reported reactivity of alkylcobalamin and derivatives as radical forming reagents [32].



(9)

To obtain a mechanistic insight into the **1**-mediated electrolysis of **3** at − 2.0 V *vs.* Ag-AgCl, the electrolysis was carried out in the presence of acetic acid-d_1 (CH_3COOD). The main product was isolated by gas chromatography and identified as a mixture of **C** and the carboxylic ester migrated product containing one deuterium, $(H_5C_2O_2C)CH_2CD(C_6H_5)(CO_2C_2H_5)$, by NMR. The deuterium incorporation ratio was 29%. This result implies that the protonation of an anionic intermediate is a possible pathway of the formation of **C**. The relatively low incorporation ratio of the deuterium ion is probably due to the proton-exchange between CH_3COOD and water involved in DMF [33,34], the proton donation from formic acid formed by the decomposition of DMF [33], and/or the proton donation from the Hofmann elimination of the *n*-Bu_4 salt [35]. The participation of the anionic intermediate in the 1,2-carboxylic ester migration is consistent with our previous study on the **1**-mediated electrolysis of diethyl 2-bromomethyl-malonate **4** [24,25]. Based on previous and present studies, the participation of a radical intermediate in the 1,2-migration of the carboxylic ester group is ruled out. Furthermore, we clarified that the key processes of the 1,2-migration are the electrochemical reactivity of the monoalkylated complexes of **1** as expressed by Eq. (10).



(10)

Based on the mechanistic investigation, mechanisms at − 1.0, − 1.5 and − 2.0 V *vs.* Ag-AgCl are proposed as shown in Fig. 3. The electrochemically generated Co(I) species of **1** induces the oxidative addition of the alkyl bromide **3** to the cobalt center with debromination. The resulting Co(III) monoalkylated complex reacts in three different ways.

(i). Electrolysis − 1.0 V vs. Ag-AgCl; upon the light irradiation, the Co—C bond of the monoalkylated complex is homolytically cleaved to form 1 and a radical intermediate. The radical intermediate abstracts a hydrogen atom before and after the 1,2-migration of a phenyl group via a radical mechanism to afford A and B, respectively.

(ii). Electrolysis − 1.5 V vs. Ag-AgCl; the one-electron-reduction of the monoalkylated complex results in cleavage of the Co—C bond to form the Co(I) species and a radical intermediate. The radical intermediate abstracts a hydrogen atom before and after the 1,2-migration of a phenyl group via a radical mechanism to afford A and B, respectively.

(iii). Electrolysis − 2.0 V vs. Ag-AgCl; the two-electron-reduction of the monoalkylated complex results in the cleavage of the Co—C bond to form the Co(I) species and an anionic intermediate, consistent with the mass and charge balance. The 1,2-migration of a carboxylic ester group proceeds via an anionic mechanism to afford C.

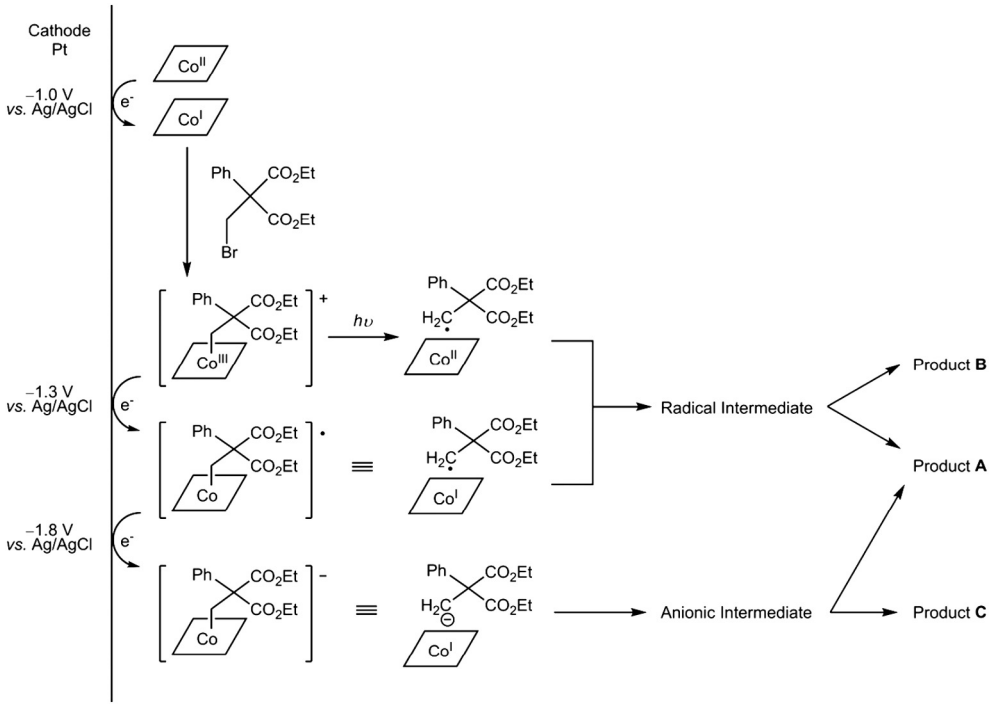


Fig. 3. Proposed mechanism of electrolysis of **3** mediated by **1** in the divided cell.

4. Conclusions

In this study, an alkyl bromide substrate **3** having two different migrating groups on the *β*-carbon (phenyl and carboxylic ester group) was applied to electrolysis mediated by the B_{12} model complex **1**. The electrolysis of **3** at − 1.0 V *vs.* Ag-AgCl along with light irradiation afforded the simple reduced product **A** as well as the phenyl migrated product **B**. The electrolysis of **3** at − 1.5 V *vs.* Ag-AgCl afforded **A** as well as **B**. The electrolysis of **3** at − 2.0 V *vs.* Ag-AgCl afforded the carboxylic ester migrated product **C** as the major product. We found that the selectivity for the migrating group can be tuned by controlling the electrolysis potential. The cathodic chemistry of the Co(III) alkylated complex of **1** is critical for the selectivity of the migrating group; the one-electron-reduction of the alkylated complex results in the 1,2-migration of the phenyl group *via* a radical intermediate while the two-electron-reduction of the carboxylic ester group *via* an anionic intermediate. This finding is a characteristic feature for the cobalt complex having the corrin ligand, and stands in contrast to the reactivity of the monoalkylated complex of **2**, the one-electron-reduction of which results in the disproportionation to the Co(I) species and the Co(III) dialkylated complex. A common feature between **1** and **2** is that the electrolysis mediated by them afforded the carboxylic ester migrated product **C** *via* ionic intermediates, which are generated by the cathodic reaction of the monoalkylated complex of **1** and the anodic reaction of the dialkylated complex of **2**, respectively. This work provides unique insights into exploiting the potential of the derivate of naturally occurring B_{12} under non-enzymatic conditions for electrochemical applications.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number JP16H01035 in Precisely Designed Catalysts with Customized Scaffolding, Grant Number JP16H06514 in Coordination Asymmetry, and Grant Number JP16H04119.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jinorgbio.2017.07.021.

References

[1] (a) P.A. Frey, Chem. Rev. 90 (1990) 1343–1357;
(b) P.A. Frey, Annu. Rev. Biochemist 70 (2001) 121–148.
[2] (a) J. Stubbe, Annu. Rev. Biochem. 58 (1989) 257–285;
(b) J. Stubbe, W.A. van der Donk, Chem. Rev. 98 (1998) 705–762.
[3] A. Jordan, P. Reichard, Annu. Rev. Biochem. 67 (1998) 71–98.
[4] G. Sawers, G. Watson, Mol. Microbiol. 29 (1998) 945–954.
[5] T. Toraya, Chem. Rev. 103 (2003) 2095–2128.
[6] B. Kräutler, B. Kräutler, D. Arigoni, B.T. Golding (Eds.), Vitamin B_{12} and B_{12}-Proteins, Wiley-VCH, Weinheim, 1998.
[7] G. Wohlfarth, G. Diekert, R. Banerjee (Ed.), Chemistry and Biochemistry of B_{12}, Wiley-Interscience, New York, 1999.
[8] W. Buckel, B.T. Golding, Chem. Soc. Rev. (1996) 329–337.
[9] K. Gruber, B. Puffer, B. Kräutler, Chem. Soc. Rev. 40 (2011) 4346–4363.
[10] Y. Murakami, J. Kikuchi, Y. Hisaeda, O. Hayashida, Chem. Rev. 96 (1996) 721–758.
[11] (a) Y. Hisaeda, K. Tahara, H. Shimakoshi, T. Masuko, Pure Appl. Chem. 85 (2013) 1415–1426;
(b) Y. Qiao, K. Tahara, Q. Zhang, X.-M. Song, Y. Hisaeda, J. Kikuchi, Chem. Lett. 43 (2014) 684–686.
[12] (a) T. Hayashi, Y. Morita, E. Mizohata, K. Oohora, J. Ohbayashi, T. Inouea, Y. Hisaeda, Chem. Commun. 50 (2014) 12560–12563;
(b) Y. Morita, K. Oohora, A. Sawada, K. Doitomi, J. Ohbayashi, T. Kamachi, K. Yoshizawa, Y. Hisaeda, T. Hayashi, Dalton Trans. 45 (2016) 3277–3284;
(c) Y. Morita, K. Oohora, E. Mizohata, A. Sawada, T. Kamachi, K. Yoshizawa, T. Inoue, T. Hayashi, Inorg. Chem. 55 (2016) 1287–1295;
(d) Y. Morita, K. Oohora, A. Sawada, T. Kamachi, K. Yoshizawa, T. Hayashi, Inorg. Chem. 56 (2017) 1950–1955.
[13] G.N. Schrauzer, Acc. Chem. Res. 1 (1968) 97–103.
[14] G. Costa, Coord. Chem. Rev. 8 (1972) 63–75.
[15] C. Rovira, K. Kunc, J. Hutter, M. Parrinello, Inorg. Chem. 40 (2001) 11–17.
[16] (a) Y. Murakami, Y. Hisaeda, A. Kajihara, Bull. Chem. Soc. Jpn. 56 (1989) 3642–3646;
(b) Y. Hisaeda, H. Shimakoshi, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), In Handbook of Porphyrin Science, Vol. 10 World Scientific, Singapore, 2010, pp. 313–370;
(c) H. Shimakoshi, Y. Hisaeda, ChemPlusChem 79 (2014) 1250–1253;
(d) H. Shimakoshi, Y. Hisaeda, Angew. Chem. Int. Ed. 54 (2015) 15439–15443;
(e) H. Shimakoshi, Y. Hisaeda, ChemPlusChem, 82 (2017) 18–29.
[17] (a) K.Ó. Proinsias, M. Giedyk, D. Gryko, Chem. Soc. Rev. 42 (2013) 6605–6619;
(b) M. Giedyk, S.N. Fedosov, D. Gryko, Chem. Commun. 50 (2014) 4674–4676;
(c) M. Giedyk, K. Goliszewska, D. Gryko, Chem. Soc. Rev. 44 (2015) 3391–3404.
[18] W.H. Tamblyn, R.J. Klingler, W.S. Hwang, J.K. Kochi, J. Am. Chem. Soc. 103 (1981) 3161–3172.
[19] C.M. Elliot, H. Hershnhart, R.G. Finke, B.L. Smith, J. Am. Chem. Soc. 103 (1981) 5558–5566.
[20] (a) Y. Murakami, Y. Hisaeda, S.-D. Fan, Y. Mastuda, Chem. Lett. (1988) 835–838;
(b) Y. Murakami, Y. Hisaeda, S.-D. Fan, Y. Mastuda, Bull. Chem. Soc. Jpn. 62 (1989) 2219–2228.
[21] K. Tahara, Y. Chen, L. Pan, T. Masuko, H. Shimakoshi, Y. Hisaeda, Chem. Lett. 40

(2011) 177–179.
[22] A. Studer, M. Bossart, Tetrahedron 57 (2001) 9649–9667.
[23] (a) H. Shimakoshi, M. Abiru, S. Izumi, Y. Hisaeda, Chem. Commun. (2009) 6427–6429;
(b) S. Izumi, H. Shimakoshi, M. Abe, Y. Hisaeda, Dalton Trans. 39 (2010) 3302–3307.
[24] Y. Hisaeda, T. Nishioka, Y. Inoue, K. Asada, T. Hayashi, Coord. Chem. Rev. 198 (2000) 21–37.
[25] Y. Murakami, Y. Hisaeda, T. Ozaki, T. Tashiro, T. Ohno, Y. Tani, Y. Matsuda, Bull. Chem. Soc. Jpn. 60 (1987) 311–324.
[26] K.P. Jensen, J. Phys. Chem. B 109 (2005) 10505–10512.
[27] M.D. Liptak, T.C. Brunold, J. Am. Chem. Soc. 128 (2006) 9144–9156.
[28] (a) H. Shimakoshi, Y. Maeyama, T. Kaieda, T. Matsuo, E. Matsui, Y. Naruta, Y. Hisaeda, Bull. Chem. Soc. Jpn. 78 (2005) 859–863;
(b) H. Shimakoshi, M. Abiru, K. Kuroiwa, N. Kimizuka, M. Watanabe, Y. Hisaeda, Bull. Chem. Soc. Jpn. 83 (2010) 170–172;
(c) K. Tahara, H. Shimakoshi, A. Tanaka, Y. Hisaeda, Bull. Chem. Soc. Jpn. 83 (2010) 1439–1446;
(d) K. Tahara, Y. Hisaeda, Green Chem. 13 (2011) 558–561;
(e) K. Tahara, K. Mikuriya, T. Masuko, J. Kikuchi, Y. Hisaeda, J. Porphyrins Phthalocyanines 17 (2013) 135–141;
(f) K. Tahara, K. Mikuriya, T. Masuko, J. Kikuchi, Y. Hisaeda, Supramol. Chem. 28 (2016) 141–150.
[29] Indeed, upon the addition of **3** to the methanol solution of the Co(I) species of **1** formed by $NaBH_4$ at 2 °C, a UV–vis spectral change was observed as shown in Figure S1a, indicating the reaction of the Co(I) species of **1** with **3**. The light irradiation of the resulting compound afforded **1** (Co(II) species) as shown in Figure S1b, indicating that this photo-sensitive compound is an alkyl complex.
[30] The spin trap technique was not applicable to the electrolysis of **3** at − 2.0 V vs. Ag-AgCl because the background signal was observed even in the absence of **1**.
[31] A.P. Esteves, D.M. Goken, L.J. Klein, L.F.M. Leite, M.J. Medeiros, D.G. Peters, Eur. J. Org. Chem. (2005) 4852–4859.
[32] K.L. Brown, Chem. Rev. 105 (2005) 2075–2149.
[33] J.A. Riddick, W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 1970, pp. 836–840.
[34] A.J. Frey, R.G. Reed, J. Am. Chem. Soc. 94 (1972) 8475–8484.
[35] A.J. Frey, R.G. Reed, J. Am. Chem. Soc. 93 (1971) 553–554.