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# Methyl-transfer reaction to alkylthiol catalyzed by a simple vitamin $B_{12}$ model complex using zinc powder

Ling Pan<sup>a,b</sup>, Keishiro Tahara<sup>a</sup>, Takahiro Masuko<sup>a</sup>, Yoshio Hisaeda<sup>a,c,\*</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan

<sup>b</sup> Department of Chemistry, Northeast Normal University, Changchun 130024, PR China

<sup>c</sup> International Research Center for Molecular Systems (IRCMS), Kyushu University, Fukuoka 819-0395, Japan

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### ABSTRACT

The catalytic methyl-transfer reaction from methyl tosylate to 1-octanethiol was carried out in the presence of a simple vitamin  $B_{12}$  model complex, [Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>], with zinc powder as the reducing reagent at 50 °C. Such a catalytic reaction proceeded via the formation and dissociation of a cobalt–carbon bond in the simple vitamin  $B_{12}$  model complex under non-enzymatic conditions. The mechanism for the methyl-transfer reaction was investigated by electronic and mass spectroscopies. The Co(I) species, which is generated from the reduction of the catalyst by the zinc powder, and its methylated CH<sub>3</sub>–Co complex were found to be indispensable intermediates.

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### 1. Introduction

The B<sub>12</sub>-dependent enzymes catalyze various molecular transformations. As examples, the rearrangement reactions as typified by the conversion of methylmalonyl-CoA to succinyl-CoA, the methylation reaction as in the synthesis of methionine, and the dehalogenation reaction of perchloroethylene [1–8]. These reactions are very interesting from the viewpoint of organic synthesis. Many B<sub>12</sub> artificial enzyme systems are reported as the biomimetic or bioinspired catalysts [9–17], but the model reactions of the B<sub>12</sub>dependent methionine synthase are limited [18–22]. In the present study, we focused on the model reaction of the B<sub>12</sub>-dependent methionine synthase in a non-enzymatic system.

The B<sub>12</sub>-dependent methionine synthase catalyzes the methyltransfer reaction from methyltetrahydrofolate (CH<sub>3</sub>–H<sub>4</sub>folate) to homocysteine as shown in Fig. 1. During the catalytic turnover, the cofactor cycles between methylcobalamin and Cob(I)alamin forms, being alternately demethylated by homocysteine and remethylated by CH<sub>3</sub>–H<sub>4</sub>folate. It is difficult to achieve such a catalytic cycle under non-enzymatic conditions, and few model studies with reasonable yields have been reported [19]. During the catalytic

\* Corresponding author at: Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan. Tel.: +81 92 802 2806; fax: +81 92 802 2807. turnover, Cob(I)alamin has been shown to be a kinetically competent intermediate.

We have reported an application for such a methyl-transfer reaction involving the methylation of arsenic trioxide by the methylated vitamin  $B_{12}$  model complexes [23,24]. Furthermore, we explored a methyl-transfer reaction from methyl tosylate (TsOCH<sub>3</sub>) to 1-octanethiol under controlled-potential electrolyses at -1.0 V vs. Ag/AgCl at 50 °C with the hydrophobic vitamin  $B_{12}$  (heptamethyl cobyrinate perchlorate, [Cob(II)7C<sub>1</sub>ester]ClO<sub>4</sub>) [25–28], which has ester groups in place of the peripheral amide moieties of the naturally occurring cobalamin and shows excellent catalytic ability in organic solvents [29], as the catalyst. The formation and formally heterolytic cleavage of the Co–CH<sub>3</sub> bond in the catalyst is confirmed to be an indispensable process in this catalytic cycle. The controlled-potential electrolysis insured the continuous Co<sup>1</sup> species, accepting the methyl group from TsOCH<sub>3</sub> and donating it to 1-octanethiol [30].

When we used a simple model complex, the diimine–dioxime type vitamin  $B_{12}$  model complex [Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] (**1** in Fig. 2), which has a similar redox behavior to the natural vitamin  $B_{12}$ , as a catalyst undergoing such a controlled-potential electrolysis [31], the catalytic methyl-transfer reaction also proceeded, although complex **1** decomposed during the electrolysis. Different from the reactions catalyzed by the hydrophobic vitamin  $B_{12}$ , the color of the reaction solution quickly changed from light green to dark when the Zn anode was initially fitted on before the controlled-potential electrolysis indicating a variation in the oxidation





E-mail address: yhisatcm@mail.cstm.kyushu-u.ac.jp (Y. Hisaeda).



Fig. 1. Cobalamin-dependent methyl-transfer reaction from methyltetrahydrofolate to homocysteine.



**1:** X = Br, Y =Br, [Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] **2:** X = CH<sub>3</sub>, Y =I, [(CH<sub>3</sub>)Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}I]

Fig. 2. Diimime-dioxime type simple B<sub>12</sub> model complex.

state of Co(III) in complex **1**. Combined with the surprising fact that the methyl-transfer reaction catalyzed by complex **1** proceeded well even without undergoing the controlled-potential electrolysis, but in the presence of the Zn anode with the other conditions unchanged, it was deduced that the Zn plate possessed a special reductive ability to  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  **1**.

Thus, we focused on the metal-promoted reductive reactions to replace the complicated controlled-potential electrolysis. We now report the diimine-dioxime type vitamin B<sub>12</sub> model complex 1 catalyzed methyl-transfer reaction from methyl tosylate to 1-octanethiol utilizing zinc powder as the reducing reagent as shown in Fig 3. Such metal-promoted reductive reactions have been successfully utilized in the Mg-promoted carbon-silvlation of carbonyl compounds and activated olefins [32-34]; Mg-promoted reductive coupling of carbonyl compounds [35-36]; Zn-promoted intramolecular conjugated addition of iodo enones [37]; and Zn-promoted one pot three-component joining reactions of  $\alpha$ ,  $\beta$ -unsaturated esters, alkyl iodides, and acylating reagents [38]. These processes usually possess advantages such as friendly to the environment, safety, simplicity and easily available. We found that our catalytic cycle from methyl tosylate to 1-octanethiol could easily proceed without decomposition of the catalyst.



Fig. 3. Methyl-transfer reaction catalyzed by simple  $B_{12}$  model complex with Zn powder as the reducing reagent.

### 2. Experimental

### 2.1. General analysis and measurements

The electronic absorption spectra were measured using a Hitachi U-3310 spectrophotometer and a 10-mm cell. The <sup>1</sup>H NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis, Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. Cyclic voltammograms were obtained using a BAS ALS-630C electrochemical analyzer. The CSI-MS was measured by an AccuTOF CS JMS-T100cs from JEOL. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length: 30 m; ID: 0.25 mm, film: 0.25 m) and helium as the carrier gas. For the measurements, the injector and detector temperatures were 250 °C, the oven temperature was initially held at 100 °C for 2 min, then increased to 240 °C at the rate of 10 °C/min. Thin layer chromatography was carried out using silica gel 60 N (spherical, neutral) as the solid phase which was purchased from Kanto Chemical, Co., Inc.

### 2.2. Materials

All solvents and chemicals were of reagent grade and used without further purification. Dry *N*,*N*-dimethylformamide (DMF) was purchased from Nakalai Chemicals and stored under an N<sub>2</sub> atmosphere. Methanol was dried and purified just before use according to the standard procedure. Tetra-*n*-butylammonium perchlorate (*n*-Bu<sub>4</sub>NClO<sub>4</sub>) was purchased from Nakalai Chemicals (Special grade) and dried at room temperature under vacuum before use. The zinc powder was purchased from Nakalai Chemicals and activated by a 5% HCl aqueous solution before use and dried under vacuum after fully washed by water and acetone. The diimine–dioxime type vitamin B<sub>12</sub> model complex **1**, [Co(III)-{(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] and [(CH<sub>3</sub>)Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}I] **2** were synthesized as already reported by our laboratory [31].

# 2.3. Cyclic voltammetry

A cylindrical three-electrode cell was used that was equipped with a 1.6-mm diameter platinum wire as the working electrode, a 25-mm platinum wire as the counter electrode and an Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. The scan rate was up to 100 mV s<sup>-1</sup> and the half-wave potential ( $E_{1/2}$ ) was calculated to be 0.56 V vs. Ag/AgCl as the  $E_{1/2}$  value for the ferrocene–ferrocenium (Fc/Fc<sup>+</sup>) couple. The dry DMF solution of [Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] **1** and *n*-Bu<sub>4</sub>NClO<sub>4</sub> (1.0 × 10<sup>-1</sup> M) were deaerated by N<sub>2</sub> gas bubbling before the measurements, and the cyclic voltammetry was carried out under an N<sub>2</sub> gas atmosphere at room temperature. The redox behaviors of [Co(III)-{(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] **1** in the presence of TsOCH<sub>3</sub> were investigated in the dark.

# 2.4. Methylation of 1-octanethiol by $[(CH_3)Co(III) \{(C_2C_3)-(DO)(DOH)pn\}I]$ **2**

The direct reaction of 1-octanethiol  $(3.2 \times 10^{-3} \text{ M})$  with [(CH<sub>3</sub>)Co(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}I] **2**  $(3.2 \times 10^{-4} \text{ M})$  was investigated in the presence of  $9.8 \times 10^{-3} \text{ M}$  ZnCl<sub>2</sub> in refluxing methanol in the dark for 24 h. The reaction solution was passed through a short silica gel column and analyzed by GC–MS with diphenyl as the internal standard.

### 2.5. Catalytic methyl-transfer reaction to 1-octanethiol

The zinc powder was activated by a 5% HCl aqueous solution and dried under vacuum for 30 min after completely washed by water and acetone. During drying, the 15 ml DMF solution (15 ml) of  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  **1** (1.8 × 10<sup>-3</sup> M) and  $TsOCH_3~(1.3\times 10^{-2}\,M)$  was deaerated by  $N_2$  gas bubbling for 20 min in a three-neck flask equipped with a condenser. The activated Zn powder (342 mg,  $5.2 \times 10^{-3}$  mol) and 1-octanethiol  $(1.2 \times 10^{-2} \text{ M})$  were then added in the dark. A color change of the reaction solution from light green to dark was observed. The mixture reacted at 50 °C for 4 h under an N<sub>2</sub> gas atmosphere. After allowing the reaction to cool to ambient temperature, the reaction solution was filtered and diluted by 80 ml water and extracted with 80 ml CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed with water  $(3 \times 50 \text{ ml})$  to completely remove the DMF and then dried with Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated and passed through a short silica gel column and analyzed by GC-MS with diphenyl as the internal standard.

### 3. Results and discussion

## 3.1. Direct reaction of 1-octanethiol with complex 2

The direct reaction of 1-octanethiol with complex 2 [(CH<sub>3</sub>)- $Co(III){(C_2C_3)(DO)(DOH)pn}I]$  (2 in Fig. 2) was carried out to examine the reactivity for the cleavage of the Co-CH<sub>3</sub> bond in complex 2 under thermodynamic conditions as shown in Eq. (1). Based on the important roles of zinc ions in the cobalamin-depended methyltransfer reaction in vivo [39] and its model studies [18,29-30], zinc chloride was added as an additive to activate the SH group in 1octanethiol to a stronger nucleophile, i.e., the S<sup>-</sup> ion. Moreover, the zinc also exists in the form of the zinc ion after being utilized as the reducing reagent. As a result, in the dark, after a 24-h reflux under a nitrogen atmosphere in methanol, 1-octanethiol could be methylated with a yield of 29% based on complex 2. Nearly no methylated product could be observed at room temperature or without the addition of ZnCl<sub>2</sub>. The methyl group could be transferred from  $Co-CH_3$  of complex 2 under thermodynamic conditions although the reactivity is not very high.



3.2. Catalytic cycle utilizing zinc powder as the reducing reagent

The catalytic methyl-transfer reaction was then carried out in DMF in the presence of 1-octanethiol,  $TsOCH_3$ , complex 1, and zinc powder in a three-neck flask under various reaction conditions as shown in Eq. (2).



The following results were obtained on the basis of the product analyses listed in Table 1: (i) The methyl-transfer reaction could be effectively achieved with a turnover number of more than four after a 4-h reaction at 50  $^{\circ}$ C in the dark as shown by entry 1 in Ta-

#### Table 1

Methyl-transfer reaction from  $\mathsf{TsOCH}_3$  to 1-octanethiol with Zn powder as the reducing reagent.^a

Entry	Catalyst	Conditions	SCH3	
			μmol <sup>b</sup>	Yield % <sup>c</sup>
1	1	50 °C, 4 h	$120 \pm 5$	498
2	1	50 °C, 2 h	85 ± 2	326
3	1	25 °C, 4 h	24 ± 2	92
4	None	25 °C, 4 h	0	-

 $^a$  The reactions were carried out in 15 ml of DMF at 50 °C under a  $N_2$  atmosphere in the dark with an excess amount of zinc powder (342 mg,  $5.2\times10^{-3}$  mol) as the reducing reagent. Initial concentration: [catalyst],  $1.8\times10^{-3}$  M; TsOCH<sub>3</sub>,  $1.3\times10^{-2}$  M; 1-octanethiol:  $1.2\times10^{-2}$  M.

<sup>b</sup> The quantity of the product is the average of at least two repeated experiments.
 <sup>c</sup> Yield is based on the initial mol of the catalyst.

ble 1. On the other hand, the catalytic methyl-transfer reaction did not proceed without complex **1**. (ii) The catalytic methyl-transfer reaction did not effectively proceed at room temperature (see entries 3 and 4 in Table 1). (iii) The quantity of the product increased with the prolonged reaction time (see entries 1 and 2 in Table 1). From these results, we concluded that such a catalytic cycle from methyl tosylate to 1-octanethiol does work well when  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  was utilized as the catalyst along with Zn powder as the reducing reagent.

### 3.3. Mechanistic aspects

To further confirm the formation of the Co(I) and Co–CH<sub>3</sub> species, the redox behavior of complex **1** was investigated in DMF by cyclic voltammetry in the presence of TsOCH<sub>3</sub> as shown in Fig. 4. The reduction potential for  $Co^{III}/Co^{II}$  was observed at -0.20 V vs. Ag/AgCl, and the redox potential of the  $Co^{II}/Co^{I}$  couple was observed at -0.64 V vs. Ag/AgCl as shown in Fig. 4(a).



**Fig. 4.** Cyclic voltammograms of  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  **1** in DMF containing 0.1 M Bu<sub>4</sub>NCIO<sub>4</sub> at room temperature: (A) **1** ( $1.0 \times 10^{-3}$  M) and (B) after the addition of TsOCH<sub>3</sub> ( $3.3 \times 10^{-2}$  M) to the solution of **1**. Sweep rate: 100 mV s<sup>-1</sup>.



**Fig. 5.** Electronic spectra observed for the 4-h reaction solution with complex **1** as the catalyst and Zn powder as the reducing reagent: (A) the reaction solution and (B) the methylated  $B_{12}$  model complex **2** in DMF.

The redox potential observed at -1.36 V vs. Ag/AgCl was attributed to the one-electron reduction of the diimine-dioxime ligand. After the addition of TsOCH<sub>3</sub>, the redox couple at -1.36 V vs. Ag/AgCl disappeared with a decrease in the peak for the oxidation of Co(I) to Co(II), and a new irreversible reduction peak at -1.42 V vs. Ag/AgCl appeared which could be attributed to the one-electron reduction of the Co-CH<sub>3</sub> complex as shown in Fig. 4(b) [31]. Such variations are consistent with the redox behavior of the hydrophobic vitamin B<sub>12</sub>, [Cob(II)7C<sub>1</sub>ester]-ClO<sub>4</sub> in the presence of TsOCH<sub>3</sub> [25]. It indicates that complex 1 could be reduced to the Co(I) species and react with TsOCH<sub>3</sub> to form the Co-CH<sub>3</sub> bond. Therefore, the zinc powder was considered to have a sufficient reducing power  $(Zn^{2+}/Zn, -0.763 V vs.)$ SHE) to reduce the  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  to the Co(I) species, accepting the methyl group from TsOCH<sub>3</sub> and donating it to 1-octanethiol.

The formation of the  $Co-CH_3$  intermediate could also be observed from the electronic spectroscopy of the reaction solution as shown in Fig. 5. After a 4-h reaction, the electronic spectrum of the reaction solution showed a different pattern with the substrate and showed an obvious peak at about 464 nm as shown in Fig. 5(A). It has an absorption similar to the methylated diimine–dioxime type complex **2** at 464 nm as shown in Fig. 5(B). Combined with the results discussed for the redox behavior of complex **1** in the presence of TsOCH<sub>3</sub>, it indicates that  $[Co(III){(C_2C_3)(DO)(DOH)pn}Br_2]$  was reduced to the super-nucleophilic Co(I) species by Zn powder and reacted with TsOCH<sub>3</sub> to form the Co–CH<sub>3</sub> intermediate. Such a CH<sub>3</sub>–Co complex could also be detected after the reaction indicating the remaining catalytic capability of complex **1**.

The reaction was followed by ESI–MS spectroscopy. When the DMF solution of complex **1** ( $1.8 \times 10^{-3}$  M) and TsOCH<sub>3</sub> ( $1.3 \times 10^{-2}$  M) was stirred for 1 h in the presence of Zn powder under N<sub>2</sub> gas atmosphere at room temperature in the dark, a peak at 397.36 was observed by ESI–MS spectroscopy as shown in Fig. 6. This peak is assigned to [CH<sub>3</sub>–Co]<sup>+</sup> of the diimine–dioxime type simple B<sub>12</sub> model complex. This result also indicates the formation of the Co–CH<sub>3</sub> intermediate during the course of the reaction.

The cleavage of the  $Co-CH_3$  bond in complex 2 was initially investigated by spectroscopic studies for the interaction between complex **2** and 1-octanethiol. The Co-CH<sub>3</sub> bond in complex **2** was rather active in the presence of 1-octanethiol. When an excess amount of 1-octanethiol was added to the DMF solution of complex **2** under aerobic conditions in the dark, the absorption maximum at 464 nm of complex 2 which is characteristic of the Co-CH<sub>3</sub> bond in the diimine-dioxime type model complex [31] decreased as shown in Fig. 7, indicating the strong interaction of the Co–CH<sub>3</sub> bond in complex 2 with 1-octanethiol. After tracking the spectrum for 3 h as room temperature, the absorption maximum at 464 nm further decreased and was consistent with that of the final reaction solution as shown in Fig. 5(A), suggesting that the Co-CH<sub>3</sub> bond in complex 2 was cleaved during the interaction with 1-octanethiol. Such an interaction is indispensable for the catalytic methyl-transfer cycle. This interaction between complex 2 and 1-octanethiol was also observed by the ESI-MS analysis of complex 2 in the presence of 1-octanethiol as shown in Fig. 8. When 100 mol-equiv. of 1-octanethiol was added to the DMF solution of complex **2**, a substitution of the axial ligand on the side opposite to the Co-CH<sub>3</sub> bond by 1-octanethiol was observed (see Eq. (3)) based on the peaks at 543.49 in Fig. 8, which corresponded



**Fig. 6.** ESI-MS spectrum for the reaction between complex 1  $(1.8 \times 10^{-3} \text{ M})$  and TsOCH<sub>3</sub>  $(1.3 \times 10^{-2} \text{ M})$  in the presence of Zn powder under N<sub>2</sub> gas atmosphere at room temperature in the dark.



Fig. 7. Electronic spectral change for the reaction between complex 2  $(2.14\times10^{-4}\,M)$  and 1-octanethiol  $(8.7\times10^{-3}\,M)$  in DMF.

to the  $[CH_3-Co-SC_8H_{17}+H]^+$  of the diimine-dioxime type simple  $B_{12}$  model complex.



In light of these results, we propose a mechanism for the catalytic methyl-transfer reaction from methyl tosylate to 1-octanethiol catalyzed by complex **1** using zinc powder as the reducing reagent as shown in Fig. 9. The central cobalt of complex **1** was reduced to the super-nucleophilic Co(I) species by efficient electrons coming from the excess amount of zinc powder. The Co(I) species facilitate the formation of the Co–CH<sub>3</sub> intermediate by the reaction with methyl tosylate. Under thermodynamic conditions, the Co– CH<sub>3</sub> bond was cleaved with the result that the methyl group was



**Fig. 9.** Proposed reaction mechanism for methyl-transfer reaction from methyl tosylate to alkylthiol catalyzed by simple  $B_{12}$  model complex in the presence of Zn powder.

transferred to the 1-octanthiol to form the methylated product. The catalyst will then be activated again to the Co(I) species in the presence of the excess amount of zinc powder.

### 4. Conclusion

In conclusion, a methyl-transfer cycle from TsOCH<sub>3</sub> to 1-octanethiol catalyzed by a diimine–dioxime type vitamin  $B_{12}$  model complex, [Cob(III){(C<sub>2</sub>C<sub>3</sub>)(DO)(DOH)pn}Br<sub>2</sub>] using zinc powder as the reducing reagent was developed under non-enzymatic conditions. A turnover behavior was observed without any decomposition of the catalyst. The formation and cleavage of the Co–CH<sub>3</sub> bond are indispensable during the catalytic methyl-transfer reaction. The total reaction mechanism for such a zinc powder mediated methyl-transfer reaction was determined by various spectroscopic



Fig. 8. Interaction of complex 2 and 1-octanethiol observed from ESI-MS spectrum in DMF with a 1:100 mol-equiv. for complex 2 and 1-octanethiol.

techniques. This reaction system is expected to apply various methyl-transfer reactions.

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