

(CO<sub>2</sub>Et)<sub>2</sub>bpy but not in 5,5'-(CO<sub>2</sub>Et)<sub>2</sub>bpy.<sup>3</sup> In addition, the Ru(II) complex of 4,4'-(CO<sub>2</sub>Et)<sub>2</sub>bpy (i.e., **3**) exhibits four extra reduction waves beyond the six observed from the Ru(II) complex of 5,5'-(CO<sub>2</sub>Et)<sub>2</sub>bpy (i.e., **2**). This can be easily understood if the reduction of the 4,4'-(CO<sub>2</sub>Et)<sub>2</sub>bpy and 5,5'-(CO<sub>2</sub>Et)<sub>2</sub>bpy ligands is primarily responsible for the reduction process of complexes **2** and **3**, respectively.

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**Registry No.** **1**, 15158-62-0; **2**, 74093-18-8; **3**, 75324-93-5; bpy, 366-18-7; 4,4'-(CO<sub>2</sub>Et)<sub>2</sub>bpy, 1762-42-1; 5,5'-(CO<sub>2</sub>Et)<sub>2</sub>bpy, 1762-46-5; 4,4'-(CO<sub>2</sub>H)<sub>2</sub>bpy, 6813-38-3; 5,5'-(CO<sub>2</sub>H)<sub>2</sub>bpy, 1802-30-8.

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### Mechanisms of Alkylation of Mercuric Ions by Alkylcobalamins

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The reactions of alkylcobalamins with electrophiles such as Hg(II) ions have been considered as direct electrophilic attacks at the  $\alpha$ -carbons.<sup>1</sup> However, our recent work on the methylation of Pt(II)/Pt(IV) couples,<sup>2</sup> diaquocobinamide,<sup>3</sup> and tetracyanoethylene<sup>4</sup> provides results that are not consistent with the S<sub>E</sub>2 mechanism. Consequently, these results are interpreted in terms of a mechanism that involves a "complexation" between the reactants and an electron-transfer process to generate a radical pair. The radical pair collapses to products. In these studies, the "complexation" was observed both kinetically and spectroscopically but the electron-transfer process was proposed mainly on the basis of kinetic observations. Nevertheless, these studies raised the question of an alternative route, i.e. the single-electron-transfer (SET) mechanism. Thus, the reactions of CH<sub>3</sub>-B<sub>12</sub> with the electrophiles might be similar to the electron-transfer reactions of alkylcobaloximes (or other B<sub>12</sub> model compounds)<sup>5</sup> and macrocyclic dimethylcobalt(III) complexes<sup>6</sup> and to the reactions of TCNE on organometallic compounds of Pb and Sn.<sup>7</sup>

The experiences of the reactions between CH<sub>3</sub>-B<sub>12</sub> and the above electrophiles inevitably led us to suspect that a reexamination of the mechanisms of reactions between alkylcobalamins and mercuric ions is warranted. A survey in the literature indicates that although previous reports on the CH<sub>3</sub>-B<sub>12</sub> methylation of mercuric ions provided some valuable information on the "medium" effects, the kinetic and mechanistic data are not sufficiently quantitative to make a case for an S<sub>E</sub>2 mechanism.<sup>8</sup> In particular, the validity of the very great difference between the dealkylation rates of Hg(OAc)<sub>2</sub> with methylaquocobinamide and Hg(OAc)<sub>2</sub> with ethylaquocobinamide<sup>8b</sup> is not totally unquestionable. Since this difference is essential for the S<sub>E</sub>2 mechanism, we decided to investigate the Hg(II) dealkylation of CH<sub>3</sub>-B<sub>12</sub> and C<sub>2</sub>H<sub>5</sub>-B<sub>12</sub> in hydrochloric acid solutions.

This note presents the results of our reexamination.

### Experimental Section

All the corrinoids used in this report were generous gifts from H. P. C. Hogenkamp.<sup>9</sup> The mercuric chloride and the other chemicals were reagent grade and were used as received. The information with regard to the chloride complex formation of Hg<sup>2+</sup> has been reported by Sillen,<sup>10</sup> whose results showed HgCl<sub>3</sub><sup>-</sup> and HgCl<sub>4</sub><sup>2-</sup> to be the dominant species for a mercuric chloride solution at 0.10 M KCl. Since the present report concerns the reactions in 1.0 M chloride solutions, the Hg(II) ions are referred to as HgCl<sub>n</sub><sup>2-n</sup> hereafter.

Pulse Fourier transformed <sup>13</sup>C (75.5 MHz) NMR spectra of the methyl-transfer products of the reactions between <sup>13</sup>CH<sub>3</sub>-B<sub>12</sub> (90% enriched) and HgCl<sub>n</sub><sup>2-n</sup> were obtained at 25 °C with a Nicolet 300 spectrometer locked to the resonance of internal D<sub>2</sub>O. The spectra were obtained under conditions of simultaneous proton noise decoupling. Chemical shifts were measured with respect to external TSP.

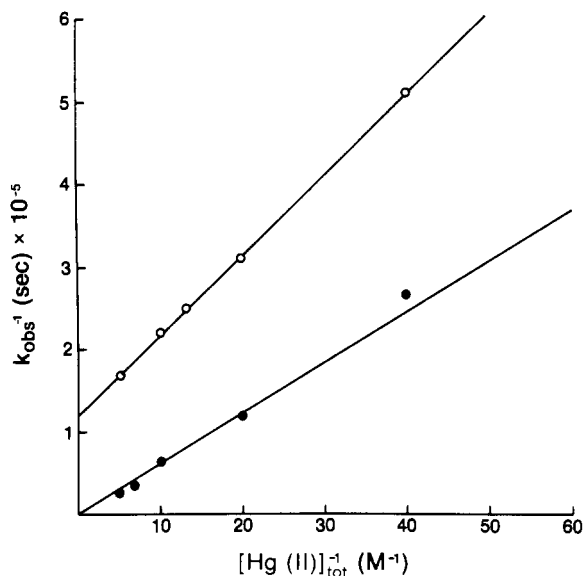
The reaction rates were monitored at 350 nm ( $\gamma$ -bands of the aquocorrinoids) with a Cary 14 spectrophotometer at 25 ± 0.3 °C under a dim light. All the rate measurements were performed under pseudo-first-order conditions in alkylcorrinoid at 1.0 M ionic strength (maintained with NaCl). The pH values were controlled in a range 0-1 with HCl. The equilibrium constant for the "complex" formation between the base-off CH<sub>3</sub>-B<sub>12</sub> and HgCl<sub>n</sub><sup>2-n</sup> was measured spectrophotometrically at 25 ± 0.3 °C.

### Results and Discussion

Addition of 10 mg of mercuric chloride to 2.5 mL of HCl solution (0.10 M) containing 2.4 mM <sup>13</sup>CH<sub>3</sub>-B<sub>12</sub> (90% enriched) resulted in a downfield shift from 0.039 ppm (base-off <sup>13</sup>CH<sub>3</sub>-Co) to 6.378 ppm. The <sup>13</sup>C resonances of the methyl-transfer products are a pseudotriplet with a spin-spin coupling constant from the outer peaks of 1576 Hz. The peak ratio is 1:10:1, corresponding to the 16.84% natural-abundance <sup>199</sup>Hg nuclei. This <sup>13</sup>C NMR study clearly demonstrates the methyl transfer between Co and Hg atoms and is in agreement with the <sup>1</sup>H NMR study of ref 8b. In the <sup>1</sup>H NMR spectrum, however, the satellites of CH<sub>3</sub>-Hg are buried under the corrin proton resonances. The corrinoid products were identified as H<sub>2</sub>O-B<sub>12</sub><sup>+</sup> spectrophotometrically. Addition of 1 equiv of HgCl<sub>n</sub><sup>2-n</sup> to an unbuffered <sup>13</sup>CH<sub>3</sub>-B<sub>12</sub> solution (2.4 mM, pH

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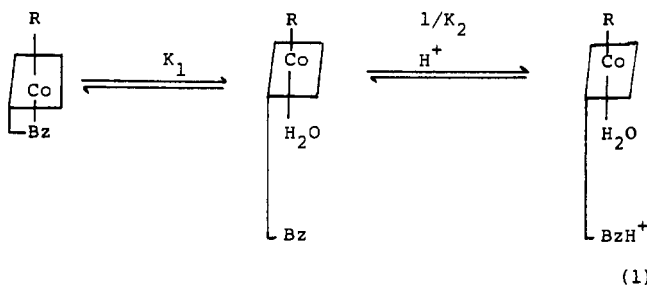
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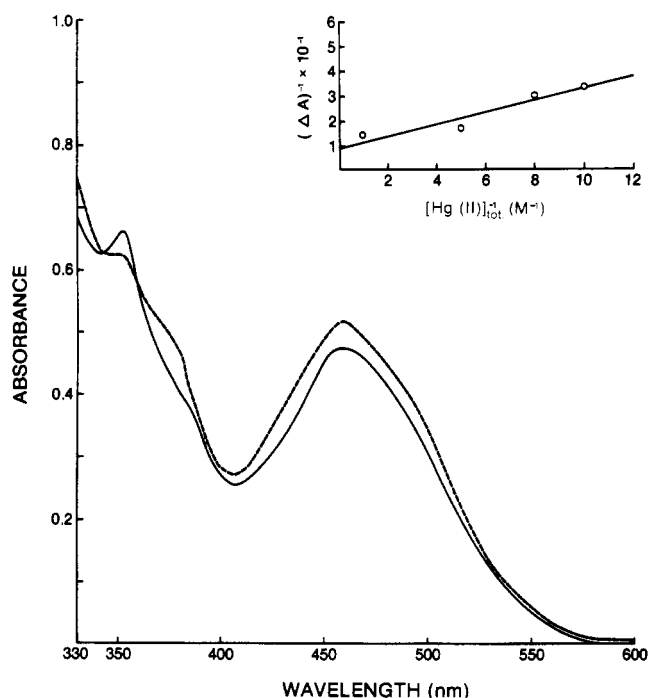
**Figure 1.** Plots of  $k_{\text{obs}}^{-1}$  vs.  $[\text{Hg(II)}]_{\text{tot}}^{-1}$  for the dealkylation of methylquo(3,5,6-trimethylbenzimidazolyl)cobamide (O) and base-off  $\text{C}_2\text{H}_5\text{-B}_{12}$  (●) by  $\text{Hg(II)}$ .  $[\text{H}^+] = 0.50 \text{ M}$ ;  $\mu = 1.0 \text{ M}$  (maintained with  $\text{NaCl}$ ); temperature =  $25 \pm 0.3 \text{ }^\circ\text{C}$ .

~6) resulted in an upfield shift from 9.80 ppm (base-on  $^{13}\text{CH}_3\text{-Co}$ ) to 0.039 ppm, indicating a base-on to base-off conversion.

The protonation of the 5,6-dimethylbenzimidazole moiety and the resulting base-on and base-off conversion can be expressed by eq 1. The  $\text{p}K_2$  is taken as 5.0, adopted from the



$\text{p}K_a$  of the protonated 5,6-dimethylbenzimidazole of  $\text{NCB}_{12}\text{CN-BzH}^+$  (1.0 M  $\text{KCl}$ ,  $25 \text{ }^\circ\text{C}$ ).<sup>11</sup> Accordingly, we have estimated the  $\text{p}K_1$  values for  $\text{CH}_3\text{-B}_{12}$  and  $\text{C}_2\text{H}_5\text{-B}_{12}$  as 2.0 and 1.3 (1.0 M  $\text{NaCl}$ ,  $23 \text{ }^\circ\text{C}$ ), respectively.<sup>12</sup> These  $\text{p}K_1$  values indicate that the 5,6-dimethylbenzimidazole base is less tightly bound to cobalt in  $\text{C}_2\text{H}_5\text{-B}_{12}$  than that in  $\text{CH}_3\text{-B}_{12}$ . In the studies of oxidative dealkylation of alkylcobalamins by oxidants such as  $\text{IrCl}_6^{2-}$ ,  $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ ,  $\text{AuCl}_4^-$ , or  $\text{PtCl}_6^{2-}$ ,<sup>13</sup> it was found that the demethylation rates decrease when  $[\text{H}^+]$  is increased even to a  $[\text{H}^+]$  range of 0.5–1 M. This is taken as an indication that the contribution from the base-on  $\text{CH}_3\text{-B}_{12}$  route is not negligible even at high acid levels. In contrast, the dealkylation rates for  $\text{C}_2\text{H}_5\text{-B}_{12}$  were found to be independent of  $[\text{H}^+]$  at  $[\text{H}^+] \geq 0.1 \text{ M}$  and were therefore assigned as the dealkylation rates for the base-off  $\text{C}_2\text{H}_5\text{-B}_{12}$ . In the present study, the dominant route for the  $\text{HgCl}_n^{2-n}$  demethylation of  $\text{CH}_3\text{-B}_{12}$  in a  $[\text{H}^+]$  range of 0.1–1.0 M is the base-on path. This is demonstrated by a sharp  $[\text{H}^+]$  dependence on the demethylation rates. Therefore, methylquo-(3,5,6-trimethylbenzimidazolyl)cobamide, which appears only in the base-off form, was chosen for the studies of the base-off  $\text{CH}_3\text{-B}_{12}$  demethylation.



**Figure 2.** The  $[\text{Hg(II)}]_{\text{tot}}$  effect on the visible spectrum of base-off  $\text{CH}_3\text{-B}_{12}$ .  $[\text{CH}_3\text{-B}_{12}] = 5.0 \times 10^{-5} \text{ M}$ ;  $[\text{Hg(II)}]_{\text{tot}} = 1.0 \text{ M}$ ;  $[\text{HCl}] = 1.0 \text{ M}$  (---). Inset: Plot of  $(\Delta A)^{-1}$  vs.  $[\text{Hg(II)}]_{\text{tot}}^{-1}$ .  $[\text{CH}_3\text{-B}_{12}] = 5.0 \times 10^{-5} \text{ M}$ ;  $[\text{HCl}] = 1.0 \text{ M}$ ; temperature =  $25 \pm 0.3 \text{ }^\circ\text{C}$ .

The reaction between methylated base-off  $\text{CH}_3\text{-B}_{12}$  and  $\text{HgCl}_n^{2-n}$  in 1.0 M  $\text{Cl}^-$  solution was first order in the methylcobalamin and first order in  $\text{HgCl}_n^{2-n}$  at relatively low concentrations but became progressively less than first order as  $[\text{HgCl}_n^{2-n}]$  was increased. The plot of  $k_{\text{obs}}^{-1}$  vs.  $[\text{HgCl}_n^{2-n}]^{-1}$  is shown in Figure 1. These rate measurements are pH independent. The reaction of base-off  $\text{C}_2\text{H}_5\text{-B}_{12}$  with  $\text{HgCl}_n^{2-n}$  at 0.5 M  $\text{HCl}$  (1.0 M  $\text{Cl}^-$ ) was first order in both  $\text{C}_2\text{H}_5\text{-B}_{12}$  and  $\text{HgCl}_n^{2-n}$ . For the purpose of comparison, the reaction rates for  $\text{C}_2\text{H}_5\text{-B}_{12}$  are also plotted in Figure 1 as  $k_{\text{obs}}^{-1}$  vs.  $[\text{HgCl}_n^{2-n}]^{-1}$ .

Two significant features are shown in Figure 1. First, the dealkylation rate for base-off  $\text{C}_2\text{H}_5\text{-B}_{12}$  is greater than that of base-off  $\text{CH}_3\text{-B}_{12}$ . Second, the demethylation of base-off  $\text{CH}_3\text{-B}_{12}$  by  $\text{HgCl}_n^{2-n}$  displays a kinetic behavior that could be interpreted in terms of an association between the reactants ( $K$ ) prior to the demethylation step ( $k$ ). Accordingly, the reaction between base-off  $\text{CH}_3\text{-B}_{12}$  and  $\text{HgCl}_n^{2-n}$  is described by eq 2 with  $K = 10 \text{ M}^{-1}$  and  $k = 9.5 \times 10^{-6} \text{ s}^{-1}$ . The de-

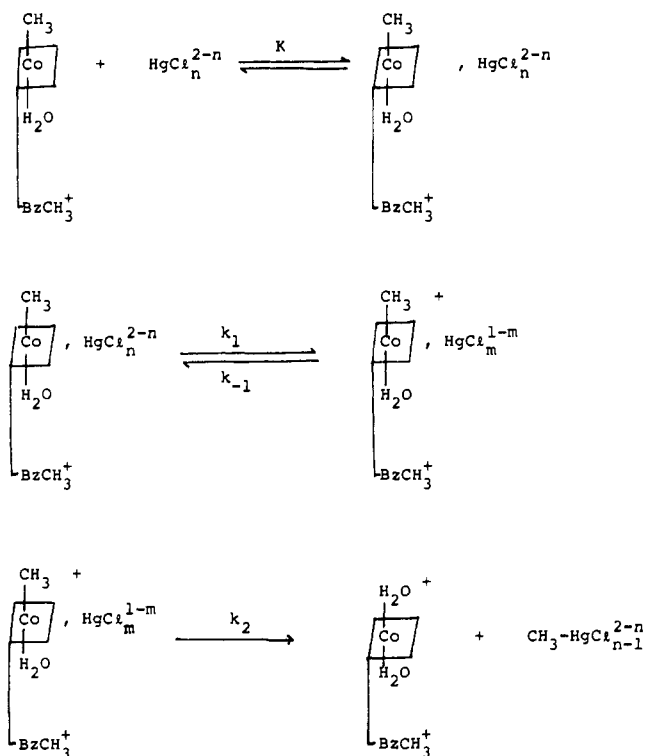
$$k_{\text{obs}} = \frac{kK[\text{HgCl}_n^{2-n}]}{1 + K[\text{HgCl}_n^{2-n}]} \quad (2)$$

alkylation mechanisms for both  $\text{CH}_3\text{-B}_{12}$  and  $\text{C}_2\text{H}_5\text{-B}_{12}$  can be unified, if it is assumed that  $K$  for  $\text{C}_2\text{H}_5\text{-B}_{12}$  is too small to be measured under the present conditions. If this assumption is true, then  $kK = 1.6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  for the dealkylation of base-off  $\text{C}_2\text{H}_5\text{-B}_{12}$  by  $\text{HgCl}_n^{2-n}$ . From Figure 1, an upper limit on  $K_{\text{Et}}$  of  $1 \text{ M}^{-1}$  is estimated, and thus the unimolecular rate constant of  $k_{\text{Et}} > 1.6 \times 10^{-4} \text{ s}^{-1}$  is obtained. Therefore, the enhancement of the ethyl over the methyl moiety is greater than a factor of 17.

The  $\text{HgCl}_n^{2-n}$  effect on the visible spectrum of base-off  $\text{CH}_3\text{-B}_{12}$  is shown in Figure 2, in which a prominent shoulder appears in the region from 360 to 390 nm. A plot of  $(\Delta A)^{-1}$  vs.  $[\text{HgCl}_n^{2-n}]^{-1}$  (inset of Figure 2), gives  $\xi$  at 370 nm for the base-off  $\text{CH}_3\text{-B}_{12}\text{-HgCl}_n^{2-n}$  complex of  $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and an equilibrium constant of  $3 \text{ M}^{-1}$ . Thus, the result from the spectrophotometric titration is in fair agreement with that obtained from kinetic measurements. The "complexation"

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Scheme I

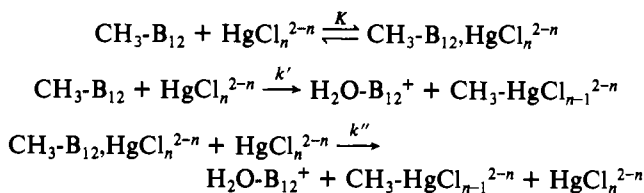


between the base-off  $\text{CH}_3\text{-B}_{12}$  and  $\text{HgCl}_n^{2-n}$  should not be confused with the Hg(II) complexation with the 5,6-dimethylbenzimidazole side chain reported in ref 8.

The major departure of the present study from the previous reports<sup>8a,b</sup> is that  $\text{HgCl}_n^{2-n}$  dealkylates  $\text{C}_2\text{H}_5\text{-B}_{12}$  with a rate greater than that of  $\text{CH}_3\text{-B}_{12}$ . It should be noted that in our studies the reactions were carried out in hydrochloric acid solution and the ionic strength was maintained at 1.0 M with NaCl. Under this condition the predominant Hg(II) species is  $\text{HgCl}_4^{2-}$ . This is not the same reactant used in several of the other papers referring to Hg(II).<sup>8</sup> Thus, while the direct electrophilic attack mechanism for the reactions between alkylcobalamins and mercuric ions cannot be ruled out at this stage, our reinvestigation does suggest an alternative mechanism that is more consistent with the data in hand (at least

for the base-off forms of alkylcobalamins). This mechanism is shown in Scheme I and is analogous to that previously proposed for the reactions with Pt(II)/Pt(IV) couples,<sup>2</sup> di-aquocobinamide,<sup>3</sup> and TCNE.<sup>4</sup>

The proposed mechanism involves a "complexation" between the reactants and an electron-transfer process. The electron-transfer step is followed by a rapid methyl radical transfer from cobalt to mercury. In an electrochemical study by Rubinson et al.,<sup>14</sup> it was reported that a single irreversible wave was observed with a peak potential of +0.87 V vs. SCE on the initial positive scan of the oxidative demethylation of  $\text{CH}_3\text{-B}_{12}$ . Methanol and  $\text{H}_2\text{O-B}_{12}^+$  were identified as the oxidative demethylation products. Their studies clearly demonstrate that the  $\text{CH}_3\text{-B}_{12}^+$  cation radical is extremely unstable. In our study, it is the subsequent rapid methyl radical transfer that allows the  $\text{HgCl}_n^{2-n}$  dealkylation of alkylcobalamins to occur by a one-electron-transfer mechanism. Under this condition,  $k$  in eq 2 represents  $k_1k_2/(k_{-1} + k_2)$ . An alternative mechanism in which the adduct is a "dead-end" complex, with the rate-limiting step in each case being simply bimolecular electron transfer, is described by



Accordingly, the reaction rate can be expressed by the rate expression

$$k_{\text{obsd}} = \frac{k[\text{HgCl}_n^{2-n}] + k''K[\text{HgCl}_n^{2-n}]^2}{1 + K[\text{HgCl}_n^{2-n}]} \quad (3)$$

Under this condition, the value of  $k'_{\text{Me}}$  would become comparable to that of  $k'_{\text{Et}}$ .

**Acknowledgment.** This research was started at the University of Minnesota and completed at Kent State University. I wish to acknowledge the generosity and kindness of Professor H. P. C. Hogenkamp, and I am also indebted to Drs. S. Philson and B. Roberts for excellent assistance in the NMR experiments.

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## Additions and Corrections

1978, Volume 17

**Glenn Bunzey and John H. Enemark\***: Molybdenum Complexes of Aliphatic Thiols. The Structures of the Syn and Anti Isomers of the Di- $\mu$ -sulfido-bis(sulfido-1,2-dimercaptoethanatomolybdate(V)) Anion,  $[\text{Mo}_2\text{S}_4(\text{S}_2\text{C}_2\text{H}_4)_2]^{2-}$ .

Page 685. In Table III the z coordinate for atom S4 should be 0.3043 (3).—John H. Enemark