Kinetics and Mechanism of Methyl Transfer from Methylcobalamin to Palladium(II)

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Abstract: The methyl transfer reaction from methylcobalamin (CH_3B_{12}) to tetrachloropalladate(II) has been monitored by visible-ultraviolet spectroscopic techniques. There are clearly two kinetically distinct steps in the reaction process. The initially established equilibrium step involves a relatively rapid complexation between $PdCl_4^{2-}$ and the methylcobalamin at the 5,6-dimethylbenzimazole nitrogen, while the subsequent slower reaction is concerned with the methyl transfer process itself. The chloride ion dependence of the overall rate process is consistent with the only predominant route of methyl transfer being the reaction of $PdCl_4^{2-}$ with *un*complexed CH_3B_{12}. The initial complexation reaction, therefore, converts much of the reactive CH_3B_{12} to the much less reactive, complex species. The ultimate products of the reaction are palladium metal, methyl chloride, aquo- and chlorocobalamin. The mechanistic pathway and the kinetic rate constants for the methyl transfer from methylcobalamin to $PdCl_4^{2-}$ are compared to the analogous transfer to Hg(II); the similarities and differences are discussed.

The reactions of heavy metal species with molecules of biological interest are currently receiving increasing attention.[1-4] Recently, considerable efforts have been directed at the understanding of the enzymatic and nonenzymatic methyl transfer from CH_3B_{12} to Hg(II).[1,5-9] This process occurs in many of our lakes and rivers to produce CH_3Hg^{II}, a mutagenic agent.[6,9,10] Additionally, it has been reported that the interaction of a wide range of metal species with vitamin B_{12} affect solubility and it is suggested that cyanide abstraction from the B_{12} coordination sphere occurs in a number of cases.[11]

Preliminary studies on the reaction of a variety of metal complexes with methylcobalamin have been reported by Agnes, *et al.*[1,12] Although detailed work in this area is lacking, it is clear that methyl transfer from methylcobalamin to metal species does not occur universally. By far, the most extensive work on a particular system has been that of DeSimone, *et al.*,[9] on the reaction of methylcobalamin with Hg(II). They have used stopped-flow kinetics to discern the kinetics and mechanism of the transfer process which proves to be similar in many ways to this present work on the $PdCl_4^{2-}$ system (*vide infra*).

In addition, a number of studies have appeared recently on the reactions of metal complexes with methylcoboloxime.[13-16] Specific attention was directed at the mechanism of (Co–C) bond cleavage and the resulting (M–C) bond formation. The understanding of the mechanistic details in these systems could contribute valuable insight into the reactions of metal complexes with methylcobalamin.

We have studied this system to explore the further generality of the methyl transfer process from methylcobalamin to transition metal complexes and to more clearly elucidate the kinetics and mechanism of this reaction. We present the first kinetic evidence indicating that the predominant route in the methyl transfer process involves metal complex ($PdCl_4^{2-}$) attack on *un*complexed CH_3B_{12}.

Experimental Section

Cyanocobalamin was purchased from Sigma Chemical Co. and aquocobalamin was a gift from the Merck Sharp and Dohme Co. The Na_2PdCl_4 was purchased from Ventron Corp. and the NaCl and $NaClO_4 \cdot H_2O$ were Fisher Certified. Methylcobalamin was synthesized by the method of Penley, *et al.*[17]

The kinetic runs were performed at 20.0 ± 0.5° and a pH of 5.0–5.8, and solutions were 0.5 *M* in NaCl unless indicated otherwise. The reaction was monitored using a Cary 14 spectrophotometer at 440 nm, a convenient wavelength at which a significantly large adsorptivity difference exists between reactants, intermediate, and final products. The extinction coefficients for all species have been reported earlier.[18-21]

Reaction rates were determined using pseudo-first-order conditions in which the $PdCl_4^{2-}$ concentration was always in at least 20-fold excess. The A_∞ values observed were, within experimental

(1) G. Agnes, H. A. O. Hill, J. M. Pratt, S. C. Ridsdale, F. S. Kennedy, and R. J. P. Williams, *Biochim. Biophys. Acta*, **252**, 207 (1971).
(2) D. R. Williams, *Chem. Rev.*, **72**, 203 (1972).
(3) B. L. Vallee and D. D. Ulmer, *Annu. Rev. Biochem.*, **41**, 91 (1972).
(4) Proceedings of the VII International Chemotherapy Congress–Coordination Complexes in Cancer Chemotherapy, Prague, Aug 1971.
(5) J. M. Wood, F. S. Kennedy, and C. G. Rosen, *Nature (London)*, **220**, 173 (1968).
(6) J. M. Wood, M. W. Penley, and R. E. DeSimone, Mercury Pollution of the Environment, International Atomic Energy Commission, Vienna, 1972.
(7) J. M. Wood and D. G. Brown, *Struct. Bonding (Berlin)*, **11**, 47 (1972).
(8) J. Lewis, R. H. Prince, and D. A. Stotter, *J. Inorg. Nucl. Chem.*, **35**, 341 (1973).
(9) R. E. DeSimone, M. W. Penley, L. Charconneau, S. G. Smith, J. M. Wood, H. A. O. Hill, J. M. Pratt, S. Ridsdale, and R. J. P. Williams, *Biochim. Biophys. Acta*, **304**, 851 (1973).
(10) J. J. Mulvihill, *Science*, **176**, 132 (1972).
(11) R. N. Havemeyer and T. Higuchi, *J. Amer. Pharm. Ass., Sci. Ed.*, **49**, 356 (1960).
(12) G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *Chem. Commun.*, 850 (1971).
(13) Methylcoboloxime is the trivial name for methylbis(dimethylglyoximato)cobalt(III).
(14) A. Adin and J. H. Espenson, *Chem. Commun.*, 653 (1971).
(15) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971).
(16) S. N. Anderson, D. H. Ballard, J. Z. Chrzastrowski, D. Dodd, and M. D. Johnson, *Chem. Commun.*, 685 (1972).
(17) M. W. Penley, D. G. Brown, and J. M. Wood, *Biochemistry*, **9**, 4302 (1970).
(18) L. I. Elding, *Inorg. Chim. Acta*, **6**, 647, 683 (1972).
(19) R. A. Firth, H. A. O. Hill, B. E. Mann, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. A*, 2419 (1968).
(20) A. W. Johnson, L. Merwyn, N. Shaw, and E. L. Smith, *J. Chem. Soc. A*, 4146 (1963).
(21) W. H. Pailes and H. P. C. Hogenkamp, *Biochemistry*, **7**, 4160 (1968).

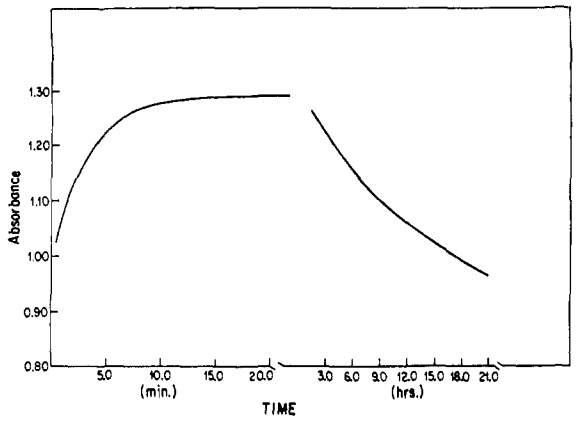


Figure 1. Absorbance change (λ 440 nm) *vs.* time for CH_3B_{12}–$PdCl_4^{2-}$ complexation reaction followed by the methyl transfer reaction. Note change in time scale.

error, identical with the superposition of the absorptions of H_2OB_{12}[22] and $PdCl_4^{2-}$ at the appropriate concentrations. Concentration ranges studied in the kinetic and formation constant analyses were $[PdCl_4^{2-}] = 1.0 \times 10^{-2}$ to 8.0×10^{-4} *M* and $[CH_3B_{12}] = 2.0 \times 10^{-4}$ to 5.0×10^{-5} *M*.

The kinetics were analyzed by conventional methods. Plots of $\log (A_{eq} - A_t)$ or $\log (A_t - A_\infty)$ *vs.* time were utilized to determine the observed rate constants for the initial and subsequent reactions, respectively. Standard least-squares routines were utilized to determine slopes and intercepts for the data, *i.e.*, rate constants, order of reaction, and k_{obsd} dependence on the $[Cl^-]$. The initial equilibrium reaction was followed over $4\tau_{1/2}$ while the much slower overall methyl transfer process was, in most cases, monitored over $3\tau_{1/2}$.

The Hitachi-Perkin-Elmer RM4-6 mass spectrometer was used to detect gaseous products evolved during the reaction.

Results and Discussion

On reaction of methylcobalamin with excess $PdCl_4^{2-}$ in 0.5 *M* chloride ion solution, the ultraviolet–visible spectrum changes relatively rapidly until within minutes a preequilibrium spectrum is observed (A_{eq}) which then very slowly decomposes to a spectrum representative of the final product species (A_∞). Figure 1 exhibits a typical absorption change with time at 440 nm, a wavelength which provides a convenient window for monitoring the entire reaction. There are clearly two distinct steps in the overall process and, since the half-times of the two steps are significantly different, one may study the reactions individually.

From a knowledge of the extinction coefficients of the reactant and product species, and "base-off" CH_3B_{12}, it is evident that the initial reaction is a *complexation* reaction involving CH_3B_{12} and $PdCl_4^{2-}$ to produce a "base-off" CH_3B_{12} species; this step clearly does not involve the transfer of the methyl group. That the transfer is involved in the second step is evident from the final spectrum which is a superposition of spectra of the appropriate concentrations of $PdCl_4^{2-}$ and H_2OB_{12}.

Initial Complexation Reaction. Figure 2 shows the spectral change observed during the initial reaction in which the peak maximum progressively moves to lower wavelength and increases in intensity. Isobestic points at 487 and 388 nm are consistent with only a single

(22) The log *K* value for chloride ion substitution in aquocobalamin is 0.1: M. J. Pratt and R. G. Thorp, *J. Chem. Soc. A*, 187 (1966). Although this indicates comparable concentrations of each species, the species have essentially identical visible spectra. Therefore, although the product species will be referred to as H_2OB_{12}, it will be understood that both species exist at equilibrium.

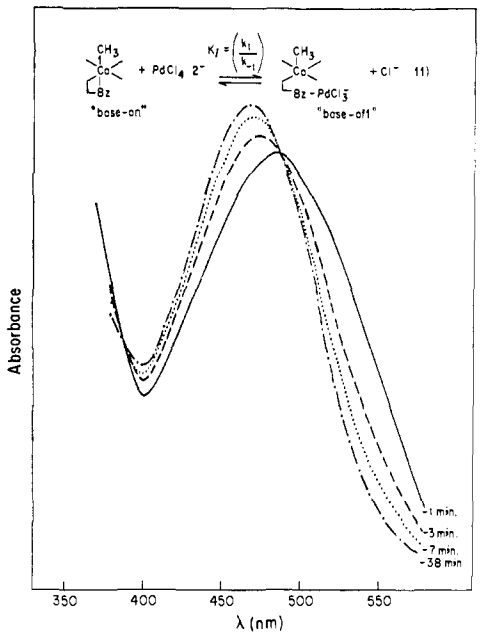
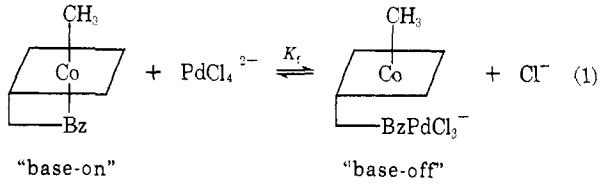


Figure 2. Typical spectral changes during initial complexation reaction. Isobestic points are at 487 and 388 nm.

chemical reaction occurring. The spectrum of the intermediate complex is very similar to that of "base-off" CH_3B_{12} or methylcobinamide in both spectral contour and absorptivity of the bands. Minor differences in the spectrum resulted from the high chloride concentration used which does not permit the equilibrium to be forced completely to the right. Due to the near coincidence of these spectra, we suggest that the Pd(II) competes successfully with the Co(III) for the nitrogen in the 5,6-dimethylbenzimidazole to produce a "base-off" CH_3B_{12} species.

The apparent equilibrium constant for reaction 1 can be determined by using varying concentrations of CH_3B_{12} and $PdCl_4^{2-}$. The apparent K_f value is $(1.5 \pm 0.6) \times 10^{+2}$.



For this reaction, $K_f = k_1/k_{-1}$ and Bz = 5,6-dimethylbenzimidazole, with the $PdCl_3$ moiety presumably bound to the nitrogen of the 5,6-dimethylbenzimidazole. Under experimental conditions, the predominant Pd(II) species in solution is $PdCl_4^{2-}$, and we have assumed that this is also the reactive species.[18] The distinctive red → yellow color change characteristic of the "base-on" CH_3B_{12} → "base-off" CH_3B_{12} transition is masked by the presence of large excesses of colored $PdCl_4^{2-}$, although the spectral change clearly indicates this process is occurring.

The order of this reaction with respect to $[PdCl_4^{2-}]$ can be determined from a plot of $\log k_{obsd}$ *vs.* $\log [PdCl_4^{2-}]$ as suggested by the approximate equation

$$\log k_{obsd} = \log k_1' + n \log [PdCl_4^{2-}] \qquad (1a)$$

where k_1' only approximates the actual k_1 value because of the existing equilibrium.

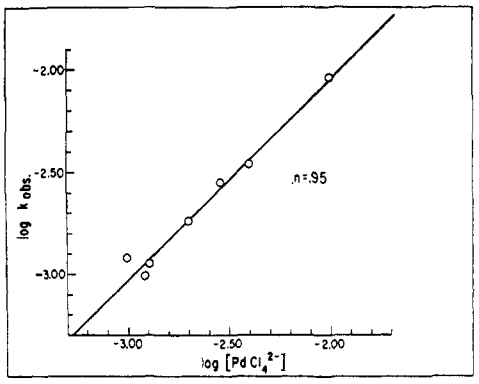


Figure 3. Plot of the log of the observed rate constant for the initial complexation reaction *vs.* the log $[PdCl_4^{2-}]$. The slope (n = 0.95) of the line indicates the first-order dependence on $[PdCl_4^{2-}]$.

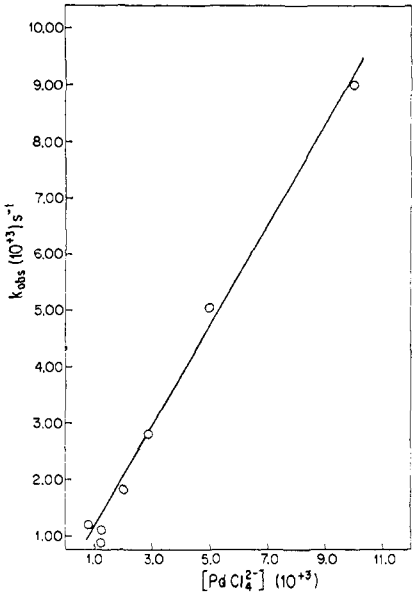


Figure 4. Plot of the observed rate constant, k_{obsd}, for the initial complexation reaction *vs.* the $PdCl_4^{2-}$ concentration. The slope yields $k_1 = 0.90\ M^{-1}\ sec^{-1}$.

Figure 3 exhibits the linear relationship with the slope (n) equal to 0.95, indicative of a first-order dependence with respect to $[PdCl_4^{2-}]$.

Determination of k_1 is most clearly seen by plotting k_{obsd} *vs.* $[PdCl_4^{2-}]$ as suggested by eq 1b, which exactly

$$k_{obsd} = k_1[PdCl_4^{2-}] + k_{-1}[Cl^-] \qquad (1b)$$

represents k_{obsd} under the reaction conditions. The slope (k_1) in Figure 4 yields $k_1 = 0.90\ M^{-1}\ sec^{-1}$. Because the intercept value is very small and the uncertainty so high, we put little significance in its value ($k_{-1}[Cl^-] \simeq (1 \pm 5) \times 10^{-4}\ sec^{-1}$) or in the corresponding value of the reverse rate constant, $k_{-1} \simeq (2 \pm 10) \times 10^{-4}\ M^{-1}\ sec^{-1}$, as determined by this method. In addition it can be determined that, for this initial step, the chloride ion does, as expected, inhibit this forward reaction.

Demethylation and the Overall Reaction. The spectral change with time for the second step in the reaction is shown in Figure 5. Note should be made that the final spectrum can be synthesized by a superposition of the absorptions for the appropriate concentrations

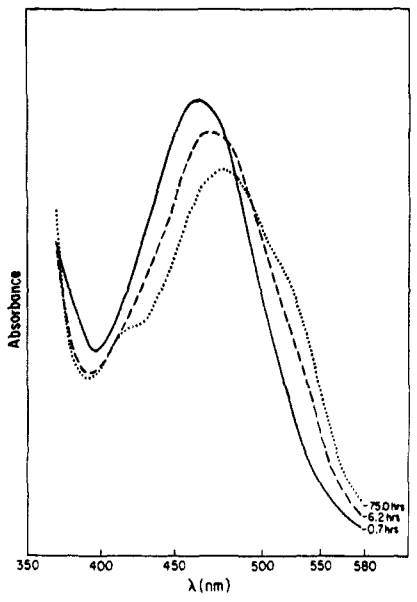


Figure 5. Typical spectral change during the methyl transfer process.

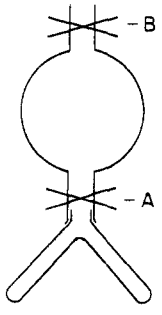


Figure 6. Reaction vessel and gas sampling device used to demonstrate CH_3Cl production. A and B indicate stopcocks in the system.

of $PdCl_4^{2-}$ and aquocobalamin. Palladium metal is observable only at the end of this reaction and is understandably the end product of the decomposition of the presumed intermediate, $CH_3PdCl_3^{2-}$. In addition to the palladium metal and H_2OB_{12}, CH_3Cl is produced. The CH_3Cl gas can be detected by mass spectroscopy; the reaction vessel and sampling device utilized is shown in Figure 6.

To demonstrate CH_3Cl production, individual solutions of CH_3B_{12} and $PdCl_4^{2-}$ (both at about $1 \times 10^{-2}\ M$ in at least 0.5 M NaCl) were syringed into the different compartments of the reaction vessel and then the frozen solutions and the gas sampling chamber were evacuated. Stopcocks A and B were then closed and the solutions were warmed, mixed, and permitted to react for 2 days at room temperature in the dark. Thereafter, the reaction vessel was cooled down carefully again to −60° and stopcock A then opened to accept any evolved product gas into the gas sampling device. The gas sampler is then closed, detached from the reaction vessel, and then attached to the mass spectrometer for analysis. Characteristic lines with the correct relative intensities were observed for CH_3Cl.

The second step in the reaction, which appears to be an electrophilic displacement of CH_3^- from CH_3B_{12} by $PdCl_4^{2-}$, could conceivably occur by a variety of plausible mechanistic pathways (reactions 2–4).

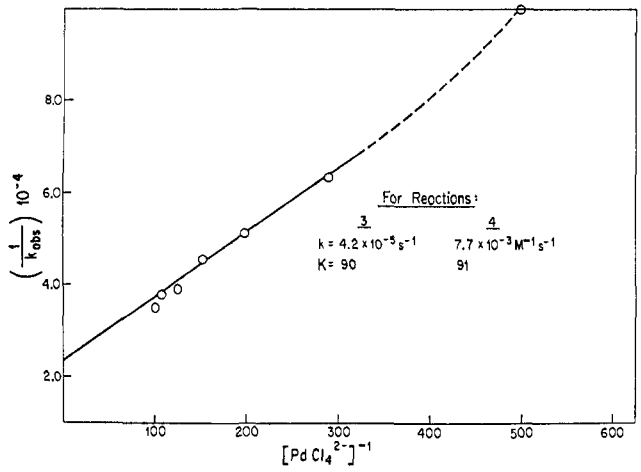
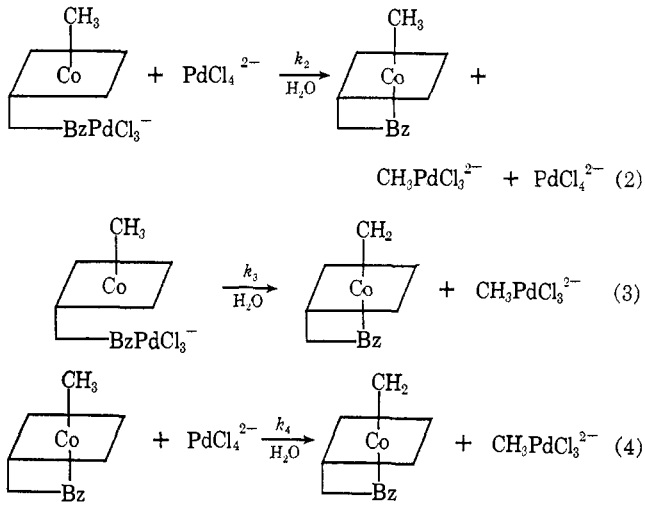


Figure 7. Plot of the reciprocal of the observed rate constant for the overall process *vs.* $[PdCl_4^{2-}]^{-}$. Values of k (the first-order and second-order rate constant for process 3 and 4, respectively) for the methyl transfer process and the apparent formation constant, K_f, can be obtained from the slope and intercept values.



Pathways 2 and 3 involve reaction of the "base-off" CH_3B_{12} intermediate with either $PdCl_4^{2-}$ or itself while reaction 4 is concerned with the reaction of $PdCl_4^{2-}$ with the *un*complexed "base-on" CH_3B_{12}. Reactions 2 and 4 are bimolecular reactions while reaction 3 involves a unimolecular decomposition of the "base-off" CH_3B_{12} species. In all cases, the product $CH_3PdCl_3^{2-}$ ultimately decomposes to palladium metal and CH_3Cl gas.

Table I lists the k_{obsd} expressions and the quantities plotted for the overall reaction involving pathways 2–4.

Table I

Reaction	k_{obsd}	Plot of
2	$k_{obsd} = \frac{k_2K[PdCl_4^{2-}]^2}{[Cl^-] + K[PdCl_4^{-2}]}$	$\frac{[PdCl_4^{2-}]}{k_{obsd}}$ *vs.* $\frac{1}{[PdCl_4^{2-}]}$
3	$= \frac{k_3K[PdCl_4^{2-}]}{[Cl^-] + K[PdCl_4^{2-}]}$	$\frac{1}{k_{obsd}}$ *vs.* $\frac{1}{PdCl_4^{2-}}$
4	$= \frac{k_4[Cl^-][PdCl_4^{2-}]}{[Cl^-] + K[PdCl_4^{2-}]}$	$\frac{1}{k_{obsd}}$ *vs.* $\frac{1}{[PdCl_4^{2-}]}$

Reaction 2 is not a viable pathway since the appropriate plot exhibits no linear relationship over the concentration range studied. The "changing slope" is negative also and both these factors clearly eliminate this pathway from serious consideration.

The same functions are plotted for reactions 3 and 4 and note should be made that the k_{obsd} expressions are identical except for the terms k_3K and $k_4[Cl^-]$ in the numerator of each expression, respectively.

The plot of the kinetic expression for reaction 3 and 4 is shown in Figure 7. A linear relationship is observed over the $[PdCl_4^{2-}]$ range of 1×10^{-2} M to at least 3×10^{-3} M. The rate constant and the apparent formation constant derived from expressions 3 and 4 are, respectively

$$k_3 = 4.2 \times 10^{-5}\ \text{sec}^{-1} \qquad K_f = 90$$

$$k_4 = 7.7 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1} \qquad K_f = 91$$

The formation constant values are of approximately the same magnitude as that obtained by the independent nonkinetic determination; therefore, the kinetic analysis adds further confidence to the magnitude of the apparent K_f value. However, these kinetic data indicate that the demethylation step is either first order in the "base-off" CH_3B_{12} complex species (pathway 3) or first order in both $PdCl_4^{2-}$ and "base-on" CH_3B_{12} (pathway 4). To distinguish between the two possible mechanistic pathways (3 and 4) and to determine if one pathway predominates in this reaction, one can utilize the fact that *each pathway is influenced differently by the chloride ion concentration.* Reaction pathway 3 has a $[Cl^-]$ dependence which appears only in the denominator of the rate expression, while pathway 4, in addition, has a direct $[Cl^-]$ dependence on the k_{obsd}.

The reaction was, therefore, also followed at a higher constant ionic strength where

$$\mu_{TOTAL} = [Cl^-] + [ClO_4^-] = 1.00\ M$$

in which $[Cl^-]$ and $[ClO_4^-]$ were varied accordingly in each run to determine the $[Cl^-]$ dependence of the overall rate.

The concentrations of $PdCl_4^{2-}$ (6.8×10^{-3} M) and CH_3B_{12} (7.3×10^{-5} M) were held constant in all runs. Under these conditions, a plot of k_{obsd}^{-1} *vs.* $[Cl^-]$ should be linear according to reaction 3, while a plot of k_{obsd}^{-1} *vs.* $1/[Cl^-]$ should be linear in accord with reaction 4. Figure 8 shows the straight line relationships. The values of the slope are necessarily different for reactions 3 and 4 and, significantly, the slope for reaction 3 is *negative* while that for reaction 4 is *positive*. A negative slope, however, cannot be explained and, therefore, eliminates reaction 3 from consideration. This study then clearly indicates that pathway 4, which is first order in $PdCl_4^{2-}$ and *un*complexed CH_3B_{12}, is the predominant route for the methyl transfer step.

DeSimone, *et al.*,[9] have previously suggested that the analogous step in the CH_3B_{12}–Hg(II) reaction is also the predominant step in the methyl transfer process. However, in this system, the reaction was not studied under conditions such that it would be possible to kinetically distinguish between the k_{obsd} expressions analogous to our eq 3 and 4. The experimental rationale for suggesting that the predominant pathway is attack of $Hg(OAc)_2$ on *un*complexed CH_3B_{12} was that methylcobinamide or "base-off" methylcobalamin both

react much slower with $Hg(OAc)_2$ than does the "base-on" methylcobalamin. This appears to be a non-sequitur in that this could only have relevance to a comparison of pathways analogous to our pathways 2 and 4.

From the kinetic studies on the Hg(II)–CH_3B_{12} system and on model systems,[9,12,14-16] there is considerable evidence to indicate an SE2 type mechanism in the methyl transfer step in these systems.[23] The kinetics of the methyl transfer process are first order in both Hg(II) and CH_3B_{12}, and also the reaction rate is reduced on going to secondary alkyls in RB_{12}.[12] That the reaction rate is increased on going from $Hg(OAc)_2$ to $Hg(ClO_4)_2$ is also consistent with an SE2 mechanism and at variance with an SEi mechanism.[12] No data are available on whether retention or inversion of configuration occurs in the alkylcobalamin system. Therefore, although the Hg(II)–CH_3B_{12} reaction is reasonably well understood now, more extensive work on the Pd(II)–CH_3B_{12} reaction is necessary before such definitive statements can be justifiably made.

Since the kinetics of methyl transfer from CH_3B_{12} to $Hg(OAc)_2$ have been reported,[9] a comparison of it with the $PdCl_4^{2-}$ system is in order.

1. The reaction profiles for both methyl transfer reactions are similar in that there are two kinetically distinct steps discernible in the overall process. The initial step can be regarded as a relatively fast complexation or association of the metal species with CH_3B_{12}, resulting in a "base-on," "base-off" preequilibrium. In both systems, the electrophilic heavy metal species competes successfully with the cobalt(III) for the lone pair of electrons on the benzimidazole nitrogen. This being the case, the initial complexation reaction, therefore, converts a significant concentration of the reactive CH_3B_{12} to the unreactive "base-off" complex. This initial reaction is followed by the slower demethylation step which is first order in both $PdCl_4^{2-}$ and CH_3B_{12} and in which the electrophilic metal species attacks the Co–C bond in the *un*complexed CH_3B_{12}. This is clearly the predominant pathway for methyl transfer in the $PdCl_4^{2-}$ system as evidenced by the rate dependence on the chloride ion concentration. It *may* logically follow now that this is also true in the Hg(II) reaction in view of other similarities between the two systems. In fact, as other metal systems are more thoroughly investigated, it could be expected that this mechanism may likely receive wider general recognition.

2. The final product common to both reactions is H_2OB_{12}.[22] However, in the $PdCl_4^{2-}$ reaction, palladium metal and CH_3Cl are ultimately formed due to the instability of (Pd–C) bonds in this environment; in the $Hg(OAc)_2$ reaction, $CH_3Hg(OAc)$ is the final product.

3. The formation constant for the initial CH_3B_{12} complexation reactions with $Hg(OAc)_2$ or $PdCl_4^{2-}$ differ in both magnitude and in units. The apparent K_f in the $Hg(OAc)_2$ reaction is 70 M, while in the $PdCl_4^{2-}$ reaction, $K_f \simeq 150$.

There is reason to suspect, however, that $Hg(OAc)_2$ may not be the predominant Hg(II) species in solution.

(23) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 563–580.

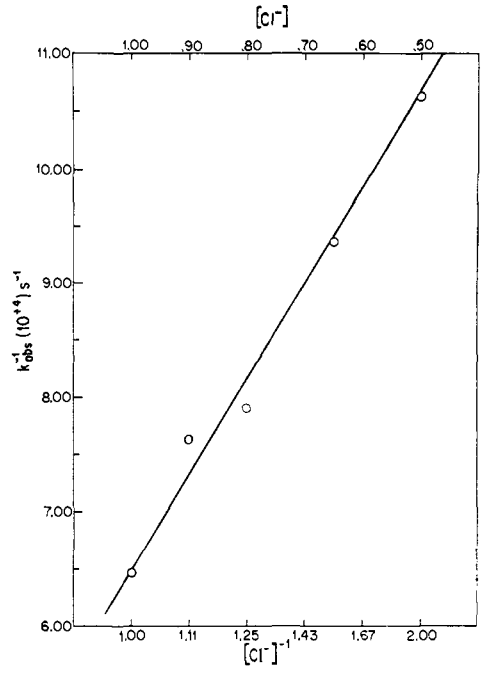


Figure 8. Plot of the reciprocal of the observed rate constant, k_{obsd}^{-1}, for the overall process *vs.* the $[Cl^-]$ and $1/[Cl^-]$ at constant ionic strength ($\mu = 1.00\ M = [Cl^-] + [ClO_4^-]$).

A species distribution calculation indicates that, at almost all conditions studied, $Hg(OAc)_4^{2-}$ appears to be the major Hg(II) species in solution.

In addition, although the two formation constants differ in form and, therefore, cannot be rigorously compared, the similar magnitudes of the K_f's can yield the deceiving impression that the affinity of Hg(II) and Pd(II) for the benzimidazole nitrogen is similar. This is certainly not the case. Although Hg(II) and Pd(II) are both considered as "soft" Lewis acids,[24] it is clear that Hg(II) binds organic nitrogen ligands tenaciously and forms stronger complexes with such ligands than do the transition metals. Formation constants for Hg(II) binding to nitrogen-containing ligands (1:1 complex) have been reported as high as 10^{+13}.[25] Therefore, a more realistic picture of the binding affinities of the two metal species for nitrogen, in competition with Co(III), must take into account the degree of dissociation of the chloride and acetate ions from $PdCl_4^{2-}$ and the Hg(II) species, respectively.[18,26] This then clearly demonstrates that the binding affinity of the Hg(II) (irrespective of the $Hg(OAc)_x$ species (x = 2, 3, or 4) and assuming the indicated stoichiometry)[9] for the benzimidazole nitrogen is many orders of magnitude greater than for the Pd(II) species.

4. The reaction of Hg(II) with CH_3B_{12} is extremely rapid (stopped-flow kinetics) in comparison to the $PdCl_4^{2-}$ reaction (Cary 14 spectrophotometer). Therefore, one would expect the analogous second-order constants in the preequilibrium (forward reactions) and in the methyl transfer steps to be significantly different in the two systems. In the case of the forward rate constant in the initial step, the rate constants are sus-

(24) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).
(25) T. H. Wirth and N. Davidson, *J. Amer. Chem. Soc.*, **86**, 4325 (1964), plus references within.
(26) "Stability Constants of Metal Ion Complexes," *Chem. Soc., Spec. Publ.*, Suppl No. 1, No. **25**, 252 (1971).

piciously similar ($PdCl_4^{2-}$, 0.90 M^{-1} sec^{-1}; Hg(II) 1.2 M^{-1} sec^{-1}). It appears from the reported data[9] that this rate constant in the Hg(II) system should be more on the order of $\simeq 10^3$ which would then appear to be in accord with the observed kinetics. The rate constants for the methyl transfer step differ by $\sim 10^4$ ($PdCl_4^{2-}$, 7.7×10^{-3} M^{-1} sec^{-1}; $Hg(OAc)_2$, 85 and 310 M^{-1} sec^{-1}).[1,9] To be sure, in comparing these systems, one must recognize that conditions are quite different. However, the Hg(II) species is clearly more electrophilic than $PdCl_4^{2-}$ and also produces slightly more of the "base-off" species, both factors contributing to the more facile methyl transfer process in the case of Hg(II).

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Reactions of Transition Metal Dihydrides. V.[1] Interaction of $(\eta\text{-}C_5H_5)_2MH_2$ (M = Mo and W) with Azo or Diazo Compounds

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Abstract: Reaction of Cp_2MoH_2 (Cp = η-C_5H_5) with an excess of azobenzene, methyl or ethyl azodicarboxylate, and azodibenzoyl proceeds *via* an incipient formation of hydridohydrazino complexes, $Cp_2MoH[\sigma\text{-}N(R)NHR]$, to a π-complex, $Cp_2Mo(PhN{=}NPh)$, or metalloheterocycles, $Cp_2MoN(COR)N{=}C(R)O$ (R = Ph, OMe, OEt). 4-Phenyl-1,2,4-triazoline-3,5-dione behaves differently to give a novel metalated heterocycle, $Cp_2Mo[\sigma\text{-}NN{=}C(OH)N(Ph)CO]_2$. A diazoalkane complex, Cp_2Mo(diazofluorene), was also prepared from Cp_2MoH_2.

We have reported[2] a detailed study of the interaction of Cp_2MoH_2 (**1**) or Cp_2WH_2 (**2**) (Cp = η-C_5H_5) with carbon–carbon homounsaturation. Novel hydrido–σ-alkyl complexes, $Cp_2Mo(H)\overset{|}{C}\overset{|}{C}H$, olefin, or acetylene complexes, $Cp_2Mo(Un)$, were isolated and characterized. Stereochemistry and mechanism of the stoichiometric olefin hydrogenation were also investigated which lend an important insight into catalytic hydrogenation. In view of the well-known activity[3] of some molybdenum complexes toward chemical as well as biological nitrogen fixation, it seems important to investigate the interactions between heterounsaturation, *e.g.*, –N=N– or dinitrogen and the dihydrides. Our preliminary study[4] with azobenzene or azodicarboxylates has now been extended to other azo or diazo compounds and the results are summarized here. In the course of our study, a closely related reaction of $[Cp_2Mo]$ or $[(Me_5C_5)_2Mo]$ with dinitrogen was reported by Thomas and Brintzinger.[5]

Interactions of various azo or diazo compounds with many d^8 or d^{10} complexes of group VIII elements have been actively investigated in our[6,7] and in several other laboratories.[8–19] The present study will serve to correlate or compare the unique behavior of group VI metal complexes with that of group VIII metal compounds.

Results

The reaction of *trans*-azobenzene with **1** was slow at room temperature, being incomplete even after 2 days.

(1) For Part IV see A. Nakamura and S. Otsuka, *Tetrahedron Lett.* 4529 (1973).

(2) (a) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972); (b) A. Nakamura, Abstracts, 5th International Conference on Organometallic Chemistry, Moscow, 1971, Vol. 2, p 550; (c) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **95**, 7262 (1973).

(3) (a) G. N. Schrauzer, G. Schlesinger, and P. A. Doemeny, *J. Amer. Chem. Soc.*, **93**, 1803 (1971); (b) G. N. Schrauzer, G. W. Kiefer, P. A. Doemeny, and H. Kisch, *ibid.*, **95**, 5582 (1973); (c) E. E. van Tamelen, J. A. Gladyzs, and J. S. Miller, *ibid.*, **95**, 1347 (1973); (d) for recent reviews, M. E. Vol'pin and V. B. Shur, "Organometallic Reaction," Vol. 1, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1970, p 55; R. W. F. Hardy, R. C. Burns, and G. W. Parshall, "Inorganic Biochemistry," Vol. 2, G. L. Eichhorn, Ed., Elsevier, Amsterdam, 1973, p 787.

(4) S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 1148 (1969).

(5) J. L. Thomas and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1386 (1972); J. L. Thomas, *ibid.*, **95**, 1838 (1973).

(6) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972); *Justus Liebigs Ann. Chem.*, in press.

(7) (a) S. Otsuka, T. Yoshida, and Y. Tatsuno, *Chem. Commun.*, 68 (1971); *J. Amer. Chem. Soc.*, **93**, 6462 (1971); (b) R. S. Dickson, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *ibid.*, **93**, 4636 (1971).

(8) H. F. Klein and J. F. Nixon, *Chem. Commun.*, 42 (1971).

(9) F. M. Hussein and A. S. Kassenally, *J. Chem. Soc., Chem. Commun.*, 3 (1972).

(10) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973), and references cited therein.

(11) (a) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 444 (1972); (b) J. Chatt and J. R. Dilworth, *ibid.*, 549 (1972).

(12) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2248 (1969).

(13) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2138, 2141 (1972), and references cited therein.

(14) F. W. B. Einstein, A. B. Gilchrist, G. W. RaynorCanham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972).

(15) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1805 (1972).

(16) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometal. Chem.*, **31**, 275 (1971); **40**, 393 (1972).

(17) M. I. Bruce, B. L. Goodal, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 558 (1973).

(18) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 176 (1973).

(19) (a) P. C. Ellgen and S. L. McMullin, *Inorg. Chem.*, 12, 2004 (1973); (b) H. Alper, *ibid.*, **11**, 976 (1972).