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if the molecule has C_{3h} symmetry, while a substantial dipole moment is expected for **3b**, reflecting the larger dipole–dipole interactions of this configuration. The dipole moment of *N*-benzoylsuccinimide, which must adopt a configuration of type **3b**, is 4.10 D.[7b]

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Kinetic Differentiation Between I_d and D Mechanisms for Axial Base–Ligand Exchange in Alkyl(base)cobaloximes

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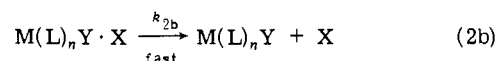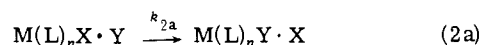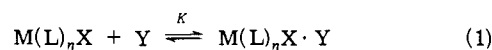
Abstract: Axial base–ligand exchange in alkyl(base)cobaloximes has been shown to occur by a purely dissociative (D) mechanism in chloroform. A method for distinguishing between closely related mechanisms solely on the basis of kinetics was demonstrated. Pyridine was found to react approximately ten times faster than tri-*n*-butylphosphine with the five-coordinate "base-off" complex produced during the ligand exchange process, even though tri-*n*-butylphosphine coordination is thermodynamically favored. A linear correlation between log K and $\bar{\sigma}$ for substitution of piperidine by various 4-substituted pyridines was found. Factors controlling thermodynamic and kinetic coordination of bases are discussed.

It has been proposed that exchange of the 5,6-dimethylbenzimidazole axial base in coenzyme B_{12} affects the reactivity of the carbon–cobalt σ-bond.[2] Considerable evidence has been presented that during enzymatic reactions which involve coenzyme B_{12} the carbon–cobalt bond is broken.[3] It is reasonable to assume that the carbon–cobalt bond may become activated for rupture by prior axial base ligand dissociation. It is significant therefore to initially study the mechanism of ligand exchange in coenzyme B_{12} or a suitable model system. The alkylcobaloximes have been shown to serve as good models for coenzyme B_{12}, the pyridine-based cobaloxime being especially appropriate due to the similarity of the pyridine and imidazole structures. For this reason, methyl(pyridine)cobaloxime was chosen as the substrate for initial study.

Considerable current interest exists in the mechanisms of ligand exchange in organometallic compounds. It has only been possible in a few cases, however, to establish the detailed nature of the mechanism. The study of a mechanism can be divided into two segments:[4] the dissection of the mechanism into elementary steps which is referred to as the stoichiometric mechanism, and the analysis of the detailed nature of the individual steps which is the study of the intimate mechanism. As was pointed out by Langford and Gray,[4] obtaining information on the intimate mechanism (e.g., determining whether the exchange is associative or dissociative in nature) is generally a relatively simple process, while establishing the stoichiometric mechanism is difficult. In most instances, a large amount of data from several different types of kinetic and stereochemical studies must be analyzed before a firm conclusion can be made concerning the stoichiometric mechanism. This situation results from the inability of kinetics to distinguish between two or more mechanisms when the exchanges are studied in coordinating solvents. For instance, for dissociative mechanisms when exchanges are performed in water, it is only possible to observe replacement of the leaving ligand by water (hydrolysis) and the subsequent replacement of water by entering ligand (anation).

In contrast, in noncoordinating solvents, two distinct dissociative mechanisms can be distinguished for reactions which proceed to completion.[4] The dissociative interchange (I_d) process involves the formation of an outer-sphere complex, $M(L)_nX \cdot Y$ (eq 1), followed by the replacement of X by Y in the outer coordination sphere (eq 2a). Then X dissociates from the outer coordination sphere (eq 2b). In most cases eq 2b is much faster than eq 2a, and, for kinetic purposes, they can be considered as a single step.

$$M(L)_nX + Y \overset{K}{\rightleftharpoons} M(L)_nX \cdot Y \qquad (1)$$

$$M(L)_nX \cdot Y \overset{k_{2a}}{\longrightarrow} M(L)_nY \cdot X \qquad (2a)$$

$$M(L)_nY \cdot X \overset{k_{2b}}{\underset{\text{fast}}{\longrightarrow}} M(L)_nY + X \qquad (2b)$$

The purely dissociative (D) mechanism (eq 3 and 4) involves dissociation of the leaving group to give an intermediate, $M(L)_n$, of reduced coordination number.

$$M(L)_nX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(L)_n + X \qquad (3)$$

$$M(L)_n + Y \xrightarrow{k_3} M(L)_nY \qquad (4)$$
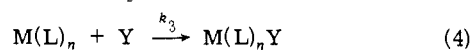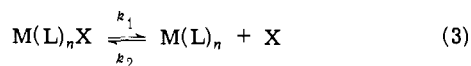
The rate expression for the I_d mechanism when the exchange is not detectably reversible is given in eq 5.

$$\text{rate} = k_{2a}K[\text{complex}][Y]/(1 + K[Y]) \qquad (5)$$

The D mechanism gives a somewhat different expression.

$$\text{rate} = k_1k_3[Y][\text{complex}]/(k_2[X] + k_3[Y]) \qquad (6)$$

Rearrangement of k_{obsd} in eq 6 gives the following:

$$1/k_{obsd} = 1/k_1 + (k_2[X]/k_3)/k_1[Y] \qquad (7)$$

The significant difference between eq 5 and 6 is that the leaving group concentration appears in one and not the other. This concentration affects the observed kinetics; the decrease in rate when additional X ligand is added to the solution is referred to as "mass-law (rate) retardation". When the reaction is carried out in water with H_2O as the leaving group, this retardation is not observed and the rate expressions (5 and 6) become identical. In this situation, the I_d and D mechanisms are kinetically indistinguishable. It is surprising, therefore, that "mass-law retardation" in nonaqueous systems has been utilized only to a minor extent in assigning mechanism. It is of course significant that a delicate balance exists between the I_d and D mechanisms and changing solvent may well cause a change in mechanism.[4]

The kinetics of substitution of the axial base in alkylcobaloximes and related cobalt complexes have been studied under a variety of conditions.[5-12] In none of the studies was the mechanism established conclusively although in all cases strong evidence was given that the intimate mechanism is dissociative (either I_d or D). In most of these studies, the exchanges were performed in water with H_2O as the leaving group. Analysis was therefore restricted by the ambiguous rate law problem mentioned above.

Results and Discussion

In light of the difficulties in distinguishing between ligand exchange mechanisms, the study of the axial base ligand exchange kinetics for methyl(base)cobaloximes was undertaken. As was made evident in the introductory section, the I_d and D mechanisms can be kinetically differentiated by mass-law retardation in a suitable noncoordinating solvent. This can only be done conveniently when conditions are chosen such that exchange proceeds to completion. In this section where the exchange mechanism is determined, all the exchanges studied proceed to completion. This was demonstrated both spectrophotometrically and by NMR spectroscopy. Therefore, the rate expressions given in eq 5 and 6 for the nonreversible I_d and D mechanisms apply. The rate expressions for the reversible I_d and D exchanges are not needed.

The exchanges were run in chloroform, a noncoordinating solvent in which cobaloximes are soluble. The method employed was that described by Wilmarth and coworkers.[13] The exchanges were followed spectrophotometrically at $25.00 \pm 0.02°$. According to the rate expression in eq 6, first-order (in cobalt complex) observed rate constants can be obtained by employing large (constant) concentrations of entering and leaving ligands. All entering and leaving ligands are uncharged as are the complexes, so ionic strength effects are unimportant. In addition, the exchanges were carried out at sufficiently low concentrations so that changes in solvent polarity due to addition of excess ligand could be ignored. The numerical values of the pseudo-first-order rate constants k_{obsd} were obtained from the slope of a

Table I. Data for Exchange of Pyridine by Tri-n-butylphosphine[a]

[phosphine]/ [cobaloxime][b]	$10^2[P(n\text{-Bu})_3]$, M	[py]/[cobaloxime] = 50 $10^4 k_{obsd}$, sec^{-1}	[py]/[cobaloxime] = 100 $10^4 k_{obsd}$, sec^{-1}
50	3.25	5.50	2.94
75	4.84	8.48	4.42
100	6.43	9.45	5.68
150	9.61	12.75	8.16
250	15.80	18.90	11.45
325	20.14		14.80
400	24.60	23.20	16.75

[a] $[Me(Co)_{Me}py] = 6.3 \times 10^{-4} M$; $25.00 \pm 0.02°$ in $CHCl_3$. [b] Approximate.

linear plot of log $(D_t - D_\infty)$ vs. time, where D_t and D_∞ refer to the measured absorbances at time t and after equilibrium was reached, respectively. In this section, the exchanges proceed to completion so D_∞ represents the absorbance after complete exchange. Values of k_{obsd} were obtained at several different entering ligand concentrations, and a plot of $1/k_{obsd}$ vs. $1/[\text{ligand}]$ was made.

Pyridine–Tributylphosphine Interchange. The initial compound studied was methyl(pyridine)cobaloxime. Since pyridine coordinates to the cobalt atom with a large equilibrium constant, the choice of ligands to replace it is limited. It has been reported[14] that tri-n-butylphosphine has a greater affinity for the cobalt center than pyridine and it was chosen to be the replacing ligand. The exchanges were run in uv cells under N_2 in degassed $CHCl_3$ due to the oxygen sensitivity of the phosphine. The results appear in Table I. The observed rate constant vs. phosphine concentration drops off from linearity at higher concentrations of phosphine, eliminating the possibility of an associative-type process. The I_d mechanism is also readily eliminated by examination of the data in Table I. As discussed previously, if the mechanism is I_d, the observed rate will not be affected by a change in the pyridine concentration while the observed rate of the D process will (compare eq 5 and 6). It is evident that there is a significant decrease in rate found when the pyridine concentration is doubled.

When the plots of $1/k_{obsd}$ vs. $1/[P(n\text{-Bu})_3]$ were made according to eq 7, straight lines were obtained as shown in Figure 1. The intercept defines $1/k_1$ while the slope is equal to $k_2[\text{pyr}]/k_1k_3$. The best line through the points was obtained by a linear least-squares data fit providing the following values (the errors are the standard deviations): 50-fold pyridine excess (eightfold range of $[P(n\text{-Bu})_3]$), intercept = 224 ± 44 sec, slope = 50.6 ± 2.5 M sec; 100-fold pyridine excess (eightfold range of $[P(n\text{-Bu})_3]$): intercept = 164 ± 20 sec, slope = 104.0 ± 1.2 M sec. As required by the kinetic expression (eq 7) the slope of the line doubled when the excess pyridine concentration is doubled. This eliminates the possibility of the I_d process occurring and provides strong support for the D mechanism. While the kinetic expression also requires the intercepts to be identical, there is a large inherent error in determining the intercept by this technique. The fact that the intercepts are within a standard deviation of each other indicates that the data adequately fit the kinetic expression. The slopes and intercepts yield the following rate constants as described above: 50-fold pyridine excess, $k_1 = (4.5 \pm 0.9) \times 10^{-3}$ sec^{-1}, k_2/k_3 = 7.1 ± 1.8; 100-fold pyridine excess, $k_1 = (6.1 \pm 0.8) \times 10^{-3}$ sec^{-1}, $k_2/k_3 = 10.0 \pm 1.4$.

Since the value of k_1 must be used to determine the k_2/k_3 ratio, a large uncertainty is also found in this ratio.

A striking difference exists between the data presented here and that of Green and coworkers.[10] They found that triphenylphosphine ($pK_a = 2.73$) reacts about ten times
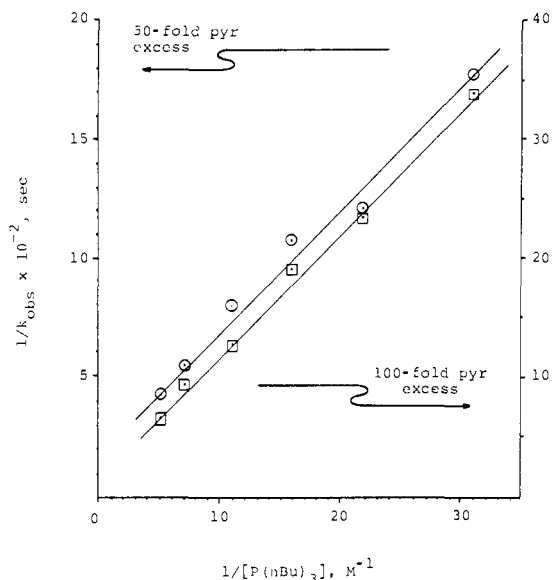
Figure 1. Replacement of pyridine by tri-n-butylphosphine. $\odot$, 50-fold excess pyridine, data plotted with respect to vertical axis on left; $\square$, 100-fold excess pyridine, data plotted with respect to vertical axis on right.

faster than either imidazole (pK_a = 6.9) or benzimidazole (pK_a = 5.5) with the five-coordinate intermediate, phenyl-1,3-bis(biacetylmonoximeimino)propanatocobalt(III) [PhCo((DOH)(DO)pn)]$^+$. The results reported in the present work show just the opposite, the nitrogen-donor base pyridine (pK_a = 5.22) reacts ten times faster than the phosphorus-donor base P(n-Bu)$_3$ (pK_a = 8.43) with the "base-off" cobaloxime. Although the cobalt complexes were different and the incoming ligands were not identical, the inversion in the rate ratios was unexpected. In both systems, the base with the lower pK_a intercepts the five-coordinate cobalt complex more rapidly, but this phenomenon may be related to steric effects as discussed below. It is possible, however, that the mechanism in the system studied by Green and coworkers[10] is I_d, not D as they suggested, making the comparison meaningless.

It is interesting that even though P(n-Bu)$_3$ is more basic than pyridine and coordinates more favorably to the cobalt due to its greater back-bonding ability, it reacts more slowly with the five-coordinate intermediate. Since it logically can be expected that P(n-Bu)$_3$ would react faster due to its basicity and back-bonding ability, the fact that it does not indicates an additional factor which favors pyridine must be dominant. It is possible that a steric effect is involved and this would favor pyridine over P(n-Bu)$_3$. However, whatever factor is operative, the differential effect must be more important in the transition state than in the product.

Piperidine–Pyridines Interchanges. In order to eliminate any possible steric factor so the electronic effects could be analyzed, a series of 4-substituted pyridines was examined. Upon reacting the various pyridines with methyl(piperidine)cobaloxime in CHCl$_3$ exactly as described previously, incomplete displacement of the piperidine was found in all cases except with 4-dimethylaminopyridine. For this reason, the reverse reaction could not be ignored, and the results were interpreted in terms of the reversible D mechanism. The D mechanism was shown in the previous section to hold for the n-Bu$_3$P-pyridine exchange and likely holds for these substituted pyridine interchanges. Evidence based on steric effects and kinetic results supporting the D mechanism for piperidine is presented below.
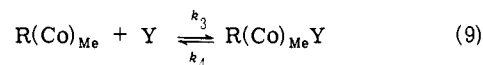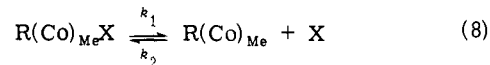
The reversible D mechanism for the alkylcobaloximes

Table II. Kinetic Data for Replacement of Piperidine by 4-Substituted Pyridines[a]

10^2[4-Substituted pyridine], M	$10^3 k_{obsd}$, sec^{-1}			10^2[4-Dimethylamino pyridine], M	$10^3 k_{obsd}$, sec^{-1}
	Pyridine	γ-Picoline	4-Acetyl-pyridine		
3.25	3.13	2.08	5.84	3.21	1.24
4.86		2.12	4.78	4.77	1.42
6.48	2.75	2.13	4.47	6.30	1.46
9.68	2.62	2.18	4.17	9.32	1.58
16.04	2.47	2.22	3.46	15.10	1.67
20.75	2.47	2.25	3.19	17.80	1.71

[a] Me(Co)$_{Me}$pip concentration is 6.3 × 10^{-4} M. Run at 25.00 ± 0.02° in CHCl$_3$.

can be represented by eq 8 and 9.

$$R(Co)_{Me}X \overset{k_1}{\underset{k_2}{\rightleftharpoons}} R(Co)_{Me} + X \qquad (8)$$

$$R(Co)_{Me} + Y \overset{k_3}{\underset{k_4}{\rightleftharpoons}} R(Co)_{Me}Y \qquad (9)$$

The expression for k_{obsd} is the following:

$$k_{obsd} = (k_1 k_3 [Y] + k_2 k_4 [X])/(k_2 [X] + k_3 [Y]) \qquad (10)$$

From this expression, it is apparent that for constant [X] the curve obtained in a plot of k_{obsd} vs. [Y] will have an intercept ([Y] = 0) of k_4, the rate constant for Y dissociation to give the five-coordinate intermediate.

The expression in eq 10 can be rearranged to give the following:

$$1/(k_{obsd} - k_4) = 1/(k_1 - k_4) + (k_2[X]/k_3)/(k_1 - k_4)[Y] \qquad (11)$$

Hence, a plot of $1/(k_{obsd} - k_4)$ vs. $1/[Y]$ will be linear with an intercept of $1/(k_1 - k_4)$ and a slope of $(k_2[X]/k_3)/(k_1 - k_4)$. When the reaction is not detectably reversible, k_4 can be ignored and eq 11 reduces to eq 7.

The data for pyridine, γ-picoline, 4-acetylpyridine, and 4-dimethylaminopyridine appear in Table II. In each case k_{obsd} was plotted vs. [4-substituted pyridine] and from these curves the intercept was estimated. The k_4 value obtained by this method was used in the plot of $1/(k_{obsd} - k_4)$ vs. $1/[4$-substituted pyridine] according to eq 11. These plots yield k_1 and the k_2/k_3 ratio allowing the overall equilibrium constant for the replacement to be calculated:

$$K = k_1 k_3/k_2 k_4 \qquad (12)$$

This calculated value was compared to the actual K measured for the displacement. By an iterative procedure the k_4 value was varied until the calculated K was identical with the measured one. The final plots appear in Figures 2–4. In all cases, except for 4-dimethylaminopyridine, this technique worked well; smooth curves could be drawn through the data points and the calculated intercept, k_4. Evidence for the accuracy of the data was provided by the fact that the k_1 values obtained in the study of pyridine, γ-picoline, and 4-acetylpyridine are effectively identical. The k_1 value represents piperidine dissociation and should be independent of the nature of the incoming ligand as was found.

For 4-dimethylaminopyridine it was not possible to obtain a k_4 value from the data which provided a calculated equilibrium constant equal to the measured one, while still giving a k_1 comparable to that obtained in the first three cases. This anomalous result cannot be attributed to a change in mechanism from D to I_d because mass-law retardation was demonstrated. This exchange proceeded to completion and the I_d mechanism does not exhibit mass-law re-
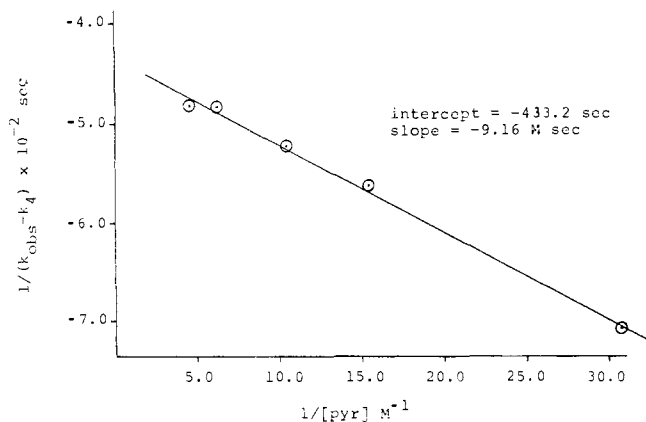
Figure 2. Replacement of piperidine by pyridine, 100-fold excess piperidine. Me(Co)$_{Me}$pip concentration is 6.3×10^{-4} M, CHCl$_3$ solvent, $25.00 \pm 0.02°$.
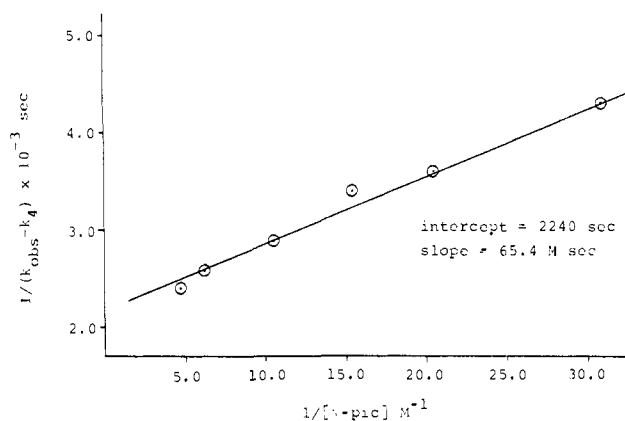
Figure 3. Replacement of piperidine by γ-picoline, 100-fold excess piperidine. Me(Co)$_{Me}$pip concentration is 6.3×10^{-4} M, CHCl$_3$ solvent, $25.00 \pm 0.02°$.

Figure 4. Replacement of piperidine by 4-acetylpyridine. 100-fold excess piperidine. Me(Co)$_{Me}$pip concentration is 6.3×10^{-4} M, CHCl$_3$ solvent, $25.00 \pm 0.02°$.

Figure 5. Hammett plot for rate constant for 4-substituted pyridine dissociation.

tardation under these conditions. Mass-law retardation was demonstrated by decreasing the excess piperidine concentration from 100-fold to 50-fold. The observed rate constant increased from 1.24×10^{-3} to 1.57×10^{-3} sec^{-1}, a 27% enhancement. An alternative explanation for the anomalous result is that the exo-nuclear anilino nitrogen can also coordinate to the base-off complex and in this manner alter the kinetics of exchange.[15]

The kinetic and thermodynamic data for the exchange of piperidine by these substituted pyridines appear in Table III. Although it was not possible to obtain the rate constants for exchange by 4-dimethylaminopyridine, the equilibrium constant was measured. Also contained in Table III are the $\bar{\sigma}$ values which are the substituent constants measured in water for substituents of the pyridine ring system.[16]

As mentioned above, the values obtained for k_1 in the first three cases are essentially identical, as expected. The k_2/k_3 ratio (representing the rate ratio for attack on the five-coordinate intermediate by piperidine vs. the 4-substituted pyridine) does not vary much for the three attacking pyridines. This is reasonable because coordination to the intermediate is a largely exothermic process resulting in minimal participation of the entering group in the transition state. Although it was hoped that some insight into the electronic factors controlling the rates of coordination of bases might be gained, these results suggest that a simple correlation does not exist with known parameters. A similar conclusion was reached when the rate constants for dissociation of the pyridines (k_4) were analyzed. When log k_4 was plot-
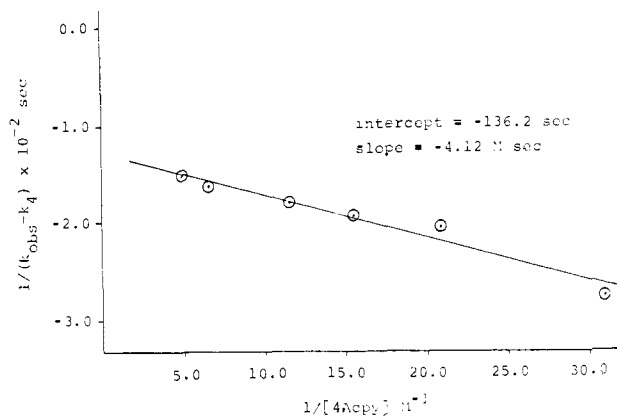
Table III. Kinetic and Thermodynamic Data for Replacement of Piperidine by 4-Substituted Pyridines[a]

Ligand	$\bar{\sigma}$ value[b]	10^3k_1, sec^{-1}	k_2/k_3	10^3k_4, sec^{-1}	K
4-Acetyl-pyridine	0.28	2.20	0.47 ± 0.04	9.54	0.49
Pyridine	0.00	2.22	0.33 ± 0.05	4.53	1.50
γ-Picoline	−0.14	2.29	0.45 ± 0.04	1.84	2.75
4-Dimethyl-amino-pyridine	−0.83				30.10

[a] Cobaloxime concentration is 6.3×10^{-4} M. Reactions were run at $25.00 \pm 0.02°$ in CHCl$_3$. [b] Substituent constant for substitution in the pyridine ring system, from ref 16.

ted against $\bar{\sigma}$ (Figure 5) a straight line was not obtained. This is taken as evidence that dissociation of the bases depends on more than merely the proton basicity of the pyridine. Although d-π back-bonding may be involved, the reverse order for the rate sequence would be predicted if this is the dominant factor. That is, k_4 for 4-acetylpyridine should be the smallest since it is the best π-electron density acceptor of the three. The fact that 4-acetylpyridine dissociation is slower than expected based on its proton basicity (in comparison to the values for pyridine and γ-picoline) suggests that d-π back-bonding may affect ligand dissociation to some extent. However, this conclusion is tenuous considering the limited amount of data.

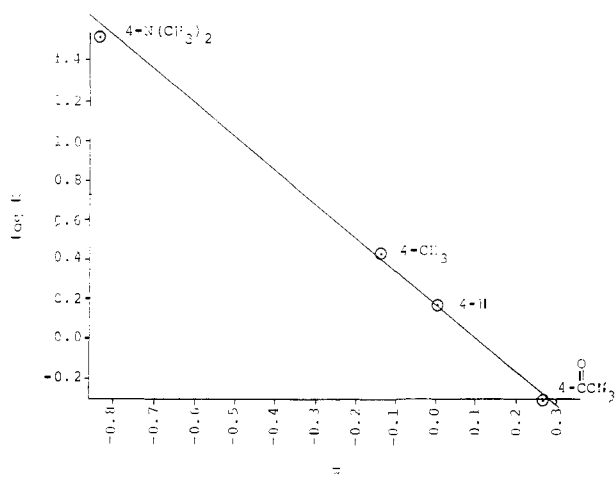In contrast to the above, a plot of log K vs. $\bar{\sigma}$ yields a

Figure 6. Hammett plot of equilibrium constant for replacement of piperidine by 4-substituted pyridines.

Table IV. Electronic Spectral Data for Methylcobaloximes[a]

Axial ligand	Wavelength, nm	Extinction coefficient
Pyridine	420	1210
Pyridine	440	708
Tri-n-butylphosphine	420	446
Piperidine	440	1030
γ-Picoline	440	675
4-Acetylpyridine	440	747
4-Dimethylaminopyridine	440	766

[a] Measured at $25.00 \pm 0.02°$ in $CHCl_3$. Cobaloxime concentration was $6.57 \times 10^{-4} M$.

straight line with $\rho = 1.64$ as shown in Figure 6. It is possible to interpret this observation in at least two different ways. Since $\bar{\sigma}$ is derived from pyridinium ion dissociation constants, the line could result from the dependence of the equilibrium constant solely on the proton basicity of the substituted pyridine, although the magnitude of the effect ($\rho = -1.64$) is small.[17] An alternate explanation is that both proton basicity and d-π back-bonding are important in coordination by pyridines. Because a straight line was obtained when log K vs. $\bar{\sigma}$ was plotted and the proton basicity of 4-substituted pyridines correlates linearly with $\bar{\sigma}$,[16] the d-π back-bonding ability must correlate linearly with $\bar{\sigma}$ as well. The small ρ value suggests that d-π back-bonding (which correlates with $\bar{\sigma}$ in the opposite direction from basicity) causes a significant decrease in the apparent magnitude of the dependence of K on basicity. It is impossible to choose between these two possibilities on the basis of the available data. Since k_1/k_2 is a constant, eq 12 requires K to be proportional to k_3/k_4. Both explanations require that the factor which causes the nonlinearity when log k_4 is plotted against $\bar{\sigma}$ (Figure 5) must affect log k_3 in the identical fashion.

Walker[19] has reported that straight lines are obtained when log K vs. pK_a is plotted for the coordination of imidazoles, pyridines, and nonaromatic cyclic amines to a cobalt porphyrin. For any given pK_a value, the coordination of an imidazole was found to be stronger than a pyridine which in turn is stronger than a nonaromatic amine. The author interpreted this in terms of d-π back-bonding, the added stability of the imidazole complexes over the pyridine compounds being due to greater d-π back-bonding in the imidazole system. The same argument was applied to the comparison of the pyridine and nonaromatic amine complexes. Although this explanation is reasonable, it is possible that the results are solely due to a steric effect. The α-hydrogens on an imidazole would produce less steric interference for nitrogen coordination than for a pyridine which in turn would be less than for a nonaromatic cyclic amine. Thus, the importance of d-π back-bonding in pyridines must still remain in question.

Two final observations concerning the data can be made, both of which fit well with the conclusion that a D mechanism is operative. The first is that the average rate constant obtained for pyridine dissociation in the study of replacement by tri-n-butylphosphine, 5.27×10^{-3} sec^{-1}, agrees well with that obtained in the study of piperidine replacement by pyridine, 4.53×10^{-3} sec^{-1}. This consistency

supplies confidence that the data are correct and that the rate equation utilized accurately describes the ligand exchange process in both cases. The second observation is that the limiting value of k_{obsd} found for replacement of piperidine by the 4-substituted pyridines is the same in each case, about 2.5×10^{-3} sec^{-1}. This provides support for the assertion that all proceed by the same mechanism. In addition, this limiting value is in very good agreement with the average k_1 value found, 2.24×10^{-3} sec^{-1}. It is a requirement of the D mechanism that the limiting k_{obsd} value equal the value for k_1. Thus, this observation is in full agreement with the conclusion that the ligand exchange is a D process.

Experimental Section

The alkylcobaloximes were synthesized either as described previously[14] or by the following procedure.

To a suspension of methyl(aquo)cobaloxime in boiling acetone a small excess of the desired axial base ligand was added. The cobaloxime rapidly goes into solution with a concomitant color change from red to yellowish orange. The hot solution was filtered and allowed to cool slowly to crystallize the product. This precipitate was filtered, washed with ether, and dried at 50° in a vacuum oven (0.5 mmHg). The NMR spectra for all the compounds are in accord with the assigned structures.

Methyl(piperidine)cobaloxime. Anal. Calcd for $C_{14}H_{28}N_5O_4Co$: C, 43.19; H, 7.24; N, 17.98. Found: C, 42.94; H, 7.15; N, 17.84.

Methyl(γ-picoline)cobaloxime. Anal. Calcd for $C_{15}H_{24}N_5O_4Co$: C, 45.34; H, 6.08; N, 17.62. Found: C, 45.21; H, 5.95; N, 17.55.

Methyl(4-acetylpyridine)cobaloxime. Anal. Calcd for $C_{16}H_{24}N_5O_5Co$: C, 45.18; H, 5.68; N, 16.46. Found: C, 45.03; H, 5.46; N, 16.73.

Methyl(4-dimethylaminopyridine)cobaloxime. Anal. Calcd for $C_{16}H_{27}N_6O_4Co$: C, 45.07; H, 6.38; N, 19.71. Found: C, 45.25; H, 6.35; N, 19.52.

Piperidine. Distilled commercial sample, bp 46-46.5° at 89 mm.

γ-**Picoline.** Distilled from barium oxide, bp 72-73° at 63 mm.

4-Acetylpyridine. Distilled from barium oxide, bp 87-89° at 7 mm.

4-Dimethylaminopyridine. Recrystallized sample from Et_2O-hexane, mp 111-112°.

Tri-n-butylphosphine. Distilled and stored under N_2, bp 107-107.5° at 7 mm.

Spectroquality chloroform from Matheson Coleman and Bell was used in all kinetic runs. All other materials used were either purified as described above or used as obtained commercially.

The ligand exchange reactions were followed spectrophotometrically with a Beckman DU spectrophotometer with the cell block maintained at $25.00 \pm 0.02°$. The exchange of tri-n-butylphosphine for pyridine was followed at 420 nm while all other exchanges were monitored at 440 nm. A standard solution of the starting cobaloxime was made up in $CHCl_3$. A 2.50-ml aliquot of this was added to a uv cell followed by the addition of the calculated amount of excess leaving ligand (either pyridine or piperidine). The uv cell was placed in the cell compartment and allowed to come to thermal equilibrium (about 0.5 hr). Finally the entering ligand was added neat by means of a syringe (the dimethylaminopyridine was added as a 250 mg/ml of $CHCl_3$ solution) and the cell quickly agitated to assure complete mixing. The timer was started and the absorbance measured at various times until equilibrium was reached. A plot of log $(D_t - D_\infty)$ vs. time was made giving a

straight line to at least 80% reaction. From the slope of this line, k_{obsd} was obtained. As described in the text, plots were then made of k_{obsd} vs. (entering ligand) and $1/k_{obsd}$ vs. $1/$(entering ligand). The best line through the data points was obtained in the latter plot by a linear least-squares data fit program. The methods for obtaining the rate constants from these plots are described in the text. Extinction coefficients at the wavelengths mentioned are given in Table IV for all compounds studied, and using these, over-all equilibrium constants were measured.

References and Notes

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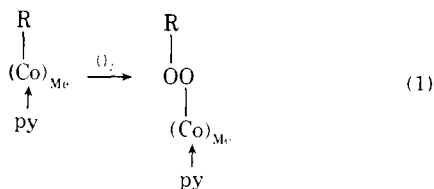(19) F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1150 (1973).

Stereochemistry and Mechanism of the Photochemical and Thermal Insertion of Oxygen into the Carbon–Cobalt Bond of Alkyl(pyridine)cobaloximes[1]

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Abstract: Photochemically induced insertion of oxygen into the carbon–cobalt bond of optically active 2-butyl(pyridine)cobaloxime occurs with complete racemization. Similarly, and in contrast to a previous report, both the photochemical and thermal reactions with optically active 2-hydroxy-1-phenethyl(pyridine)cobaloxime yield no optically active dioxy product. The apparent difference in results between this and previous work is believed to arise from the practical difficulties of measuring optical rotations of highly colored solutions. Photolysis of 5-hexenyl(pyridine)cobaloxime under suitable conditions yields almost entirely the cyclized product cyclopentylmethyldioxy(pyridine)cobaloxime. The cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical is well documented, and the formation of cyclized product is evidence that the reaction proceeds through the intermediacy of free radicals. Evidence regarding possible mechanisms was obtained. Addition of pyridine significantly retards the rate of axial pyridine ligand exchange by tri-*n*-butylphosphine, which indicates that ligand exchange occurs through a dissociative mechanism. However, addition of excess pyridine does not affect the rate of the oxygen insertion reaction, and this eliminates several previously proposed mechanisms which have involved the formation of a "base-off" complex during the oxygen insertion process. The preferred mechanism for the photolytic reaction involves a base-off complex, but it arises differently than has been suggested earlier. In contrast, the thermal reaction does not proceed through the base-off complex. In addition, photochemically induced ligand exchange is demonstrated for these complexes.

Considerable current interest exists in the reaction between cobalt complexes and molecular oxygen.[3–9] Recently, Gaudemer and coworkers have shown that, in the presence of oxygen, stable dioxy adducts can be obtained from alkyl(pyridine)cobaloximes.[10] When R is a benzylic or allylic

$$\underset{py}{\overset{R}{\underset{\uparrow}{\overset{|}{(Co)_{Me}}}}} \xrightarrow{O_2} \underset{\underset{py}{\overset{\uparrow}{(Co)_{Me}}}}{\overset{R}{\underset{|}{\overset{|}{OO}}}} \qquad (1)$$

moiety, the insertion reaction proceeds either thermally in the dark or photochemically.[11] Simple alkyl derivatives do not react at moderate temperatures except when irradiated.[12] The reactions proceed well regardless of the R group, and there is no report of an organocobaloxime that does not give the dioxy product when treated as described. The thermal (dark) reactions are generally carried out at room temperature, while the photolysis reactions may be carried out at lower temperatures using light filtered through copper sulfate solution.[13]

This facile reaction gives quantitative yields in some cases[1,10] and has been reported to be stereospecific,[10,14] with an assignment of possible stereochemistry in one case.[14] This observation has important biochemical and mechanistic[15] implications. The alkylcobaloximes serve as models for coenzyme B_{12},[17] and several proposed mechanisms for conversions mediated by B_{12} involve alkylcobalt complexes as intermediates. Some transformations catalyzed by B_{12} dependent enzymes including propanediol