References and Notes

(1) (a) Partial support of this research by the National Institutes of Health (AM 14341) and the National Science Foundation (MPS 72 0509LA02) is gratefully acknowledged. (b) Additional support in the form of a fellowship and academic leave for C.Y.M. from Nanyang University, Singapore, is also gratefully acknowledged. (c) Preliminary reports of these studies have been made at the VIth IUPAC Symposium on Photochemistry, Aix-en-Provence, France, July 1976 (paper no. 26, p 79), and the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, Abstracts, No. INOR-8.
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Mechanism of Hydrogen Evolution from Hydridocobaloxime

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Received May 19, 1977

Abstract: The forward rate of the reaction $2HCo(dmgH)_2P(n\text{-}C_4H_9)_3 = H_2 + 2Co(dmgH)_2P(n\text{-}C_4H_9)_3$ has been determined in methanol–water solutions as a function of perchloric acid concentration, 0.003–0.10 M. The reaction proceeds by two parallel pathways, with respective first-order and second-order dependences upon the concentration of hydridocobaloxime. Once allowance is made for an H^+-dependent equilibrium with $K_H = 1.3 \times 10^2$ M^{-1}, which we interpret to be the protonation of oxime oxygens (a reaction known in related complexes), the first-order term proceeds at a rate directly proportional to $[H^+]$, and the second-order term is independent of $[H^+]$. Deuterium labeling experiments were also carried out. The reaction appears to proceed by parallel heterolytic and homolytic cleavage of the hydrogen–cobalt bond.

Introduction

Hydrido complexes of cobalt(III) are conjugate acids of the corresponding cobalt(I) complexes. Thus Schrauzer and Holland[1] have isolated and characterized the hydride of bis(dimethylglyoximato)cobalt (or cobaloxime). They find, that with an axial tri-*n*-butylphosphine base, the pK_a for transformation of H(Co)B to $(Co)B^-$ is ~10.5 in 50% aqueous methanol (eq 1).

$$HCo(dmgH)_2P(n\text{-}C_4H_9)_3 \rightleftharpoons H^+ + Co(dmgH)_2P(n\text{-}C_4H_9)_3^- \quad (1)$$

These two cobalt complexes are capable of independent existence and reactivity. For example, at pH ≥11 reaction with $CH_2{=}CHX$ (X = CN, CO_2R, etc.; B = py) produces $XCH_2CH_2Co(dmgH)_2B$, whereas in neutral solution $CH_3CH(X)Co(dmgH)_2B$ is formed.[2,3] Similarly phenylacetylene reacts with $DCo(dmgH)_2py$ to give stereospecific cis addition (eq 2), in contrast to the trans addition of the nucleophilic cobalt(I) anion.[4]

The deuterated complex, prepared from BD_4^- + $ClCo^{III}(dmgH)_2py$ in MeOH, not MeOD, nevertheless transfers D to the organic substrate in reaction 2. This estab-

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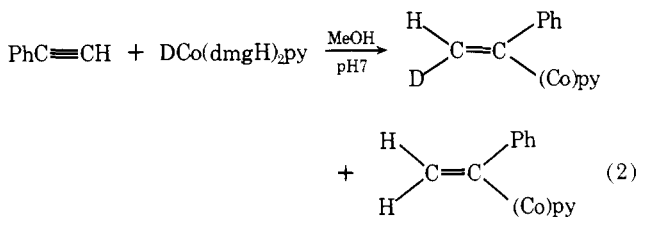


(2)

lishes that exchange of hydrogen bound to cobalt with the acidic proton of the methanol solvent occurs more slowly than does the overall chemical reaction under these approximately neutral conditions.

We are concerned here with the acidity of hydrogen bound to cobalt, and more directly in the present paper with the mechanism of evolution of molecular hydrogen and formation of cobalt(II) cobaloxime as in eq 3. This equilibrium is drawn to completion at high $[H^+]$ owing to the very rapid[5] conversion of the cobalt(II) cobaloxime to Co_{aq}^{2+} and free H_2dmg.

$$2HCo(dmgH)_2P(n\text{-}Bu)_3 \rightleftharpoons H_2 + 2Co(dmgH)_2P(n\text{-}Bu)_3 \quad (3)$$

The purpose of this work is to study the mechanism of this reaction, by determining both the rate expression for disappearance of the hydride complex and the isotopic composition of hydrogen evolved from protiated starting material upon reaction in deuterated solvent.

Three studies in the literature bear on the mechanism of reaction 3: (1) Tackett, Collat, and Abbott[6] have studied the rate of decomposition of B_{12s}, cobalt(I) cobalamin, or, in strongly acidic solution, hydridocobalamin, by virtue of a protonation equilibrium analogous to eq 1 but with $pK_a \sim 1$;[7] (2) DeVries[8] and Burnett, Connolly, and Kemball[9] have measured the forward and reverse rates of reaction for the pentacyanocobalt complexes $HCo(CN)_5^{3-}$ and $Co(CN)_5^{3-}$, analogous to the cobaloximes of reaction 3; (3) Simandi et al.[10] have determined the rate of reaction of cobalt(II) cobaloxime with H_2 in aqueous methanol solutions containing pyridine.

The most fundamental of questions concerning the overall transformation of the hydrido complex shown in eq 3 is whether a so-called hydrogen atom transfer or one-electron pathway is preferred, in which case "direct" formation of H_2 from a bimolecular reaction between two molecules of the hydride is expected, or whether a hydride transfer or two-electron pathway ($H^- \rightarrow H^+$) is preferred. In the latter case a Co(III) complex would be formed as a reaction intermediate and would react in a subsequent rapid reaction.[11] The first of these mechanisms corresponds to reaction 3 being an elementary step, and we show the essence of the second in eq 4 and 5.

$$HCo(dmgH)_2PBu_3 + H_3O^+ \rightarrow H_2OCo(dmgH)_2PBu_3^+ + H_2 \quad (4)$$

$$HCo(dmgH)_2PBu_3 + H_2OCo(dmgH)_2PBu_3^+ \rightarrow 2Co(dmgH)_2PBu_3 + H_3O^+ \quad (5)$$

Experimental Section

Materials. Chloro(tri-*n*-butylphosphine)cobaloxime was prepared by Schrauzer's general procedure.[12] The reduced cobaloxime ($Co(dmgH)_2B^-$ and/or $HCo(dmgH)_2B$, depending on pH) was prepared by reduction of $ClCo(dmgH)_2P(n\text{-}C_4H_9)_3$ with sodium borohydride under an atmosphere of nitrogen purified by passage through a scrubbing tower containing Cr(II). For kinetic experiments the complex was prepared in solution by reduction with a roughly equimolar quantity of borohydride at $\sim 10^{-4}$ M OH^- in 40% methanol-water.

The solid hydrido complex, $HCo(dmgH)_2P(n\text{-}C_4H_9)_3$, was prepared for use in the isotopic labeling experiments by the published method,[1] with an additional rapid washing of the solid by oxygen-free 1 M perchloric acid to decompose any borohydride possibly remaining. The solid was then quickly filtered and dried under vacuum for 1 h, and used the same day for the isotopic determinations.

Deuterated methanol-d_1 (CH_3OD) was prepared from D_2O and solid sodium methoxide, and was collected by distillation. Its purity was confirmed by an NMR measurement.

Methods. The kinetic runs were monitored by following the decrease in concentration of $HCo(dmgH)_2P(n\text{-}C_4H_9)_3$ at its absorption maximum at 610 nm ($\epsilon \sim 1 \times 10^4$ M^{-1} cm^{-1}). Depending upon the anticipated reaction rate, this determination was made using a Cary 14 recording spectrophotometer or a Canterbury SF-3A stopped-flow spectrophotometer. The reaction was initiated by mixing with a dilute, oxygen-free solution of perchloric acid.

The isotopic composition of the hydrogen gas evolved from decomposition of $HCo(dmgH)_2P(n\text{-}C_4H_9)_3$ in $MeOD/D_2O$ was determined mass spectrometrically.[13] The freshly prepared solid hydride was placed in the side arm of an evacuable vessel containing $MeOD/D_2O$ in the main chamber and dilute $HClO_4$ in deuterated solvent in the other. (Although $HClO_4$, not $DClO_4$, was used, the mole fraction of acidic protio hydrogen is so low, <0.01, that the solvent and acid are effectively all deuterated.) Depending on the purpose of the experiment at hand, the complex was either first dissolved with stirring in the neutral solvent, followed by addition of D^+ from the side arm, or else this order of addition was reversed. The solution was then frozen in liquid nitrogen and the noncondensable gases were allowed to flow into the mass spectrometer. The ion currents for H_2^+, HD^+, and D_2^+ were recorded and corrected for background contributions.

Results

Kinetic Determinations. The pattern of kinetic behavior in many experiments proved to be complex, although in some circumstances, notably a low concentration of hydridocobaloxime and high $[H^+]$, 4.6×10^{-5} M cobalt and >0.02 M H^+, the kinetics during the larger part of each run conformed to the simple pseudo-first-order rate expression

$$-d[H(Co)]/dt = k_1[H(Co)] \quad (6)$$

Values of k_1 were computed from the absorbance (D) readings by a standard plot of log $(D_t - D_\infty)$ vs. time. The rate constant was determined over a modest range of concentrations and ionic strengths, and proved to be independent of these variations, the average value being $k_1 = 6.4 \pm 0.3 \times 10^{-3}$ s^{-1} at 25.0 °C.

The complications became apparent from the analysis of data in this range of $[H^+]$ for runs with higher initial concentrations of the hydrido complex, as well as in all the runs at $[H^+]$ <0.02 M. The attempted pseudo-first-order rate plots were curved upward at the start of each run, although in most cases (except at the very lowest $[H^+]$, <0.007 M) the latter 20% or so of reaction again followed a linear relationship between log $(D_t - D_\infty)$ and time, with the same (±10%) limiting rate constant, $\sim 6.4 \times 10^{-3}$ s^{-1}, as in the family of runs which followed pseudo-first-order kinetics throughout. This suggested to us that a mixed first-order and second-order rate expression was needed to describe the kinetics over the entire range:

$$\frac{-d[H(Co)_T]}{dt} = k_1[H(Co)_T] + k_2[H(Co)_T]^2 \quad (7)$$

where the designation $[H(Co)_T]$ is used to indicate the sum of the concentrations of two forms of the hydridocobaloxime as shown in the equilibrium

$$HCo(dmgH)_2P(n\text{-}C_4H_9)_3 + H^+ \overset{K_H}{\rightleftharpoons} HCo(dmgH)(dmgH_2)P(n\text{-}C_4H_9)_3^+ \quad (8)$$

Confirmation of eq 7 is found in the plots of log $(rate)_t$ vs. log $[H(Co)_T]_t$. The "rate" was evaluated at various intervals during the run as $\Delta(D)/2\Delta t$, and the concentration used was that of the hydride complex at the midpoint of that interval. Two runs are shown[14] in Figure 1, both at 0.0755 M H^+, the

Table I. Kinetic Data[a] for Mixed First-Order–Second-Order Kinetics

Time, s	$(D_t)^b$	$(e^\alpha)^c$
0	1.331	1.000
8.4	1.105	0.871
12.4	1.010	0.815
16.4	0.950	0.785
20.4	0.875	0.740
24.4	0.820	0.710
28.4	0.768	0.680
32.4	0.722	0.654
36.4	0.678	0.628
40.4	0.640	0.607
44.4	0.605	0.587
48.4	0.575	0.572
52.4	0.543	0.551
56.4	0.516	0.535
60.4	0.490	0.520
64.4	0.470	0.510
68.4	0.448	0.497
72.4	0.429	0.487
76.4	0.410	0.475
84.4	0.377	0.457
92.4	0.347	0.439
100.4	0.320	0.423
108.4	0.296	0.408
124.4	0.260	0.391
144.4	0.220	0.366
152.4	0.210	0.365
∞	0.031	

[a] In 40% CH_3OH–H_2O at 25.0 °C with $[H(Co)_T]_0 = 7.38 \times 10^{-5}$ M. $[H^+] = 0.0755$ M, ionic strength 0.0755 M. [b] Absorbance readings at λ 610 nm in a cell of 2.00 cm optical path. [c] $\alpha = \ln [(D_t - D_\infty)/(D_0 - D_\infty)] + k_1 t$, calculated using $k_1 = 6.4 \times 10^{-3}$ s^{-1}.

one with $[H(Co)_T]_0 = 7.38 \times 10^{-5}$ M, the other with $[H(Co)_T]_0 = 1.6 \times 10^{-5}$ M. For purposes of comparison lines of slopes 2 and 1 are shown, and it is readily seen that the apparent reaction order progresses between these limits as expected for a reaction following eq 7.

The existence of the equilibrium shown in reaction 8, and the value $K_H = 1.3 \times 10^2$ M^{-1}, are justified from the kinetic data, as indicated later. For the moment, however, we can analyze the kinetic data according to eq 7, using a constant value of 6.4×10^{-3} s^{-1} for k_1 and computing a value for k_2. (The ultimate data analysis is such that k_1 should in fact be a function of $[H^+]$, and therefore vary from run to run, as in the expression $k_1 = k_1^0[H^+]/(1 + K_H[H^+])$. In some runs $K_H[H^+] \gg 1$, such that $k_1 \sim k_1^0/K_H$, independent of $[H^+]$; in others at lower $[H^+]$, <0.02 M, the k_2 term becomes so dominant that the k_1 term is of minor importance.)

Integration of the rate expression in eq 7 yields

$$\ln \left\{ \frac{[H(Co)_T]_0(k_1 + k_2[H(Co)_T])}{[H(Co)_T](k_1 + k_2[H(Co)_T]_0)} \right\} = k_1 t \qquad (9)$$

which, after expression in terms of absorbance readings, can be rearranged to

$$\exp \left\{ \ln \frac{D_t - D_\infty}{D_0 - D_\infty} + k_1 t \right\} = \exp \alpha = \frac{k_1}{k_1 + k_2[H(Co)_T]_0} + \frac{k_2[H(Co)_T]_0(D_t - D_\infty)}{(k_1 + k_2[H(Co)_T]_0)(D_0 - D_\infty)} \qquad (10)$$

such that the plot of the left-hand side vs. $D_t - D_\infty$ is linear. The value of k_2 is calculated from the relation

$$k_2 = \frac{(\text{slope})(k_1)(D_0 - D_\infty)}{(\text{intercept})[H(Co)_T]_0} \qquad (11)$$

Data for a particular run are shown in Table I, with the corresponding kinetic plot given in Figure 2. For this run as well

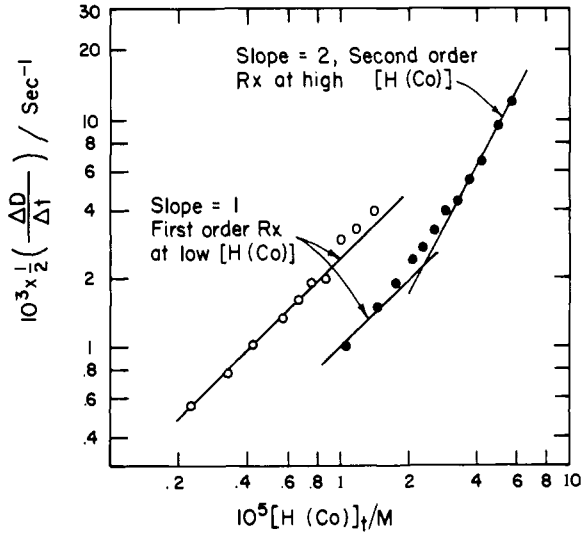


Figure 1. Log-log plot of average reaction rate, expressed as Δ absorbance/2Δ time, with the mean concentration of hydridocobaloxime in the interval over which the rate was evaluated. The two runs have $[H^+]$ = 0.0755 M, with initial concentrations of 7.38×10^{-5} and 1.63×10^{-5} M $HCo(dmgH)_2P(n\text{-}C_4H_9)_3$. (The absorbances were measured in cells of 2- and 5-cm optical path, respectively, which accounts for a factor of 2.5 difference in the rate of absorbance change between runs.)

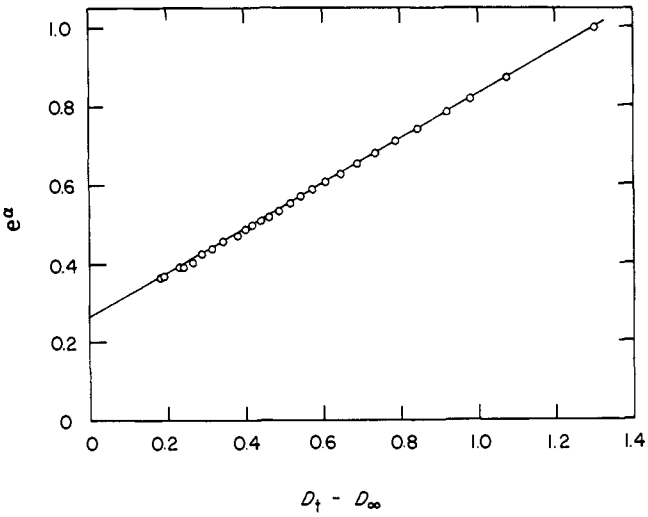


Figure 2. Plots for mixed first-order and second-order kinetics according to eq 10 for the data of Table I; the line shown yields $k_2 = 240$ M^{-1} s^{-1}.

as all the others, the data were fit quite well by the rate law eq 7. An alternative method based on a nonlinear least-squares computation[15] was used to analyze the kinetic data according to the expression of eq 12, fitting absorbance readings as a function of time to the relation given, calculating k_2 with k_1 fixed at the desired value.

$$D_t = D_0 + \frac{(k_1 + k_2[A]_0)[\exp(k_2 t) - 1](D_\infty - D_0)}{(k_1 + k_2[A]_0)\exp(k_2 t) - k_2[A]_0} \qquad (12)$$

Both methods gave comparable results. The graphical treatment for the run shown in Figure 2 gave $k_2 = 2.40 \times 10^2$ M^{-1} s^{-1}, and the computer calculation with the value of k_1 fixed at 6.4×10^{-3} s^{-1} gives $k_2 = 2.46 \pm 0.04 \times 10^2$ M^{-1} s^{-1}. Similarly good agreement was obtained in all other reactions. The case shown is one for which both the first-order and second-order terms contribute appreciably, and the value of k_2 was dependent upon the choice of k_1. The first-order kinetic term becomes of declining importance at lower $[H^+]$, and al-

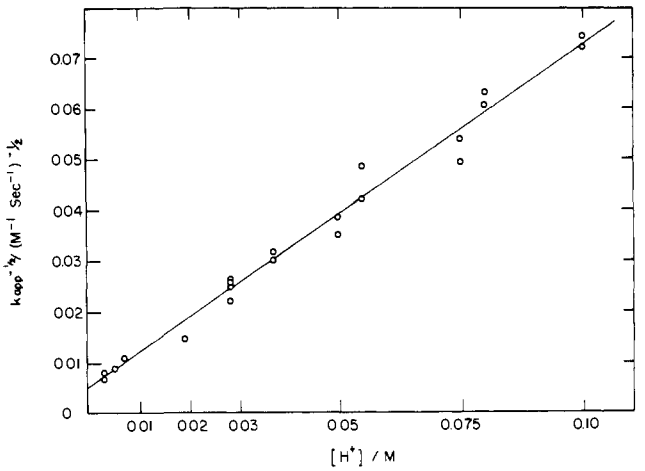


Figure 3. Hydrogen-ion dependence of k_2 shown in the linear variation of $1/(k_2)^{1/2}$ with $[H^+]$ according to eq 13.

though our ultimate formulation leads us to expect that k_1 will decline with decreasing $[H^+]$ as $[H^+]/(1 + 130[H^+])$, the choice of the k_1 value becomes immaterial at low $[H^+]$. At 0.0189 M H^+, for example, the values of $10^{-3}k_2$ are 5.12, 5.19, and 5.38 M^{-1} s^{-1} for respective values of 10^3k_1 = 5.5, 4.0, and 0 s^{-1}.

The values of k_2 for each experiment are summarized in Table II, and we wish now to formulate its functional dependence upon $[H^+]$. A number of forms were tried, but the only simple (i.e., two-parameter) function which gives a satisfactory fit is given by

$$k_2 = k_2^0/(1 + K_H[H^+])^2 \quad (13)$$

a relation which offers the further advantage of a ready mechanistic interpretation (see Discussion). A test of this relation is the linearity of the plot of $(k_2)^{-1/2}$ vs. $[H^+]$, shown in Figure 3. Least-squares fit[15] of the data yields the values $k_2^0 = 3.43 \pm 0.24 \times 10^4$ M^{-1} s^{-1}, $K_H = 1.3 \pm 0.1 \times 10^2$ M^{-1}.

Deuterium Tracer Determinations. The isotopic composition of the hydrogen evolved from decomposition of the exclusively protio complex in exclusively (>0.99) deuterio solvent (CH_3OD/D_2O) was determined. Experiments were done under two separate sets of conditions, each designed to elucidate the isotopic course of one reaction pathway over the other.

The experiment designed to emphasize the second-order kinetic term was performed by dissolving a relatively high concentration, $\sim 7 \times 10^{-3}$ M, of the hydride in neutral methanol-d_1 then adding the dilute solution of $DClO_4$ in D_2O to provide $\sim 3 \times 10^{-3}$ M D^+. The dihydrogen produced was mainly H_2, the mass spectrometrically determined ratios being H_2:HD:D_2 = 400:20:1.

The experiment designed to emphasize the first-order kinetic term was conducted at high $[D^+]$, 0.3 M, and low [H(Co)]. The solution of $DClO_4$ in CH_3OD/D_2O was first prepared; then the solid hydride was added in small increments from the side arm of the reaction vessel, such that one portion was largely decolorized before the next was added. The ratio of gases was H_2:HD:$D_2 \sim$ 1:3:3.

Interpretation and Discussion

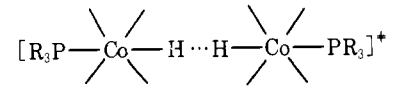
The second-order kinetic term and the functional form of the variation of k_2 with $[H^+]$ as shown by eq 13 are consistent with a mechanism having the bimolecular reaction of an unprotonated hydridocobaloxime as the rate-limiting step. The postulation of the equilibrium of eq 8 for hydridocobaloxime is exactly parallel to known and analogous processes for alkylcobaloximes.[16-19] Provided that only the unprotonated form reacts, this formulation then agrees with eq 13 in that the fraction of the total hydridocobaloxime which is unprotonated is

$$\frac{[HCo(dmgH)_2P(n\text{-}C_4H_9)_3]}{[HCo(dmgH)_2P(n\text{-}C_4H_9)_3] + [HCo(dmgH)(dmgH_2)P(n\text{-}C_4H_9)_3]} = \frac{1}{1 + K_H[H^+]} \quad (14)$$

The rate-limiting step in the second-order path thus appears to be that of eq 15, with $k_{15} = k_2^0/2 = 1.7 \times 10^4$ M^{-1} s^{-1}.

$$2HCo(dmgH)_2B \xrightarrow{k_{15}} H_2 + 2Co(dmgH)_2B \quad (15)$$

This suggests to us an activated complex in which the bond between the two hydrogen atoms is being formed directly, as in the configuration



The tracer determination provides strong support for this formulation in that H_2 rather than HD or D_2 is the major product in an experiment in which >99% of the acidic hydrogens are deuterium.

The value of K_H also deserves comment. Hydridocobaloxime with $K_H = 1.3 \times 10^2$ M^{-1} is considerably more basic than are

Table II. Kinetic Data[a] for Reaction of Hydridocobaloxime According to the Equation $-d[H(Co)_T]/dt = k_1[H(Co)_T] + k_2[H(Co)_T]^2$

$[H^+]$, M	μ, M	$10^5[H(Co)_T]_0$, M	10^3k_1, s^{-1}[b]	$10^{-2}k_2$, M^{-1} s^{-1}
0.100	0.100	0.20	6.2	
0.100	0.100	4.86	(6.4)	1.9
0.100	0.100	7.60	(6.4)	1.8
0.100	0.100	7.60	(6.4)	1.9
0.0755	0.100	0.20	6.2	
0.0755	0.0755	1.63	6.8	
0.0755	0.0755	3.04	(6.4)	2.62
0.0755	0.0755	5.13	(6.4)	2.48
0.0755	0.0755	5.13	(6.4)	2.71
0.0755	0.0755	7.38	(6.4)	2.46
0.0755	0.0755	7.38	(6.4)	2.47
0.0750	0.100	0.20	(6.4)	
0.0750	0.100	4.86	(6.4)	3.4
0.0750	0.100	7.6	(6.4)	4.1
0.0550	0.055	8.5	(6.4)	4.2
0.0550	0.055	8.5	(6.4)	5.6
0.050	0.100	0.20	6.1	
0.050	0.100	4.86	(6.4)	6.7
0.050	0.100	7.60	(6.4)	8.1
0.037	0.037	8.64	(6.4)	10.9
0.037	0.037	8.65	(6.4)	9.9
0.0283	0.0650	1.63	6.8	
0.0283	0.0283	1.63	6.5	
0.0283	0.0283	5.00	(6.4)	15.8
0.0382	0.0283	7.80	(6.4)	15.0
0.0382	0.0650	7.80	(6.4)	14.7
0.0283	0.101	7.80	(6.4)	21.0
0.0189	0.0189	8.80	(6.4)	50.5
0.0070	0.0070	5.38		83.7
0.0070	0.0070	5.38		84.8
0.0050	0.0050	5.38		125.
0.0030	0.0030	5.38		156.
0.0030	0.0030	5.38		222.

[a] At 25.0 °C in 40% methanol-water. [b] Values of k_1 determined in a given experiment are shown; a value of k_1 shown in parentheses was not determined, but was set at the value shown for the calculation of k_2; no entry for k_1 is made in runs where k_1 was not included.

the structurally similar alkylcobaloxime, $RCo(dmgH)_2H_2O$ (R = CH_3, K_H = 3.5 M^{-1}; R = C_2H_5, K_H = 4.2 M^{-1}; etc.[16,17,19]). We assume that the analogous chemistry, namely, protonation of an oxime oxygen, is occurring. The larger value of K_H seems consistent with the NMR assignment for hydridocobaloxime,[2] the resonance at δ 6.0 ppm suggesting a polarization $H^{\delta+}$-$Co^{\delta-}$ of the cobalt-hydrogen bond.

A further point of comparison concerning the second-order kinetic term should be noted. The cobalt(II) complexes $Co(CN)_5^{3-}$ and $pyCo(dmgH)_2$ both react with H_2[8-10] at a rate given by $k[H_2][Co(II)]$,[2] and in the case of the cobalt(II) cobaloxime only the five-coordinate form proved reactive.[10] The rate thus passes through a maximum with variation of pyridine concentration, as both the dipyridine and the pyridine-free forms proved largely unreactive. The hydrogenation equilibrium for the pentacyanocobaltate system at 25 °C has $K_{eq} = 6.2 \times 10^{-6}$ M for

$$2HCo(CN)_5^{3-} = H_2 + 2Co(CN)_5^{3-} \quad (16)$$

and the reaction rate law is

$$-d[HCo(CN)_5^{3-}]/dt = k_{16}[HCo(CN)_5^{3-}]^2 - k_{-16}[Co(CN)_5^{3-}]^2[H_2] \quad (17)$$

The value of the rate constant k_{16} is 5×10^{-3} M^{-1} s^{-1}, considerably smaller than the value $k_2^0 = 3.4 \times 10^4$ M^{-1} s^{-1} found in the present work for $HCo(dmgH)_2P(n\text{-}C_4H_9)_3$.

Ignoring for the moment any difference between the phosphine and pyridine axial bases on the cobaloxime, the equilibrium constant for the reaction

$$2HCo(dmgH)_2B = H_2 + 2Co(dmgH)_2B \quad (18)$$

can be estimated from the quotient of forward and reverse rate constants, using $k_2^0/2$ determined in the present work for k_{18} and Simándi's value[10] for k_{-18}. Thus $K_{18} = 1.7 \times 10^4$ M^{-1} $s^{-1}/2.2 \times 10^3$ M^{-2} s^{-1} = 8 M. Even if the difference between B = py and $P(n\text{-}C_4H_9)_3$ is not negligible, these data are sufficient to show that hydridocobaloxime is considerably less stable (by ~4.3 kcal/mol Co-H) to dissociation to H_2 and (Co^{II}) than is $HCo(CN)_5^{3-}$.

We now return to a consideration of the first-order pathway, for which the rate was found to be independent of $[H^+]$ in the region $[H^+] > 1/K_H$; where the predominant species of hydridocobaloxime is the protonated form. Thus the first-order dependence upon $[H(Co)_T]$ under these conditions, eq 6, is really to be interpreted in terms of either of the equivalent rate expressions of eq 19.

$$-d[H(Co)_T]/dt = k_1[HCo(dmgH)(dmgH_2)P(n\text{-}C_4H_9)_3^+] \quad (19a)$$

$$-d[H(Co)_T]/dt = k_1'[HCo(dmgH)_2P(n\text{-}C_4H_9)_3][H^+] \quad (19b)$$

The latter suggests a hydride transfer process forming Co(III):

$$R_3P\text{—}Co\text{—}H\cdots HO^+H_2 \xrightarrow{k_1'} R_3P\text{—}Co\text{—}OH_2^+ + H_2 \quad (20)$$

If this mechanism is correct, $k_1' = k_1K_H/2 = 0.42$ M^{-1} s^{-1}. Two further results bear on this proposal, the first being the rate of reaction between Co(III) and Co(I). If eq 20 is indeed the rate-limiting step along this pathway, then it must be followed by a still more rapid conversion of (Co^{III}) to $Co(dmgH)_2$ by reaction with a second reduced cobaloxime as shown in eq 5. We have determined the rate of this reaction, and find a second-order rate constant of 3.6×10^5 M^{-1} s^{-1} (at 25 °C in 20% acetone-methanol with $[OH^-] = 5 \times 10^{-5}$ M) for reaction of $ClCo^{III}(dmgH)_2P(n\text{-}C_4H_9)_3$ and the anionic cobalt(I) complex, $Co^I(dmgH)_2P(nC_4H_9)_3^-$ (see also ref 11).

A second result related to this pathway concerns the isotopic tracer result at high $[H^+]$. According to eq 20, we expect only HD, whereas comparable quantities of H_2 and D_2 are found as well. The H_2 may arise from residual contributions from the second-order pathway, whereas D_2 may be produced if slow exchange between complex and solvent occurs prior to hydrogen evolution. The exchange rate of $HCo(dmgH)_2B$ and solvent has not been determined, but an exchange rate comparable to that of hydrogen evolution is not unreasonable considering the relatively low rate of the latter under comparable conditions. We note that $HCo(CN)_5^{3-}$ reacts with OH^- only rather slowly,[20] and similar chemistry could apply to hydridocobaloxime as well.

A direct comparison between k_1 or k_1' and the corresponding term for B_{12s} would be interesting, but the existing kinetic data[6] are rather limited. Moreover, the major species of B_{12s} is the Co(I) anion since $pK_a \sim 1$ for hydridocobalamin.[7]

Finally it is interesting to consider that the answer we have found to the question of one-equivalent vs. two-equivalent mechanisms for hydrogen evolution is a dual one. Both mechanisms operate under suitable conditions. Considering the reverse reaction dealing with the activation of the H_2 molecule for cleavage, our finding in the light of the principle of microscopic reversibility is that both heterolytic and homolytic pathways for hydrogen activation function in parallel. This situation is analogous to the reaction of $Ag^+(aq)$ with H_2 for which Webster and Halpern[21] find similar parallel pathways.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Basic Energy Sciences. Helpful discussions with Dr. M. D. Johnson and partial support from a joint NATO Research Grant are gratefully acknowledged.

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(14) Note that the actual rates at [H(Co)] concentrations where the two runs overlap differ by a factor of 2.5, consistent with absorbance readings for the two runs in cells having 2- and 5-cm optical paths. The path length difference was not divided out so as to separate the two runs in this graphical display.
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