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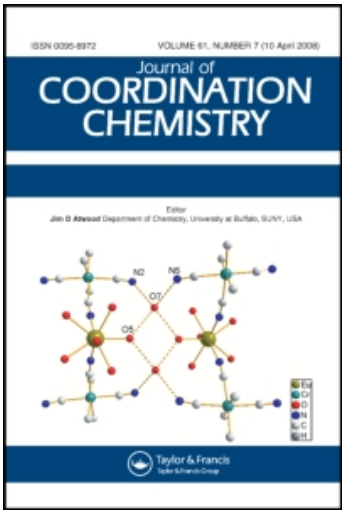

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AUTOCATALYTIC REDUCTION OF PYRIDINECOBALOXIME(III) BY MOLECULAR HYDROGEN

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In the presence of added cobaloxime(II), hydroxopyridinecobaloxime(III) is autocatalytically reduced by molecular hydrogen in methanol at 20°C. The sigma-shaped volumetric curves were evaluated by computer simulation of the system of differential equations corresponding to a 4-step mechanism. The key reduction step is presumably H-atom transfer from hydridocobaloxime(III) to cobaloxime(III). The lower limit of its rate constant is $k_4 = (5.0 \pm 0.5) \times 10^4\ M^{-1}\ sec^{-1}$ at 20°C. Hydridopyridinecobaloxime(III) is thermodynamically unstable, its estimated formation equilibrium constant being $(3.9 \pm 0.6) \times 10^{-4}\ M^{-1}$. The possible role of cobaloxime(I) species is discussed.

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INTRODUCTION

Bis(dimethylglyoximato)cobalt(II), referred to also as cobaloxime(II), is known to react with molecular hydrogen at room temperature, its reactivity being enhanced by added pyridine.[1–7] According to previous studies, the hydrogen absorbed is consumed for the hydrogenation of coordinated dimethylglyoxime and the hydridocobaloxime intermediate cannot be isolated from these systems.[1]

Under the above conditions, cobaloxime(III) derivatives are unreactive toward molecular hydrogen. We have found that they can be reduced in an autocatalytic reaction. In this paper, we report on the reduction of pyridinebis(dimethylglyoximato)cobalt(III) effected by added pyridinecobaloxime(II).

EXPERIMENTAL

Cobaloxime(II) solutions were prepared *in situ* under strictly anaerobic conditions from cobalt(II) perchlorate, dimethylglyoxime, sodium hydroxide and pyridine. Cobaloxime(III) solutions were prepared *in situ* by air-oxidation of the corresponding cobaloxime(II) solutions. Analytical grade chemicals were used throughout. H_2 absorption curves were recorded volumetrically after mixing deaerated and H_2-saturated solutions of the components.

Spectrophotometric measurements were carried out on a Beckman ACTA MIV instrument. The calculations were performed on a CDC-3300 computer.

RESULTS AND DISCUSSION

The volumetric H_2 absorption curve of a 1.0×10^{-3} M methanol solution of pyridinecobaloxime(II), $Co^{II}py$, prepared under anaerobic conditions is shown in Figure 1 (A). The concentration of py was selected so as to ensure maximum formation of the 1:1 mixed complex.[8] Upon the addition of 6.0×10^{-3} hydroxopyridinecobaloxime(III), $Co^{III}OH(py)$, prepared separately by air oxidation of $Co^{II}py$, a sigma-shaped H_2-absorption curve (Figure 1, B) is observed. The volumetric curve of a 7.0×10^{-3} M $Co^{II}py$ solution (Figure 1, C) is also given for comparison; here $[Co^{II}py]$ is equal to the *overall* cobaloxime concentration corresponding to curve B.

The amount of H_2 absorbed up to the beginning of the linear section of curve B (t_1) corresponds to 2.77×10^{-3} M hydrogen, which is almost exactly the amount required for the reduction of the added $Co^{III}py$ to $Co^{II}py$. Clearly, after complete reduction, the system behaves as if only $Co^{II}py$ were present: the slope of the linear section is equal to that of curve C. At the end of the sigmoid curve, the UV–VIS spectrum of the solution corresponds to that of a 7.0×10^{-3} M pyridinecobaloxime(II) solution.

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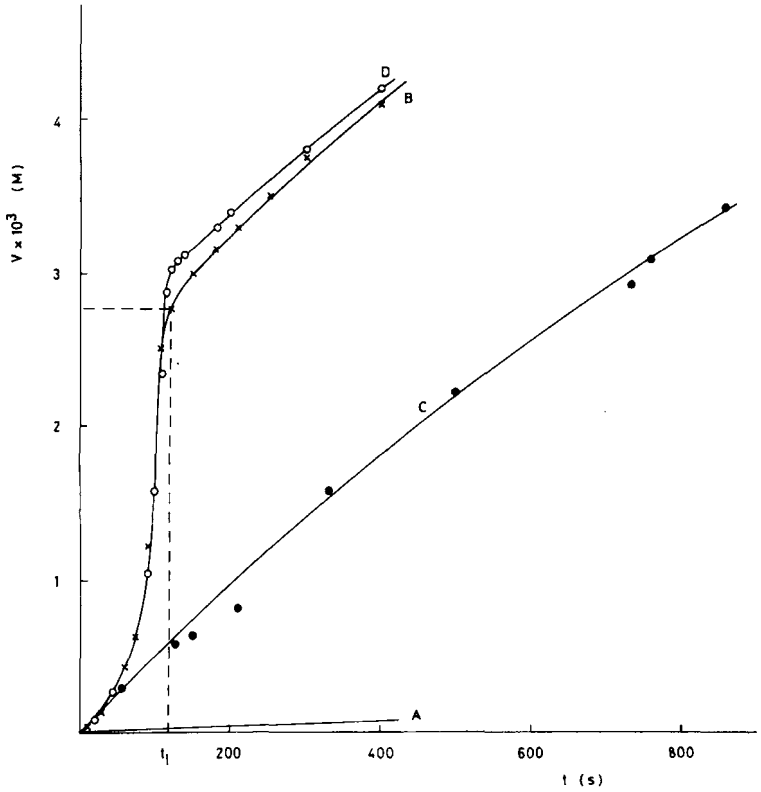

FIGURE 1 H_2-uptake in the presence of cobaloxime(II); T = 20°C, solvent: methanol

A) $[Co^{II}]_0 = 1 \times 10^{-3}$ M, $[Co^{III}]_0 = 0$, $[py]_T = 0.16$ M;

B) $[Co^{II}]_0 = 1 \times 10^{-3}$ M, $[Co^{III}]_0 = 6 \times 10^{-3}$ M, $[py]_T = 0.16$ M;

C) $[Co^{II}]_0 = 7 \times 10^{-3}$ M, $[Co^{III}]_0 = 0$, $[py]_T = 0.16$ M;

D) computer simulated curve: $[Co^{II}]_0 = 1 \times 10^{-3}$ M, $[Co^{III}]_0 = 6 \times 10^{-3}$ M, $[py]_T = 0.16$ M (for rate constants see Table I).

Comparison of the curves in Figure 1 leads to the following conclusion. Added cobaloxime(III) strongly increases the rate of H_2-uptake from the very beginning: the initial slope of curve B exceeds that of curve A appreciably. The accumulation of $Co^{II}py$ produces a further acceleration of H_2-absorption, then the rate gradually decreases to the value corresponding to curve C.

The fact that at all times during the reduction of the added cobaloxime(III) the rate is higher than could be expected from the actual $Co^{II}py$ concentration indicates a different rate-determining step for the autocatalytic process. The observed behaviour can be interpreted in terms of the following mechanism. In the absence of cobaloxime(III), steps (1)–(3) have been assumed to occur;[2,7,9] in this scheme (1) and (2) are pre-equilibria, and (3) is rate-determining (Co*py is an intermediate with a $>C{=}N-$ group hydrogenated to $>CH{-}NH-$). The existence of (H_2)Copy is assumed to avoid the assumption of a ternary collision, which would otherwise be required to account for the overall third order kinetics. Since no straightforward bonding picture can be given for this type of species,[10] molecular H_2 is thought to be held by unspecified weak interactions for times just permitting an encounter with $Co^{II}py$. The alternative of $Co^{II}py$ dimerization followed by reaction with H_2 seems less likely as the dimer would form at the expense of its reaction center.

$$Co^{II}py + H_2 \overset{K_1}{\rightleftharpoons} (H_2)Copy \qquad (1)$$

$$(H_2)Copy + Co^{II}py \overset{K_2}{\rightleftharpoons} 2HCopy \qquad (2)$$

$$2HCopy \xrightarrow{k_3} Co^{*}py + Co^{II}py \qquad (3)$$

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The rate law corresponding to scheme (1)–(3) is of the form[2,3,9] (V is the amount of H_2 absorbed, mol/dm^3):

$$dV/dt = k_{obs}[H_2][Co^{II}py]^2 \qquad (a)$$

where $k_{obs} = K_1 K_2 k_3 = K_1(k_2/k_{-2})k_3$.

Added cobaloxime(III) suppresses ligand hydrogenation (3) by opening up a fast, competitive route for the consumption of hydridocobaloxime(III) via step (4).

$$HCopy + Co^{III}OH(py) \xrightarrow{k_4} 2Co^{II}py + H_2O \qquad (4)$$

As a consequence, the formation of $HCo^{III}py$, i.e. the activation of H_2, will become rate-determining. As a first approximation, we assume that step (1) remains a pre-equilibrium, however, step (2) will be slow and practically irreversible and step (3) is absent. Taking into account that

$$[Co^{II}py] = \frac{([Co^{II}]_0 + 2V)\beta_1[py]}{1 + \beta_1[py] + \beta_2[py]^2} = ([Co^{II}]_0 + 2V)A \qquad (b)$$

and replacing k_{obs} by k^*_{obs} in rate Eq. (a), we obtain the following integrated expression:

$$\frac{1}{2V} = -\frac{1}{[Co^{II}]_0} + \frac{1}{2k^*_{obs}[H_2][Co^{II}]_0^2 A^2} \cdot \frac{1}{t} \qquad (c)$$

Here $k^*_{obs} = K_1 k_2$ and β_1 and β_2 are the products of the successive stability constants of $Co^{II}py$ and $Co^{II}py_2$[8]

$$\beta_1 = \frac{[Co^{II}py]}{[Co^{II}][py]} \qquad \beta_2 = \frac{[Co^{II}py_2]}{[Co^{II}][py]^2}$$

and $[Co^{II}]_0$ is the initial total cobaloxime(II) concentration, i.e.

$$[Co^{II}]_0 = [Co^{II}] + [Co^{II}py] + [Co^{II}py_2]$$

(the free py concentration was taken equal to $[py]_T$). The plot based on Eq. (c) (Figure 2) is linear for the accelerating section of curve B but serious deviations occur in the vicinity of the decelerating part. From the linear section of the plot, $K_1 k_2 = 1500\ M^{-2}\ sec^{-1}$, in excellent agreement with a previous value obtained using styrene as a scavenger for hydridopyridinecobaloxime(III).[11]

The breakdown of Eq. (c) is obviously due the decreasing cobaloxime(III) concentration, which vitiates the assumption that step (4) is irreversible and fast compared with step (2). This has the important consequence that ligand hydrogenation step (3) makes gradually increasing contributions to H_2-absorption.

The neglect-free kinetic treatment of reactions (1)–(4) requires the solution of the following system of differential equations:

$$w_1 = dV/dt = K_1 k_2 [Co^{II}py]^2 [H_2] - k_{-2}[HCopy]^2 \qquad (d)$$

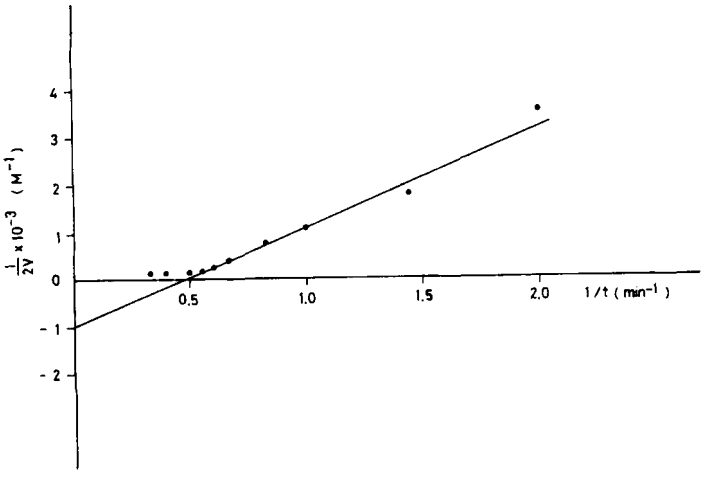

FIGURE 2 Plot of curve B (Figure 1) according to Eq. (c).

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$$w_2 = d[HCopy]/dt = 2w_1 - k_4[HCopy]\cdot[Co^{III}OH(py)] - 2k_3[HCopy]^2 \quad (e)$$

$$w_3 = d[Co^{III}OH(py)]/dt = -k_4[HCopy]\cdot[Co^{III}OH(py)] \quad (f)$$

$$w_4 = d[Co^{*}py]/dt = k_3[HCopy]^2 \quad (g)$$

Eqs. (d), (e) and (f) being independent. The underlying assumptions are that /i/ step (1) is a pre-equilibrium; /ii/ step (2) is reversible; /iii/ step (3) is not suppressed; and /iv/ step (4) occurs at a finite rate. It should be noted that no steady state assumption is made for $HCo^{III}py$.

Apparently, Eqs. (d)–(f) cannot be integrated in an exact form. The consistency of these rate equations with mechanism (1)–(4) was demonstrated by means of computer simulation based on a numerical integration routine for "stiff" differential equations.[12] The value of K_1k_2 derived from the ascending section was accepted as correct. The starting value of k_{-2} was estimated from the assumption that the combined equilibrium constant for steps (1) and (2), i.e. K_1k_2/k_{-2}, permits a maximum $HCo^{III}py$ concentration equal to about 1% of the overall $Co^{II}py$ present. This is justified by the fact that upon acidification of a pyridinecobaloxime(I) solution, prepared by conducting the reaction of $Co^{II}py$ with H_2 in excess NaOH,[1] 0.5 mol H_2 is immediately released for each mole of cobaloxime, which implies that no appreciable amounts of $HCo^{III}py$ may exist in methanol solutions. The low equilibrium concentration of $HCo^{III}py$ is in line with the failure to isolate it from reacting $Co^{II}py/H_2$ systems (no excess NaOH) and with the lack of excess H_2 over the dissolved amount, as shown by freeze-thaw-pump experiments.

The starting value of k_3 was estimated from the ratio $k^{*}_{obs}/k_{obs} = k_{-2}/k_3$ and the actual value of k_{-2}. This ratio can be determined experimentally, therefore, its value was regarded as fixed in all simulation runs. The initial value of k_4 was set two orders of magnitude higher than that of $K_1k_2[H_2]$.

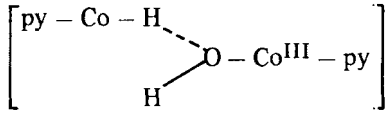
Simulations were first performed with the set of constants thus obtained. In order to explore the effect of the individual rate constants on the shape of the simulated H_2-absorption curve, we varied each constant in turn over a wide range, keeping the other two constants fixed. The shape of the simulated H_2-absorption curve is rather sensitive to the values of the constants k_{-2}, k_3 and k_4. The set of rate constants listed in Table 1 produces agreement between the measured and simulated curves within the experimental error (Figure 1, curve D). The upper and lower limits of each value correspond to the threshold at which deviations from the experimental curve noticeably exceed the experimental error.

TABLE I
Rate constants at 20°C, obtained from computer simulation (K_1k_2 not varied).

K_1k_2	=	$1500 \pm 150\ M^{-2}sec^{-1}$
k_{-2}	=	$(3.8 \pm 0.3) \times 10^6\ M^{-1}sec^{-1}$
k_3	=	$(1.0 \pm 0.1) \times 10^5\ M^{-1}sec^{-1}$
k_4	$\geqslant$	$(5.0 \pm 0.5) \times 10^4\ M^{-1}sec^{-1}$

As the value of k_{-2} derived from the simulation is independent of K_1k_2 (determined graphically), it is justified to calculate the formation equilibrium constant for $HCo^{III}py$ (steps 1 and 2) as $K_1k_2/k_{-2} = (3.9 \pm 0.6) \times 10^{-4}\ M^{-1}$. This result is in line with the failure to isolate $HCo^{III}py$ from, and to detect reversibly bound H_2 in, reacting cobaloxime(II) solutions. The thermodynamic instability of $HCo^{III}py$ precludes direct determination of K_1K_2, therefore, the above estimate may be of value for comparison purposes. Espenson[13] estimated K_1K_2 for $HCoP(n\text{-}Bu)_3$ to be $0.13\ M^{-1}$, which is in agreement with the present result in as much as both data indicate the instability of hydridocobaloxime(III) species to dissociation to H_2 and cobaloxime(II).

Step (4) is the simplest possibility for hydroxocobaloxime(III) reduction. Mechanistically, it probably involves hydrogen atom transfer via the following transition state



The present results are formally also consistent with an alternative (or simultaneous) reduction path occurring via the known cobaloxime(I) complex:[1]

$$HCo^{III}py \rightleftharpoons Co^{I}py^{-} + H^{+} \quad (4a)$$

$$Co^{I}py^{-} + Co^{III}OH(py) \longrightarrow 2Co^{II}py + OH^{-} \quad (4b)$$

Reaction (4b) is well known for analogous vitamin B_{12} derivatives[14,15] and has recently been subjected to detailed kinetic analysis.[16] The disproportionation of cobaloxime(II), i.e. the reverse of (4b), has been investigated[1,17,18] but little mechanistic information is available on this process.

Under the conditions used, however, the presence of cobaloxime(I) cannot be detected spectrophotometrically in methanol but this species is clearly

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visible in aqueous methanol, and in methanol at higher basicities. The evaluation of the contribution from path (4a)–(4b) would require a study of the pH dependence of the rate, which is not feasible owing to disporportionation of cobaloxime(II) in the presence of excess sodium hydroxide.[1] Another argument against the involvement of cobaloxime(I) under the present experimental conditions is the following. If one replaces step (4) by steps (4a) and (4b) in the mechanism, then the quantity corresponding to k_4 will have to be regarded as $K_{4a}k_{4b}$, where K_{4a} is the acid dissociation constant of HCopy. Obviously, k_{4a} cannot exceed the diffusion-controlled value of about $10^{10}M^{-1}sec^{-1}$, which sets an upper limit of $5 \times 10^4/10^{10} = 5 \times 10^{-6}$ on K_{4a}. (k_{4a} is probably closer to the value of $5.8 \times 10^3\ M^{-1}sec^{-1}$ reported[16] for the analogous reaction of vitamin B_{12s} and hydroxocobalamin). A pK of 5.3 or smaller would require cobaloxime(I) to be the predominant product of the reaction between cobaloxime(II) and H_2 in slightly alkaline solutions, which is, however, not the case.[11] Cobaloxime(I) formation is only observed in the presence of 4×10^{-3} M and more NaOH.[7]

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