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THE EFFECT OF PYRIDINE ON THE HYDROGEN ABSORPTION PROCESS OF BIS(DIMETHYLGLYOXIMATO)COBALT(II)

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The initial hydrogen absorption rate of the methanolic solution of isolated pyridinecobaloxime was measured manometrically at 30°C. The rate dependence on the cobaloxime concentration was varied with excess pyridine added to the solution. The results gave the mechanistic elucidation for the hydrogen absorption process.

Bis(dimethylglyoximato)cobalt(II) (cobaloxime, $Co(Hdmg)_2$) is known to react with molecular hydrogen under moderate conditions to form hydridocobaloxime[1] and catalyzed certain hydrogenation reactions in the liquid phase.[2,3] Simándi and his coworkers have reported on the kinetics of the reaction of cobaloxime which formed in situ by mixing methanolic solutions of cobalt(II) perchlorate, dimethylglyoxime and NaOH in the presence of pyridine and styrene as an axial base and a scavenger for hydridocobaloxime, respectively.[4] Their results showed that the initial rate of the hydrogen absorption depends on the second order of the complex concentration in the case of both $Co(Hdmg)_2$ and $Co(Hdmg)_2Py$. In the previous investigation, we have obtained different results on this point. Namely, first order dependence on $Co(Hdmg)_2$ concentration was shown for the hydrogen absorption rate in THF.[5] The difference prompts us to reexamine precisely the kinetics of the hydrogen absorption reaction of the isolated pyridinecobaloxime $[Co(Hdmg)_2Py]_2$ in methanol.

Experimental

The Isolation of Pyridinecobaloxime $[Co(Hdmg)_2Py]_2$. ---- According to the method of Schrauzer and Windgassen,[1] cobalt(II) acetate tetrahydrate, dimethylglyoxime and pyridine were mixed in molar ratio 1:2:1 in methanol under the atmosphere of nitrogen. Resulting precipitate was filtered and purified by methanol.

The Kinetical Measurement. ---- The initial hydrogen absorption rate was measured by means of a Warburg type manometer at 30°C. The testing methanolic solutions were made so as to contain 3-50mM of the complex $Co(Hdmg)_2Py$. The molar ratio of total pyridine to the complex were varied from 1 to 8 by the addition of prescribed amount of pyridine to the solution. Since the pressure differences through the manometric measurements are not more than 2.3mmHg, the rate is not substantially affected.

The Calculation of the Rate Equation. --- The calculation of the each constant in the proposed equation was made on a HITAC 8700/8800 operating system in the Computer Centre at the University of Tokyo. Details will be reported in another paper.[9)]

Results and Discussion

Pyridinecobaloxime is known to be isolated as the dimer[1)] and to maintain the activities for a long time even in the air.[6)] In methanol it dissociates completely to the monomer, and the following successive coordination equilibria are readily achieved in the solution.

$$\text{(Co)} + \text{Py} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{(Co)Py}$$

$$\text{(Co)Py} + \text{Py} \underset{}{\overset{K_2}{\rightleftharpoons}} \text{(Co)Py}_2$$

(Co) =cobaloxime, Py = pyridine

In general, the reactivity of cobaloxime toward molecular hydrogen is accelerated by the axial coordination of the fifth ligand, i.e. the formation of $Co(Hdmg)_2B$. However, it was previously shown that the hexacoordinated complex $Co(Hdmg)_2B_2$ does not absorb molecular hydrogen.[5)]

In order to elucidate the mechanism of this molecular hydrogen absorption reaction, we examined precisely the dependence of the initial hydrogen absorption rate on the complex concentration. When the molar ratio of pyridine to cobaloxime was varied by the addition of pyridine to the methanolic solution of the isolated complex $[Co(Hdmg)_2Py]_2$ at 30°C, the reaction order of the complex was varied as shown in Fig. 1. The maximum order (ca. 2nd) was obtained where the ratio Py/(Co) was approximately 2. It was found that the addition of excess pyridine decreases the cobaloxime order. On the other hand, although the rate was depressed by excess pyridine by the formation of $Co(Hdmg)_2Py_2$,[5)] the maximum rate was varied with the complex concentration (Fig. 2). The rate dependence on the hydrogen partial pressure was almost 1st order and invariable by the variation of the ratio Py/(Co). In the case of cobaloxime without axial base, which prepared in situ from $CoCl_2$, dimethylglyoxime and NaOH in methanol, the reaction order was ca. 1.2 for the complex concentration. The points are expressed by blank circles in the Figures.

Since the resulting rate dependence are different, 1st order for $Co(Hdmg)_2$ and 2nd order for $Co(Hdmg)_2Py$ species in the solution, the hydrogen absorption mechanism might be somewhat different with each other. As for $Co(Hdmg)_2Py$, Simándi's proposal would not be deniable. Namely, the addition of molecular hydrogen to cobaloxime (step 1) is a rapid preequilibrium, and the hydrogen cleavage between two molecules of cobaloxime (step 2) is rate-determining. However, in the absence of pyridine the rate-determining step is replaced with step 1, which then becomes irreversible.

$$(Co) + H_2 \longrightarrow H_2(Co) \qquad (1)$$

$$H_2(Co) + (Co) \longrightarrow 2\,H(Co) \qquad (2)$$

The difference can be explained by the stabilization of the molecular hydrogen adduct $H_2Co(Hdmg)_2Py$ with the trans coordination of pyridine ligand. This is attributable to the more extensive delocalization of the unpaired electron of pyridinecobaloxime along with Z axe.

Decreasing trends of the reaction order with increasing amount of pyridine suggest that the other process including pyridine becomes influential for the initial rate in place of step 2. Heterolytic splitting of hydrogen molecule has been proposed to appear particularly in the media of moderately high basicity where the driving force is provided by the stabilization of released proton.$^{8)}$ In this case, excess pyridine might act as a proton acceptor and accelerate the H-H bond cleavage in the following manner.

$$H_2(Co)Py + Py \longrightarrow H(Co)Py + HPy^+ \qquad (3)$$

The overall initial hydrogen absorption rate can be then expressed by the linear combination of the above mentioned items.

$$r = k_1\big[(Co)\big] + k_2\big[(Co)Py\big]^2 + k_3\big[(Co)Py\big]\big[Py\big] \qquad (4)$$

The rate constants k_1-k_3 and the formation constants K_1-K_2 were determined by means of an iteration procedure performed on a desital computer, based on the variation of the rate with the Py/(Co) ratios. The calculated values are : $k_1 = 1.32\times10^{-2}$ (1/min), $k_2 = 5.98$ (l/mol min), $k_3 = 0.30$ (l/mol min), $K_1 = 192$ (l/mol), and K_2 = 17 (l/mol). The calculated formation constant K_1 showed a fairly good agreement with the value obtained by Rockenbauer by means of the esr spectral method.[7)] In a similar way, the formation constants with respect to several bases other than pyridine were calculated. Details will be presented in another paper.[9)]

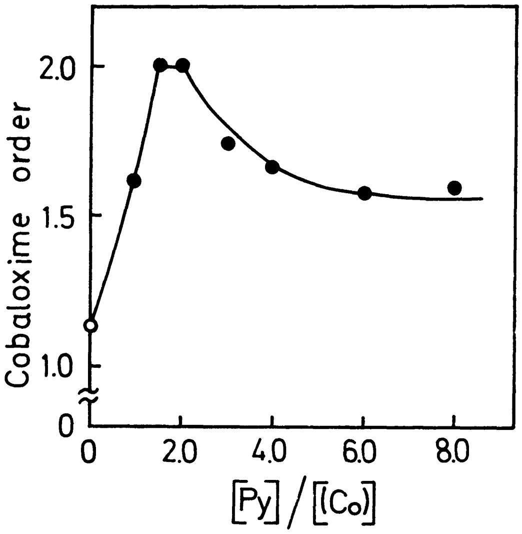

Fig. 1. Correlation between cobaloxime order and Py/(Co) ratios.

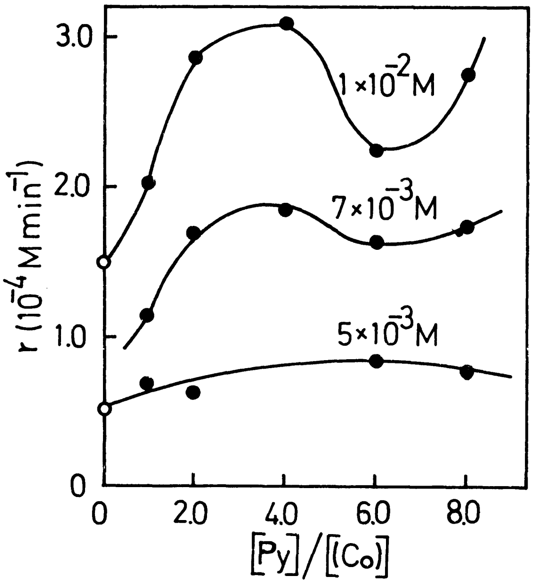

Fig. 2. Variation of the initial rate with Py/(Co) ratios.

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