The Hydrogenation of Benzil Catalyzed by Cobalt(II) Dimethylglyoxime Complex

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Kinetic studies on the catalytic hydrogenation of benzil to benzoin by bis(dimethylglyoximato)cobalt(II), $Co(Hdmg)_2$, were carried out by varying the concentration of $Co(Hdmg)_2$ and pyridine. The initial rate of the hydrogenation reaction was first order with respect to the overall cobalt concentration at a constant overall pyridine concentration. On the other hand, the rate passed through a peak as the overall pyridine concentration was increased at a constant overall cobalt concentration. The peak was observed at $[py]_T=$ 130 mmol dm^{-3}, where the square bracket denotes the concentration in the liquid phase. These results show that the initial reaction rate, V_{in}, can be expressed by the following rate equation,

$$V_{in} = k[Co(Hdmg)_2]\frac{58[py]_T}{1+58[py]_T},$$

where, k=1.1 min^{-1}.

It has been known that bis(dimethylglyoximato)-cobalt(II), $Co(Hdmg)_2$, referred to as cobaloxime, shows a catalytic activity for the hydrogenation of certain unsaturated organic compounds in the presence of bases such as pyridine.[1] The influence of the concentration of cobalt and pyridine on the rate of hydrogenation has been studied by various researchers. Simandi and coworkers studied the hydrogenation of free dimethylglyoxime added in excess of the amount required for cobaloxime formation at a constant pyridine concentration.[2] Due to the influence of the cobalt concentration, they observed that the initial rate of the hydrogenation was second order with respect to the overall cobalt concentration. Yamakawa and coworkers studied the hydrogenation of benzil in the presence of 4,4′-trimethylenebis(pyridine) as a base at a constant ratio of the cobalt and the base.[3] They also found that the initial rate of hydrogenation was second order with respect to the overall cobalt concentration. In a previous paper, we reported that a plot of the reaction rate vs. the overall cobalt concentration gave a sigmoidal curve for benzil hydrogenation at a constant cobalt-pyridine ratio.[4]

Due to the influence of base concentrations, Yamakawa and coworkers reported that the initial reaction rate increased and remained constant as the concentration of base was increased.[3] Tylrik and coworkers studied the asymmetric hydrogenation of benzil in the presence of quinine or morpholine.[5] They also reported that the initial reaction rate increased and remained constant as the concentration of the base was increased.

The second-order dependence of the reaction rate on the cobalt concentration implies that two molecules of cobaloxime(II) are required to activate one molecule of H_2.[2] Although, due to the influence of the concentration of base, a mechanism in which excess base act as a proton acceptor and accelerate the H–H bond cleavage has been proposed,[2,6,8] no kinetic model that can quantitatively explain the dependency of the reaction rate on the base concentration has ever been proposed for catalytic hydrogenation by $Co(Hdmg)_2$.

In this work, kinetic studies on the catalytic hydrogenation of benzil to benzoin by $Co(Hdmg)_2$ were carried out. From the rate data obtained for various concentrations of $Co(Hdmg)_2$ and pyridine, it was found that the initial reaction rate was first order with respect to the overall cobalt concentration at a constant pyridine concentration and that the initial reaction rate passed through a peak as the pyridine concentration was increased at a constant overall cobalt concentration. These results could be successfully interpreted by a rate law which shows a first-order dependence on the concentration of $Co(Hdmg)_2py$ at a constant pyridine concentration. A kinetic model that can quantitatively explain the dependency of the reaction rate on the concentration of pyridine was also proposed.

Experimental

A 27 cm^3 methanol solution of $Co(Hdmg)_2$ was prepared by mixing $Co(NO_3)_2\cdot 6H_2O$, dimethylglyoxime (H_2dmg), and NaOH in a ratio of 1:2:2 under a hydrogen atmosphere. The preliminary hydrogen uptake (H_2 uptake) was initiated by the injection of an appropriate amount of pyridine and a 1.5 cm^3 deoxygenated toluene solution of benzil to the reaction vessel under vigorous stirring. Just before the preliminary H_2 uptake was completed, 1.5 cm^3 of the methanol solution of benzil was again injected. The hydrogenation was carried out under an atmospheric pressure of hydrogen at 20 °C and was followed by measuring the volume of the H_2 uptake using a gas burette.

The H_2 uptake rate was almost constant at the first ca. 1—5 min and then droped. Therefore, the average volume of the H_2 uptake during the 2nd and 3rd minute was taken as the initial reaction rate, V_{in}. This rate was found to increase and to saturate with increased stirring. The rate measurement was performed under conditions where the rate was independent of stirring. The reproducibility for measurements of the H_2 uptake rate was good. An analysis by gas chromatography showed that benzoin was the only product of the reaction.

Results

During this experiment, the same methanol solution of $Co(Hdmg)_2$ and pyridine was repeatedly used four times for the hydrogenation of 1.5, 1.5, 3.0, and 1.5 mmol benzil according to the method described in the Experimental section. After each incremental addition of benzil, the initial H_2 uptake rate was measured. As a typical example, Fig. 1 shows that the initial rate increased after the first run and then became almost constant over the 2nd—4th runs. The results show that the initial rate of H_2 uptake was independent of the concentration of benzil, in agreement with results from the literature.[2,4] It can also be seen from Fig. 1 that the decomposition of $Co(Hdmg)_2$ or its pyridine adducts is negligible under the present experimental conditions. However, it is not clear why the rate of the lst run is lower compared with those of the other runs. Therefore, in all the experiments described here, the initial H_2 uptake rate of the 2nd run was taken as a measure of the catalytic activity in order to obtain a reproducible hydrogenation activity.

Figure 2 shows the dependence of the initial rate of H_2 uptake on $[Co]_T$ for the hydrogenation of benzil at a constant $[py]_T$, where $[Co]_T$ is the initial overall $Co(Hdmg)_2$ concentration and $[py]_T$ is the initial overall pyridine concentration. It can be seen from Fig. 2 that the initial rate of H_2 uptake (V_{in}) is first order with respect to $[Co]_T$,

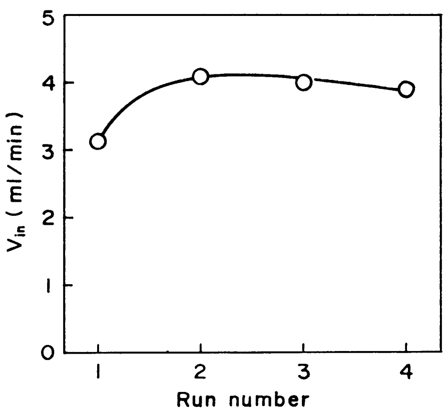

Fig. 1. Activity change of $Co(Hdmg)_2$–pyridine system for the hydrogenation of benzil.
$[Co]_T$: 13 mmol dm^{-3}, $[py]_T$: 330 mmol dm^{-3}, volume of catalytic solution: 30 cm^3, Temp: 20 °C, H_2 pressure: 1 atm, [benzil]: 25 mmol dm^{-3}.

$$V_{in} = k[Co]_T. \quad (1)$$

It can also be seen from Fig. 2 that the initial rate of H_2 uptake increases and then passes a peak as $[py]_T$ increases at a constant$[Co]_T$. The peak was observed at $[py]_T$=130 mmol dm^{-3}. As a typical example, the initial H_2 uptake rate at $[Co]_T$=13 mmol dm^{-3} was ploted against $[py]_T$ using the data in Fig. 2. This plot was indicated in Fig. 3 by a open circle.

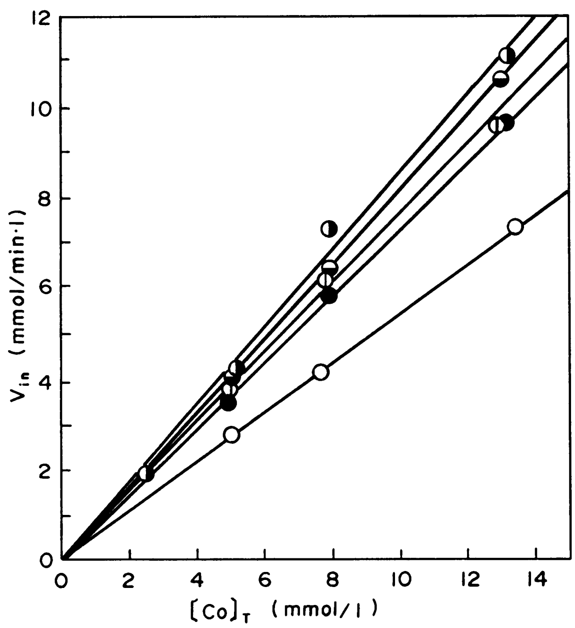

Fig. 2. Dependence of the initial rate of H_2 uptake (V_{in}) on $[Co]_T$.
$[py]_T$=33 (○), 66 (◐), 130 (◑), 330 (◒), and 530 mmol dm^{-3} (●).

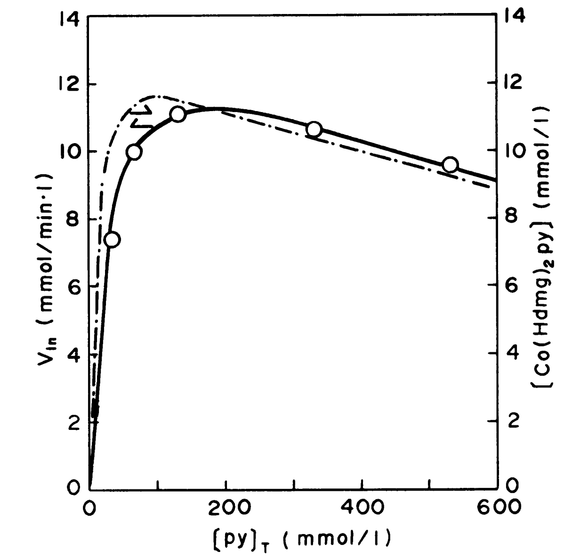

Fig. 3. Plots of V_{in} vs. $[py]_T$ (○: experimental, ——: calculated from Eq. 9) and plots of $[Co(Hdmg)_2py]$ vs. $[py]_T$ (–·–·–: calculated by using K_1=186 and K_2=0.75 dm^3 mol^{-1}). $[Co]_T$=13 mmol dm^{-3}.

Discussion

In a solution containing $Co(Hdmg)_2$ and pyridine, the following successive coordination equilibria are readily achieved.

$$Co(Hdmg)_2 + py \overset{K_1}{\rightleftharpoons} Co(Hdmg)_2py \tag{2}$$

$$Co(Hdmg)_2py + py \overset{K_2}{\rightleftharpoons} Co(Hdmg)_2py_2 \tag{3}$$

The stepwise stability constants (K_1 and K_2) were determined using the visible absorption spectra.[2] The calculated values are: K_1=186 and K_2=0.75 $dm^3\ mol^{-1}$.

According to the literature,[2,5,7] $Co(Hdmg)_2py_2$ dose not interact with molecular H_2. In the present experiment, the hydrogenation of benzil by $Co(Hdmg)_2$ did not occur in the absence of pyridine, indicating that $Co(Hdmg)_2$ shows no catalytic activity. Therefore, only $Co(Hdmg)_2py$ can be considered to be active for the hydrogenation of benzil.

The concentration of $Co(Hdmg)_2py$ can be calculated from $[Co]_T$ and $[py]_T$ by using the stepwise stability constants in Eqs. 2 and 3. Introducing the relation between $[Co]_T$ and $[Co(Hdmg)_2py]$, the plots of V_{in} vs. $[Co]_T$ in Fig. 2 were re-formed to the plots of V_{in} vs. $[Co(Hdmg)_2py]$. The plots are shown in Fig. 4. It can be seen from Fig. 4 that at a fixed pyridine concentration the initial H_2 uptake rate is linearly proportional to the concentration of $Co(Hdmg)_2py$ as is given by the following rate equation.

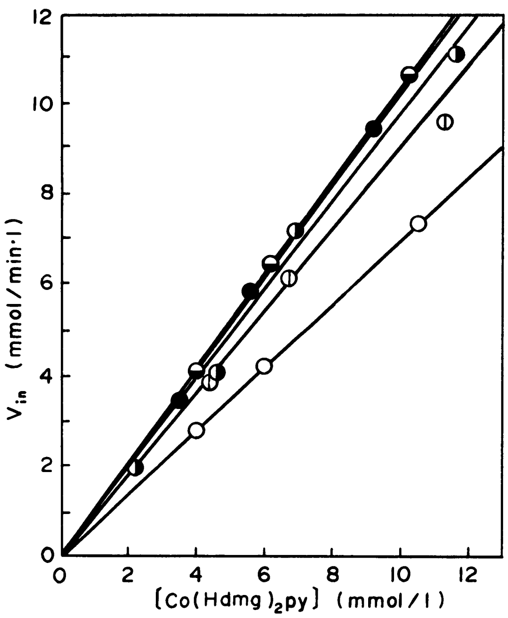

Fig. 4. Plot of V_{in} vs. $[Co(Hdmg)_2py]$.
$[py]_T$ ($mmol\ dm^{-3}$)=33 (○), 66 (⦶), 130 (◑), 330 (⊖), and 530 (●).

$$V_{in} = k[Co(Hdmg)_2py] \tag{4}$$

The value of k, that is $V_{in}/[Co(Hdmg)_2py]$, was determined by the slope of the plot in Fig. 4 at each pyridine concentration and Fig. 5 shows the plot of $V_{in}/[Co(Hdmg)_2py]$ vs. $[py]_T$. As is shown in Fig. 5, the value of $V_{in}/[Co(Hdmg)_2py]$ increases and saturates upon increasing the pyridine concentration.

It has been proposed that excess pyridine acts as a proton acceptor and accelerates the H-H bond cleavage in the following manner.[5-7]

$$H_2 + Co(Hdmg)_2py + py \longrightarrow py\cdots H\cdots H\cdots Co(Hdmg)_2py \tag{5}$$

The plot in Fig. 5 also indicate that excess pyridine acts as catalysts together with $Co(Hdmg)_2py$ (in agreement with the literature). The simplest rate law which could be expected for the plot in Fig. 5 is given in Eq. 6.

$$k = k_1\frac{K[py]_T}{1+K[py]_T} \tag{6}$$

By uing Eq. 6, Eq. 4 leads to Eq. 7.

$$V_{in} = k_1[Co(Hdmg)_2py]\frac{K[py]_T}{1+K[py]_T} \tag{7}$$

Thus, the result shown in Fig. 5 was for an analysis according to Eq. 7. It is convenient to transform Eq. 7 into one that gives a straight-line plot. This can be done by taking the reciprocal of both side of Eq. 7 to give Eq. 8,

$$\frac{[Co(Hdmg)_2py]}{V_{in}} = \left(\frac{1}{k_1K}\right)\frac{1}{[py]_T} + \left(\frac{1}{k_1}\right), \tag{8}$$

where the quantities within the parentheses are constant. The plot of $V_{in}/[Co(Hdmg)_2py]$ vs. $[py]_T$ in Fig. 5 was transformed to a plot of $[Co(Hdmg)_2py]/V_{in}$ vs. $1/[py]_T$. As can be seen in Fig. 6, $[Co(Hdmg)_2py]/$

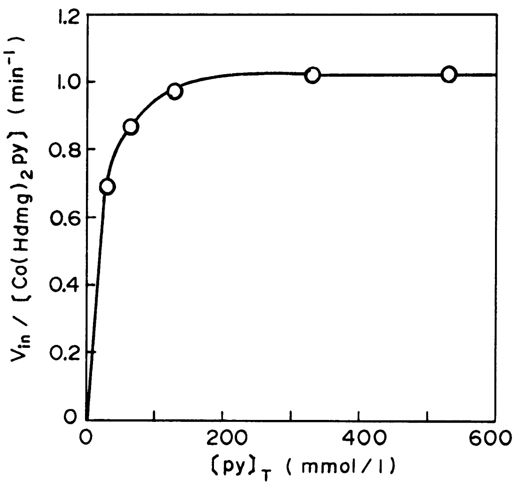

Fig. 5. Plot of $V_{in}/[Co(Hdmg)_2py]$ vs. $[py]_T$.

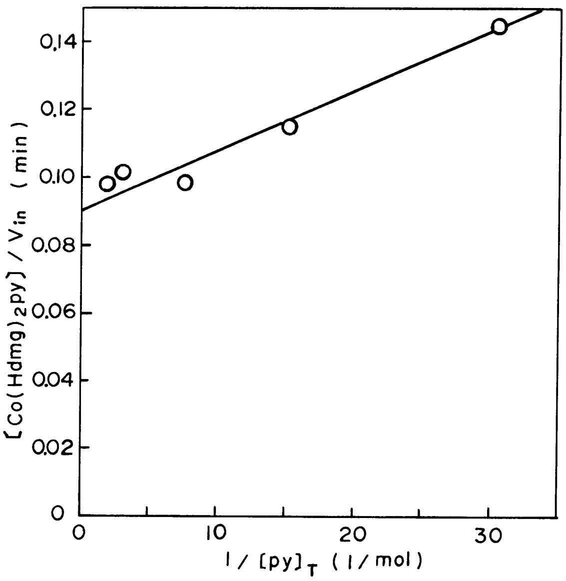

Fig. 6. Plot of $[Co(Hdmg)_2py]/V_{in}$ vs. $1/[py]_T$.

V_{in} is almost linearly proportional to $1/[py]_T$. This confirms the validity of the rate law.

The values of k_1 and K in Eq. 8 can be calculated from the slope and the intercept of the plot in Fig. 6. Finnally, the rate law was expressed as

$$V_{in} = 1.1(\text{min}^{-1})[Co(Hdmg)_2py]\frac{58[py]_T}{1+58[py]_T}. \quad (9)$$

The plot of $[Co(Hdmg)_2py]$ vs. $[py]_T$ at a constant $[Co]_T$ was calculated from $[Co]_T$ and $[py]_T$ using the stepwise stability constants in Eqs. 2—3. As a typical example, a plot at $[Co]_T$=13 mmol dm^{-3} is shown in Fig. 3 by a broken line. It can be seen from the plots that the concentration of $Co(Hdmg)_2py$ increased and passes a peak as the pyridine concentration increases. As is shown in Fig. 3, the concentration of pyridine at which the plot of $Co(Hdmg)_2py$ vs. $[py]_T$ shows a peak clearly deviates from that at which the plot of V_{in} vs. $[py]_T$ shows a peak. On the other hand, the V_{in} value which was calculated from Eq. 9 was ploted against $[py]_T$. This plot is shown in Fig. 3 by a real line. An excellent fit was observed between the calculated plot of V_{in} vs. $[py]_T$ and the experimental plot of V_{in} vs. $[py]_T$. This also suggest the validity of Eq. 9.

The value of V_{in} was calculated from Eq. 9 at a constant ratio of $[py]_T/[Co]_T$, and the values were ploted against $[Co]_T$. The plot showed a sigmoidal curves. This is the reason why the reaction rate is reported to be second order with respect to $[Co]_T$[3] or why the plot of V_{in} vs. $[Co]_T$ showed a sigmoidal curve[4] for the hydrogenation of benzil at a constant ratio of $[py]_T/[Co]_T$. However, the second-order dependence on $[Co]_T$ for the hydrogenation of dimethylglyoxime at a constant pyridine concentration[2] could not be interpreted by Eq. 9. The hydrogenation rate of dimethylglyoxime is much lower than that of benzil. Therefore, the mechanism of the hydrogenation of dimethylglyoxime may be different from that of benzil.

References

1) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **44**, 283, 583, (1971).

2) L. I. Simandi, E. Budo-Zahonyi, Z. Szeverenyi, and S. Nemeth, *J. Chem. Soc., Dalton Trans.*, **1980**, 276.

3) S. Yamakawa, I. Yasumori, and E. Miyazaki, Preprint of 37th National Meeting of Chemical Society of Japan, April, 1978, Abstr. No. 2Q14.

4) K. Mita, K. Hotta, and S. Watanabe, *Nippon Kagaku Kaishi*, **1978**, 1583.

5) S. Tyrlik, M. M. Kucharska, and I. Wolochowicz, *J. Mol. Catal.*, **6**, 393, (1979).

6) T. Yamaguchi and R. Miyagawa, *Chem. Lett.*, **1978**, 89.

7) T. Yamaguchi and T. Tsumura, *Chem. Lett.*, **1973**, 409.

8) K. Mita, K. Hotta, and S. Watanabe, *Nippon Kagaku Kaishi*, **1979**, 1299.