BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1172—1177 (1970)

A Novel Reduction in the Presence of Precipitated Metals. II. The Behavior of Precipitated Metals and Water in Catalytic Reduction

Koji SAKAI, Masayoshi ISHIGE,[*1] Ken-ichi WATANABE and Kazuo HATA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received September 26, 1969)

The ppt-metal-catalyzed reduction, which is performed by refluxing the substrates with water in the presence of ppt-metals, was investigated in detail. The participation of water as a hydrogen donor was demonstrated by the fact that benzaldehyde was reduced to the corresponding deuterated alcohols when heated with D_2O in the presence of ppt-Ni. The scope of the reduction was established by the reaction of cyclohexanone with ppt-metals and water. The most preferable H_2O/cyclohexanone molar ratio was found to be about 15 : 1. The reaction was accelerated when a 0.25N aqueous solution of sodium chloride was used instead of water. It was found that the order of the abilities of various ppt-metals to decompose water is different from that of the abilities to catalyze the reduction of cyclohexanone. The values of the activation energies for the reduction catalyzed by ppt-Ni and ppt-Ni,Co were found to be 4.0 kcal/mol and 7.5 kcal/mol respectively. From these facts, it was concluded that the ppt-metal-catalyzed reduction consists of two steps: the reaction of water with zinc or zinc compounds to supply a hydrogen source necessary for the hydrogenation, followed by ordinary catalytic hydrogenation.

In previous papers,1,2) the utilization of precipitated metals (abbreviated as ppt-metals) as catalysts for the reduction of various compounds, with water as the hydrogen donor, has been described. The reduction was easily attained by refluxing with water in the presence of ppt-metal, the co-existence of any acids or bases being unnecessary. It has already been proposed2) that this catalytic reaction might involve a reaction step similar to that in the ordinary catalytic hydrogenation. The present paper will deal with an extensive study of this reaction, a study covering the behavior of water and the function of catalyst metals.

Results

Deuteration of Benzaldehyde with D_2O. In order to provide direct evidence for the participation of water as a hydrogen donor, the reduction of benzaldehyde with D_2O in the presence of ppt-Ni was investigated.

The experiment was carried out in a sealed tube by heating benzaldehyde with 99.75% D_2O in the presence of ppt-Ni; deuterated benzyl alcohol was thus obtained in a good yield. However, the attempt to determine the deuterium distribution in the product by the spectroscopic method failed because of the rapid exchange between the D and H in the hydroxyl group by means of the moisture in the air. Therefore, the product, which was assumed to be a mixture of C_6H_5–CHD–OD and

---

[*1] Present address: Chemical Laboratory, Ochanomizu University, Ootsuka, Bunkyo-ku, Tokyo.

1) K. Sakai and K. Watanabe, This Bulletin, **40**, 1548 (1967).

2) K. Sakai, M. Ishige, H. Kono, I. Motoyama, K. Watanabe and K. Hata, *ibid.*, **41**, 1902 (1968); M. Ishige, K. Sakai, K. Watanabe and K. Hata, *Shokubai* (*Catalyst*) (Tokyo), **11**, 50 (1969).

C_6H_5–CD_2–OD, was completely changed to C_6H_5–CHD–OH and C_6H_5–CD_2–OH by vigorous shaking with a large amount of water. The NMR spectrum of the sample thus obtained showed only three sharp singlets, at τ 2.85, 5.60, and 6.35; these singlets are assignable to phenyl, methylene, and hydroxyl protons, and the intensities correspond to 5, 0.4, and 1 protons respectively. From the proton intensities in NMR, the ratio between C_6H_5–CHD–OH and C_6H_5–CD_2–OH was estimated to be approximately 40 : 60. The IR spectram of the deuterated alcohols showed an intense band at 2200 cm^{-1} assignable to the stretching vibration of the CD group. The disappearance of the OD band at 2510 cm^{-1} showed the complete exchange of the D in the hydroxyl group for H. The absorption bands in the 650—900 cm^{-1} region, observed in a *n*-hexane solution (0.014 mol/*l*), distinctly showed the presence of a monosubstituted benzene ring, thus demonstrating that no deuterium exchange of ring protons had occurred during the reduction.

These experimental results prove that water acts as a hydrogen donor as well as a solvent in this reduction. This participation of D_2O as a hydrogen donor in the reduction led to the suggestion that this reduction with D_2O would be useful for the synthesis of various deuterated organic compounds as a simpler method than the well-known reduction with $LiAlD_4$ or $NaBD_4$.

The Reduction of Cyclohexanone Using a Varying Amount of Water. Though the presence of water is indispensable for the reduction, the use of an excess of water may be unfavorable because of the low concentration of the reactants. We tried to ascertain the adequate quantity of water suitable for the reduction by using cyclohexanone as a substrate. The reduction reaction of cyclohexanone to cyclohexanol in the presence of ppt-Ni was apparently first-order in the disappearance of the ketone. Typical examples of the apparent first-order rate constants of cyclohexanone in the reactions with various quantities of water are summarized in Table 1. In order to keep the reaction mixture homogeneous, a given quantity of dioxane was added to the aqueous solution. As is shown in Table 1, when a comparatively small quantity of water is used the rate constant increases with the increase in the quantity of water used. However, the reaction rate gradually decreased when the quantity of water exceeded a certain limit, as had been expected from the decreased concentration of cyclohexanone. The most favorable result was obtained when the H_2O/cyclohexanone mole ratio was about 15 : 1 (Exp. 3).

TABLE 1. THE EFFECT OF WATER ON THE RATE OF THE REDUCTION OF CYCLOHEXANONE UNDER REFLUXING

cyclohexanone 9.8 g (0.1 mol), ppt-Ni 20 g

Exp. No.	Water *ml*	Water mol	Dioxane *ml*	Concentration of cyclohexanone %	Rate constant $k(\times 10^2)$ (hr^{-1})
1	16.2	0.9	13	24.8	6.49
2	21.6	1.2	13	21.8	11.30
3	27.0	1.5	15	18.8	13.30
4	32.4	1.8	16	16.7	11.10
5	37.8	2.1	20	14.4	9.00
6	43.2	2.4	20	13.3	9.34

The Promoting Effect of Sodium Chloride[2,3] on the Reduction of Cyclohexanone. The ppt-Ni is generally prepared by the rapid addition of a hot aqueous solution of nickel chloride to slushy zinc dust. When nickel nitrate was used in place of nickel chloride, a ppt-Ni with a lower catalytic activity was obtained. On the other hand, when a nickel chloride solution containing a suitable amount of sodium chloride was used, the activity of the ppt-Ni increased. These findings suggest that the catalytic properties are greatly affected by a small amount of contaminant in the catalyst. In order to get further information on the effect of the chloride ion, the rates of the reduction of cyclohexanone with ppt-Ni in the presence of an aqueous sodium chloride solutions of various concentrations were compared with each other. The results are given in Table 2. As is shown in the table, the reaction was accelerated by the addition of sodium chloride, the most favorable concentration found to be 0.25N. On the other hand, no promoting effect on the reaction was observed when a potassium chloride was used instead of sodium chloride.

TABLE 2. THE EFFECT OF NaCl ON THE REDUCTION OF CYCLOHEXANONE

Cyclohexanone 9.8 g; Dioxane 13 *ml*; Aqueous NaCl solution 18 *ml*; ppt-Ni 20 g

Exp. No.	Concentration of NaCl N	Rate constant $k(\times 10^2)$ (hr^{-1})
7	0.000	5.21
8	0.080	5.40
9	0.165	4.31
10	0.250	8.58
11	0.500	6.74

X-Ray diffraction studies revealed the composition of the ppt-Ni. As is shown in Fig. 1, the X-ray diffraction diagram[1,4] of ppt-Ni showed several sharp bands assignable to Zn, Zn(OH)Cl, and ZnO. Besides these constituents, ppt-Ni

---

[3] T. Nakabayashi, *J. Amer. Chem. Soc.*, **82**, 3900 (1960).

[4] Y. Urushibara, M. Kobayashi, S. Nishimura and H. Uehara, *Shokubai* (*Catalyst*) (Tokyo) **12**, 163 (1956).

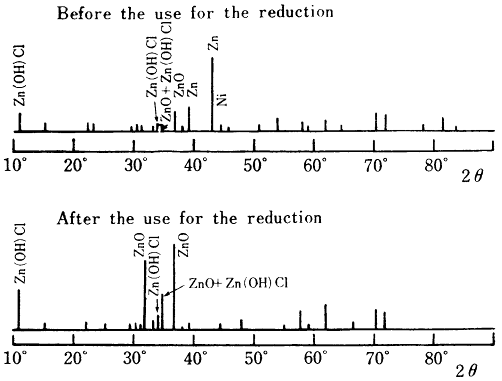


Fig. 1. X-ray diffraction diagrams of ppt-Ni.

also contains Ni, $ZnCl_2$, and $Zn(OH)_2$, though they are not revealed in the X-ray diffraction diagram. On the other hand, a ppt-Ni recovered after being used for the reduction by refluxing with water showed a different diffraction diagram, one in which the bands of Zn disappeared almost completely, while those of ZnO and Zn(OH)Cl were enhanced. This implies that the Zn and $ZnCl_2$ in the ppt-Ni were converted into ZnO, $Zn(OH)_2$, and Zn(OH)Cl in the course of the reaction. It is noteworthy that, when the reaction was carried out in a sodium chloride solution, a remarkable increase in Zn(OH)Cl was observed in the recovered ppt-Ni. From these experimental results, it is concluded that the reaction of water with zinc or zinc chloride is responsible for the supply of hydrogen necessary for the hydrogenation.

The Relationship between the Volume of Generated Hydrogen and That of the Reacted Hydrogen in the Reduction of Cyclohexanone. The reduction with water in the presence of ppt-Ni may be supposed to be composed of two steps: the generation of hydrogen from water and the reduction of organic compounds with the hydrogen.

It has been shown that the generation of hydrogen from water is attributable to the reaction of zinc in the catalyst with water, and also to the difference in ionization potential between zinc and other metals, such as nickel, in the ppt-metal, because the reaction of water with zinc dust alone is extraordinarily slow. Therefore, the amount of hydrogen generated during the reaction depends greatly upon the kind of ppt-metal used. It has previously been reported that the ppt-metal is not useful for ordinary catalytic hydrogenation.[2] However, it has been found*[2] that cyclohexene can be hydrogenated under an ordinary pressure of hydrogen in the presence of ppt-Ni, though the reaction velocity is slow. In this hydrogenation, the activity of the catalyst was found to be dependent on the procedure of its preparation and on the amount of nickel in it. Therefore, it may be presumed that the behavior of ppt-metals in the reduction step is analogous to that of the ordinary hydrogenation catalysts. In this step, metals other than zinc in the ppt-metals, such as nickel or cobalt, may play an important part, while zinc may serve for the step of decomposing water.

In the present study, the activities of several ppt-metals were compared for each of the two steps. The hydrogen gas generated when water was refluxed with the ppt-metal alone was introduced into a gas burette and then estimated volumetrically. The volume of hydrogen gas generated when the reaction was carried out in the presence of cyclohexanone under the same conditions was measured in a similar way. Then the volume of hydrogen reacted with cyclohexanone was calculated and compared with the amount of cyclohexanol, determined by gas chromatography. The results are listed in Table 3.

As may be seen in the table, the abilities of the ppt-metals to decompose water were found to increase in the order: ppt-Ni<ppt-Cu<ppt-Ni, Co<ppt-Ni,Cu. This order may be expected if the ability of the ppt-metal to produce hydrogen originates mainly in the difference in ionization potential between the metal in question and zinc.

On the other hand, the ability of each ppt-metal to catalyze the reduction of cyclohexanone was considered to be represented by the ratio of the amount of hydrogen reacted with cyclohexanone

TABLE 3. THE RELATIONSHIP BETWEEN VOLUME OF GENERATED HYDROGEN AND OF THE REACTED HYDROGEN

ppt-metal 0.8 g; H_2O 1.4 m*l*; dioxane 1 m*l*; cyclohexanone 0.5 g; reaction time 2.5 hr

Catalyst	Volume of generated H_2		Hydrogen reacted $V_1—V_2$	Ratio of reacted hydrogen	Yield of cyclohexanol
	in the absence of cyclohexanone V_1 (m*l*)	in the presence of cyclohexanone V_2 (m*l*)	V_3 (m*l*)	V_3/V_1 (%)	(%)
ppt-Ni	90.6	56.5	34.1	38	24
ppt-Cu	120.6	106.4	14.2	12	15
ppt-Ni,Co	138.3	96.4	41.9	30	25
ppt-Ni,Cu	160.5	142.8	17.7	11	9

---

*[2] A private communication from Y. Urushibara and H. Tomoda.

to the total amount of hydrogen generated by the decomposition of water. The catalytic activity may also be represented by the yield of cyclohexanol. As may be seen in Table 3, the ratio of the amount of reacted hydrogen was approximately parallel to the yield of cyclohexanol. Thus, the catalytic abilities of the ppt-metals were found to increase in the order: ppt-Ni,Cu<ppt-Cu<ppt-Ni<ppt-Ni,Co. This order coincides with that of the catalytic activities of the corresponding Urushibara catalysts which are prepared from these ppt-metals. The fact suggests that the reduction step of the ppt-metal-catalyzed reaction may be similar to that of oridnary catalytic hydrogenation.

The Relative Activities of ppt-Metals in the Reduction of Cyclohexanone.[2] The rate constant was determined for the reduction of cyclohexanone by water in the presence of several ppt-metals. The results are summarized in Table 4 and Fig. 2.

Table 4. The rate constants of the reduction of cyclohexanone at 111.5±2°C catalyzed by various ppt-metals

Cyclohexanone 0.26 ml; H_2O 0.68 ml; dioxane 0.50 ml; ppt-metal 0.4 g; in a sealed tube

Catalyst	Rate constant $k(\times 10^2)(\mathrm{hr}^{-1})$
ppt-Ni,Co	24.5
ppt-Ni,Fe	17.1
ppt-Ni	14.8
ppt-Co	7.17
ppt-Cu	3.76
ppt-Ni,Cu	1.75
ppt-Fe	0.924

The relative activities are found to be in the order: ppt-Fe<ppt-Ni,Cu<ppt-Cu<ppt-Co<ppt-Ni<ppt-Ni,Fe<ppt-Ni,Co. This order is approximately analogous to what has been proposed on the basis of a comparison of the yields of the reduction products.[2]

The Effect of Temperature on the Reduction of Cyclohexanone. The rate constant of the reduction of cyclohexanone was observed at various reaction temperatures; the results are shown in Table 5. Figure 3 shows the Arrhenius plots of the rate constants shown in Table 5. The values of the activation energies and the activation entropies were calculated (from Fig. 3) to be 4.0 kcal/mol and −72 e.u./mol, and 7.5 kcal/mol and −59 e.u./mol, respectively, for the reductions catalyzed by ppt-Ni and by ppt-Ni,Co.

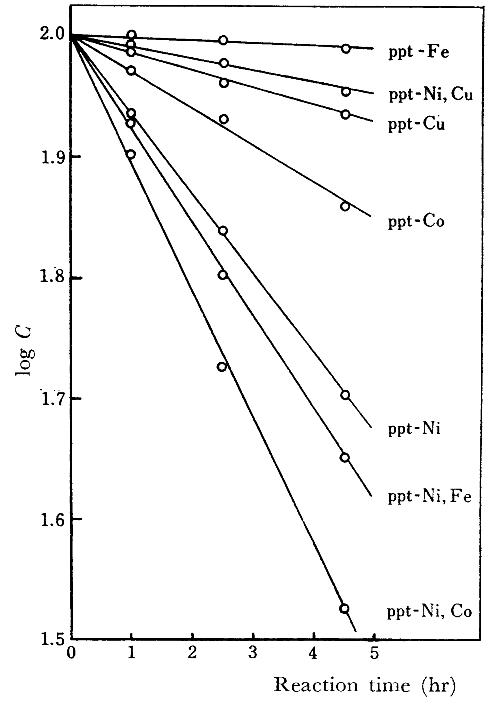


Fig. 2. The first order rate plots for the reduction of cyclohexanone.

$$C=\frac{[\text{cyclohexanone}]}{[\text{cyclohexanone}]+[\text{cyclohexanol}]}\times 100,$$

where [ ] denotes the molar concentration.

Discussion

A mixture of dioxane and water has proved to be an excellent solvent for studies of the ppt-metal-catalyzed reaction because dioxane is almost entirely indifferent to the reaction. Besides the indifference of dioxane to the reaction, the dioxane-water mixed

Table 5. The rate constants of the reduction of cyclohexanone under various reaction temperature (71—100°C)

Reaction temp.		$k(\times 10^2)(\mathrm{hr}^{-1})$		$\log k$	
°C	$1/T\ (\times 10^3)$	ppt-Ni	ppt-Ni,Co	ppt-Ni	ppt-Ni,Co
71.0	2.91	4.40	5.39	−1.35655	−1.28641
80.0	2.83	5.26	7.38	−1.29901	−1.13194
90.0	2.75	5.61	8.78	−1.25104	−1.05651
100.0	2.68	6.90	12.20	−1.16115	−0.91304

Cyclohexanone 0.26 ml; H_2O 0.68 ml; dioxane 0.50 ml; ppt-metal 0.40 g

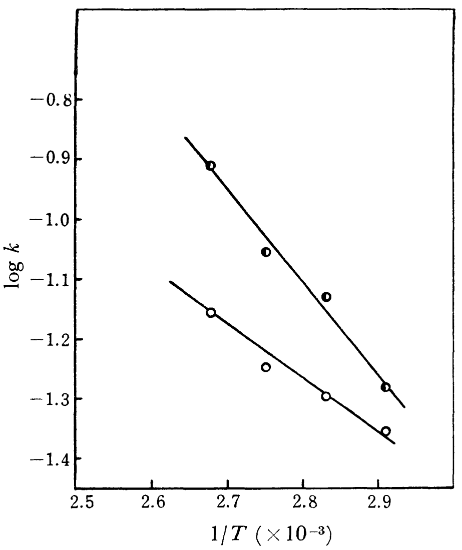
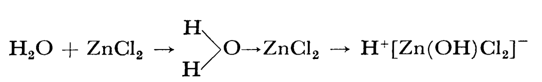


Fig. 3. The Arrhenius plots for the reduction reaction of cyclohexanone.
—◐— ppt-Ni,CO —○— ppt-Ni

solvent*3 has the following merits: (1) it can dissolve almost all organic compounds, (2) it can easily be separated from the reaction mixture in most cases, and (3) the closeness of the boiling points of the two components of the solvent makes it easy to keep the reaction temperature constant, even during refluxing over a long period.

It has been demonstrated, by an X-ray diffraction study, that ZnO and Zn(OH)Cl are produced during the reduction reaction by refluxing with water.*4 The increase in ZnO suggests that the difference in ionization potentials between a catalyst metal, such as nickel, and zinc may lead to the decomposition of water through a coordination of the water to the zinc. The increase in Zn(OH)Cl may be explained in terms of the participation of $ZnCl_2$, which is necessarily present in ppt-metal. The catalytic behavior of such metal halides as Lewis acids is well known.[5] In a ppt-metal-catalyzed reduction, a donor-acceptor complex may be formed by the combination of water, as a Lewis base, with zinc chloride in the ppt-metal, thus, leading to a protonic acid,[6] for example:



$$H_2O + ZnCl_2 \rightarrow \begin{matrix} H \\ H \end{matrix}\!\!>\!O\!\rightarrow\!ZnCl_2 \rightarrow H^+[Zn(OH)Cl_2]^-$$

The formation of Zn(OH)Cl during the reaction may be through this protonic acid.

The activation energy of the catalytic hydrogenation of cyclohexanone with U–Ni–B at room temperature under an ordinary pressure was reported by Nishimura to be 5.3 kcal/mol.[7] The value resembles that of the ppt-Ni-catalyzed reduction of cyclohexanone by water. This fact suggests that the function of ppt-Ni as a catalyst is similar to that of the ordinary hydrogenation catalysts.

Whereas the Clemmensen-type reduction of a ketone often affords dimerization of rearrangement products, the ppt-Ni-catalyzed reduction never produces such by-products. However, when the reduction of ketones in the presence of ppt-Ni was carried out in an acidic or an alkaline solution,*5 a different result, one which rather resembles that of the Clemmensen reduction, was observed.

In ppt-metals used as catalysts, active sites for hydrogenation are presumably arranged on the surface of such metals as nickel and cobalt, not on the surface of zinc. This presumption is supported by the facts that, on the one hand, the rate of reduction is dependent on the kind of ppt-metal, and that, on the other hand, the rate stays constant in spite of the consumption of zinc during the reaction.

The fact that the activation energy for ppt-Ni differs from that for ppt-Ni,Co suggests the intervention of a transition state in which cyclohexanone forms a certain complex with the catalyst metal. Thus, the mechanism of the reduction may be considered to be as follows. The coordination of water to zinc or zinc chloride leads to a protonic acid, through which hydrogen is then transferred to active sites for the hydrogenation on the surface of nickel or cobalt. The following step is the reaction of cyclohexanone and hydrogen, each of which is adsorbed on the active sites of the catalyst metal, in just the same way as in ordinary catalytic hydrogenation.

Experimental

Materials. *Benzaldehyde.* Commercial benzaldehyde was purified by fractional distillation under reduced pressure.

Deuterium Oxide. Commercial 99.75% D_2O (Showa Denko K. K.) was used.

Cyclohexanone. Commercial cyclohexanone was purified as follows. About 100 m*l* of commercial cyclohexanone was stirred with a solution of potassium dichromate (4 g) and concentrated sulfuric acid (5 m*l*) in 50 m*l* of water at room temperature. When the color of the

---

[*3] The high suitability of dioxane-water mixtures as solvents for physico-chemical studies has been verified by several authors; *cf.*, *e. g.*, G. Åkerlöf and O. A. Short, *J. Amer. Chem. Soc.*, **58**, 1241 (1936); F. Hovorka, R. A. Schaeffer and D. Dreisbach, *ibid.*, **58**, 2264 (1936).

[*4] It has been reported that the Raney alloy reacted with, and was developed by, water, thus forming bayerite; S. Nishimura, This Bulletin, **32**, 61 (1959).

5) Edited by A. Ozaki, K. Tanabe, K. Tamaru and S. Nishimura, "Shokubai Kogaku Koza (Catalytic Engineering)," Vol. 10, Chijinshokan & Co., Tokyo (1967), p. 107.

6) H. Meerwein, *Ann. Chem.*, **455**, 227 (1927); *Angew. Chem. Int. Ed. Engl.*, **5**, 335 (1966).

7) S. Nishimura, *Nippon Kagaku Zasshi*, **79**, 56 (1958).

[*5] Y. Urushibara and H. Tomoda, unpublished work.

solution turned dark green (after about 30 min), the cyclohexanone layer was separated, washed with water several times, dried over anhydrous magnesium sulfate, and distilled. A fraction boiling at 153—154°C was collected. The purity of the sample was verified by gas-chromatographic analysis to be over 99%.

The Reduction of Benzaldehyde with D_2O. A mixture of 1 m*l* of benzaldehyde, 4 m*l* of D_2O, and 3 g of ppt-Ni was heated at 100°C in a sealed tube for 12 hr. After the reaction was over, the reaction mixture was filtered quickly. The filtrate was extracted with ether, and the solid on the filter was washed with ether. All the ethereal solution was combined, and the ether was carefully evaporated away. The residue was shaken vigorously with an excess of water to exchange the D in the hydroxyl group for H, and the deuterated benzyl alcohol was extracted with ether.

Kinetic Measurements. *(1) The Reduction of Cyclohexanone with H_2O* (Table 1). In a 100-m*l*, three-necked, round flask equipped with a reflux condenser, a given amount of water and dioxane (shown in Table 1) was placed together with 9.8 g of cyclohexanone (0.1 mol). The solution was heated to 92.5°C, and then 20 g of ppt-Ni (containing 2 g of nickel) was rapidly added. While the mixture was kept at a constant temperature, 0.2—0.3 m*l* portions of the suspending solution were pipetted out at appropriate intervals. Each sample was kept standing for a while until a small amount of the suspending particles had settled, and was then analyzed by gas chromatography.

(2) The Activity of ppt-Metals (Table 4). For each run of the experiment, several sealed ampoules were prepared, each of them containing 0.26 m*l* of cyclohexanone, 0.50 m*l* of dioxane, 0.68 m*l* of water, and 0.4 g of ppt-metal. The tubes were immersed side by side in an oil bath which had been previously kept at 111.5±2°C. At definite intervals tubes were taken out, one after another, and cooled to 0°C with ice. The composition of the reaction mixture was analyzed immediately by gas chromatography. The decrease in the concentration of cyclohexanone was plotted on a graph for each ppt-metal (Fig. 3).

(3) Measurement of the Hydrogen Gas Liberated (Table 3). In a round, 20-m*l* flask connected to a gas-burette through a reflux condenser, 1 m*l* of dioxane and 1.4 m*l* of water were placed. The mixture was heated to boiling, and then 0.8 g of a ppt-metal was rapidly added. After heating for 2.5 hr, the volume of hydrogen generated was measured by a gas-burette. Another run was carried out by the same procedure and under the same conditions except that it was in the presence of 0.50 g of cyclohexanone. Besides the measurement of the volume of the hydrogen generated, cyclohexanol produced in the solution was analyzed by gas chromatography.

The authors wish to express their hearty thanks to Professor Dr. Michio Kobayashi for his helpful advice and discussions.