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The Catalytic Dehydrogenation, Dehydroxylation and Dehydroxymethylation of Benzyl Alcohol. I. The Scope and the Kinetic Study

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Benzyl alcohol was dehydrogenated to benzaldehyde when it was heated in the presence of various metal catalysts. It was found that the dehydrogenation was accompanied by a reductive dehydroxylation and dehydroxymethylation which led to the production of toluene and benzene respectively. The compositions of the products, which mainly consisted of benzaldehyde, toluene, and benzene, were greatly affected by the chemical nature of the catalysts used. The results of the reactions in a sealed tube or in an authoclave suggested that a pseudo-equilibrium between benzyl alcohol and benzaldehyde was attained during the reaction in a closed system. The formation of CO_2, CH_4, and other hydrocarbons as gaseous products was also observed. From these results, the catalytic dehydrogenation, dehydroxylation, and dehydroxymethylation were assumed to proceed competitively *via* a certain metal benzyl complex which is formed as an adsorbed transition complex upon the catalyst metal.

It has previously been reported[1] that a novel redox reaction was observed between benzyl alcohol and some kinds of unsaturated organic compounds, such as styrene and mesityl oxide, in the presence of nickel catalysts. In these reactions, benzyl alcohol was mainly converted into benzaldehyde by dehydrogenation (Eq. (1)), but reductive dehydroxylation (Eq. (2)) and dehydroxymethylation

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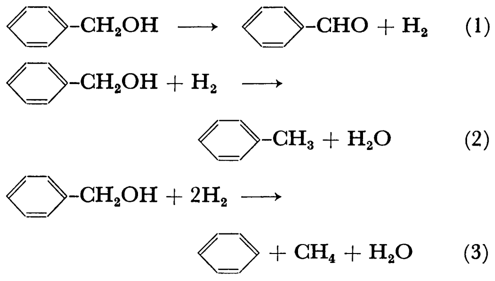
1) K. Sakai, T. Ito and K. Watanabe, This Bulletin, **39**, 2230 (1966).

(Eq. (3)) were also found to take place to some extent.



The behavior of benzyl alcohol in these reactions was considered to be much more complicated; for example, in addition to the formation of CH_4, the generation of CO_2 and of some other gaseous hydrocarbons was observed. Furthermore, the composition of the products from the alcohol was characteristically affected by the nature of the catalysts used. Nishimura[2] has also shown that the reactivity and selectivity in the hydrogenation of benzyl alcohol are dependent upon the species of the catalysts used. Thus, the study of the dehydrogenation, dehydroxylation and dehydroxymethylation of benzyl alcohol may provide an insight into the nature of the reactivity and selectivity in catalysis. For a further investigation of the relation between the catalytic reaction and the nature of the catalysts, the reactions of benzyl alcohol have been studied in the presence of various kinds of solid catalysts, including metals and metal oxides.

Results and Discussion

Benzyl alcohol afforded benzaldehyde, toluene, and benzene when heated at 140—180°C with various metal catalysts. In addition, the generation of CO_2, CH_4, and some other hydrocarbons was observed, accompanied by the formation of benzene by dehydroxymethylation.

Some experiments were carried out by refluxing under ordinary pressure; in these experiments, when the refluxing was continued for a long time, a change in the quality of the catalyst was necessarily brought

Table 1. The reactions of benzyl alcohol under ordinary pressure
benzyl alcohol 6 m*l*; catalyst 1.0 g; refluxed at 160°C for 24 hr

Catalyst	Alcohol reacted (%)	Composition of products[a)] (mol %)			Selectivity × 10^2		k_{alc}[b)] (hr^{-1}) × 10^3
		PhH	$PhCH_3$	PhCHO	PhH/PhCHO	$PhCH_3$/PhCHO	
ppt-Ni	99	1.2	38.8	60.0	2.0	64.8	96.0
$Cu_2Cr_2O_5$	51.8	—	7.7	92.3	—	8.3	30.4
S-Ni	25.0	9.6	11.2	79.2	12.0	14.3	12.0
$Ni_2Cr_2O_5$	17.4	—	2.3	97.7	—	2.4	7.8
ppt-Cu	9.1	—	26.4	73.6	—	35.9	3.9
NiO	7.2	—	4.2	95.8	—	4.4	3.1

a) The gaseous products, such as CO_2 and CH_4, are ignored.
b) The first order rate constants of the diminution of benzyl alcohol.

Table 2. The reaction of benzyl alcohol in a closed vessel

Reaction vessel	Catalyst	Alcohol reacted (%)	Composition of products[a)] (mol %)			Selectivity × 10^2		k_{alc}[b)] (hr^{-1}) × 10^4
			PhH	$PhCH_3$	PhCHO	PhH/ PhCHO	$PhCH_3$/ PhCHO	
Autoclave	ppt-Ni	40.5	1.5	52.8	45.7	3.3	115	216
	R-Ni (W-7)	44.7	19.4	42.6	38.0	51.0	112	246
	U-Ni-A	30.3	3.0	39.3	57.7	5.2	68.1	149
Sealed tube	S-Ni	21.2	28.8	46.7	24.5	117	190	98.8
	$Cu_2Cr_2O_5$	4.7	—	trace	<100	—	—	19.2
	$ZnCr_2O_4$	1.8	—	trace	<100	—	—	7.7
	Al_2O_3	1.4	—	trace	<100	—	—	5.8

Reaction in an autoclave: benzyl alcohol 24 m*l*, catalyst 4 g, heated at 155°C for 24 hr
Reaction in a sealed tube: benzyl alcohol 2 m*l*, catalyst 0.333 g, heated at 157°C for 24 hr
a) The quantity of gaseous products is ignored.
b) The first order rate constant of the diminution of benzyl alcohol.

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[2] S. Nishimura and M. Hama, *ibid.*, **39**, 2467 (1966); S. Nishimura, *ibid.*, **32**, 103 (1959); **32**, 1158 (1959).

about by the reaction with the benzaldehyde and/or benzoic acid which was formed during the reaction. The other experiments were practiced in a sealed tube or in an autoclave in order to avoid the volatilization and oxidation of the products. After the reaction was over, the reaction mixture was analyzed by gas chromatography. The results of representative experiments are summarized in Tables 1 and 2. The catalysts used were precipitated nickel (ppt-Ni), precipitated copper (ppt-Cu), Raney nickel (R-Ni), Urushibara nickel A (U-Ni-A), stabilized nickel (S-Ni), copper chromium oxide ($Cu_2Cr_2O_5$), nickel chromium oxide ($Ni_2Cr_2O_5$), zinc chromium oxide ($ZnCr_2O_4$), aluminum oxide (Al_2O_3), and nickel oxide (NiO).

The activities of these catalysts are represented in terms of the corresponding first-order rate constants of the catalytic reaction of the alcohol (k_{alc}), which were approximately calculated from the amount of unreacted alcohol. From these results, it was found that the activity of ppt-Ni is much better in dehydrogenation rather than those of the other catalysts, and that the compositions of the reaction products vary remarkably depending upon the species of the catalysts; for example, the mol percentage of toluene in the products was not very different between the different nickel catalysts used, whereas the formation of benzene was markedly influenced by the kind of catalyst, the relative yield being suppressed in the following order: S-Ni>R-Ni>U-Ni-A>ppt-Ni. It is noteworthy that benzene was not produced in the presence of metal oxide catalysts, such as $Cu_2Cr_2O_5$, $ZnCr_2O_4$, and Al_2O_3. From the viewpoint of the formation of benzene during the reaction, the catalysts used can be roughly classified into three categories: (a) the catalysts, such as S-Ni and R-Ni (W-7), which afford a large quantity of benzene. They are mainly composed of nickel crystals or crystallites; (b) the catalysts, such as ppt-Ni and U-Ni-A, which give a small quantity of benzene. Ppt-Ni, which is the precursor of U-Ni-A, is supposed to have the surface structure of an alloy-like crystal composed of nickel and zinc,[3] and (c) ppt-Cu or oxide-type catalysts which exhibit no activity giving benzene. Considering these facts, it can be assumed that the nickel crystals are generally effective in the formation of benzene.

With a veiw to getting further information on the process of the reactions of benzyl alcohol, the change in the composition of the reaction mixture was followed by gas-chromatographic analysis at successive intervals. The results of the reaction, in which benzyl alcohol was refluxed under orindary pressure in the presence of S–Ni (S 10), are shown in Fig. 1; those of the same reaction practiced in a sealed tube are illustrated in Fig. 2. Figures 1 and 2 indicate that the alcohol always reacts in the

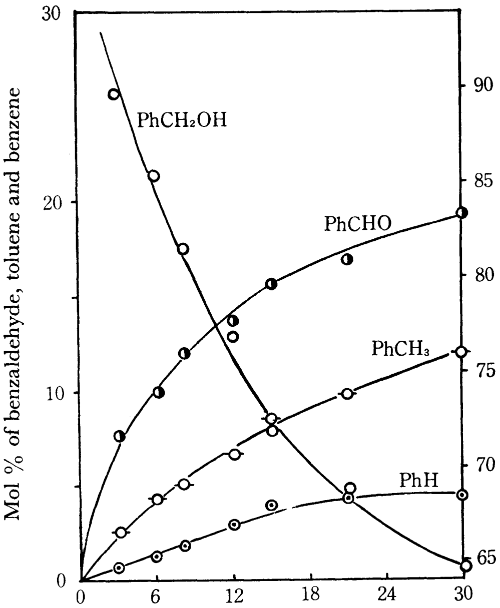

Fig. 1. The change of the composition of the reaction mixture.
substrate: benzyl alcohol, catalyst: stabilized nickel (S 10), conditions: refluxing under the ordinary pressure

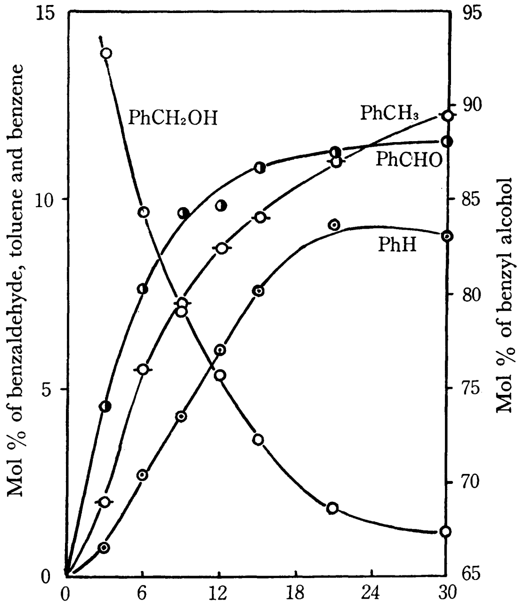

Fig. 2. The change of the composition of the reaction mixture.
substrate: benzyl alcohol, catalyst: stabilized nickel (S 10), conditions: heated at 157°C in a sealed tube

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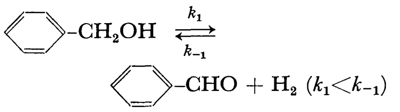
[3] S. Taira, "Catalytic Engineering," Vol. 10, ed. by Catalysis Society of Japan, Chijin Shokan & Co., Tokyo (1967), pp. 498—499.

first order. In the reaction in a sealed tube, benzaldehyde and benzene increased successively in the early stages, but the rate of their formation was found to decline after the elapse of 12 hr, while toluene went on increasing.

In the redox reaction shown in Eq. (4), the rate constant of the oxidation of the alcohol (k_1) was supposed to be smaller than that of the reverse reaction (k_{-1}), because the oxidation potential of benzaldehyde is comparatively high.[4]



(4)

Thus, in the state of equilibrium between benzyl alcohol and benzaldehyde, the alcohol may be predominant. Therefore, in the closed reaction system, the reduction of benzaldehyde, which corresponds to the reverse reaction in Eq. (4), may proceed concurrently with the dehydrogenation of benzyl alcohol until the pseudo-equilibrium shown in Eq. (4) is attained in the reaction system. The consumption of hydrogen produced by the dehydrogenation of benzyl alcohol will lead to the disadvantageous reductive dehydroxylation and dehydroxymethylation of the alcohol according to Eqs. (2) and (3). Of these competitive reactions, the latter was found to be more strongly suppressed (Fig. 2). This is conceivable not only because the C–C bond is more difficult to hydrogenolyze than the C–O bond, but also because the dehydroxymethylation (Eq. (3)) requires twice as much hydrogen as does dehydroxylation (Eq. (2)).

One piece of evidence leading to this conclusion comes from the results of the reactions carried out with various amounts of a nickel catalyst (S-Ni) in sealed tubes; the influence of the change in the amount of catalyst in the reactions is summarized in Table 3 and Fig. 3. As is shown in Fig. 3, a linear proportionality was observed between the amount of the catalyst and the logarithm of the rate constant. The linear relation equation can be approximately represented as follows:

$$\log k_{alc} = 6.20 \times 10^{-2} \cdot W - 2.20 \qquad (5)$$

where W is the weight of the catalyst (in gram).

The composition of each product in the reaction mixture of the above reactions is given in Fig. 4. It can be found from Figs. 3 and 4 that the rate constant of the overall reaction of benzyl alcohol and the yields of toluene and benzene increased with an increase in the amount of the catalyst. However, the yield of benzaldehyde decreased in spite of the increase in the rate of the overall reaction of benzyl alcohol. Therefore, it may be

Table 3. The reactions of benzyl alcohol in the presence of varied amount of stabilized nickel catalyst in a sealed tube

benzyl alcohol 1.0 ml; heated at 160° for 24 hr

Weight of catalyst (g)	k_{alc} (hr^{-1}) $\times 10^2$	$\log k_{alc}$
0.100	0.977	−2.010
0.167	1.19	−1.922
0.250	1.95	−1.710
0.333	2.40	−1.620
0.500	5.36	−1.271

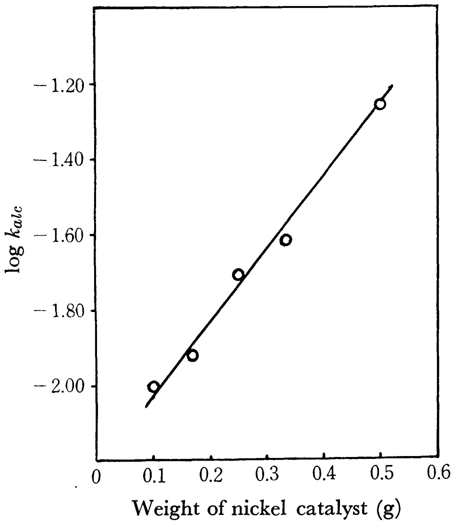


Fig. 3. Relation between k_{alc} and weight of nickel catalyst by the reactions in sealed tubes.

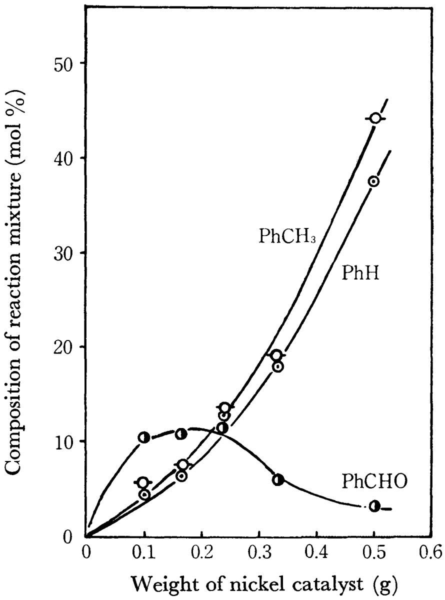


Fig. 4. The composition of products by the reactions of benzyl alcohol in the presence of varied amount of stabilized nickel catalyst in sealed tubes.

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[4] The values of E_0 and $-\Delta F$ for benzaldehyde are 197 mV and 9.1 kcal (25°C); H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, *J. Amer. Chem. Soc.*, **71**, 3622 (1949).

TABLE 4. THE REACTIONS OF BENZYL ALCOHOL IN THE PRESENCE OF VARIED AMOUNT OF STABILIZED NICKEL CATALYST UNDER ORDINARY PRESSURE

benzyl alcohol 30 ml; refluxed at 150°C for 6 hr

Weight of catalyst (g)	k_{alc} (hr^{-1}) $\times 10^2$
3.0	0.766
5.0	1.11
7.5	1.66
10	2.20
15	3.33

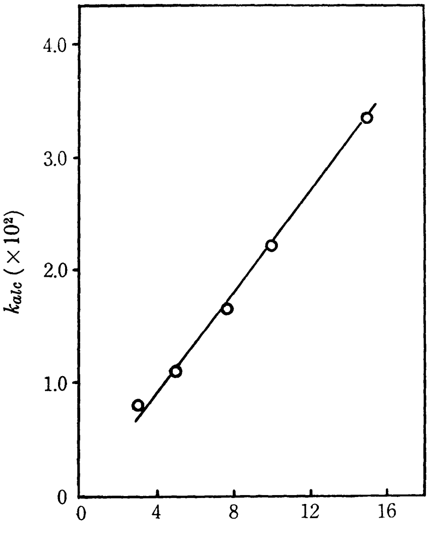

Fig. 5. Relation between k_{alc} and weight of nickel catalyst by the reactions under ordinary pressure.

assumed that the faster the dehydragenation reaction proceeds due to an increase in the amount of the catalyst, the more readily the pseudo-equilibrium shown in Eq. (4) will be attained, resulting in the promotion of the formation of benzene and toluene.

Other experiments to observe the effect of the amount of the catalyst were carried out by refluxing benzyl alcohol under ordinary pressure. The results are shown in Table 4 and Fig. 5. A linear relationship was similarly observed between the rate constant of the overall reaction of benzyl alcohol and the amount of the catalyst. The relation can be represented as in the following equation:

$$k_{alc} = 2.21 \times 10^{-3} \cdot W \qquad (6)$$

In contrast to the results in a closed reaction system, the decrease in the formation of benzaldehyde with the increase in the catalyst amount (see Fig. 4) was observed in an open reaction system under ordinary pressure. Thus, it was found that hydrogen plays an important role in determining the compositions of the products. In the closed reaction system, the high pressure of hydrogen, which is brought about by the dehydrogenation, necessarily leads to a decrease in the final yield of benzaldehyde. On the other hand, it may be advantageous to promote the formation of toluene and benzene by the reductive dehydroxylation and dehydroxymethylation. This consideration is fairly consistent with the results of another experiment in which the variation in the composition of the products under various hydrogen pressures was observed (Fig. 6). Consequently, it was concluded that the selectivity of this reaction is dependent not only upon the nature of the catalyst used, but also upon the pressure of hydrogen in the reaction system.

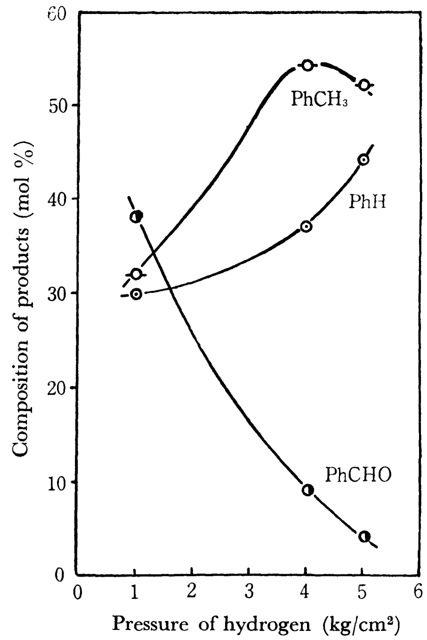

Fig. 6. The composition of products by the catalytic reactions of benzyl alcohol under varied pressure of hydrogen.

benzyl alcohol 24 ml; catalyst: stabilized nickel 4 g

It was established that benzaldehyde cannot be an intermediate in the formation of toluene or benzene, because the benzaldehyde itself was completely recovered unchanged when it was heated in the presence of a nickel catalyst in a sealed tube for more than 24 hr. The formation of methane in the dehydroxymethylation of primary alcohol has already been reported.$^{5)}$ In the present study the generation of a small quantity of another gaseous hydrocarbon besides methane was observed by gas-

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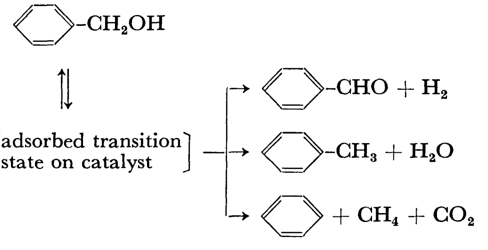
5) V. N. Ipatieff, G. Czajkowski and H. Pines, *ibid.*, **73**, 4098 (1951); H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **76**, 771 (1954); H. Pines, M. Shamaiengar and W. S. Postle, *ibid.*, **77**, 5099 (1955).

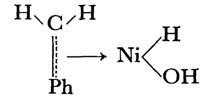
chromatographic analysis; it was assumed to be either ethane or propane on the basis of its retention time. The formaldehyde, which might be expected in dehydroxymethylation, could not be detected by any test with 2,4-dinitrophenylhydrazine, Fehling's solution, and Schiff's reagent.

It is noticeable that the generation of carbon dioxide was observed as another by-product of the dehydroxymethylation. Carbon dioxide was detected by gas-chromatographic analysis and by the formation of a $BaCO_3$ precipitate when a gaseous product was introduced into a saturated aqueous solution of $Ba(OH)_2$.

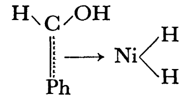
The mode of the adsorption of benzyl alcohol on the catalyst and the mechanism of the catalytic reaction are not entirely clear, but it is considered that the general scheme of the reaction may well be represented as follows, assuming the intervention of an adsorbed transition state on the catalyst:



McQuillin *et al.*[6] have proposed a mechanism of the hydrogenolysis of benzylic compounds in which the reaction was presumed to proceed through a metal benzyl complex. If the formation of a π-benzyl complex intermediate in hydrogenolysis is established, it is conceivable that a similar complex, at least one of nickel, is involved in the dehydroxymethylation and dehydroxylation of benzyl alcohol in the presence of a catalyst. This consideration seems to be fairly consistent with the complicated reaction course of benzyl alcohol. Since nickel metal plays an important role in the cleavage of α-carbon from the benzene ring by dehydroxymethylation reaction, a strong interaction of nickel with the phenyl group may be expected in the adsorbed transition complex. Considering the simultaneous formation of CO_2 and CH_4 in the dehydroxymethylation, and the high yield of cyclohexylmethanol in the hydrogenation,[2,7] of benzyl alcohol, it was supposed that the formation of a π-benzyl intermediate involves the removal of either a hydrogen atom or a hydroxyl group from α-carbon, thus giving a metal benzyl complex, I or II :



(I)



(II)

The preference for the alternative removal of either the hydrogen or hydroxyl group is probably dependent upon the chemical nature of the catalyst metal and on the reaction conditions. From the fact that scarcely no formation of benzene was observed when precipitated copper or oxide-type catalysts were used, it is reasonable to consider that the reaction in the presence of these catalysts might take place through another reaction path, without any formation of the metal complex.

Experimental

Benzyl Alcohol. Commercial benzyl alcohol of an extra pure degree was refined by distillation. The fraction boiling at 100—101°C/20 mmHg was collected. The sample was proved to be pure by gas chromatography.

The Reaction under Ordinary Pressure. In a 50-m*l* three-necked flask fitted with a Dimroth condenser and a thermometer was placed 6 m*l* of benzyl alcohol (6.25 g). The flask was then heated to 160°C, and 1.0 g of a catalyst was added through a side-neck when the contents reached a constant temperature.

Small portions of the reaction mixture were periodically taken out with a pipet and analyzed by gas chromatography: column, 1 m of 30% Silicone grease DC on Celite 480 (30—40 meshes) and 2 m*l* of 20% Apiezon grease on Chromosorb W (60—80 meshes); column temp., 150—163°C; flow rate, 40—60 m*l*/min; carrier gas, H_2.

The Reaction in a Sealed Tube. Benzyl alcohol (2.00 m*l*) and a catalyst (0.333 g) were heated at 157°C for 24 hr in a sealed tube. After the reaction was over, the tube was cooled by ice; then the reaction mixture was analyzed by gas chromatography immediately after the tube was opened. For the kinetic study in a closed reaction system, several sealed tubes with the same contents were prepared. The tubes were succesively taken out from the heating bath at adequate intervals and the reaction mixture was analyzed as has been mentioned above.

The Reaction in an Autoclave. Benzyl alcohol (24 m*l*) and a catalyst (4 g) were placed in a 200-m*l* autoclave. After the air in the autoclave had been completely displaced by hydrogen gas, the mixture was heated at 155°C for 24 hr under 1.0 kg/cm^2 pressure of hydrogen without stirring. After the reaction was over, portions of the gaseous product were introduced into various kinds of reagents in order to detect the formation of CO_2 and formaldehyde. The liquid products were analyzed by gas chromatography. Some of the gaseous products were also detected by gas chromatography.

The authors wish to express their hearty thanks to Dr. Ken-ichi Watanabe for his helpful encouragement.

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6) I. Jardine and F. J. McQuillin, *J. Chem. Soc.*, *C*, **1966**, 458; D. A. Denton, F. J. McQuillin and P. L. Simpson, *ibid.*, **1964**, 5535; A. M. Khan, F. J. McQuillin and I. Jardine, *ibid.*, *C*, **1967**, 136; *Tetrahedron Lett.*, **1966**, 2649.

7) H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931); R. Mozingo, C. Spencer and K. Folkers, *J. Amer. Chem. Soc.*, **66**, 1859 (1944); K. Taketomo, Y. Nishimura, T. Hiraki, S. Akitomo and K. Kawamoto, Preprints for the 20th Annual Meeting of the Chemical Society of Japan, Tokyo (April, 1967), Vol. III, p. 278.