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The Catalytic Reaction of Alcohols with Reduced Copper[1]

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The catalytic properties of a reduced copper catalyst in reaction to ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, 2-phenylethanol, 1-phenylethanol, 3-phenyl-1-propanol, cinnamyl alcohol, propionaldehyde, *n*-propyl propionate, and a mixture of ethyl alcohol and propionaldehyde were studied. The present investigation has been undertaken in order to find out whether or not the activity and the selectivity of reduced copper are affected by the method of the preparation of catalysts and the structure of alcohols used as the reactants, and to clarify the mechanism of the formation of the esters and ketones obtained from aliphatic alcohols. It has been found that, over reduced copper, saturated aliphatic alcohol gives considerable amounts of the corresponding aldehyde and ester. The formation of the ester may be explained by a hemiacetal mechanism. The hydroxyl group of aliphatic alcohol is very resistant to hydrogenolysis. However, with the phenyl-substituted alcohols the carbon-to-oxygen bond is easily broken.

Studies concerning the catalytic reaction of primary alcohol with various catalysts have been reported by many investigators.[2] Especially, Adkins *et al.*[2b] and Dunbar[2c] reported that, when *n*-butyl alcohol was passed over copper-chromium oxide catalysts, there were at least four important types of reactions: (1) dehydrogenation, (2) dehydration, (3) aldol condensation, and (4) ester formation by the Tischenko reaction. Dolgow *et al.*[2p] found that, on a pure copper catalyst, ethyl alcohol at 220°—300°C gave almost pure acetaldehyde and that, in the presence of a promoter, ethyl acetate was also formed, in amounts increasing with the concentration of the promoter. Further, Eto[2o] reported that the copper catalyst strongly accelerated ester formation by the Tischenko reaction.

It has been well known that the aromatic nuclear catalytic hydrogenation of benzyl-type oxygen compounds is accompanied by the hydrogenolysis of carbon-oxygen linkage.[3] The catalytic hydrogenation and hydrogenolysis of allyl alcohol, benzyl alcohol, and cinnamyl alcohol over Raney nickel, palladium on charcoal, palladium(H), Adams' platinum, ruthenium, rhodium on alumina, nickel on kieselguhr, copper-chromium oxide, palladium boride, and reduced copper as the catalysts have been investigated by many wokers.[4]

The preparation of copper catalysts and the production of acetone and oily products (isobutyl methyl ketone and diisobutyl ketone) from isopropyl alcohol have been reported in detail in previous papers.[5] It has been found that two distinct types of copper catalysts are obtained, according to the precipitants, and that the activity and the selectivity of the catalyst are affected by the reducing agent used in the preparation of the copper catalyst.

The present investigation includes an extension of this method to aliphatic primary alcohols and aromatic alcohols. Certain tendencies regarding the structure of alcohol, the ease of dehydrogenation, the ester forma-

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tion, and the hydrogenolysis over reduced copper catalyst have been discussed. Further, this research has been undertaken in order to clarify the mechanism of the formation of the ester and the ketone.

Experimental

Reactants. The aliphatic alcohols, such as ethyl alcohol, *n*-propyl alcohol, and *n*-butyl alcohol, were purified, after being dried with calcium oxide, by distillation through a fractionating column. Propionaldehyde, *n*-propyl propionate, 2-phenylethanol, 1-phenylethanol, 3-phenyl-1-propanol, and cinnamyl alcohol were purified by being dried with anhydrous sodium sulfate, followed by fractional distillation under ordinary pressure or reduced pressure. The reactants used in this experiment showed no impurity in gas-chromatographic analysis. (Columns of PEG-6000, tricresyl phosphate, and silicone DC-550 were used.)

Preparation of Catalysts. The precipitates used in this research were identical with the Cu VII and Cu IX which were described in a preceding paper.[5] The Cu VII was prepared as follows: A solution of 30 g of cupric nitrate hexahydrate in 900 m*l* of distilled water was kept at 22°C. A sodium hydroxide solution prepared from 15 g of sodium hydroxide and 300 m*l* of distilled water was brought to the same temperature and added rapidly to the stirred copper nitrate solution. After the mixture had been stirred at this temperature for 30 min, the precipitate was washed well with distilled water by decantation, collected on a glass filter, dried in an electric oven at 105°C for 20 hr, powdered in an agate mortar, and finally stored in a stoppered bottle. The Cu IX was prepared by the same method except for the precipitant (K_2CO_3: 25 g) and the volume of distilled water (500 m*l*) used to dissolve it. These precipitates were reduced in the following ways. When hydrogen was used as the reducing agent, the hydrogen was passed at the rate 750—900 m*l* per hr. The reduction temperature was always below 185°C. In the case of the reduction of the precipitate with carbon monoxide, the flow rate of carbon monoxide was 800—900 m*l* per hr, and the reduction temperature was always below 140°C.

Apparatus and Procedure. The apparatus employed was exactly the same as that previously described.[5] The precipitate (10 g) to be reduced was placed in a Pyrex reaction tube. The furnace was heated to the reduction temperature and kept at this temperature for the period of reduction. The reducing agent was passed through the tube at a regular velocity, and the resulting catalyst was then heated to the reaction temperature. Experiments were performed at 220, 250, and 300°C under ordinary pressure, and the reactants were passed through the tube at a constant flow rate. The reaction products coming from the reaction tube were condensed by passing them through a condenser cooled with ice and were collected by two traps cooled with ice. The volume of gas evolved during the period of the reaction was measured at intervals of 30 min. All the values given in the present research are averages of two or three measurements under constant reaction conditions.

Identification and Analysis of the Reaction Products. The liquid products were identified by comparing them with authentic samples by gas chromatography. (Columns of tricresyl phosphate, PEG-6000, silicone DC-550, diethylene glycol succinate, and Hyprose SP-80 were used. For the determination of water, a 3-m column packed with Shimalite F impregnated with PEG-1000 was used.) In addition, the reaction products were dried over anhydrous sodium sulfate and then fractionally distilled, and the constituents of the fraction were identified by observing the formation of the derivatives[6] and the infrared absorption. The gaseous products were analyzed by gas chromatography. (Columns of activated charcoal, molecular sieve-13X, hexamethyl phosphoramide, tricresyl phosphate, acetonylacetone, and dimethyl sulfolane were used.) The gaseous products could not be determined quantitatively. The quantitative analysis of the liquid products in this experiment was performed by gas chromatography.

Results and Discussion

The influences of the reaction temperatures, the precipitants, and the reducing agents on the activity and the selectivity of the copper catalyst are summarized in Tables 1, 2, 4, 5, 6, 7, and 8. Experiment Nos. 11—14 of Table 2 and Experiment Nos. 15 and 16 of Table 3 were carried out in order to explain the formation mechanism of the ester and the ketone obtained by this experiment. The fluctuation in the yields of the reaction products obtained by the repeated experiments was less than 1 per cent. Since the reactants were not changed in the absence of the catalysts over a range of temperatures from 220°C to 300°C, the changes shown in Tables 1—8 do not involve the simple pyrolysis of the reactants. Further, since the evolution of the gas is constant during the reaction period, it may be concluded that the sustained activity of catalyst holds over the period of the operation.

Influences of the Precipitants and the Reducing Agents on the Catalytic Action of Reduced Copper toward Aliphatic Primary Alcohols. As may be seen from the amounts of unreacted alcohol shown in Tables 1, 2, and 4, the conversion of primary alcohol to the reaction product (aldehyde, ester, ketone, *etc.*) in the presence of the copper catalyst depends upon the temperature at which the reaction is carried out; it has been found that the yield of the reaction product increases rapidly with a rise in the reaction temperature. Dehydrogenation and the formation of the ester are the chief reactions when the catalytic reaction of aliphatic primary alcohol is carried out at 220—300°C. Even at atmospheric pressure, a considerable amounts of ester may be formed, especially at a higher temperature (300°C). From the amounts of alkenes and water present in the reaction products, it was shown that dehydration has never been a troublesome factor in studies with the aliphatic alcohol at temperatures below 300°C. As may be seen from Experiment Nos. 2 and 5 of Table 1 and Experiment Nos. 7 and 10 of Table 2, the yield of the reaction product is also affected by the sort of precipitant; it has been found that when the copper catalyst prepared with sodium hydroxide is used, the yield of the reaction product increases. As may be seen from Experiment Nos. 2 and 4 of Table 1 and Experiment Nos. 7 and 9 of Table 2, the copper catalysts prepared by treatment with hydrogen and carbon monoxide as the reducing agents are nearly equal in the yields of the reaction product, but there are the distinct differences in the amounts of aldehyde and

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[6] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, New York (1956).

TABLE 1. INFLUENCES OF THE PRECIPITANTS, THE REDUCING AGENTS AND THE REACTION TEMPERATURES ON THE CATALYTIC ACTION OF REDUCED COPPER TOWARD ETHYL ALCOHOL

Experiment No.	1	2	3	4	5
Precipitate	CuVII				CuIX
Reducing agent	H_2	H_2	H_2	CO	H_2
Reaction temp. (°C)	220	250	300	250	250
Ethyl alcohol (g)	17.37	17.21	16.79	18.83	17.77
Velocity (g/hr)	7.6	7.1	7.1	8.7	6.9
Liquid product (g)	16.63	16.43	15.94	16.15	16.92
Composition of liquid product (%)					
Acetaldehyde	11.4	19.3	24.0	14.7	19.3
Ethyl acetate	15.5	18.7	23.5	22.6	11.5
Acetone	0.4	1.2	3.8	0.8	0.5
Acetic acid	T	T	0.7	T	T
Aldol	0.1	0.3	0.5	T	0.1
Crotonaldehyde	0.1	0.2	0.3	T	0.1
Butyraldehyde	0.1	0.2	0.4	T	0.1
2-Buten-l-ol	0.1	0.2	0.3	0.4	0.1
n-Butyl alcohol	0.2	0.4	1.0	0.3	0.2
Methyl alcohol	T	T	T	T	T
Water	T	T	T	T	T
Unidentified product	0.2	0.2	0.5	0.4	0.2
Unreacted alcohol	71.9	59.3	45.0	60.8	67.9
Gas collected[a)] (*l*)	2.25	3.28	4.31	3.26	2.94

T: Trace

a) The gaseous products evolved were found to consist of hydrogen, methane, ethylene, ethane, and carbon dioxide with the exception that carbon monoxide was observed in the case of the reduction of precipitate with carbon monoxide.

TABLE 2. THE CATALYTIC PROPERTIES OF REDUCED COPPER TOWARD *n*-PROPYL ALCOHOL, PROPIONALDEHYDE AND *n*-PROPYL PROPIONATE

Experiment No.	6	7	8	9	10	11	12	13	14
Precipitate	CuVII				CuIX	CuVII			
Reducing agent	H_2	H_2	H_2	CO	H_2	H_2	H_2	CO	H_2
Reaction temp. (°C)	220	250	300	250	250	250	300	250	250
Reactant	*n*-Propyl alcohol					Propionaldehyde			*n*-Propyl propionate
Reactant charged (g)	18.93	18.73	19.16	19.00	17.16	16.19	17.72	18.96	18.08
Velocity (g/hr)	7.7	6.9	7.2	8.4	6.5	7.1	6.9	7.5	7.0
Liquid product (g)	17.97	17.72	17.99	17.93	16.20	15.15	16.59	17.38	17.02
Composition of liquid product (%)									
Propionaldehyde	11.3	15.8	22.9	11.7	17.1	—	—	—	0.3
n-Propyl propionate	9.2	14.4	19.5	20.2	11.8	0	0	0	—
Diethyl ketone	5.0	7.1	8.6	4.2	1.4	0	0	0	0.3
Propionic acid	T	0.3	0.5	T	T	2.4	4.3	2.3	0.4
n-Propyl alcohol	—	—	—	—	—	2.6	4.6	2.9	0.3
Ethyl alcohol	0.2	0.5	0.9	0.2	0.2	0	0	0	0
Methyl alcohol	0.1	0.2	0.3	0.1	0.1	0	0	0	0
Water	T	T	T	T	T	T	T	T	T
Unidentified product	0.3	1.1	1.1	1.2	0.2	T	T	0.7	0.2
Unreacted reactant	73.9	60.6	46.2	62.4	69.2	95.0	91.1	94.1	98.5
Gas collected[a)] (*l*)	1.92	2.21	5.00	2.30	2.06	0.19	0.31	0.17	0.13

T: Trace

a) Gaseous products

n-Propyl alcohol: hydrogen, propylene, carbon dioxide, methane, ethane, and carbon monoxide

Propionaldehyde: carbon dioxide, hydrogen, carbon monoxide, and ethane

n-Propyl propionate: propylene and carbon dioxide

TABLE 3. THE REACTION BETWEEN ETHYL ALCOHOL AND PROPIONALDEHYDE IN THE PRESENCE OF REDUCED COPPER[a)]

Experiment No.	15	16
Reducing agent	H_2	CO
Reaction temp. (°C)	250	250
Reactant charged		
Ethyl alcohol (g)	15.35	15.20
Propionaldehyde (g)	19.28	19.32
Velocity (g/hr)	8.0	10.5
Liquid product (g)	33.20	32.88
Composition of liquid product (%)		
Acetaldehyde	3.9	4.1
Ethyl acetate	T	0.8
Ethyl propionate	15.4	7.8
Methyl ethyl ketone	0.6	0.2
n-propyl alcohol	4.8	4.1
Ethyl alcohol	30.4	34.5
Propionaldehyde	44.7	48.4
Unidentified product	0.2	0.1
Gas collected[b)] (*l*)	0.69	0.57

T: Trace

a) The precipitate (CuIX) prepared with potassium carbonate was used.

b) The gaseous products evolved contain hydrogen, carbon dioxide, ethylene, carbon monoxide, and ethane.

TABLE 4. THE CATALYTIC PROPERTIES OF REDUCED COPPER[a)] TOWARD *n*-BUTYL ALCOHOL

Experiment No.	17	18	19
Reaction temp. (°C)	220	250	300
n-Butyl alcohol (g)	18.63	19.13	19.32
Velocity (g/hr)	6.2	6.5	5.9
Liquid product (g)	17.78	18.23	18.37
Composition of liquid product (%)			
Butyraldehyde	16.2	20.1	24.2
n-Butyl-*n*-butyrate	5.7	15.0	20.9
Di-*n*-propyl ketone	0.2	0.6	5.3
Butyric acid	T	T	0.1
n-Propyl alcohol	T	0.2	0.5
Ethyl alcohol	T	0.2	0.3
Methyl alcohol	T	0.1	0.2
Water	T	T	T
Unidentified product	0.3	0.1	0.8
Unreacted alcohol	77.6	63.7	47.7
Gas collected[b)] (*l*)	1.42	2.06	3.57

T: Trace

a) The copper catalyst, prepared by treatment with sodium hydroxide followed by reduction with hydrogen, was used.

b) The gaseous products evolved contain hydrogen, carbon dioxide, 1-butene, methane, ethane, propane, and carbon monoxide.

TABLE 5. THE CATALYTIC PROPERTIES OF REDUCED COPPER TOWARD 2-PHENYLETHANOL

Experiment No.	20	21	22
Precipitate[a)]	CuVII		CuIX
Reaction temp. (°C)	250	300	250
2-Phenylethanol (g)	21.54	22.00	23.46
Velocity (g/hr)	12.6	12.1	12.5
Liquid product (g)	20.12	20.64	21.80
Composition of liquid product (%)			
Phenylacetaldehyde	17.7	9.8	8.2
Ethylbenzene	26.7	44.6	14.1
Toluene	10.8	33.3	6.9
Styrene	0.7	0.2	2.7
Methanol	0.1	T	0.2
Water	4.9	7.8	2.9
Unidentified product	0.1	0.1	6.6
Unreacted alcohol	39.0	4.2	58.4
Gas collected[b)] (*l*)	0.93	2.29	1.14

T: Trace

a) These precipitates were prepared by reduction with hydrogen.

b) The gaseous products contain hydrogen and carbon monoxide.

TABLE 6. THE CATALYTIC PROPERTIES OF REDUCED COPPER TOWARD 1-PHENYLETHANOL

Experiment No.	23	24	25
Precipitate[a]	CuVII		CuIX
Reaction temp. (°C)	250	300	250
1-Phenylethanol (g)	20.28	20.50	21.76
Velocity (g/hr)	11.7	11.7	12.8
Liquid product (g)	18.99	19.09	20.23
Composition of liquid product (%)			
Phenyl methyl ketone	49.4	49.6	53.1
Ethylbenzene	43.1	42.8	39.4
Styrene	T	T	T
Water	7.2	7.4	6.7
Unidentified product	0	0	0
Unreacted alcohol	0.3	0.2	0.8
Gas collected[b] (*l*)	0.25	0.21	0.88

T: Trace
a) These precipitates reduced with hydrogen were used.
b) The gaseous products consist of hydrogen.

TABLE 7. THE CATALYTIC PROPERTIES OF REDUCED COPPER TOWARD 3-PHENYL-1-PROPANOL

Experiment No.	26	27	28
Precipitate[a]	CuVII		CuIX
Reaction temp. (°C)	250	300	250
3-Phenyl-1-propanol (g)	19.77	20.00	21.07
Velocity (g/hr)	13.2	11.9	12.0
Liquid product (g)	18.31	18.50	19.49
Composition of liquid product (%)			
Phenylpropanal	13.9	33.3	12.5
n-Propylbenzene	11.4	28.4	4.8
β-Methylstyrene	2.4	9.8	1.6
Allylbenzene	0.7	1.6	0.2
Ethylbenzene	T	0.4	T
Methanol	T	T	T
Toluene	T	T	T
Ethanol	T	T	T
Water	2.1	6.3	1.2
Unidentified product	0.4	0.1	8.7
Unreacted alcohol	69.1	20.1	71.0
Gas collected[b] (*l*)	0.63	1.02	0.70

T: Trace
a) These precipitates reduced with hydrogen were used.
b) The gaseous products consist of hydrogen and the trace of carbon monoxide.

the ester in the reaction products; it has been found that the formation of the ester from alcohol is more increased by the use of the carbon monoxide-reduced copper catalyst than by the use of the hydrogen-reduced one. Judging from the values listed in Tables 1, 2, and 4, the yield of the reaction product under comparable conditions decreases with an increase in the molecular weight of alcohol. As is shown in Table 1, the copper catalyst is a good catalyst for the dehydrogenation of alcohol and for the ester formation, but it has a poor catalytic activity for aldol condensation. In the catalytic reaction of aliphatic primary alcohol, there are at least three important types of reactions which occur when primary alcohols are passed over reduced copper: (1) dehydrogenation, (2) ester formation, and (3) ketone formation.

The Mechanism of the Formation of the Main Products Obtained by the Catalytic Reaction of Aliphatic Alcohols. Many investigators[1] have found that aliphatic alcohols of *n* carbon atoms can be readily converted to the esters of 2*n* carbon atoms and to symmetrical ketones of $2n-1$ carbon atoms by vapor-phase contact with various catalysts. Especially, Komarewsky *et al.*[2e] reported that, in the presence of a chromium oxide catalyst, primary alcohols ranging from *n*-propyl to *n*-octadecyl alcohol can be converted to ketones by the following mechanism: (1) the dehydrogenation of alcohol to aldehyde, (2) the aldol condensation of aldehyde, (3) the removal of the carbon monoxide from the CHO group of the aldol, leaving a secondary

TABLE 8. THE CATALYTIC PROPERTIES OF REDUCED COPPER[a] TOWARD CINNAMYL ALCOHOL

Experiment No.	29	30	31
Reaction temp. (°C)	260	280	300
Cinnamyl alcohol (g)	49.62	50.24	51.18
Velocity (g/hr)	14.9	15.8	15.9
Liquid product (g)	45.49	46.59	47.56
Composition of liquid product (%)			
Cinnamaldehyde	24.9	26.1	28.4
3-Phenylpropionaldehyde	43.5	41.1	33.3
β-Methylstyrene	19.1	20.6	22.3
Allylbenzene	2.1	2.3	2.9
3-Phenyl-1-propanol	0.8	1.0	1.2
Propylbenzene	1.1	1.4	2.3
Styrene	T	T	T
Ethylbenzene	T	0.2	0.4
Phenylacetylene	2.5	2.8	3.6
Methanol	T	T	T
Water	3.5	3.5	3.9
Unidentified product	0.6	1.0	1.7
Unreacted alcohol	1.9	0	0
Gas collected[b] (*l*)	0.06	0.05	0.02

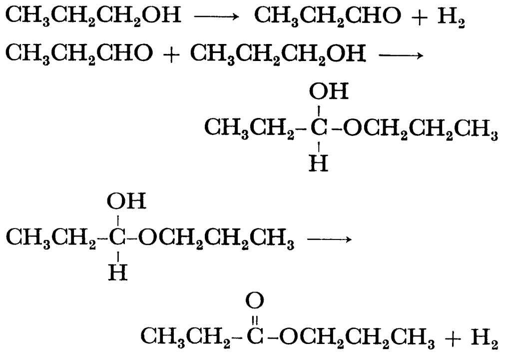
T: Trace

a) The copper catalyst, prepared by treatment with sodium hydroxide followed by reduction with hydrogen, was used.

b) The gaseous products evolved consist of hydrogen.

alcohol, and (4) the dehydrogenation of this alcohol to ketone. On the other hand, the mechanism[7] of the conversion of ethyl alcohol into acetone was examined by Kagan and his co-workers,[8] who considered that ethyl acetate was an important intermediate in the chain of reactions involved. Dolgow and Golodnikow[9] showed that, upon passing alcohol over an activated copper catalyst or mixed catalysts (copper, nickel, zinc oxide, zirconium oxide, *etc.*) at atmospheric pressure and at 250°—300°C, a mixture of the ester and the ketone was obtained, and that the reaction was proceeded by an ester mechanism. The ester was obtained by the processes[10] to be shown below.

In the present research, propionaldehyde, *n*-propyl propionate, and a mixture of ethyl alcohol and propionaldehyde were selected for the study of the reaction mechanism. As is shown in Experiment Nos. 11—13 of Table 2, when propionaldehyde was passed over a copper catalyst, the aldehyde did not condense to give the ester, and small amounts of propionic acid and *n*-propyl alcohol were obtained. Further, as is shown in Table 3, when a mixture of ethyl alcohol and propionaldehyde was passed over reduced copper, the amount of ethyl propionate found in the reaction product was considerably higher than that of ethyl acetate. From these results, the presence of significant quantities of ester in the reaction product may be explained by a hemiacetal mechanism, as in the following schemes:



$$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CHO + H_2$$

$$CH_3CH_2CHO + CH_3CH_2CH_2OH \longrightarrow CH_3CH_2\text{-}\overset{OH}{\underset{H}{C}}\text{-}OCH_2CH_2CH_3$$

$$CH_3CH_2\text{-}\overset{OH}{\underset{H}{C}}\text{-}OCH_2CH_2CH_3 \longrightarrow CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2CH_3 + H_2$$

In the absence of the alcohol, propionaldehyde reacts to give only small amounts of acid and alcohol. These products seem to be obtained by a catalytic reaction between aldehyde and water. As is shown in Experiment No. 14 of Table 2, when *n*-propyl propionate was passed over a copper catalyst, the diethyl ketone, propionic acid, *n*-propyl alcohol, and propionaldehyde in the liquid product and the propylene and carbon dioxide in the gaseous product were obtained. Judging from these results, the formation of ketones from primary alcohols with reduced copper is probably accounted for by the Kagan process:[8]

$$2C_2H_5COOC_3H_7 \longrightarrow C_2H_5COC_2H_5 + C_3H_7OH + C_3H_6 + CO_2$$

Adkins[3d] found that when a mixture of primary alcohol and hydrogen was passed over Raney nickel at 250°C, hydrocarbon was obtained by the steps

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[7] $4\ C_2H_5OH \longrightarrow 4\ CH_3CHO + 2\ H_2$
$4\ CH_3CHO \longrightarrow 2\ CH_3COOC_2H_5 \xrightarrow{2H_2O} 2\ CH_3COOH + 2\ C_2H_5OH$
$2\ CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$

[8] M. J. Kagan, I. A. Sobolew, and G. D. Lubarsky, *Ber.*, **68**, 1140 (1935).

[9] B. N. Dolgow and G. V. Golodnikow, *Zh. Obshch. Khim.*, **24**, 987, 1167, 1364 (1954).

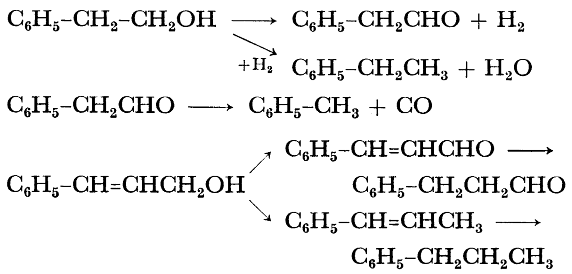
[10] Dolgow *et al.* proved that ethyl acetate is not primarily formed from $2C_2H_5OH \rightarrow CH_3COOC_2H_5 + 2H_2$, but, rather, by the condensation: $2CH_3CHO \rightarrow CH_3COOC_2H_5$, and that acetaldehyde, formed by the direct dehydrogenation of ethyl alcohol, is the intermediate product.

shown below.[11] Judging from the above results and from the gaseous products (alkane) obtained by this experiment, lower alcohols, such as ethyl alcohol and methyl alcohol, that were little produced by the catalytic reaction of *n*-propyl alcohol seem to be obtained by hydrogenolysis. In the case of ethyl alcohol, aldol condensation may also occur in the presence of reduced copper.

The Catalytic Properties of Reduced Copper toward Aromatic Alcohols. As may be seen from the amounts of unreacted alcohol shown in Tables 5—8, the conversion of aromatic alcohol to a reaction product varies considerably with the sort of alcohol. The percentage conversion of 2-phenylethanol is lower than that for 1-phenylethanol; this illustrates the effect of the primary or secondary nature of the alcohol on the ease of the catalytic reactions. Further, over reduced copper, 3-phenyl-1-propanol is less reactive than cinnamyl alcohol. As may be seen from Table 5, when 2-phenylethanol was passed over two types of reduced copper, heated at 250 and 300°C respectively, it was transformed into phenylacetaldehyde, ethylbenzene, toluene, styrene, methanol, and water as the liquid products. At high temperatures, the yields of toluene and carbon monoxide increased, while the yield of phenylacetaldehyde decreased. As may be seen from Table 8, cinnamyl alcohol, when passed over reduced copper heated at 260, 280, and 300°C, was converted into cinnamaldehyde, 3-phenylpropionaldehyde, β-methylstyrene, allylbenzene, 3-phenyl-1-propanol, propylbenzene, styrene, ethylbenzene, phenylacetylene, methanol, and water. Judging from the chromatograms (Columns: PEG-6000 and tricresyl phosphate) of the liquid products, the unidentified products listed in Experiment No. 22 of Table 5 and in Experiment No. 28 of Table 7 consist of a single compound. Accordingly, when the copper catalyst prepared with potassium carbonate as the precipitant was used, a different reaction seems to have occurred.

The Mechamism of the Formation of the Main Products Obtained by the Catalytic Reaction of Aromatic Alcohols. Adkins *et al.*[4d] reported that 3-phenyl-1-propanol was considerably more resistant to hydrogenolysis than 2-phenylethanol, and that, as a phenyl group became more distant from hydroxyl group, the hydrogenolysis of the carbon-oxygen linkage became more difficult. In the present research, when 3-phenyl-1-propanol was passed over the reduced copper, a large amount of *n*-propylbenzene was obtained.

The competitive hydrogenation of C=C and C=O in cinnamaldehyde over a palladium boride catalyst was studied by Kawai *et al.*[4g]; they reported that the reaction proceeded by the steps shown below.[12] Judging from the reaction products obtained by this experiment, it seems reasonable that the main products obtained by the catalytic reactions of 2-phenylethanol and cinnamyl alcohol with reduced copper were formed through the following schemes:



$$\begin{array}{l} C_6H_5\text{-}CH_2\text{-}CH_2OH \longrightarrow C_6H_5\text{-}CH_2CHO + H_2 \\ \qquad\qquad\qquad\quad \searrow^{+H_2}\ C_6H_5\text{-}CH_2CH_3 + H_2O \\ C_6H_5\text{-}CH_2CHO \longrightarrow C_6H_5\text{-}CH_3 + CO \\ \qquad\qquad\qquad\quad \nearrow C_6H_5\text{-}CH{=}CHCHO \longrightarrow \\ C_6H_5\text{-}CH{=}CHCH_2OH \qquad\quad C_6H_5\text{-}CH_2CH_2CHO \\ \qquad\qquad\qquad\quad \searrow C_6H_5\text{-}CH{=}CHCH_3 \longrightarrow \\ \qquad\qquad\qquad\qquad\qquad C_6H_5\text{-}CH_2CH_2CH_3 \end{array}$$

The hydrogenolysis apparently does not occur to any great extent on the catalytic reaction of the aliphatic primary alcohol with the reduced copper. However, with such aromatic alcohols as 2-phenylethanol, 1-phenylethanol, 3-phenyl-1-propanol, and cinnamyl alcohol, this is an important side-reaction. The extent of the hydrogenolysis will, therefore, depend upon the structure of the starting alcohol.

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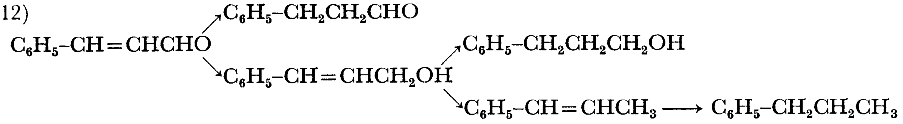
[11] $RCH_2OH + H_2 \longrightarrow RH + CH_3OH \qquad CH_3OH + H_2 \longrightarrow CH_4 + H_2O$

[12]



$$\begin{array}{l} \qquad\qquad\qquad \nearrow C_6H_5\text{-}CH_2CH_2CHO \\ C_6H_5\text{-}CH{=}CHCHO \qquad\qquad\qquad\qquad\qquad \nearrow C_6H_5\text{-}CH_2CH_2CH_2OH \\ \qquad\qquad\qquad \searrow C_6H_5\text{-}CH{=}CHCH_2OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \searrow C_6H_5\text{-}CH{=}CHCH_3 \longrightarrow C_6H_5\text{-}CH_2CH_2CH_3 \end{array}$$