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Catalytic Dehydrogenation of Secondary Alcohols with Reduced Copper. VI.[1] The Dehydrogenation of Isopropyl Alcohol (Part III)*1

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In order to determine whether the condensing activity of reduced copper is affected by the mode of preparation of the catalyst, the condensation of isopropyl alcohol to isobutyl methyl ketone, diisobutyl ketone, and isobutylmethylcarbinol was studied with catalysts prepared in different ways. It was found that the copper catalyst obtained by the hydrogen treatment of the oxide prepared from copper nitrate and an excess of sodium hydroxide was the most suitable catalyst for the condensation of isopropyl alcohol to isobutyl methyl ketone and diisobutyl ketone, and that the copper catalyst prepared with potassium carbonate was the most suitable catalyst for the dehydrogenation of isopropyl alcohol to acetone with no side reaction.

In a previous study,[2] it was found that isobutyl methyl ketone and diisobutyl ketone could be prepared in one step by passing isopropyl alcohol over various forms of copper catalysts heated at 220°C and 250°C, and that the relative amounts of the compounds in the reaction products depended not only upon the reaction temperature, but also upon the mode of preparation of the catalyst.

Adkins *et al.*[3] found that the nickel catalyst prepared by precipitation with ammonium carbonate was more active in the hydrogenation than those prepared with other precipitants (sodium hydroxide, sodium carbonate and sodium bicarbonate). Frolich *et al.*[4] reported that an active catalyst for the decomposition of methanol could be obtained by adding ammonia to a solution of copper nitrate.

Palmer[5] studied the influence of the reducing agents on the copper catalyst, which was used as the catalyst for the dehydrogenation of ethyl alcohol; he reported that the activity of the copper catalyst prepared with hydrogen was greater than those treated with methanol and with carbon monoxide.

No detailed study of the effect of solvents used in the preparation of copper catalysts on the dehydrogenation of a secondary alcohol have been reported.

The object of the present work is to discover how the precipitant, the solvent, and the reducing agent used in the preparation of a catalyst influence the activity and the selectivity of the catalyst, and to find the most suitable conditions and the best catalyst for the formation of isobutyl methyl ketone and diisobutyl ketone from isopropyl alcohol. Experiments were carried out at several temperatures between 185°C and 325°C; four different precipitants, six solvents, and three reducing agents were used.

Experimental

Preparation of Catalysts. The precipitates (Cu VII—Cu XXIV) were prepared as shown in Table 1. As a typical run, Cu XV 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. An ammonia solution prepared from 12 g of ammonia (30%) 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 the time given in the table, powdered in an agate mortar, and finally stored in a stoppered bottle.

The precipitates were reduced in the following ways. When hydrogen was used as the reducing agent, the hydrogen was passed at the rate of 750—900 m*l* per hour over 10 g of the precipitate; the reduction temperature was always below 185°C. In the case of the reduction of the precipitate with isopropyl alcohol vapor, the isopropyl alcohol was charged at the rate of 10—11 g per hour, while the reduction temperatures were 185, 220, 250 and 325°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 hour, and the reduction temperature was always below 140°C.

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[1] K. Kawamoto, This Bulletin, **34**, 799 (1961).

*1 The major part of this research was presented at the Chugoku Shikoku Local Meeting of the Chemical Society of Japan, Matsuyama, November, 1963.

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[2] K. Kawamoto, This Bulletin, **34**, 161, 795 (1961).

[3] H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931); L. W. Covert and R. Connor, *J. Am. Chem. Soc.*, **54**, 1651 (1932).

[4] P. K. Frolich, M. R. Fenske and D. Quiggle, *ibid.*, **51**, 61 (1929).

[5] W. G. Palmer, *Proc. Roy. Soc.*, **A99**, 412 (1921).

TABLE 1. PREPARATION OF PRECIPITATES

Precipitate	Precipitant and amount		Solvent			Time of drying
			Alcohol and volume		Distilled water	
		g		m*l*	m*l*	hr
Cu VII	NaOH	15			300	20
Cu IX	K_2CO_3	25			500	10
Cu XV	NH_4OH	12			300	20
Cu XVI	$(NH_4)_2CO_3$	16			300	20
Cu XVII	NaOH	15	CH_3OH	300		20
Cu XVIII	NaOH	15	C_2H_5OH	300		20
Cu XIX	NaOH	15	n-C_3H_7OH	250	50	20
Cu XX	NaOH	15	n-C_4H_9OH	250	50	20
Cu XXI	NaOH	15	i-C_3H_7OH	250	50	20
Cu XXII	NaOH	15	s-C_4H_9OH	250	50	20
Cu XXIII	K_2CO_3	25	CH_3OH	300	200	10
Cu XXIV	K_2CO_3	25	C_2H_5OH	300	200	10

Apparatus and Procedure. The apparatus employed was similar to that used in the previous investigation, with the exception that an electrically heated furnace was used. A definite amount (10 g) of the precipitate was placed in the Pyrex reaction tube (18 mm in inside diameter and 1 m in length), which was set in an electrically heated furnace of the horizontal type. 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; the resulting catalyst was then heated to the reaction temperature. Experiments were performed at 185, 220, 250, 300, and 325°C under ordinary pressure, and isopropyl alcohol was passed through the tube at a constant flow rate. The reaction products coming out of the reaction tube were removed by being passed through a condenser cooled with ice water, supplemented by two traps which were cooled with ice. The volume of gas evolved was determined by allowing it to displace the water from a 2 *l* graduated cylinder. All the values given in the present research are averages of two to three measurements under constant reaction conditions.

Analysis of the Products. The reaction products (acetone, isobutyl methyl ketone, diisobutyl ketone, and isobutylmethylcarbinol) were identified by comparing them with authentic samples obtained by gas chromatography. In addition, the reaction products were dried with anhydrous sodium sulfate and then fractionally distilled, and the constituents of the cut were identified by their boiling points, densities, refractive indices, and the formation of the corresponding derivatives. All derivatives for the identification of the reaction products were made by the Shriner, Fuson, and Curtin method.[6] Acetone was present in a fraction boiled at 56—56.5°C. From this fraction, the 2,4-dinitrophenylhydrazone, mp 128°C, and the semicarbazone, mp 187°C were obtained. The fraction of isobutyl methyl ketone gave the semicarbazone, mp 133—133.5°C, and the 2,4-dinitrophenylhydrazone, mp 93.5—94°C. The fraction of diisobutyl ketone gave the 2,4-dinitrophenylhydrazone, mp 92—92.5°C, and the semicarbazone, mp 122—122.5°C. The fraction of isobutylmethylcarbinol gave the phenylurethane, mp 142—143°C. No formation of unsaturated or hydroxy ketones, such as mesityl oxide, phorone or diacetone alcohol, were detected in the reaction products of any of the experiments. The gaseous product, when analyzed by gas chromatography, has found to be hydrogen. The reaction products were analyzed quantitatively by gas chromatography using a Shimadzu-Type GC-2B and a Shimadzu-Type CG-2C apparatus. A 5-m column of PEG-6000 was used at an operating temperature of 100°C and at a flow rate of 22.0 m*l*/min of helium. For the determination of water, a 3-m column packed with Shimalite F impregnated with PEG-1000 was used at 100°C with a hydrogen carrier at 11.5 m*l*/min. Further, the content of acetone was determined by the hydroxylamine method.[7]

Results and Discussion

The influence of the precipitant, the solvent, and the reducing agent used in the preparation of catalyst on the activity and the selectivity of the copper catalyst is summarized in Tables 2 and 3; the amounts of reaction products given in these tables are reproducible within 1 per cent. The evolution of gas measured at intervals of 15—20 min was found to be constant during the reaction time. Therefore, it was concluded that the sustained activity of the catalyst held over the period of the operation. Little dehydration of isopropyl alcohol to propylene seems to occur at temperatures below 325°C.

Influences of the Precipitants and the Solvents on the Dehydrogenating Activity and the Condensing Activity of Reduced Copper. As shown in Table 2, the dehydrogenating activity and the condensing activity of a copper catalyst vary considerably with the sort of precipitant and

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

7) M. Katsuno, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **46**, 112 (1943).

TABLE 2. INFLUENCES OF THE PRECIPITANTS AND THE SOLVENTS ON THE DEHYDROGENATING ACTIVITY AND THE CONDENSING ACTIVITY OF REDUCED COPPER (Reaction temp.: 250°C)

Precipitant		NaOH							K$_2$CO$_3$			NH$_4$OH	(NH$_4$)$_2$CO$_3$
Precipitate Solvent		Cu VII H$_2$O	Cu XVII CH$_3$OH	Cu XVIII C$_2$H$_5$OH	CuXIX n-C$_3$H$_7$OH	Cu XX n-C$_4$H$_9$OH	Cu XXI i-C$_3$H$_7$OH	Cu XXII s-C$_4$H$_9$OH	Cu IX H$_2$O	Cu XXIII CH$_3$OH	Cu XXIV C$_2$H$_5$OH	Cu XV H$_2$O	Cu XVI H$_2$O
Isopropyl alcohol	g	38.8	38.6	39.0	39.4	39.3	38.6	38.6	39.2	39.4	39.2	38.8	38.8
Velocity	g/hr	11.7	11.4	9.8	12.1	11.8	12.5	12.1	11.5	12.3	10.8	10.0	8.4
Reaction product	g	34.6	34.7	34.9	35.2	35.0	34.9	34.7	35.9	35.9	35.9	34.6	35.0
Composition of reaction product													
Acetone	%	47.6	54.7	55.8	84.8	84.4	86.1	85.9	90.2	79.8	80.3	81.1	58.8
Isobutyl methyl ketone	%	19.8	16.7	16.4	T	T	T	T	0	0	0	2.6	12.5
Diisobutyl ketone	%	16.0	13.4	13.6	T	T	T	T	0	0	0	2.1	10.3
Isobutylmethylcarbinol	%	2.1	1.6	1.7	0	0	0	0	0	0	0	0.2	1.4
Unidentified product	%	0.8	0.9	0.7	0	0	0	0	0	0	0	0	0.6
Water	%	7.9	6.5	6.5	0	0	0	0	0	0	0	1.0	4.9
Unreacted alcohol	%	5.8	6.2	5.3	15.2	15.6	13.9	14.1	9.8	20.2	19.7	13.0	11.5
Gas collected	l	9.11	9.71	10.11	12.11	11.89	11.93	11.98	12.80	11.34	11.31	11.50	10.01

T: Trace

TABLE 3. INFLUENCES OF THE REDUCING AGENTS AND THE REACTION TEMPERATURES ON THE DEHYDROGENATING ACTIVITY AND THE CONDENSING ACTIVITY OF REDUCED COPPER

Precipitate		Cu VII												Cu IX	
Reducing agent		Isopropyl alcohol									Carbon monoxide				
Reduction temp. °C Reaction temp. °C		185*	185 250	220*	220 250	250*	250 250	250 325	325*	325 325	140 220	140 250	140 300	140 250	140 300
Isopropyl alcohol	g	54.4	38.8	54.6	38.7	54.3	38.7	38.8	54.2	38.8	38.9	38.2	38.7	38.6	38.9
Velocity	g/hr	10.8	10.8	10.9	12.0	10.7	11.1	12.5	11.0	12.0	9.5	11.3	9.5	10.3	11.8
Reaction product	g	51.3	35.9	53.5	36.5	53.3	35.9	36.4	52.4	36.1	34.7	36.6	34.8	35.4	35.6
Composition of reaction product															
Acetone	%	58.0	82.6	72.5	82.2	78.8	83.9	95.5	92.4	96.1	59.4	46.7	83.5	74.3	92.5
Isobutyl methyl ketone	%	0	5.2	0	5.5	4.8	4.9	0	0	0	9.1	20.0	7.7	0	0
Diisobutyl ketone	%	0	1.2	0	1.3	1.2	1.2	0	0	0	3.9	17.0	2.0	0	0
Isobutylmethylcarbinol	%	0	0.5	0	0.5	0.4	0.4	0	0	0	1.6	2.4	0.3	0	0
Unidentified product	%	0	0	0	0	0	0	0	0	0	0.3	0.9	0.3	0	0
Water	%	4.4	1.2	4.2	1.3	5.5	1.1	0	4.4	0	2.8	8.2	1.8	0	0
Unreacted alcohol	%	37.6	9.3	23.3	9.2	9.3	8.5	4.5	3.2	3.9	22.9	4.8	4.4	25.7	7.5
Gas collected	l	9.27	11.87	12.91	12.06	15.33	11.96	13.67	19.37	13.56	9.25	10.13	12.76	10.91	13.11

* These columns show the products obtained when isopropyl alcohol was passed over the catalyst as the reducing agent at the temperatures described.

with the sort of solvent. Although the influence of the reaction temperature on the dehydrogenating activity of reduced copper is not listed in this table, at the highest reaction temperature (325°C) the catalyst prepared by the treatment with hydrogen of the precipitate (Cu IX) obtained by using potassium carbonate as a precipitant gave the highest yield of acetone (97.0%). The dehydrogenating activity of various copper catalysts is in the following order with respect to the precipitants: $K_2CO_3 > NaOH > (NH_4)_2CO_3 > NH_4OH$. Furthermore, it was found that the catalyst prepared by the treatment of Cu IX with hydrogen acted only to dehydrogenate isopropyl alcohol to acetone at all temperatures; the catalyst prepared by the treatment with hydrogen of the precipitates (Cu VII, Cu XV and Cu XVI) obtained by using sodium hydroxide, ammonia, and ammonium carbonate acted similarly at the highest temperature, but at lower temperatures (185—250°C) they gave not only acetone but also isobutyl methyl ketone, diisobutyl ketone, and isobutylmethylcarbinol. The copper catalyst prepared by precipitation with sodium hydroxide was more active in the condensation of isopropyl alcohol than those catalysts precipitated with ammonia and ammonium carbonate. The proportion of diisobutyl ketone in the condensation products increased with a rise in the reaction temperature.

From the fact that the copper catalyst obtained by using an excess of ammonium carbonate caused the condensation reaction, and that the copper catalyst prepared with an excess of potassium carbonate did not cause this reaction, it does not appear that this condensation was caused by traces of alkali contaminating the catalyst. Considering the information in the previous paper,[2] the formation of higher ketones in the present research seems to be attributable to the effect either of traces of water or of a lower oxide of copper in the catalysts.

When the precipitate prepared from ammonia water was used, the evolution of NO_2 gas in the course of reduction of the precipitate with hydrogen was noticed; this gas seems to be attributable to the nitrate ions remaining as an impurity in the precipitate. NO_2 gas tended to exert a strongly negative influence on the velocity of reduction, the reduction time being fifty hours. However, the gas had no appreciable change on the dehydrogenating activity.

Cu XVII and Cu XVIII, prepared in methyl alcohol and ethyl alcohol respectively as solvents, were nearly equal in their activity for the production of both the condensation product and acetone. When the reaction temperature was carried out at lower temperatures (220—250°C), Cu XX, prepared in butyl alcohol, had a relatively poor activity for the formation of the condensation product. However, at the reaction temperature of 220°C the copper catalysts obtained by the treatment with hydrogen of the precipitates (Cu XVII, Cu XVIII, Cu XIX, Cu XXI and Cu XXII) prepared in the other alcohols did give the condensation product. There was thus a marked difference in activity between the copper catalyst prepared in a higher alcohol and those prepared in lower alcohols with respect to the relative amount of condensation product formed. The maximum conversion to the higher ketones resulted when water was used as the solvent; the formation of the condensation product increased in the following order with respect to the solvent: water>methanol, ethanol>2-propanol > 2-butanol > 1-propanol > 1-butanol. When the copper catalyst prepared in a higher alcohol was used at a low temperature, it gave a large quantity of unreacted alcohol. This seems to be caused by the adsorption of the higher alcohol on the catalyst. Because of the small extent of the condensation reaction, the degree of dehydrogenation was excellent over the catalyst prepared in the higher alcohol. When the copper catalysts obtained by the treatment with hydrogen of the precipitates (Cu XXIII and Cu XXIV) prepared with potassium carbonate in alcohols were used at 220—250°C, isopropyl alcohol yielded acetone and hydrogen, but not higher ketones. It has been found by Suito and Takiyama[8] that considerable differences in particle size occur with changes in the solvents used in preparing the precipitates. Accordingly, the dehydrogenating activity and the condensing activity of the copper catalyst is presumed also to depend on the particle size, which may vary with changes in the solvents.

Influence of Reducing Agents on the Dehydrogenating Activity and the Condensing Activity of Reduced Copper. The influence of the reducing agents and the reaction temperatures on the activity of the copper catalyst is shown in Table 3. The condensing activity of the copper catalyst varies considerably with the sort of reducing agent, the catalyst prepared by treatment with hydrogen showed the largest activity for condensation reaction. On the contrary, the reduction of the precipitate with isopropyl alcohol vapor, in place of hydrogen, prevented the formation of any condensation products. The fact that only a small amount of higher ketones was obtained when the catalyst reduced by isopropyl alcohol was used is interesting; probably, the most effective and simplest way to suppress the formation of condensation products is to use precipitates reduced with isopropyl alcohol. When the copper catalyst, prepared by treatment with sodium hydroxide followed by reduction with carbon monoxide, was used at 300°C, the condensation product was obtained, while the copper catalyst prepared with potassium

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[8] E. Suito and K. Takiyama, This Bulletin, **28**, 305 (1955).

carbonate acted only to dehydrogenate isopropyl alcohol to acetone at all temperatures.

The dehydrogenation activity of reduced copper catalysts depends also upon the temperature at which the oxide is reduced with the reducing agent and upon the velocity with which the reducing agent is passed over the oxide. The reduction of copper oxide with hydrogen is an exothermic reaction; the heat of reaction may accumulate on a part of the catalyst. Accordingly, this may cause sintering. On the other hand, when isopropyl alcohol was used as the reducing agent, the catalytic activity of dehydrogenation was not affected by the reducing temperature.

When isopropyl alcohol was passed over reduced copper, a small amount of isobutylmethylcarbinol was obtained. This compound is formed by the hydrogenation of isobutyl methyl ketone. Further, the present authors*3 have found that the copper catalysts changed *l*-menthol to *l*-menthone, *d*-isomenthone, thymol, isomenthol and neomenthol, and allyl alcohol to acrolein, propargylaldehyde, propionaldehyde, and *n*-propyl alcohol, and the mixture of cyclohexene and hydrogen to cyclohexane. The reduced copper, therefore, is an effective catalyst for the hydrogenation.

Pease and Stewart(9) found that the addition of carbon monoxide to materials lowered the hydrogenation activity of a copper catalyst. When, however, the copper catalysts prepared by the reduction with carbon monoxide or hydrogen were used, isobutylmethylcarbinol was obtained. In this case, therefore, carbon monoxide seems to act somewhat as a poison with regard to the copper catalyst.

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*3 The results of their, investigation were presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966; some of them were also presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

9) R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, **47**, 1235 (1925).