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

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Although there are a large number of patents and are latively small number of reports concerning the vapor phase dehydrogenation of isopropyl alcohol to acetone, the majority deal with the use of copper in some form as the catalysts. Sabatier[2] found that reduced copper heated at 200∼300°C is a suitable catalyst for the dehydrogenation of alcohols to aldehydes or ketones with no side reaction, and he showed that isopropyl alcohol, in the presence of reduced copper, is dehydrogenated to acetone slowly at 150°C, and rapidly and smoothly in the whole range of temperatures between 250°C and 430°C without the formation of a large amount of propylene. This method was improved by Bouveault[3], Armstrong[4] and Palmer[5]. A remarkable addition to the knowledge of the contact action of reduced copper was made by Komatsu[6], who found that reduced copper has the property of promoting not only the dehydrogenation but also dehydration of alcohols and that isopropyl alcohol is transformed into acetone and propylene by exposure to high temperature (300°C). Platonow et al.[7] found that in the presence of copper dehydrogenation of isopropyl alcohol at 300°C furnishes 53.2% of the theoretical yield of acetone. Moreover, Katsuno[8] reported the synthesis of acetone from isopropyl alcohol, using copper-active-carbon or copper-kieselguhr as a catalyst. Dunbar and Arnold[9] also used a copper-chromium-oxide catalyst with considerable success in the dehydrogenation of isopropyl alcohol.

The reduced copper is little used at present for the industrial synthesis of ketones from alcohols. However, copper is considered as the most important component in the majority of widely used mixed catalysts. Therefore, the behavior of the reduced copper catalyst will be of special interest for the interpretation of the mechanism of catalysis with mixed copper catalysts.

Earlier, Frolich et al.[10] found that the copper catalyst prepared by precipitation with sodium hydroxide is more active in the decomposition of methanol than that precipitated with ammonia, and Fischer and Meyer[11] studied the influence of the precipitants on the

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[1] Previous paper, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 681 (1959).

* The major part of this research was presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April 3, 1958.

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[2] P. Sabatier and J. B. Senderens, *Compt. rend.*, **136**, 738, 921, 983 (1903); P. Sabatier and J. B. Senderens, *Bull. soc. chim. France*, (3) 33, 263 (1905); P. Sabatier, "Die Katalyse in der Organischen Chemie", Akademische Verlagsgesellschaft m. b. H., Leipzig (1927).

[3] L. Bouveault, *Bull. soc. chim. France*, (4) 3, 119 (1908).

[4] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, **A97**, 259 (1920).

[5] W. G. Palmer, *Proc. Roy. Soc.*, **A98**, 13 (1920); W. G. Palmer, ibid., **A99**, 412 (1921); W. G. Palmer, ibid., **A101**, 175 (1922); W. G. Palmer and F. H. Constable, ibid., **A106**, 250 (1924).

[6] S. Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A7**, 85 (1924).

[7] M. S. Platonow, S. B. Anissimow and W. M. Krascheninnikowa, *Ber.*, **69**, 1050 (1936).

[8] M. Katsuno, *J. Soc. Chem. Ind. Japan*, (*Kogyo Kagaku Zasshi*), **45**, 1026 (1942); M. Katsuno, ibid., **46**, 109 (1943).

[9] R. E. Dunbar and M. R. Arnold, *J. Org. Chem.*, **10**, 501 (1945).

[10] P. K. Frolich, M. R. Fenske, L. R. Perry and N. L. Hurd, *J. Am. Chem. Soc.*, **51**, 187 (1929).

[11] F. Fischer and K. Meyer, *Brennstoff Chem.*, **12**, 225 (1931).

nickel-thoria-kieselguhr catalyst, which is used as a catalyst for the Fischer-Tropsch synthesis. For this catalyst potassium carbonate was the best precipitant and the preparation using sodium hydroxide or potassium hydroxide was virtually inactive. Further, Niwa and Yamaguchi[12] reported that the activity of the copper catalyst prepared with sodium hydroxide is greater than that treated with ammonium carbonate.

As no comparative study of the action of reduced copper catalysts prepared with a number of precipitants upon secondary alcohols has been reported, the present work has been undertaken to discover how the reaction temperature and the precipitant influence the activity and the behavior of the catalysts, and furthermore to find the most suitable condition and the most suitable catalyst for the preparation of acetone from isopropyl alcohol. Experiments were carried out at several temperatures between 185°C and 325°C, and five different precipitants, i. e. sodium hydroxide, potassium hydroxide, potassium carbonate, sodium bicarbonate and potassium bicarbonate, were used.

Experimental

Purification of Isopropyl Alcohol and Acetone.—The isopropyl alcohol used in this research was purified, after being dried with anhydrous potassium carbonate, by fractionation through a Widmer column: b. p. 82~82.5°C, n_D^{25} 1.3753, d_4^{25} 0.7811. Acetone was also purified in an analogous manner: b. p. 56.2~56.3°C, n_D^{25} 1.3564, d_4^{25} 0.7844.

Preparation of Catalysts.—Komatsu and Kurata[13] previously found that the reduced copper catalysts derived from copper sulfate and copper nitrate act to promote both dehydrogenation and dehydration of *l*-menthol. The degree of dehydration, however, was smaller with the catalyst prepared from copper nitrate than with that from copper sulfate under the same conditions. Consequently, the present author used copper nitrate as the starting material to prepare the dehydrogenation catalyst. Copper nitrate was prepared from electrolytic copper and nitric acid, and was purified by recrystallization. The catalysts are classified into Cu I, II, III, IV and V, as shown in Table I. These catalysts were prepared similarly except for the species and amount of the precipitant. For example, Cu I was prepared as follows: A solution of 30 g. of cupric nitrate hexahydrate in 900 ml. of distilled water was kept at 90°C. A sodium hydroxide solution, prepared from 300 ml. of distilled water and 15 g. of sodium hydroxide, was brought to the same temperature and added rapidly to the stirred copper nitrate solution. After the mixture was stirred at this temperature for 30 min., the precipitate was washed by decantation with a copious amount of warm water (at 70°C), collected on a glass filter, dried in an electric oven at 105°C for 10 hr., powdered in an agate mortar and finally stored in a stoppered bottle. It has been reported[14] that the occluded or absorbed impurities (mainly anions) in the preparation of reduced copper influence the activity. Accordingly, to minimize the inclusion of such impurities dilute solutions were used for precipitation and the resulting precipitates were then washed well with distilled water by decantation. The chemicals used were of the purest reagent grade and all vessels were washed with nitric acid and rinsed with distilled water.

TABLE I. PREPARATION OF CATALYSTS

Catalyst	Precipitant	Amount of precipitant g.	Distilled water ml.	Color of catalyst
Cu I	NaOH	15	300	black
Cu II	KOH	24	500	black
Cu III	K_2CO_3	25	500	dark brown
Cu IV	$NaHCO_3$	30	300	yellowish green
Cu V	$KHCO_3$	40	400	yellowish green

Apparatus.—The apparatus, illustrated diagrammatically in Fig. 1, is designed to measure the ratio of dehydrogenation and dehydration by the catalysts. Hydrogen coming from the reservoir (A) was passed through a tube (C) containing heated copper gauze to remove the oxygen present in the hydrogen by converting it into water, and then through a bottle (D) containing a 30% sodium hydroxide solution

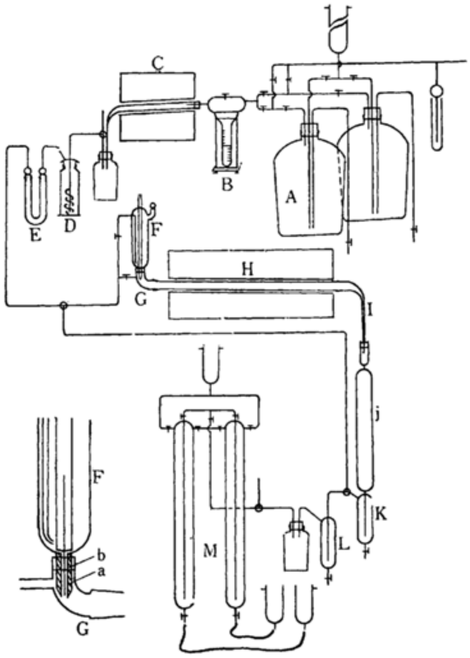

Fig. 1. Apparatus.

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[12] M. Niwa and M. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 73, 159, 162 (1952).

[13] S. Komatsu and M. Kurata, *Mem. Coll. Sci. Kyoto Imp. Univ.*, A8, 147 (1925).

[14] H. Hasegawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 58, 334 (1955).

and a solid sodium hydroxide tube (E). The hydrogen flow was measured by passing it through a calibrated flowmeter (B). The reaction tube (H) was a hard glass tube of 1 m. length and 18 mm. inside diameter, and was set in a combustion furnace and in this tube 10 g. of the catalyst to be used was spread in a length of approximately 70 cm. This tube was inclined at an angle of about 5° to insure proper drainage of the liquid product and the temperature was measured by a thermometer at a position of 30 cm. from the exit end of the catalyst bed. A rate of flow of the sample can be kept approximately constant by varying the extent of the insertion of the tungsten wire (a) into the capillary (b) (Fig. 1), and connecting the funnel (F) with a receiver (K) to keep the pressure equal. The sample is vaporized through a vaporizer (G) before reaching the catalyst. This vaporizer was made of a hard glass tube filled with glass wool and heated to a desired temperature by a heater. The reaction tube was connected with a condenser (J) by means of an adapter (I). The liquid product condensed was collected in a receiver (K) and uncondensed vapor was absorbed in water in a bottle (L). Noncondensable gas was collected in a gas-holder (M).

Procedure.—The catalyst was placed in the reaction tube and the apparatus was tested for gas-tightness. After the tube was filled with hydrogen, the furnace was heated to the reduction temperature, and was kept at this temperature for the period of reduction. Care was taken during the reduction to avoid the overheating of the catalyst as the reaction is exothermic, and the reduction temperature was always below 185°C. The standard flow rate of hydrogen (measured at room temperature) was 750~900 ml. per hour. The reduction was continued until the color of the catalyst changed from black or yellowish green to reddish purple and then the hydrogen supply was stopped and the resulting catalyst was heated to the operating temperature. Experiments were performed at 185, 250, 305 and 325°C under the ordinary pressure, and in the case of the copper catalyst precipitated with sodium hydroxide, further experiments were carried out at 220°C and 280°C, and during the run which lasted for several hours, the temperature was maintained within about ±5°C of the desired temperature. A definite weight of the alcohol or acetone was supplied from the dropping funnel (F) at the predetermined rate. The vapor coming out from the reaction tube was condensed by passing through a condenser cooled with ice water and the escaped gas from the condenser was passed into ice-cooled distilled water (50 ml.) to catch condensable products completely. The noncondensable gas which came out of the receiver (L) was collected in a gas-holder and its volume was measured from time to time. At the end of the run, the weight of liquid products collected in the receiver, that absorbed by water in the bottle, and the volume of noncondensable gas in the gas-holder were measured. The condensed product and the water solution in the bottle were combined. If an oily product

TABLE II. INFLUENCE OF PRECIPITANTS AND TEMPERATURES ON DEHYDROGENATION OF ISOPROPYL ALCOHOL

Exp. no.	Precipitant	Temp. °C	Isopropyl alcohol g.	Velocity g./hr.	Acetone g.	Oily product g.	Gas collected l.	Percentage of conversion* %
1	NaOH	185	39.69	10.82	21.78	0	8.57	57.9
2	KOH	185	38.81	12.25	19.71	0	7.95	54.9
3	K_2CO_3	185	39.04	11.71	18.39	0	7.38	50.7
4	$NaHCO_3$	185	38.83	11.95	19.95	0	8.06	55.7
5	$KHCO_3$	185	39.02	12.01	20.55	0	8.26	56.7
6	NaOH	220	39.49	10.53	20.06	9.26	9.64	65.5
7	NaOH	250	39.59	10.55	18.60	11.53	9.07	61.4
8	KOH	250	38.66	12.21	19.69	9.97	9.91	68.7
9	K_2CO_3	250	39.24	12.07	24.46	5.25	10.87	74.3
10	$NaHCO_3$	250	38.87	11.66	30.92	0	12.35	85.2
11	$KHCO_3$	250	38.78	11.08	30.96	0	12.36	85.5
12	NaOH	280	39.63	10.56	26.98	4.24	11.39	77.0
13	NaOH	305	39.18	11.47	33.55	0	13.63	93.3
14	KOH	305	38.86	11.96	33.51	0	13.63	94.1
15	K_2CO_3	305	39.36	11.52	34.33	0	13.51	92.0
16	$NaHCO_3$	305	38.93	12.29	34.77	0	13.75	94.7
17	$KHCO_3$	305	38.82	11.65	35.11	0	13.89	95.9
18	NaOH	325	38.96	11.40	34.41	0	13.91	95.7
19	KOH	325	38.87	11.96	34.43	0	14.03	96.7
20	K_2CO_3	325	39.32	11.80	35.15	0	13.87	94.6
21	$NaHCO_3$	325	38.91	11.12	35.44	0	14.01	96.6
22	$KHCO_3$	325	38.91	11.39	35.62	0	14.07	97.0

* Calculated from the volume of the gaseous product collected in each experiment on the assumption that original isopropyl alcohol is transformed completely into gases such as hydrogen or propylene.

was formed, this was separated from the water layer and washed with a known volume (20 ml.) of distilled water. If the oily product was not formed, the aqueous solution was analyzed by the method described below.

Analysis of the Products.—The aqueous solution was recognized to consist of acetone and unchanged isopropyl alcohol by the preparation of the 2,4-dinitrophenylhydrazone and the phenylurethan, respectively, and the content of the acetone was determined by the hydroxylamine method[15]. The reliability of this analytical method was checked by titrating a known sample of acetone and the result was found to be correct within experimental errors. The oily product, which was obtained in some of the experiments, was dried with anhydrous sodium sulfate and then fractionally distilled through a Widmer column. Isobutyl methyl ketone was present in a fraction that showed the properties: b. p. 110∼125°C, n_D^{25} 1.3963, d_4^{25} 0.7908, and a semicarbazone, m. p. 133∼133.5°C and a 2,4-dinitrophenylhydrazone, m. p. 93.5∼94°C were obtained and showed no depression of the melting points when mixed with the known derivatives of isobutyl methyl ketone. Diisobutyl ketone was found mainly in a fraction as follows: b. p. 160∼170°C, n_D^{25} 1.4115, d_4^{25} 0.8012, and it was identified on the basis of the preparation of the 2,4-dinitrophenylhydrazone, m. p. 92∼92.5°C and the semicarbazone, m. p. 122∼122.5°C which were shown to be the corresponding derivatives of diisobutyl ketone by the mixed melting point determination. The formation of unsaturated and hydroxy ketones such as mesityl oxide, phorone and diacetone alcohol, was not detected in the oily product.

Results and Discussion

The influence of the precipitants and reaction temperatures on the activity and the selectivity of the copper catalysts is summarized in Table II. Experiments were controlled so as to regulate the reducing condition of the precipitate* with hydrogen as far as possible and further to maintain the constancy of the velocity of the isopropyl alcohol passing over the catalyst. To find the difference in the reaction products on varying the reaction temperature and the optimum temperature for dehydrogenation, the catalytic reaction was performed at 185, 250, 305 and 325°C. Since isopropyl alcohol was not changed in the absence of the catalysts over the range (185∼325°C) of temperatures, the changes shown in Table II do not involve the simple pyrolysis of isopropyl alcohol. The yield of acetone shown in Table II does not necessarily represent the maximum yield but is an average of three or four experiments under the constant operating condition. However the fluctuation in the yields of acetone and of the oily product obtained by the repeated experiments was less than 1 per cent, and thus within the limit of experimental error in the determination of acetone.

Influence of the Reaction Temperatures on the Dehydrogenating Activity of Reduced Copper.—The dehydrogenating activity of the various copper catalysts depends upon the temperature at which the reaction is carried out. Using a copper catalyst, the equilibrium constant for the reaction of isopropyl alcohol to form acetone and hydrogen has been measured[16]. Though the results obtained by various workers show little agreement, it is accepted that the equilibrium transfers to the direction of dehydrogenation at the reaction temperature above 220°C. Consequently, at low temperatures the copper catalyst has a poor activity for dehydrogenation. In the present research all catalysts act to promote dehydrogenation of isopropyl alcohol at high temperatures, and at the highest reaction temperature (325°C) the dehydrogenation of isopropyl alcohol to acetone is the highest.

Influence of the Precipitants on the Dehydrogenating Activity of Reduced Copper.—As shown in Table II, the dehydrogenating activity of the copper catalysts varies considerably with the sort of precipitants, and the catalyst prepared by the treatment with potassium bicarbonate showed the largest activity. On the contrary, the catalyst prepared with sodium hydroxide showed the smallest activity. The dehydrogenating activity of the copper catalysts prepared with various precipitants is in the following order: $KHCO_3 > NaHCO_3 > K_2CO_3 > KOH > NaOH$.

The author presumed that the catalysts prepared with alkali bicarbonates possess a capillary or a porous structure on account of the evolution of carbon dioxide at precipitation or the hydrogen treatment, and this is one of the reasons for the large dehydrogenating activity of the catalysts.

The Relation between the Amount of Gas Evolved and that of Acetone Produced.—When the oily product was not formed, the difference between the theoretical yield of acetone and the percentage of conversion was a few per cent. Therefore, the dehydration of isopropyl alcohol to propylene seems to occur little at temperatures below 325°C. Accordingly, the dehydration is not an important factor from the viewpoint of dehydrogenation. When the

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[15] M. Katsuno, *J. Soc. Chem. Ind. Japan*, (*Kogyo Kagaku Zasshi*), **46**, 112 (1943).

* Copper compound prepared from copper nitrate by "precipitant".

[16] G. S. Parks and H. M. Huffman, "Free Energies of Some Organic Compounds", Reinhold Pub. Corp., New York (1932), p. 22; H. J. Kolb and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **67**, 1084 (1945); A. H. Cubberley and M. B. Mueller, ibid., **68**, 1149 (1946).

oily product was not formed, a proportional relation was found between the amount of the gas evolved and that of acetone produced, namely the greater the amount of the evolved gas, the greater the amount of acetone. This is reasonably accounted for by considering that both the gas and acetone result from the dehydrogenation of isopropyl alcohol. Also the amount of the gas collected increased proportionally with the temperature rise.

The Relation between the Amount of Gas Evolved and the Reaction Time.—A test was made by the following method to see whether the catalytic activity is kept constant during the whole reaction time or not. The amount of gas evolved (Table II) was measured at intervals of 15~20 min. and the volumes of the evolved gas reduced to the normal state were plotted against the reaction time in Fig. 2. Since the evolution of the gas is constant during the reaction time as seen in Fig. 2, it is concluded that the sustained activity of the catalyst holds over the period of the operation. Thus the constancy of the activity of the catalyst can be detected by inspecting the amount of the gas evolved.

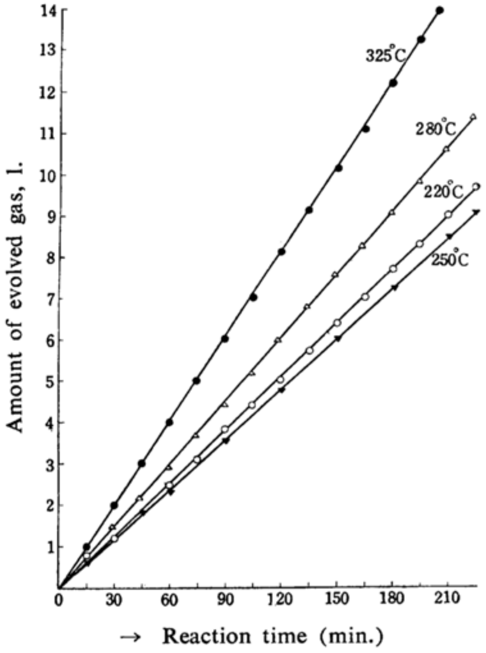
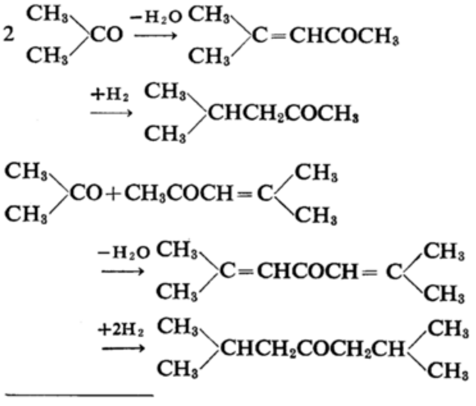


Fig. 2. The amount of evolved gas as a function of the reaction time for various temperatures (precipitant: NaOH)

Two Types of Reduced Copper Catalysts.—It was found that there are two distinct types of reduced copper catalysts. One of them catalyzes the decomposition of isopropyl alcohol to acetone and hydrogen; that is, promotes dehydrogenation. Cu IV and Cu V belong to this type. The other type catalyzes the conversion of isopropyl alcohol into isobutyl methyl ketone and diisobutyl ketone together with acetone and hydrogen, that is, promotes both dehydrogenation and condensation. Cu I, Cu II and Cu III belong to this type. Further, there is a distinct difference in color before reduction between these two types of catalysts. As shown in Table I, the precipitates prepared with sodium hydroxide, potassium hydroxide, and potassium carbonate are black or dark brown in color. On the contrary, those prepared with potassium bicarbonate and sodium bicarbonate have a yellowish green color. Cu I and Cu II were nearly equal in the activity for the production of both the oily product and acetone, and Cu III has a relatively poor activity for the formation of the oily product. Also Cu IV and Cu V were entirely inactive to the production of the oily product. There is thus a marked difference of activity between the copper catalysts prepared with alkali hydroxides and those prepared with alkali bicarbonates with respect to the relative amount of acetone formed. Cu I and Cu II are especially convenient for preparing isobutyl methyl ketone and diisobutyl ketone. The new synthetic process of these ketones, which consists in passing isopropyl alcohol over Cu I or Cu II under the atmospheric pressure at 220~250°C, is now proposed as one which has not yet been observed with a copper catalyst alone.

Mechanism of the Condensation Reaction.—Lassieur[17] found that a mixture of acetone and hydrogen, when it is passed over reduced nickel at 200~300°C, yields mesityl oxide, isobutyl methyl ketone, phorone and diisobutyl ketone. Concerning the mechanism of this reaction he showed that acetone undergoes condensation to give mesityl oxide and phorone, and these unsaturated ketones are then reduced by hydrogen.



$$2\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle CO \xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle C=CHCOCH_3$$

$$\xrightarrow{+H_2} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle CHCH_2COCH_3$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle CO+CH_3COCH=C\langle\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

$$\xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle C=CHCOCH=C\langle\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

$$\xrightarrow{+2H_2} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!\rangle CHCH_2COCH_2CH\langle\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

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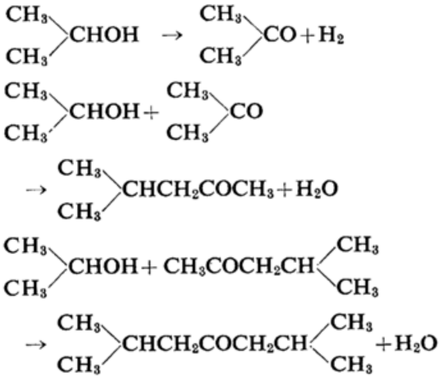
[17] M. A. Lassieur, *Compt. rend.*, **156**, 795 (1913).

On the other hand, Ipatieff and Haensel[18] found that in the presence of a copper-alumina or a copper-zinc-oxide-alumina catalyst, a mixture of isopropyl alcohol and acetone is converted into isobutyl methyl ketone and diisobutyl ketone, and that in the absence of isopropyl alcohol, acetone reacts to give only small amounts of mesityl oxide and phorone, and they reported that isobutyl methyl ketone is obtained by a regular ketonic condensation of acetone to diacetone alcohol and then a hydrogen disproportionation between isopropyl alcohol and diacetone alcohol.

$$2\ CH_3COCH_3 \rightleftarrows (CH_3)_2COHCH_2COCH_3$$
$$(CH_3)_2COHCH_2COCH_3+CH_3CHOHCH_3$$
$$\rightarrow (CH_3)_2CHCH_2COCH_3+CH_3COCH_3+H_2O$$

In the present research, isobutyl methyl ketone and diisobutyl ketone were obtained from isopropyl alcohol with the copper catalyst prepared with sodium hydroxide or potassium hydroxide, but the formation of mesityl oxide, diacetone alcohol and phorone was not observed. Further, it was confirmed that, when the catalytic reaction is carried out with acetone alone under a condition similar to that in the experiment with isopropyl alcohol, acetone is not changed. It is generally recognized that hydrogen atoms of a methyl group adjacent to a carbonyl group are reactive. From these considerations, the formation of the reaction products obtained by the present author can be illustrated by the following schemes:



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH \rightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO+H_2$$
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH+\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO$$
$$\rightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHCH_2COCH_3+H_2O$$
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH+CH_3COCH_2CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$
$$\rightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHCH_2COCH_2CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. +H_2O$$

Further, the following results have been obtained by the present author: (1) Alicyclic alcohols (cyclohexanol and *l*-menthol) do not undergo alcohol-ketone condensation under a condition similar to that employed for isopropyl alcohol[1], consequently giving no higher ketones. (2) When *sec*-butyl alcohol is passed over reduced copper, 5-methyl-3-heptanone together with ethyl methyl ketone is formed.* From these results it seems that the condensation reaction takes place when three hydrogen atoms are attached to the alpha carbon atom of a carbonyl group, but is not favored when only two hydrogen atoms are attached. The alcohols which on dehydrogenation can yield ketones containing a methyl group adjacent to the carbonyl group can condense with the ketones produced.

Up to the present, isobutyl methyl ketone has been prepared by the following method: Acetone is first condensed in the presence of bases to give diacetone alcohol, and this diacetone alcohol is dehydrated by heating with an acid such as sulfuric acid to give mesityl oxide, and then the mesityl oxide thus formed is hydrogenated in the presence of a copper catalyst to give isobutyl methyl ketone. It is of interest that isobutyl methyl ketone can be prepared in one step by passing isopropyl alcohol over reduced copper as described above.

Summary

In order to determine whether the dehydrogenating activity of reduced copper is affected by the species of precipitants in the preparation, the dehydrogenation of isopropyl alcohol to acetone was studied by using five different precipitants, i. e. sodium hydroxide, potassium hydroxide, potassium carbonate, sodium bicarbonate and potassium bicarbonate. The dehydrogenation was the highest with no side reaction at 305~325°C, especially when potassium bicarbonate was used as precipitant.

When the copper catalysts, prepared with sodium hydroxide, potassium hydroxide and potassium carbonate, were used, condensation together with dehydrogenation occurred. The formation of higher ketones is explained by the assumption of intermolecular dehydration between acetone and original isopropyl alcohol.

The author wishes to express his hearty thanks to Professor T. Matsuura for his kind guidance and valuable suggestions throughout this work.

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[18] V. N. Ipatieff and V. Haensel, *J. Org. Chem.*, 7, 189 (1942).

* Presented at the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.