Dehydrogenation of Secondary Alcohols with Reduced Copper. V[1]. *Catalytic Dehydrogenation of sec-Butyl Alcohol**

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The preparation of copper catalysts, and the production of acetone and oily products (isobutyl methyl ketone and diisobutyl ketone) from isopropyl alcohol were described in detail in the previous papers[1,2], and it has been found that two distinct types of copper catalysts are obtained according to the precipitants. One type catalyses the decomposition of isopropyl alcohol to acetone and hydrogen. The other type catalyses the conversion of isopropyl alcohol into isobutyl methyl ketone and diisobutyl ketone together with acetone and hydrogen. That is to say, the copper catalysts prepared by reducing precipitates obtained by adding a solution of potassium bicarbonate or potassium carbonate to a solution of copper nitrate at 22°C gave the highest yield of acetone when used at the highest reaction temperature (325°C). On the other hand, the copper catalyst prepared by the reduction of the precipitate obtained from sodium hydroxide and copper nitrate at 22°C showed the greatest activity for the condensation of isopropyl alcohol. The

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

* The major part of this research was presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

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

TABLE I. INFLUENCE OF PRECIPITANTS AND THE REACTION TEMPERATURE ON THE DEHYDROGENATION OF *sec*-BUTYL ALCOHOL

Expt. No.	Precipitant	Temp. °C	*sec*-Butyl alcohol g.	Velocity g./hr.	Reaction product					Ketone in aq. soln. g.	Gas collected l.	Yield of ketone* mol. %	Percentage of conversion** %
					Yield g.	n_D^{25}	d_4^{25}	Ketone g.	Unchanged alcohol, g.				
1	NaOH	185	40.03	9.61	38.58	1.3862	0.8077	19.99	16.29	0.37	6.60	52.3	54.5
2	K_2CO_3	185	40.22	10.49	39.24	1.3840	0.8061	23.77	13.60	0.58	7.86	62.2	64.6
3	NaOH	220	40.08	10.02	38.76	1.3862	0.8105	26.15	7.67	0.52	8.61	68.4	71.0
4	K_2CO_3	220	40.03	11.72	38.59	1.3807	0.8057	28.90	8.22	0.82	9.45	76.3	78.1
5	NaOH	250	39.99	10.00	38.58	1.3802	0.8100	31.49	4.38	0.83	10.32	83.1	85.3
6	K_2CO_3	250	39.45	10.76	38.86	1.3793	0.8073	32.13	5.21	0.92	10.58	86.1	88.7
7	NaOH	280	40.07	10.23	38.41	1.3781	0.8077	33.40	3.44	0.91	10.95	88.0	90.3
8	K_2CO_3	280	40.22	10.06	38.38	1.3775	0.8060	34.68	2.70	0.98	11.33	91.2	93.2
9	NaOH	305	40.03	11.44	38.20	1.3777	0.8076	34.82	1.60	1.06	11.41	92.1	94.2
10	K_2CO_3	305	40.26	11.24	38.29	1.3774	0.8044	36.13	0.94	1.03	11.77	94.9	96.7
11	NaOH	325	40.06	10.23	38.40	1.3775	0.8081	35.42	1.43	1.10	11.63	93.7	96.0
12	K_2CO_3	325	40.22	10.63	38.46	1.3779	0.8081	36.20	0.55	1.17	11.86	95.5	97.5

* This value was an average of three determinations under the constant operating condition, but the fluctuation in the yield of ethyl methyl ketone obtained by the repeated experiments was less than 1%.

** The percentage of the volume of the gaseous product to the theoretical calculated on the assumption that original *sec*-butyl alcohol were transformed completely either into the ketone and hydrogen or into butylenes and water.

TABLE II. THE PROPERTIES OF DISTILLED FRACTIONS OF EXPERIMENT No. 3

Fraction	B. p. °C	Yield %	n_D^{25}	d_4^{25}	Ketone %	Unchanged alcohol %
1	72.5～ 80	40.31	1.3788	0.8221	81.14	8.52
2	80 ～ 85	19.58	1.3799	0.8050	77.99	19.71
3	85 ～ 90	14.14	1.3818	0.7990	66.82	32.16
4	90 ～100	10.11	1.3897	0.8007	25.77	73.01
5	100 ～155	1.51	1.4016	0.8060	—	—
6	155 ～158	12.53	1.4129	0.8162	—	—
7	residue	0.34	1.4194	—	—	—

TABLE III. THE PROPERTIES OF DISTILLED FRACTIONS OF EXPERIMENT No. 4

Fraction	B. p. °C	Yield %	n_D^{25}	d_4^{25}	Ketone %	Unchanged alcohol %
1	71.5～80	36.45	1.3782	0.8170	86.84	6.09
2	80 ～85	41.15	1.3782	0.8016	83.45	16.09
3	85 ～90	7.29	1.3814	0.7999	69.12	30.78
4	90 ～98	11.45	1.3907	0.8022	19.32	79.12
5	residue	1.68	1.4032	—	—	—

TABLE IV. THE PROPERTIES OF DISTILLED FRACTIONS OF EXPERIMENT NO. 11

Fraction	B. p. °C	Yield %	n_D^{25}	d_4^{25}	Ketone %	Unchanged alcohol %
1	71.5~80	66.84	1.3770	0.8136	93.07	1.48
2	80 ~81	29.36	1.3770	0.8006	94.71	4.50
3	residue	1.17	1.3852	—	—	—

TABLE V. THE PROPERTIES OF DISTILLED FRACTIONS OF EXPERIMENT NO. 12

Fraction	B. p. °C	Yield %	n_D^{25}	d_4^{25}	Ketone %	Unchanged alcohol %
1	71.5~80	67.00	1.3772	0.8100	94.12	0.66
2	80 ~80.8	28.50	1.3772	0.8000	96.32	3.06
3	residue	1.24	1.4085	—	—	—

highest yield of the condensation products was obtained with the catalyst at the reaction temperature of 220°C.

The present paper describes the results of similar experiments with *sec*-butyl alcohol and the two types of catalysts. In the present research, one type was prepared with potassium carbonate, and the other type with sodium hydroxide. The vapor phase dehydrogenation of *sec*-butyl alcohol was carried out with these two types of catalysts at several temperatures between 185 and 325°C.

Up to the present, there have been a large number of patents and a few reports about the vapor phase dehydrogenation of *sec*-butyl alcohol to ethyl methyl ketone, and the majority deal with the use of copper mixed with other metals. Dunbar and Arnold[3] found that in the presence of a copper-chromium-oxide catalyst, the dehydrogenation of *sec*-butyl alcohol at 300~325°C furnishes 68% of ethyl methyl ketone.

Experimental

Purification of *sec*-Butyl Alcohol.—Commercial extra pure *sec*-butyl alcohol was purified by being dried with quick lime, followed by fractional distillation. B. p. 98.7~99.2°C, n_D^{25} 1.3950, d_4^{25} 0.8029.

Preparation of Catalysts. — The two specimens of copper catalysts used in the present research are identical with Cu VII and Cu IX which were described in the preceding paper[1].

Apparatus and Procedure. — The apparatus for the dehydrogenation was exactly the same as that previously described[2]. The precipitate (10 g.) to be reduced was placed in the reaction tube. After the tube was filled with hydrogen, the furnace was heated to the reduction temperature below 185°C. Hydrogen was passed through the tube at the rate of 750~900 ml. per hour, and *sec*-butyl alcohol was passed under the ordinary pressure over the catalyst heated to 185, 220, 250, 280, 305 and 325°C, respectively. The vapor coming out from the reaction tube was condensed by passing it through a condenser cooled with ice water and the gas escaping from the condenser was scrubbed with ice-cooled distilled water (50 ml.) to remove the ethyl methyl ketone and the unchanged alcohol from the hydrogen stream. The volume of the non-condensable gas was measured at intervals of 15~30 min. At the end of a run, the weight of liquid products and of that absorbed by the distilled water were measured.

Analysis of the Products.—The relative content of ethyl methyl ketone and unchanged *sec*-butyl alcohol in the liquid product was determined by the hydroxylamine method[4] and the acetic anhydride-pyridine method[5], respectively. The product in the aqueous solution was recognized to be ethyl methyl ketone by the preparation of its 2,4-dinitrophenylhydrazone (m. p. 118°C) and semicarbazone (m. p. 144°C), and further its content was determined by the hydroxylamine method. The reliability of these analytical methods was checked by titrating the known samples of ethyl methyl ketone and *sec*-butyl alcohol, respectively. The result was found to be correct within experimental errors. The liquid product was dried with anhydrous sodium sulfate in every case, and then fractionally distilled through an electrically heated Widmer column. As examples, the properties of distilled fractions of Experiments No. 3, 4, 11 and 12 in Table I are shown in Tables II, III, IV and V.

Fractions 1, 2 and 3 in Table II correspond in physical constants to ethyl methyl ketone. The 2,4-dinitrophenylhydrazone and semicarbazone melted at 118 and 144°C, respectively, both alone and in admixture with the corresponding derivatives of authentic ethyl methyl ketone. From Fraction 4 a phenylurethan was obtained, which was identified as that of *sec*-butyl alcohol by mixing with an authentic specimen. Fraction 6 gave a crystalline

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

[4] M. Katsuno, *J. Soc. Chem. Ind., Japan* (*Kōgyō Kagaku Zassi*), **46**, 112 (1943).

[5] C. L. Ogg, W. L. Porter and C. O. Willits, *Ind. Eng. Chem. Anal. Ed.*, **17**, 394 (1945).

semicarbazone melting at 95~96°C which was identified with the semicarbazone of 5-methyl-3-heptanone[6]. Judging from the physical constants of this fraction, the semicarbazone and the formation of isobutyl methyl ketone from isopropyl alcohol as described previously, it seems that Fraction 6 (b. p. 155~158°C) consists mainly of 5-methyl-3-heptanone. The formation of unsaturated and hydroxy ketones such as 5-methyl-4-hepten-3-one and 5-methyl-5-hydroxy-3-heptanone was not detected in the reaction product. As shown in Table III, no fraction corresponding in the boiling point to 5-methyl-3-heptanone was found in the reaction product obtained by employing the copper catalyst prepared with potassium carbonate.

Results and Discussion

The results are summarized in Table I. In the range of 185 to 325°C *sec*-butyl alcohol does not decompose in the absence of catalysts. Consequently the changes observed in the present research do not involve the simple pyrolysis of *sec*-butyl alcohol. The yield of ethyl methyl ketone and the percentage of conversion recorded in Table I do not necessarily represent the maximum values. The difference between the yield of ethyl methyl ketone and the percentage of conversion was a few per cent. Therefore, the dehydration of *sec*-butyl alcohol to butylenes seems to occur little at temperatures below 325°C, and the yield of total ethyl methyl ketone agrees closely with the value calculated from the amount of the escaping gas in each experiment.

Influence of the Reaction Temperature on the Dehydrogenating Activity of Reduced Copper.— In Fig. 1 the yield of ethyl methyl ketone is plotted against the reaction temperature. As seen from Tables I—V and Fig. 1, the rates of the dehydrogenation of *sec*-butyl alcohol to ethyl methyl ketone and that of the conversion of *sec*-butyl alcohol to 5-methyl-3-heptanone depend upon the reaction temperature. The reaction products obtained at the higher temperatures contained more ethyl methyl ketone than those obtained at the lower temperatures, and the conversion of *sec*-butyl alcohol to ethyl methyl ketone was very high at the highest reaction temperature (325°C) so that unchanged *sec*-butyl alcohol was scarcely found in the reaction products. The higher ketone was not obtained at all or only a little was obtained except in Experiment No. 3, where 5-methyl-3-heptanone was produced along with ethyl methyl ketone.

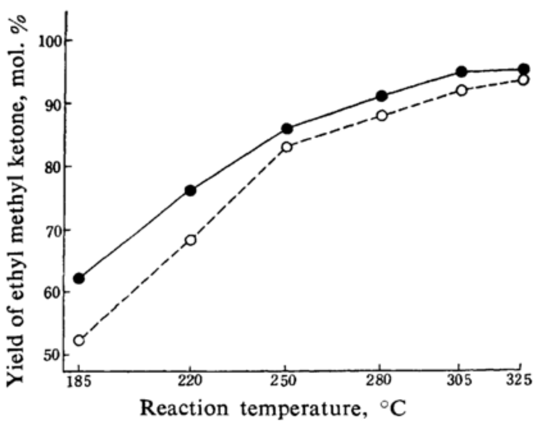

Fig. 1. The effect of temperature on the dehydrogenation of *sec*-butyl alcohol with two types of copper catalysts.

●: Catalyst prepared with potassium carbonate.

○: Catalyst prepared with sodium hydroxide.

The volume of the evolved gas, mainly consisting of hydrogen, is plotted against the reaction time in Figs. 2 and 3, which show that the activity of the catalysts holds over the period of the operation. Further, a parallelism exists between the amount of gas evolved and the temperature.

Two Types of Reduced Copper. — As in the case of isopropyl alcohol, the copper catalyst prepared with potassium carbonate promotes dehydrogenation alone, but that prepared with sodium hydroxide catalyses not only dehydrogenation but also condensation reactions.

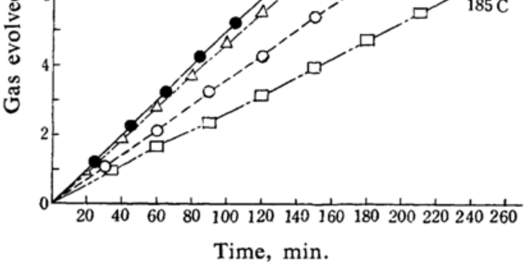

Fig. 2. Relation between volume of gas evolved and time of reaction at various temperatures (Precipitant in the preparation of catalyst; NaOH).

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6) 5-Methyl-3-heptanone was prepared according to Powell and Secoy's method: Ethyl methyl ketone was first condensed in the presence of powdered barium oxide, and the 5-methyl-4-hepten-3-one thus formed was reduced selectively over platinum catalyst to give 5-methyl-3-heptanone, and its semicarbazone melted at 95~96°C. S. G. Powell and C. H. Secoy, *J. Am. Chem. Soc.*, 53, 765 (1931).

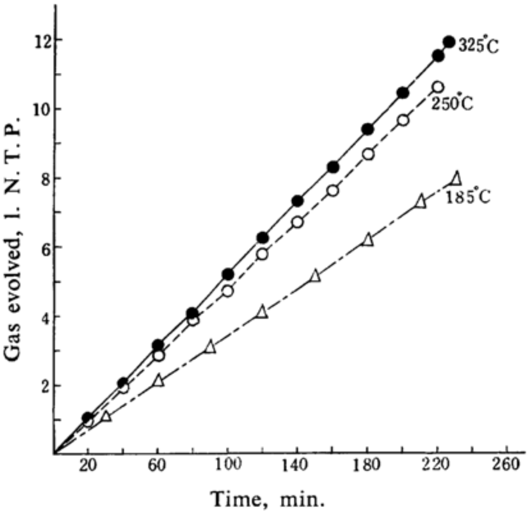

Fig. 3. Relation between volume of gas evolved and time of reaction at various temperatures (Precipitant in the preparation of catalyst; K_2CO_3).

The Activity of Dehydrogenating Various Secondary Alcohols to the Corresponding Ketones. — The copper catalyst prepared by reduction of the precipitate obtained by adding an excess of a dilute sodium hydroxide solution to an aqueous solution of cupric nitrate changed isoborneol⁷⁾ to camphor (yield 96%) at 220°C, *l*-menthol⁸⁾ to menthones (*d*-isomenthone and *l*-menthone) (yield 74%) and a small amount of thymol under similar conditions, and cyclohexanol⁸⁾ to cyclohexanone (yield 63%) and a trace of phenol. In the case of isopropyl alcohol¹⁾, the yield of acetone amounted to about 93% at 325°C, while at 220°C the yield of acetone decreased to 35% with the formation of the condensation products, isobutyl methyl ketone and diisobutyl ketone. *sec*-Butyl alcohol behaved similarly, giving a condensation product (5-methyl-3-heptanone) along with ethyl methyl ketone at 220°C but the latter alone did so at higher temperatures with greater ease than isopropyl alcohol.

Thus the copper catalyst is suitable for dehydrogenating secondary alcohols to the corresponding ketones, but the dehydrogenating and the condensing abilities of the copper catalyst vary with the species of alcohols, and it seemed that the alcohols which possess a methyl group adjacent to the hydroxylated carbon atom give rise to the condensation reaction.

5-Methyl-3-heptanone. — Up to the present, 5-methyl-3-heptanone has been prepared by the following methods: (1)⁶˒⁹⁾ *sec*-Butyl alcohol is first dehydrogenated to ethyl methyl ketone, and the latter is condensed in the presence of alkali or calcium carbide to give 5-methyl-4-hepten-3-one and then the unsaturated ketone thus formed is hydrogenated to 5-methyl-3-heptanone. (2)¹⁰⁾ It is prepared by treating *sec*-butyl alcohol with ethyl methyl ketone in the vapor phase under pressure in the presence of a mixed catalyst with dehydrogenating and dehydrating properties. A new synthetic process for 5-methyl-3-heptanone, consisting in passing *sec*-butyl alcohol over reduced copper under the atmospheric pressure at 220°C, is now proposed.

Summary

It was confirmed that ethyl methyl ketone and 5-methyl-3-heptanone are produced from *sec*-butyl alcohol with reduced copper alone. Two distinct types of reduced copper were prepared by precipitation with sodium hydroxide and with potassium carbonate. They differ somewhat in their ability to promote dehydrogenation of *sec*-butyl alcohol and differ greatly in their power to bring about condensation. The copper catalyst prepared with potassium carbonate acts to dehydrogenate *sec*-butyl alcohol at all the temperatures examined (185~325°C), giving ethyl methyl ketone, but the catalyst prepared with sodium hydroxide acts to dehydrogenate and to condense simultaneously at a certain temperature (220°C), giving 5-methyl-3-heptanone along with ethyl methyl ketone, and this affords a new synthetic method for 5-methyl-3-heptanone. *sec*-Butyl alcohol was converted into ethyl methyl ketone in 94~96% yield with no side reaction by passing it over these catalysts at 325°C.

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7) T. Matsuura and K. Kawamoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 94 (1959).

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