The Catalytic Dehydrogenation of Alcohols with Reduced Copper under Ultraviolet Light[1]

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In order to investigate whether or not the dehydrogenation activity of the reduced copper is affected by ultraviolet light, the reaction of such alcohols as ethanol, 1-propanol, 2-propanol, and 1-butanol was carried out with reduced copper and ultraviolet light at 250°C. It was found that the conversion of alcohols and the yield of aldehydes were larger with the reduced copper under ultraviolet light than without the light, and that aldol condensation for the ethanol reaction was recognizable when the reduced copper catalyst was used without ultraviolet light.

Many papers have reported on the decomposition of alcohols with copper catalysts.[3-6] The main products of the formation of a complex[4,7] between the alcohols and the copper catalysts were found to be aldehydes, ketones, and esters. On the other hand, the photochemical reaction of alcohols has been carried out recently.[8,9]

It has been reported that the radical formation of alcohol under ultraviolet light produced mainly RR'-$\dot{C}$OH,[9] from which aldehyde, pinacol, and so on were obtained. Although the photo-oxidation of such reactants as alcohol, water, and carbon monoxide has been studied with ZnO[10] sensitized by ultraviolet light, the reaction of gaseous alcohol in the presence of a reduced copper catalyst and ultraviolet light has not been carried out. Accordingly, the present work was carried out in order to study the difference between the catalytic reaction of alcohols with the reduced copper alone and that with the reduced copper under ultraviolet light. It was found that the yield of aldehydes and the conversions of ethanol, 1-propanol, and 1-butanol increased considerably with the catalytic reaction under ultraviolet light, with the exception of 2-propanol, and that 1-butanol might be formed from ethanol through an aldol condensation mechanism with the catalyst without ultraviolet light.

Experimental

Preparation of Catalyst. Copper nitrate, the starting material, was prepared from electrolytic copper and nitric acid.

A mixture of 20 g of electrolytic copper in an aqueous solution of nitric acid (90 g of 60% HNO_3 and 90 m*l* of distilled water) was heated gradually on a sand bath.

After the electrolytic copper has been completely dissolved, the solution was diluted with the same amount of distilled water and filtered through a glass filter. The diluted solution was evaporated below 60°C to give crystals of cupric nitrate hexahydrate. The blue crystals were dried under reduced pressure for several hours. A solution of 30 g of cupric nitrate hexahydrate, prepared by the method described above 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 a 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 precipitates were reduced in the following ways. When hydrogen (or carbon monoxide) was passed through at the rate of 750—900 m*l* per hour over 10 g of the precipitate, the reduction temperature was always below 180°C in the case of hydrogen and below 140°C in the case of carbon monoxide, and the reduction time was 4—5 hr.

Apparatus and Procedure. The apparatus employed was similar to that used in the previous investigation,[6] with the exception that a low-pressure mercury lamp (UL1—8 DQ 80 W made by Ushio Electric Co., Ltd.) was inserted into the center of the reaction tube (Fig. 1). A definite amount (10 g) of the precipitate was spread in a Pyrex reaction tube (reaction part: 35 mm in inside diameter and 550 mm long), which was then 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 the reduction.

The resulting catalyst was then heated to the reaction temperature (250°C) under ordinary pressure. The alcohols (ethanol, 1-propanol, 2-propanol, and 1-butanol) purified by the ordinary method were passed through the tube at a constant flow rate of 7.2 to 9.3 g per hour (carrier gas, nitrogen).

1) The major part of this research was presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March 31, 1969.

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4) W. G. Palmer and F. H. Constable, *Proc. Roy. Soc.* (London), **106A**, 250 (1924).

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9) G. Gibson, *Trans. Faraday Soc.*, **53**, 914 (1957); D. Ingram, *ibid.*, **54**, 1304 (1958).

10) I. Komuro, Y. Fujita, and T. Kwan, This Bulletin, **32**, 884 (1959); J. Kuriacose and M. C. Markham, *J. Catal.*, **1**, 498 (1962); E. Bauer and C. Neuweiler, *Helv. Chim. Acta*, **10**, 901 (1921); A. Berna, *J. Phys. Chem.*, **68**, 2047 (1964); W. Doerffler and K. Hauffe, *J. Catal.*, **3**, 156 (1964).

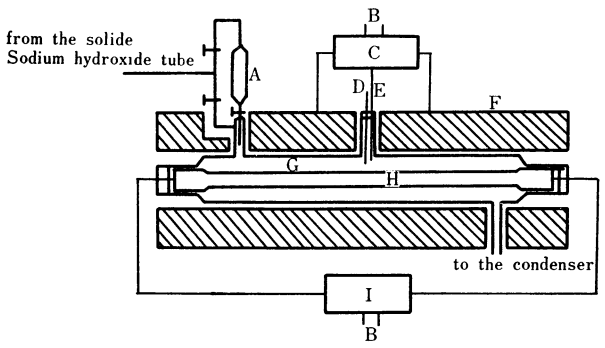


Fig. 1. Apparatus.
A: Funnel, B: Electric source, C: Temp. regulator, D: Thermometer, E: Thermocouple, F: Electric furnace, G: Reaction tube, H: Mercury lamp, I: Voltage stabilizer.

The reaction products coming out of the reaction tube were removed by being passed through a condenser filled with ice water, supplemented by two traps which were cooled with dry ice and acetone. The volume of gas evolved was determined by allowing it to displace the water from a graduated 2-*l* cylinder.

All the values given in the present research are averages of two to three measurements under constant reaction conditions, as Tables 1—4 show.

Analysis of the Products. The reaction products were identified by comparing them with authentic samples obtained by gas chromatography. In addition, the liquid products were dried over 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 the derivatives for the identification of the reaction products were made by the Shriner, Fuson, and Curtin method.[11]

The reaction products were analyzed quantitatively by gas chromatography, using a Shimadzu Type GC-2C apparatus. A 5-m column of the filler (polyethylene glycol-6000, tricresyl phosphate, silicone DC-550 and diethylene glycol succinate in the case of the liquid products, and activated charcoal, molecular sieve-13X, hexamethylphosphoramide, tricresyl phosphate, acetonylacetone and dimethylsulfolane in the case of the gaseous products) was used at an operating temperature of 100°C and a flow rate of 22.0 m*l*/min of helium. For the determination of the water, a 3-m column packed with Shimalite F impregnated with polyethylene glycol-1000 was used at 100°C, with a hydrogen carrier and at 11.5 m*l*/min.

Results and Discussion

Tables 1—5 show the results of the present experiments.

Table 1. Catalytic dehydrogenation of ethanol with reduced copper under ultraviolet light
(Reaction temp.: 250°C)

Experiment No.	1	2	3	4	5	6
Catalyst	Abs.	Pres.	Pres.	Pres.	Pres.	Pres.
Reducing agent	—	H_2	CO	H_2	CO	Non
Ultraviolet light	Irra.	Non	Non	Irra.	Irra.	Irra.
Ethanol used (g)	20.82	20.10	20.02	19.86	20.05	19.99
Liquid products (g)	19.86	19.02	19.02	18.53	18.19	18.65 17.89[b]
Conversion[a] (%)	2.01	38.28	37.91	66.59	65.92	65.62[c]
Composition of Liquid Products (%)						
Ethanal	1.2	18.1	13.8	29.7	21.8	49.9
Ethyl acetate	—	16.8	21.2	25.4	33.9	12.6
Propanone	0.4	1.6	1.4	10.2	8.9	1.9
Aldol	—	0.3	T	0	0	0
2-Butenal	—	0.2	0.2	0	0	0
Butanal	—	0.2	0.2	0	0	0
2-Buten-1-ol	—	0.2	0.2	0	0	0
1-Butanol	—	0.4	0.4	T	T	T
2,3-Butanediol	T	—	—	T	T	T
2-Propanol	0.2	—	—	0.4	0.4	0.4
1-Propanol	T	—	—	T	T	T
Methanol	0.1	0.1	0.1	0.3	0.3	0.3
2-Butanol	0.1	—	—	0.2	0.1	0.1
Water	T	T	T	T	T	(0.76 g)
Unidentified product	T	0.4	0.4	0.4	0.5	0.4
Unreacted alcohol	98.0	61.7	62.1	33.4	34.1	34.4

Abs.: absent. Pres.: present. Irra.: irradiated. T: trace.
a) The conversion was given by 100·(grams of liquid product - grams of unreacted alcohol) divided by grams of liquid product.
b), c) The values were obtained by means of excluding water from the liquid products. The value in parentheses shows the weight of water formed.

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

TABLE 2. CATALYTIC DEHYDROGENATION OF 1-PROPANOL WITH REDUCED COPPER UNDER ULTRAVIOLET LIGHT
(Reaction temp.: 250°C)

Experiment No.	1	2	3	4	5	6
Catalyst	Abs.	Pres.	Pres.	Pres.	Pres.	Pres.
Reducing agent	—	H_2	CO	H_2	CO	Non
Ultraviolet light	Irra.	Non	Non	Irra.	Irra.	Irra.
1-Propanol used (g)	19.98	19.96	19.99	20.07	19.95	19.68
Liquid products (g)	19.35	19.00	18.84	19.26	18.50	19.10 18.46[b]
Conversion[a] (%)	1.81	37.32	36.78	62.62	62.38	62.19[c]
Composition of Liquid Products (%)						
Propanal	1.1	15.4	10.3	30.3	20.4	48.2
Propyl propionate	—	13.7	19.2	20.8	31.2	9.6
3-Pentanone	—	6.4	5.6	8.6	7.9	1.5
Ethanol	0.2	0.5	0.4	0.6	0.6	0.6
Methanol	T	0.2	0.2	0.2	0.2	0.3
3,4-Hexanediol	T	—	—	T	T	T
2-Butanol	0.2	—	—	0.4	0.4	0.4
2-Methyl-1-propanol	—	—	—	0.3	0.2	0.2
Hexane	T	—	—	T	T	T
Ethanal	0.2	—	—	T	T	T
Propanone	0.1	—	—	T	T	T
Water	T	T	T	T	T	(0.64 g)
Unidentified product	T	1.1	1.1	1.4	1.5	1.4
Unreacted alcohol	98.2	62.7	63.2	37.4	37.6	37.8

Abs.: absent. Pres.: present. Irra.: irradiated. T: trace.
a) The conversion was given by 100·(grams of liquid product - grams of unreacted alcohol) divided by grams of liquid product.
b), c) The values were obtained by means of excluding water from the liquid products. The value in parentheses shows the weight of water formed.

TABLE 3. CATALYTIC DEHYDROGENATION OF 1-BUTANOL WITH REDUCED COPPER UNDER ULTRAVIOLET LIGHT
(Reaction temp.: 250°C)

Experiment No.	1	2	3	4	5	6
Catalyst	Abs.	Pres.	Pres.	Pres.	Pres.	Pres.
Reducing agent	—	H_2	CO	H_2	CO	Non
Ultraviolet light	Irra.	Non	Non	Irra.	Irra.	Irra.
1-Butanol used (g)	20.07	19.98	19.91	19.96	19.98	19.92
Liquid products (g)	18.44	18.84	18.61	18.05	17.96	19.11 18.52[b]
Conversion[a] (%)	1.08	35.77	35.20	60.50	60.30	58.42[c]
Composition of Liquid Products (%)						
Butanal	0.7	18.9	13.7	30.2	22.8	48.4
Butyl butyrate	—	15.7	20.2	26.7	33.9	6.7
4-Heptanone	—	0.5	0.3	0.5	0.4	0.5
1-Propanol	0.2	0.2	0.2	0.3	0.4	0.4
Ethanol	T	0.2	0.2	0.2	0.2	0.2
Methanol	T	0.1	0.1	0.1	0.1	0.1
2-Pentanol	0.2	—	—	0.5	0.5	0.4
2-Methyl-1-butanol	0.1	—	—	0.2	0.3	0.2
3-Methyl-1-butanol	T	—	—	0.1	0.1	0.1
Ethanal	T	—	—	T	T	T
Propanone	T	—	—	T	T	T
Water	T	T	T	T	T	(0.59 g)
Unidentified product	0.2	0.4	0.5	1.7	1.6	1.4
Unreacted alcohol	98.6	64.0	64.8	39.5	39.7	41.6

Abs.: absent. Pres.: present. Irra.: irradiated. T: trace.
a) The conversion was given by 100·(grams of liquid product - grams of unreacted alcohol) divided by grams of liquid product.
b), c) The values were obtained by means of excluding water from the liquid products. The value in parentheses shows the weight of water formed.

Table 4. Catalytic dehydrogenation of 2-propanol with reduced copper under ultraviolet light
(Reaction temp.: 250°C)

Experiment No.	1	2	3	4	5	6
Catalyst	Abs.	Pres.	Pres.	Pres.	Pres.	Pres.
Reducing agent	—	H_2	CO	H_2	CO	Non
Ultraviolet light	Irra.	Non	Non	Irra.	Irra.	Irra.
2-Propanol used (g)	19.86	20.05	20.04	19.96	19.86	19.93
Liquid products (g)	18.28	17.84	18.43	18.62	18.44	20.39 19.42[b]
Conversion[a] (%)	1.81	90.19	90.61	92.37	92.68	91.19[c]
Composition of Liquid Products (%)						
Propanone	1.4	53.3	52.1	75.9	90.1	90.1
4-Methyl-2-pentanone	—	16.6	17.2	9.8	1.6	0.1
2,6-Dimethyl-4-heptanone	—	11.9	12.4	2.3	T	0
4-Methyl-2-pentanol	—	1.7	1.9	0.6	T	0
2,3-Dimethyl-2,3-butanediol	T	—	—	T	T	T
Water	T	5.6	6.0	2.8	T	(0.97 g)
2,3-Dimethylbutane	T	—	—	0.3	0.3	0.3
2-Butanol	0.2	—	—	0.4	0.4	0.4
Ethanal	0.2	—	—	0.3	0.3	0.3
Ethanol	T	—	—	T	T	T
Unidentified product	T	1.1	1.0	T	T	T
Unreacted alcohol	98.2	9.8	9.4	7.6	7.3	8.8

Abs.: absent. Pres.: Present. Irra.: irradiated. T: trace.

a) The conversion was given by 100·(grams of liquid product - grams of unreacted alcohol) divided by grams of liquid product.

b), c) The values were obtained by means of excluding water from the liquid products. The value in parentheses shows the weight of water formed.

Table 5. Catalytic reaction of alcohols with copper catalyst under ultraviolet light
Gaseous Products

Reactant	Catalyst	Light	Product
Ethanol	Pres.	Abs.	H_2, C_2H_4, CO, CO_2
	Pres.	Pres.	H_2, CH_4, C_2H_6, C_2H_4, n-C_4H_{10}, CO, CO_2
1-Propanol	Pres.	Abs.	H_2, C_3H_6, CO, CO_2
	Pres.	Pres.	H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, CO, CO_2
1-Butanol	Pres.	Abs.	H_2, 1-C_4H_8, CO, CO_2
	Pres.	Pres.	H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, n-C_4H_{10}, 1-C_4H_8, CO, CO_2
2-Propanol	Pres.	Abs.	H_2, CO
	Pres.	Pres.	H_2, CH_4, C_2H_6, C_3H_8, C_3H_6, CO

Pres.: present. Abs.: absent.

Comparison of the Copper Catalyst under Ultraviolet Light with the Non-irradiated Copper Catalyst. In the case of the gaseous reaction of ethanol, as is shown in Table 1, the conversion in the presence of the copper catalyst under ultraviolet light was much larger than that without the light.

The conversion of ethanol under only ultraviolet light was smaller than all those obtained in the presence of the copper catalyst.

As is shown in Tables 1—3, the conversion of 1-propanol and 1-butanol had an inclination similar to that of ethanol, but it was found that the conversions of the primary alcohols decreased slightly in proportion to the molecular weights of the primary alcohols. As is shown in Table 4, the conversion of 2-propanol in the presence of the catalyst and the light was almost the same as that obtained with the catalyst without the light. In the case of the catalytic reaction of 2-propanol, it is considered that the 2-propanol reaction differs from those of other primary alcohols by having the reactive α-hydrogen atom.

The total amounts of the main products of the alcohols, such as the aldehydes, the esters and the ketones, accounted for over 95% of the conversions of the present alcohols for both the catalytic reaction under ultraviolet light and the reaction without the light. The aldol condensation was observed with the catalytic reaction of ethanol in the absence of the light, but it did not occur quite as in the cases of the other alcohols.

The formation of diols by the use of ultraviolet light

was observed in the cases of ethanol, 1-propanol, and 2-propanol, but not in the case of 1-butanol. The gaseous products are shown in Table 5. When the reaction of alcohol in the presence of the catalyst and ultraviolet light was compared with that in the presence of the non-irradiated catalyst, more gaseous products were found to be formed under the former reaction conditions.

Comparison between the Reduced Copper Catalysts. As is shown in Table 1, the formation of ethanal from ethanol by dehydrogenation was more increased by the use of the hydrogen-reduced copper catalyst than by the use of the carbon monoxide-reduced copper catalyst and was further promoted by ultraviolet light. The same tendency was observed in the formation of propanal and butanal from 1-propanol and 1-butanol respectively, as is shown in Tables 2 and 3. As is shown in Table 4, the formation of propanone from 2-propanol by dehydrogenation was remarkably accelerated by ultraviolet light. The conversion of 2-propanol into propanone with the carbon monoxide-reduced catalyst under ultraviolet light was above 90% in all the products (included the unreacted alcohol). The aldehydes and the ketone mentioned above were obtained in any small amounts under ultraviolet light without the catalyst. Esters were obtained in larger quantities by the use of a reduced copper catalyst treated with carbon monoxide than with one reduced with hydrogen, and the production was further promoted by ultraviolet light. From the results mentioned above, it was found that the formation of the esters occurred preferentially with the carbon monoxide-reduced catalyst, and that the copper catalyst treated with hydrogen as the reducing agent was suitable for the formation of the aldehyde. The above facts suggest that the different structures of the catalyst surface are formed by the different reducing agents used. As Table 1 shows, the yield of propanone, which seems to have been formed by the secondary reaction process of ethanol, was nearly proportional to that of ethanal from ethanol. A similar tendency was also observed in the formation of 3-pentanone from 1-propanol, but little 4-heptanone was formed from 1-butanol.

Non-reduced Copper Catalyst. As is shown by Experiment No. 6 in Tables 1—3, the yield of aldehydes, such as ethanal from ethanol, propanal from 1-propanol, and butanal from 1-butanol, was the largest, and much more water was formed than under other experimental conditions. The hydrogen formed by dehydrogenation and the non-reduced copper catalyst might react to form water on the surface of the catalyst.

Formation Mechanism of the Main Products from Ethanol in the Presence of the Catalyst. From the facts mentioned above, the reaction mechanism of ethanol is considered to be as follows.

The main products, such as ethanal and ethyl acetate, appear to be formed by the following schemes:[5,12,13]

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

$$C_2H_5OH + CH_3CHO \rightarrow$$

$$CH_3CH(OH)OC_2H_5 \xrightarrow{-H_2} CH_3COOC_2H_5$$

The formation of propanone from ethanol with a catalyst can probably be presented by Kagan's process,[14] with the result that ethylene and carbon dioxide are formed:

$$2CH_3COOC_2H_5 \rightarrow$$

$$CH_3COCH_3 + C_2H_5OH + C_2H_4 + CO_2$$

Judging from such gaseous products as methane and hydrogen, methanol, which was little produced in a catalytic reaction, seems to be formed by hydrogenolysis:[13]

$$C_2H_5OH \xrightarrow{H_2} CH_3OH + CH_4$$

The ethylene in gas products is considered to be provided by dehydration,[13] also. Morgan and Kagan proposed the following mechanism for the formation of alcohol by aldol condensation and hydrogenation as follows:[15]

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO \xrightarrow[H_2]{-H_2O}$$

$$CH_3CH_2CH_2CHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH$$

Accordingly, 1-butanol seems to be formed by the aldol condensation of ethanal, which is itself the product of the primary catalytic reaction process of ethanol. Aldol condensation was not observed under ultraviolet light. On the other hand, one of the present authors has previously reported that the main reaction mechanism of 2-propanol with the copper catalyst is represented by the steps shown below.[6]

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$$

$$(CH_3)_2CHOH + (CH_3)_2CO \rightarrow$$

$$(CH_3)_2CHCH_2COCH_3 + H_2O$$

$$(CH_3)_2CHOH + CH_3COCH_2CH(CH_3)_2 \rightarrow$$

$$(CH_3)_2CHCH_2COCH_2CH(CH_3)_2 + H_2O$$

2-Methyl-2-pentanol may be formed from 4-methyl-2-pentanone by hydrogenation.

Photochemical Reaction Mechanism of Ethanol. As is shown in Table 6, the photochemical reaction of ethanol seems to proceed without a catalyst, judging from the products obtained in the present work and from the results previously reported.[8,9]

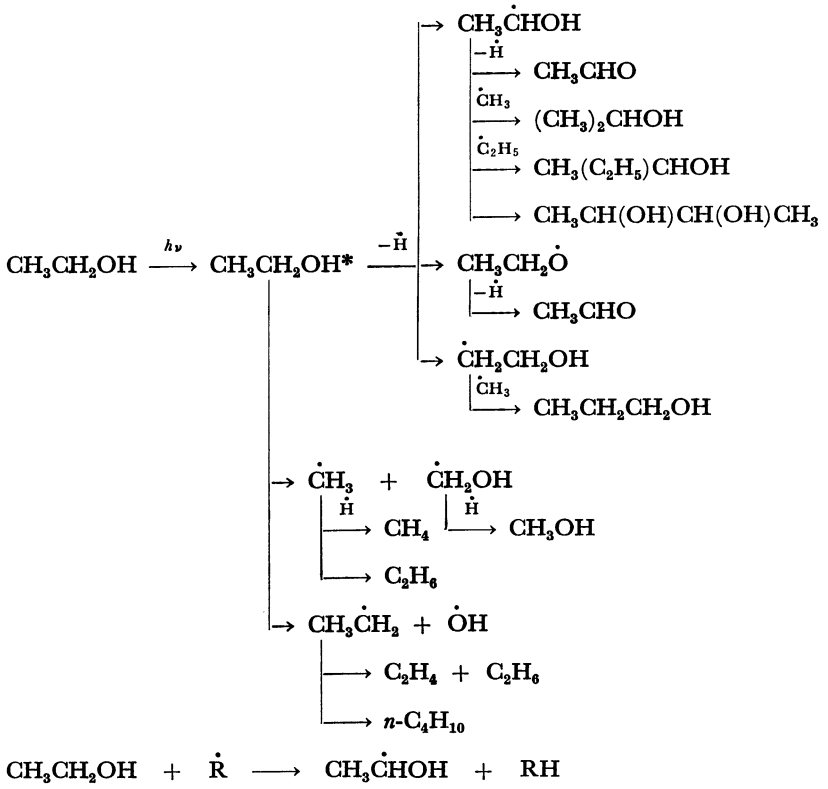
12) W. G. Palmer, *Proc. Roy. Soc.* (London), **98A**, 13 (1920); H. Adkins, K. Folkers, and M. Kinsey, *J. Amer. Chem. Soc.*, **53**, 2714 (1931); M. Ya. Kagan, and O. M. Podurovskaya, *J. Appl. Chem. (U. S. S. R.)*, **5**, 378 (1932); B. N. Dolgov and T. V. Nizovkina, *Zh. Obshch. Khim.*, **19**, 1125 (1949); B. N. Dolgov, T. V. Nizovkina, and I. M. Strouman, *Sbornik Statei Obshch. Khim.*, **2**, 1288, 1293 (1953).

13) B. N. Dolgow, "Die Katalyse in der Organischen Chemie," Veb Deutscher Verlag Der Wissenschaften, Berlin (1963).

14) M. Ya. Kagan, I. A. Sobolev, and G. D. Lyubarskii, *Ber.*, **68B**, 1140 (1935).

15) G. T. Morgan, *Proc. Roy. Soc.* (London), **127A**, 240 (1930); G. T. Morgan and D. V. N. Hardy, *Chem. Ind.* (London), **1933**, 518; M. Ya. Kagan, G. D. Lyubarskii, and S. F. Fedorov, *J. Appl. Chem. (U. S. S. R.)*, **7**, 135 (1934).

Table 6. Photochemical reaction scheme
(Reactant: Ethanol)



Reaction Process of Alcohol with the Catalyst under Ultraviolet Light. The reaction of the alcohols with the catalyst under ultraviolet light promoted the formation of aldehydes and esters, and their conversions, except in the case of 2-propanol, were much accelerated by ultraviolet light. By the use of the non-reduced copper catalyst under the light, the formation of aldehyde from alcohol was especially remarkable.

However, the conversion of alcohol under ultraviolet light without the copper catalyst was small. Accordingly, it is considered that the scarcely no decomposition of alcohol occurs under ultraviolet light without the catalyst, and that the main products were almost all formed by the catalytic reaction of alcohol. The facts mentioned above may be represented by the two following reaction processes.

The first is:

$$S \xrightarrow{h\nu} S^*$$

$$R + S^* \rightarrow R\cdots\cdots S^* \rightarrow \text{Products} + S$$

where:

S, catalyst; R, alcohol; h, Plank's constant, and ν, the frequency of ultraviolet light.

As is shown in Table 1, no aldol condensation was observed under ultraviolet light, but it occurred slightly with the non-irradiated catalyst. The above facts suggest that the surface of the catalyst was altered slightly by the irradiation of ultraviolet light. One of the present authors has previously reported that the formation of higher ketones from 2-propanol with the reduced copper catalyst seems to be attributable to the effect either of a trace of water or of a lower oxide of copper in the catalyst.[6] Also, from the fact that the copper catalyst reduced in the present work was reddish purple, it seems to include such oxides of copper as Cu_2O,[16] which shows photoconductivity, though no strong and sharp absorption of copper and copper compounds has been observed in the range of ultraviolet light.[17] Accordingly, we consider that the copper catalyst gives rise to electrons and positive holes which may enhance the activity of the catalyst when irradiated under ultraviolet light. The above process has been reported for the ZnO - O_2 system by Kwan.[18]

16) T. S. Moss, "Photoconductivity in the Elements," Academic Press, New York (1953); R. H. Bube, "Photoconductivity of Solids," John Wiley, New York (1960).

17) Miner (1903), Tool (1910), Mecke and Ley (1924), and French and Lowry (1924). In "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. V, ed. by J. W. Clarence, McGraw Hill Book Co., New York and London (1933), pp. 249, 330.

18) T. Kwan, "Photochemistry and Its Application," ed. by M. Koizumi *et al.*, Kagaku Dojin Tokyo, Tokyo (1965), pp. 101—119.

The reaction schemes described in the above report are as follows:

$$M \xrightarrow{h\nu} M^* \xrightarrow{O_2} MO_2^*(MO_2) \xrightarrow{B} M + BO_2 \quad (1)$$

$$M \xrightarrow{h\nu} M^* \xrightarrow{B} MB^*(MB) \xrightarrow{O_2} M + BO_2 \quad (2)$$

where M is a photocatalyst and B is the reactant oxidized. In the present work, oxygen was not present in the reaction system.

Accordingly, it is considered that the photo-response may occur in the adsorption of alcohol on the surface of the present catalyst, as is shown in Scheme (2).

The second is:

$$R + S \rightarrow R\cdots\cdots S \xrightarrow{h\nu} (R\cdots\cdots S)^* \rightarrow \text{Products} + S$$

Although alcohols like ethanol show the absorption in the extreme range of ultraviolet light,[19] the wavelength of its absorption seems to be shifted[20] when it is adsorbed on the surface of the catalyst. Accordingly, an intermediate state like an activated complex seems to be excited by ultraviolet light, and its decomposition seems to be promoted. When the reaction with the copper catalyst under ultraviolet light was compared with that in the presence of the non-irradiated copper catalyst, the species of the main products, such as ethanal, ethyl acetate, and propanone, were, in the case of ethanol, almost the same in both the experiments, and the yields of the main products increased in all the main products upon irradiation of ultraviolet light. Moreover, the total amounts of the main products accounted for over 95% of the conversions of the primary alcohol for both the catalytic reaction under the light and the reaction without the light. From the above facts, it can be considered that the direction of the catalytic reaction with the catalyst and the light may be almost the same as that of the catalytic reaction without the light, and that the reaction velocity may be accelerated by the irradiation. In the case of the first process, the species of the main products with the catalyst under ultraviolet light may differ somewhat from those obtained with the catalyst alone, so the state of the non-irradiated catalyst might be altered considerably by ultraviolet light. Accordingly, the second reaction process may occur rather than the first process. The tendency of the catalytic reactions of 1-propanol and 1-butanol was similar to that of ethanol. In the case of 2-propanol, the dehydrogenation may be more rapid than that of the primary alcohols,[7] so 2-propanol may have a reactive α-hydrogen atom, though the second process is considered to be valid for the catalytic reaction under the light. Accordingly, the yield of propanone by the catalytic dehydrogenation may be especially large and may be further promoted by ultraviolet light.

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