# Studies on Catalytih Action, IV.
# A New Function of Reduced Copper.

By

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While engaged on the study of the camphor series, the author made use of the principle proposed by Prof. Paul Sabatier[1] for obtaining menthone by passing menthol on the reduced copper heated at 320°, which was prepared from copper oxide of the following composition, according to the direction of P. Sabatier[2].

$$CuO = 99.89 \; ; \; Fe_2O_3 = \text{trace} \; ; \; Al_2O_3 = 0.025 \; ;$$
$$CaO = 0.046 \; ; \; MgO = 0.006 :$$

Contrary to expectation, the reaction product was found to consist of menthene instead of menthone; the product obtained from 30 grm. menthol, amounting to 25 grm. was separated from 1 c.c. of water formed simultaneously, and fractionated after drying with anhydrous sodium sulphate, in the following three portions :

| | | |
|---|---|---|
| 1. | 160– 198° | 9.3 grm. |
| 2. | 198—208° | 3.9 ,, |
| 3. | 208—210° | 11.7 ,, |

The last fraction was found to consist of unchanged menthol, and the other fractions, after repeated fractional distillation, were separated into two portions :

| | | |
|---|---|---|
| 1. | 165—167° | 4.7 grm. |
| 2. | 208—210° | 4.5 ,, |

The first fraction was confirmed by elementary analysis to consist of menthene, and the determination of the physical constants :

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[1] La catalyse en chimie organique, 254 (1920).
[2] Ibid., 18.

$C = 86.01$; $H = 13.09$ (theory requires $C = 86.87$; $H = 13.13$ for $C_{10}H_{16}$)
$d_4^{25} = 0.8081$ ; $n_D^{25} = 1.4456$.

So far as we could ascertain[1], when secondary alcohol passed through a heated glass tube, in presence of reduced copper, dehydrogenation was effected perfectly, yielding hydrogen and ketone, while metallic oxides such as thoria or alumina act as catalysts of dehydration, promoting the decomposition of the alcohol into olefine hydrocarbone and water. In the present case, however, it seems proper to ascribe the formation of menthene from menthol to the catalytic action of the reduced copper, in other word, metallic copper promotes the decomposition of menthol into menthene and water.

Does the reduced copper act, like thoria, as catalyst of dehydration at high temperature? In order to ascertain the catalytic action of the reduced copper toward alcohols, 8 grm. copper oxide of the composition[2] were spread in a layer inside of a 75 cm. glass tube and reduced at 180° to a metallic copper on which ethyl alcohol purified by distillation on calcium oxide, was passed and the reaction tube was maintained at a temperature 320°. The vapours escaped from the reaction tube, condensed by passage through a condenser cooled with ice-water, the escaped gas from the condenser carried with it a small quantity of the liquid reaction product, which recovered by passing the gas through the second empty flask cooled with ice-water, and then through an absorption vessel containing bromine.

The reaction product in the condenser was found to consist of unchanged alcohol and acetaldehyde, and the latter was confirmed by Schiff's reagent and also identified by transforming it into aldelyde

1   Sabatier : La catalyse chimi. organ., p. 92, 250, 254 ; W. D. Bancroft ; Applied colloid chemistry, 44, 60 (1921) ; K. G. Falk : Catalytic action, 50, 156 (1922) ; C. Engler and J. Weissberg : Vorträge d. Autoxydation, 98, 149 (1904) ; P. Sabatier & B. Kubota : C. R., 172, 733 : 173, 17, 212 (1921) ; G. Woker : Die Katalyse, II, 397 (1915) ; G. G. Henderson : Catalysis in industrial chemistry, 121, 145 (1919) ; A. Skita : u. Kataly. Reduk. Org. Verb., 66,72 (1912) ; W. Ipatiew : Ber. D. Chem. Ges., 34, 3587 (1901) ; 36, 1993 (1903) ; 37, 2961 (1904).

2   $CuO = 99.88$ ; $Fe_2O_3 = 0.007$ ; $CaO = 0.050$ ; $MgO = 0.017$.

ammonia. The other reaction product in the absorption vessel was recognised by its property of decolourising bromine to be ethylene, and this was confirmed by the analysis after purification by fractional distillation.

The substance B. p. 129—130°, gave on analysis Br = 85.23 (theory requires Br = 84.87 for $C_2H_4Br_2$).

It is a well-known fact that when ethyl alcohol[1] is passed through a heated glass tube, it begins to decompose at about 500°, two reactions taking place simultaneously, namely (1) dehydration of the alcohol, with the formation of water and ethylene, and (2) dehydrogenation, resulting in the product of hydrogen and acetaldehyde :

1.  $C_2H_5OH = CH_2CH_2 + H_2O$.

2.  $C_2H_5OH = CH_3CHO + H_2$
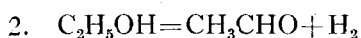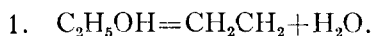
Such decomposition of the alcohol by heat may follow at a red heat but it shows no appreciable decomposition below 400°. In presence of catalysts these reactions can be brought about with greater velocity and at lower temperatures. Reduced copper, as the author has actually observed in the cases of menthol and ethyl alcohol acts to promote both reactions-dehydration and dehydrogenation, when alcohol is brought under the conditions described above, notwithstanding that it has the universal sanction of chemists reduced copper is the sole catalyst which perfectly induces dehydrogenation or hydrogenation.

On referring the literature[2], we have, however, noticed that diphenyl carbinol when heated to its boiling point (298°), suffers partial decomposition into water and benzhydrol ether, and the reaction seems to effected by a catalytic influence, transforming the carbinol by the action of heat (210—220°), in presence of copper powder, into the ether with the yield of 75% and accompanied with the formation of some diphenyl keton.

In the same manner, isopropyl alcohol B. p. 82°, from Kahlbaum,

1   M. Berthelot and E. Jungfleisch : Traité élém. chimi. organ., 1, 245 (1908) ; W. Ipatiew : Ber. D. Chem. Ges., 34, 3579 (1901) ; 35, 1047 (1902).

2   Ber. D. Chem. Ges., 36, 2823 (1903) ; Beilstein : Handbuch d. Organ. Chem., 3rd. ed., Il, 1077.

purified by distillation, was passed at the rate of one grm. per 20 seconds over the reduced copper heated at $300^{\circ}$.

Acetone formed by the reaction, was separated from unchanged alcohol by precipitating it as a mercury complex compound $(2HgSO_4 3HgO)_3 4CO(CH_3)_2$ with the Deniger reagent[1], which after separation and purification was analysed with the following results :

Hg = 77.5, theory requires Hg = 76.15.

The olefine hydrocarbone formed simultaneously with acetone was converted into the bromine derivative which after being fractionated into tow portions, was analysed :

1.   130—140°          0.3 grm.
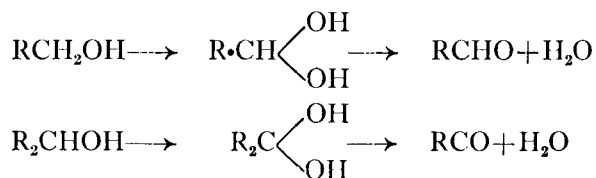1.   140—150°          0.5 grm.

1st.  fraction : Br=80.58 ;

2nd. fraction : Br=80.03 ; theory requires Br=79.0 for $C_3H_6Br_2$.

It was confirmed that isopropyl alcohol, in the presence of the reduced copper, transforms by exposure to high temperature into acetone and propylene.

The mechanism of such decomposition of alcohols into aldehydes or ketones, in presence of the reduced copper, may be explained either by the dehydrogenation theory proposed by P. Sabatier[2] and also by H. Wieland[3], or by the dehydration theory.

In the oxidation, according to the latter view, a free oxygen atom inserts itself between the hydrogen atom and the carbon atom which the hydroxyl group is joined in the molecule of alcohol.   α-Glycohol which is assumed to be formed in a moment as an intermediate product in the course of oxidation, being splitted off water, and its anhydride-aldehyde or ketone, resulted as will be seen in the following scheme :

$$RCH_2OH \longrightarrow R{\cdot}CH{\Big\langle}{}^{OH}_{OH} \longrightarrow RCHO+H_2O$$

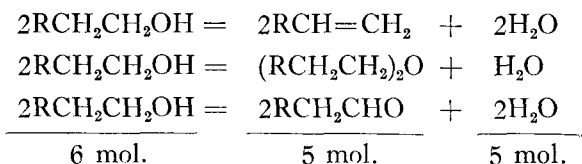$$R_2CHOH \longrightarrow R_2C{\Big\langle}{}^{OH}_{OH} \longrightarrow RCO+H_2O$$

1  C. R., 127, 963 (1898).

2  La catalyse en chimie organique, 58, 60 (1920).

3  Ber. D. Chem. Ges., 45, 2606 (1912) ; 55, 3639 (1922).

The author, however, sides with the latter view for the explanation of the catalytic oxidation of the alcohol.

In generaly the direct transformation of alcohols into hydrocarbons and oxygen compourds by chemical means or pyrogenetic contact action may be represented in the following reactions :

$$2RCH_2CH_2OH = 2RCH{=}CH_2 + 2H_2O$$
$$2RCH_2CH_2OH = (RCH_2CH_2)_2O + H_2O$$
$$2RCH_2CH_2OH = 2RCH_2CHO + 2H_2O$$

| 6 mol. | 5 mol. | 5 mol. |
|---|---|---|

When the reactions proceed simultaneously as shown in the equations, the quantity of water generated by the reactions should be of the same molecular proportion as that of the substances formed by the transformation.

In order to see, if there may exist some relation between the amount of water and that of the compounds which were formed by the reaction, the author carried the experiment of passing 18 grm. hexahydrophenol over the reduced copper heated at 320°, during an interval of 8 hours. One grm. of water, 15.5 grm. oily substance $d_{1}^{25'} = 0.8874$, were obtained as a reaction product, and the latter separated from water, dried with anhydrous sodium sulphate, was subjected to fractional distillation under ordinary pressure :

| Fraction | | Yield | |
|---|---|---|---|
| | | in grm. | in mol. |
| 1. | 80—90° | 2.4 | 0.024 |
| 2. | 90—150° | 0.1 | |
| 3. | 150—165° | 4.8 | 0.024 |
| 4. | 175—200° | 0.6 | |
| 5. | above 200° | 0.2 | 0.001 |
| | | | 0.048 |

The first fraction again purified by repeated distillations with metallic sodium and the fraction B. p. 82—83°, with the yield 2 grm. was confirmed to consist of tetrahydrobenzene by its analysis and also by measurement of the physical constants :

$C = 87.84$ ; $H = 12.29$ ; $d_4^{25} = 0.8076$ ; $n_D^{25} = 1.440$.

The third fraction assumed to be a mixture of hexahydrophenol and cyclohexanone, was treated with hydroxylamine to separate the latter substance as an oxime, from the former. The oxime thus isolated amounting to 1.2 grm. (69% of the fraction) was purified by recrystal-lization from petroleum ether solution, and was analysed with these results :

$C = 64.26$ ; $H = 9.95$ ; $N = 11.5$ (by Kejeldal's method), theory requires $C = 63.66$ ; $H = 9.80$ ; $N = 12.38$ for $C_6H_{11}NO$.

The elementary analysis and M. p. 98—89°.5, agree with those of cyclohexanone oxime[1].

The analytical results of the 4th and 5th fractions are as follows :

4th. fraction : $C = 74.4$ ; $H = 9.4$ ; $O = 16.2$ (by difference).

5th. ,,　　　　$C = 77.4$ ; $H = 9.9$ ; $O = 12.7$ ( ,,　　,, 　).

It seems that the 5th fraction by the analytical results, consists mainly of di-hexahydrophenyl ether[2] requiring $C = 79.1$ ; $H = 12.1$ ; $O = 8.8$.

The yield of the compounds being 0.048 mol., agrees approximately with that of water (0.055 mol) generated simultaneously during the reaction. Hence, we have to confess that the formation of unsaturated hydrocarbons by dehydration of alcohol, was actually effected by the catalytic action of reduced copper as it promotes the oxidation of alcohol. Though the mechanism of the reactions under such conditions, was not at all decided, the author suggests that the reduced copper surely promotes the dehydration of alcohol.

It may naturally be considered that the reduced copper is also capable, under different conditions, of exercising a catalytic influence in promoting the oppsite reaction of dehydration. The reactions of the hydration of nitriles usually brought about with the aid of catalysts such

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1　A. Baeyer : Lieb. Ann., **278**, 102 (1893).

2　W. Ipatiew and O. Philipow : Ber. D. Chem. Ges., **41** 1001 (1908) ; S. Komatsu and S. Kumamoto : These Memoirs, **6**, 48 (1922).

as thoria and acids, which were also accelerated in presence of reduced copper, resulted in amides from the mixturs of nitriles and water, these results will be communicated in the next article.

The formation of α-campholenic acid[1] from camphoroxime, reduced copper and hydrogen at 200°, of benzoic acid[2] from acetophenonoxime and of menthonyl acid[3] from menthonoxime under the same conditions, should be explained by the same mechanism which was applied in the reaction forming benzamide from benzonitrile and water at 200° in presence of the reduced copper, namely, the hydration of nitriles which were formed as an intermediate compound from the oximes by the Beckmann rearrangement or the so-called nitrile decomposition[4], nitriles by addition of water transformed into acid amides and then into acids successively.

The new catalytic action of the finely divided reduced copper will be studied further in my laboratory.

The author is indebted to Messrs.  M. Ishimasa and M. Kurata for assistance in some of the experiments.

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1   S. Komatsu and S. Yamaguchi : These Mencoiss **6**. 245 (1923).

2   Unpublished work by Yamaguchi.

8   Unpublished work with S. Kurata.

4   A-Kötz and O. Wunstorf : J. prak. Chem., (2), **88**, 519 (1913).