Studies on Catalytic Action, XIX.
Catalytic Action of Reduced Copper upon Methyl Alcohol.

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Thermal decomposition of the primary alcohols of the aliphatic series, will take place, as indicated by M. Berthelot in his investigation into the decomposition of ethyl alcohol[1], in the following manner:

$$RCH_2OH \begin{cases} \nearrow H_2O + R'CH{:}\,CH_2 \quad \ldots\ldots\ldots\ldots (1) \\ \searrow H_2 + RCHO \quad \ldots\ldots\ldots\ldots\ldots\ldots (2) \end{cases}$$

Reduced copper, according to Professor P. Sabatier[2], promotes only the oxidation of alcohols (2), and it has been used for the preparation of formaldehyde from methyl alcohol on a large scale with very satisfactory results.

However, both reactions of the primary alcohols, as indicated by S. Komatsu[3], and also by T. Hara[4], in their investigation of the catalytic action of reduced copper on alcohols, were accelerated by the presence of the catalyst, though its effect is not entirely the same for both the reactions. It is, therefore, very interesting to extend the catalytic action of various types of reduced copper upon methyl alcohol in order to see what the catalytic effect of the metal would be.

The catalyst[5] used in the present experiment was Cu I prepared from

1 C. R., 33, 210 (1851).
2 Ibid., **136**, 738, 921, 983 (1903).
3 These Memoirs: A. **7**, 85 (1924).
4 Ibid., A. **9**, 405 (1925).
5 B. Masumoto: Ibid., A. **10**, 175 (1927).

copper hydroxide gel; Cu IV, from a basic copper nitrate of a grey colour; and Cu VII from copper oxide prepared by ignition of its nitrate.

In the experiment, 15·0 grm. of copper oxide mentioned above was reduced with a slow current of hydrogen at a temperature 180–200°, and methyl alcohol purified by distillation over quicklime, (B. p. 66–67) was passed, at the rate of 5 or 10 grm. an hour, over the catalyst heated to the required temperature (200, 300, 350, 400, 500 & 600). Formaldehyde

No.	Catalyst	Reaction temp.	Rate of passing per hour	Yield	
				CH_2O%	C_2H_4%
1	Cu I	350°	5 grm.	6·2%	0·1%
2		〃	10 〃	6·2〃	0·1〃
3		400	5 〃	9·1〃	0·1〃
4		〃	10 〃	9·1〃	0·1〃
5		500	5 〃	10·9〃	0·1〃
6		〃	10 〃	10·9〃	0·2〃
7		600	5 〃	19·9〃	0·1〃
8		〃	10 〃	19·9〃	0·1〃
9	Cu IV	350	5 〃	7·2〃	0·1〃
10		〃	10 〃	7·2〃	0·1〃
11		400	5 〃	7·2〃	0·1〃
12		〃	10 〃	7·2〃	0·1〃
13		500	5 〃	9·8〃	0·1〃
14		〃	10 〃	19·5〃	0·1〃
15		600	5 〃	9·8〃	0·1〃
16		〃	10 〃	19·5〃	0·1〃
17	Cu VII	200	5 〃	2·1〃	1·0〃
18		〃	10 〃	2·1〃	2·0〃
19		300	5 〃	2·1〃	0·2〃
20		〃	10 〃	2·1〃	0·5〃
21		350	5 〃	3·1〃	0·05〃
22		〃	10 〃	3·1〃	0·2〃
23		400—430	5 〃	12·0〃	0·7〃
24		〃	10 〃	13·8〃	2·1〃
25		500	5 〃	12·7〃	3·0〃
26		〃	10 〃	19·1〃	1·5〃
27		600	5 〃	34·4〃	0·3〃
28		〃	10 〃	34·4〃	trace

and other reaction products which escaped from the reaction vessel were collected separately in receivers; the formaldehyde which was collected in the first receiver containing water, was determined as to its quantity by means of a sodium sulphite solution; and unsaturated hydrocarbon was fixed with bromine water in a second receiver, determined quantitatively after being purified by fractional distillation (B. p. 130–170).

The results of the experiments are shown in the table.

As will be seen from the table, the methyl alcohol was decomposed at higher temperatures, and in the presence of reduced copper, into formaldelyde and hydrogen on the one side, and on the other into ethylene and water.

The decomposition of alcohol into formaldehyde and hydrogen is generally effected at higher temperature, and also accelerated especially in presence of Cu VII; Cu I and Cu IV show no difference in the catalytic influence on the oxidation of alcohol. The formation of the aldehyde is favourable when the alcohol was passed rapidly on Cu IV heated at high temperatures such as 500° and 600°. Lower temperatures, on the contrary, are convenient for the formation of ethylene which is also accelerated much more through the catalytic action of Cu VII. To our interest, there is a minimum yield of the hydrocarbon when the reaction happens in presence of Cu IV and Cu VII at a temperature about 350°.

Although the formation of ethylene takes place, generally in a less degree when compared with that of aldehyde, there is no doubt that the reduced coppers behave toward alcohol in dehydrating in a similar manner to other primary alcohols. The mechanism of the formation of ethylene from the alcohol was proposed, in which reduced copper acts catalytically to separate the water molecules from methyl alcohol, forming in this way the methylene radical, which is then polymerized into ethylene, admitting for a momentary existence a divalent carbon compound, as Nef has already suggested in his research on the divalent nature of carbon in organic compounds[1],

$$CH_3OH \longrightarrow CH_2 + H_2O$$
$$2CH_2 \longrightarrow CH_2 : CH_2.$$

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1 J. Am. Chem. Soc., **26**, 1549 (1904).