

# Studies on Catalytic Action, XI. Catalytic Activity of Reduced Copper, I.

By

Shigeru Komatsu and Masao Kurata.

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In the fourth paper on this subject<sup>1</sup>, it was shown that reduced copper promotes dehydration of alcohols, yielding menthene from menthol. Repeating the same experiment, however, one of the authors(S.K.) and T. Yukitomo<sup>2</sup> have observed that the greater part of menthol at 300° was transformed into thymol and the remainder into menthone, menthene and cymene. Such transformations of menthol seem highly probable when referred to the experimental results by one of us(S.K.) and B. Masumoto<sup>3</sup> on the catalytic action of reduced copper on cyclohexanol.

The marked difference in the behaviour of reduced copper toward menthol as mentioned above leads the authors to consider that the catalytic activity of the catalyst will be affected in different degrees by the presence of some poison, or by the method of its preparation, since we do not find as yet any definite proof to deny any one of two observations that menthol was decomposed into menthene and water in one way, by the presence of reduced copper, and in the other way into cymene, menthene, menthone and thymol.

⊙ The present study was, therefore, undertaken to give some experimental support for the idea that the catalytic activity of reduced copper

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1 These Memoirs, 7, 85(1923).

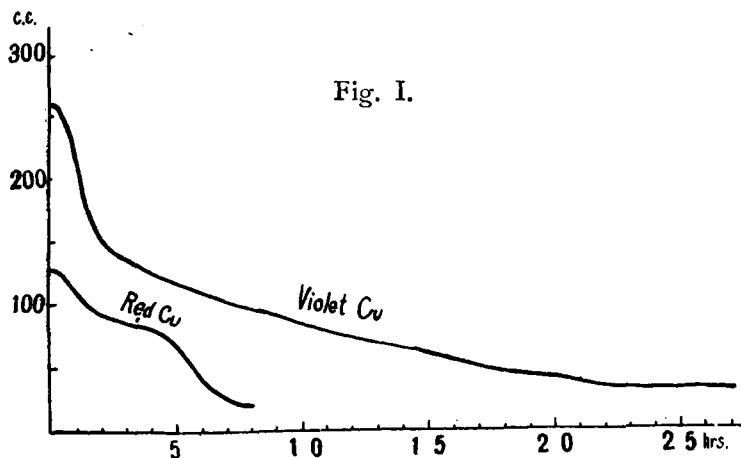
2 Ibid.

3 Ibid.

will be affected by the process of its formation.

#### I. ACTIVITY OF THE CATALYST ON 1-MENTHOL.

In the experiment, menthol M. p.  $43^{\circ}$ ,  $[\alpha]_D = -49.9^{\circ}$  was passed at



the rate of 9 gramm. per hour, over reduced copper at  $300^{\circ}$ , obtained from copper oxide by reduction with hydrogen which was prepared from purified copper sulphate and caustic soda solution; the amount of hydrogen gas evolved by the reaction, was measured, from time to time, for five minutes each, and the results calculated under normal conditions, were plotted in Fig. I.

By comparison with them, we can ascertain approximately the oxidizing activity of the catalyst. The activity of the catalytic actions of reduced copper can also be compared by determination of the yield of the fractions which were divided by fractional distillation repeated eight times. The yield of thymol and menthone in each experiment was determined as usual, of higher fractions and that of menthene and cymene was determined of the lower fractions by means of the index of refraction, and the results are shown in gramm. per cent and also in mol. per cent as seen in the tables I and II. In experiments, 1 and 2, the reaction products were divided into two or three portions which were collected separately in the course of the reaction and examined one by one.

Table I.

No. of the catalyst used	1		2			3	4	5
Portion of products	1	2	1	2	3	—	—	—
Fraction (in%)	78	22	7	44	49	—	—	—
Time for passing (in hr.)	5	2½	1½	10½	14½	½	1	1

Yield in grm. per cent.

Menthene	61	87	31	60	75	27	99.6	100
Cymene	8	1	11	2	1	4	0.4	0
Menthone	1	4	0	22	20	13	0	0
Thymol	30	8	58	16	4	56	0	0

Table II.

Yield in mol. per cent.

No. of catalyst used	1		2			3	4	5
Portion of products	1	2	1	2	3	—	—	—
Menthene	62	88	33	62	77	30	99.6	100
Cymene	9	1	12	2	1	4	0.4	0
Menthone	1	3	0	21	19	12	0	0
Thymol	28	8	55	15	3	54	0	0

1. Copper oxide used in the first experiment was prepared from copper sulphate (Jap. pharm.) with an excess of sodium hydroxide solution, washed with hot water 35 times, and was reduced with pure hydrogen, passing at the rate of 110 c.c. per minute, at 200°. The colour of the reduced copper was red.

2. When, however, copper oxide prepared by the method described in (1), was reduced with a slow current of hydrogen at 200°, at the rate of 33 c.c. per minute, it resulted in a violet-coloured copper.

3. Copper oxide prepared from purified copper sulphate and an excess of hot sodium hydroxide solution, was reduced with pure hydrogen at 200° passing at the rate of 60 c.c. per minute, and yielded red-coloured copper.

When menthol was passed on reduced copper prepared by methods (1), (2) and (3), each heated at 300°, the evolution of hydrogen gas in each case was noticed, but this was gradually diminished with time as may be seen in the results indicated in Fig. 1, and menthene, cymene and thymol were actually observed to be formed, though the yield of these compounds, depending on the catalyst employed, was not entirely the same in each case.

4. Copper oxide prepared from purified copper sulphate and a slight excess to the equivalent quantity of sodium hydroxide solution to precipitate copper as a hydroxide, washed with hot water 30 times, and reduced with pure hydrogen, at the rate of 84 c.c. per minute, at 200°, and the evolution of SO<sub>2</sub> gas in the course of reduction was noticed. The colour of the reduced copper was red.

When this reduced copper was used as catalyst, no evolution of hydrogen was perceived during the reaction, and menthene was found to be the sole substance formed by the reaction and assumed to be the result of the dehydration of menthol.

The authors' attention was naturally directed to the examination of the source of sulphur dioxide, since it was believed that the evolution of the gas had an intimate connection with the formation of menthene or the dehydration of menthol. The source of the gas was then ascribed to the decomposition of a basic copper sulphate, the presence of which in copper hydroxide precipitated from copper sulphate solution with a slight excess to the equivalent quantity of sodium hydroxide solution, was highly probable, when referred to Williamson's experiment<sup>1</sup> on the formation of a basic copper sulphate.

When basic copper compound is reduced with hydrogen, it should be decomposed into copper and sulphur dioxide, and the latter will act on reduced copper to destroy the oxidizing activity, and accordingly reduced copper previously exposed to the poisonous action of sulphur dioxide, when used as a catalyst, will promote only the dehydration of menthol, resulting in menthene and water.

5. For confirmation of the idea above-mentioned, that sulphur dioxide formed during reduction of basic copper sulphate associated with copper oxide, acts on reduced copper to retard its oxidizing activity only, the gas was passed on reduced copper prepared according to the directions described in (3) at 200°, the colour of the reduced copper was changed

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<sup>1</sup> J. Phys. Chem., 27, 789 (1923).

from red to yellowish brown, and then passed pure hydrogen at 180°. It resulted again in a reddish-coloured copper.

When menthol was passed on this copper heated at 300°, it yielded menthene and water but not menthone, cymene or thymol as observed in case (4). And thus, our hypothesis that the catalytic activity of reduced copper will be affected by the method of its preparation was proved experimentally.

The following conclusions were drawn from the experimental results above-mentioned :

1. Reduced copper prepared from copper sulphate through copper oxide, acts on menthol at 300° to oxidize both hydrogen atoms of the hydroxyl group, and cyclohexane nucleus, and simultaneously to dehydrate catalytically, resulting in cymene, menthene, menthone and thymol as reaction products.

2. The catalytic activity of reduced copper as oxidizing and dehydrating agent depends on the velocity of the reduction of its oxide, and also on the process of preparation of the latter.

3. Reduced copper obtained by the reduction of copper oxide formed by the interaction of copper sulphate and an excess of sodium hydroxide solution, promotes catalytically both the oxidation and the dehydration of menthol, while that formed from copper sulphate with no excess of sodium hydroxide exerts a positive influence on dehydration only.

4. "Red copper" formed from copper oxide by reduction with a rapid current of hydrogen exerts a stronger effect on the dehydration of menthol than the "violet copper" prepared with a slow current of hydrogen while the effect on the oxidizing action is reversed.

5. The oxidizing activity of reduced copper was markedly diminished with time, but the dehydrating activity remained constant through the reaction, and this phenomenon should be ascribed to the accumulation of some poisonous substance on the surface of the catalyst<sup>1</sup>.

6. The oxidizing activity of "red copper" was diminished more quickly than that of "violet copper".

7. Sulphur dioxide acts to exert a strongly negative influence on the oxidizing activity of reduced copper.

## II. ACTIVITY OF THE CATALYST ON MENTHONE.

90 grm. of l-menthone,  $d_4^{25} = 0.8892$  ;  $n_D^{25} = 1.4425$  ;  $[\alpha]_D = -27.12^\circ$ ,

<sup>1</sup> See later experiment.

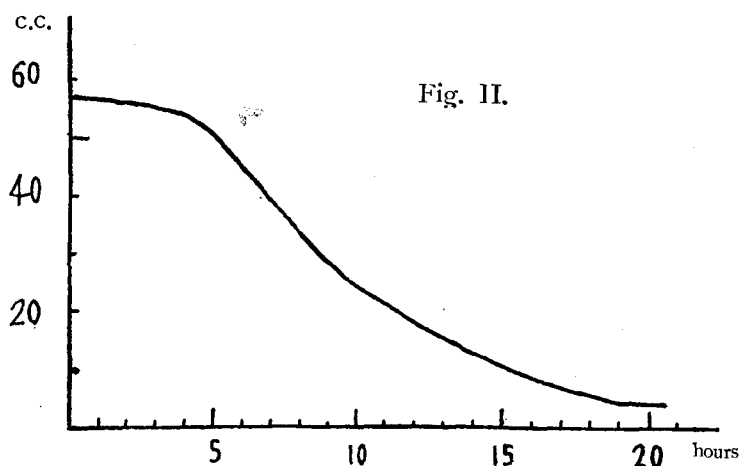
were passed, in an interval of 28 hours, on reduced copper at 300° obtained from 8 gm. copper oxide described in (3), and the reaction product was divided into two parts; the first part was collected from the product formed during the first 10 hours and the second from that of the next 10 hours respectively, and both showed the following physical constants:

	First part.	Second part.
Colour	colourless	pale yellow
$d_4^{25}$	0.9229	0.8926
$n_D^{25}$	1.4950	1.4753
$[\alpha]_D$	+ 0.41	+ 4.48

After repeated fractional distillation of each part, the following results were obtained:

	First part.	Second part.
	(yield in mol. per cent.)	
Menthene cymene	32	45
Thymol	68	55
<u>Changed menthone</u>	96	92
<u>Used menthone</u>		

Amount of hydrogen gas generated during the reaction, which collected, time to time; for five minutes each was plotted in Fig.2. When the results were compared with the yield of the reaction products of both parts, it was learned that results analogous to those derived from the experimentations on menthol, with respect to the oxidizing and dehydrating activities of the catalyst, should be obtained.



It has been observed that, as mentioned in the case of menthol, the evolution of hydrogen gas decreased with time, which indicated a retardation in the velocity of oxidation.

One thing which is necessary in order to account for the phenomenon, is that the piling up of reaction products on the surface of the catalyst will prevent the substance from reacting to it.<sup>1</sup>

When the evolution of hydrogen gas was markedly decreased, the operation was interrupted, a dry current of air was passed for some time to sweep away menthone and other volatile substances. Copper oxide was then heated in a current of dry air as in the case of elementary analysis, and water and carbon dioxide formed by combustion of a substance condensed on the surface of the catalyst during the operation, were collected separately as usual, and then the proportion of carbon and hydrogen in the substance was calculated:

Sample	CO <sub>2</sub>	H <sub>2</sub> O	C	H	Ratio(C:H)
(1) 2.0604 grm.	0.0501 grm.	0.0154 grm.	0.663%	0.084%	1:1.53
(2) 2.2331 "	0.0414 "	0.0166 "	0.506 "	0.083 "	1:1.97

Feb., 1924. Laboratory of Organic- and Bio-Chemistry.

<sup>1</sup> W. D. Bancroft: Applied Colloid Chemistry, p. 47 (1921).