

Studies on the Camphor Series, XII.
Catalytic Activity of
Various Reduced Coppers on l-Menthol.

By

Teikichi Hiraidzumi.

(Received April 11, 1927)

In the previous article, Prof. S. Komatsu and M. Kurata¹ have noted that the variability in the catalytic behaviour of reduced copper toward l-menthol, is affected greatly by the process by which the catalyst is prepared from various copper salts. Recently, Dr. B. Masumoto² in our laboratory, has observed on the catalytic action of various forms of copper oxide on pinene hydrochloride that the formation and physical nature of camphene depend on the modes of preparation of these catalysts, and these facts led the writer to undertake the present research.

The catalysts used in the experiment were prepared from the oxides of copper by reduction with hydrogen at 200°, and these were obtained by the writer according to the directions given by Dr. B. Masumoto in his paper above mentioned.

The density, and the bulk gravity (the volume occupied by one gram of the material when shaken down in a stoppered tube), of the catalysts were measured, and these properties seem to have some analogy to the colour of reduced metals, as will be seen in Table I. In Table I, Cu I was obtained from copper hydroxide gel from copper nitrate and a

¹ These Memoirs, A, **8**, 147 (1925).

² Ibid., **10**, 175 (1927).

potassium hydroxide solution and heated at 250° - 300° . Cu II was prepared from crystalline copper hydroxide obtained from basic copper nitrate. Cu III was obtained from amorphous copper hydroxide. Cu IV, from basic copper nitrate of a grey colour by ignition at 250° - 300° . Cu V, from black copper oxide which was formed from copper nitrate and 20 % ammonia water. Cu VI, from the copper oxide obtained from basic copper nitrate and excess of ammonia water and ignited at 250° . Cu VII, from the copper oxide resulting from the ignition of copper nitrate at 250° - 300° .

Table I.

| | d_4^{25} | bulk gravity | colour |
|---------------------|------------|--------------|----------------|
| Cu I. Colloidal gel | 5.8135 | 0.1720 | dull red |
| Cu II. Crystalline | 4.9504 | 0.2020 | brownish black |
| Cu III. Amorphous | 4.2832 | 0.2335 | black |
| Cu IV. | 5.4193 | 0.1845 | dull red |
| Cu V. | 5.2543 | 0.1903 | brown |
| Cu VI. | 5.3630 | 0.1862 | reddish brown |
| Cu VII. Ignited | 5.7683 | 0.1774 | vermilion |

In the experiment, 5 grm. of every copper oxide were reduced at 200° with hydrogen as usual, and menthol, M. p. 41° , $[\alpha]_D = -49^{\circ}.0$, was passed with almost equal rate over catalysts heated to 250° . By the reaction, hydrogen gas, water and oily substance were noticed to formed. However, the quantity of these reaction products and the nature of the constituents of oily substance are largely depend upon the kind of the catalyst, though the conditions under which the reaction was proceeded were kept in a similar manner.

The amount of hydrogen gas evolved by the reaction was measured, from time to time, for every five minutes, which was plotted against time and the results are shown in Fig. 1, 2, 3, 4, 5.

The oily substance, formed by the reaction with some water, was separated from the water layer, its physical constants measured, and then fractionated by distillation in a Witmer flask into the following three parts;

| | |
|---------------|-------------------------------|
| 1st. fraction | to 190° |
| 2nd. ,, | 190° - 210° |
| 3rd. ,, | above 210° |

The first fraction was distilled on metallic sodium and the fraction, B. p. 164° - 167° , was designated as menthene after confirmation of its

physical constants. The second fraction, B. p. 190° - 210° , was noticed in one case, on standing for a while, to be solidified in a mass, and in other cases remained in a liquid state, and in the former case the fraction was confirmed to consist mostly of unchanged menthol from its physical nature, while in its oily state it was composed of a mixture of menthol and menthone. The proportion of the two components in the oily mixture was estimated by means of phthalic anhydride and semicarbazid, transforming the alcohol into a phthalic acid ester and the ketone into its semicarbazone. The third fraction which boils above 210° , was assigned

Fig. 1. Cu VI.

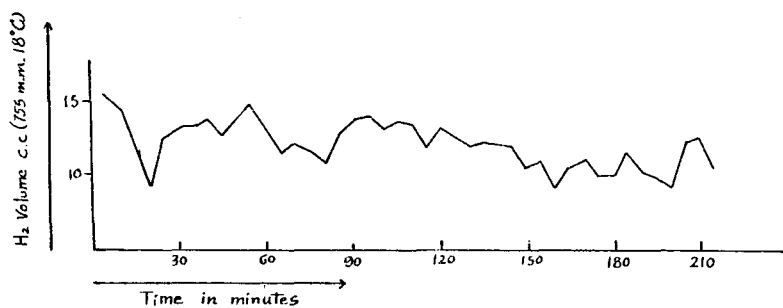


Fig. 2. Cu V.

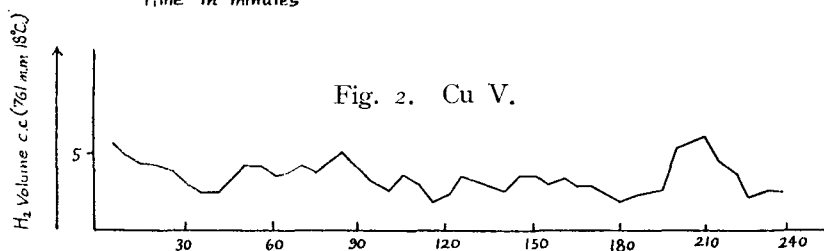


Fig. 3. Cu VII.

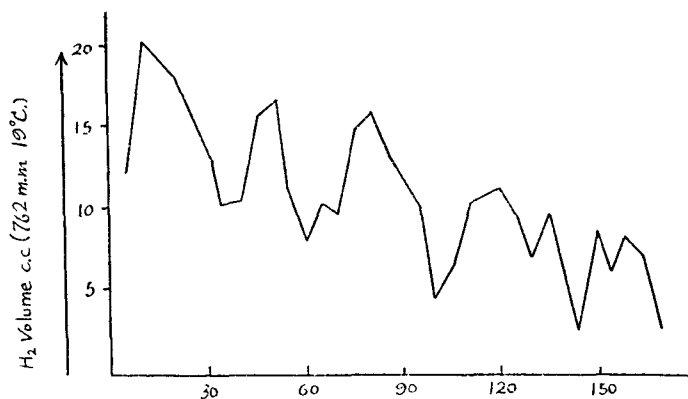


Fig. 4. Cu II.

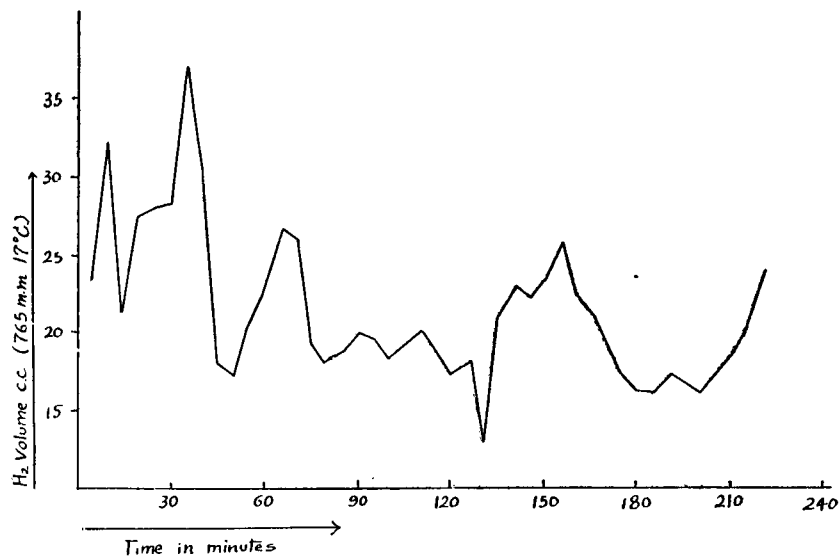
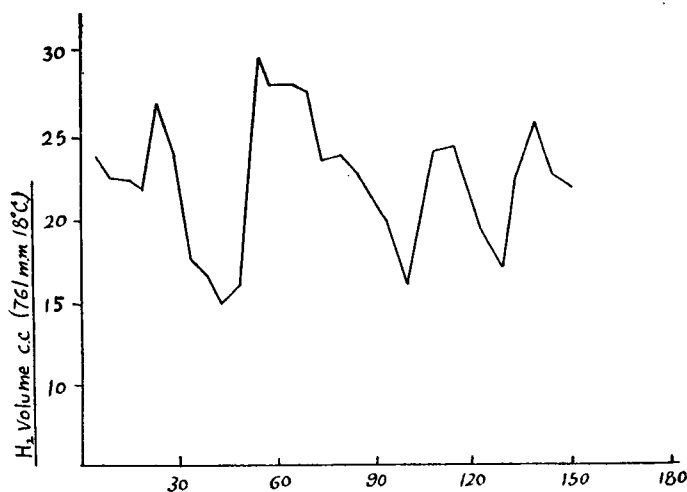


Fig. 5. Cu III.



to be thymol from its physical and chemical properties. The results of the experiment are shown in Table II.

As will be seen in that Figures, when menthol was passed on Cu I and Cu IV, no gas was evolved; while with other kinds of copper a certain amount of hydrogen gas was noticed to evolved, and its quantity

Table II.

| Catalyst | Cu I | Cu VII | Cu IV | Cu VI | Cu V | Cu II | Cu III | |
|--------------------------|------------------------|-----------|-----------|---------------|-----------|----------------|-----------|-----------|
| Density of CuO | 5.814 | 5.768 | 5.419 | 5.363 | 5.254 | 4.950 | 4.283 | |
| Colour of Reduced Cu | dull red | vermilion | dull red | reddish brown | brown | brownish black | black | |
| Grm. Passed per hour | 6.7 | 6.9 | 6.9 | 5.2 | 4.8 | 7.7 | 7.5 | |
| Menthol (grm.) | 20. | 20. | 8.5 | 20. | 20. | 30. | 20. | |
| Reaction Product (grm.) | 17. | 19. | 7.0 | 17. | 19. | 29. | 19. | |
| Reaction product | $[\alpha]_D$ | -21°·2 | +12°·1 | -47°·0 | +3°·0 | -33°·3 | -4°·9 | -2°·3 |
| | n_D^{25} | 1.4478 | 1.4488 | — | 1.4456 | 1.4479 | 1.4520 | 1.4673 |
| | d_4^{25} | 0.8505 | 0.8913 | — | 0.8899 | 0.8913 | 0.9029 | 0.8785 |
| Production of Water | + | — | — | — | — | — | + | |
| Fraction I (Menthen?) | B.p. | 165°-170° | — | — | 180°-200° | 160°-180° | 189°-200° | 160°-190° |
| | $[\alpha]_D$ | +7°·1 | — | — | +2°·0 | +3°·0 | +7°·0 | +2°·43 |
| | n_D^{25} | 1.4427 | — | — | 1.4463 | — | 1.4460 | 1.4493 |
| | d_4^{25} | 0.8113 | — | — | — | — | — | 0.8234 |
| | yield % | 49. | — | — | 6.0 | 2.6 | 2.0 | 46. |
| Fraction II | B.p. | — | 202°-209° | — | 202°-208° | 202°-206° | 204°-208° | — |
| | $[\alpha]_D$ | — | +12°·2 | — | +4°·4 | +14°·1 | -4°·9 | — |
| | n_D^{25} | — | 1.4468 | — | 1.4474 | — | 1.4487 | — |
| | d_4^{25} | — | 0.8913 | — | 0.8925 | — | 0.8944 | — |
| | yield % | — | 92.6 | — | 77. | 50. | 80. | — |
| Menthone | M.p. of Semicarbazone | — | 173°-176° | — | — | 169°-172° | — | — |
| | M.p. | 41°-42° | — | 43° | — | 40°-42° | — | — |
| | $[\alpha]_D$ | -50°·2 | — | -48°·1 | — | -50°·2 | — | — |
| | yield % | 45.8 | — | 95. | — | 31. | — | 25. |
| Menthol | M.p. of acid phthalate | — | — | — | — | 104°-110° | — | 100°-108° |
| | yield % | — | — | — | — | — | — | — |
| Fraction III (Thymol) | M.p. | — | — | — | — | 43°-44° | 44° | |
| | yield % | — | — | — | — | 2.0 | 14. | |

depending largely upon the nature of catalyst, with Cu V and Cu VI, the evolution of the gas is constant during the experiment, while with Cu VII, it shows a gradual decrease with the progress of the reaction. With Cu II and Cu III, the curves for hydrogen gas show a zigzag form which indicates that the reaction in presence of the catalysts will be more complicated than in the other cases, and such an idea of the reaction will be foretold on the appearance of water in the reaction product.

In the case of Cu III, some quantity of water was noticed to form by the reaction, because of this water the reaction product was emulsified.

The formation of water by the reaction was also observed with Cu I. The reaction product, however, in this case seem to differ in nature from those of Cu III, since no hydrogen gas was noticed to evolve in the former as stated above. With Cu I and Cu IV, there is a similarity in the fact that no hydrogen gas is formed in the reaction; while they differ with regard to the formation of water. The behaviour of Cu IV, Cu VII, Cu VI, Cu II and Cu V toward menthol seems to be similar in the fact that no water is formed, but there is a difference in the formation of hydrogen gas.

Such a difference in the formation of water and hydrogen gas by the reaction with various catalysts was also noticed in the chemical nature of the oily reaction products in some measure; the products which were formed in presence of Cu I and Cu III, are alike in the quantity of menthene, but differ in the occurrence of thymol, and these facts were manifested in the formation of hydrogen gas and water. In other words, with Cu I, the dehydration of menthol takes a prominent part in the reaction; while with Cu III, the dehydration and the oxidation of menthol take place simultaneously, and the former catalyst serves as a dehydrating agent, and the latter as dehydrating and oxidizing agent. Cu II behaves toward menthol as a dehydrating and oxidizing agent just like Cu III, the oxidizing action of the former, however, is different in details from the latter, forming menthone as a principal reaction product.

The catalytic action of Cu VII, Cu VI and Cu V is similar to Cu II in producing menthone, but the rotatory power of menthone formed by the action of the three former catalysts is different from that formed by the last one. The catalytic activities of these reduced coppers, therefore, differ greatly from each other in detail though they are practically similar in the main points of reaction. Analogous phenomena may be noticed in the menthene fraction with these catalysts.

In summary, Cu VII, as noticed already by Sabatier on the catalytic action of reduced copper, acts on menthol as an oxidizing catalyst forming

menthone, and other catalysts except Cu I, act to promote the oxidation of menthol, but the activities of these catalysts differ from each other, especially those of Cu II and Cu III, possessing the faculty to remove the hydrogen atoms of the polymethylene ring, consequently Cu VII is the most convenient catalyst for making menthone from menthol, and Cu VI, Cu V and Cu II may be used as catalysts for this purpose, and Cu III is in like manner a good catalyst for the preparation of thymol.

Cu I acts on menthol to dehydrate it, with the formation of menthene, which is similar in catalytic activity to alumina or thoria; and Cu III, as will be seen in the results shown in Table II acts as a dehydrating catalyst.

The reduced coppers will be divided from the stand-points of catalytic activity toward menthol, into two classes, the first group which acts to promote the oxidizing action of menthol, as we noticed with reduced nickel, to which Cu VII belongs; and the second group acts on menthol to promote dehydration, and Cu I belongs to this group. Other reduced coppers have both of these catalytic actions, though the activity of these actions differs according to the processes by which these catalysts are prepared from nitrate.

The activity and nature of the catalytic actions of these catalysts are independent of their specific gravity but seem to depend upon the mode of the formation of the catalysts, and their nature may be ascribed to the special features of the catalysts.

This research was carried out at the suggestion and under the direction of Prof. S. Komatsu, to whom the writer wishes to express his sincere thanks.

April 1926.

Laboratory of Organic- and Bio-Chemistry.
