Studies on Catalytic Action, XV.

Catalytic Activity of Reduced Copper, II.

By

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The conclusions stated in the previous article,[1] which were drawn from the experimental results of the activity of reduced copper on l-menthol, indicate clearly one reason for variability in the catalytic behavior of the metal with the variation in the mode of preparing catalyst—the velocity of the reduction of its oxide, and also the process of the preparation of the oxide. The variable adsorptive capacity of the material, in general, would account for a variadle catalytic behavior, and it was believed that there was a parallelism between adsorption and catalytic activity.[2] Kelber[3] and Armstrong and Hilditch[4] have shown with nickel such a relationship between adsorptive power and catalytic activity ; nickel oxide per se gave a moderately active catalyst when reduced at about 300,° reduction of the same material at 450–500° gave a product of but feeble activity, and the former was found to take up ten times of hydrogen gas compared with the latter.

It seems that reduced copper shows similar variability to nickel in adsorptive power with variation in the mode of preparation referring to the experiment by Brown and Henke[5] on the catalytic reduction of nitrobenzene with copper catalyst ; and moreover, they have stated that copper oxide prepared by ignition of the nitrate at 450° and reduced at a lower temperature, the resulting catalyst is active, but deteriorates

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1 These Memoirs.

2 W. D. Bancroft : J. Phys. Chem., **27**, 802 (1923).

3 Ber. D. Chem. Ges., **49**, 55, 1868 (1916).

4 Fourth Report on Coll. Chem., 1922. p. 333.

5 J. Phys. Chem., **26**, 715 (1922).

rapidly, presumably more readily than the same catalyst obtained by reduction at 314.°

Reduced copper, however, acts, as we conjectured, as an oxidizing agent as well as a dehydrating one, and accordingly it was doubtful whether these catalytic activities would be affected equally by the mode of preparation or by the action of some poisonous substances.

The present investigation was, therefore, undertaken in the anticipation of settling this question by comparing the catalytic behavior of reduced copper toward menthol, which was obtained from the oxide precipitated from the nitrate by means of an alkali, and that from copper sulphate in the same manner, since it was suggested from the previous experiment that sulphur dioxide tends to exert a strongly negative influence on the oxidizing activity of the catalyst.

On the other hand, the apparent density of various type of copper oxide was measured in a manner similar to that used by Armstrong and Hilditch in the case of nickel oxide, and the results were compared with the catalytic activity of reduced copper, derived from the corresponding oxide.

Table I.

	Copper Oxide	Density
1	Copper sulphate and an excess of sodium hydroxide	5·47
2	„ „ „ 2 mol „ „ „	5·42
3	Copper nitrate and an excess of sodium hydroxide	6·08
4	„ „ „ ammonia water	6·05
5	„ „ by ignition	6·06

In the experiment, the same menthol M. p. 43°; B. p. 211–212°; $[\alpha]_D = -49.9°$, used in the previous experiment[1], was passed over reduced copper heated at 200° and 300° respectively, obtained from

(1)   5 grm. copper oxide by reduction with hydrogen at 200° and 300,° which was prepared from purified copper sulphate and (a) an excess of sodium hydroxide solution, (b) ammonia water, and from purified copper nitrate and (c) an excess of sodium hydroxide, (d) ammonia water, from

(2)   10 grm. copper oxide by ignition of the nitrate, and

(3)   5 grm. copper oxide prepared from 1 mol copper sulphate and 2 mol caustic soda solution,

(4)   2·8 grm. basic copper sulphate by reduction with hydrogen at

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1   S. Komatsu and M. Kurata: Loc. cit.

the temperatures, which were prepared according to the direction of Williamson,[1]

(5) by reduction of 2·8 grm. basic copper nitrate formed by the interaction of copper nitrate and ammonia,.

(6) copper sulphate reduced with pure hydrogen at 250°[2],

(7) a mixture of copper oxide (a) and basic copper sulphate (4) by reduction at 200° and

(8) a mixture of copper oxide (a) and copper sulphate by reduction at 200.°

The amount of hydrogen gas evolved by the reaction was measured for five minutes each when the reaction was carried on for one, two and three hours, and the results calculated under normal conditions were shown in table III.

The reaction product was subjected to fractional distillation in a Witmer flask[3] after being dried with anhydrous sodium sulphate, and the fraction boiling to 180° was distilled twice on metallic sodium, and the content of cymene and menthene in it was determined by means of index of refraction, the fraction B. p. 200–220° was treated with hydroxylamine following the directions of Beckmann[4] to separate menthols[5] from the menthones formed by oxidation of the former, the rotatory power of the oxime was observed in 10% alcohol solution in 1 dm. tube, and the last fraction boiling above 220,° was regarded as thymol.

The results are shown in the following tables II and III.

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1 J. Phys. Chem., **27**, 789 (1923).

2 Copper sulphate heated at 200° in presence of hydrogen shows no appreciable change, while at 250° it was noticed to be decomposed into metallic copper and sulphur dioxide: $CuSO_4 = Cu + SO_2 + 2H_2O$.

3 Helv. Chim. Acta, **7**, 59 (1924).

4 J. prak. Chem., (2), **55**, 17 (1897).

5 It was supposed that some isomers of menthol and menthone should be formed and their existence in the reaction product will be discussed in the next article.

Table II.

Kinds of copper oxides	Reduction temp.	Reaction temp.	Gm. passed per hr.	Time for passing	Fractions, in wt. %			Fraction to 180°			Ratio, % Changed menthol / Used menthol
					to 180°	180–200°	200–220°	n_D^{25}	Menthene %	Cymene %	
CuSO$_4$ +2NaOH (3)	200°	300°	2·2	2¾	100	0	0	1·4478	89·5	10·5	100
	300°	,,	11·0	½	100	0	0	1·4515	80·7	19·3	100
	200°	200°	3·1	2	41	0	59	1·4476	90·2	9·8	41
Basic copper sulphate (4)	,,	300°	0·5	5	86	5	9	1·4500	96·5	3·5	91
Basic copper sulphate (1) (b)	,,	,,	4·5	1	18	5	77	1·4496	84·9	15·1	19
	,,	,,	7·7	1	10	2	88	1·4562	93·8	6·2	10
	300°	,,	9·5	1	4	2	94	1·4493	85·7	14·3	4
CuSO$_4$ (6)	250°	,,	2·9	1½	0	1	99	—	0	0	0
Copper oxide+Basic Copper sulphate (7)	200°	,,	17·8	1	49	2	49	—	—	—	50
Copper oxide+CuSO$_4$ (8)	,,	,,	2·9	1½	76	6	18	1·4485	87·8	12·2	81

It was noticed, in all cases of the preparation of reduced copper by reduction, evolution of SO$_2$ gas, and that no hydrogen gas was generated during the reaction with the reduced metal. The reaction products, in each case, when subjected to distillation, were distilled out below 220°, and the fraction B. p. 200–220° being solidified at ordinary temperature, was assumed to be composed of menthol.

1. The results of the catalytic reaction of l-menthol in presence of reduced copper derived from both copper sulphate and copper nitrate are alike generally, but differ in some detail; the catalyst acts to promote both oxidation and dehydration of menthol, yielding thymol, menthone, menthene and cymene, and the yield of the latter two substances, however, is smaller in case the reduced copper from copper nitrate and an excess of alkali was used as a catalyst than that of the catalyst from copper sulphate prepared and used under same conditions.

2. Such a variable catalytic activity of the catalyst would be accounted for the variation in the mode of preparation, in other words mostly for the source of the catalyst from which the oxide was prepared. Since reduced copper derived from a basic copper sulphate behaves quite different from that from a basic copper nitrate; in the former case it acts simply as dehydrating agent yielding menthene and cymene and the latter substance should be regarded naturally to be formed catalytically from menthene, by the reaction shown in the following scheme: menthene——➤ cymene + menthane, while the catalyst obtained in another way acts principally as oxidizing agent with some formation of menthene, and cymene and secondary reaction products as was observed in (2), in which reduced copper derived from the oxide by ignition of the nitrate was used as catalyst.

3. As a matter of fact, reduced copper prepared from copper sulphate acts on menthol as oxidation and dehydration agent in one way, and on the other, only as dehydrator, according to the method of its preparation, while the same metal from copper nitrate acts principally as an oxidizing agent no matter what process was used for the preparation of the catalyst. It was, therefore, borne in mind that a very toxic substance—sulphur dioxide—which would suppress only the oxidizing activity of the catalyst, would be evolved from copper sulphate remaining as an impurity in copper oxide, during reduction of the oxide with hydrogen, and the experimental fact which indorses the present idea, has been described in the previous article.

4. It was recommended, consequently to get menthene from menthol, reduced copper prepared from copper sulphate and an equivalent quantity of sodium hydroxide, would be conveniently used at 300° as catalyst.

5. Metallic copper from the oxide prepared from both nitrate and sulphate with an excess of caustic soda solution, reduced at 200°, may be employed at 200° for the preparation of menthone, which also will be obtained with fruitful results, by the aid of reduced copper from the oxide obtained by ignition of the nitrate by reduction at 200.°

Reduced copper obtained from copper oxide by reduction at 200° and heated at 200° acts to promote the ketone-formation, whilst the same heated at 300° the thymol-formation; for the preparation of the ketone by dehydrogenation of the alcohol, it was suggested, according to the authors' experiment, the temperature of the reaction is better in every respect maintained at 200–245°, though it was usually believed much more advantageous to keep the catalyst at 300° for the purpose,[1] since in the latter treatment the ketone formed by exidation reverts by virtue of the catalyst at high temperature to phenol by further loss of hydrogen of the hexamethylene ring similar in result to the case in which reduced nickel was employed.[2]

6. It was a noteworthy fact that the rotatory power of the menthone oxime shows no constant value, which seems to depend on the factors: (1) the source of the catalyst, (2) the method of preparation of the catalyst and also (3) the temperature at which the catalyst was maintained during the reaction; the ketone derived at higher temperature or by using the catalyst obtained at higher temperature shows a lower rotatory power of the oxime than that which resulted at a lower temperature or by the action of the catalyst obtained at a lower temperature, and the true nature of the variability of the optical rotatory power of menthone, will be discussed in the next article.

7. The belief cherished by many chemists that finely divided copper has no dehydrating action on alcohol and that it has no activity to oxidize the hydrogen of the hexamethylene ring, must now be modified by the above experiments, since that properly reduced copper acts essentially as a catalyst for the dehydrogenation and dehydration of alcohol and also performs easily the oxidation of the hydrogen of hexamethylene ring, though the activity of these actions depends largely on the mode of its preparation.

8. In comparing the catalytic activity of the catalyst prepared according to various methods (reduced at 200°), the results obtained by passing 5 grm. of menthol in intervals of 5 minutes at 300°, were cited here again.

In the table IV. Hobs. and Hcalc. are the results measured actually during the reaction and calculated, by means of the chemical equations mentioned under the table, from the quantity of the reaction products.

1　W. D. Bancroft: J. Phys. Chem., **27**, 853 (1923); E. F. Armstrong and T. P. Hilditch: Fourth Report on Colloid Chem., (1922), p. 333.

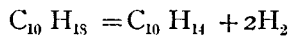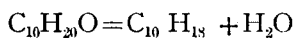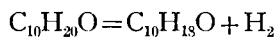2　P. Sabatier: La catalyse en chimie organique, p. 251, 246 (1922).

Table III.

Kinds of copper oxides	Reduction temp.	Reaction temp.	Gm. passed per hr.	Time for passing	Vol. H₂ hr. 1	Vol. H₂ hrs. 2	Vol. H₂ hrs. 3	to 180°	180–200°	200–220°	220–225°	225°–230°	n_D^{21}	Menthene %	Cymene %	Menthon %	Menthol %	Thymol above 220 %	Oxime $[\alpha]_D$	Menthene	Cymene	Menthon	Thymol	Ratio % changed menthol / used menthol
CuSO₄+Excess NaOH (1) (a)	200°	200°	5·3	1	34			(2) 0	1	99	0	0	—	—	—	47	53	0	-11·1°	0	0	100	0	47
	"	"	2·7	2	60																			
	300°	"	7·6	3½	11	—	15	2	1	97	0	0	1·4532	75	25	20	80	0	-17·9°	6·7	2·3	91	0	22
	200°	300°	8·6	1	198			3	1	3	2	90	1·4581	63	37	20	20	60	—	1·8	1·2	0·6	96·4	99·4
	300°	"	4·8	3	195	—	124	(2) 7	1	1 (a)	1	90	1·4580	63	37	—	—	—	—	4·4	2·6	trace	93	99·5
	"	"	3·8	1	187																			
	"	"	5·4	3	188	—	172																	
Cu(NO₃)₂+Excess NaOH(1)(c)	200°	200°	4·9	3	34	—	15	0	0	100	0	0	—	—	—	46	54	—	-7·6°	0	0	100	0	46
	300°	"	5·1	1	29			0	0	100	0	0	(2) —	—	—									
	"	"	5·1	2	57	43		0	0	100	0	0				38	62	0	-6·6°	0	0	100	0	38
	200°	300°	9·3	4	189	—	171	0·9	0·4	1·3	1·3	96·1	(2) 1·4659	43	57	13	27	60	—	1·2	0·3	0·1	99·4	99·6
	"	"	6·1	2	177	129		0	1·5	1·5 (1)	3	94												
	300°	"	7·5	2⅙	150	123		1	0	2 (1)	3	94	1·4643	47	53	—	—	—	—	0·5	0·5	trace	99	99
Cu(NO₃)₂+NH₄OH (1) (d)	200°	200°	3·2	2⅔	20			0	0	100	0	0	—	—	—	22	78	0	-26·7°	0	0	100	0	22
	300°	"	4·3	2	13			0	0	100	0	0	(2) —	—	—									
	"	"	6·0	2	12	7		0	0	100	0	0				27	73	0	-30·8°	0	0	100	0	27
	200°	300°	5·6	4	172	—	77	1	3	61	10	25	(2) 1·4594	59	41	56	8	36	-11·6°	0·3	0·2	39	60·5	95
	"	"	6·3	2	118	48		0	2·5	67	16	14·5												
	300°	"	7·5	1	124			5	5	37	19	33	1·4640	47	53	55	0	45	-5·4°	2·4	2·6	22	73	100
	"	"	4·6	4	197	—	70	1	2	55	15	27	1·4631	50	50	52	7	41	-15·9°	0·5	0·5	30	69	96
Cu(NO₃)₂ By ignition (2)	200°	200°	6·0	1⅙	—			0	0	100	0	0	—	—	—	33	67	0	-22·5°	0	0	100	0	33
	"	"	5·4	2	25			0	0	100	0	0	—	—	—	27	73	0	-29·9°	0	0	100	0	27
	300°	"	7·2	1	8			(2) 0	0	100	0	0	—	—	—	24	76	0	-31·9°	0	0	100	0	24
	"	"	3·2	1	13			0	0	100	0	0												
	200°	300°	12·9	3½	42	21	16	1	1	89	2	7	1·4647	46	54	77	8	15	-12·1°	0·46	0·54	75	24	93
	"	"	7·3	1⅙	67			0	1	88	3	8	—	—	—	—	—	—	—	—	—	—	—	—
	300°	"	9·0	1½	59			1·5	1·5	85	3	9	1·4699	32	68	71	22	7	-28·0°	0·6	1·4	75	23	81

(1) It was regarded to be composed equally of menthol and thymol.

(2) The reaction products obtained under the same conditions, combined together and then were analysed.

Table IV.

Source of catalyst	Yield in mol %				H. gas in c.c.	
	Menthene	Cymene	Menthone	Thymol	obs.	calc.
Copper sulphate with an excess of caustic soda.	3	2	0.4	94.6	190	180
Copper nitrate with an excess of caustic soda.	0.3	0.4	0.1	99.2	170	186
Copper nitrate with ammonia.	1	1	30	68	150	147
„ „ by ignition.	0.5	1	75	23.5	50	91

$$C_{10}H_{20}O = C_{10}H_{18}O + H_2$$
$$C_{10}H_{20}O = C_{10}H_{18} + H_2O$$
$$C_{10}H_{18} = C_{10}H_{14} + 2H_2$$
$$C_{10}H_{20}O = C_{10}H_{12}O + 4H_2$$

When the catalytic activity of the catalyst measured by means of the quantity of hydrogen generated by the reaction, compared with the specific gravity of the catalyst shown in the table I, there seems to exist a relationship similar to that noticed by Armstrong and Hilditch[1] with the nickel catalyst, between them.

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

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1 Loc. cit.