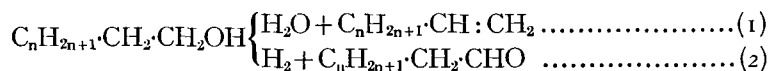# Studies on Catalytic Action, XVII.
Catalytic Actions of Various Types of Reduced Copper upon Alcohols.

By

Tohoru Hara.

Berthelot[1] has observed that when ethyl alcohol passed through a glass tube heated to high temperatures, the formation of ethylene and aldehyde began about $500°$.   Other primary alcohols[2] suffer by heat analogous reactions with ethyl alcohol, which will be represented in the following schemes:

$$C_nH_{2n+1}\cdot CH_2\cdot CH_2OH \begin{cases} H_2O + C_nH_{2n+1}\cdot CH:CH_2 \dots\dots\dots\dots\dots (1) \\ H_2 + C_nH_{2n+1}\cdot CH_2\cdot CHO \dots\dots\dots\dots (2) \end{cases}$$

In the presence of a catalyst, such as copper, cobalt, nickel, iron, platinum[3], and palladium[4], the dehydrogenation of alcohols (1) is promoted, and on the contrary, by the contact action of the oxide of a metal such as alumina,[5] thoria and the blue oxide of tungsten[6], the dehydration (2) takes place prominently.   According to P. Sabatier and J. -B. Sendrens[7], reduced copper heated at about $200°—300°$ is the sole catalyst for the oxidation of primary and secondary alcohols into aldehydes and ketones respectively, without any side-reaction.   Recently a remarkable addition has been made by S· Komatsu[8], to our knowledge of the contact action of reduced copper

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1   C. R., **33**, 210 (1851).
2   W. Ipatief: Ber. D. Chem. Ges., **34**, 596, 3579 (1901).
3   P. Sabatier and J. -B. Sendrens: C.R., **136**, 738, 921 (1903).
4   H. Wieland: Ber. D. Chem. Ges., **45**, 484 (1912).
5   W. Ipatief: Ibid., **36**, 1990 (1903).
6   P. Sabatier and A. Mailhe: C.R., **146**, 1376 (1908); **147**, 16, 106 (1908).
7   Ibid., **136**, 738, 921, 983 (1903).
8   These Memoirs, A. **7**, 85 (1924).

that reduced copper has the property of promoting not only the oxidation
of alcohol, but also its dehydration, and the new catalytic action of the
metal was confirmed by S. Komatsu and B. Masumoto[1] with their findings
that cyclohexanol, when passed over reduced copper at 200° and 300°,
yielded phenol and cyclohexene, besides cyclohexanone[1,2], and that l-menthol,
under conditions similar to those in the experiment with cyclohexanol, was
transformed into menthone, thymol[3], and menthene[4].   And recently Komatsu
and Kurata[5] have investigated comprehensively the catalytic action of reduced
copper prepared in various ways on l-menthol, and they came to the
conclusion that the reduced coppers from the standpoint of the catalytic
activities at about 300°, would be classified into the following three types:

Type of reduced copper from the oxide formed by	Main Reaction Products at 300°		Catalytic Action.
1st. Cu I. $CuSO_4 + 2NaOH$,	Menthene, $4/5 - 9/10$ parts		Dehydration
	Cymene, $1/5 - 1/10$ parts		
2nd. Cu II. $CuSO_4$ + excess NaOH,	Thymol, $19/20$ parts		Dehydrogenation (cyclohexane ring)
3rd. Cu III. by ignition of $Cu(NO_3)_2$.	Menthone, $3/4$ parts		Dehydrogenation (OH-group)
	Thymol, $1/4$ parts		Dehydrogenation (cyclohexane ring)

In order to see whether the statements above-mentioned of the catalytic
actions would have some general application, the present writer has examined
the results obtained by passing some primary and secondary alcohols on
the three types of reduced copper above-mentioned heated at 230° and
330° respectively.

I. PREPARATION OF CATALYSTS[6]

To the hot aqueous solution of copper sulphate purified by recrys-
tallisation, an equimolecular quantity of caustic soda solution was added
speedily and the precipitate thus formed, washed immediately by decantation
with water until not a trace of SO_4 - ion could be found in the washing,
then filtered and dried in an air bath at about 100°. The oxide, thus obtained,
— both the oxide and metallic copper were confirmed to contain a trace of

1   These memoirs, **9**, 15 (1925).
2   P. Sabatier and J. –B. Sendrens: Ann. Chim. phys., (8), **4**, 466 (1905). Cyclohexanol
     by the contact action of reduced copper at about 300°, was decomposed into hydrogene
     and cyclohexanone.
3   S. Komatsu and T. Yukitomo: These memoirs, A. **8**, 65 (1925).
4   S. Komatsu and M. Kurata: Ibid., *A.* **8**,35 (1925).
5   Ibid., A. **8**, 147 (1925).
6   S. Komatsu and M. Kurata: These memoirs, A. **8**, 148 (1925).

basic copper sulphate[1],— was reduced to metallic copper (denoted by Cu I).

To the hot aqueous solution of purified copper sulphate an excess of caustic soda solution was added. The precipitate was washed well with hot water, filtered and dried in an air bath as before. It contained neither neutral nor basic sulphate, and was reduced to metallic copper (denoted by Cu II).

The copper oxide obtained by the ignition of purified copper nitrate, was reduced as usual to metallic copper (denoted by Cu III).

In each experiment, 10 grm. (in Cu I and Cu II) or 20 grm. (in Cu III) of cupric oxide were reduced with a slow current of pure hydrogen at 220°–230°, and alcohol vapour was passed at 230° and 330° respectively. The reaction products were fractionated carefully with a Witmer flask, and then treated in the proper way, where necessary, to separate the constituents.

Before and after each experiment, l-menthol was passed on the reduced copper used in the experiment, and the activity of the catalyst was tested by examination of the reaction products.

II. EXPERIMENTS.

1. Ethyl Alcohol.

According to P. Sabatier and J.–B. Sendrens[2], the alcohol, in presence of reduced copper, began to decompose at 200° into aldehyde which was noticed to form quantitatively at from 250° to 350°. When, however, the alcohol purified by distillation on lime, B. p. 78°, passed on the three types of reduced copper, reaction products of the following compositions were obtained:

	Cu I.		Cu II.			Cu III.	
Reaction temp.	230°	330°	230°	330°		230°	330°
No. of exp.	82	83	101	102	103	112	113
Total alc. pass, (grm.)	13	13	12	63	8	11	9·5
Alc. pass. (grm. p. h.)	8·7	8·7	8	8	8	8·3	6·8
React. prod. (grm.)	11	11	11	43	5	10	8·5
Fraction	—	—	—	—	—	—	—
30° – 70° (aldehyde) (grm.)	0	0	3·5	23	2·5	0	2
70° – 85° (alcohol) (grm.)	10	10	7·0	13	2·0	9·5	6
85° – 105° (grm)	0	0	0	2	0	0	trace
105° – 117° (acetic acid) (grm.)	—	—	—	3	—	—	—

1 Cu I is quite different in this respect from the Cu I described in the XVIth article of this series, since the latter contains neither neutral copper sulphate nor basic salt.

2 C. R., **136**, 738, 922 (1903).

As may be seen from the table, Cu I has no catalytic action at 330° on the alcohol. Cu III shows the catalytic action to decompose the alcohol into aldehyde, which has been already noticed by P. Sabatier and J.-B. Sendrens, while Cu II at 230° and 330° acts on alcohol to yield aldehyde, acetic acid and acetic ester. The occurrence of the last substance in the reaction products of No. 101, 102 & 103 was noticed by its characteristic odour.

2. Isoamyl Alcohol.

It was obtained from a fusel oil, and purified by the fractional distillation in a Witmer flask, B. p. 129°-130°. The experimental results obtained by passing the alcohol on the reduced coppers, are as will be seen in the following table quite different from those obtained previously by P. Sabatier and J.-B. Sendrens[1].

	Cu I.		Cu II.		Cu III		
Reaction temp.	230°	330°	230°	330°	230°	300°	330°
No. of exp.	65	66	88	10	76	77	17
Total alc. pass. (grm.)	9	10	8	138	17	15	12
Alc. pass. (grm. p. h.)	9	9	7	7·6	10	10	8
React. prod. (grm.)	8	9·5	7	134	15	13	10
Acid (calc. as isovaleric acid) (%)	-	-	-	-	0·2	0·85	-
Fraction	-	-	-	-	-	-	-
90°-120° (aldehyde)	0	0·7	1·6	73·5	2	7	4·5
120°-135° (alcohol)	7·5	8	3·9	42	11	3	1·8
135°-175° (ester, acid)	0	0·7	-	13	-	-	2
Loss and residue.	0·5	0·1	0·5	1·5	0·5	1	1·7
Sum	8	9·5	6	130	13·5	11	10

With Cu I, Cu II and Cu III at 330°, isovaleric acid and its isoamyl ester were obtained and further investigations on the formation of these compounds will be reported in another article by S. Kumamoto of our laboratory.

3. Benzyl Alcohol.

The alcohol from the Schimmel Co, was purified by distillation, B. p. 202°, and used in the experiment. It was reported by P. Sabatier and J.-B. Sendrens[2] that the decomposition of the alcohol, in presence of reduced copper began above 300°. The author's experimental results, however quite different from those of the others, are as follows:

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[1] C. R., **136**, 923 (1903).
[2] C. R., **136**, 984 (1903).

	Cu I.		Cu II.		Cu III.	
React. temp.	$230°$	$330°$	$230°$	$330°$	$230°$	$330°$
No. of exp.	62	63	60	61	74	75
Total alc. pass. (grm.)	20	20	20	20	20	20
Alc. pass. (grm. p. h.)	9	10	8	8	10	10
React. prod. (grm.)	19	19	19	19	19	19
Water layer (grm.)	0	0	0·4	2	0	a few drops
Oily layer (grm.)	19	19	18·6	17	19	19
Acid (calc. as benzoic acid) (%)	neutral		3	5·6	0·5	1·4
Fraction						
$110° - 160°$ (toluene)	0	0·5	7	8·3	2·3	2
$160° - 190°$ (aldehyde)	0	0	5·2	4·3	8·4	14
$190° - 210°$ (alcohol)	17·5	17	1·5	0·4	2·8	trace
Residue & loss.	0·5	0·5	1·3	2·0	2·5	1
Sum	18	18	15	15	16	17

With Cu II and Cu III, the formation of benzoic acid (M. p. $120°$ – $121°$) was evident, and on the other hand, no ester was observed to be formed in any case. Toluene was noticed to be formed when Cu I was used as catalyst at $330°$, and with Cu II and Cu III at $230°$ and $330°$, and the yield of the hydrocarbon, in the presence of Cu II, was increased with the temperature; while in the presence of Cu III the relation between the yield and the temperature was reversed. Cu I shows the catalytic action on this alcohol at $330°$, while other coppers show it already at $230°$, and especially was it remarked with Cu II.

In the following table the yield of reaction products was shown in mol per alcohol.

1. Ethyl alcohol.

Type of reduced copper	Cu I.		Cu II.			Cu III.	
Reaction temperature	$230°$	$330°$	$230°$	$330°$	$330°$	$230°$	$330°$
Aldehyde	0	0	33	58	58	0	25
Unchanged alcohol	100	100	77	37	45	100	75
Acetic acid	–	–	–	7	–	–	–

2. Isoamyl alcohol

Type of reduced copper	Cu I.		Cu II.		Cu III.		
Reaction temperature	$230°$	$330°$	$230°$	$330°$	$230°$	$300°$	$330°$
Aldehyde	0	8	29	59	15	70	60
Unchanged alcohol	100	88	71	34	85	30	24
Isovaleric acid and its isoamyl ester		4	–	7	–	–	16

3. Benzyl alcohol.

Type of reduced copper	Cu I.		Cu II.		Cu III	
Reaction temp.	230°	330°	230°	330°	230°	330°
Toluene	0	4	53	64	19	14
Aldehyde	0	0	34	28	60	84
Unchanged alcohol	100	96	10	·3	20	—
Benzoic acid	0	0	3	5	1	2

When primary alcohol (ethyl, isoamyl and benzyl alcohols) was passed over the three types of reduced copper above-mentioned heated at 230° and 330° respectively, aldehyde is formed accompanied always with the formation of an acid, though the quantity of the latter substance is small compared with that of aldehyde. The formation of aldehyde is much more effective when Cu II is employed, especially in the oxidation of the lower member of aliphatic alcohol, and the yield of aldehyde (in mol per cent) when Cu III is used as catalyst, is proportional to the molecular weight of alcohol and also to the reaction temperature. In the oxidation of benzyl alcohol, Cu III serves as a good catalyst while Cu II tends to promote the formation of toluene, and both reactions are much more favorable at higher temperature.

Reduced Cu I thus, promotes the dehydration of primary alcohols with the exception of ethyl alcohol used in the experiment, under the conditions mentioned above. The catalytic actions of Cu II and Cu III toward primary alcohol seem to be different in their activities, from those toward menthol[1] and cyclohexanol[2], and therefore, some secondary alcohols were passed over the reduced coppers in the same way as were the primary alcohols, and the reaction products were examined to compare their catalytic activities.

According to W. Ipatief[3], secondary alcohol also undergoes dehydration and dehydrogenation by heating at dull red heat. Consequently, the transformations of the secondary alcohols by heat in presence of the catalysts, is very interesting, especially in comparison of the results with those of primary alcohols.

4. Isopropyl Alcohol.

Aceton (B. p. $57^\circ - 58^\circ$) was reduced according to the directions of P. Sabatier and J. -B. Sendrens[4] with reduced nickel and hydrogen at $115^\circ - 125^\circ$, and isopropyl alcohol (B. p. $80^\circ - 82^\circ$) was isolated from the reaction product by fractional distillation in a Witmer flask. When this

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1   Loc. cit.
2   Loc. cit.
3   Ber. D. Chem. Ges., **34**, 599 (1901)
4   C. R., **137**, 302 (1903).

alcohol was passed on reduced copper heated at 230° and 330° respectively, acetone was formed as the main reaction product as noticed previously by P. Sabatier and J. -B. Senderens[1], as will be shown in the following table:

	Cu I.		Cu II.		Cu III.	
React. temp.	230°	330°	230°	330°	230°	330°
No. of Exp.	80	81	89	90	78	79
Total alc. pass. (grm.)	13	13	10	10	15	15
Alc. pass. (grm. p. h.)	6·5	6·5	10	10	5·4	5·4
React. prod. (grm.)	12	12	8·5	8	13	12
Fraction						
56°–70° (acetone)	0	0	7	7	5·3	9
70°–83° (alcohol)	10	9·5	1	0·5	4·9	1·9
Loss & residue	1	1·5	0·5	0·5	2·8	1·1
Sum	11	11	8·5	8	13	12

5. Methyl Isobutyl Carbinol.

For the preparation of the alcohol, methyl isobutyl ketone obtained by passing an equimolecular mixture of acetic acid and isovaleric acid over thoria heated at 400°–450°[2], was reduced with reduced nickel and hydrogen at 130°–150°[3]. Methyl isobutyl carbinol (B. p. 129°–131°), thus obtained, after being purified by fractional distillation, was passed on reduced copper heated at 230° and 330°, and methyl isobutyl ketone and unsaturated hydrocarbon were obtained. These reaction products were mentioned by Ipatief as obtainable by heating alcohol alone at 600°–700°[4]. But the relative amount of the ketone and hydrocarbon in the reaction product depends largely on the type of the catalyst employed in the reaction, and also on the conditions (temperature, etc.,) under which the alcohol was treated, as will be seen in the table.

	Cu I.		Cu II.		Cu III.	
React. temp.	230°	330°	230°	330°	230°	330°
No. of exp.	84	85	86	87	91	92
Total alc. pass. (grm.)	7	10	7	6	10	10
Alc. pass. (grm. p. h.)	6	6	7	6	7·5	7·5
React. prod. (grm.)	6	9	5·5	5	9	9·5

1 C. R., **136**, 984 (1903).
2 J. –B. Sendrens: Ibid., **149**, 996 (1909).
3 P. Sabatier and J. –B. Sendrens: Ibid., **137**, 301 (1903).
4 W. Ipatief: Ber. D. Chem. Ges., **34**, 599 (1901).

Fraction.

60° – 80° (hexene)	o	o 8	o	o	o	2·3
80° – 105°	o	–	o	o	o	0·3
105° – 120° (ketone)	0·5	0·6	3·3	3·8	2·5	4·5
120° – 127°			0·5	0·5	0·5	trace
127° – 132° (carbinol)	4·1	7·0	1·0	trace	5·0	trace
Loss & residue	0·9	0·6	0·7	0·2	0·5	0·7
Sum	5·5	9	5·5	4·5	8·5	7·8

The main part (1·6 grm.) of the first fraction (Cu III) distilled out at 63° – 66° and was ascertained to be hexene by its decolerising action upon bromine water and also by the determination of its physical constants: $D_{25}^{25} = 0\,674$; $n_D^{25} = 1\cdot3810\cdot$

6. Di isobutyl Carbinol.

Isovaleric acid (B. p. 175° – 177°) from Kahlbaum was passed over thoria heated at 400° – 450°[1], and di-isobutyl ketone, thus obtained and purified, boils at 162° – 164°, and shows $d_4^{25} = 0\cdot791$; $n_D^{26} = 1\cdot4078$. Di-isobutyl carbinol was obtained by reducing the ketone above-mentioned with reduced nickel and hydrogen at 150° – 155°[2]. It boils at 172° – 175° and shows $d_4^{25} = 0\,8143$; $n_D^{25} = 1\cdot4152$.

The catalytic action of reduced copper heated at 230° and 330° respectively on the carbinol was studied as usual and the following results were obtained:

	Cu I.		Cu II.		Cu III.	
React. temp.	230°	330°	230°	330°	230°	330°
No. of exp.	96	97	104	105	93	94
Total alc, pass, (grm.)	10	10	6	6	5	6
Alc. pass. (grm. p. h.)	5	5	6	6	5	7
React. prod. (grm.)	9·3	8·5	5·5	5·5	4	5·5
Fraction						
1. 120° – 155° (nonene)	o	3·7[i]	o	0·4	o	1·1[vi]
2. 155° – 161° ⎫ (ketone)	o		o	2·8[iv]	o	
3. 161° – 168° ⎭	0·5	1·4	3·8[ii]	2·2[v]	0·5	3·0
4. 168° – 171° (carbinol)	8·2	1·4	1·4[iii]	trace	2·7	0·6
Loss & residue	0·8	0·5	0·3	0·1	0·3	0·3
Sum	9	7	5·5	5·5	3·5	5

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1 J. -B. Sendrens: C.R., **148**, 927 (1909); **149**, 213 (1909).

2 Amouroux: Bull. Soc. Chim., (4), **7**, 154 (1910):
A. Malihe: Ibid., (4), **15**, 327 (1914).

Of some fractions, the density and index of refraction were determined, as will be seen in the following table, for the identification of nonene and di-isobutyl ketone in the fractions, which should be formed by the reaction from the alcohol, and the presence of nonene in the fractions (i) and (vi) was also evident by the decolorising action of the fractions on bromine water.

Fractions	d_4^{26}	n_D^{26}	Remarks
i	0·731	1·4092	Mostly nonene
ii	0·793	1·4088	Mostly isovalerone
iii	0·803	1·4098	Isovalerone and carbinol
iv	0·790	1·4078	Mostly isovalerone
v	0·801	1·4078	Mostly isovalerone

The major part (1·8 grm.) of the first fraction (Cu I) distilled out at $138° - 148°$ and its physical constants were determined: $d_{25}^{25} = 0·751$; $n_D^{25} = 1·4060$.

7. Methyl Phenyl Carbinol.

Acetophenone ($d_4^{25} = 1·0269$; $n_D^{25} = 1·5234$) from Kahlbaum was reduced with metallic sodium in boiling ethyl alcohol solution[1], and the main part of the reaction product consists of the fraction which boils from $93° - 95°$ at 20 mm. ($d_4^{25} = 1·0082$; $n_D^{25} = 1·5234$), shows a reddish-brown colour with conc. sulphuric acid, and yields with hydroxylamine no trace of the oxime.

On passing the carbinol over reduced copper heated to the required temperature, the reaction product was obtained, which by the various treatments described below, gave the results shown in the table.

The reaction product was fractionated under reduced pressure and the following portions were obtaided:

	Fraction		Yield	Remark
(I) Cu I. at 330° (Exp. 110)	1. 60° – 80°	40 mm.	3·2 grm.	Mostly stylene
	2. 80° – 115°	″	0·6 ″	Carbinol
(II) Cu II. at 330° (Exp. 107)	1. 40° – 80°	35 mm.	1·7 ″	Mostly ethyle benzene
	2. 80° – 115°	″	6 0 ″	Acetophenone
(III) Cu III. at 330° (Exp. 111)	1. 55° – 85°	50 mm.	1·5 ″	Mostly stylene
	2. 85° – 118°	″	3·2 ″	Carbinol

The first fraction (Cu I) was redistilled under 40 mm. and the main

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1 A. Klages and P. Allendorf: Ber. D. Chem. Ges., **31**, 1003 (1898).

part (2·4 grm.) boiled at $50° - 53°$, showing $d_{25}^{25} = 0.9021$; $n_D^{25} = 1.5406$, and was ascertained by its physical constants to be composed mostly of stylene, and also by transforming it into the dibromo-derivative of M. p. $70° - 71°$.

The second fraction giving no trace of the oxime on being treated with hydroxylamine, was also ascertained from their physical constants to be composed of unchanged carbinol.

First fraction (Cu II) by the determination of the physical constants ($d_{25}^{25} = 0.8711$; $n_D^{26} = 1.4948$) was ascertained to consist mostly of ethyl benzene, with some stylene, the existence of the latter being also indicated by its decolorising action on bromine water. The second fraction boils at $118° - 120°$ under 65 mm. ($d_{25}^{25} = 1.0214$; $n_D^{25} = 1.5274$) and was confirmed to consist mostly of acetophenone, since 2·0 grm. of this fraction yielded with hydroxylamine 2·2 grm. of acetophenone oxime which recrystallised from petroleum benzine melted at $58° - 59°$.

The first fraction (Cu III) consists mostly of the fraction (1·0 grm.) which boils at $68° - 70°$, mm. ($d_{25}^{25} = 0.9045$; $n_D^{26} = 1.5354$), and 0·8 grm. of which yielded with bromine 1·6 grm. of stylene dibromide of M. p. $66° - 68°$. The second fraction (Cu III) was again distilled under 80 mm. pressure, and the main part (B. p. $122° - 125°$) shows the physical constants: $d_{25}^{25} = 1.0107$; $d_4^{25} = 1.0078$; $n_D^{26} = 1.5252$, and yields no trace of the oxime of acetophenone.

8. Diphenyl Carbinol.

Benzophenone (M. p. $48°$) from Kahlbaum was reduced with zinc dust in a caustic soda solution[1], and carbinol was isolated in pure state from the crude reaction product (M. p. $63° - 65°$) by recrystallisation from petroleum benzine and melted at $68° - 69°$. Benzhydrol ether[2], benzophenone[3,4] sym-tetraphenyl ethane and diphenyl methane[3] were described by many investigators as being derived from diphenyl carbinol by heating it at about $300°$. In presence of finely divided copper[5] the alcohol decomposes into benzophenone and benzhydrol ether at $205° - 220°$, while at $255° - 270°$ it yields benzophenone, sym-tetraphenyl ethane and diphenyl methane. When, however, the vapour of the alcohol was passed over reduced copper heated at $250°$, benzophenone was formed by the dehydrogenation of the

1   K. Elbs: J. prak. Chem., **33**, 184 (1886).

2   Ed. Linnemann: Lieb. Ann., **133**, 9 (1865).

3   U. Nef: Ibid., **298**, 236 (1897).

4   E. Knoevenagel and W. Heckel: Ber. D. Chem. Ges., **36**, 2816 (1903).

5   E. Knoevenagel and W. Heckel: Ibid. **36**, 2825 (1903).

alcohol, which was then converted by catalytic action into diphenyl methane and sym-tetraphenyl ethane[1]. The experiment with the alcohol was carried out by the writer with the following results.

I. Exp. No. 100. 5 grm. pure benzhydrol were passed over reduced Cu I, at 330° in an interval of one hour, and liquid and crystalline reaction products were obtained. The latter substance amounted to 0 5 grm., and was ascertained to be sym.-tetraphenyl ethane from its melting point of 206° – 208°, and the liquid product was divided into 2 parts by fractional distillation; (1) B. p. 270° – 280°, yielded 0·4 grm. consisting of diphenyl methane, (2) B. p. 290° – 310°, yielded 1·5 grm. consisting of benzophenone, which was confirmed by its chemical reactions, and also by the determination of the M. p. of the oxime (138° – 140°).

II. Exp. No. 95. 5 grm. pure diphenyl carbinol were passed over reduced Cu II, at 330° in an interval of one hour, and 2·5 grm. liquid and 0·4 grm. crystalline reaction products were obtained. The latter substance was identified as sym.-tetraphenyl ethane from its melting point of 208° – 209°, and the former was fractionated: (1) B. p. 160° – 180°, with a yield of 0 5 grm., consisting mainly of diphenyl methane; and (2) B. p. 180° – 210°, with a yield of 1·6 grm., composed mostly of benzophenone, since 1·0 grm. of the fraction yielded with hydroxylamine, 0·5 grm. of the oxime, M. p., 138° – 139° after being recrystallized from petroleum benzine.

9. Cyclohexanol.

It was prepared from phenol (B. p. 180° – 182°) by reduction with reduced nickel and hydrogen at about 180°[1] and the reaction product was distilled after being treated with conc. sodium bisulphite solution, and then with dilute (5 %) caustic soda solution, to remove the ketone and unchanged phenol from the carbinol, and the fraction which boiled at 159° – 161° ($d_1^{25} = 0.9451$; $n_D^{25} = 1.4602$), was collected, and used as a sample in the following experiments.

(I) Exp. No. 51. 7 grm. of pure hexahydrophenol were passed over reduced Cu I at 330° in an interval of 1·5 hours, and 0·8 grm. of the water layer and 6.3 grm. of an oily layer were obtained. 4·1 grm. of the upper oily part decolorising bromine water but showing no violet colour with ferric chloride, were divided into two parts by distillation: fraction (1) B. p. 80° – 90°, with a yield of 3·5 grm, and showing the following

1   P. Sabatier: La Catalyse en Chimie Org., 1920, 282.

2   P. Sabatier and J. -B. Sendrens: C. R., **137**, 1025 (1903).

physical constants: $d_4^{25} = 0.8100$; $n_D^{25} = 1.4440$, and consequently was confirmed as consisting mostly of cyclohexene, (2) the second fraction, B. p. $150° - 160°$ with a yield of 0.3 grm. yielded with conc. sodium bisulphite solution an additional compound which indicates the occurrence of cyclohexanone in the fraction.

(II) Exp. No. 48. 10 grm. of pure hexahydrophenol were passed over reduced Cu II at $330°$ in an interval of 2 hours, and 8 grm. of the reaction product were obtained, and fractionated (7.5grm.) into 4 parts which were ascertained as usual to be composed of the following constituents:—

Fraction	Yield	Remark
(1) $75° - 95°$	0.3 grm.	Mostly of cyclohexene
(2) $95° - 150°$	0.4 ″	—
(3) $150° - 175°$	0.5 ″	Ketone reaction negative
(4) $175° - 185°$	5.7 ″	Mostly of phenol; it gives a violet coloration with ferric chloride.

(III) Exp. No. 118. 7 grm. of pure cyclohexanol were passed over reduced Cu III at $330°$ in an interval of 1.5 hours, and 6 grm. of the reaction product were obtained, which rapidly decolorised a potassium permanganate solution but gave no colour reaction with ferric chloride. The main part of the product distilled out between $150° - 160°$, and 2.0 grm. of the fraction yielded 2.2 grm. of an additional product with a conc. sodium disulphite solution, and accordingly the fraction was assumed to consist mostly of cyclohexanone.

10. Laevo-Menthol.

l-menthol (M. p. $43°$) was passed over the three types of reduced copper heated at $330°$, and results similar to those observed previously by S. Komatsu and M. Kurata[1] were obtained: in presence of Cu I, it was transformed mostly into menthene (B. p. $165° - 170°$), in presence of Cu II, into thymol (B. p. $225° - 227°$; M. p. $48° - 50°$), and in presence of Cu III, menthone (B. p. $205° - 207°$) was the principal reaction product.

11. Dextro-Borneol.

(I) Exp. No. 68. 30 grm. of d-borneol (M. p. $205° - 205.5°$) were passed over reduced Cu I at $330°$ in an interval of one hour, and 25 grm. of crystalline reaction products with some water were obtained and the former was fractionated into 3 parts:

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1 Loc. cit.

	Fraction	Yield	Remark
1.	$155° - 180°$	15 grm.	Mostly camphene
2.	$180° - 200°$	3 ″	—
3.	$200° - 215°$	5 ″	Gives no oxime.

The major part (10 grm.) of the first fraction distilled out between $155° - 165°$ (M. p. $50° - 52°$), and was condirmed as consisting of camphene by its chemical and physical properties.

(2) When d-borneol was passed on reduced Cu II and on Cu III at $330°$, it was converted entirely into camphor in both cases. The experimental results above-mentioned, harmonize with those observed by B. Masumoto[1], but do not coincide well with the experimentation of other chemists.

In the following table, the yield of reaction products, including unchanged alcohol, at $230°$ and $330°$, is shown in a ratio of mol per cent.

1. Isopropyl alcohol.

	Cu I.		Cu II.			Cu III.	
Reaction temp.	$230°$	$330°$	$230°$	$330°$	$330°$	$230°$	$330°$
Acetone	0	0	88	90	93	52	83
Unchanged alcohol	100	100	12	10	7	48	17

2. Methyl isobutyl carbinol.

	Cu I.		Cu II.		Cu III.	
Reaction temp,	$230°$	$330°$	$230°$	$330°$	$230°$	$330°$
Hexene	0	11	0	0	0	38
Ketone	11	7	79	100	38	62
Unchanged alcohol	89	82	21	0	62	0

3. Di-isobutyl carbinol.

	Cu I.		Cu II.		Cu III.	
Reaction temp.	$230°$	$330°$	$230°$	$330°$	$230°$	$330°$
Nonene	0	58	0	8	0	25
Ketone	6	21	90	92	15	63
Unchanged alcohol	94	21	10	0	85	12

4. Methyl phenyl carbinol at $330°$.

	Cu I.	Cu II.	Cu III.
$C_6H_5 \cdot CH : CH_3$	85	(+)	35
$C_6H_5 \cdot CH_2 \cdot CH_3$	–	24	–
$C_6H_5 \cdot CO \cdot CH_3$	0	76	0
$C_6H_5 \cdot CHOH \cdot CH_3$	15	(+)	65

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1 These Memoirs, A, 9, 219 (1925).

5. Diphenyl carbinol at 330°.

	Cu I. mol %	Cu II. mol %
$C_6H_5 \cdot CO \cdot C_6H_5$	73	68
$C_6H_5 \cdot CH_2 \cdot C_6H_5$	15	23
sym. tetra phenyl ethane	12	9

6. Cyclohexanol at 330°.

	Cu I.	Cu II.	Cu III.
Cyclohexene	95	8	–
Cyclohexanone	5	0	Mostly cyclohexanone
Phenol	0	83	–
Unchanged subst.	–	9	–

7. l-Menthol at 330°.

Cu I.	Mostly menthene.
Cu II.	Mostly thymol.
Cu III.	Mostly menthone.

8. d-Bornol at 330°,

	Cu I.	Cu II.	Cu III.
Camphene	74	0	–
Camphor	0	Mostly camphor	Mostly camphor
Borneol	26	–	–

Eight secondary alcohols were passed over the three types of reduced copper heated at 230° and 330° respectively and both of the reactions — dehydrogenation and dehydration, were observed to be promoted as in the case of the primary alcohols. The velocity of these reactions is greater in the secondary alcohols than in the primary ones due to the unstability of these compounds toward heat.

The yield of unsaturated hydrocarbon from alcohol by the contact action of Cu I, under the same conditions, is proportional to the molecular weight of the alcohol used, and also depends upon the nature of the radicals combined with the carbon atom linked to the hydroxyl group, being in mol per cent, 0, 11 and 85 with dimethyl, methyl isobutyl and menthyl phenyl carbinols, and 0, 58 and 27 with dimethyl, di-isobutyl and diphenyl carbinols respectively.

These facts considered from a different point of view, indicate that a relation should exist between the facility of dehydration and the electronic character of the radicals in a molecule of alcohol. Such a relationship between the yield of the ketone and the chemical structure of alcohol was also noticed in the catalytic action of Cu II and Cu III, as will be shown in the table. To the interest of the present writer, the alcohol which

gives much yield of unsaturated hydrocarbon by the contact action of Cu
I suffers in the least degree dehydrogenation in presence of Cu II, and
the results obtained by the contact action of Cu III on alcohols, indorse
the correctness of the observation with regard to the dehydration and
dehydrogenation above-mentioned.

The influence of temperature on the activities of the catalysts is
marked with Cu I and Cu III, which will be illustrated with the following
experimental data: the yield of nonene from di-isobutyl carbinol at 230°
and 330° is 0:58 with Cu I, and 0:25 with Cu III, respectively, and
that of di-isobutyl ketone is 6:21 and 15:63 in the corresponding cases,
while the yield of the ketone with Cu II is 90:82.

As we often have reported that the specific effect of the catalytic
action of reduced copper is very marked at about 300°, and to study the
catalytic action of the three types of the catalyst the experimental results
(in mol %) obtained from alcohols (both primary and secondary) by passing
on them at 330° were again tabulated:

Alcohol and the reaction products at 330° in mol %	Cu I.	Cu II.	Cu III.
1. Ethyl alcohol			
Aldehyde	0	58	25
Acetic acid	–	7	(+)
Acetic ester	–	(+)	–
Unchaged alcohol	100	35	75
2. Isoamyl alcohol			
Aldehyde	8	59	60
Valeric acid and its amylester	4	7	16
Unchanged alcohol	88	34	24
3. Benzyl alcohol			
Toluene	4	64	14
Benzaldehyde	0	28	84
Benzoic acid	0	5	2
Unchanged alcohol	96	3	–
4, Isopropyl alcohol			
Acetone	0	93	83
Unchanged alcohol	100	7	17
5. Methyl isobutyl carbinol			
Hexene	11	0	38
Ketone	7	100	62
Unchanged alcohol	82	0	0

Alcohol and the reaction products at 330° in mol %	Cu I.	Cu II.	Cu III.
6. Di-isobutyl			
Nonene	58	8	25
Ketone	21	92	63
Unchanged alcohol	21	0	12
7. Methyl phenyl carbinol			
Stylene	85	(+)	35
Ethylbenzene	–	24	–
Acetophenone	0	76	0
Unchanged alcohol	15	(+)	65
8. Benzhydrol			
Benzophenone	73	68	–
Diphenylmethane	15	23	–
Sym-tetraphenylethane	12	9	–
9. Cyclohexanol			
Cyclohexene	95	8	(+) mostly cyclo-hexanone
Cyclohexanone	5	0	
Phenol	0	83	0
Unchanged alcohol	–	9	–
10. l-Menthol	mostly menthene	mostly thymol	mostly menthone
11. d-Borneol			
Camphene	74	0 mostly camphor	0 mostly camphor
Camphor	0		
Unchanged borneol	26	–	–

In the following table, (a) the molar ratio of the changed alcohols to the unchanged ones in the reactions, (b) and (c) the yields in mol per cent of the unsaturated hydrocarbon and carbonyl compound in the reaction product excluded unchanged alcohol, are shown:

	Cu I.			Cu II.			Cu III.		
	a	b	c	a	b	c	a	b	c
1. Ethyl alcohol	0:100	0	0	65:35	0	89	25:75	0	100
2. Isoamyl alcohol	12:88	0	66	66:34	(+)	89	76:24	(+)	87
3. Benzyl alcohol	4:96	–	0	97:3	–	29	100:0	–	84
4. Isopropyl alcohol	0:100	0	0	93:7	0	100	83:17	0	100

	Cu I.			Cu II.			Cu III.		
	a	b	c	a	b	c	a	b	c
5. Methyl isobutyl carbinol									
	18:82	61	39	100:0	0	100	100:0	.38	62
6. Di-isobutyl carbinol									
	79:21	74	26	100:0	8	92	88:12	29	71
7. Methyl phenyl carbinol									
	85:15	100	0	100:(+)	(+)	76	35:65	100	0
8. Benzhydrol									
	100:(+)	–	(+)	100:(+)	–	(+)	–	–	–
9. Cyclohexanol									
	100:0	95	5	91:9	9	(91 phenol)	mostly changed	(+)	mostly cyclohexanone
10. l-Menthol									
	mostly changed	mostly menthene	–	mostly changed	–	(mostly thymol)	mostly changed	–	mostly menthone
11. d-Borneol									
	74;26	100	0	mostly changed	–	mostly camphor	mostly changed	–	mostly camphor

From the experimental results shown in the tables above-mentioned, the following summary was obtained:

Reduced Cu I acts on alcohols to promote principally their decomposition into unsaturated hydrocarbons and water, and the reaction velocity, sa may be seen in the table, was varied with the alcohol, though the passing of the alcohols on the catalyst was kept at a definite rate, due to the difference of the structure of the alcohols; secondary alcohols (RR'CHOH) which are composed of the " electro-negative" radical (R, R') are dehydrated easily, with the exception of benzhydrol.

Reduced Cu II accelerates mostly the dehydrogenation of alcohols, especially of secondary alcohols of the aliphatic series; the dehydrogenation velocity of methyl isobutyl carbinol is greater than that of methyl phenyl carbinol. In the case of alcohols of the cyclohexane series, as noticed previously by S. Komatsu and T. Yukitomo, the dehydrogenation being quite different from that of the secondary alcohols of the other series, will take place of the hydrogen atoms of hexamethylene ring to form phenols. The dehydration by the contact action of the catalyst, takes place in the least degree compared with the other reaction

Reduced Cu III accelerating both the dehydrogenation and the dehydration of alcohol, though their activities are of different degrees, which resembles in facilitating the oxidation of alcohol, with reduced Cu II, and on the other band, behaves like reduced Cu I in its dehydrogenating action. Although the reduced Cu II promotes catalytic oxidation of the
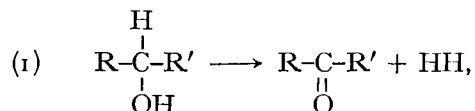
primary alcohols more energetically than Cu III does, the transformation
of the alcohols of the cyclohexane series into the carbonyl compound was
carried out with a fruitful yield when Cu III was used as a catalyst,
owing to the fact that the removal of the hydrogen atoms of hexamethylene
ring will take place to the least extent in this case while this reaction
occurs prominently in case Cu II was used.

The activity of the dehydrogenating action of these catalysts is greatest
with Cu II, and of the dehydrating with reduced Cu I, and as a catalyst
reduced Cu III stands between the two in every respect.

As to the explanation of the promotion of the dehydration of alcohol
in presence of Cu I, it will be considered that the action would be caused
by the presence of some substance such as basic copper sulphate, as an
impurity in the catalyst, and the occurrence of which has been confirmed
actually by analysis of the oxide from which reduced Cu I was obtained.
The writer, however, came to have the same opinion as S. Komatsu[1]
with regard to the catalytic action of reduced copper, that the reduced
copper, in general, promotes the dehydrogenation of alcohol, and also is
capable, under certain conditions, of exercising a catalytic influence in
promoting dehydration, since Cu III, which has no trace of such an
impurity as is associated with Cu I, performs catalytically the dehydration
of alcohol, though the catalytic activity is small when compared with its
oxidizing one; and also to confirm the statement made by S. Komatsu
and M. Kurata[2], that the catalytic activities of reduced copper will depend
largely on the modes of preparation of its oxide, and also on the reaction
temperature under which substrates come into contact with the catalyst.

## III. MECHANISM OF THE CATALYTIC ACTION OF REDUCED COOPPER.

The mechanism of the catalytic action of reduced copper — dehydration
and dehydrogenation — will be interpreted in the following two ways:
the first explanation which is similar to H. Wieland's hypothesis[3] proposed
already for the catalytic oxidation of organic compounds, is that the
substrate — alcohol, when it comes into contact with the catalyst, is activated
under the influence of the catalyst to promote the two reactions represented
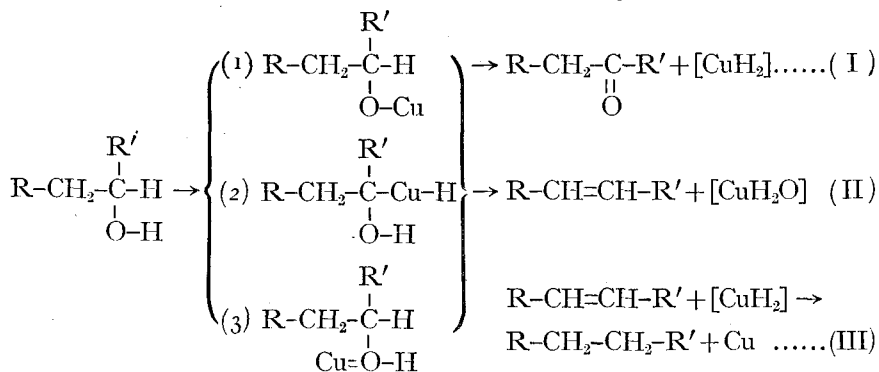by the schemes;

$$(1) \qquad R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R' \longrightarrow R-\overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle O}{||}}{C}}-R' + HH,$$

1   Loc. cit.
2   Loc. cit.
3   Ber. D. Chem. Ges., **45**, 2606 (1912); **46**, 3327 (1913); **47**, 2085 (1914); **55**, 3639 (1922).

$$(2) \quad R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-R' \longrightarrow R-CH:CH-R' + H_2O,$$
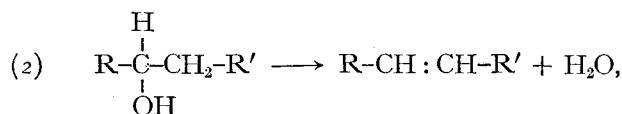
and the rate of the reactions will be illustrated by the relative quantity of the carbonyl compounds and the unsaturated hydrocarbons formed at different cases, and in the present case, reduced copper plays a rôle in the reactions as a carrier of hydrogen atoms or water molecules, therefore alcohols are catalytically oxidated or dehydrated. When, however, a reducible substance such as an unsaturated compound formed by consequence of the dehydration appears in the reaction system, it will be combined by virtue of the reduced copper with hydrogen generated from the reaction by the catalytic oxidation. The second interpretation seems, however, to explain more accurately the mechanism of the catalytic actions than the above explanation, and runs thus: an alcohols when passed as a vapour over finely divided copper, according to the recent view of contact action which has been already accepted by S. Komatsu and T. Hiraizumi[1] in their investigation on Beckmann's rearrangement, would be condensed in a thin layer on the surface of the catalyst, thus temporarily forming a copper compound — a hydrogen atom of the molecule being replaced by the metal (1), copper inserts itself between the hydrogen atom and the carbon atom to which the hydroxyl group is joined (2), or the catalyst is added directly to the alcohol to form an oxonium compound, without any disturbance of the molecular structure (3), — which then decomposes into a carbonyl compound and metallic hydride (I) or unsaturated hydrocarbon and metal hydrate (II). When unsaturated hydrocarbon and metallic hydride are present in one reaction system, they will react to from a saturated compound, and copper will be generated in a free state (III), and the chemical reactions will be illustrated in the following schemes:

$$R-CH_2-\underset{\underset{O-H}{|}}{\overset{\overset{R'}{|}}{C}}-H \rightarrow
\begin{cases}
(1)\ R-CH_2-\underset{\underset{O-Cu}{|}}{\overset{\overset{R'}{|}}{C}}-H \\[2em]
(2)\ R-CH_2-\underset{\underset{O-H}{|}}{\overset{\overset{R'}{|}}{C}}-Cu-H \\[2em]
(3)\ R-CH_2-\underset{\underset{Cu=O-H}{|}}{\overset{\overset{R'}{|}}{C}}-H
\end{cases}$$

$\rightarrow R-CH_2-\underset{\underset{O}{\overset{||}{}}}{C}-R' + [CuH_2] \ldots\ldots(I)$

$\rightarrow R-CH=CH-R' + [CuH_2O] \ (II)$

$R-CH=CH-R' + [CuH_2] \rightarrow$
$R-CH_2-CH_2-R' + Cu \ \ldots\ldots(III)$

1 These Memoirs, A, **8**, 273 (1925).

The type of reduced copper used as catalyst and the chemical and electrical characters of the hydrocarbon radicals (R and R') of the alcohols, were obviously regarded by the writer as important factors for determining the direction of the reaction (I) or (II).

The catalytic action of reduced copper on alcohol in vitro, according to the opinion of the present writer, is compatible, in the mode of reactions, with the biochemical catalysis in vivo, and the mechanism of the latter phenomenon will naturally be explained by applying the hypothesis described above on the contact action of the metal.

Many hypotheses have already been proposed by A. Bach, C. Engler, H. Wieland, T. Thurnberg, F. –G, Hopkins and O. Warburg for the explanation of the vital phenomenon. According to the peroxide theory by A. Bach[1] and C. Engler[2], an autoxidisable (C. E.) or easily oxidisable substance (A. B.) combines first with molecular oxygen, and then oxygen was generated by decomposition in an active state, which then enters again into the reaction. H. Wieland[3], on the contrary, considers, from his experimental results described above on milk and on an organic compound, that the hydrogen atoms in the molecule of the reactant by the catalytic influence of some easily reducible substance which is present in the reaction system, will be influenced to allow itself to be detached easily from the molecule by the so-called hydrogen acceptor — a non activated oxygen molecule or any other easily reducible substance. The Wieland hydrogen acceptor theory was supported by T. Thurnberg's[4] investigation on "hydrogen transportase" and also extended recently by F. –G. Hopkins[5] to the glutathion hypothesis.

The writer, however, supports Bach and Engler's peroxide theory for the explanation of the catalytic oxidation in living organisms, resulting from the combination of the oxygen atom with the molecule of the tissues and replacement of the hydrogen atom by oxygen, which was lately supported by O. Warburg[6] in his research titled: "Sauerstoffübertragender Bestandteil des Atmungsferments." With regard to the explanation of the biochemical oxidation caused by the splitting off of hydrogen, the present writer's opinion being different from Wieland's explanation, and is that a catalyst — an organic or inorganic substance, which occurs in the tissues,

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1   C. R., **124**, 951 (1897).
2   C. Engler and W. Wild: Ber. D. Chem. Ges., **30**, 1669 (1897); C. Engler and J. Weissberg: Studien über die Vorgänge der Autoxydation, Braunschweiz, 1904.
3   Ber. D. Chem. Ges., **55**, 3639 (1922).
4   Chem. Centralbl., 1920, III, 390.
5   Biochem. J., **15**, 286 (1921); Bull. Soc. Chim. Bio., **5**, 761 (1923).

forms a compound with reactants, though its combination is momentary and in an unstable state, and the oxidation will be performed in the course of the decomposition of the compound, as mentioned in the catalytic action of reduced copper on alcohol.

CONCLUSION.

(1) Catalytic actions of the three types of reduced copper upon various alcohols are studied.

(2) Reduced copper, in general, accelerates both the dehydrogenation and the dehydration of an alcohol, and the velocity of the reactions are manifested in different degrees by the difference of the chemical structure of the alcohol and also by the difference in the type of catalyst.

(3) Reduced Cu I. promotes mostly the dehydration of alcohols.

(4) Reduced Cu II. principally accelerates the dehydrogenation of alcohols — hydrogen atoms both of the hydroxyl group and of the hexamethylene ring.

(5) Reduced Cu III. promotes both the dehydrogenation and the dehydration of alcohol, though the latter action is quite a minor affair compared with the former one.

(6) In the catalytic action of reduced copper, the union of the catalyst and reactant was made, which being probably labile at a high temperature will be decomposed in forming any one of the carbonyl compounds and unsaturated hydrocarbon or both.

(7) The hypothesis for the mechanism of the catalytic action of reduced copper in vitro was extended to the explanation of the biochemical oxidation in vivo.

The author wishes to express his heartiest thanks to Professor Shigeru Komatsu for his kind directions and encouragement during this investigation

June, 1925. Laboratory of Organic- and Bio-Chemistry.

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1 Biochem. Zs., **145**, 461 (1924); Ber. D. Chem. Ges., **58**, 1001 (1925).