

Studies on Catalytic Action, XIV.
A Comparative Study of the Catalytic Activity
of Reduced Copper, Reduced Nickel
and Thoria, II.

BY

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I. THE CATALYTIC ACTION OF THE CATALYSTS
ON CYCLOHEXYLAMINE.

In the tenth paper of this series,¹ on the catalytic action of the divided metals and metallic oxide on cyclohexanol at 200° and 300°, it was shown that reduced nickel acts principally as oxidizing catalyst and thoria promotes mostly the dehydration of the alcohol, whilst reduced nickel performs the latter action in the least degree, and reduced copper stands as a catalyst between these catalysts in every respect.

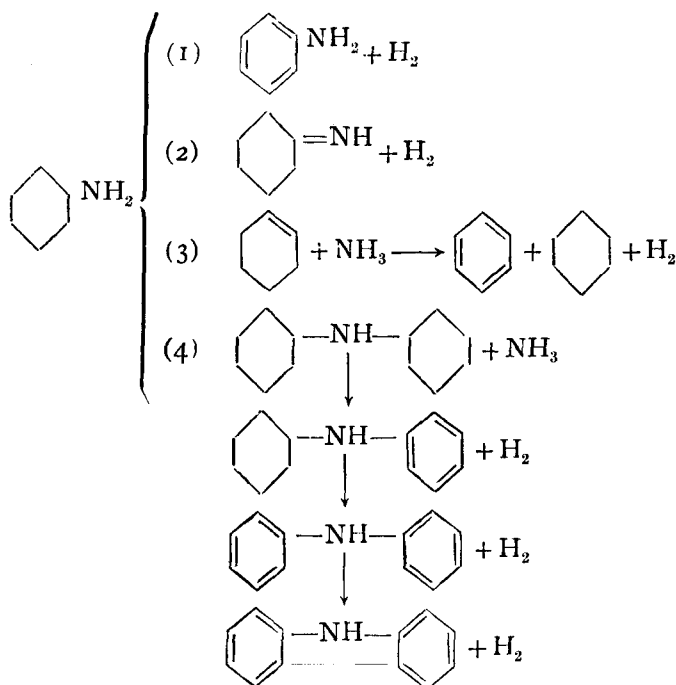
The authors have then extended the study to cyclohexylamine and examined whether the catalytic activity of these catalysts would be changed when the amine comes into contact with them at high temperature, by the presence of the NH₂ group combined with the carbon atom of hexamethylene ring instead of the OH group in cyclohexanol, since the varying absorptive capacity of the catalysts, with reactant or resultant, would account for such a specific activity of the catalyst.

As to the reaction products from cyclohexylamine by the catalytic action of the metals at a high temperature, it will be supposed to be the hydrocarbons² (benzene, cyclohexane and other hydrocarbons) derived from cyclohexene formed by the decomposition of the amine, aniline, dicyclohexylamine, cyclohexylphenylamine, diphenylamine and carbazol by

¹ S. Komatsu and B. Masumoto: These Memoirs.

² S. Komatsu and B. Masumoto: Loc. cit.; N. Zelinsky and G. Pavlow: Ber. D. Chem. Ges., **57**, 1066 (1924).

referring to the experimental results¹ obtained in the course of the catalytic hydrogenation of aniline in the presence of reduced nickel at 195,^o and the reactions by which they are produced from cyclohexylamine are formulated in the following schemes :



Schemes (1), (3), and (4) are compatible with the formation of phenol, benzene and other hydrocarbons and ether from alcohol (hexahydrophenol). The reaction (2) corresponds to the ketone-formation in the case of cyclohexanol, and the actual existence of the imine in the reaction products, however, will be discussed in full detail in another article, though the authors have not yet succeeded in getting it in a pure state owing to its unstable nature towards water.

Such compounds as mentioned above except cyclohexylimine which is supposed to be formed by the catalytic action of the catalysts on cyclohexylamine, were prepared by the present authors, in a pure state, by the catalytic reduction of aniline at 180^o in the presence of reduced nickel, following the direction proposed by Prof. P. Sabatier and Senderens.² The physical constants of cyclohexylamine, dicyclohexylamine and

¹ P. Sabatier and Senderens: C. R., **138**, 457 (1906).

² Loc. cit.

cyclohexylphenylamine were measured from the samples purified by repeated fractional distillation under reduced pressure :

Table I.

	Cyclohexylamine ¹	Dicyclohexylamine ²	Cyclohexylphenylamine ³
B. p.	133-135°	132-134° 23 mm.	{ 156°.5 23 mm. 151-153° 19 mm.
d_{4}^{25}	0.8636	0.9109	0.9897
n_{D}^{25}	1.4530	1.4787	1.5508

Cyclohexylamine.

Aniline, purified by fractional distillation for 3 times, B. p. 183-184°, was passed with pure hydrogen over reduced nickel heated at 178-180° and the fraction boiling to 180° of the reaction product was treated with dry carbon dioxide gas in its ethereal solution, whereas cyclohexylamine with some dicyclohexylamine was precipitated as a carbonate from the solution, separated by filtration, dried and decomposed into a free base with fused caustic potash and then distilled. The fraction B. p. 133-135° was used in this experiment.

Nickel.

15 gm. of nickel oxide, prepared from nickel plate and pure nitric acid, as usual, were spread out in a hard glass tube of 100 cm. length and 1.9 cm. diameter, to a length of 75 cm., and then was reduced with pure hydrogen at about 280°.

Copper.

12 gm. cupric oxide obtained in the same manner as described in the previous article from purified copper sulphate and an excess of caustic soda solution, was reduced with a slow current of pure hydrogen at about 180°.

- 1 A. v. Baeyer: *Lieb. Ann.*, **278**, 88 (1893); Markonikoff: *Ibid.*, **502**, 1 (1898); Sabatier and Senderens: *C. R.*, **138**, 457 (1906); W. Ipatiew: *Ber. D. Chem. Ges.*, **41**, 991 (1908); Amouroux: *Bull. Soc. Chim.*, (4), **9**, 214 (1911); Willstätter and Hatt: *Ber. D. Chem. Ges.*, **45**, 1471 (1912); A. Skita and W. Berendt: *Ibid.*, **52**, 1519 (1919).
- 2 Sabatier and Senderens: *Loc. cit.*; W. Ipatiew: *Loc. cit.*
Amouroux: *Loc. cit.*; Willstätter and Hatt: *Loc. cit.*; Skita and Berendt: *Loc. cit.*
- 3 Sabatier and Senderens: *Loc. cit.*; W. Ipatiew: *Loc. cit.*

Thoria.

This was prepared from thorium nitrate by ignition as usual.

Method of Analysis.

The sample was passed over the catalyst heated at the required temperature (200° and 300°) and then a slow current of pure hydrogen gas was passed into the reaction tube after the reaction was completed and cooled to room temperature, to sweep out completely any ammonia gas and other reaction products which might have remained in it.

The liquid reaction product was condensed in the receiver connected to the reaction tube by an adapter, which carried a spiral condenser cooled with iced water to condense a volatile matter likely to escape with the gases from the receiver. One end of the condenser was immersed into dilute hydrochloric acid in an absorption vessel to catch ammonia gas generated by the reaction.

The liquid reaction product in the receiver was found to consist of benzene and other hydrocarbons, unchanged cyclohexylamine, aniline, cyclohexylimine, dicyclohexylamine, cyclohexylphenylamine, diphenylamine and carbazol. The presence of carbazol in the reaction products from cyclohexylamine by the catalytic action of the reduced metals was not noticed previously by any investigator. It was, however, observed by the authors that some crystals were deposited at the end of the reaction tube and that their colour changed from white to blue on the apparatus being opened after the reaction had ended. Such observations indicated the presence of diphenylamine and carbazol in the product, and these were actually confirmed in isolating by fractional crystallization in a crystalline state; one melting at 54° and other crystals (melt at 238°) which yielded a picrate melting at the same temperature as carbazol picrate (M. p. 182°).

It was then fractionated under ordinary pressure into three parts; the first fraction boiling to 100°, the second fraction B. p. 100–200°, and the third fraction boiled above 200°. The fraction boiling to 100°, consisted mainly of benzene with some other hydrocarbons formed by the catalytic decomposition of the amine as shown in the scheme (3). The second fraction B. p. 100–200°, indicating by chemical reactions the presence of unchanged cyclohexylamine and other basic compounds, was treated with dry carbon dioxide gas of its ether solution under cooling with a mixture of ice and salt, whereas cyclohexylamine was thrown out as a carbonate from the solution.

The ethereal solution separated from the insoluble carbonate, was distilled to get rid of the solvent and the oil remaining in the flask was then subjected to fractional distillation and was divided into three parts;

the fraction B. p. 100–175° was designated cyclohexylamine which escaped from the carbon dioxide treatment described above, the fraction B. p. 175–190° was treated in its ethereal solution with dry hydrochloric acid gas and the hydrochloride precipitated and separated by filtration from the solution was found to be composed of cyclohexylimine and aniline salts by its chemical properties and melting point determination, and the fraction boiling above 190° was combined together with the higher fraction boiling above 200° mentioned above, and was then treated in the following manner:

The combined fraction was subjected to fractional distillation under 25–30 mm., after the solvent was completely driven off, and was divided into 4 portions:

Fraction	(1)	B. p.	under 29 mm. to 140°
"	(2)	"	140–160°
"	(3)	"	160–170°
"	(4)	"	above 170°

The presence of dicyclohexylamine and cyclohexylphenylamine in both fraction (2) and (3), was confirmed by their behavior toward a mixture of conc. sulphuric and nitric acids and also by determination of the melting point of the picrate, since the former forms a picrate (M. p. 171–172°) whilst the latter shows an orange-coloured reaction to the mixed acid, and the phenomena can be used to distinguish these bases from diphenylamine and also from each other. The proportion of these bases in the fractions (2) and (3) can be determined indirectly by means of the index of refraction. To illustrate the quantitative analysis of the bases, we cite here the example of the case, a copper catalyst used at 300°.

Table II.

	Fraction (31 mm.)	Yield	n_D^{25}	Remark
(1)	to 140°	0.1 grm.	—	Colourless, aniline and cyclohexylimine.
(2)	140–160°	4.6 "	1.5030	Colourless } dicyclohexylamine and Light yellow } cyclohexylphenylamine.
(3)	160–173°	4.9 "	1.5420	
(4)	above 173°	9.5 "	—	Brown, cyclohexylphenylamine.

The second and third fractions were combined together and then fractionated again under 30 mm.

Table III.

Fraction	Yield	n_D^{25}	Remark
1. 141-144°	0.3 gm.	1.4871	Mostly dicyclohexylamine.
2. 144-148°	2.60 "	1.4870	Pure dicyclohexylamine.
3. 148-152°	0.63 "	1.4894	Mostly dicyclohexylamine.
4. 152-160°	0.30 "	1.4954	Dicyclohexylamine and cyclohexylphenylamine.
5. 160-167°	0.60 "	1.5275	
6. 167-171°	4.00 "	1.5560	Pure cyclohexylphenylamine.
7. above 171°	0.70 "	—	Mostly diphenylamine.

From the figures shown in the table III, the amount of dicyclohexylamine and of cyclohexylphenylamine in the fractions (4) (B. p. 152-160°) and (5) (B. p. 160-167°) will be calculated, and accordingly their proportion in the fractions (2) and (3) in the table II was assigned to be 3.53 gm. and 4.51 gm. respectively.

The higher fraction boiling above 173° in table II and also in table III, was treated with hydrochloric acid in its ethereal solution, and cyclohexylphenylamine was thus separated from the diphenylamine associated with it.

When carbazol is present in the reaction product as in the case of experiments (1) and (2), it was separated from diphenylamine by the difference of the solubility of their hydrochlorides in an alcohol solution.

When, however, 11.0 gm. of the sample (cyclohexylamine) were passed in an interval of 4.5 hours, on 40 gm. of thoria heated at 300°, 9.0 gm. of the liquid reaction product and 0.06 gm. ammonia were obtained. The liquid product was fractionated as usual into the following 5 portions:

Table IV.

Fraction	Yield
1. 110-127°	0.30 gm.
2. 127-140°	7.60 "
3. 140-150°	0.50 "
4. 150-190°	0.30 "
5. residue	0.25 "
	8.95 gm.

The second fraction mostly distilled out at 134° and was confirmed to be composed entirely of cyclohexylamine.

Thus, it was learned that thoria, even at 300°, shows no appreciable catalytic action toward the base.

The analytical results of the reaction products in the four experiments are shown in the following tables :

Table V.

No. of expt.	Catalyst	Reaction temp.	Cyclohexylamine used	Time required for passage
1.	Nickel	200°	18.0 gm.	8.5 hours
2.	"	300°	20.0 "	8.5 "
3.	Copper	200°	17.0 "	7.0 "
4.	"	300°	19.3 "	8.5 "

No. of expt.	Rate of passing per hour	Reaction product		Unchanged amine
		Solid and liquid	Ammonia gas	
1.	2.1 gm.	15.0 gm.	0.86 gm.	4.80 gm. (32.0 %)
2.	2.3 "	16.0 "	1.00 "	trace (0 %)
3.	2.4 "	13.2 "	0.55 "	6.90 " (50.18%)
4.	2.2 "	16.5 "	0.96 "	4.75 " (27.21%)

No. of expt.	Benzene and other hydrocarbons	Aniline	D.cyclohexylamine	Cyclohexylphenylamine	Diphenylamine	Carbazol
1.	trace (gm.)	0.82 gm.	5.82 gm.	2.73 gm.	0.25 gm.	0.10 gm.
2.	1.95 "	8.45 "	—	—	5.07 "	0.53 "
3.	—	—	6.30 "	—	—	—
4.	trace "	1.10 "	4.40 "	5.80 "	0.25 "	—

Table VI.

Yield in mol% (without ammonia).

No. of expt.	Benzene and other hydrocarbons	Aniline	Dicyclohexylamine	Cyclohexylphenylamine	Diphenylamine	Carbazol
1.	trace	15.3	54.0	27.1	2.6	1.0
2.	1.68	61.0	—	—	20.1	2.1
3.	—	—	100.0	—	—	—
4.	trace	16.7	34.4	46.8	2.1	—

Yield in mol% (with ammonia).

No. of expt.	Ammonia	Hydrocarbons	Aniline	Dicyclohexylamine	Cyclohexylphenylamine	Diphenylamine	Carbazol
1.	46.74	trace	8.15	28.78	14.41	1.37	0.55
2.	28.29	12.03	43.72	—	—	14.43	1.53
3.	48.20	—	—	51.80	—	—	—
4.	44.38	trace	9.30	19.11	26.05	1.16	—

Table VII.

No. of expt.	Changed amine	Ratio (200°:300°)
1. Ni 200°	68.0 %	1:1.47
2. Ni 300°	100.0 "	
3. Cu 200°	49.82 "	1:1.46
4. Cu 300°	72.79 "	

Table VIII.

No. of expt.	Oxidation	Deamination
1. Ni 200°	34.9 %	63.1 %
2. " 300°	71.9 "	28.1 "
3. Cu 200°	—	100.0 "
4. " 300°	44.0 "	56.0 "

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

1. Reduced nickel acts at 200° and 300° on cyclohexylamine as oxidation and deamination catalyst. Reduced copper, also, promotes both actions at these temperatures, whilst thoria behaves not at all appreciably on the amine even at 300°.
2. The behavior of reduced copper on the amine at lower temperatures seems to be quite different in its action as deamination agent, from that of the same catalyst on cyclohexanol under the same condition. Such difference in behavior of the catalyst toward two substances should be attributed to the variability of the absorptive power of the catalyst of the resultants or reactants.
3. The catalytic behavior of reduced nickel at 200° towards cyclohexylamine, in the oxidation as well as in the deamination, is alike both

qualitatively and quantitatively to that of reduced copper at 300°, and the latter catalyst at 200° promotes only the deamination of the amine forming dicyclohexylamine as a principal reaction product.

4. The yield of the oxidation product by nickel catalyst was increased with the temperature from 34.9% at 200° to 78.9% at 300° whilst that of the deamination product was reversed, and the ratio of both reaction products at 200° and 300° is 2.06 and 0.44 respectively.

5. Reduced copper shows similar variability to nickel in catalytic activity with the variation of the reaction temperature, *i. e.* the ratio of the deamination product at 200° and 300° is 0.56.

6. In reaction (1) reduced nickel serves as a convenient catalyst at 300°, and reduced copper heated at 200° may be employed as the most suitable one in getting dicyclohexylamine from cyclohexylamine, and the former reaction is compatible with the formation of phenol by reduced nickel at 300° from cyclohexanol, and the latter one to the ether formation from alcohol.

7. Reduced nickel is apt to remove the hydrogen atoms combined with the carbon atom of the hexamethylene ring resulting in aniline and diphenylamine from cyclohexylamine, and this reaction, however, was made noticeable in a small degree by the presence of reduced copper which acts to promote oxidation of one cyclohexyl radical of dicyclohexylamine. Consequently, reduced nickel may be used as a good catalyst for the preparation of diphenylamine and carbazol from dicyclohexylamine, and reduced copper, in the same way, as the sole catalyst in getting cyclohexylphenylamine.

8. A matter of much interest was that the chemical constituents of the reaction product obtained from aniline by reduction with reduced nickel at 195° by P. Sabatier coincided quantitatively with the authors' results, as shown in the experiment, the result of passing cyclohexylamine over the same catalyst at 200° as shown in the following table:

Table IX.

	Benzene	Aniline	Cyclohexyl- amine	Dicyclohexyl- amine	Cyclohexyl- phenyl- amine	Di- phenyl- amine
Aniline $\xrightarrow[190^\circ]{Ni+H}$	trace	trace	30%	30%	30%	trace
Cyclohexyl- amine $\xrightarrow[200^\circ]{Ni}$	trace	5%	30%	39%	18%	1.6%

Accordingly, the yield of cyclohexylamine by catalytic reduction of aniline would not exceed the amount of 30%, unless a special device was employed to protect the transformation of the amine into dicyclohexylamine by condensation, such as that proposed by Ipatiew¹ using high temperature and high pressure, as we often experienced in the course of catalytic reduction at high temperature, or that by A. Skita and W. Berendt² using platinum black as a catalyst in an acid solution.

II. MECHANISM OF THE REACTION.

The formation of dicyclohexylamine, cyclohexylphenylamine, diphenylamine and carbazol from cyclohexylamine by catalytic action of the finely divided metals was explained by the scheme of reaction (4), as mentioned above.

For the confirmation of this assumption, dicyclohexylamine and cyclohexylphenylamine were passed separately on reduced nickel and reduced copper both heated at 300° respectively, and the reaction products in each case were examined quantitatively, the procedure of the analysis of the products is the same as mentioned in above cases, and the results are as follows:

Table X.

1. Dicyclohexylamine					
Catalyst	Sample passed	Reaction time	Reaction product changed	Unchanged substance	Ammonia
Ni	20.00 gm.	10 hrs.	17.40 gm.	—	0.15 gm.
Cu	24.00 "	9 "	12.98 "	9.82 gm.	0.02 "
2. Cyclohexylphenylamine					
Ni	20.50 "	10.5 "	18.00 "	—	0.08 "
Cu	22.00 "	21 "	8.50 "	10.75 "	0.01 "

¹ W. Ipatiew: Ber. D. Chem. Ges., **41**, 991, (1908).

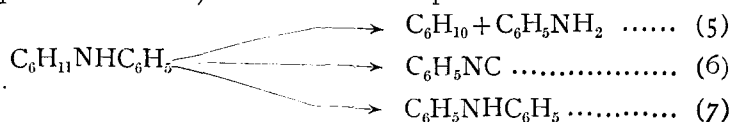
² A. Skita and W. Berendt: Ber. D. Chem. Ges., **52**, 1519 (1919).

Table XI.
Yield (mol%).

Catalyst	NH ₃	1. Dicyclohexylamine			C ₆ H ₁₁ NHC ₆ H ₅	(C ₆ H ₅) ₂ NH	$\begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4-\text{C}_6\text{H}_4 \end{array}$
		C ₆ H ₆ +C ₆ H ₁₂	C ₆ H ₁₁ NH ₂	C ₆ H ₅ NC			
Ni	8.11	25.03	25.02	—	—	36.01	5.65
Cu	1.52	trace	2.93	2.37	90.11	3.07	—
2. Cyclohexylphenylamine							
Ni	3.27	26.05	20.14	—	—	48.28	2.26
Cu	0.84	24.20	27.31	2.11	—	45.54	—

It was thus proved experimentally that cyclohexylamine was transformed step by step, as we anticipated, by the catalytic action of reduced metals into dicyclohexylamine, cyclohexylphenylamine, diphenylamine and then carbazol.

It should be explained that some of the cyclohexylphenylamine would be decomposed by the catalytic action of the finely divided metals into aniline and hydrocarbons on the way to diphenylamine, as shown in scheme (5), since the yield of these reaction products is, as may be seen in the experimental results, in the same mol. per cent.



As a matter of fact, when reduced copper was employed as catalyst, isonitrile was noticed to be formed and the cause of its formation was attributed, as it was suspected, to the partial decomposition of cyclohexylphenylamine, owing to the disruption of the hexamethylene ring as shown in scheme (6).

The formation of carbazol, however, was observed only when reduced nickel was used as a catalyst and the yield of the compound was proportional to that of the ammonia and there arose a supposition that some relationship between their formation might exist, which remained as a question to be decided in the future.

Thus, the behavior of reduced copper and reduced nickel toward cyclohexylphenylamine is almost the same, essentially, but toward dicyclohexylamine it is quite different, since the former catalyst is apt to oxidize the latter substance into cyclohexylphenylamine whilst by the latter one the oxidation proceeded further to yield diphenylamine and carbazol.

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