increase the free-fatty-acid content, in which case this loss is greater. It has been shown that on some poor types of deodorizers the free-fatty-acid content of the distillate may amount to three times as much as could be accounted for by the free-fatty-acid content of the original oil.

Volatile Matter Lost during Deodorization

	Per cent
Coconut	0.40
Cottonseed and peanut	0.12–0.35
Soy and corn	0.35–0.75
Beef tallow and oleostearin	1.5 –1.75

The volatile loss is determined by the difference between incoming and outgoing scale weights, after correcting for condensed distillate. Soluble distillate is included as volatile loss, unless determined in the condensing water.

Summary of Losses Due to (A) Impurities in Oil Purchased and (B) Refining Processes

	Cotton	Corn	Peanut	Soy	Coconut
Moisture	0.27	0.27	0.27	0.27	0.39
Gasoline insoluble[a]	.11	.11	.11	.11	0.037
Phosphatides	0.488	.....	.....	.....	.....
Other nonfatty acid material	0.272	.....	0.30	0.50	0.200
Glycerol loss by saponification	0.080	.....	0.035	0.035	0.000
Loss by emulsion	0.150	.....	0.150	0.150	0.075
Solubility loss	0.000	0.000	0.000	0.000	0.065
Glycerol loss by hydrolysis	.....	.....	.....	.....	0.057
Volatility loss	0.250	0.550	0.250	0.550	0.449
Bleaching loss	0.450	0.450	0.450	0.450	0.240
Total	2.270	1.380	1.565	2.065	1.513

[a] Includes all dirt, solid organic matter (meal), and colloidal meal.

The Catalytic Ammonolysis of Beta-Naphthol and Chlorobenzene in the Vapor State[1]

By A. M. Howald with Alexander Lowy

University of Pittsburgh, Pittsburgh, Pa.

β-Naphthol and chlorobenzene mixed with ammonia were passed in the vapor state at definite temperatures over various contact materials. Alumina was the best catalyst found for the ammonolysis of β-naphthol. Good yields of β-naphthylamine (90 to 95 per cent of the naphthol used) were obtained over a range of conditions.

A study of the yield of β-naphthylamine obtained as depending on the catalyst, temperature, ratio of the reactants, and the rate of their flow over the catalyst was made. Curves showing the effect of the temperature and rate of flow of the yield of β-naphthylamine were obtained.

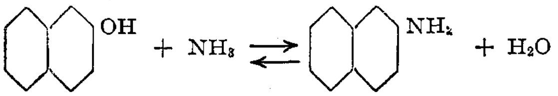
Some conversion of chlorobenzene to aniline was effected. Yields were low (up to 7 per cent) and the catalyst depreciation was rapid. Reduced metals of the iron group were the only contact materials found to catalyze appreciably the ammonolysis of chlorobenzene.

PART I. CONVERSION OF BETA-NAPHTHOL TO BETA-NAPHTHYLAMINE*

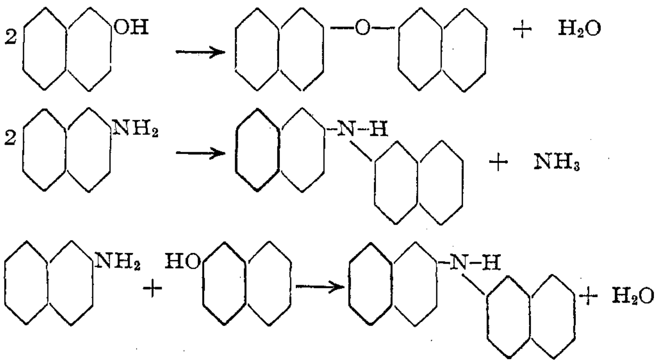
This study of the vapor-phase ammonolysis of β-naphthol was undertaken for several reasons. In the first place, while this reaction was tried and found to be successful in the preparation of aliphatic amines[2] from alcohols, yet the action of ammonia on the phenols and naphthols has not been studied. Then too, β-naphthylamine is a valuable dye intermediate and is prepared commercially in quantity. However, the autoclave reaction now in use is necessarily an intermittent one, while a vapor-phase reaction could be made continuous. Also, since the reaction of ammonia on β-naphthol has already been successfully catalyzed by a homogeneous catalyst[3] in liquid systems, a study of it in the gaseous state from the viewpoint of heterogeneous catalysis might help to correlate these two branches of catalytic phenomena.

References to the literature on the preparation of β-naphthylamine by the autoclave process are given below.[4]

Various reactions might be expected to take place when mixtures of β-naphthol vapor and ammonia gas are passed over contact masses. A primary reaction to give β-naphthylamine according to the following equation



as well as some others according to the equations:



etc., seemed probable.

Experimental Part

The experimental apparatus is shown in Fig. 1. It was built with three objects in mind—namely, to get a definite and known mixture of ammonia gas and β-naphthol vapor, to bring this mixture into contact with a catalytic mass at a known temperature, and to collect the products of the reaction.

The general method of conducting experiments, most of which were of 1-hr. duration, was as follows:

The inner tube *t* of the vaporizer V was replaced by a shorter one not reaching to the surface of the β-naphthol B in the vaporizer. Stopcock c_4 was turned off the tubes U_1 and U_2 and to a waste ammonia line and c_1 and c_2 turned in such a manner as either to shunt ammonia from T by or through the wash bottles W_1, W_2, W_3, and W_4, as the experiment required. A slow stream of ammonia was passed through the whole train for about 15 min. thoroughly flushing it out. The furnace F was brought slowly to the required temperature, and the external heating coils H_1 and H_2 turned on. The furnace having reached the required temperature the heating liquid L in the outer jacket of the vaporizer V was made to boil and the flow of ammonia through the flowmeter M

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[1] Received August 21, 1922. Abstract of a thesis presented by A. M. Howald in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1922.

* Patent applied for.

[2] *Compt. rend.*, **148** (1909), 898.

[3] *J. prakt. Chem.*, [2] **69** (1904), 49.

[4] *Ibid.*, [1] **32** (1870), 286; *Ibid.*, [1] **32** (1870), 540; *Ber.*, **13** (1880), 1298; *Ibid.*, **13** (1880), 1850; **14** (1881), 2343; **16** (1883), 19; D. R P. 14,612 (1880); 117,471 (1900); 121,683 (1901); 123,570 (1901); 126,536 (1901); *J. prakt. Chem.*, [2] **69** (1904), 49; **70** (1904), 345; **71** (1905), 433; **75** (1907), 249; **77** (1908), 403.

adjusted by means of the valve v_2 to the rate required by the particular experiment. Next, the short inner tube of the vaporizer was replaced by a long one so that the ammonia would bubble through the molten β-naphthol. After 10 min. more, the reaction tube and catalyst having been flushed with the gaseous mixture of naphthol and ammonia, the bulb C was replaced by a similar clean one and the time recorded. At a definite time 2 to 5 min. later c_4 was turned to pass the ammonia through U_1 into the weighed tubes U_2 and U_3.

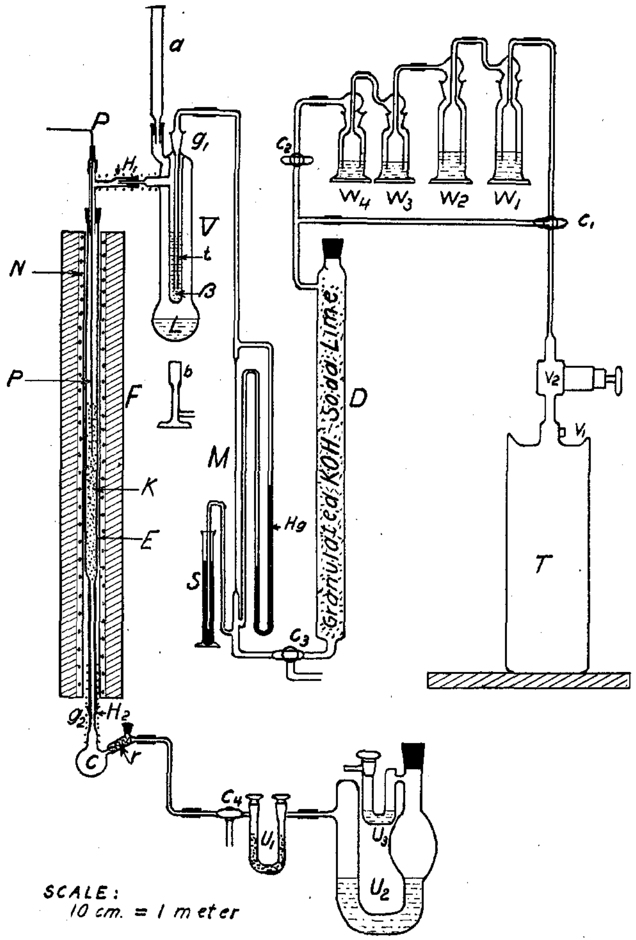

FIG. 1

T, cylinder of anhydrous ammonia.
v_1 and v_2, two valves in series.
c_1, c_3, c_4, 3-way stopcocks.
W_1, W_2, W_3, and W_4, wash bottles for purification of NH_3.
c_2, stopcock.
D, drying tower.
M, glass flowmeter of the capillary and manometer type, calibrated to read grams of ammonia per hour.
S, mercury-seal safety outlet.
V, vaporizer in which the entering ammonia bubbled through a column of molten β-naphthol, B, kept at a constant temperature by the vapors of a liquid, L, kept boiling in an outer jacket. *t* is an inner small bore tube by which the ammonia entered, g_1 a ground joint, and *a* an air condenser to return the boiling liquid L.
H_1 and H_2, two resistance-wire heating coils covered with asbestos cloth by means of which the ammonia and β-naphthol vapor mixture was kept hot between the vaporizer and the furnace F, and between the furnace and the bulb C, in which the reaction products condensed.
P, copper-constantan couple pyrometer extending into the center of the reaction tube.
C, bulb condenser connected to the reaction tube by a ground joint, g_2.
K, catalyst held in the Pyrex reaction tube E.
U_1, U-tube containing granulated KOH for drying the unused ammonia.
U_2 and U_3, two U-tubes in series filled with water and concentrated sulfuric acid, for collecting and weighing the unused ammonia.
F, special 1.2-m. tube furnace of which N is the nichrome heating coil. The furnace was built on a 1.2-m. length of 1.5-in. iron pipe, covered with a thin layer of asbestos cloth and alundum cement, wound with a nichrome coil, then covered with another layer of asbestos cloth and alundum cement, and finally encased in a length of "85 per cent magnesia" 3-in. pipe covering. The furnace temperature was controlled within a 5- to 10-degree range with a sliding rheostat.
r, glass wool.

A series of experiments could then be made by merely replacing the condenser bulb C and the ammonia collecting tubes U_2 and U_3. The solid products were collected in most cases for 1 hr., the ammonia for but 50 min. and calculated to 60 min.

METHOD OF ANALYSIS

The following method of analysis adapted to the determination of β-naphthylamine on small samples in the presence of β-naphthol and β-dinaphthylamine was devised.

A 0.0500 to 0.1000-g. sample was placed in a 25-cc. beaker which had been weighed together with a stirring rod and a 15-cc. Gooch crucible. The sample in the beaker was then dissolved in 10 cc. of dry ether (distilled over fused calcium chloride) and saturated under a desiccated bell-jar with dry hydrochloric acid gas. (Fig. 2) It was then filtered through the Gooch crucible (without suction) and washed five times with a saturated solution of hydrogen chloride in ether. No attempt was made to remove all the precipitate from the beaker, but it was thoroughly washed by decantation. Finally, the outside of the crucible was washed once or twice to remove any soluble deposit left by evaporation of the ether. The precipitate of β-naphthylamine hydrochloride with the crucible stirring rod and beaker was then dried to constant weight at 95° to 100° C. (1 to 2 hrs.) and the weight of hydrochloride was multiplied by the factor 0.797 to give the weight of mononaphthylamine. On distilling off the ether from the filtrate and drying the residue at 50° C., it was weighed as combined naphthol and β-dinaphthylamine.

The analytical method was checked against known amounts of the pure substances, as follows:

TABLE I—CHECK ANALYSIS AGAINST KNOWN AMOUNTS OF PURE SUBSTANCES

β-Naphthylamine Used G.	β-Naphthylamine Found G.	β-Naphthol Used G.	β,β-Dinaphthylamine Used G.	Combined Naphthol and β,β-Dinaphthylamine Used G	Combined Naphthol and β,β-Dinaphthylamine Found G.
0.0614	0.0610	Not weighed	Not weighed	0.0434	0.0437
0.1105	0.1107	Not weighed	Not weighed	0.0485	0.0480
0.2042	0.2045	0.1347	None	0.1347	......
0.1353	0.1337	0.1990	None	0.1990	0.1971

Instead of weighing the β-naphthylamine hydrochloride, it may be determined by titrating its hydrochloric acid content, using phenolphthalein as the indicator.

A preliminary series of experiments was conducted using anhydrous ammonia of coal-tar origin and with aluminium oxide on pumice as the catalytic mass. Poisoning of the catalyst was quite rapid when the ammonia gas was passed only through a soda lime and granulated potassium hydroxide tower. This catalyst depreciation could be, almost if not entirely, overcome by adding to the train wash bottles of alkaline permanganate (W_1 and W_2 of Fig. 1), ammoniacal silver sulfate (W_3), and concentrated potassium hydroxide solution (W_4).

However, in the subsequent experiments, synthetic ammonia requiring no purification was used. A large quantity of alumina catalyst was also prepared at once at this point, so that all the experiments to follow in which alumina was used were performed from this batch of catalyst. One hundred and thirty-five cc. were chosen as a standard amount of catalyst to be used and were taken for all experiments where a different amount is not specifically stated.

Several series of experiments were conducted to determine the effect of the temperature on the yield of β-naphthylamine. Two separate ratios of ammonia to β-naphthol were used by employing dimethylaniline and nitrobenzene of boiling points 191° to 193° C. and 204° to 205° C., respectively, in the outer jacket of the vaporizer. Results for each charge of catalyst are tabulated separately.

For the first series, a meter reading of 4 cm., corresponding to a flow of 5.05 g. of ammonia per hour, was chosen, and dimethylaniline was used as the heating liquid in the vaporizer. The condition and results of the series appear in Table II, and the yields of β-naphthylamine are plotted against temperature as Curve II. (Fig. 3)

TABLE II

Expt.	Temp. °C.	Time in Min.	NH_3 Caught in U_2,U_3 G.	Solids Caught in C. G.	β-Naphthylamine in Solid Condensate %	Naphthol, β,β-Dinaphthylamine, etc. %
1	350	60	5.02	2.36	19.8	....
2	400	60	5.08	2.03	40.6	58.6
3	450	60	....	2.55	91.0	8.0
4	500	60	4.70	1.92	88.1	12.8
5	430	60	4.96	1.55	89.9	10.5
6	450	60	4.52	2.18	90.8	9.2
7	470	60	4.48	2.15	89.0	10.5
8	415	60	4.20	....	79.3	20.4

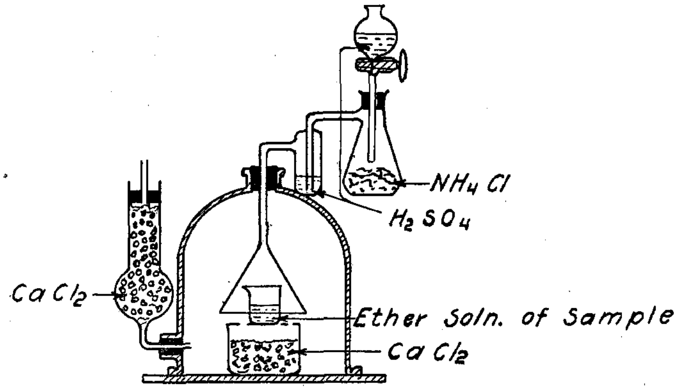

FIG. 2

These results (Curve II) show an optimum yield of β-naphthylamine between 430° and 450° C., which decreases very rapidly between 430° and 400° C. The analyses tabulated are the average of two determinations.

In the next series nitrobenzene was used in the vaporizer and the same temperature range was covered. The duration of each experiment was 1 hr., as before.

TABLE III

Expt.	Temp. °C.	Meter Reading G. NH_3	NH_3 Caught in U_2, U_3 G.	Wt. of Solids Caught G.	β-Naphthylamine in Solid Condensate %	Naphthol, β,β-Dinaphthylamine %
1	350	5.05	5.00	3.39	21.4	78.4
2	400	5.05	5.07	3.31	36.9	63.3
3	450	5.05	4.72	2.40	69.0	30.5
4	500	5.05	4.74	2.38	82.2	20.1

Yields of β-naphthylamine from Table III appear as Curve V. It will be noticed that the yields of β-naphthylamine are everywhere lower than when the vaporizer contained dimethylaniline (Curve II) and that the optimum temperature is higher. That the temperature is higher for a maximum yield when the vaporizer is heated with a higher boiling liquid can be explained by the greater rate of passage of β-naphthol over the catalyst under these conditions.

In the next series the vaporizer was once more heated with dimethylaniline, but the rate of flow of ammonia was decreased to half that used in the experiments of Table II. The conditions and results for this series are given in Table IV, and the yields of β-naphthylamine are plotted as Curve IV.

TABLE IV

Expt.	Temp °C.	Time in Min.	Meter Reading in G. NH_3	NH_3 Caught in U_2, U_3 G.	Solids Caught G.	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	415	60	2.52	2.47	1.06	92.2	7.7
2	450	60	2.52	1.93	.70	95.5	5.0
3	500	60	2.52	1.84	1.07	89.5	9.8
4	400	60	2.52	1.96	.97	88.3	11.8
5	350	60	2.52	2.10	1.06	30.9	67.9

Since decreasing the rate of flow of the vapor mixture (Table IV as compared with Table II) increased the yield of amine, indicating that equilibrium had not been attained, it was decided to conduct a series of experiments in which both the rate of flow of the vapor mixture and the volume of catalyst used should be reduced to one-half their values in the experiments of Table II. In this way was to be determined whether or not the relative yields of amine at a given temperature depended only on the rate of flow per unit volume of the catalyst.

The experiments under these conditions are recorded in Table V.

TABLE V

Expt.	Temp. °C.	Time in Min.	Meter Reading in G. NH_3	NH_3 Caught in U_2,U_3 G.	Solids Caught G.	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	350	60	2.52	2.33	0.91	34.0	....
2	400	60	2.52	2.39	0.93	90.1	9.7
3	450	60	2.52	2.43	1.11	87.8	12.7
4	500	60	2.52	2.39	1.05	88.2	11.7

The percentages of naphthylamine in Table V are plotted as Curve III. It is only at the higher temperatures (range of maximum catalyst efficiency) that this curve coincides, within the experimental error, with Curve II.

TABLE VI

Expt.[a]	Reading of Meter in G. NH_3	NH_3 Caught in U_2, U_3 G.	Solids Caught G.	Ratio by Weight NH_3 Solids	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	2.52	1.93	0.70	2.88	95.5	5.0
2	5.05	4.52	2.18	2.07	90.8	9.2
3	6.30	5.96	2.12	2.91	86.0	14.4
4	10.05	....	4.15	2.43	59.0	40.3

[a] Experiments 3 and 4 were made with one charge of catalyst in the order named. Experiments 1 and 2 are taken from Tables II and IV, respectively.

Some experiments in which the rate of flow of the ammonia was varied are tabulated as Table VI. In each case the va-

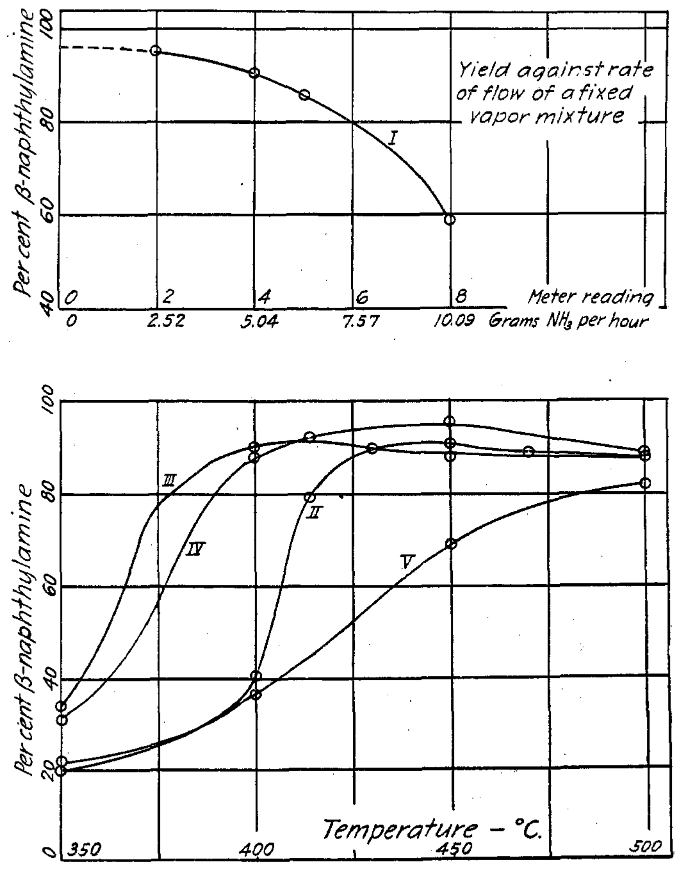

FIG. 3

porizer was heated with boiling dimethylaniline so that approximately a constant ratio of ammonia to naphthol was obtained. The duration of each experiment was 1 hr. and the temperature was kept constant at 450° C.

The results given in Table VI appear as Curve I. The yield of β-naphthylamine increases as the speed of passage over the catalyst decreases. The curve extrapolated to zero speed should give, therefore, the equilibrium concentrations.

A long-period experiment was performed to test the durability of the alumina catalyst. One hundred and thirty-five cc. of catalyst were used with a flow of ammonia of 5.05 g. per hour at the optimum temperature (450° C.) for that rate of flow, as read from Table II and Curve II. It was conducted on two consecutive days for 9 and 7 hrs., respectively. The regular vaporizer was replaced by a 500-cc. flask held in an oil bath kept at 196° to 197° C. by a gas-regulating thermostat. The receiver was also made larger.

Owing to inequalities in the depth of immersion of the tube by which the ammonia bubbled through the β-naphthol, less solid product was obtained per hour on the second than on the first day. The weights were 21.6 and 11.9 g., corresponding to an hourly rate of 2.4 and 1.7 g., respectively. The analysis of the product obtained was as follows:

	β-Naphthylamine %	Naphthol, etc. %
First day (9 hrs.)	85.5	15.4
Second day (7 hrs.)	90.7	9.3
Total product	87.3	13.3

Evidently, the catalyst had not depreciated materially during 16 hrs. The higher yield during the last 7 hrs. is accounted for by the lower hourly rate.

The product from the last 7 hrs. of the long-period experiment was analyzed for β,β-dinaphthylamine by the method of Lee,[5] and Jones, in which it is obtained as a residue insoluble in hot 1 : 30 hydrochloric acid. Two analyses on a 5-g. sample gave 4.57 and 4.58 per cent of insoluble residue, which gave melting points of 165° and 166.5° C. (uncorrected). The melting point of pure β,β-dinaphthylamine is 171° C. That the insoluble residues contained no β-naphthol was shown by the fact that one of them when washed with 200 cc. of boiling 0.96 specific gravity ammonium hydroxide lost no appreciable weight. Calling the difference between the sum of the percentages of the two amines and one hundred, the percentage of β-naphthol present, the complete analysis of this sample becomes:

β-Naphthylamine	90.7 per cent
β,β-Dinaphthylamine	4.6 per cent
β-Naphthol, etc.	4.7 per cent

Some experiments were conducted using titania- and thoria-bearing pumice as the catalytic masses. They are given below in Table VII, together with one experiment in which the reaction chamber was filled with pumice alone.

TABLE VII

CATALYST	Expt.	Temp. ° C.	Time Min.	NH_3 by Meter G.	NH_3 in U_2,U_3 G.	Solids in G.	β-$C_{10}H_7NH_2$ %	$C_{10}H_7OH$ and β,β-$(C_{10}H_7)_2NH$, etc. %
Titania	1	445	65	6.82	6.46	....	43.4	55.7
	2	500	60	6.30	5.88	2.58	63.5	36.4
	3	445	60	6.30	6.25	....	40.9	58.4
Thoria	1	445	60	6.30	5.31	....	18.0	....
	2	500	60	6.30	....	1.62	19.7	78.9
	3	445	60	6.30	4.06	2.01	20.9	80.0
Pumice	1	450	60	5.05	4.91	1.88	16.7 17.1	....

The titania was prepared by stirring 35 g. of titanium tetrachloride dissolved in concentrated hydrochloric acid into 150 g. of granulated pumice of the same grain size as used in previous experiments. Most of the hydrochloric acid was then evaporated, an excess of concentrated aqua ammonia added, the whole evaporated and ignited to dull redness in a muffle furnace.

The thoria was prepared by stirring a solution of 50 g. of hydrated thorium nitrate with 150 g. of pumice, adding an excess of ammonia, evaporating, and igniting to redness.

PART II. AMMONIA ON CHLOROBENZENE

It seemed probable that the halogen atom as well as the hydroxyl group could be replaced by the amino group by the action of ammonia in the vapor phase, if a suitable catalyst could be found. Indeed, chlorobenzene,[6] like β-naphthol, has already been successfully subjected to ammonolysis in an autoclave in the presence of a catalyst.

Earlier[7] attempts to replace halogen atoms on the benzene nucleus by the action of ammonia were unsuccessful in the case of the monosubstituted derivatives, but it was soon discovered that additional negative groups on the nucleus, especially in the ortho and para positions, made a halogen atom comparatively easy to replace. More recently the more difficult task of substituting the amino group for halogen in derivatives of benzene containing only halogen atoms has been accomplished.[8] In most cases pressure and a catalyst were used.

Quick[6] has made a study of catalysts and yields working chlorobenzene and *p*-dichlorobenzene, using the methods outlined in the patents referred to above. He found copper sulfate, cuprous chloride, cuprous bromide, cuprous iodide, and cupric chloride to be active catalysts, while salts of iron, nickel, and cobalt, metallic mercury, metallic copper, mercuric chloride, and sodium acid sulfite were inactive.

The primary reaction between chlorobenzene and ammonia, if applied above the dissociation temperature of ammonium chloride, can be represented by the equation:

$$C_6H_5Cl + NH_3 = HCl + C_6H_5NH_2$$

However, on cooling, any excess of ammonia would react with the hydrogen chloride formed to give ammonium chloride.

In addition to this primary reaction, other reactions according to the following equations might be expected:

$$3C_6H_5Cl + 2NH_3 \longrightarrow 3C_6H_6 + 3HCl + N_2 \qquad (1)$$

This equation is probable since hydrogen has been shown[9] to reduce chlorobenzene to benzene in the presence of reduced nickel and iron which are also known to decompose ammonia into hydrogen and nitrogen.

$$2C_6H_5Cl \longrightarrow Cl.C_6H_4.C_6H_4.Cl + H_2 \qquad (2)^{10}$$

$$6C_6H_5Cl + 2NH_3 \longrightarrow N_2 + 3C_6H_5.C_6H_5 + 6HCl \qquad (3)^{9}$$

Also an amine, if formed, might react further according to one of the following equations:

$$C_6H_5NH_2 + C_6H_5Cl \longrightarrow C_6H_5.NH.C_6H_5 + HCl \qquad (4)^{11}$$

$$2C_6H_5NH_2 \longrightarrow C_6H_5.NH.C_6H_5 + NH_3 \qquad (5)^{12}$$

EXPERIMENTAL PART

As preliminary experiments indicated the formation of some aniline by the reaction of ammonia upon chlorobenzene in the vapor state, an apparatus was devised to study the course of the reaction. The final form used is shown in Fig. 4. The furnace at F (not shown) was the same as used in

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[5] Private communication.

[6] *J. Am. Chem. Soc.*, **42** (1920), 1033.

[7] *Ann.*, **104** (1857), 225; **121** (1862), 358.

[8] *J. prakt. Chem.*, [2] **48** (1894), 465; D. R. P. 202,170 (1908); 204,848 (1908); Brit. Patent 3847; Fr. Patent 397,443; D. R. P. 204,951 (1908); Fr. Patent 397,495; *Ber.*, **47** (1914), 3165.

[9] Rideal and Taylor, "Catalysis in Theory and Practice," p. 179.

[10] *Ann.*, **189** (1877), 138.

[11] *Ber.*, **36** (1903), 2382; D. R. P. 187,870 (1907).

[12] *Z. Chem.*, **2** (1866), 438.

Part I (Fig. 1), as were the flowmeter and ammonia-washing train, which are not repeated in Fig. 4. The essential differences in the apparatus consisted in the device for obtaining the vapor mixture and in the condenser used in collecting and withdrawing samples of the product.

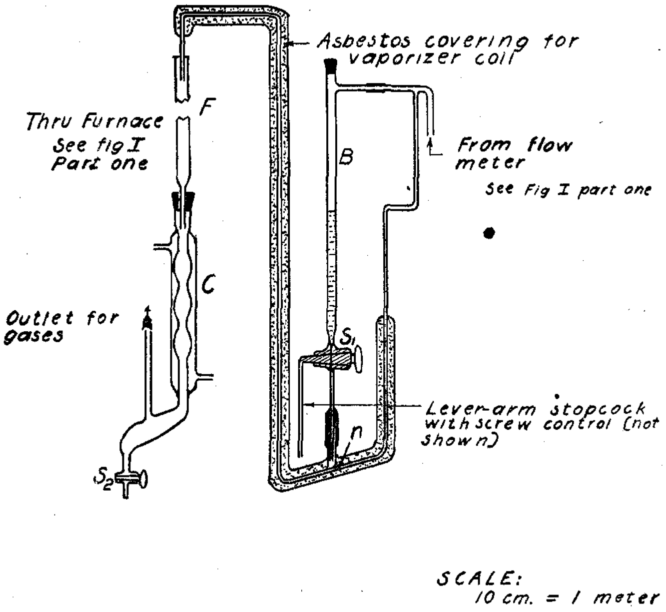

FIG. 4

The chlorobenzene was contained in a buret, B, with a long-armed stopcock, S, fitted with a screw regulator by means of which a constant flow of chlorobenzene could be made to drop into a vaporizer at *n*, where it met the incoming stream of ammonia. The mixture then passed up through the vaporizer which was heated above the boiling point of chlorobenzene by means of a nichrome coil, and passed into the furnace F. By means of a stopcock, S_2, on the condenser C a sample of the liquid product could be withdrawn at any time. A nickel-nichrome couple was used in measuring the temperature.

A method of analysis for aniline was devised based on the fact that the hydrogen chloride contained in its hydrochloride can be titrated with alkali, using phenolphthalein as the indicator.

With the apparatus as described, reduced nickel was tried as the catalyst. In preparing it, 100 g. of pure hydrated nickel nitrate were dissolved in water and the solution poured over 100 g. of granulated pumice screened to pass a 4-mesh standard sieve, but held on an 8-mesh sieve. The mixture was well stirred while evaporating to dryness and then ignited in porcelain over a burner until no more nitric oxide fumes were evolved. A 2-ft. length of it was then charged into the center of the reaction tube and reduced there with hydrogen at 350° C. until no more water was evolved. The hydrogen used was electrolytic hydrogen, as obtained in cylinders, and was purified by passing through wash bottles containing solutions of KOH and Ag_2SO_4, and finally dried by passing over fused $CaCl_2$. When the reduction was complete, the stopcocks were turned so as to replace the flow of hydrogen by ammonia, and the apparatus was then ready for an experiment.

The results and conditions of experiments with the first nickel catalyst are tabulated below. (Table VIII)

Experiment 1 showed promise, but in Experiment 4, conducted under identical conditions, the yield of aniline was only one-sixth as great. This could only be explained by catalyst poisoning.

TABLE VIII

Expt.	Time	Temp. ° C.	C_6H_5Cl Used Cc.	NH_3 Liters	Molar Ratio $C_6H_5Cl : NH_3$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	380	30	21.7	1:2.5	27	5.80
2		480				24	1.30
3		360				32.5	0.51
4		380				32	0.93

A second nickel catalyst prepared as before was used at 380° C., with a greater excess of NH_3 over C_6H_5Cl, and the results with it are given in Table IX.

TABLE IX

Expt.	Time	Temp. ° C.	C_6H_5Cl Cc.	NH_3 Liters	Molar Ratio $NH_3 : C_6H_5Cl$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	380	15	21.7	5 : 1	14	7.35
2						14	5.60

Reduced iron gave results very similar to those obtained with nickel. It was prepared by distributing 100 g. of hydrated ferric nitrate over 100 g. of granulated pumice of the same grain size as used for nickel. It was ignited to ferric oxide, charged into the catalyst tube, and reduced with hydrogen at 550° C. Table X contains the results of experiments conducted with this catalyst.

TABLE X

Expt.	Time	Temp. ° C.	C_6H_5Cl Cc.	NH_3 Liters	Molar Ratio $C_6H_5Cl : NH_3$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	480	15	21.7	1 : 5	15.5	7.35
2		380				....	.75
3		480				....	3.23

480° C. was evidently a more favorable temperature than 380° C. The same diminishing effectiveness as for the nickel catalyst was apparent.

A new charge of the iron oxide was prepared and reduced as before, and it was then subjected for 5 hrs. to a stream of ammonia gas of the speed used in the experiments of Table X. The idea in this was to determine if the catalyst were being poisoned by an impurity in the ammonia. That this was not the case was shown, as this iron when used according to the conditions of Experiment 1, Table X, gave 7.2 per cent aniline.

Reduced cobalt gave lower results than either nickel or iron. It was prepared by dissolving 100 g. of hydrated $Co(NO_3)_2$ in water, pouring the solution on 100 g. of granulated pumice, evaporating, igniting, and reducing as with iron and nickel. The temperature of reduction was 480° C. The results of a continuous 2-hr. experiment with cobalt, in which the product for each half hour was separately analyzed, is given in Table XI.

TABLE XI

Half-Hour Period	Temp. ° C.	C_6H_5Cl Cc.	NH_3 G.	Molar Ratio $C_6H_5Cl : NH_3$	$C_6H_5NH_2$ %
1	480	15	6.37	1 : 2.5	1.30
2	480				1.05
3	380				1.02
4	480				0.85

The poisoning in each case was probably due to chloride formed in the reaction, as it has been known for some time that the halides[13] are extremely deleterious in their action on metallic catalysts of the iron and platinum groups as used for hydrogenations.

An attempt was made to find some material which would catalyze the production of aniline and which would no be poisoned. Some of the substances giving little or no catalysis were: metallic copper (380° and 580° C.), reduced molybdenum (380° and 480° C.), platinum black (280° and 380° C.), cocoanut charcoal (380° and 580° C.), vanadium pentoxide (480° C.), titania, etc. Of the nonmetallic substances used none showed appreciable catalysis.

Bromobenzene, iodobenzene, and *p*-dichlorobenzene were subjected to the action of ammonia in the presence of iron in a manner analogous to that used with chlorobenzene. No very promising results were obtained.

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[13] Sabatier, "La Catalyse en Chimie Organique," **1913** edition, p. 23.