

HIGH PRESSURE CATALYTIC AMMONOLYSIS OF ALCOHOLS

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Sabatier and Mailhe,¹ for the first time, obtained a mixture of primary, secondary, and tertiary amines by passing vapours of alcohols and ammonia over thoria heated to 360° C. E. g and Kaz. Smolensky² obtained 53 per cent. ethylamines by passing ammonia and alcohol over alumina at 330–350° C. Brown and Reid³ studied the joint catalytic dehydration of ammonia and aliphatic alcohols on blue tungsten oxide, special silica gel etc. and found that the special silica gel gave the maximum yield of amines. Dorrel,⁴ under the optimum conditions, obtained only 17.6 per cent. ethylamines in presence of alumina. Briner *et al.*⁵ in a similar investigation with methyl alcohol reported 52.7 per cent. yield of amines at 405° C. Arnold⁶ found that higher concentrations of ammonia in ammonolysis increased the yield of primary amines. Nickel,⁷ Copper⁸ and aluminum silicates⁹ were also employed as catalysts for ammonolysis at atmospheric pressures. Shuykin *et al.*¹⁰ found that when oxides of iron, chromium, etc., were mixed with alumina, during ammonolysis, the yields of amines were brought down. Andrews¹¹ used aluminium and diammonium phosphates for the ammonolysis of alcohols. Basic aluminium phosphate is reported^{12, 13} to give higher yields of amines in ammonolysis. Herold¹⁴ reported the formation of isoheptyl amines by heating the alcohol with ammonia at 300–450° C. in presence of hydrated alumina. Olin *et al.*¹⁵ claimed 91.6 per cent. yield of butyl amines when reduced nickel was employed as catalyst at 159° C. Ishikuro¹⁶ patented a method of obtaining high yields of amines by passing alcohol and ammonia over heated kaolin or mixture of alumina and silicic acid gel. Popov¹⁷ carried out the ammonolysis of isobutyl alcohol over activated charcoal, platinised silica gel, etc., and found that a maximum yield of 27 per cent. was obtained with activated charcoal at 400–450° C. Heinemann *et al.*¹⁸ produced butylamines in 58 per cent. yield using activated bauxite as catalyst. They stated that their yield was higher than the yields reported in literature. These authors, however, did not mention anything about the claims made in the patent literature. In addition, the authors found that the iron oxide in the bauxite acted as a promoter whereas Shuykin¹⁰ *et al.* stated that it was a retarder.

Scroutch,¹⁹ Smeykal,²⁰ and Arnold²¹ reported high yields (95 per cent.) of higher aliphatic amines by the reaction of alcohols and ammonia at high temperatures and pressures (50–100 atm.). Hasche²² and Davy²³ produced amines by spraying alcohols into ammonia in presence of a dehydrating catalyst at 150–250° C. and 400–450 p.s.i. Egly *et al.*²⁴ noticed that the increase of pressure from 10–200 p.s.i.

nearly doubled the yield of amines in the lower temperature range (300° C.). They also noticed that the presence of water in the feed reduced the formation of tertiary amine. Koslov²⁵ reported that the decomposition of cyclohexanol to cyclohexene could be suppressed by increasing the reaction pressure. Davies²⁶ patented a method of obtaining 96 per cent. butylamines by carrying out the reaction over a copper catalyst at 240–300° C. and 10–15 atm. pressure.

It is evident from the above literature that most of the information with respect to ammonolysis of alcohols is patented and the details are not available. There are also some controversies regarding the claims made. The position regarding the pressure ammonolysis is even less satisfactory since the few publications are all covered by patents. It is clear, therefore, that a detailed study of the ammonolysis is desirable.

Mechanism of the reaction

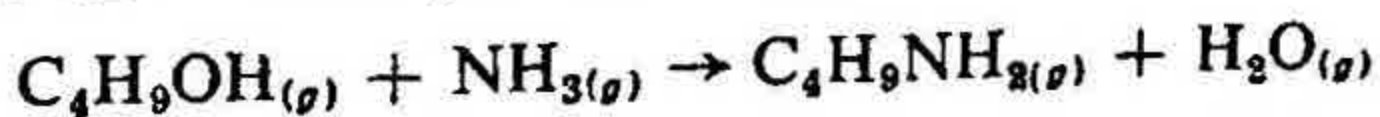
Sabatier and Mailhe have assumed that alcohols form an unstable ester with the metallic oxide (catalyst) and this ester reacts with ammonia giving amine and water, the dehydration of the alcohol to unsaturated hydrocarbons being only a side reaction. The primary amine, thus formed, will again react with the alcohol in presence of the catalyst to yield the secondary amine which in turn will give rise to the tertiary amine.

But Groggins and Stirton²⁷ are of the opinion that addition of alcohol and ammonia may occur to form ammonium alcoholate, which in presence of a dehydrating agent decomposes into amine and water. According to these authors the decomposition of the alcohol, in presence of a catalyst, to olefine and subsequent addition of H-NH₂ is also possible.

The present work helps us to determine which of these mechanisms is a prominent factor in the ammonolysis of alcohols.

Thermodynamics

The following are the thermodynamic values calculated for the reaction:—



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|--|------------------------|
| 1. Heat of reaction: ΔH at 25° C. | 5370 cal. /g. mol. |
| 2. Free energy of reaction: ΔF at 25° C. | 7690 cal./g. mol. |
| 3. Equilibrium constant at 25° C. and 1 atm. (Kp.) | 2.328×10^{-6} |
| 4. Equilibrium constant at 300° C. and 1 atm. | 1.816×10^{-4} |
| 5. Equilibrium constant at 300° C. and 20 atm. | 1.882×10^{-4} |

The above values indicate that the reaction is endothermic to the extent of 5,370 cal. /g. mol. and that the reaction is of doubtful promise but may be feasible under altered conditions, since the value of ΔF (7,690) lies between 0 and 10,000. The value for equilibrium constant indicates that at 300° C. and 20 atm. pressure only about 1 per cent. of the amine can be formed. But the literature¹⁸ already cited shows that the maximum yield obtained is about 58 per cent.

In view of the meagre literature in the high pressure ammonolysis of alcohols and the controversial claims made regarding the yields and mechanisms, the present paper aims at a systematic investigation of high pressure ammonolysis.

EXPERIMENTAL

Reagents used.—Liquid ammonia supplied by Messrs. Mysore Chemicals and Fertilizers Ltd., in a 60 lb. ammonia cylinder and ethylene (98.5 per cent. pure) supplied by Indian Oxygen Co., in a 40 cft. cylinder were used. All the alcohols of Merck's quality were refluxed with calcium for 8 hours and distilled in an all-glass apparatus.

Catalysts.—Alumina catalysts were prepared from 1 M solutions of the following salts: aluminium nitrate, aluminium chloride, aluminium sulphate, and alum. In all these preparations 6 N ammonia was used as the precipitant. The precipitate was washed free of the soluble electrolytes and dried slowly at room temperature till the whole mass became gritty and then at 110° C. Further activation was carried out in the reactor as described later. The γ -alumina was prepared according to the procedure given by Selwood.²⁸ Silica gel catalyst was prepared by mixing equal quantities of pure water glass (sp. gr. = 1.118) and C.P. nitric acid (sp. gr. = 1.109) simultaneously in a glass jar with vigorous stirring. The gel was allowed to set overnight, washed free of acid and dried in the usual way.

The promoted alumina catalysts with 2.5 per cent. ferric oxide, 5 per cent. thoria, 5 per cent. zirconia as promoters were prepared from the mixed solutions of the corresponding nitrates using 6 N ammonia as the precipitant. But in the case of alumina-molybdena (10 per cent. MoO_3) catalyst aluminium hydroxide was mixed with the requisite quantity of ammonium molybdate solution. The slurry was evaporated to dryness and converted to oxides during activation.

Apparatus.—The apparatus used in the high pressure experiments consisted essentially of a high pressure reactor (bomb.), a high pressure condenser, gauges, valves, etc. The assembly of apparatus is given in Fig. 1.

The high pressure reactor (R), supplied by American Instrument Co. ('aminco'), was made of chrome-vanadium steel capable of withstanding 1,000 atm. pressure at 400° C. The capacity of the reactor was 134.5 ml. with 1" i.d. and 3" o.d. It has screwed caps on each side with a provision for a thermowell to record the temperature. A tight-fitting stainless steel tube was used as a liner. The reactor was provided with an external electrical heating circuit and a Sunwic regulator. The temperature was measured by a calibrated iron-constantan thermocouple correct to $\pm 2^\circ \text{C}$.

The pressure condenser was fabricated from a nickel-chrome-molybdenum steel (1" i.d. and 1 13/16" o.d.) with a capacity of 30 ml. The pressure head was screwed to the inside body of the condenser and the gas tightness was achieved by a soft annealed copper gasket. The pressure head had an 'aminco' type gas inlet which was connected to a three-way valve as shown in the figure. The condenser was tested hydraulically to 100 atm. pressure before use.

The valves, connectors, etc., used in the assembly were of 'aminco' type capable of withstanding 1,000 atm. The alloy tubings were solid drawn 1/16" i.d. and 1/4" o.d. The Budenberg gauges were calibrated by means of a dead weight tester.

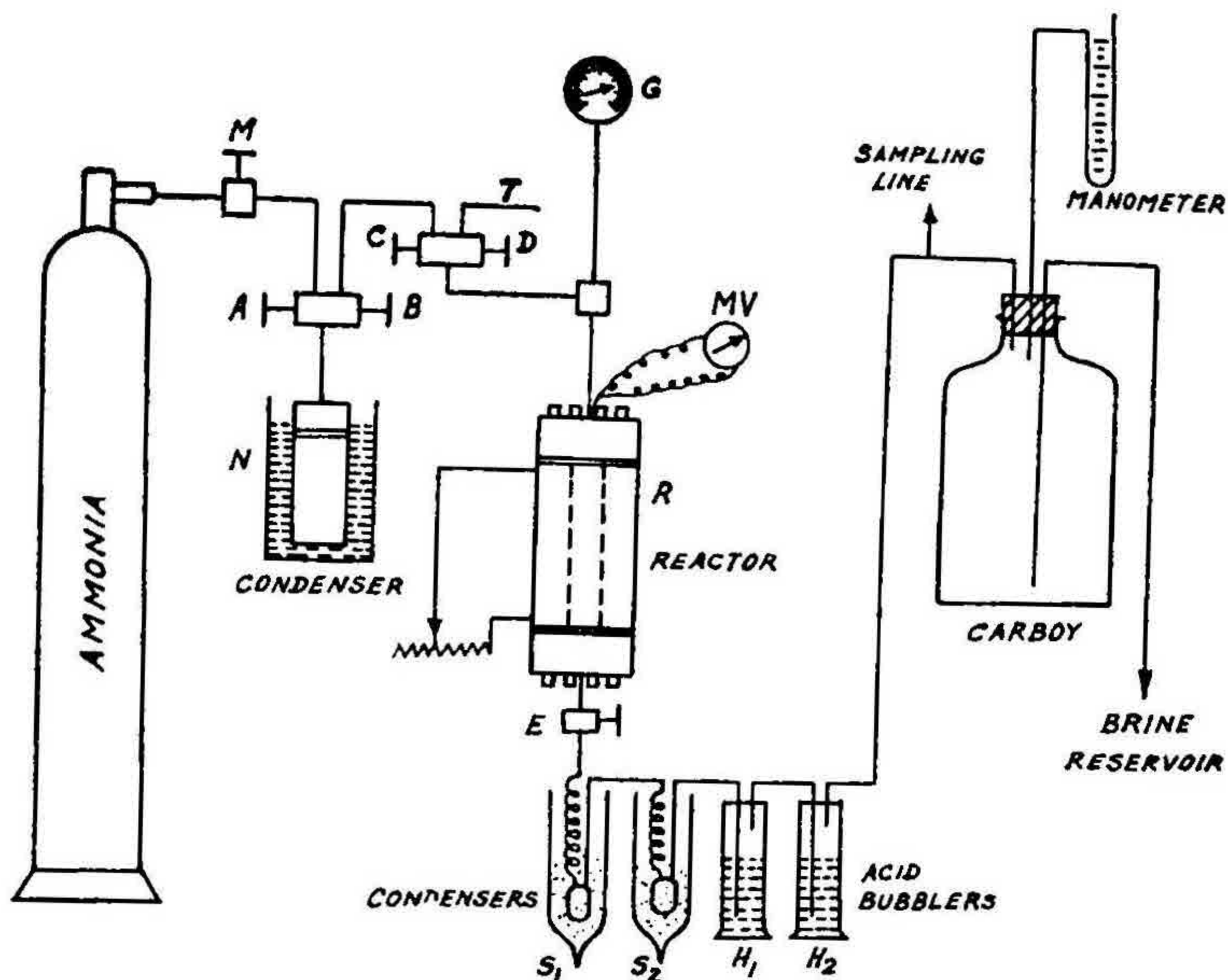


FIG. 1. Apparatus for Reactions at High Pressure.

Procedure.—Twenty ml. of the catalyst was charged into the thoroughly cleaned and dried reactor (R) and it was closed. The bomb was tested for leaks at a slightly higher pressure than was expected, by compressing air through the bleeder valve D. The air was let out and the catalyst was activated by passing dry air (free from CO_2) through T at the requisite temperature, the valve E serving as the outlet for the air. After the activation the valves D and E were closed and the reactor was cooled to room temperature. The reactor (R) and the condenser (N) were evacuated by a Cenco pump connected to T and by opening the valves A, B, C and D (M & E closed). The valves B, C and D were then closed and a required amount of alcohol was sucked into the reactor (R) through E. Condenser (N) was cooled to -7°C . by means of freezing mixture and M was opened for about 20 minutes to condense the ammonia inside the condenser. The valves M and A were then closed and B and C were opened. The liquid ammonia from the condenser was distilled into the reactor (R) by replacing the freezing mixture with hot water (45°C .) for about 20 minutes. Since the volume of the condenser was known the quantity of ammonia transferred into the reactor could be calculated. The quantity of liquid

ammonia that condensed in N was also determined by passing the gas into a known excess of dilute acid and estimating the amount of acid neutralised. The valve C was then closed and the furnace was switched on. The pressures developed were noted at different temperatures during heating. The bomb was maintained at the desired temperature for various intervals and the products were discharged slowly through E into two spiral glass condensers S_1 and S_2 cooled in freezing mixture. The uncondensed gases were scrubbed by dilute sulphuric acid in the bubble s H_1 and H_2 to absorb the gaseous ammonia. The residual gasses were collected in a carboy over saturated brine. After the complete discharge of products dry nitrogen was passed for about 20 minutes through T to sweep away the residual products into the condensers.

For experiments where hydrogen and nitrogen were used, the gases were boosted up to 2,000 psig. in a booster pump and transferred to the reactor through D.

The assembly of apparatus used for the experiments carried out at atmospheric pressures is shown in Fig. 2. The reactor was of 1" \times 12" Pyrex glass tube tapered and bent at the exit end as shown in the figure. The first half of the reactor was

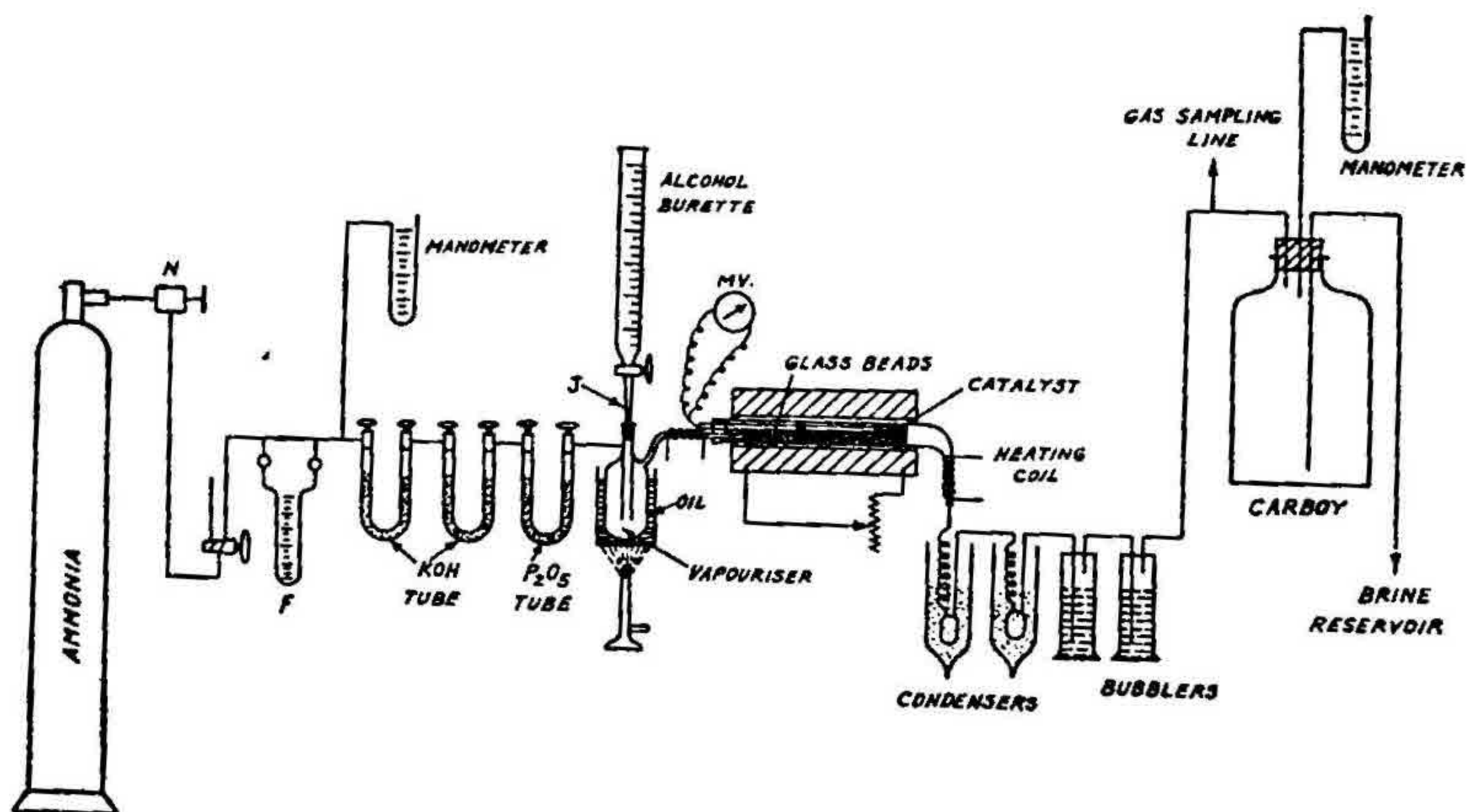


FIG. 2. Apparatus for Reactions at Atmospheric Pressure.

filled with glass beads to act as preheater and the second half with 20 ml. of catalyst which was held in position by two plugs of glass-wool on each side. The catalyst was activated by passing dry air at 300° C. as measured by a calibrated iron-constantan thermocouple.

After the activation, the system was flushed with pure dry nitrogen. Ammonia was then passed through the flow meter (F), the drying train and the catalyst. The alcohol was run from the burette into the vaporiser, heated on oil-bath, through

the calibrated jet (J). The mixture of alcohol vapour and ammonia were then passed over the catalyst. After the steady condition had reached, the liquid products were condensed in the spiral condensers and the ammonia was scrubbed by dilute acid in the bubblers for a known time. The residual gas was collected in a carboy over brine.

Analysis.—The total basic nitrogen (ammonia and amines) was estimated from the liquid products by acidifying the products with a known excess of acid and then back titrating the acid with standard alkali. The acid consumed gives the amount of amines and ammonia in the liquid products.

The total amines were estimated by the method of Weber and Wilson.²⁹ The method is based on the selective precipitation of ammonia by yellow mercuric oxide in presence of sodium hydroxide-sodium carbonate solution. The amines present do not react with the reagent (yellow mercuric oxide) under these conditions. After removing the ammonia, the amines were distilled into a known excess of acid and the acid determined by titration with alkali. From the amount of acid used the total moles of amines could be calculated.

After the titration the solution was further acidified and evaporated to a small volume and kept for the analysis of secondary and tertiary amines. The primary amine was determined from the solution by measuring the volume of the nitrogen evolved on reaction with nitrous acid by employing Van Slyke's³⁰ amino nitrogen apparatus. The tertiary amine remains unaffected with nitrous acid whereas the secondary amine forms the nitroso amine. After destroying the primary and secondary amine from the solution, the tertiary amine was distilled with alkali into a known excess of acid and the excess acid determined by titration with alkali.

In cases where the individual amines were not determined the results are given as "per cent. amines" which indicate the number of moles of amine formed from 100 moles of alcohol. But when all the three amines are determined the results are given as "per cent. alcohol converted to various amines".

The gaseous products were analysed by employing Orsat's gas analysis apparatus following the standard methods of adsorption. Hydrogen was determined by the partial combustion of the gas over copper oxide at 280–90° C. while the hydrocarbons were determined by the explosion method.

RESULTS

To establish the optimum conditions for the ammonolysis of alcohols, butyl alcohol was chosen since the amines formed in this case had higher boiling points and could be separated easily.

The catalyst employed for these experiments was alumina prepared from aluminium nitrate and the temperature of activation was the same as the temperature at which the experiment had to be conducted. The conditions, the reactants, and the results of these experiments are given in Table I.

TABLE I

Effect of Temperature on the Ammonolysis of Butyl Alcohol

Butyl alcohol = 10 ml.

Catalyst = 20 ml. alumina

Ammonia = 5.8 litres (N.T.P.)

Initial pressure = 140 psig.

Ammonia/alcohol = 2.37 (Mol. ratio)

Time of reaction = 2.5 hours

No.	Temp. °C.	Final pressure after heating Psig.	% Amines	% Alcohol converted to		
				Olefins	Paraffins	Total hydrocarbon
1	250	300	3.66
2	275	400	10.95
3	300	420	12.77
4	325	450	12.44	1.21	..	1.21
5	350	600	11.90	6.46	3.07	9.53
6	375	700	9.13	6.93	6.37	13.30
7	400	800	8.68	7.54	11.91	19.45
8	425	800	8.56	17.63	18.56	36.19

The results of the table indicate that the yield of amines increases with temperature up to 325° C. after which the formation of hydrocarbons starts, with a simultaneous diminution in the yield of amines. Finally at 425° C. the per cent. amines formed is only 8.6 whereas the decomposition of alcohol is 36 per cent. Since a maximum yield of 12.8 per cent. amines was obtained at 300° C., this was taken as optimum temperature for the subsequent experiments.

Effect of ammonia concentration.—To determine the optimum ammonia/alcohol ratio, experiments were carried out on the same variety of catalyst and the results are given in Table II.

It is clear from the table that a maximum of 25 per cent. amines is obtained at ammonia/alcohol ratio of 11.37. Decomposition of alcohol to hydrocarbons does not take place under these conditions. The effect of ammonia on the nature of the products formed is also given in the table, where it is seen that at high ammonia/alcohol ratio primary amine predominates while at a low ratio more of secondary and tertiary amines are formed. The percentages of secondary and tertiary amines formed, however, have no definite relation to the ammonia/alcohol

TABLE II
Effect of Concentration of Ammonia

Temperature = 300 °C.
Time = 2.5 hours

Catalyst = 20 ml. Al₂O₃
Initial pressure = 140 psig.

No.	Butyl alcohol ml.	Ammonia alcohol (mol. ratio)	Final pressure after heating psig.	% Amines	% Alcohol converted to amines			
					Prim-ary	Second-ary	Terti-ary	Total
1	2.5	11.37	300	24.75	21.85	2.89	4.34	29.08
2	4.0	5.50	280	23.16	17.08	9.58	3.87	30.53
3	5.0	3.67	300	19.74	13.36	7.63	7.73	28.72
4	10.0	2.02	420	12.14	7.72	5.80	5.42	18.94
5	15.0	1.20	450	5.73	2.94	2.67	4.36	9.97
6	20.0	0.84	500	3.07	1.47	1.25	2.92	5.64

ratio. These results are in agreement with the results reported in literature.^{4, 6} Since the yield is quite high at an ammonia/alcohol ratio of six, this was taken as the optimum ratio for further studies.

Effect of time on the reaction.—Figure 3 represents the effect of time on the per cent. amines formed at 300° C. These results show that the reaction takes place quite rapidly during the first 30 minutes during which about 13 per cent. amines are formed. It reaches a maximum of 23.4 per cent. in the next 2 hours after which it remains constant. In all these experiments a constant pressure (300 psig.) was indicated showing thereby that no hydrocarbons were obtained even after 5 hours. It can therefore be concluded that the amines formed are quite stable and do not decompose under the experimental conditions. Subsequent experiments were carried out for 2.5 hours since this time was quite adequate for the attainment of equilibrium conditions.

Effect of water.—Ammonolysis of alcohols involves elimination of 1 mole of water for every mole of amine formed. Presence of water in the feed should, therefore, inhibit the formation of the amine. The results obtained (Fig. 4) confirm this view-point. Even with a molecular ratio of water to alcohol of 0.2 (about 95 per cent. butyl alcohol) the per cent. amines is reduced from 25 to 24. From the curve it is seen that the relation is linear up to a water/alcohol ratio of 2.5, after which the rate of diminution of amine falls. It is interesting to note that in all these experiments no hydrocarbons are produced.

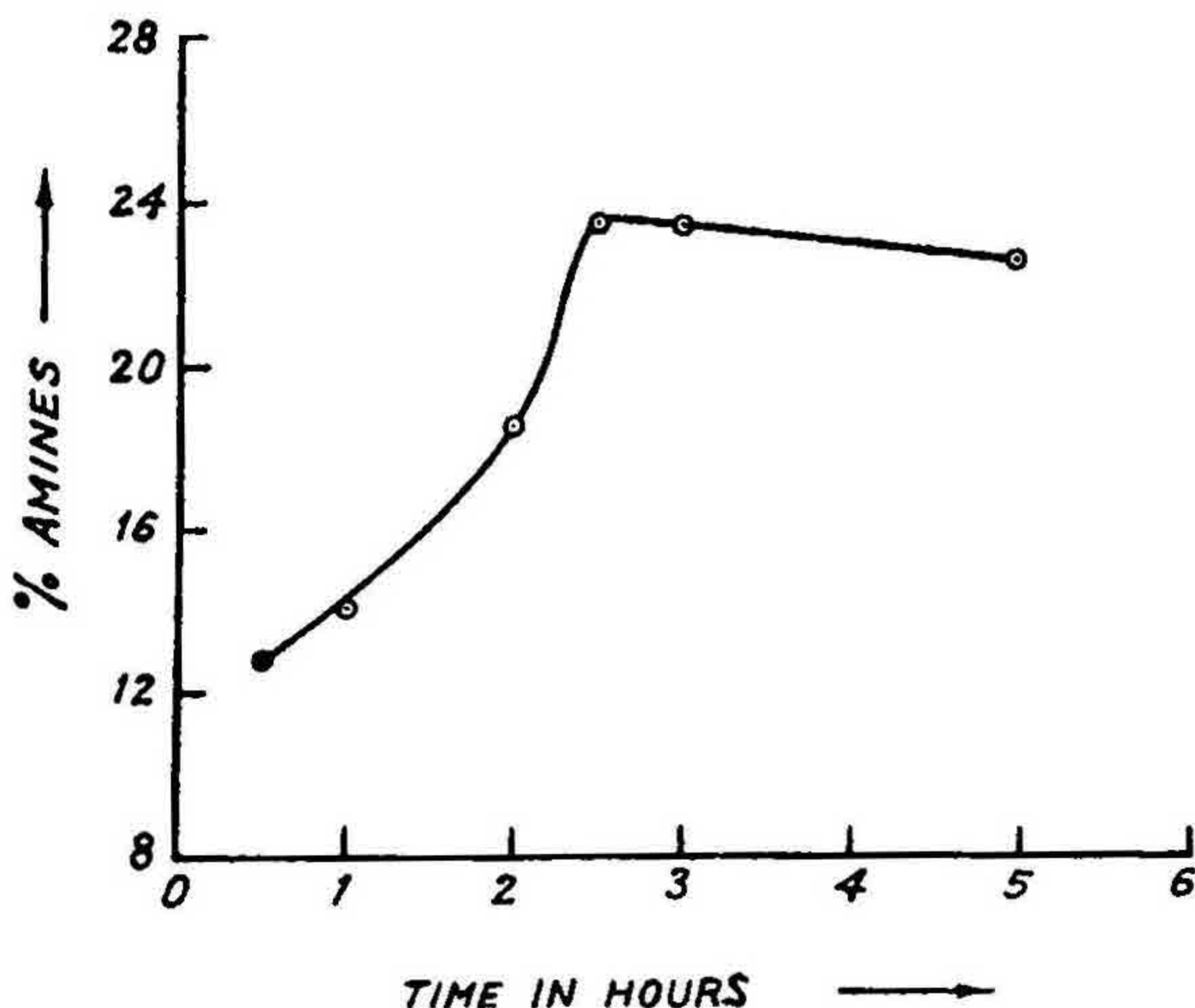


FIG. 3. Effect of Time on the Reaction.

When the catalyst was activated at 300° C. under the above experimental conditions it was invariably noticed that the catalyst had about 10 per cent. water. Since water had a deleterious effect on the per cent. conversion of alcohol into amines, it is of interest to find out whether a further desiccation of the catalyst would increase the per cent. yield of amines during ammonolysis. For this purpose the catalyst was activated in a combustion tube by passing dry air at 300° C. and 425° C. After the activation, the sample was quickly cooled in a desiccator and the amount of water present was determined by ignition of the catalyst in a platinum crucible to constant weight. The water contents were 10.5 and 4.4 per cent. respectively. The catalyst was also activated in vacuum at the above two temperatures where the amount of water retained was considerably reduced (7 and 1.8 per cent. respectively).

Ammonolysis was carried out employing 2.5 ml. of butyl alcohol at 300° C. for 2.5 hours in presence of 20 ml. of the above alumina samples. The per cent. amines obtained was practically same (23–25) with all the 4 samples although their water contents varied from 2–10 per cent. indicating thereby that the water present in the catalyst does not in any way retard the formation of amines.

Effect of pressure.—In order to determine the effect of pressure on ammonolysis, experiments were carried out at 300° C. for 2.5 hours, employing 4 ml. of butyl alcohol in presence of 20 ml. of alumina catalyst with hydrogen and nitrogen as additional pressure producing media. The initial and final pressure were 1,100 and 2,750 psig. in the case of hydrogen and 1,000 and 2,650 psig. in the case of nitrogen respectively. But the per cent. amines formed were only 11.7 and 8.4 in

the cases. It is clear, therefore, that the increase of gas pressure inhibits the reaction. This may be due to the wall effect of the inert gas, which will decrease the number of fruitful collisions between the reactants.

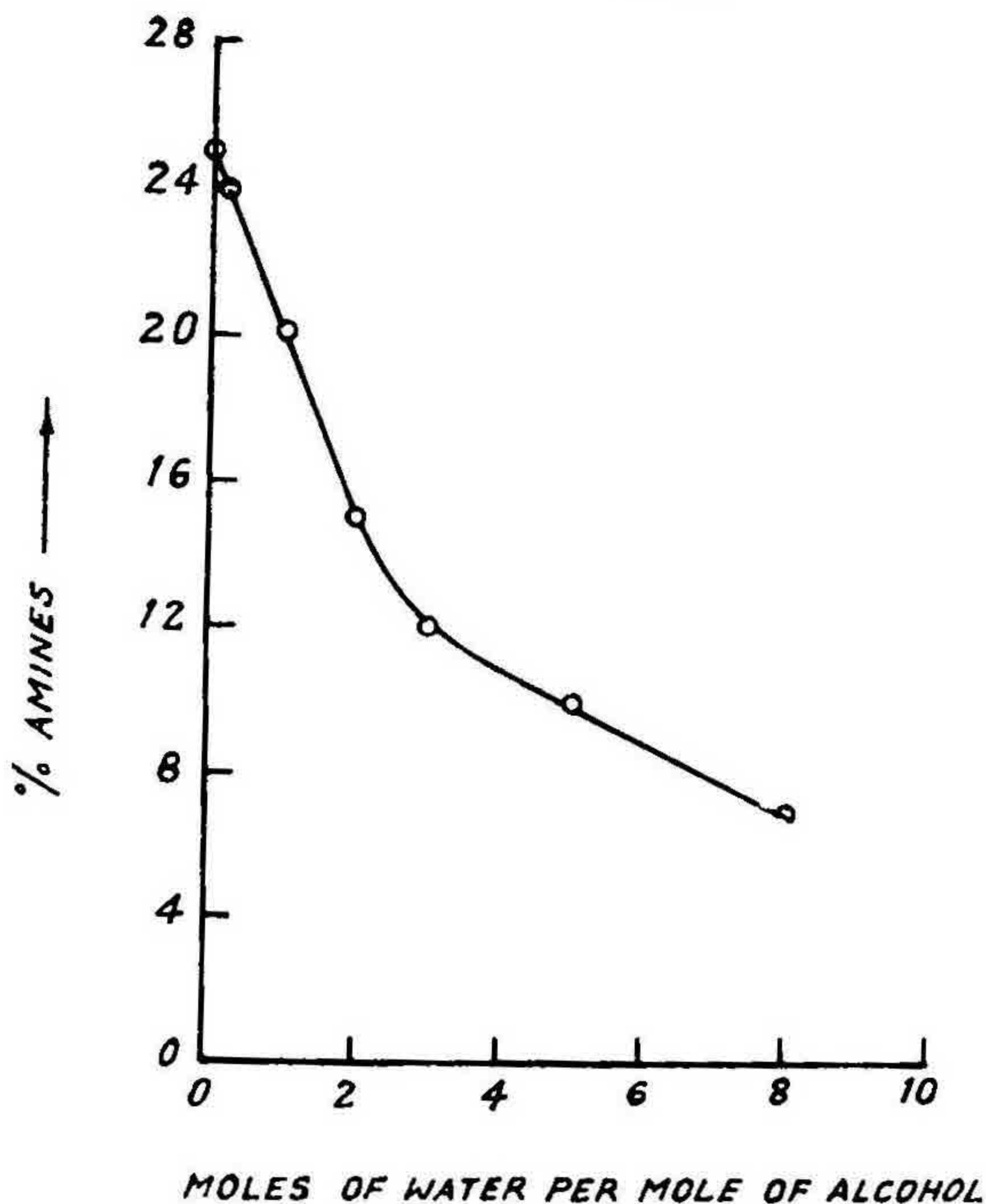


FIG. 4. Effect of Water.

The reaction pressure was therefore varied by changing the quantities of the reactants, keeping ammonia/alcohol ratio about 6 throughout and the results are given in Table III.

As seen from the results the per cent. amines formed is reduced gradually from 24.6 to 4.2 as the pressure of the system is raised from 300 to 4,800 psig. although the total quantities of the amines formed increased with the increase of pressure (*i.e.*, reactants).

Catalysts prepared from various aluminium salts.—In order to get an idea of the porosity of the alumina samples prepared, the adsorption capacity of each of the sample for water was determined. Weighed quantities of activated samples were kept in a desiccator containing water and the desiccator was evacuated. They were then allowed to remain in contact with water vapour for a definite period and

TABLE III
Effect of Pressure

Temperature = 300° C. Time = 2.5 hours		Catalyst = 20 ml. Al ₂ O ₃ Initial pressure = 140 psig.				
No.	Butyl alcohol ml.	Ammonia litres (N.T.P.)	Ammonia alcohol (Mol. ratio)	Final pressure Psig.	% amines	% amines × vol. of alcohol
1	2.0	2.92	6.0	200	23.45	46.90
2	2.5	5.95	8.6	300	24.58	61.45
3	5.0	10.32	8.4	600	13.58	67.90
4	10.0	18.74	7.7	2450	6.37	63.70
5	20.0	28.02	5.7	4800	4.20	84.00

the vacuum was then released and the samples weighed. This process was repeated until constant weights were obtained and the results are given in Fig. 5.

These results indicate that about 18 hours were required to reach equilibrium in each case and that the samples precipitated from aluminium nitrate and aluminium chloride have the highest porosities while γ -alumina has the least.

The results of ammonolysis carried out with these samples are given in Table IV.

TABLE IV
Activity of the Various Catalysts

Butyl alcohol = 2.5 ml. Ammonia = 3.7 litres (N.T.P.) Ammonia/alcohol = 6. (Mol.)		Temperature = 300° C. Time = 2.5 hours. Catalyst volume = 20 ml.		
No.	Method of preparation of alumina	Porosity expressed as g. of water per g. of Al ₂ O ₃	Final pressure Psig.	% amines
1	Prepared from aluminium nitrate..	0.3692	300	24.58
2	Prepared from aluminium chloride	0.3521	300	19.48
3	Prepared from alum	0.3228	300	11.54
4	Prepared from aluminium sulphate	0.3151	300	18.49
5	γ -alumina	0.2736	300	18.12

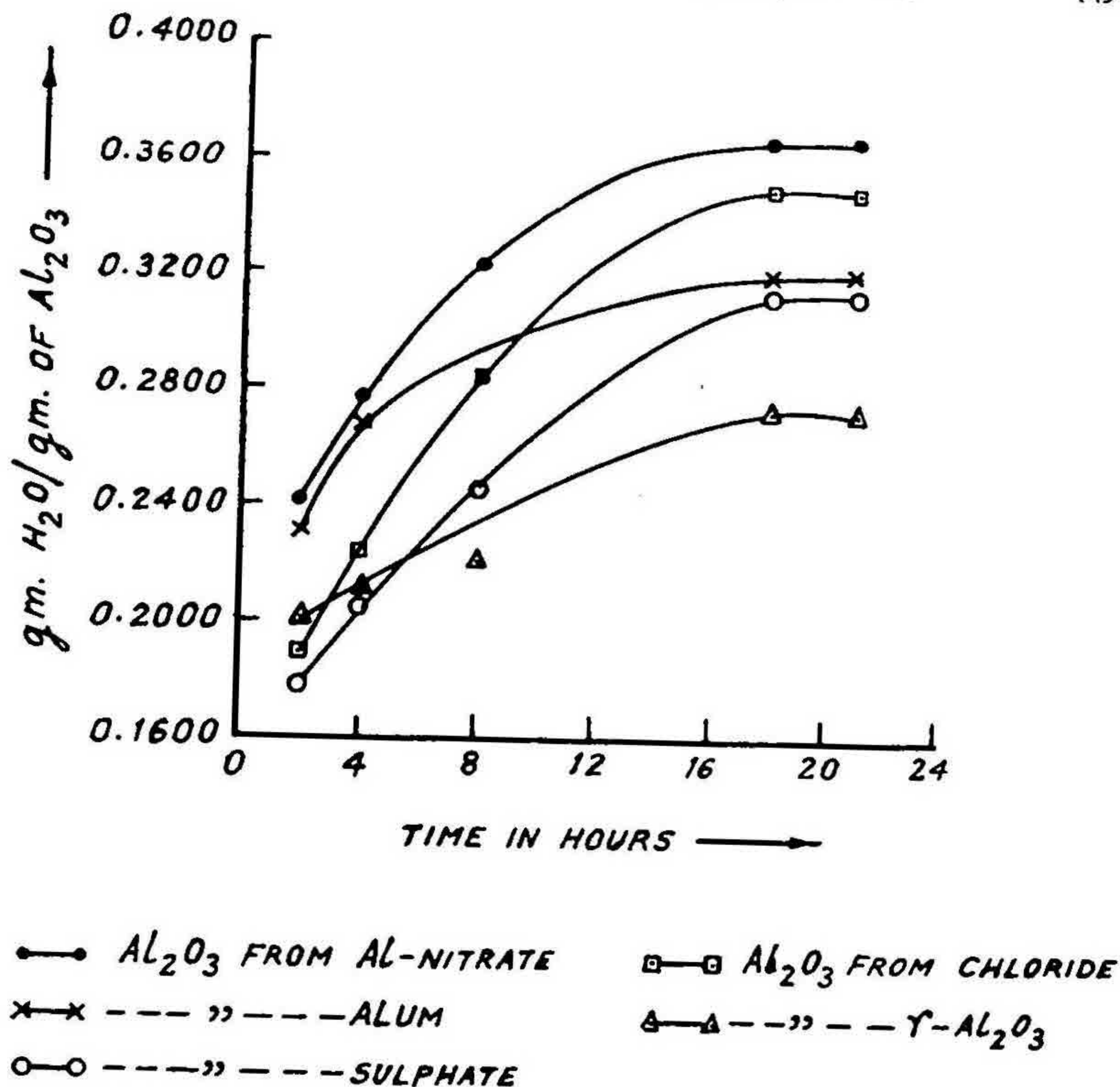


FIG. 5. Adsorption of Water on Alumina.

As can be seen from the results, with the exception of the catalyst prepared from potassium alum, the decrease in the activity of the catalysts is in the same order as the decrease in their porosity. But the decrease in porosity and the decrease in activity are not proportional. It may be concluded, therefore, that the porosity is not the only criterion for the activity of the catalysts. The poor yield in the case of alumina prepared from potassium alum may be due to the poisoning effect of traces of potassium that is invariably associated with this alumina. But in the case of alumina prepared from aluminum nitrate, the adsorbed nitrate impurity can easily be decomposed at the temperature of activation, thus giving a surface without any catalytic poison, enhancing the catalytic activity.

Promoters.—Experiments were conducted to find out the effect of oxides of iron ($Fe_2O_3 = 2.5$ per cent.), thorium ($ThO_2 = 5$ per cent.), zirconium ($ZrO_2 = 5$ per cent.) and molybdenum ($MoO_3 = 10$ per cent.) in the catalyst under the

optimum conditions and the per cent. amines obtained respectively were 14, 13, 16 and 10 indicating thereby that all the oxides incorporated in the alumina catalyst diminish the yield of amines. The results agree with those reported by Shuykin¹⁰ although Heinemann¹³ has reported that the iron oxide plays a very important role in the catalytic activity. No decomposition of alcohol to hydrocarbons was observed in all these experiments. It can therefore be concluded that the oxides used do not act as promoters; in fact they act as catalytic inhibitors.

Catalyst volume.—5, 10 and 20 ml. of alumina prepared from aluminium nitrate were employed for this purpose and the per cent. amines obtained are 26, 29 and 25 respectively under the optimum conditions. Without any catalyst 4.5 per cent. amines are formed. This may be due to the catalytic action of the walls of the reactor. The variation of per cent. amines with different volumes does not appear to be considerable. Since 10 ml. sample has yielded slightly higher per cent. amines, this volume of catalyst was employed in subsequent experiments.

Ammonolysis of aliphatic alcohols.—With the optimum conditions obtained for the ammonolysis of butyl alcohol, the studies were extended to other aliphatic alcohols and the results are given in Table V.

It is seen from the table that a maximum of 38 per cent. conversion to amines is obtained in the case of *n*-butyl alcohol and the conversion in all other alcohols is less. The conversion in the case of isopropyl alcohol is less than that in the *n*-propyl alcohol. This diminution in conversion in the case of secondary alcohols has also been observed by Popov.¹⁷ There is no regularity in the conversions with the increase of chain-length in the normal alcohols.

Ammonolysis with silica gel catalyst.—Since the reaction involves elimination of water, it is of interest to study the efficiency of a similar dehydrating agent. An experiment was therefore carried out with 20 ml. silica gel at 300° C. under similar conditions of experiments given in Table V. The per cent. amines obtained was 26.3 which was nearly equivalent to the yield obtained with alumina. Even in this case, no hydrocarbons were produced. It was concluded, therefore, that silica gel can act as efficiently as alumina in the ammonolysis of alcohols.

Ammonolysis at atmospheric pressure.—The results of the experiments carried out at atmospheric pressure are given in Table VI. The alumina employed was prepared from aluminium nitrate.

In the two experiments carried out with alumina only 13 and 16.7 per cent. amines are obtained. But 10 per cent. of alcohol is converted to butylene in each case. It is surprising to find that in the case of silica gel the reaction is practically negligible (1.6%) with very little formation of olefins (0.4 per cent.), while in pressure reaction it is as effective as alumina. This indicates that a pressure reaction is essential if silica gel is employed as the catalyst, while in the case of alumina a pressure reaction not only gives a higher yield but also inhibits the formation of olefins.

TABLE V

Ammonolysis of Aliphatic Alcohols

Alcohol = 2.5 ml.

Temperature = 300° C.

Catalyst = 10 ml. Al₂O₃

Time = 2.5 hours

No.	Alcohol	Ammonia Alcohol (mol. ratio)	Final pressure psig.	% Amines	% Alcohol converted to amines			
					Prim- ary	Second- ary	Terti- ary	Total
1	Ethyl..	.. 3.96	270	22.39	21.38	0.83	1.75	23.96
2	<i>n</i> -propyl-	.. 6.02	270	22.58	13.98	11.31	8.13	33.42
3	Iso-propyl-	.. 4.38	270	21.65	15.69	6.37	8.33	30.39
4	<i>n</i> -butyl-	.. 5.88	270	28.74	22.97	4.53	10.57	38.07
5	Iso-butyl-	.. 7.23	240	27.64	19.78	11.13	6.76	37.67
6	<i>n</i> -amyl-	.. 5.07	245	23.20	19.67	3.32	5.55	28.57
7	Iso-amyl-	.. 6.02	225	25.84	21.07	3.87	8.49	33.45
8	<i>n</i> -hexyl-	.. 7.79	260	19.56	16.82	3.43	3.08	23.33

TABLE VI

Ammonolysis at Atmospheric Pressure

Butyl alcohol = 6 ml.

Temperature = 300° C.

Catalyst volume = 20 ml.

Time of run = 1 hour

No.	Catalyst	Liquid space velocity of alcohol	Ammonia Alcohol (Mol. ratio)	% Amines	% Alcohol converted to olefins
1	Alumina	.. 0.3	2.0	13.08	10.32
2	Alumina	.. 0.3	2.0	16.70	9.96
3	Silica gel	.. 0.3	2.0	1.62	0.40

Decomposition studies of alcohols.—The results of Table V indicate that no hydrocarbons are formed in spite of the fact that the alcohols are heated in presence of alumina. To find out whether this is merely the pressure effect or the effect of

excess of ammonia, 2.5 ml. of alcohols were heated at 300° C. in presence of alumina for 2.5 hours in absence of ammonia. It is surprising to find, from the results, that only in the case of normal and iso propyl alcohols there is a high conversion (22 per cent.) to olefins, whereas in the case of other alcohols it is less than 5 per cent. But in presence of ammonia no hydrocarbon is produced even in the case of propyl alcohol. It can therefore be concluded that ammonia suppresses the decomposition of alcohols to olefins.

Reaction of ammonia with other organic compounds.—In order to ascertain the mechanism of ammonolysis, the reaction of ammonia with ethylene, ethyl ether and some alicyclic compounds were carried out and the results are given in Table VII.

TABLE VII

Reaction of Ammonia with Organic Compounds

Temperature = 300° C.

Catalyst = 10 ml. alumina

Time = 2.5 hours

No.	Compound	G. mol.	Ammonia Compound (mol. ratio)	Final pressure psig.	% Amines
1	Ethylene	0.0933	1.20	850	Nil
2	Ethyl ether	0.0506	4.70	275	9.75
3	Cyclohexanol	0.0455	4.00	220	5.94
4.	Cyclohexanol	0.0455	5.97	240	5.44
5	Cyclohexene	0.0498	5.21	170	0.53
6	Dipentene	0.0322	5.89	155	0.84
7	α -pinene	0.0322	4.48	155	0.48

As can be seen from the table no amine is formed when ammonia and ethylene are subjected to the optimum conditions of ammonolysis. But ethyl ether gives about 10 per cent. amines during ammonolysis. Cyclohexanol also yields the amine (6 per cent.) while the corresponding unsaturated compound (cyclohexene) yields only a trace of the cyclohexyl amine. Dipentene and α -pinene also behave in a similar manner. It can therefore be concluded that the olefin production is not the intermediate step in the ammonolysis of alcohols.

ADSORPTION STUDIES

The extent of adsorption of ammonia and butanol, individually as well as in presence of each other were determined at various temperatures. 11.2 litres

(N.T.P.) of ammonia was introduced into the evacuated bomb having no catalyst and the pressures developed at various temperatures were noted. After removing ammonia the bomb was cooled and evacuated. Similarly the pressure-temperature curves for 10 ml. of butanol and a mixture of 11.2 litres (N.T.P.) of ammonia and 10 ml. of butanol were determined. Pressure-temperature curves for 11.2 litres of ammonia, 10 ml. of butanol and the mixture of these two were also determined in presence of 14 g. of alumina and 9 g. of silica gel respectively and the results are given in Table VIII.

These results indicate that in the absence of the catalyst at low temperatures the combined pressure of the mixture of ammonia and butanol is higher than the sum of the individual pressures of the two reactants, although this difference is gradually reduced with an increase in temperature. This may partly be due to the space occupied by the liquid butanol in the reaction vessel. In presence of alumina and silica the sum of the pressures of the individual components agrees fairly closely with the pressures for the mixture. These results are in accordance with expectation since there is no volume change for the formation of the amine from the reactants. The results also indicate that both in the case of alumina and silica the fall of pressure due to the adsorption of ammonia is always (at all temperatures) greater than that due to butanol. It is clear, therefore, that the adsorption of ammonia is higher than that of butanol.

From the diminution in pressure of the gases in presence of catalysts, the amount of butanol and ammonia adsorbed by the catalysts at different temperatures and pressures was calculated and the results are given in Table IX.

These results indicate that the adsorption of butanol on alumina is more or less constant, while in the case of silica gel the amount of adsorption increases with the increase of pressure. It has to be pointed out that the total adsorption noticed is a function of two opposing factors, the adsorption increasing with the increase in pressure and diminishing with the increase in temperature. For the adsorption of butanol on alumina these two factors seem to cancel each other with the result that the total adsorption has remained practically constant. In the case of silica, on the other hand, the amount of butanol adsorbed has increased with the increase in temperature and pressure, indicating thereby that the pressure effect on adsorption is higher than the temperature effect. In fact the adsorption of butanol on silica gel at any particular temperature is 3-5 times higher than that on alumina surface. The total adsorption of ammonia has increased with an increase in temperature (and pressure) both with alumina and silica gel. As in the previous case the pressure effect on adsorption seems to be more prominent than the temperature effect. The quantity of ammonia taken up by silica gel is nearly twice as much as that with alumina. It is interesting to note that in spite of the high capacity for adsorption by silica gel for both the reactants, the total yield of amines is nearly equivalent to that with alumina. This indicates that the specific activity of the two catalysts is nearly the same although the total adsorption of the reactants greatly differs.

TABLE VIII

High Pressure Adsorption of Reactants on Catalysts

Butanol = 10 ml.

Catalyst: (1) Alumina. = 14 g. (4.4 ml.).

Ammonia = 11.2 lit.

(2) Silica Gel = 9 g. (4.2 ml.).

Volume of the Reactor = 134.5 ml.

Temp. °C.	Pressure PSIG.								
	Blank			Alumina			Silica Gel		
	Butanol	Ammonia	Mixture	Butanol	Ammonia	Mixture	Butanol	Ammonia	Mixture
140	34	345	465	95	275	330	22	275	330
160	50	395	540	44	320	385	35	320	370
180	65	455	605	58	355	435	50	355	410
200	80	505	670	73	395	480	60	385	445
220	95	560	750	87	430	540	70	420	480
240	110	620	815	102	480	585	82	460	520
260	125	685	880	116	535	650	90	510	570
280	140	770	940	130	600	720	100	570	640
300	150	880	1020	140	685	820	110	640	725

TABLE IX
High Pressure Adsorption of Reactants on Catalysts

Temp. °C.-	Alumina				Silica Gel			
	Butanol Vapour		Ammonia		Butanol Vapour		Ammonia	
	Equilibrium pressure psig.	Adsorption c.c. at N.T.P. per g.	Equilibrium pressure psig.	Adsorption c.c. at N.T.P. per g.	Equilibrium pressure psig.	Adsorption c.c. at N.T.P. per g.	Equilibrium pressure psig.	Adsorption c.c. at N.T.P. per g.
140	31.5	2.16	310.0	30.20	28.0	7.38	310.0	46.98
160	47.0	2.47	357.5	30.87	42.5	9.60	357.5	48.01
180	61.5	2.75	405.0	39.33	57.5	9.18	405.0	61.19
200	76.5	2.63	450.0	41.44	70.0	11.71	445.0	70.33
220	91.0	2.89	495.0	46.99	82.5	14.06	490.0	78.72
240	106.0	2.78	550.0	48.63	96.0	15.11	540.0	86.32
260	120.5	3.01	610.0	50.16	107.5	18.21	597.5	91.01
280	135.0	3.22	685.0	54.78	120.0	20.05	670.0	100.2
300	145.0	3.11	782.0	60.63	130.0	19.35	760.0	116.1

GENERAL DISCUSSION

Reaction mechanism.—Groggins and Stirton²⁷ suggested that during the ammonolysis of alcohol the function of alumina is to produce the olefins (by dehydration) which are then supposed to react with ammonia to give amines. But the evidence obtained by the present investigation shows that the olefin formation is not essential for the production of the amine. Thus in the case of propyl alcohol the olefin produced in the absence of ammonia is 22 per cent. while the per cent. amines formed is about 22 (Table V). In the case of butyl alcohol the corresponding olefin formation is only 2.5 per cent., while the per cent. amine is nearly 29. In the case of amyl and higher alcohols olefins are not produced in any detectable quantities yet the per cent. amines formed is between 20 and 25. It is thus clear that the olefin formation has no direct relationship with the amine formation. When ethylene is allowed to react with ammonia in presence of the same catalyst no detectable quantity of ethyl amine is formed (Table VII). This is another convincing evidence against the production of olefins as intermediate compounds in the formation of amines.

The olefin formation need not be essential even in the case of alicyclic compounds. Thus cyclohexanol will give rise to 6 per cent. of the corresponding amine while cyclohexene gives hardly 0.5 per cent. amine under similar experimental conditions (Table VII). It can therefore be concluded that olefin formation need not be postulated as intermediate step in the ammonolysis of alcohols.

Extent of formation of the amines.—Calculations based on thermodynamic considerations indicate a value of 2.3×10^{-6} for the equilibrium constant for the formation of butyl amine from the corresponding alcohol and ammonia at atmospheric temperature and pressure. The value of the equilibrium constant is increased to 1.8×10^{-4} at 300° C. and atmospheric pressure and further to 1.9×10^{-4} at 300° C. and 20 atm. The above values indicate that an increase in the temperature would enhance the production of the amine. Similarly an increase in pressure at high temperature would also increase the amount of amine formation. These general predictions are qualitatively borne out by the experimental values obtained in this section. Thus in Table I the per cent. amines produced has increased from 3.6 to 12.8 when the temperature is increased from 250° to 300° C., the pressure remaining in the neighbourhood of 400 psig. With further increase in temperature the per cent. amines get reduced (8.6 at 425° C.). This is evidently due to the side reactions that take place in the reaction mixture. Thus at 425° C. nearly 36 per cent. of the alcohol employed is converted into hydrocarbons, while at 300° C. the hydrocarbons are hardly detectable.

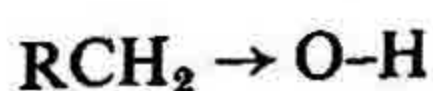
The low value (1.9×10^{-4}) of equilibrium constant for the reaction at 300° C. and 20 atm. shows that when equilibrium is reached the amount of the amine formed must be about 1 per cent., but actually the quantity of the amine formed is 30–40 per cent. under most favourable conditions. The increase in the production of the amine is due to one or more of the following causes:

(1) The alumina or silica gel employed as catalyst can adsorb the water vapour produced in the reaction and the equilibrium may be shifted towards the formation of the larger amounts of the amine. The high pressure of the reaction system may also favour the adsorption of the water vapour to a large extent in spite of the high temperature (300° C.).

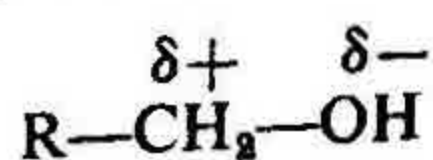
(2) In the calculation of the equilibrium constants, empirical methods have been employed in calculating the value of some factors. For example the critical constants for butyl amine have been calculated from the boiling point data making use of an empirical equation. It has also been assumed that the heat of reaction (ΔH) remains constant between the temperatures 25° C. and 300° C., while calculating the values of equilibrium constant at different temperatures. These approximations would greatly alter the quantitative nature of the calculations.

Influence of pressure on the reaction.—In the formation of amines particularly at high temperatures, no volume changes occur. Hence according to LeChatelier's principle the production of the amine must be independent of pressure. However, the experimental results indicate that there is a large increase in the production of the amine at elevated pressures. This may be due to the imperfectness of the gaseous system under consideration. The compressibility coefficients may be different for various gases in the system and this may help in getting higher yield of amines. Also since the most favourable temperature (300° C.) is below the critical temperature of water (374.5° C.), it is possible that an increase of pressure, by causing condensation of a part of water, would result in an increased yield. Similar reactions have also been noticed in the catalytic decomposition of paraffins. It has been found in this laboratory (unpublished results) that when kerosene is subjected to cracking the amount of gasolenes produced increases with an increase in the pressure, although the reverse reaction should have taken place according to LeChatelier's principle.

Electronic interpretation of the observed reaction.—In the case of alcohols it is known that the electron releasing tendency is greater with the alkyl group than with the hydrogen atom attached to the oxygen and can be represented thus:



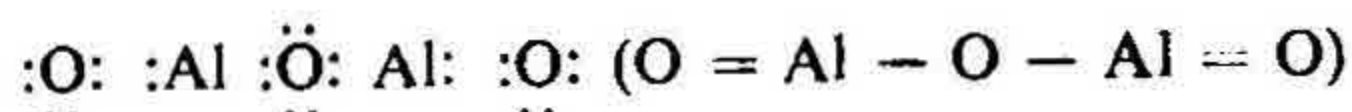
This is also borne out by the fact that the dipole moments of the alcohols are in the neighbourhood of 1.7×10^{-18} electrostatic units. The electron releasing tendency would give rise to a positive charge to the carbonium ion and negative charge to the oxygen atom of the hydroxyl group and can be represented as follows:—



In the case of ammonia the seat of attack is the lone pair of electrons on the nitrogen. Since in the ground state of the alcohol molecule, the α -carbon atom carries a fractional positive charge ($\delta+$) it is not sufficiently activated due to its weak electrophilic character. Hence no reaction between the alcohol and ammonia

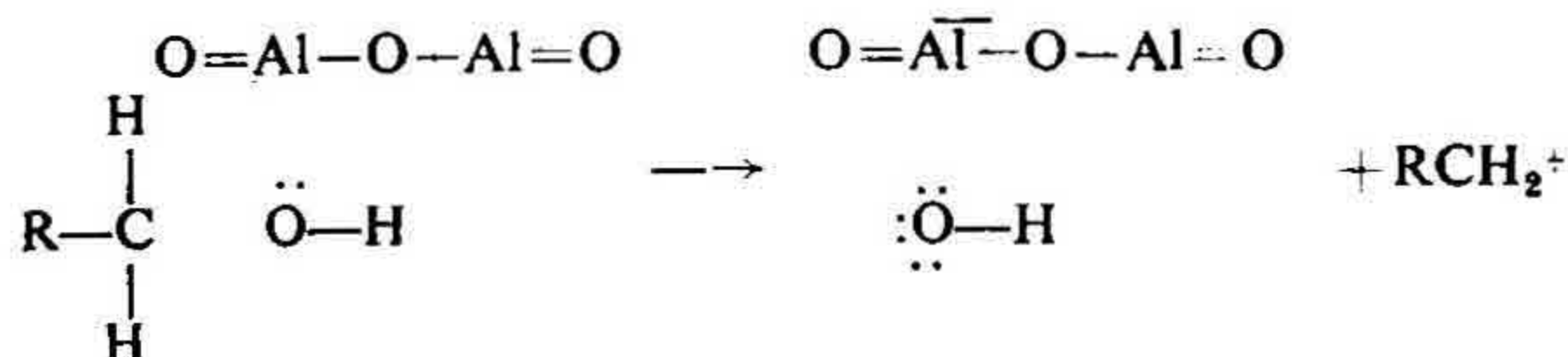
can be expected unless in the presence of an activating agent which will enhance the net positive charge on the α -carbon atom. This can be expected to be brought about by the catalyst employed.

The alumina catalyst has the following electronic configuration for the aluminum and the oxygen atoms:

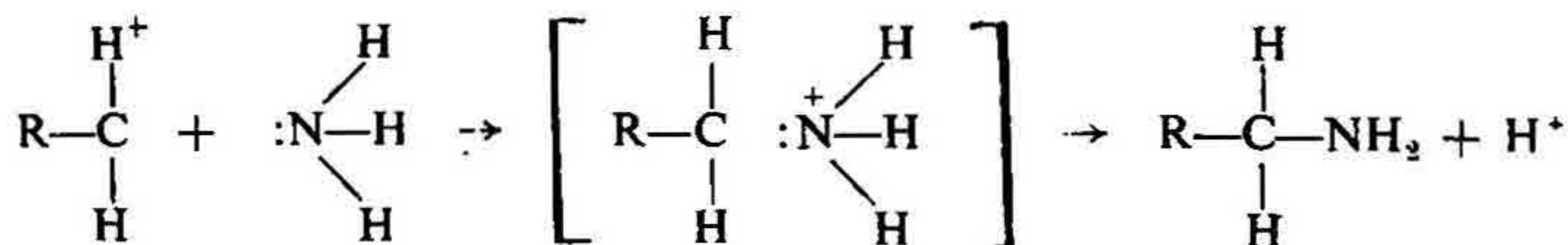


From this structure it is clear that the aluminum atom is in a position to accept two more electrons according to the theory of "Lewis acid", *i.e.*, aluminum will be highly electrophilic and can co-ordinate with alcohol or ammonia.

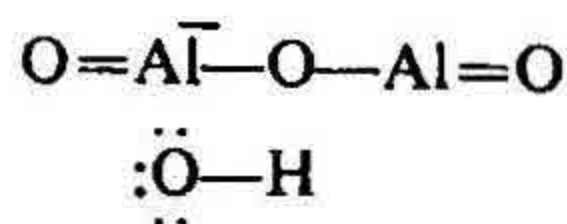
In the case of alcohol the formation of a co-ordinated complex with aluminum can be represented as follows:



The RCH_2^+ that is so obtained can immediately react with the ammonia present to form the amine and liberating the proton



The proton thus liberated will combine with



to produce the original alumina and water.

Although the adsorption of alcohol at the surface of the catalyst is found to be comparatively less than the adsorption of ammonia (Table IX) yet the carbonium ion formed seems to be sufficiently large to bring about the reaction. It can therefore be concluded that the excess ammonia adsorbed at the surface of the catalyst would only facilitate the formation of amine by supplying a large surface concentration of the ammonia gas. In the case of silica gel also it can readily be shown that the silicon atom is electrophilic and is therefore analogous in character to the alumina.

Effect of alkyl group.—The electron releasing power of various normal alkyl groups for the homologous series does not vary appreciably with the chain-length. It can therefore be expected that the amine formation is practically independent of the chain-length. Results of Table V indicate that the per cent. amines is more or less the same for the various normal alcohols in accordance with expectation.

That carbonium ion is mainly responsible for the reaction between ammonia and alcohol is further confirmed by the fact that olefinic compounds do not yield the amines when they come into contact with ammonia under pressure. In fact according to LeChatelier's principle an olefin can be expected to react with ammonia under pressure since there is volume reduction. But this reaction does not proceed in practice as shown in Table VII where it is noticed that ethylene and ammonia do not give any detectable yield of ethyl amine, while ethyl alcohol and ammonia give nearly 23 per cent. (Table V) amines. This reaction can also be explained by the electronic theory. Ethylene is a symmetrical molecule and the carbon atom in ethylene has no tendency to get polarised since both the carbon atoms are equal in their electrophilic nature. This is further confirmed by a value of zero for the dipole moment of ethylene gas. Hence ethylene cannot form $C_2H_4^+$ although it may come in contact with a catalyst which is capable of accepting electrons.

Reaction rates with alumina and silica catalysts at atmospheric pressures.—When silica is employed as catalyst at atmospheric pressures, the per cent. amines formed is only 1.6 (Table VI), while the corresponding yield with alumina is 13–16 per cent. At 300 psig., however, the per cent. amines formed is about 25 in both cases. The surprisingly low efficiency of silica gel at atmospheric pressure may be due to its low dehydrating capacity at atmospheric pressure. This is further supported by the fact that the amount of olefins obtained with alumina (10 per cent.) is higher than the amount (0.4 per cent.) obtained with silica gel (Table VI). One other factor may also contribute towards the low efficiency of silica gel as a catalyst. The values for adsorption given in Table IX indicate that the total adsorption of both alcohol and ammonia falls rapidly with the lowering of pressure and temperature especially in the case of silica gel. The diminution in adsorption of reactants can also diminish the velocity of the formation of the amine. It can therefore be concluded that at comparatively low pressures alumina works as a better catalyst than silica gel.

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