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THE CATALYTIC PREPARATION OF METHYLAMINE FROM METHYL ALCOHOL AND AMMONIA[1]

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Except for the methods which use prussic acid and acetamide as raw materials, the most useful processes for the preparation of methylamine are those which start with some derivative of methyl alcohol or with formaldehyde which is itself prepared by the oxidation of methyl alcohol. We have therefore sought for a method by which methylamine, preferably free from secondary and tertiary amine, may be procured directly from methyl alcohol without intermediate steps.

Sabatier and Mailhe[2] have found that various alcohols react with ammonia when the vapors are passed over thorium oxide at 350–370°; water is eliminated and the primary amine is formed. They have found also that primary amines react with alcohols in the same way to yield secondary amines and have reported the preparation of a number of primary and secondary amines and of some secondary amines containing dissimilar groups. They did not work with methyl alcohol; their materials in every case were such that the products could be separated by ordinary distillation and they did not report the yields.

We find that the reaction between methyl alcohol and ammonia in presence of hot thorium oxide results in the conversion of a portion of the materials into methylamine and have studied the reaction under various conditions by collecting the products in hydrochloric acid and analyzing the mixed chlorides. The best results are secured at 325–330° and the yield drops off very sharply both above and below this temperature. At higher temperatures, especially above 380°, the catalyst becomes coated with carbonaceous material and the methyl alcohol is decomposed with the formation of carbon monoxide and hydrogen along with methane and some formaldehyde. Since the use of this reaction for the preparation of methylamine involves the separation of that substance from unchanged ammonia,[3] we have made no effort to increase the

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[1] The present work was undertaken on behalf of the Ordnance Department, and this report if it is published with the permission of the Chief of Ordnance.

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

[3] The method described by Valton, *J. Chem. Soc.*, **127**, 40 (1925), has special advantages for the explosives maker. The mixture of methylamine and ammonia is absorbed in an alcohol solution of 2,4-dinitrochlorobenzene. On standing overnight at ordinary temperature the methylamine reacts and the next morning 2,4-dinitromethylaniline is crystallized out practically pure and in practically quantitative amount. The ammonia reacts only on longer standing. Tetryl or 2,4,6-trinitrophenylmethylnitramine may be obtained from 2,4-dinitromethylaniline by simple nitration.

yield by the use of an excess of ammonia. The separation of methyl alcohol from methylamine, on the other hand, is easy and we have made experiments to determine what excess of methyl alcohol must be used to secure the largest conversion of methyl alcohol into methylamine. The results indicate that 80–83% of a mole of ammonia per mole of methyl alcohol will bring about the maximum conversion, namely, that of about 32.5% of the methyl alcohol into methylamine. The product, although formed in the presence of methyl alcohol, contains no secondary or tertiary amine.

Discussion of Experiments

The methyl alcohol which was used was the ordinary commercial material and the ammonia was obtained from a cylinder of the liquefied gas.

The catalyst was prepared according to the method of Kramer and Reid,[4] and consisted of fragments of pumice, between 6 and 12 mesh, impregnated with 3 times its own weight of thorium oxide (from the nitrate). It had been heated in a current of air at 270° for the decomposition of the nitrate and finally at 400° until the issuing gases no longer reddened litmus paper. After the catalyst had become coated with carbonaceous material by use at 380° and above, it was conveniently regenerated by heating at 380°, first with steam, then with nitrogen peroxide, and finally with steam again.

The reaction chamber consisted of an electrically heated quartz tube of 27 mm. internal diameter and about 125 cm. long. The catalyst occupied a length of about 1 meter. The temperature was determined by means of a thermocouple inside the tube. The ammonia was admitted from a cylinder of the liquefied gas and its amount was determined by a calibrated flowmeter of the standard orifice type to which was connected an inclined U-tube to permit of more accurate control. The alcohol was admitted from a vaporizer which consisted of a distilling flask heated in an oil-bath and equipped with a dropping funnel from which the alcohol dropped into the flask, where it was immediately vaporized. The pressure in the distilling flask and in the upper part of the dropping funnel was equalized by a connecting glass tube. The escaping gases from the reaction were absorbed by 25% hydrochloric acid which trickled down an absorption tower consisting of a glass condenser jacket filled with short pieces of glass tubing. At the end of each run a considerable amount of condensed water and methyl alcohol was found entrapped in the cold exit end of the quartz tube. This was added to the acid liquor from the absorption tower, the whole was evaporated to dryness and the residue, after baking at 105°, was analyzed for chlorine by titration with silver nitrate. Since tests showed that the product contained no secondary or tertiary amine, it was possible to calculate the amount of methylamine hydrochloride which was mixed with the ammonium chloride.

A series of runs was carried out for the purpose of determining the best temperature for the reaction and the most favorable relative concentration of the reacting gases. Each run required two hours for the passage of the materials through the catalyst chamber. The yields, in the table below, are the percentages of ammonia which was converted into methylamine.

If these data are plotted, the three curves have a maximum at about the

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[4] Kramer and Reid, This Journal, **43,** 883 (1921).

TABLE I

YIELDS OF METHYLAMINE

Gram molecules of NH_3	0.5	0.75	1.0
Gram molecules of CH_3OH	1.0	1.0	1.0
Temp., °C.	Yield, %	Yield, %	Yield, %
275	31.5	26.1	14.7
280	...	28.4	...
285	...	...	23.1
290	33.8	29.5	16.7
300	...	24.5	22.0
305	38.4	...	...
310	...	29.6	...
315	39.9	...	...
325	41.6; 41.7	37.5	...
330	41.5	42.4	25.5; 24.1
335	33.8	...	25.9
350	29.0; 30.6	35.5	23.0
360	33.8; 34.6	28.4	21.8
370	28.0	...	...
375	...	19.6	...
385	...	...	16.1
400	21.2	9.1; 8.0	...
500	19.5	4.5	10.5

same point, namely, at 325–330°, and all three drop away rapidly on both sides of the maximum. We infer that 325–330° is the best temperature for the reaction. When the results at 330° are recalculated in terms of the percentage of methyl alcohol converted to methylamine, and are compared with the percentage of the theoretically required ammonia which was used, we have the following.

Theoretical ammonia, %	50.0	75.0	100.0
Methyl alcohol converted, %	20.75	31.8	25.5; 24.1

The curve representing these data has a maximum at a point which corresponds to about 80–83% of the theoretical ammonia and to about 32.5% of the methyl alcohol converted into methylamine.

In the experiments at higher temperatures it was noticed that an offensive odor, resembling that of decayed cabbage, came from the apparatus—the higher the temperature the stronger the odor. An examination of the chlorides for the amines, putrescine and cadaverine, was without result. An analysis of the gaseous products gave no clue to the nature of the odor but showed that the methyl alcohol had been broken down to form the primary and secondary products which would be expected in accordance with the earlier findings of other investigators. In the run at 475° in which 0.75 mole of ammonia was used, the gases were scrubbed thoroughly with hydrochloric acid, collected and analyzed. The results are shown in Column I.

	I—%	II—%
Carbon dioxide	4.40	6.40
Unsaturated hydrocarbons	1.14	1.30
Oxygen	1.83	1.41
Hydrogen	55.75	53.91
Carbon monoxide	21.20	20.60
Methane	6.80	9.33
Nitrogen (by difference)	8.88	7.05
Nitrogen with oxygen from air leakage	7.32	5.64
Net nitrogen	1.56	1.41

In another experiment methyl alcohol vapor without ammonia was passed through the catalyst chamber at 475°, the gases were bubbled through water and the water was found to give a strong test with the fuchsine aldehyde reagent—indicating formaldehyde. The composition of the gases is shown in Col. II above. Since ammonia is appreciably decomposed into its elements at 475°, the nitrogen of the first experiment may be accounted for, and that of the second is probably to be explained by supposing that some ammonia was left in the catalyst chamber from the earlier runs. The presence of carbon monoxide and hydrogen is in agreement with the observation of Ghosh and Baksi,[5] who passed methyl alcohol vapor over a mixture of copper oxide with thorium oxide at 215° and obtained a gas which consisted of carbon dioxide 2.6%, carbon monoxide 13.2%, methane 5.2% and hydrogen 78.5%. Sabatier and Senderens[6] had previously produced methane, and Orlow[7] had produced ethylene, from the hydrogenation of carbon monoxide.

The reaction between methyl alcohol and ammonia which produces water and methylamine takes place, theoretically, without change of volume, and we have not studied the effect of pressure upon it. Since the most favorable temperature, 325–330°, is below the critical temperature of water, 365°, it is possible that an increase of pressure by causing a condensation of part of the water would result in an increased yield.

Summary

Methylamine is formed when methyl alcohol and ammonia are passed over a hot thorium oxide catalyst. The best temperature appears to be 325–330° and the best relative concentration about 0.80–0.83 mole of ammonia per mole of methyl alcohol. Under the best conditions nearly one-third of the methyl alcohol is converted into methylamine.

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[5] Ghosh and Baksi, *Quart. J. Ind. Chem. Soc.*, [III] **4,** 415 (1926).

[6] Sabatier and Senderens, *Ann. chim. phys.*, [8] **4,** 418 (1905).

[7] Orlow, *Chem. Zent.*, **80,** I, 735 (1909).