XXIX.—*The Preparation of Methylamine from Ammonium Methyl Sulphate.*

By William Smith Denham and Lionel Frederick Knapp.

Werner (T., 1914, **105**, 2762), who observed that methylamine is produced when ammonium methyl sulphate is heated, followed acidimetrically the progress of the change to temperatures up to 275°, and regards it as being represented essentially by the equation $NH_4 \cdot SO_4Me = NH_3Me \cdot SO_4H$, although at temperatures above 240° a small quantity of ethylene is formed owing to a subsidiary reaction. He records the separation under favourable conditions of an 85·6 per cent. yield of methylamine. The methyl sulphates of the substituted ammonium bases behave similarly when heated, and the discoverer suggests that those reactions may be found of practical value for the preparation of the substituted methylammonium bases.

The results now communicated, obtained in an investigation of Werner's reaction undertaken with the object of utilising it for the preparation of methylamine, indicate that, under the conditions observed, the reaction is less simple than represented above, and that, at any temperature at which a noticeable transformation of ammonium methyl sulphate occurs, a mixture is produced containing ammonium, methylammonium, dimethylammonium, trimethylammonium, and (probably) tetramethylammonium salts, as, indeed, is implied in Werner's statement that "the further progress and limit of the isomeric transformation may be expressed by the general equations:

$$NH_2RR' \cdot SO_4Me = NHRR'Me \cdot SO_4H$$
$$NHRR'R'' \cdot SO_4Me = NRR'R''Me \cdot SO_4H,"$$

for, once some methylamine is produced, the melted mass may be considered, as pointed out by Werner, to contain methylamine methyl sulphate among other salts.

It is evident that the formation of secondary and tertiary amines need not become apparent in the acidimetric values, since, as indicated by equations given below, an interconversion of the amines may cause no alteration in the amount of free acid present. The products of the transformation were therefore separated approximately, and from these analyses it is concluded that, by heating ammonium methyl sulphate alone, about 25 to 30 per cent. of the ammonia can be converted into methylamine. When the period of heating is prolonged, the proportion of dimethylamine and trimethylamine (taken together) in the product increases, but the absolute amount of methylamine does not alter very much.

Methylamine is produced when a mixture of the sulphate of ammonium, dimethylamine, and trimethylamine is heated, and this supports the view that in the melted mass obtained by heating ammonium methyl sulphate, a state of equilibrium is attained or approximated to in which, as expressed by the equations

$$2NH_3Me{\cdot}SO_4H \rightleftharpoons NH_4{\cdot}SO_4H + NH_2Me_2{\cdot}SO_4H,$$
$$2NH_2Me_2{\cdot}SO_4H \rightleftharpoons NH_3Me{\cdot}SO_4H + NHMe_3{\cdot}SO_4H,$$

salts of methylamine and ammonium are opposed. The addition of ammonium salts to the ammonium methyl sulphate may therefore be expected to increase the yield of methylamine, an expectation which is in accordance with the fact. When one equivalent of ammonium sulphate was mixed with ammonium methyl sulphate, a distinct improvement was observed in the yield of methylamine, but the mixture does not melt very readily, and, possibly on account of the imperfect fusion, the yield was not further increased when two equivalents of ammonium sulphate were added. Of the few other ammonium salts which it appeared to be practicable to use, ammonium benzenesulphonate was chosen. With ammonium methyl sulphate, this salt forms an easily fusible mixture, from which a greatly increased yield of methylamine is obtained, whilst the proportion of dimethylamine and trimethylamine produced (taken together) is greatly diminished.

The possibility that the beneficial effect of the presence of ammonium benzenesulphonate may be related to the known methylating action of methyl benzenesulphonate was not investigated; although this possibility might account for an increased yield of methylamine, it does not explain the alteration in the relative proportions of methylamine on the one hand and dimethylamine and trimethylamine on the other if we suppose the subsequent transformations to be reversible. No further sulphonation of the benzene residue was observed, and the improved yield cannot therefore be ascribed to a partial removal in this way of free sulphuric acid, the presence of which, indeed, does not appear to be harmful and is probably necessary.

The employment of gaseous ammonia suggests itself as a means of neutralising the free acid (supposing that desirable) and of supplying at the same time an increased concentration of ammonium salts, and an improved yield of methylamine was indeed obtained when ammonia in regulated amounts was admitted to the reaction vessel, but the method is inconvenient. At the ordinary temperature, ammonia reacts with ammonium methyl sulphate with the evolution of heat, probably owing to the occurrence of the following or some similar reaction,

$$NH_4 \cdot SO_4Me + NH_3 = NH_4 \cdot SO_3 \cdot NH_2 + MeOH,$$

and no methylamine is produced.

It is concluded that, to obtain the best yield of methylamine by means of Werner's reaction, the ammonium methyl sulphate should be heated for one hour and a-half at 260° or at a slightly higher temperature, when the yield of methylamine is about 27 per cent. of the theoretical yield; when a mixture of ammonium methyl sulphate with two equivalents of ammonium benzenesulphonate is heated under conditions otherwise the same, the yield of methylamine is nearly 50 per cent. of the theoretical.

EXPERIMENTAL.

In most of the experiments summarised in the following tables, 1/10th gram-molecule (12·9 grams) of ammonium methyl sulphate contained in a test-tube was heated in an oil-bath. Excess of sodium hydroxide was added to the aqueous solution of the product, and the liberated bases were distilled, usually under diminished pressure, into aqueous hydrochloric acid. The hydrochloric acid solution of the amines was then evaporated, at first on the water-bath under atmospheric pressure, and finally in a vacuum until the weight was constant. The dried mass was extracted twice by boiling with absolute alcohol, using 50 c.c. of alcohol for the first extraction and 25 c.c. for the second, and the residue of ammonium chloride was washed with 25 c.c. of cold alcohol. (When very large quantities of ammonium salts were present, a preliminary extraction was made with much alcohol, and the residue from the evaporation of the solution thus obtained was then extracted as above.) After removing the alcohol by distillation from the united alcoholic extracts and washings, the residual mixture of ammonium chloride and amine hydrochlorides was dried until constant in weight, and in some experiments this residue was extracted twice by boiling it with chloroform, using 50 c.c. of the solvent each time. According to Bresler (*Ann. Chim. anal.*, 1901, **6**, 28; compare Behrend, *Annalen*, 1884, **222**, 119), methylamine hydrochloride is insoluble in hot chloroform, whilst the hydrochlorides of dimethylamine and trimethylamine dissolve quite readily. When ammonium chloride alone was boiled with 50 c.c. and 25 c.c. of alcohol successively, the united extracts gave on evaporation 0·55 gram of ammonium chloride, and in the calculation of the "yield of methylamine" from the weight of the alcoholic extract, 0·55 gram has been deducted as an approximate correction for the ammonium chloride present. The "yield" thus found is employed merely as a conventional method of comparing the results of experiments when more accurate methods of comparison are not available, for the alcoholic extract contained the hydrochlorides of dimethylamine and trimethylamine, and probably more ammonium chloride than was allowed for. The residue from the extraction with chloroform contained, besides methylamine hydrochloride, the ammonium chloride present in the alcoholic extract, and in calculating the "yield of methylamine" from the quantity of product dissolved by alcohol, but undissolved by chloroform, the same weight (0·55 gram) was first deducted. In several experiments, the proportion of methylamine in the residue from the extraction with chloroform was determined by Francois' method (*Compt. rend.*, 1907, **144**, 857), that is, by fixing the ammonia with yellow mercuric oxide and titrating the methylamine in the filtrate.

In each of the experiments of which the results are summarised in this table, a tube containing 20 grams of ammonium methyl sulphate was placed in an oil-bath already heated to the desired temperature and removed after thirty minutes, the contents of the tube being at the maximum temperature for periods varying between fifteen and twenty minutes. Two-fifths of the product (derived from 8 grams of ammonium methyl sulphate) were used for titration, and from the remainder the amine hydrochlorides were prepared and extracted with alcohol, as described above. Although the part of the product treated in this way was derived from only 12 grams of ammonium methyl sulphate, the same approximate correction was made for the ammonium chloride present as in the experiments in which 12·9 grams were used, since the same quantities of alcohol were employed in the extractions. Werner's results by titration after fifteen minutes' heating at nearly equal temperatures are given for comparison. The "yields of methylamine" are expressed as percentages of the theoretical yield if complete transformation occurred. The weight of methylamine hydrochloride from 12 grams of ammonium methyl sulphate would then be 6·27 grams.

Effervescence occurred in all cases, especially in 3 and 4, where the temperatures in the tubes rose above that of the bath, but both the effervescence and the evolution of heat slackened after a few minutes. The fused products from experiments 1 and 2 were slightly yellow; those from 3 and 4 were dark reddish-brown.

TABLE I.

No. of experiment.	I. Total duration of heating Minutes.	I. Period at maximum temperature.	II. Amine hydrochlorides dissolved by alcohol (grams).	III. Yield of methylamine calculated from III after correction for NH_4Cl.	IV. Yield of methylamine from titration.	V. "Isomeric change" at nearly equal temperatures (Werner).
				Per cent. of theoretical yield.		
1	30	16 min. at 160—165°	0·61	1·0	2·2	11·5 (160°)
2	30	18 ,, 200—205°	1·17	10·0	23·8	25·8 (200—205°)
3	30	22 ,, 255—260°	3·94	54·1	89·6	85·9 (250—260°)
4	30	22 ,, 274—275°	4·19	58·1	95·6	97·2 (275°)

Table II.

In the experiments summarised here, the period of heating was longer. 12·9 Grams of ammonium methyl sulphate were used for each experiment, the theoretical yield of methylamine hydrochloride being 6·75 grams.

The temperatures are those of the bath, initially at the ordinary temperature.

I.			II.	III.
No. of experiment.	Duration of heating. Hours.	Temperature, etc.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	Yield of methylamine calculated from II after correction for ammonium chloride. Percentage of the theoretical yield.
5	100	100°	0·69	2·1
6	7	5 hours up to 168°. 2 hours at 160—168°.	0·70	2·2
7	6½	2 hours up to 206°. 4½ hours at 196—206°.	3·24	39·9
8	6	3 hours up to 255°. 3 hours at 230—255°.	3·89	49·5
9	1⅔	1 hour up to 272°. ⅔ hour at 240—272°.	4·52	58·8

Partial Solubility of the Amine Hydrochlorides in Chloroform.—Table III shows the proportion of the alcohol-soluble product.

Table III.

12·9 Grams of ammonium methyl sulphate were heated in each experiment, the theoretical yield of methylammonium chloride being 6·75 grams.

I.			II.	III.	IV.	V.
					Percentage of the theoretical yield.	
No. of experiment.	Duration of heating. Mins.	Temperature.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	Yield of methylamine calculated from II after correction for ammonium chloride.	Yield of methylamine calculated from III after correction for ammonium chloride.
10	18	230—234°	3·0	2·1	36·3	23·0
11	17	254—258°	3·74	2·44	47·3	28·0
12	16	From room temperature to 260°	3·47	2·62	43·3	30·1

found to be insoluble in chloroform. The results are confirmed by those displayed in later tables. In experiments 10 and 11, the vessels containing the ammonium methyl sulphate were placed in an oil-bath already heated to the required temperature. In experiment 12, the ammonium methyl sulphate was heated in sixteen minutes from the ordinary temperature to 260°, and then removed from the bath, when the temperature of the melted salt remained at about 260° for a minute or two, and then fell slowly.

Nitrogen in the Still Residue.—In experiment (10), after the volatile bases had been removed by prolonged distillation of the alkaline solution of the product obtained on heating the ammonium methyl sulphate, the residue in the distillation flask was neutralised with sulphuric acid and evaporated to dryness. The dried residue was found to contain nitrogen.

Effect of Ammonia on the Transformation.—In experiment (13) (table IV), a very slow current of ammonia was passed into the salt after it had been melted and heated to 170°; in experiment (14), the flask containing the salt was heated rapidly to 220°, and then attached to a reservoir of ammonia gas under a pressure of 100 mm., in addition to the atmospheric pressure; and in experiments (15), (16), and (17), ammonia, similarly under a slightly increased pressure, was present from the beginning. If the yield of methylamine were theoretical, and if all the acid formed were neutralised by ammonia, the total weights of hydrochlorides in column III would be 12·1 grams (5·35 grams of ammonium chloride and 6·75 grams of methylamine hydrochloride).

Table IV.

12·9 Grams of ammonium methyl sulphate were heated in each experiment. The oil-bath and contents were heated from the ordinary temperature. The temperatures are those of the bath.

	I.		II.	III.	IV.
No. of experiment.	Duration of heating. Hours.	Temperature.	Weight of amine hydrochlorides. Grams.	Weight of amine hydrochlorides dissolved by alcohol. Grams.	Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of the theoretical yield.
13	3¼	1¼ hours at 234°	8·89	4·32	55·9
14	3¼	2 ,, 260°	7·13	4·93	64·9
15	3⅓	2 ,, 260°	7·48	5·14	68·0
16	2¾	2 ,, 240°	11·27	4·59	59·9
17	2⅔	2 ,, 260° (reached 270°)	12·15	4·52	58·8

Effect of Ammonium Sulphate on the Transformation.—Table V summarises the results of a study of the effect on the yield of methylamine of the duration of heating and of the presence during the reaction of different proportions of ammonium sulphate. In this series, the percentage of methylamine was determined by François' method, already referred to, in that portion of the amine hydrochlorides which was dissolved by alcohol, but undissolved by chloroform.

Estimation of the Dimethylamine and Trimethylamine in the Chloroform-soluble Part.—The following percentages of dimethylamine and trimethylamine hydrochlorides were found in the chloroform-soluble portions obtained in experiments 19 and 24, using Bertheaume's method (*Compt. rend.*, 1910, **150**, 1251), that is, by precipitating the trimethylamine as periodide and estimating volumetrically the trimethylamine in the precipitate and the dimethylamine in the solution:

	Dimethylamine hydrochloride. Per cent.	Trimethylamine hydrochloride. Per cent.
Chloroform-soluble portion from experiment 19	67·4	64·8
Chloroform-soluble portion from experiment 24	27·0	31·6

Although the comparison is not complete, since in experiment 28 the percentage of methylamine in the chloroform-insoluble portion was not estimated, the results tabulated above indicate that two equivalents of ammonium benzenesulphonate are as effective as four. With the larger proportion of ammonium benzenesulphonate, the mixture did not fuse so readily.

Examination of the Residual Benzenesulphonate.—In experiment 25, the amines were liberated by the addition of baryta, the excess of which was removed from the residue in the distilling flask after the distillation by means of carbon dioxide. The solution was then evaporated to dryness, and the barium estimated in the dried product.

Found: Ba=30·7.

$(C_6H_5\cdot SO_3)_2Ba$ requires Ba=30·4, and $C_6H_4(SO_3)_2Ba$ requires Ba=36·7 per cent.

General Comparison of Experiments made at about 260°.—In table VII are assembled those experiments in which ammonium methyl sulphate was heated for different periods at about 260°, with and without the addition of ammonia or of an ammonium salt. Two experiments made in closed vessels (29 and 30) are included.

TABLE V.

12·9 Grams of ammonium methyl sulphate were heated in each experiment. One equivalent of ammonium sulphate = 1/20 mol. = 6·6 grams. Experiments 18—23 were made simultaneously, using the same oil-bath, which was heated from the ordinary temperature. The temperatures are those of the bath.

No. of experiment.	I. Weight of ammonium sulphate added. Grams.	II. Duration of heating. Hours.	II. Temperature.	III. Weight of amine hydrochlorides dissolved by alcohol. Grams.	IV. Weight of amine hydrochlorides dissolved by alcohol but undissolved by chloroform. Grams.	V. Percentage of methylamine hydrochloride by analytical estimation in substance (col. IV) undissolved by chloroform.	VI. Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of theoretical yield.	VII. Yield of methylamine calculated from IV after correction for ammonium chloride. Percentage of theoretical yield.	VIII. Yield of methylamine by analytical estimation of methylamine (IV and V). Percentage of theoretical yield.
18	None	1½	¾ hour at 260°	4·57	2·74	66·1	59·6	32·4	26·8
19	6·6	1½	,,	4·99	3·14	70·5	65·8	38·4	32·8
20	13·2	1½	,,	4·81	3·01	61·7	63·1	36·4	27·5
21	None	3	2¼ hour at 260°	4·54	2·63	68·2	59·1	30·8	24·6
22	6·6	3	,,	4·49	3·02	70·5	58·3	36·3	31·5
23	13·2	3	,,	4·74	2·95	68·6	62·1	35·6	30·0
24	66·0 (10 equivalents)	2	1 hour at 260°	4·39	2·89	69·2	56·9	34·7	29·6

Effect of Ammonium Benzenesulphonate on the Transformation.

TABLE VI.

12·9 Grams of ammonium methyl sulphate were heated in each experiment, except in experiment 25, where 6·45 grams were used and other substances in proportion. The figures shown in the table for experiment 25 are the actual figures multiplied by two to facilitate comparison. One equivalent of ammonium benzenesulphonate = 17·5 grams.

	I.	II.		III.	IV.	V.	VI.	VII.	VIII.
No. of experiment.	Weight of ammonium benzene-sulphonate added. Grams.	Duration of heating.	Temperature.	Weight of amine hydro-chlorides dissolved by alcohol. Grams.	Weight of amine hydro-chlorides dissolved by alcohol but undissolved by chloroform. Grams.	Percentage of methylamine by analytical estimation in substance (col. IV) undissolved by chloroform.	Yield of methylamine calculated from III after correction for ammonium chloride. Percentage of theoretical yield.	Yield of methylamine calculated from IV after correction for ammonium chloride. Percentage of theoretical yield.	Yield of methylamine by analytical estimation of methylamine (IV and V). Percentage of theoretical yield.
25	17·5	1½ hours	Heated from ord. temp. 20 min. at 250—260°.	4·82	3·68	—	63·3	46·4	—
26	35·0	1½ ,,	Heated from ord. temp. 55 min. at 250—260°.	5·02	4·35	75·5	66·2	56·3	48·7
27	35·0	18 min.	Ammonium methyl sulphate added to ammonium benzenesulphonate already heated to 250—260°.	4·52	3·89	—	58·8	49·5	—
28	70·0	1½ hours	Heated from ord. temp. 1 hour at 250—260°.	5·24	4·29	—	71·0	55·4	—

TABLE VII.

I.		II.		III.	IV.	V.	VI.
No. of experiment.	Addition	Duration of heating.	Temperature.	From titration.	From amine hydrochloride soluble in alcohol after correction for ammonium chloride.	From amine hydrochloride soluble in alcohol but insoluble in chloroform after correction for ammonium chloride.	By analytical estimation of the methylamine.
				Yield of methylamine as percentage the theoretical yield.			
12	None.	16 min.	ord. temp. to 260°.	—	43·3	30·1	—
11	,,	17 ,,	254—258°.	—	47·3	28·0	—
3	,,	30 ,,	22 min. at 255—260°.	89·6	54·1	—	—
18	,,	$1\frac{1}{2}$ hours.	45 min. at 260°.	—	59·6	32·4	26·8
29	None (closed vessel).	$1\frac{1}{2}$,,	1 hour at 250—260°.	—	58·5	33·3	—
21	None.	3 ,,	$2\frac{1}{4}$ hours at 260°.	—	59·1	30·8	24·6
14	Ammonia.	$3\frac{1}{4}$,,	2 hours at 260°.	—	64·9	—	—
15	,,	3 ,,	2 hours at 260°.	—	68·0	—	—
19	1 equivalent $(NH_4)_2SO_4$.	$1\frac{1}{2}$,,	45 min. at 260°.	—	65·8	38·4	32·8
30	1 equivalent $(NH_4)_2SO_4$ (closed vessel).	$1\frac{1}{2}$,,	45 min. at 260°.	—	56·0	34·8	—
22	1 equivalent $(NH_4)_2SO_4$.	3 ,,	$2\frac{1}{4}$ hours at 260°.	—	58·3	36·3	31·5
20	2 equivalents $(NH_4)_2SO_4$.	$1\frac{1}{2}$,,	45 min. at 260°.	—	63·1	36·4	27·5
23	,, ,,	3 ,,	$2\frac{1}{4}$ hours at 260°.	—	62·1	35·6	30·0
24	10 equivalents $(NH_4)_2SO_4$.	2 ,,	1 hour at 260°.	—	56·9	34·7	29·6
25	1 equivalent $C_6H_5{\cdot}SO_3NH_4$.	$1\frac{1}{2}$,,	20 min. at 250—260°.	—	63·3	46·4	—
27	2 equivalents $C_6H_5{\cdot}SO_3NH_4$.	18 min.	255—260°.	—	58·8	49·5	—
26	,, ,,	$1\frac{1}{2}$ hours.	55 min. at 250—260°.	—	66·2	56·3	48·7
28	4 equivalents $C_6H_5{\cdot}SO_3NH_4$.	$1\frac{1}{2}$,,	1 hour at 250—260°.	—	71·0	55·4	—

Methylamine from a Mixture of the Sulphates of Ammonium, Dimethylammonium, and Trimethylammonium.—Five grams of the mixed hydrochlorides of dimethylamine and trimethylamine, obtained in the extractions with chloroform, were mixed with an excess of sodium hydroxide solution, and the liberated bases were distilled into an aqueous solution of 6 grams of sulphuric acid. The solution was neutralised with ammonia (but the presence of some free acid would doubtless have been advantageous), and the residue, after evaporation to dryness, was heated at 270° for a short time. The bases were converted into the hydrochlorides and extracted with alcohol, and then with chloroform, which dissolved 1·55 grams. After purification of the portion insoluble in chloroform, 0·44 gram of methylamine hydrochloride was obtained.

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