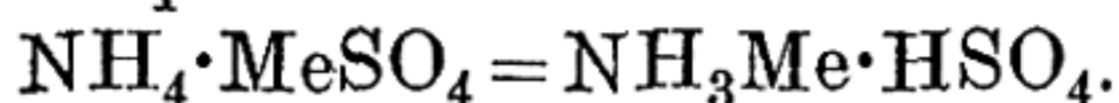


The Isomeric Transformation of Ammonium Methyl Sulphate, and of Substituted Ammonium Methyl Sulphates; the Interaction of Amines and Methyl Sulphate. By EMIL ALPHONSE WERNER.

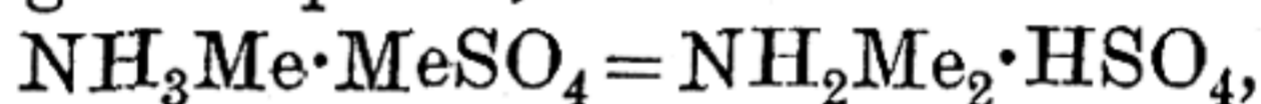
J. Chem. Soc. 105, 2762-2769 (1914)

IN a recent communication (this vol., p. 925) containing an account of the study of the decomposition by heat of the methyl sulphates of certain isocarbamides, it was pointed out that ammonium methyl sulphate can evidently undergo isomeric change when heated, in accordance with the equation:

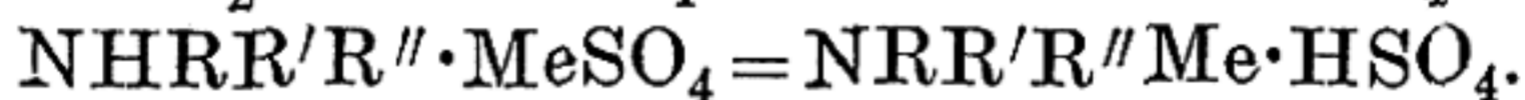
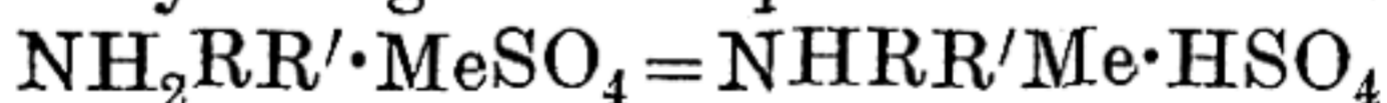


This interesting reaction, which does not appear to have been hitherto recorded, was only noticed as a qualitative change in connexion with the investigation referred to above. A more intimate study of the change has now been made, the results of which have shown that an isomeric transformation on the line indicated above is apparently a property common to all substituted ammonium methyl sulphates, where such an interchange in the position of a hydrogen atom and a methyl group is possible.

Thus when methylammonium methyl sulphate, the simple preparation of which from ammonia and methyl sulphate is described further on, is heated it gradually changes to the isomeric dimethylammonium hydrogen sulphate,



and the further progress and limit of the isomeric transformation may be expressed by the general equations:

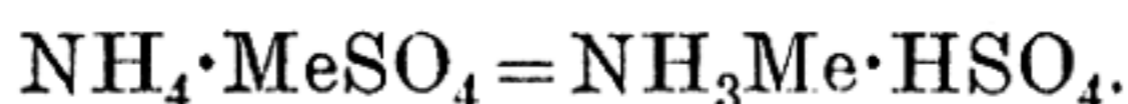


Whilst the alcohol radicles may be variants, the isomerisation appears to be restricted to the methyl sulphates, since neither ammonium ethyl sulphate nor ammonium *n*-propyl sulphate was found to undergo any isomeric change. Decomposition with the formation of ammonium hydrogen sulphate and ethylene and propylene respectively was the only result of the action of heat on these two salts.

The results of a quantitative study of the extent of isomeric change with rise of temperature in the case of ammonium and methylammonium methyl sulphates are given in the tables below; the time of heating was fifteen minutes in all the experiments; this comparatively short period was chosen, as preliminary experiments showed that the velocity of the isomeric change was chiefly a func-

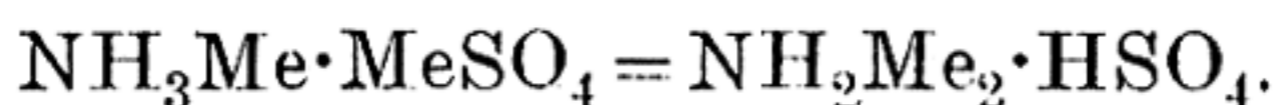
tion of the temperature. Since the methyl sulphates under investigation were found to be neutral in reaction, the progress of the change was readily measured by determining the acidity developed in the product at the end of each experiment.

TABLE I.*



Temperature.	Per cent. of isomeric change.	Temperature.	Per cent. of isomeric change.
110—120°	7.0	220—230°	46.3
135—145	9.4	240—250	73.4
160	11.3	250—260	85.9
180—185	14.3	275	97.2
200—205	25.8		

TABLE II.*



Temperature.	Per cent. of isomeric change.	Temperature.	Per cent. of isomeric change.
100—105°	2.6	210—220°	34.1
135—140	6.4	230—240	50.4
150—155	7.2	250—260	81.3
170—175	8.3	275	97.8
190—200	13.9		

* The numbers for the temperatures from 240° upwards are slightly higher than the true values, on account of the small amount of secondary change referred to in the experimental part.

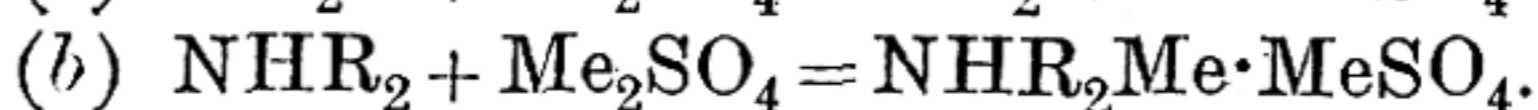
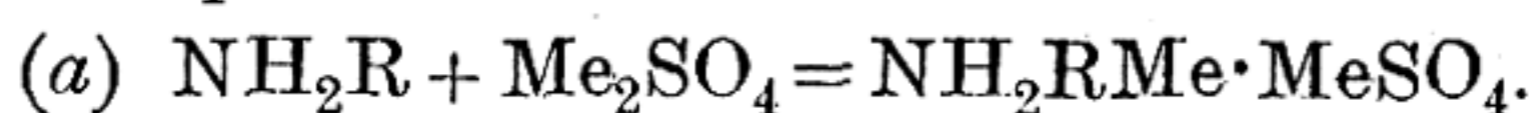
It will be seen from the above that in both cases the amount of isomeric change is small until a temperature of about 220° is reached; beyond this it proceeds rapidly, and is almost complete at 275°, and with the exception of a slightly greater amount of isomerisation for the lower temperatures in the case of ammonium methyl sulphate there is practically no difference in the general order of the change for these two salts. The influence of time on the velocity of isomeric change is small even just below 220°; thus in the case of ammonium methyl sulphate after heating for one hour at 200—205° the percentage of isomerisation was raised from 25.8 (for fifteen minutes) to 34.2, whilst with the methylammonium salt at 210—220° there was an increase from 34.1 to 46.9 per cent. for the same difference in period.

A few different types of substituted ammonium methyl sulphates have been examined, all of which apparently undergo an isomeric change, and in the case of derivatives containing more complex alkyl groups or a phenyl group this proceeds more readily than with the methyl sulphates recorded above; for example, methyl-dipropylammonium and phenyldimethylammonium methyl sul-

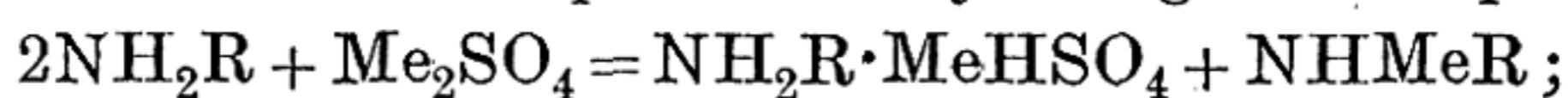
phates were found to undergo isomeric change to the extent of about 35 and 48 per cent. respectively at 140°, whilst even at 100° there was a very appreciable amount of change.

It is hoped to make a systematic quantitative study of a number of different methyl sulphates as soon as opportunity permits.

As regards the mechanism of this isomeric change it appears very probable that dissociation, as the first step towards more stable equilibrium, precedes the formation of the isomeride; thus when ammonium methyl sulphate is heated it will dissociate with the production of methylamine and sulphuric acid rather than ammonia and the very unstable methyl hydrogen sulphate, and from the union of the dissociation products the still more stable methylammonium hydrogen sulphate will be formed. This explanation is in agreement with the conditions under which the isomeric change has been shown to take place, and also with the fact that the methyl sulphates of the feeble (benzenoid) ammonium bases undergo isomerisation readily at correspondingly lower temperatures. Considered from a practical point of view, the recognition of this general isomeric change is likely to prove of some value, since it appears to place in our hands a method more simple than any of those hitherto available for the preparation of various substituted methylammonium bases, more particularly on account of the ease with which the methyl sulphates may be prepared from the interaction of the amines and methyl sulphate, in accordance with the general equations:



It also explains certain discrepancies in the results which have been published hitherto with regard to the above reactions. Thus, whilst Claesson and Lundvaal (*Ber.*, 1880, **13**, 1699) have shown that ammonia and aniline respectively react with methyl sulphate according to equation (a), they state that in the case of diethylamine and methyl sulphate the products formed are diethylammonium and dimethyldiethylammonium methyl sulphates, and more recently Ullmann (*Annalen*, 1903, **327**, 104), who has examined the behaviour of aniline and a number of its different homologues towards methyl sulphate, has arrived at the conclusion that in the case of aromatic amines the interaction does not follow the course described by Claesson and Lundvaal (*loc. cit.*), but for primary amines is to be represented by the general equation:



for example, with aniline the products formed are stated to be aniline methyl sulphate, methylaniline, and a certain amount of dimethylaniline. The experimental conditions adopted, more especi-

ally by Ullmann, were such that much heat was allowed to develop during the interactions, with the result that more or less isomeric change must have taken place, to which cause must be attributed the different conclusions arrived at regarding the general order of the interaction. The results of experiments with several different amines, aliphatic and aromatic, have shown that if care be taken to avoid anything more than a slight development of heat, the reactions with methyl sulphate proceed in a perfectly straightforward manner in accordance with equations (a) and (b); practically quantitative yields of the substituted ammonium methyl sulphates have been obtained without any trouble.

EXPERIMENTAL.

Preparation of, and Action of Heat on, Ammonium Methyl Sulphate.

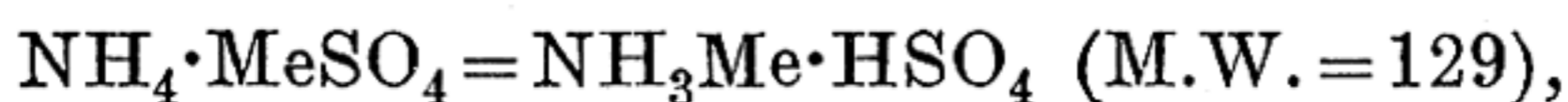
The following method of preparation was found to give a fairly good yield of the above salt in a high degree of purity. The product obtained after heating a mixture of 50 grams of pure methyl alcohol and 100 grams of pure sulphuric acid on the water-bath for half-an-hour was cooled and directly neutralised by addition of powdered commercial ammonium carbonate until, with the occasional addition of a small quantity of water, a pasty, faintly alkaline mass was obtained; this was extracted with about 150 c.c. of boiling methyl alcohol, the cold solution was poured off from any ammonium sulphate which separated, and concentrated to about half the volume by careful distillation. While hot the solution was again poured off from any substance which had separated, and on cooling it set to a mass of thin, plate-like crystals with a satiny lustre. After a further recrystallisation from absolute methyl alcohol the salt was obtained quite free from even a trace of sulphate, and was almost neutral in reaction; 32 grams of pure ammonium methyl sulphate were obtained from 50 grams of methyl alcohol.

The pure salt melts* at 137° , and is exceedingly hygroscopic; it is less soluble in ethyl alcohol than in methyl alcohol, hence the preference of the latter solvent for its purification.

In order to study the progress of the isomeric change, a series of test-tubes containing weighed quantities of the well-dried salt were heated in a bath of glycerol for fifteen minutes to the desired temperature; the bulb of a thermometer, passed through a loosely-fitting cork, was kept immersed in the fused salt during each

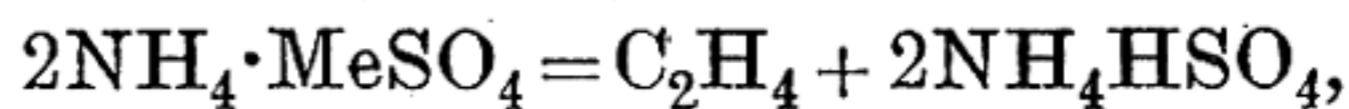
* When slowly heated the salt may be found to melt at 125° , as a result of a certain amount of isomeric change.

experiment. The product was dissolved in water and titrated directly with *N*-sodium hydroxide, methyl-orange being used as indicator. On account of the very hygroscopic nature of the salt it was not advisable to attempt to weigh out a similar quantity for each experiment; from the equation:



it will be readily seen that 1.29 grams of ammonium methyl sulphate would require, after complete isomerisation, 10 c.c. of *N*-sodium hydroxide for neutralisation, hence the values for a molecular proportion were calculated from the titration results obtained in the different experiments, and as these numbers expressed in terms of percentage of isomeric change are given under table I, the full details would be of no particular interest, and have therefore been omitted.

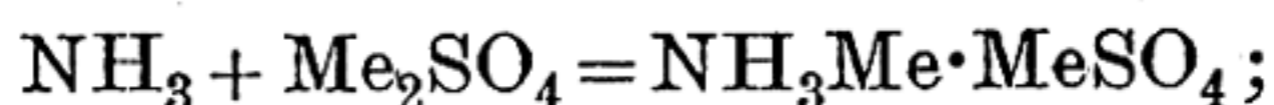
When ammonium methyl sulphate was heated to about 240° and upwards, a slight evolution of gas commenced after five minutes' heating, and continued very slowly to the end of the experiment; this was found to be ethylene, the result of a secondary decomposition, namely,



which to a very slight extent accompanies the main isomeric change. From 20 grams of ammonium methyl sulphate, after heating under the most favourable conditions, 8.9 grams of methylamine hydrochloride were ultimately obtained, corresponding with 85.6 per cent. of the theoretical yield for complete isomerisation; hence the secondary decomposition referred to above has no serious influence on the main change.

Preparation of, and Action of Heat on, Methylammonium Methyl Sulphate.

This salt was readily prepared, in quantitative yield, by passing a current of dry ammonia into a solution of pure methyl sulphate in about fifteen times its volume of benzene until the product, after keeping for one hour, had a slight odour of ammonia, the flask containing the solution being immersed in ice-cold water. The salt gradually separated in micro-crystalline form; it was quite colourless, neutral in reaction, and gave an absolutely negative result when tested with barium chloride solution. The dry salt melts at 52°, and is very hygroscopic; its purity was confirmed by analysis, and hence the reaction is correctly represented by the equation:



the formation of some ammonium methyl sulphate, recorded by

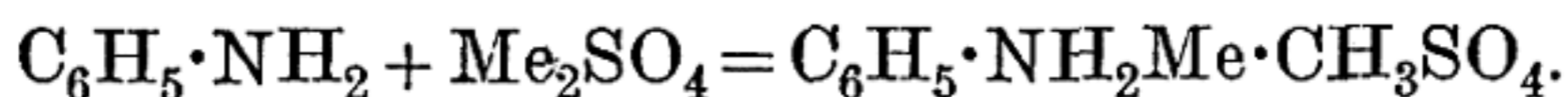
Claesson and Lundvaal (*loc. cit.*), was probably due to the presence of some methyl hydrogen sulphate in the ester used by them.

The examination of the progress of the isomeric change when methylammonium methyl sulphate is heated was carried out exactly as in the case of the ammonium salt; the results so obtained are given under table II.

Interaction of Amines and Methyl Sulphate.

The ester used in these experiments was purified from any acid impurities by shaking it with a solution of sodium hydroxide until neutral; the separated ester was then dried over anhydrous sodium sulphate, and used directly without redistillation.

Expt. I. Aniline and Methyl Sulphate (equal molecular proportions).—To a solution of 9.3 grams of freshly distilled aniline in 75 c.c. of pure benzene, 12.6 grams of methyl sulphate dissolved in 25 c.c. of benzene were added; there was very slight development of heat, and after a short time, minute, thin, glistening plates began to separate. After twenty-four hours these were collected, washed with benzene, and dried over sulphuric acid and afterwards for a short time in a vacuum. The weight obtained was 21.1 grams, whilst theory requires 21.9 grams if the reaction proceeded in accordance with the equation:



An aqueous solution of the product gave no precipitate with barium chloride solution, and on the addition of bleaching-powder solution and a few drops of dilute sulphuric acid, a deep indigo-blue colour was developed,* a reaction characteristic of methylaniline (Found, $\text{SO}_4 = 44.02$. $\text{C}_8\text{H}_{13}\text{O}_4\text{NS}$ requires $\text{SO}_4 = 43.83$ per cent.).

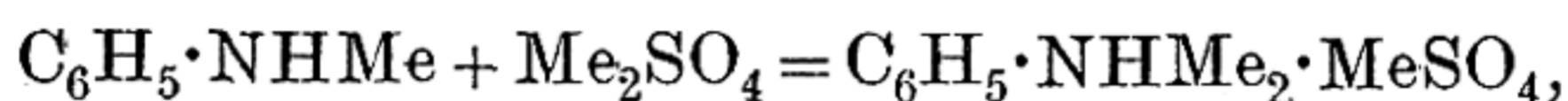
Phenylmethylammonium methyl sulphate melts at 159° , and undergoes isomeric change very readily; this was strikingly demonstrated in the benzene filtrate from the preparation, which retained a small quantity of the salt in solution, in the following manner: a portion of the benzene solution was evaporated to dryness on the water-bath, and the residue gave a copious precipitate with barium chloride solution, and, on addition of bleaching-powder solution, a deep orange-red colour was at once developed, a reaction characteristic of dimethylaniline. The original benzene solution when shaken with distilled water gave no reaction with barium chloride, but when previously heated for a few minutes on the water-bath and again shaken with water, on applying the test reagent a precipitate

* It is generally stated that methylaniline gives no colour with bleaching-powder solution, but this is only true of the free base; on acidification an intense indigo-blue colour is quickly developed.

of barium sulphate was immediately formed as a result of the isomeric change.

The experiment was repeated, using an excess of aniline, and the weight of crystalline precipitate obtained was practically the same as before, the excess of aniline being found unchanged in the benzene filtrate, thus proving that the interaction takes place strictly in accordance with the equation given above, and that the failure to recognise the isomerisation which takes place so readily was responsible for the erroneous explanation of the change given by Ullmann (*loc. cit.*).

Expt. II. Methylaniline and Methyl Sulphate (equal molecular proportions).—To 10.7 grams of pure methylaniline dissolved in 75 c.c. of benzene, 12.6 grams of methyl sulphate dissolved in twice its volume of benzene were added; a clear, pale yellow oil gradually separated, without any appreciable evolution of heat, and after twenty-four hours this was collected. The weight obtained was 32 grams; the theoretical yield of phenyldimethylammonium methyl sulphate formed in accordance with the equation:



would be 23.3 grams. The oil when added to water rapidly dissolved with the separation of some benzene, and any attempt to expel the latter from the oil by heat was accompanied by evidence of isomeric change having taken place during the process. By leaving the oil for a week in a vacuum over sulphuric acid a product quite free from benzene was finally obtained. The viscous residue, which showed no signs of crystallisation, was not analysed, but gave all the reactions of a salt of dimethylaniline, and no other product could be detected in the original benzene separated from the oil, the yield of which corresponded very closely with a compound of the salt with a molecular proportion of benzene which would require 31.1 grams. This property of forming a feeble compound with benzene has already been noticed by Claesson and Lundvaal (*loc. cit.*) in the case of ethylaniline ethyl sulphate.

Expt. III. Dipropylamine and Methyl Sulphate (equal molecular proportions).—This experiment was carried out as in the previous case, with 10.1 grams of dipropylamine and 12.6 grams of the ester, a clear, almost colourless oil quickly separating with slight evolution of heat. The yield of oil was 30.8 grams, whilst the theoretical yield of methyldipropylammonium methyl sulphate would be 22.7 grams, and for a compound with one molecular proportion of benzene 30.5 grams. In this case also an attempt to expel benzene from the oil by heat was accompanied by isomeric change. The product, freed from benzene by the means mentioned under Expt. II, was a viscous liquid, the aqueous solution of which gave

no precipitate with barium chloride solution, and on distillation with potassium hydroxide gave methyldipropylamine, which was identified by the analysis of its hydrochloride (Found, Cl=23.44. Calc., Cl=23.43 per cent.).

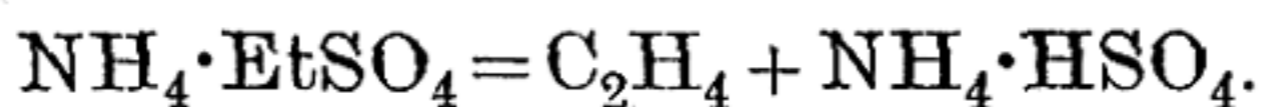
Experiments II and III were repeated, using an excess of the respective amine; in each case this excess was found unchanged in the benzene separated from the precipitated oil, proving that with secondary amines also the reaction with methyl sulphate is between equal molecular proportions and in accordance with the general equations already given.

*Note on Ammonium Ethyl Sulphate and Ammonium
n-Propyl Sulphate.*

Pure ammonium ethyl sulphate was readily prepared in very good yield by directly neutralising crude ethyl sulphuric acid (prepared in the usual manner) with commercial ammonium carbonate, absolute alcohol being used for the extraction and recrystallisation of the ammonium salt. The yield was 58 grams of the pure compound from 50 grams of ethyl alcohol, no attempt being made to recover a further quantity from the mother liquor. The pure salt crystallises from alcohol in thin, flat, rhomboidal prisms, which have been easily obtained in a length of 4—5 cm., and possessing a brilliant, satin-like lustre.

Ammonium ethyl sulphate melts at 97° (not 62°, as stated in various works of reference), and is not notably hygroscopic, which is also contrary to the published statements.

When heated the salt decomposed rapidly at about 220° with the evolution of ethylene; after fifteen minutes at this temperature the amount of decomposition was 55 per cent., in accordance with the equation:



No ethylamine could be detected in the residue, thus proving the absence of any isomeric change.

Ammonium *n*-propyl sulphate (m. p. 132°) was obtained in good yield from crude *n*-propylsulphuric acid in a manner similar to that stated above. The pure salt, which is very hygroscopic, decomposed rapidly at 150—160° with the evolution of propylene and without any evidence of isomeric change.