

XLVII.—*The Action of Heat on the Salts of Tetramethylammonium.*

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THE following experiments on the action of heat on the tetramethylammonium salts were undertaken in order to ascertain in what respects the compound ammonium salts when subjected to the action of heat resembled, and also in what points they differed from, the corresponding phosphorus and sulphur salts.

The action of heat on a considerable number of the trimethylsulphine salts (chiefly the salts of sulphur acids) has been investigated by Crum-Brown and Blaikie (*J. pr. Chem.* [2], **23**, 395); whilst the action of heat on the tetramethylphosphonium salts is the subject of a separate paper by one of us (p. 636), but the decomposition that the tetramethylammonium salts suffer when heated has only been studied in a very few cases. Hofmann (*Ber.*, **14**, 494) has noticed that the hydroxide is easily decomposed by heat—



whilst Thompson (*Ber.*, **16**, 2339) has found that the cyanide volatilises unchanged.

The salts that tetramethylammonium hydroxides form with the more common acids have not received much attention since Hofmann discovered these interesting compounds nearly 40 years ago. Duvillier and Buisine (*Ann. Chim. Phys.* [5], **23**, 331) have shown that methyl nitrate, and also methyl bromide, when heated with methylamine or with dimethylamine, yield tetramethylammonium compounds, but they did not prepare many of the salts. Hofmann mentions that crystalline salts can be prepared by neutralising the base with sulphuric, oxalic, or nitric acids, and he also prepared the chloride, but he gives no details as to the solubility, crystalline form, or other properties of these compounds. The bromide and cyanide have been prepared by other workers, and also a number of double salts; but the chief work on the tetramethylammonium compounds seems to have been directed towards the preparation of a number of addition products, obtained by the action of chlorine, bromine, or iodine on the halogen salts (Waltzien, *Annalen*, **99**, 1; Stahlschmidt, *Jahresber.*, 1863, 403; Dobbin, *J. Chem. Soc.*, Trans., 1886, 846).

The starting point from which we prepared all our salts was the iodide of tetramethylammonium. It was made according to the method suggested by Hofmann. Methyl alcohol saturated with ammonia gas was digested with methyl iodide in sealed tubes at a temperature of 100—120°. It was found better to put the methyl

iodide in a separate tube (open at one end), and not to mix it with the ammoniacal methyl alcohol till after the tube which contained both had been sealed. The yield varied considerably in different tubes, several tubes, after heating for only a few hours, being filled with crystals, while the yield in other tubes, even on prolonged heating at a temperature of  $140^{\circ}$ , did not seem to be materially increased. We believe this was due possibly to the presence of small quantities of water in the methyl alcohol. The iodide of tetramethylammonium can be easily separated from the iodide of ammonium, and from the hydriodides of mono-, di-, and tri-methylamine by crystallisation from water, in which it is not very soluble. The mean of several analyses of the salt gave 63.1 per cent. of iodine, the theoretical amount required by  $(\text{CH}_3)_4\text{NI}$  being 63.2 per cent. iodine.

When this salt is heated, it decomposes at a temperature not much short of a low red heat without melting, giving trimethylamine, free iodine, and other products. It probably first splits up into trimethylamine, and iodide of methyl—



and at the high temperature both the trimethylamine and the iodide of methyl are partially decomposed (the latter almost completely).

*Action of Heat on Bromide of Tetramethylammonium.*

This salt was prepared by neutralising hydroxide of tetramethylammonium with hydrobromic acid, and evaporating the solution over the water-bath. On allowing the salt to remain over sulphuric acid in a vacuum, it soon crystallised. An analysis of the salt gave the following results: 0.430 salt took 27.7 c.c. decinormal  $\text{AgNO}_3$  solution = 51.5 per cent. bromine; theory for  $(\text{CH}_3)_4\text{NBr}$  = 51.9 per cent. bromine. It forms needle-shaped crystals which are deliquescent, and their solubility in water is considerably greater than that of the iodide; 100 c.c. of water at  $15^{\circ}$  dissolve 55.26 grams of the salt.

The salt on heating to  $300^{\circ}$  in a vacuum gave off no gas, but on raising the temperature above  $360^{\circ}$  the salt sublimed and condensed again on the walls of the tube (which was used as a condenser and was surrounded by a freezing mixture) in the form of a white powder. This solid was analysed, and from a bromine determination proved to be pure bromide of tetramethylammonium. (It contained 51.6 per cent. bromine.) At the end of the experiment, the whole of the salt had sublimed, and scarcely a trace of permanent gas had been evolved. Evidently the bromide on heating dissociates—



and the two gases at once recombine on cooling.

*Action of Heat on Chloride of Tetramethylammonium.*

The chloride was prepared by treating the iodide with hydroxide of silver, and neutralising the base thus obtained with hydrochloric acid. The solution was evaporated over the water-bath to the consistency of a syrup, and allowed to stand in a vacuum over sulphuric acid, when it soon crystallised. Attempts made to determine its solubility in water were unsuccessful, on account of its great solubility; it is also deliquescent. The salt was heated in a vacuum at 150° till perfectly dry, when a chlorine determination gave 32·4 per cent. of chlorine:  $(\text{CH}_3)_4\text{NCl}$  contains 32·4 per cent. Cl.

When the salt is heated to above 360°, it decomposes completely without the slightest charring, yielding trimethylamine and a gas which burnt with a greenish flame, and behaved in every way like chloride of methyl. In one experiment, 3·52 grams of salt yielded 750 c.c. of gas. The theoretical yield of methyl chloride would be about 800 c.c. The trimethylamine was converted into the chloroplatinate, and gave the following numbers on analysis.

0·144 gram salt gave 0·0527 gram Pt = 36·60 per cent. Pt. Theory for  $(\text{Me}_3\text{HNCl})_2\text{PtCl}_4$  = 36·93 per cent. Pt.

The gas was also analysed:—

Gas taken .....	8·0 c.c.
Gas and oxygen .....	31·0 „
After explosion and the addition of a few drops of water .....	19·8 „
After addition of caustic soda.....	12·0 „

This shows that one volume of the gas on explosion with excess of oxygen yields nearly its own volume of carbon dioxide, which is the amount required by methyl chloride. The decomposition of the chloride is nearly quantitative, and can be expressed by the following equation:—

*Action of Heat on Fluoride of Tetramethylammonium.*

After the extremely neat manner in which the chloride decomposed when heated, we had every reason to expect that the fluoride would decompose in an analogous manner, yielding trimethylamine and methyl fluoride, and the decomposition, besides being of interest in illustrating the general method of decomposition of the tetramethylammonium salts, would also be useful in the preparation of organic fluorine compounds.

Although fluorine itself has recently been isolated, still, on account of the great difficulty of uniting fluorine with carbon, the number of organic compounds where fluorine is combined with hydrocarbon radicles of the paraffin series is small, and their properties have not been much studied.

The salt was prepared in a manner similar to that employed in the manufacture of the chloride. The base was neutralised with hydrofluoric acid, and evaporated over the water-bath to a syrup. This solidified on cooling to a solid mass of radiating crystals. They were, however, by no means dry, for on heating at  $100^{\circ}$  in a vacuum, a considerable amount of water was lost. Great difficulty was experienced in drying the salt completely, and it could only be accomplished by prolonged heating in a vacuum at  $160^{\circ}$ . A determination was made of the amount of water contained in the salt which had been dried over sulphuric acid.

0.900 gram salt heated at  $160^{\circ}$  in a vacuum lost 0.150 gram  $H_2O = 16.6$  per cent.  $H_2O$ .

	Theory for $Me_4NF.H_2O$ .	Found.
$H_2O$ . . . . .	16.2 per cent.	16.6 per cent.

The tube in which the salt was heated was not etched, showing that no hydrofluoric acid had been liberated. Some of the dried salt was analysed:—

- I. 0.500 gram salt gave 0.1975 gram  $CaF_2 = 19.2$  per cent. fluorine.
- II. 0.2727 gram salt gave 0.1186 gram  $CaF_2 = 21.1$  per cent. fluorine.

	Calculated for $Me_4NF$ .	Found.	
		I.	II.
F. . . . .	20.4 per cent.	19.2	21.1 per cent.

The great difference in the percentage of fluorine found is possibly due to the great difficulty in obtaining the salt pure and dry at the same time, for if the salt be heated even as high as  $160^{\circ}$  in a vacuum it is not perfectly anhydrous, and if the temperature be raised above that point it begins to slowly decompose.

When the salt is heated to  $180^{\circ}$  in a vacuum it begins to decompose, and yields trimethylamine and a gaseous substance. During the first experiments made on the action of heat on this salt, the trimethylamine was condensed by passing the products of the decomposition through a U-tube surrounded by a freezing mixture. Subsequently it was found better to absorb the trimethylamine by pumice-

stone moistened with sulphuric acid (which absorbed only the trimethylamine). The trimethylamine obtained was converted into the chloroplatinate, and analysed (0.362 gram salt gave 0.132 gram Pt = 36.6 per cent.; theory for  $(\text{Me}_3\text{HNCl})_2\text{PtCl}_4 = 36.9$  per cent. Pt).

The amount of tetramethylammonium fluoride which was decomposed was also noticed, as well as the amount of gas evolved. 2.614 grams of the fluoride gave 400 c.c. of gas, which proved to be fluoride of methyl. This gas was first prepared by Dumas and Peligot (*Annalen*, **15**, 59), by heating together potassium fluoride and potassium methyl sulphate. The gas prepared by heating the fluoride of tetramethylammonium was slightly soluble in water, but more so in alcohol; it burnt with a blue flame, yielding hydrofluoric acid, and it had a pleasant odour. On analysis, it yielded its own volume of carbon dioxide:—

Taken of gas.....	8.0 c.c.
Gas and oxygen .....	51.0 ,,
After explosion.....	39.0 ,,
After addition of caustic soda .	31.0 ,,

thus showing that 8.0 c.c. of gas yielded 8.0 c.c. of carbon dioxide. The fluoride of tetramethylammonium, therefore, decomposes in a manner similar to the chloride:—



*Action of Heat on Nitrate of Tetramethylammonium.*

The salt was prepared by the action of silver nitrate on the iodide. Evaporated over the water-bath to a small bulk, the solution crystallises in long needles; when pure, it does not seem to be perceptibly deliquescent. Several grams of the salt were heated. No decomposition occurred till the temperature had risen to above 300°. Slight blackening then took place, but it was found that if the temperature was kept just at the melting point of the salt, nearly the whole of it decomposed without much charring. A yellow liquid was found in the condensing apparatus, and a small quantity of gas was produced, consisting chiefly of nitric oxide, but on treatment with oxygen and water there remained a small amount, which from its properties seemed to be methyl nitrate; the quantity, however, was too small for identification. The yellow distillate was alkaline, and smelt strongly of trimethylamine, it was, therefore, warmed with water, in order to free it from the base, and then treated with a small quantity of pure caustic soda; on warming, a further quantity of trimethylamine

was evolved, which gave the characteristic chloroplatinate. The remaining caustic soda solution was treated with carbon dioxide, and evaporated to dryness, it was then extracted with absolute alcohol, and the alcoholic solution of the sodium salt evaporated to dryness. Thus treated a small quantity of a soluble sodium salt was obtained. An attempt to prepare the silver salt was unsuccessful, owing to the reduction of the salt to metallic silver; with mercurous salts a similar reduction took place, and the sodium salt itself gave carbon monoxide when heated with strong sulphuric acid; the salt in question was, therefore, probably sodium formate. From this it will be seen that the decomposition of the nitrate is complex, trimethylamine alone being formed in any quantity. If methyl nitrate is also formed, it is decomposed, yielding as oxidation products, formic acid, &c., and as reduction products, methyl nitrite and nitric oxide.

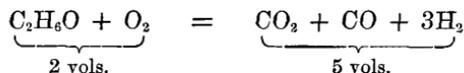
*Action of Heat on Nitrite of Tetramethylammonium.*

This salt was prepared by treating a solution of iodide of tetramethylammonium with nitrite of silver. It is deliquescent, and much more soluble in water than the nitrate. When subjected to the action of heat, it decomposed at a temperature above 300° with great rapidity; trimethylamine was produced, and at the same time a small quantity of an orange-coloured oxide of nitrogen mixed with a considerable amount of some other gas was given off. On treatment with caustic soda, there was little diminution in volume, but on adding oxygen the orange peroxide of nitrogen was produced, which dissolved in the caustic soda solution. About half of the gas collected consisted of nitric oxide, and the remainder was inflammable. This residual gas was mixed with an equal volume of oxygen (under the supposition that it was methyl nitrite), and exploded in a eudiometer. The result was unexpected, for the two volumes of mixed gases became nearly five volumes, and the remaining gas was inflammable; evidently the oxygen used was not nearly sufficient for its combustion, and another experiment was, therefore, made with the following quantities:—

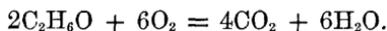
Gas used . . . . .	5·0 c.c.
Gas and oxygen . . . . .	37·0 „
After explosion . . . . .	24·0 „
After treatment with caustic soda . . . . .	14·4 „

Thus 5·0 c.c. of the gas yielded 9·6 c.c. of carbon dioxide, or nearly twice the volume, and the remaining gas in the eudiometer was nearly pure oxygen. This proved that the gas under examination

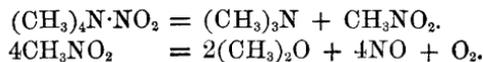
did not contain nitrogen, and also that two atoms of carbon were present in the molecule; in all probability the substance was methyl ether. For when mixed with its own volume of oxygen, and exploded, two volumes would give five volumes of mixed and inflammable gases:—



whilst if it were exploded with excess of oxygen it should yield twice its volume of carbon dioxide:—



Evidently, then, when the nitrite is heated, it is decomposed into trimethylamine and nitrite of methyl, the latter being further decomposed into methyl alcohol, nitric oxide, and oxygen:—



The nitric oxide and oxygen on cooling combined, forming some of the higher oxides of nitrogen, which probably united with the trimethylamine.

#### *Action of Heat on Acetate of Tetramethylammonium.*

The hydroxide of tetramethylammonium was neutralised with acetic acid in order to produce this salt; the solution was evaporated, and solidified to a mass of needle-shaped crystals when allowed to stand in a vacuum over sulphuric acid. The salt was highly deliquescent. When heated, it melted at about 70°, and a small quantity of water distilled; at 190—200°, complete decomposition took place. The condenser, which was surrounded by a freezing mixture, contained a liquid, which on the addition of water separated into two layers, one of which proved to be an aqueous solution of trimethylamine, whilst the other was acetate of methyl. This was proved beyond doubt by the boiling point, 57—58° (methyl acetate, b. p. 56°), and by its conversion into methyl alcohol and sodium acetate on treatment with caustic soda. The sodium acetate was converted into the corresponding silver salt, and then analysed. 0.5395 gram salt gave 0.348 Ag = 64.5 per cent.; theory for  $\text{AgC}_2\text{H}_3\text{O}_2 = 64.6$  per cent. Ag. Some of the liquid b. p. 57.8°, was shaken with a concentrated solution of acid sulphite of sodium, but no crystalline double salt was formed. The decomposition of the acetate is, therefore, quite simple:—



*Action of Heat on Benzoate of Tetramethylammonium.*

This salt was prepared in the same way as the acetate. It is a deliquescent salt, but could be obtained in the form of long needles by allowing the salt to remain over sulphuric acid in a vacuum. When it was heated, it melted at 220—230°, and at once decomposed. There was no charring, and the whole of the salt distilled by the time the temperature had risen to 250°. No gas was produced by the action of heat. The distillate was completely liquid, and separated into two layers when water was added, the one an aqueous solution of trimethylamine, the other a liquid which when dried over calcium chloride and distilled, boiled at 198° (methyl benzoate, b. p. 199°). It did not contain nitrogen, and in order to be sure that it was methyl benzoate it was boiled with caustic soda. The distillate contained methyl alcohol, and from the residue containing the sodium benzoate, the silver salt was prepared. 0.230 gram salt gave 0.110 gram Ag = 47.1 per cent. Ag; theory for  $\text{AgC}_7\text{H}_5\text{O}_2 = 47.1$  per cent. Ag. An analysis was also made of the chloroplatinate of trimethylamine. 36.5 per cent. Pt was found, while the theory for  $(\text{Me}_3\text{HNCl})_2\text{PtCl}_4 = 36.7$  per cent. Pt. The benzoate decomposes in exactly similar manner to the acetate:—

*Action of Heat on Sulphate of Tetramethylammonium.*

This salt was obtained by neutralising the base with sulphuric acid. It is crystalline and very deliquescent, and, before the last traces of water could be removed, it had to be heated to about 160° in a vacuum. An analysis of some of the salt thus dried gave the following numbers:—

0.4342 gram salt gave  $\text{BaSO}_4$  0.417 gram = 39.57 per cent.  $\text{SO}_4$ .

Theory for  $(\text{Me}_4\text{N})_2\text{SO}_4$ ..... = 39.34     ,,     ,,

The remainder of the salt was carefully heated (5.72 grams). It melted at 280°, and at once began to decompose. The temperature was kept as near as possible to 290°, till all effervescence had ceased and the loss that the 5.72 grams had suffered was 1.42 grams. The whole of this was found to be due to the trimethylamine, no other substance passing over into the condenser. The salt on cooling solidified to a mass of deliquescent crystals which were broken up and analysed. They were found to contain sulphur, but their solution in water was not precipitated by a barium salt. The sulphur, therefore, had to be determined by a combustion of the substance (which Dr. Plimpton

kindly undertook, using his new method for analysing such compounds).

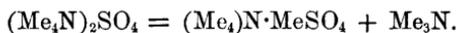
0.196 gram salt gave 0.2517 gram  $\text{BaSO}_4 = 17.63$  per cent. S.

A determination of carbon and hydrogen was also made.

0.497 gram salt gave 0.590  $\text{CO}_2$  and 0.3765  $\text{H}_2\text{O} = 32.38$  per cent. C and 8.41 per cent. H.

	Calculated for $(\text{CH}_3)_4\text{N} \cdot (\text{CH}_3)\text{SO}_4$ .	Found.	
		I.	II.
C .....	32.47	—	32.38
H .....	8.11	—	8.41
S .....	17.29	17.63	—
N .....	7.56	—	—
O .....	34.60	—	—

The first decomposition which the sulphate of tetramethylammonium suffers is the loss of trimethylamine, whereby it is converted into the methyl sulphate of tetramethylammonium.



The 5.72 grams which were used should lose on heating 1.38 grams of trimethylamine, and the amount found was 1.42 gram. The further action of heat on the methyl sulphate of tetramethylammonium was complex; under these circumstances part of the salt passed over into the condenser unchanged, while compounds possessing a very strong smell, recalling that of sulphide of methyl, were formed. There was also produced in small quantities a highly crystalline substance which resembled dimethylsulphone, and much charred matter remained behind in the distilling flask.

#### *Action of Heat on Oxalate of Tetramethylammonium.*

Two methods were employed for the preparation of this salt—one by the action of oxalic acid on the base, the other by the action of silver oxalate on the iodide. A deliquescent salt was obtained by both methods, and was most difficult to obtain anhydrous. When allowed to remain in a vacuum over sulphuric acid, a crust formed on the surface of the salt, while the underlayer remained in a liquid state for weeks. The only method which gave at all a dry product was heating the salt in a vacuum at  $160^\circ$ . An analysis of some of the dry salt was made.

0.590 gram salt gave 0.1355  $\text{CaO} = 36.35$  per cent.  $\text{C}_2\text{O}_4$ .

Theory for  $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4$ ..... = 37.28     ,,     ,,

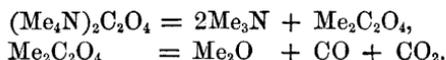
The rest of the salt was subjected to the action of heat. Scarcely any decomposition occurred below  $360^\circ$ , whilst above that temperature

the salt seemed to slowly sublime without melting; decomposition occurred at the same time, for trimethylamine and a gas were evolved. When the salt was more strongly heated, however, the evolution of gas became more rapid. The gas seemed to be composed of carbon dioxide mixed with nearly its own volume of carbon monoxide; a small quantity of an inflammable gas was also present. In two experiments made with weighed quantities of the oxalate, the following amounts of gas were obtained:—

I. 2·5 grams salt gave 500 c.c. of gas composed of 225 c.c. of carbon dioxide, 225 c.c. of carbon monoxide, and 50 c.c. of inflammable gas.

II. 2·4 grams salt gave 450 c.c. gas composed of 205 c.c. carbon dioxide and 205 c.c. of carbon monoxide and 40 c.c. of inflammable gas.

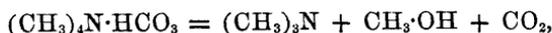
As far as could be ascertained, no methyl oxalate was formed; this was obviously due to the extremely high temperature at which the oxalate decomposed. Trimethylamine was formed in considerable quantity and was converted into the chloroplatinate and analysed. The decomposition of this salt is therefore not a simple one, owing to the high temperature at which it occurs. Probably methyl oxalate and trimethylamine are first formed, and the former at once decomposes into carbon dioxide, carbon monoxide, and other substances, perhaps methyl ether.



The amount of carbon dioxide and carbon monoxide evolved by the 2·4 grams and 2·5 grams respectively agrees fairly well with the amount required by theory; 2·4 grams should yield about 230 c.c., whilst 2·5 grams should yield about 245 c.c. of mixed gases.

*Action of Heat on the Acid Carbonate of Tetramethylammonium.*

A solution of the base saturated with carbon dioxide was evaporated, first over the water-bath and finally over sulphuric acid in a vacuum. The salt was crystalline but highly deliquescent, and could only be obtained anhydrous by prolonged heating in a vacuum. When subjected to the action of heat it began to decompose at 180° with effervescence, but more rapidly at a temperature of 210—220°. Trimethylamine, methyl alcohol, and carbon dioxide were the only substances produced. This decomposition,



seemed to be nearly quantitative: 3 grams of the salt yielded 280 c.c. of carbon dioxide, the theoretical yield according to the above equation being about 500 c.c. Attempts were made to prepare the normal carbonate by dividing a solution of the base into two equal parts, saturating one with carbon dioxide, and then adding the other half to it. On evaporating, and leaving the salt for two months in a desiccator, a white, friable, crystalline, deliquescent salt was obtained. This salt, when heated, gave exactly the same results as the acid carbonate, and was probably a mixture of the acid carbonate with hydroxide of tetramethylammonium. Not a trace of carbonate of ethyl was produced. Possibly, therefore, the normal carbonate does not exist.

A few other salts were examined, the hydrosulphide, the acid sulphite, and the phosphate. The hydrosulphide is a very deliquescent salt, and when heated to about 200° easily decomposes into trimethylamine and methyl mercaptan. The acid sulphite crystallises fairly easily from concentrated solutions, and is not very deliquescent; on heating this salt, it melted at 180° and gave off some water of crystallisation, leaving a white salt behind; this did not melt or decompose till the temperature had risen above 300°, it then split up in a complicated manner, yielding trimethylamine, methyl alcohol, sulphur dioxide, and small quantities of a volatile, crystalline substance with a high boiling point, but it was not obtained in amount sufficient for purification. Traces also of sulphide of methyl were apparent.

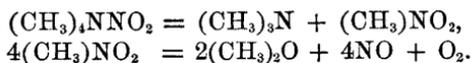
The phosphate of tetramethylammonium is also a deliquescent salt. It was prepared by shaking a solution of the iodide with phosphate of silver; the solution thus obtained was strongly alkaline. With ammonium nitromolybdate, it gave a light-yellow precipitate which contained tetramethylammonium phosphate and molybdic acid. When the phosphate was heated at a very high temperature, it decomposed, giving trimethylamine and methyl alcohol which distilled, while metaphosphoric acid remained in the flask.

#### *Conclusion.*

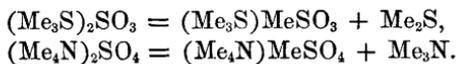
It appears, therefore, that the action of heat on the salts of tetramethylammonium is usually of a simple nature, and trimethylamine is always produced. If the salt heated be one which decomposes at a low temperature, trimethylamine and a salt of methyl are the only substances produced. This is seen in the case of the fluoride, acetate, &c.,



but if the salt decomposes only at a high temperature, it is often the case that the salt of methyl (which is no doubt at first produced) is decomposed; for instance, the nitrite, oxalate, &c.



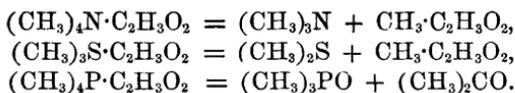
One salt alone decomposed in an unexpected manner, namely, the normal sulphate, but Crum-Brown and Blaikie (*loc. cit.*) have noticed that when the hyposulphite and sulphite of trimethylsulphine are heated, a similar splitting up of the molecule takes place—



It will be seen that the salts experimented with may be divided into two groups: firstly, those which are easily acted on by heat, and which decompose at a temperature of about 200°; secondly, those which are more stable, and are only decomposed at temperatures above 300°. Those belonging to the first class are the hydroxide, carbonate, acetate, benzoate, fluoride, and hydrosulphide; whilst those which belong to the second class are the iodide, bromide, chloride, oxalate, nitrate, &c.

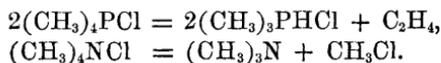
Another point of interest is the solubility in water of the salts of tetramethylammonium, which seems to be in many cases exactly the reverse of the solubility of the ammonium salts, for the iodide of tetramethylammonium is the least soluble of the tetramethylammonium compounds with the halogens, the fluoride and chloride the most soluble. Amongst the other salts, the oxalate and sulphate are highly deliquescent, whilst the nitrate is scarcely even hygroscopic.

When the action of heat on the tetramethylammonium salts is compared with the action of that agent on the corresponding phosphorus and sulphur compounds, it is seen that the decomposition which they undergo is similar. This is shown in the case of the acetate—



The apparent difference in decomposition which the phosphorus salt suffers is at once explained when we remember the intense affinity of that element for oxygen. Phosphorus, sulphur, and nitrogen are a group of elements which show a regular gradation in their affinity for oxygen and electronegative elements. When once phosphorus is

combined with oxygen, it is usually no easy matter to separate these two elements, consequently we find the method of decomposition of the tetramethylphosphonium salts containing oxygen differing in this respect from the corresponding ammonium compounds. The decomposition of the tetramethylphosphonium and the tetramethylammonium chlorides by heat also illustrates this difference—



As sulphur does not possess such a strong attraction for oxygen as phosphorus, yet still possessing more than nitrogen for that element, we find that the sulphine salts resemble both the compound ammonium and phosphonium salts in their behaviour when heated.

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