XLVIII.—*Action of Heat on the Salts of Tetramethylphosphonium.*

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THE action of heat on the salts of tetramethylphosphonium was undertaken partly to complete a series of experiments which had been made on the general method of decomposition of phosphonium salts when heated (*Phil. Mag.*, Aug., 1886, p. 183; *ibid.*, June, 1887, p. 27), and partly to compare their decomposition with that of the tetramethylammonium salts when similarly treated.

The iodide of tetramethylphosphonium was the starting point for the preparation of the other salts. It was prepared according to the method recommended by Hofmann (*Ber.*, **4**, 208); phosphonium iodide being heated with purified wood-spirit in sealed tubes at 180°. The iodide thus obtained was recrystallised from alcohol and ether. It gave no free phosphine when boiled with caustic soda, and a determination of iodine was made (58·9 per cent. and 58·7 per cent. iodine; theory for $(\text{CH}_3)_4\text{NI} = 58\cdot2$). The iodide when heated does not decompose easily, but at a temperature above 300° complicated decomposition occurs, free iodine and other products being formed.

Hofmann has already tried the action of heat on the hydroxide; he found that it split up into trimethylphosphine oxide and marsh-gas—

On repeating his experiment, the same result was obtained; 7 grams of the iodide were converted into hydroxide, and on heating this sub-

stance to a temperature of 115° complete decomposition occurred, 690 c.c. of gas were evolved, and a crystalline substance (trimethylphosphine oxide) remained in the flask. The gas proved to be pure methane (5.3 c.c. gave 5.2 c.c. of carbon dioxide), and the theoretical yield, according to the above equation, should be about 720 c.c. The trimethylphosphine oxide which remained in the flask was distilled. On redistillation, it was obtained as a highly crystalline and deliquescent substance; boiling point (corr.) $214-215^{\circ}$; melting point (corr.) $137-138^{\circ}$. Hofmann gives no analysis or melting or boiling point of this substance.

0.310 gram gave 0.440 CO_2 and 0.275 H_2O = 38.71 per cent. C and 9.85 per cent. H. Theory for $(\text{CH}_3)_3\text{PO}$ = 39.13 per cent. C and 9.78 per cent. H.

When mixed with chloride of platinum and hydrochloric acid, a chloroplatinate was obtained which crystallised from concentrated solutions, sometimes in magnificent orange plates, at other times in needle-shaped crystals.

I. 1.0945 gram heated at 90° lost 0.030 gram = 2.74 per cent. H_2O .

II. 0.583 gram gave 0.1635 Pt = 28.04 per cent. Pt.

III. 0.748 gram gave 0.204 Pt + 63.0 c.c. AgNO_3 (decinormal) = 27.27 Pt + 29.90 Cl.

IV. 0.352 gram gave 0.196 PO_2 + 0.141 H_2O = 15.18 per cent. C + 4.45 per cent. H_2O .

	Theory for $3\text{Me}_3\text{PO}, 2\text{HCl}, \text{PtCl}_4, \text{H}_2\text{O}$.	Found.	
		I.	II.
C	15.34	15.18	—
H	4.40	4.45	—
Pt	27.89	27.27	28.04
Cl	30.20	29.90	—
H_2O	2.54	2.74	—

These results were unexpected, for the oxide of triethylphosphine and tribenzylphosphine give, with platinic chloride, chloroplatinates containing $4(\text{C}_2\text{H}_5)_3\text{PO}, \text{H}_2\text{PtCl}_6$ and $4(\text{C}_7\text{H}_7)_3\text{PO}, \text{H}_2\text{PtCl}_6$.

Action of Heat on Chloride of Tetramethylphosphonium.

This salt was prepared by adding hydrochloric acid to a solution of the hydroxide till it was neutral. On evaporation, a very deliquescent crystalline salt was obtained which gave with chloride of platinum an insoluble chloroplatinate crystallising in glittering yellow octahedra. 8 grams of the chloride were heated: the salt did not

melt till the temperature was above 300° , and it did not decompose till the bottom of the flask was hot enough to colour the Bunsen flame yellow. Eventually 800 c.c. of gas were collected and a solid crystalline substance had distilled. The gas consisted almost entirely of ethylene; an analysis of it was made, when 8.5 c.c. gave 16.5 c.c. of carbon dioxide, and the remainder was nearly all absorbed by bromine, giving a liquid b. p. 132.4° , and which was therefore dibromomethylene. The crystalline solid was soluble in water and had an acid reaction. It contained chlorine, and when treated with caustic soda trimethylphosphine was liberated as an oily liquid which rapidly volatilised on warming, and caught fire at the mouth of the tube. The chloride therefore decomposes as follows:—

probably methylene is first produced during the decomposition of the chloride, but at once polymerises and becomes ethylene.

Action of Heat on Sulphate of Tetramethylphosphonium.

The sulphate was prepared by the action of sulphate of silver on iodide of tetramethylphosphonium. The excess of sulphate of silver which had dissolved was precipitated by the careful addition of sulphuretted hydrogen, and the solution was then made neutral with a small quantity of the hydroxide. On evaporation, a very deliquescent salt was obtained, which crystallised in thick needles. When mixed with a concentrated solution of aluminium sulphate and allowed to stand, no octahedral crystals could be obtained, or any double salt which seemed at all like an alum.

When heated, the solid sulphate decomposed at a temperature above 300° , only just melting, and much charring occurred. The distillate was crystalline and when treated with a little water did not entirely dissolve. The aqueous solution was separated from the crystals, and when redistilled gave pure oxide of trimethylphosphine, b. p. 214.5° , and m. p. 137.8° . The crystals which had been separated from the trimethylphosphine oxide proved to be the sulphide of trimethylphosphine. They melted at 105° , and when boiled with water rapidly volatilised; when warmed with a solution of a silver salt, they gave a black metallic mirror of silver sulphide.

Action of Heat on Benzoate of Tetramethylphosphonium.

This was made by neutralising a solution of the base with benzoic acid. This salt was also very soluble in water, and when obtained in

the crystalline condition it rapidly deliquesced if left in contact with the air. 20 grams of this salt were heated, but no decomposition occurred below 250° , and between that temperature and 300° the whole of the contents of the flask distilled over. During the decomposition, a little gas was formed which was chiefly carbon dioxide. In the receiver, a highly crystalline substance collected, which when treated with water dissolved and formed two layers which were separated. The lower layer proved to be an aqueous solution of trimethylphosphine oxide which on redistillation gave 8 grams of nearly pure oxide of trimethylphosphine (b. p. 214.5°), whilst the upper layer contained traces of trimethylphosphine and toluene, but when distilled the thermometer rose almost at once to 190° , and the whole of the substance passed over between that temperature and 210° . On redistillation most of it passed over at a temperature near 200° and seemed to consist of methyl phenyl ketone (b. p. 200°). Methyl phenyl ketone, however, is a solid which melts at 20° . The fraction $199-202^{\circ}$ could not be made to solidify till it was cooled below 0° , and the crystals so formed melted again below 10° . The substance was unchanged when boiled with caustic soda solution, (and therefore was not methyl benzoate), when oxidised with chromic acid solution, it yielded formic and benzoic acids. From the above results, the benzoate decomposes almost completely as follows:—

while a small portion decomposes—

Several other salts were experimented with, but as their method of decomposition is similar to that of the same salts of tetrethylphosphonium, only a short account of them is necessary.

The acetate when heated decomposed in a manner similar to the benzoate, chiefly into trimethylphosphine oxide and acetone; traces of ethyl acetate and trimethylphosphine were also observed.

The acid carbonate decomposed at a temperature a little above 100° into trimethylphosphine oxide, carbon dioxide, and methane. When the salts of tetramethylphosphonium are compared with the salts of tetrethylphosphonium, they show great similarity in their method of decomposition by heat, but owing to the greater stability of the methyl-group, the changes effected by the heating are not so complicated. The chief decomposition is always (in the case of oxy-salts) into the oxide of trimethylphosphine, sometimes accompanied by a ketone, sometimes, as in the case of the sulphate, by other products. This change was first pointed out as occur-

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ring, in the paper by Professor Letts and the author (*loc. cit.*), on the tetrethylphosphonium salts. But it is more clearly seen, and the decomposition occurs more neatly, when the tetramethylphosphonium salts are heated. The decomposition of tetramethylphosphonium chloride resembles that of the tetrethylphosphonium salt, whilst the decomposition of the sulphate into the sulphide and oxide of trimethylphosphine exactly resembles the decomposition of the sulphate of tetrethylphosphonium. The comparison with the tetramethylammonium salts has already been made in the paper by Dr. Lawson and the author in the preceding paper.