XXVI.—*Notes on Pyrophosphodiamic Acid.*

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SINCE the paper of the late Mr. Holmes and myself, in which the formula of Pyrophosphodiamic acid was established,* I have made several new observations on this body. I propose throwing them together under the three headings of Characteristic Test, Methods of Preparation, and Compounds.

Characteristic Test.

The ready formation of ferric pyrophosphamate from an acid solution of a pyrophosphodiamate affords a very good test for this substance. If it be an insoluble salt that is to be examined, it should be dissolved or decomposed by cold dilute sulphuric acid; and, if a solution, it should be rendered strongly acid, with sulphuric acid if possible, but other acids will answer the purpose though they are more likely to destroy the compound sought for. To this acid solution a few drops of a ferric salt should be added; sufficient to colour it distinctly red. On heating this mixture the presence of pyrophosphodiamic acid is shown by the appearance of a haziness in the warmer currents, which soon extends itself over the whole liquid, and the ferric pyrophosphamate separates in small white flocculent masses. If the acid be present in large quantity, the liquid will become gelatinous. As far as I know, no other ferric compound of a similar appearance can be produced by heating any very acid solution, but the fact of the precipitate being really the pyrophosphamate may be further proved by its solubility in ammonia. Occasionally the precipitate will not form till the mixture is fairly boiling. The reaction which takes place may be thus expressed:—

But the question arises, Is there no other compound that will give the pyrophosphamate under similar circumstances? There are amides of pyrophosphoric acid which contain a larger amount of the elements of ammonia, and these do give the same reaction; but

* Chem. Soc. J. xvii, p. 225.

whether in doing so they pass through the intermediate stage of the diamic acid it is impossible to say. Thus the weak aqueous solution which is obtained when pyrophosphotriamic acid is treated with hot water gives this reaction; but there is little fear of confounding the triamic with the diamic acid, on account of the almost insolubility of the one, and the extreme solubility of the other. There exist, however, two substances, or two modifications of the same substance, intermediate in composition between the diamic and triamic acids, which yield the ferric pyrophosphamate with the greatest facility. It is necessary, therefore, to have some means of distinguishing these. Their salts seem in general less soluble than the pyrophosphodiamates; but there is a much more trustworthy means of recognition, and one that has the advantage of being applicable to quantitative separation. Pyrophosphodiamic acid is very soluble both in water and in alcohol, but the higher compounds, though water dissolves them freely, are thrown down from their aqueous solution on the addition of common spirits of wine. The alcoholic solution may be tested for the diamic acid by the iron test, but it should be diluted with about an equal volume of water before it is heated, so as to ensure a sufficiently high temperature to effect the transformation into the pyrophosphamate.

Methods of Preparation.

The reactions by which pyrophosphodiamic acid is produced are very numerous; indeed, there would seem to be a great tendency in the elements to arrange themselves in this particular form. Most of the processes, however, give at the same time a larger or smaller quantity of the higher compound which is insoluble in alcohol.

In the papers already referred to the following three methods were pointed out:—

1st. By decomposing chlorophosphuret of nitrogen with an alcoholic solution of an alkali, or even by the slow action of water.

2nd. By saturating phosphoric anhydride with dry ammonia-gas.

3rd. By acting on oxychloride of phosphorus with dry ammonia at a low temperature. Two molecules of ammonia are absorbed, as is shown by the increase of weight—about 22 per cent.; and I have reason to believe that the resulting white solid mass is a mixture of chloride of ammonium and an amidated oxychloride. The following will be the expression of this first stage of the reaction:—

which on the addition of water splits up thus:—

The last two methods of producing this acid may be modified in a way which saves time and trouble, namely, by using the strongest aqueous ammonia, sp. gr. 0·880, instead of the dry gas. Thus phosphorus may be burnt in a large vessel containing some ammonia at the bottom. In this case there is a white substance produced which is insoluble in water or acids, and which renders the solution milky, and is very difficult to separate from the liquid containing the pyrophosphodiamate of ammonium. Again, oxychloride of phosphorus may be dropped continuously into aqueous ammonia, when pyrophosphodiamic acid is produced, perhaps without the intervention of the amidated oxychloride—

Akin to this last method is the following:—

4th. By throwing pieces of pentachloride of phosphorus into the strongest aqueous solution of ammonia. The reaction is very violent, and it is desirable to cool the vessel in which it is performed. An insoluble white flocculent substance appears in small quantity, which gives reactions characteristic of pyrophosphotriamate of ammonium, while the solution made decidedly acid, and heated with a ferric salt, gives the ferric pyrophosphamate. This is due to a mixture of pyrophosphodiamic acid and the higher compound. It is hardly credible that no phosphoric acid is produced, but the magnesium test fails to detect any in the tribasic condition.

This experiment was performed quantitatively. 0·65 grm. of pentachloride of phosphorus gave 0·035 grm. of pyrophosphotriamate of ammonium, and 0·305 grm. of ferric pyrophosphamate.

Phosphorus as pyrophosphotriamate..	0·0113	gram. or 11·7 %
„ „ pyrophosphamate	0·0762	„ 78·9 „
Loss.....	0·0091	„ 9·4 „
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Original phosphorus.....	0·0966	„ 100·0

A considerable part of this small loss must be due to the escape of dense fumes on bringing the two bodies into contact. The main reaction seems to be—

If the solution of ammonia be not very strong, phosphate and chloride of ammonium are the only products.

5th. By saturating oxychloride of phosphorus with dry ammonia-gas at 100°C ., or thereabouts. It then takes up four molecules, and on the addition of water there is formed a mixture of the insoluble triamic with the soluble diamic acid, and generally a large quantity of the intermediate compound. The production of the pyrophosphodiamic acid probably takes place in these two stages:—

and

6th. By boiling for a long time a solution of pyrophosphotriamic acid in water, especially if some hydrochloric acid be present.

This is an intermediate step in the reduction of the amide to phosphoric acid.

7th. By treating the acid intermediate in composition between the triamic and the diamic acid with a large amount of some other acid, even acetic; or by decomposing its salts with a strong acid.

8th. By dissolving pyrophosphotriamic acid or a pyrophosphotriamate in sulphuric acid, either quite strong or mixed with a very small quantity of water. Heat is required to effect the solution, and it must not be continued long, lest the action proceed too far. The acid solution diluted with water and neutralized, gives no precipitate, showing that the pyrophosphotriamic acid is really

decomposed, while it gives the ferric pyrophosphamate only on boiling.

9th. By heating pyrophosphotriamic acid to 250° C., and treating the resulting mass with water. There are other products of decomposition.

10th. By dissolving in strong sulphuric acid the substance obtained by saturating oxychloride of phosphorus with dry ammonia at 300° C., and washing the resulting mass with water. The body thus formed differs from pyrophosphotriamic acid, and on analysis gave numbers very different from Schiff's phosphamide (phosphotriamide). It requires the assistance of heat to dissolve it, and apparently stronger acid than is needed in the case of pyrophosphotriamic acid.

11th. By heating Gerhardt's phosphamide with sulphuric acid.

Compounds.

It has already been shown that pyrophosphodiamic acid is bibasic, the silver-salt, for instance, being $\text{P}_2\text{N}_2\text{H}_4\text{Ag}_2\text{O}_5$, or $\text{P}_2(\text{NH}_2)_2\text{Ag}_2\text{O}_5$. In such a case it would be likely enough that compounds should be obtained in which only one of the two atoms of hydrogen is replaced by a metal, or in which a part of the remaining hydrogen is so replaced, as with the triamic acid. I have not, however, succeeded in forming any other silver-salt; but the barium-salt produced in different ways is certainly not uniform in composition, and one portion of it is often much more soluble in hydrochloric acid than another portion. Still I have never isolated any definite salt other than the bimetallic $\text{P}_2\text{N}_2\text{H}_4\text{Ba}_2\text{O}_5$.

Ammonium-salt. In my first paper on this subject* there are some experiments recorded which enable us to determine the composition of the ammonium-salt. A known weight of chlorophosphuretted of nitrogen was decomposed by an alcoholic solution of ammonia, and the resulting salts were evaporated to dryness in a water-bath, and weighed. As nothing is, or ought to be, pro-

* Chem. Soc. Qu. J. iii, 360.

duced in this reaction except the chloride and pyrophosphodiamate of ammonium, it is easy to reckon the amount of alkaline base which has entered into combination.

I.	0.2135	grm.	of $P_3N_3Cl_6$	yielded	0.387	grm.	of salts.
II.	0.2553	"	"	"	0.469	"	"
III.	0.7035	"	"	"	1.2505	"	"

These numbers are in the proportion of

I.	100 : 181.2
II.	100 : 183.7
III.	100 : 177.7

and they indicate that the pyrophosphodiamate of ammonium produced contained 2 molecules of the base and was therefore $P_2N_2H_4(NH_4)_2O_5$, which theoretically should give an increase of

$$100 : 182.8.$$

Metallic Salts.—According to the notes of Mr. Holmes, a neutral solution of mixed pyrophosphodiamate and chloride of ammonium gives with soluble salts of silver barium and zinc, the bimetallic salts that have been analysed; with chloride of strontium and calcium, white flocculent precipitates, readily soluble in acids, but insoluble in ammonia; with chloride of cadmium and manganese similar white precipitates, soluble both in acids and ammonia; with chloride of copper and of nickel blue flocculent precipitates, and with chloride of cobalt a similar violet compound, all soluble either in ammonia or acids. All these precipitates are believed to be, more or less, soluble in chloride of ammonium. It was found at the same time that no precipitate was given with solutions of corrosive sublimate, ferric or chromic sulphate, alum, sulphate of magnesium, or the tartrate of potassium and antimony.

I may also add that a slightly acid solution of pyrophosphodiamic acid gives a white flocculent precipitate with a solution of lead, and a more granular precipitate with a solution of tin, both of which are easily dissolved by nitric acid. The uranic compound is exceedingly soluble in acids, and is dissolved like the oxide by carbonate of ammonium.

Acid.—In recent experiments, pyrophosphodiamic acid has never been obtained in a crystalline form, as stated in my original paper; and I believe that when pure it closely resembles phosphoric acid itself in its physical properties.

Ether.—In the same paper I described an aromatic oil, which makes its appearance when chlorophosphuret of nitrogen is decomposed in the presence of ether or alcohol. It was concluded from its products of decomposition that this liquid is deutazophosphoric (pyrophosphodiamic) ether. Later observations have served to confirm this view ; but no quantitative analysis has recently been made. The only determination of the carbon and hydrogen was unsatisfactory, since a large quantity of unburnt charcoal or hydrocarbon was found after the combustion in the bulb that had been used to contain the liquid. However, notwithstanding this loss, there was obtained 14·4 % of carbon and 4·5 % of hydrogen, which indicates more than 1 molecule of ethyl, and leads to the belief that the compound was probably $P_2N_2H_4(C_2H_5)_2O_5$, which, if completely burnt, should have given 20·6 % of carbon, and 6 % of hydrogen.