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I.—*On Pyrophosphotriamic Acid.*

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IT was my intention, in conjunction with my assistant and friend, Mr. J. D. Holmes, to follow up our previous papers on some of the amides of phosphoric acid* with a more complete investigation of the whole subject. But our paper on the action of ammonia on sulphochloride of phosphorus was scarcely printed, when Mr. Holmes was taken seriously ill, and his death, last midsummer, has deprived the world of a careful experimenter and a good man. I feel his loss the more because he had many thoughts and observations connected with these compounds of phosphorus, which he never committed to writing. On looking over our notebooks, I find a tolerably complete history of a remarkable acid amide, which, with a few additional experiments, will form the present communication.

If dry ammonia gas be allowed to stream slowly into a flask containing oxychloride of phosphorus, kept cool by being immersed in water, the liquid is gradually converted into a white solid mass by the absorption of two equivalents of ammonia. If at that point the flask be immersed in water at 100° C., the mass will be found capable of absorbing two more equivalents of ammonia, and on the addition of water to the white substance thus produced, there results an insoluble amide, the subject of the present inquiry. In order to obtain it pure, the oxychloride of phosphorus employed must be free from pentachloride, but it is not necessary to attempt to free it from hydrochloric acid. During the latter portion of the

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* Journal Chem. Soc., 1864, p. 225, and 1865, p. 1.

process it is desirable to break up the solid mass from time to time, in order that all parts of it may be exposed to the gaseous ammonia; and if this be properly done, the contents of the flask will be found to have increased in weight nearly, if not quite, 44 per cent.

The white amorphous powder produced by the action of water must be washed with cold water till the washings give no indication of a chloride, and then it is better to finish the washing with a little dilute alcohol.

The compound thus obtained is tasteless, but when moistened it reddens blue litmus paper, and it effervesces with solutions of alkaline carbonates. When suspended in solutions of metallic salts, it usually decomposes them, entering into combination with the metal, and that in the presence of the liberated acid. These salts, so easily formed, are all insoluble or very sparingly soluble in water, like the acid itself, even the salts of the alkalis. Another remarkable circumstance connected with this acid is, that it is capable of combining with 1, 2, 3, or 4 atoms of the base, according to the peculiarities of the metal itself, or the way in which it is presented.

This compound, though almost insoluble in water, is very slowly attacked by it, especially at a high temperature, with the production of pyrophosphodiamic acid. When boiled with dilute hydrochloric acid, it is speedily resolved into phosphoric acid and ammonia, pyrophosphodiamic acid being an intermediate product. When heated with strong sulphuric acid, it instantly dissolves, and this solution also contains pyrophosphodiamic acid.

The following analyses were made of different preparations of the substance dried at 100° C.:—

I. 0·3315 grm. boiled with hydrochloric acid, and the ammonia determined in the usual manner, gave 1·243 grm. of ammonio-chloride of platinum.

II. 0·197 grm. gave 0·755 grm. of ammonio-chloride of platinum.

III. 0·197 grm. decomposed in the same way gave 0·247 grm. of pyrophosphate of magnesium.

IV. 0·2595 grm. gave 0·987 grm. of ammonio-chloride of platinum.

V. 0·2445 grm. gave 0·309 grm. of pyrophosphate of magnesium.

VI. 0·1845 grm. regained from its ammonium salt, gave 0·705 grm. of ammonio-chloride of platinum.

VII. 0·225 grm. of substance regained from its combination with copper gave 0·2825 grm. of pyrophosphate of magnesium.

VIII. 0·320 grm. burnt with oxide of copper gave 0·114 grm. of water.

These numbers, when reckoned to 100 parts, give

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Phosphorus	—	—	35·02	—	35·29	—	35·38	—
Nitrogen	23·54	24·03	—	23·85	—	23·96	—	—
Hydrogen	—	—	—	—	—	—	—	3·93

agreeing very closely with the numbers deduced from the formula $P_2N_3H_7\Theta_4$.

	Calculated.		Mean of Analyses.
Phosphorus	62	35·43	35·23
Nitrogen	42	24·00	23·84
Hydrogen	7	4·00	3·93
Oxygen	64	36·57	—
	175	100·00	

This may be viewed as the third member of the series of amides of pyrophosphoric acid, of which the first two have already been described by me; and it should by analogy be termed pyrophosphotriamic acid.

Pyrophosphoric acid .... $P_2 \quad H_4\Theta_7$
Pyrophosphamic acid .... $P_2NH_5\Theta_6$ or $P_2(NH_2)\,H_3\Theta_6$
Pyrophosphodiamic acid .... $P_2N_2H_6\Theta_5$ or $P_22(NH_2)H_2\Theta_5$
Pyrophosphotriamic acid .... $P_2N_3H_7\Theta_4$ or $P_23(NH_2)H\,\Theta_4$

The reaction by which this substance is produced by the treatment of oxychloride of phosphorus with ammonia and water in succession may be briefly expressed thus:—

$$2(PCl_3\Theta + 4NH_3) + 2H_2\Theta = P_2N_3H_7\Theta_4 + 6HCl + 5NH_3,$$

just as in the production of pyrophosphodiamic acid formerly described—

$$2(PCl_3\Theta + 2NH_3) + 3H_2\Theta = P_2N_2H_6\Theta_5 + 6HCl + 2NH_3,$$

but in both cases there are intermediate products not recognized in the above equations. I reserve the fuller consideration of what takes place when ammonia is passed over oxychloride of phosphorus till a future occasion.

SALTS.

If the rational formula of this acid be that above given, it might be expected that only one equivalent of hydrogen would be replaceable by a metal, or, in other words, that pyrophosphotriamic acid would be monobasic, just as the -diamic acid is bibasic, and the -amic acid is tribasic. The analysis of its salts shows indeed that such monobasic compounds are produced with the alkali-metals and many others, but it also shows that most metals are capable of displacing one or more equivalents of that hydrogen which we are apt to consider as more intimately associated with the nitrogen.

SILVER-SALTS.—*Monometallic.*—If a solution of nitrate of silver be added to an aqueous solution of pyrophosphotriamic acid, it gives a white gelatinous precipitate. But it is not easy to prepare in this way a quantity sufficient for analysis, and a portion so produced gave a determination of silver, which led to the conclusion that the salt was impure. A better method is to suspend the acid in cold water, and add a solution of nitrate of silver, when a flocculent precipitate subsides, and becomes granular. It is white, amorphous, and insoluble in water; dilute nitric acid or ammonia will dissolve out a little silver, and leave the pure monometallic salt. This salt is decomposed at once by hydrochloric acid; and this affords a ready means for its analysis, as the pyrophosphotriamic acid itself is converted on boiling into phosphoric acid and ammonia, which can be determined in the usual way.

The following determinations were obtained:—

I. 0·259 grm. of silver-salt, washed with dilute ammonia, gave 0·133 grm. of chloride of silver, and 0·208 of pyrophosphate of magnesium.

II. 0·241 grm. similarly washed gave 0·122 grm. of chloride of silver, and 0·581 grm. of ammonio-chloride of platinum.

III. 0·298 grm. of salt, washed with dilute nitric acid, gave 0·1515 grm. of chloride of silver, and 0·235 grm. of pyrophosphate of magnesium.

IV. 0·285 grm., similarly washed, gave 0·145 grm. of chloride of silver, and 0·679 grm. of ammonio-chloride of platinum.

This agrees closely with what ought to be obtained from a substance having the composition $P_2N_3H_6Ag\Theta_4$.

	Calculated.		I.	II.	III.	IV.
Phosphorus ..	62	21·98	22·42	—	22·01	—
Nitrogen	42	14·89	—	15·11	—	14·94
Hydrogen	6	2·13	—	—	—	—
Silver	108	38·30	38·64	38·09	38·26	38·29
Oxygen	64	22·70				
	282	100·00				

Trimetallic.—If a feebly ammoniacal solution of nitrate of silver be added to a solution of pyrophosphotriamic acid, there precipitates a yellowish salt. Or if the monometallic compound just described be treated with such an ammoniacal salt of silver in excess, it becomes of a bright yellow colour, heavy, granular, and easily washed by decantation. When dry it forms an orange-yellow powder. Dilute nitric acid, or ammonia, converts it at once into the white monometallic salt. Acetic acid attacks it but slowly, even when strong and at a boiling temperature. It was analysed by decomposition with hydrochloric acid.

I. 0·509 grm. of the yellow salt gave 0·442 grm. of chloride of silver, and 0·675 grm. of ammonio-chloride of platinum.

II. 0·5745 grm. gave 0·4995 grm. of chloride of silver, and 0·252 grm. of pyrophosphate of magnesium.

III. 0·286 grm. gave 0·2485 grm. of chloride of silver, and 0·3695 grm. of ammonio-chloride of platinum.

IV. 0·404 grm. gave 0·3515 grm. of chloride of silver, and 0·183 grm. of pyrophosphate of magnesium.

These numbers agree well with the composition $P_2N_3H_4Ag_3\Theta_4$.

	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus ..	62	12·50	—	12·25	—	12·65
Nitrogen	42	8·47	8·32	—	8·10	—
Hydrogen	4	0·81	—	—	—	—
Silver	324	65·32	65·34	65·46	65·39	65·48
Oxygen ..	64	12·90	—	—	—	—
	496	100·00				

These two silver-salts, white and yellow, and their ready convertibility into one another, afford a good test for pyrophosphotriamic acid.

BARIUM-SALTS.—*Monometallic.*—This salt was prepared by diffusing the acid through a solution of chloride of barium, and carefully neutralising the liberated hydrochloric acid by a few drops of ammonia. It was decomposed by hydrochloric acid, the different constituents being determined in the usual way.

I. 0·429 grm. gave 0·2045 grm. of sulphate of barium, and 1·1795 grm. of ammonio-chloride of platinum.

II. 0·3465 grm. gave 0·1665 grm. of sulphate of barium, and 0·3145 grm. of pyrophosphate of magnesium.

These numbers indicate the formula $P_2N_3H_6BaO_4$.

	Calculated.		Found.	
			I.	II.
Phosphorus ..	62	25·56	—	25·34
Nitrogen	42	17·31	17·24	—
Hydrogen	6	2·47	—	—
Barium	68·6	28·28	28·06	28·27
Oxygen	64	26·38	—	—
	242·6	100·00		

Dimetallic.—When pyrophosphotriamic acid was suspended in an excess of an ammoniacal solution of chloride of barium, it combined with twice as much of the metal.

The following analyses were made :—

I. 0·2335 grm. of salt gave 0·174 grm. of sulphate of barium, and 0·4895 grm. of ammonio-chloride of platinum.

II. 0·2445 grm. gave 0·1835 grm. of sulphate of barium, and 0·1793 grm. of pyrophosphate of magnesium.

These indicate the composition $P_2N_3H_5Ba_2O_4$.

	Calculated.		Found.	
			I.	II.
Phosphorus ..	62	20·00	—	20·48
Nitrogen	42	13·54	13·14	—
Hydrogen	5	1·60	—	—
Barium	137·24	4·23	43·84	44·18
Oxygen	64	20·63	—	—
	310·2			

LEAD-SALTS. — Lead is capable of entering into combination with pyrophosphotriamic acid in three different proportions.

Monometallic.—If the acid be treated with a solution of nitrate of lead, the result is a mixture of the compounds of 1 and 2 atoms of the metal. If, however, the solution be rendered decidedly acid with nitric acid, a pure mono-metallic salt may be produced. 0·203 grm. of the acid thus treated gave 0·327 grm. of salt, which indicates a compound of the formula $P_2N_3H_6PbO_4$. The excess of weight being due to the addition of lead, and the removal of a corresponding amount of hydrogen, gives the following percentage:—

	Calculated.	Found.
Lead ..	37·3 per cent.	38·1 per cent.

Dimetallic.—To produce this compound the acid was suspended in water, and an excess of a strong but slightly acid solution of acetate of lead was added. A dense white granular precipitate was the result. It was analysed in the usual way.

0·354 grm. of salt gave 0·2805 grm. of sulphate of lead, and 0·2035 grm. of pyrophosphate of magnesium.

This agrees sufficiently with the formula $P_2N_3H_5Pb_2O_4$.

	Calculated.		Found.
Phosphorus ..	62	16·32	16·05
Nitrogen	42	11·05	—
Hydrogen......	5	1·32	—
Lead..........	207	54·47	53·95
Oxygen........	64	16·84	—
	380	100·00	

This compound is not turned yellow by iodide of potassium, except on the addition of hydrochloric acid.

Trimetallic.—When pyrophosphotriamic acid was warmed with basic acetate of lead, it combined with a larger portion of the metal. The following analyses were made:—

I. 0·3405 grm. of salt gave 0·321 grm. of sulphate of lead, and 0·1535 of pyrophosphate of magnesium.

II. 0·2365 grm. gave 0·175 grm. of sulphide of lead, and 0·3165 grm. of ammonio-chloride of platinum.

This agrees with the formula $P_2N_3H_4Pb_3\Theta_4$.

	Calculated.		Found.	
			I.	II.
Phosphorus ..	62	12·85	12·59	—
Nitrogen	42	8·70	—	8·39
Hydrogen	4	0·83	—	—
Lead	310·5	64·35	64·40	64·08
Oxygen	64	13·27	—	—
	482·5	100·00		

Thallium-salt.—Pyrophosphotriamic acid treated with nitrate of thallium gives a heavy white compound, which is easily decomposed by rather strong nitric acid.

Copper-salts.—Both neutral and ammoniacal salts of copper give up their metal to pyrophosphotriamic acid.

Monometallic.—The acid when treated with a solution of nitrate of copper to which some drops of nitric acid had been added, gave a pale blue compound. On analysis this was found to contain rather more copper than a pure monometallic salt should have done; but it consisted mainly, in all probability, of such a compound.

Dimetallic.—0·164 grm. of the acid, digested awhile with a solution of acetate of copper, gave a greenish salt, which, when dried at 100° C., weighed 0·215 grm. These numbers indicate that two equivalents of hydrogen had been replaced by copper, though perhaps the conversion had not been complete. The increased weight ought, by calculation, to have been 0·220.

If some of the acid be thrown into a solution of a copper-salt in excess of carbonate of ammonium, an effervescence takes place, and there results a green powder, insoluble in ammonia, but from which dilute acids dissolve out the copper.

I. 0·236 grm. of this salt gave 0·080 grm. of oxide of copper, and 0·646 grm. of ammonio-chloride of platinum.

II. 0·304 grm. gave 0·103 grm. of oxide of copper, and 0·285 grm. of pyrophosphate of magnesium.

This was certainly $P_2N_3H_5Cu_2\Theta_4$.

	Calculated.		Found.	
			I.	II.
Phosphorus	62	26·25	—	26·18
Nitrogen	42	17·78	17·17	—
Hydrogen	5	2·12	—	—
Copper	63·2	26·76	27·04	27·03
Oxygen	64	27·09	—	—
	236·2	100·00		

Zinc-salt.—The acid decomposes chloride of zinc, forming a white pyrophosphotriamate.

Cadmium-salt.—It forms a white compound also, when treated with chloride of cadmium.

Iron-salt.—*Monometallic.*—If the acid be digested with a solution of ferrous sulphate, a salt of a yellow-drab colour is produced, which resists the solvent power of dilute acids. 0·075 grm. of substance increased in this way to 0·089 grm., which points to the formula $P_2N_3H_6FeΘ_4$. The salt obtained ought to have weighed 0·086 grm.; but it probably contained a trace of ferric oxide mixed with the ferrous compound.

I have not succeeded in preparing any ferric pyrophosphotriamate, though the attempt has been made with ferric chloride, acetate, and ammonio-citrate. This is the more remarkable, as pyrophosphamic acid and phosphoric acid itself show such a readiness to combine with iron in that condition.

Cobalt-salt.—*Dimetallic.*—The acid, digested with a slightly ammoniacal solution of nitrate of cobalt, forms a compound of a beautiful violet colour, not decomposed by dilute hydrochloric, and but slowly by dilute sulphuric acid. 0·136 grm. gave thus 0·177 grm. of salt, which is sufficiently near to the theoretical amount to show that the composition was $P_2N_3H_5Co_2Θ_4$.

	Calculated.	By synthesis.
Cobalt ..	25·6 per cent.	24·3 per cent.

The same salt seems to be produced when the acid is treated with an ordinary solution of chloride of cobalt: but an analytical experiment gave also in this case less than the required percentage of metal.

Nickel-salt.—A feebly ammoniacal solution of sulphate of nickel gives a bright green pyrophosphotriamate.

MANGANESE-SALT.—Chloride of manganese gives a yellowish salt of this acid.

CHROMIUM-SALT.—A green compound may be produced by means of acetate of chromium.

MAGNESIUM-SALT.—This was produced by warming the acid with an ammoniacal solution of magnesia, and washing with water containing a little ammonia, and afterwards with pure water. On analysis, it appeared to be a mixture of monometallic and dimetallic salts.

POTASSIUM-SALT.—*Monometallic.*—Pyrophosphotriamic acid decomposes carbonate of potassium without dissolving. The white, almost insoluble salt is readily decomposed by acids. The following determinations were made:—

I. 0·312 grm. of salt gave 0·356 grm. of potassio-chloride of platinum.

II. 0·329 grm. gave 0·3402 grm. of pyrophosphate of magnesium.

III. 0·2985 grm. gave 0·3355 grm. of potassio-chloride of platinum.

This agrees with the numbers deduced from the formula $P_2N_3H_6K\Theta_4$.

	Calculated.		Found.		
			I.	II.	III.
Phosphorus ..	62	29·10	—	28·87	—
Nitrogen	42	19·72	—	—	—
Hydrogen	6	2·82	—	—	—
Potassium	39	18·31	18·17	—	17·95
Oxygen	64	30·05	—	—	—
	213	100·00			

AMMONIUM-SALT.—The acid forms a similar sparingly soluble ammonium-compound, which cakes together in small white lumps, and readily parts with the base when treated with dilute acids in the cold.

I. 0·129 grm. of salt gave 0·5945 grm. of ammonio-chloride of platinum.

II. 0·2095 grm. gave 0·9805 grm. of ammonio-chloride of platinum.

III. 0·3423 grm. gave 0·3995 grm. of pyrophosphate of magnesium.

IV. 0·220 grm. gave 1·014 grm. of ammonio-chloride of platinum.

This indicates the compound $P_2N_3H_6(NH_4)\Theta_4$.

	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus ..	62	32·29	—	—	32·61	—
Nitrogen	56	29·17	28·90	29·34	—	28·90
Hydrogen	10	5·21	—	—	—	—
Oxygen	64	33·33	—	—	—	—
	192	100·00				

Mercury-salt.—*Tetrametallic.*—It was observed early in the investigation that if pyrophosphotriamic acid be boiled with oxide of mercury, the oxide loses its colour and forms a white compound which is insoluble in dilute nitric or hydrochloric acid. This mercury-salt may be also prepared by diffusing the acid through a solution of corrosive sublimate, but Mr. Holmes seems always to have employed a slightly acid solution of the double chloride of mercury and ammonium. It is a heavy, white, granular powder, which becomes yellowish, and eventually dark-coloured, when exposed to light. Iodide of potassium first turns it scarlet, and then dissolves out the mercury. The following analyses were made:—

I. 0·4175 grm. of salt gave 0·3405 grm. of sulphide of mercury.

II. 0·5405 grm. gave 0·4405 grm. of sulphide of mercury.

III. 0·276 grm. gave 0·224 grm. of sulphide of mercury, and 0·3305 grm. of ammonio-chloride of platinum.

IV. 0·3415 grm. gave 0·277 grm. of sulphide of mercury, and 0·1305 grm. of pyrophosphate of magnesium.

These numbers require the formula $P_2N_3H_3Hg_4\Theta_4$.

	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus	62	10·86	—	—	—	10·67
Nitrogen	42	7·35	—	—	7·50	—
Hydrogen......	3	0·53	—	—	—	—
Mercury	400	70·05	70·31	70·25	69·96	69·92
Oxygen..	64	11·21	—	—	—	—
	571	100·00				

PLATINUM-SALT.—When pyrophosphotriamic acid is treated with a strong aqueous solution of platinic chloride, a bulky, yellowish compound is formed. This is entirely decomposed when washed with water, in presence of the liberated acid; but it may be safely washed with alcohol, and then water has not the same effect upon it. 0·097 grm. of the original acid gave 0·207 grm. of this platinum-compound, which shows that two equivalents of the metal must have entered into combination, displacing, no doubt, four equivalents of hydrogen; the formula being $P_2N_3H_3Pt''_2\Theta_4$.

	Calculated.	Found.
Platinum ..	53·7 per cent.	54·1 per cent.

An attempt to prepare a salt of gold in a similar manner was unsuccessful.

The rational formula $P_2(NH_2)_3H\Theta_4$ has been given above for this pyrophosphotriamic acid, but the elements are susceptible of another arrangement, which brings them more closely in accordance with the formula of pyrophosphoric acid, and indicates four equivalents of hydrogen as in a different position to the remaining three.

Pyrophosphoric acid .. .. $P_2H_4\Theta_7$

Pyrophosphotriamic acid .. .. $P_2H_4\left\{\begin{matrix}\Theta_4\\(NH)_3\end{matrix}\right\}$

The following table exhibits at a glance the number of hydrogen atoms displaced by different metals, as far as the salts have been hitherto examined quantitatively:—

	1 eq.	2 eqs.	3 eqs.	4 eqs.
Ammonium..............	Yes	—	—	—
Potassium	Yes	—	—	—
Magnesium..............	?	?	—	—
Barium	Yes	Yes	—	—
Lead...................	Yes	Yes	Yes	—
Copper.................	?	Yes	—	—
Iron...................	Yes	—	—	—
Cobalt	—	Yes	—	—
Silver	Yes	—	Yes	—
Mercury	—	—	—	Yes
Platinum...............	—	—	—	Yes