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CLXXIII. *On the Compounds of Phosphoric Acid with Aniline.*
By EDWARD CHAMBERS NICHOLSON, Esq.

OF the inorganic acids there is none so remarkable for the number and variety of the compounds it forms with bases as phosphoric acid. The peculiar and complex reactions of the salts of this acid were first satisfactorily explained by Prof.

* *Annalen der Chemie*, Bd. xxxvii. S. 155.

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Graham, in his well-known paper published in 1833*. The modifications of phosphoric acid by its amount of water of hydration, giving rise to pyrophosphoric and metaphosphoric acid, beautifully explained all that was enigmatical in the observed reactions.

Prof. Graham's excellent experiments have added a great deal to our knowledge of phosphoric acid; the study, however, of this acid and its salts is by no means exhausted. I consequently hope that any contribution to the subject will be accepted.

The following experiments, which were instituted in the laboratory of the Royal College of Chemistry, relate to the combination of phosphoric acid with a large and interesting group of bodies, viz. the organic alkaloids. It is curious that this class of salts has not been hitherto examined; indeed the composition of scarcely any phosphate of an organic base has been satisfactorily ascertained.

It was a very interesting question, whether these bases, which with monobasic acids comport themselves exactly the same as mineral oxides, were capable of combining with polybasic acids in the same remarkable proportions. In the absence of experiments, the only points which were known from whence we might, by way of analogy, have inferred any similarity in these compounds with the inorganic phosphates, are the salts of ammonia with phosphoric acid; ammonia being as it were the type of all the organic bases. A phosphate of ammonia indeed is known, containing two equivalents of the volatile alkali; but it still remained to be decided whether any true organic alkaloid unites in the proportions of two or more equivalents with one equivalent of phosphoric acid.

The only analysis of a phosphate with an organic alkali is published by Regnault†. This chemist determined the carbon and hydrogen in phosphate of strychnine. Regnault considered the salt which he analysed as a compound of 1 equiv. of phosphoric acid, 1 equiv. of strychnine and water,

However, Regnault's formula of strychnine has been corrected by Professor Liebig‡, who showed that this base contains one equivalent of carbon more, *i. e.*

* Phil. Trans. of Royal Society of London, part 2, 1833. Researches on the Arseniates, Phosphates and Modifications of Phosphoric Acid, by Thos. Graham, Esq., M.A., F.R.S.E., Professor of Chemistry in the Andersonian University of Glasgow.

† Liebig's *Annalen*, vol. xxvi. p. 37.

‡ Ibid. vol. xxvi. p. 58.

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it is therefore evident that the composition of Regnault's phosphate is to be expressed by the formula

as Professor Liebig* already remarks, and, as may be seen from the following comparison of the per-centages corresponding to this formula with his analytical results, which I have calculated with the new atomic weights of carbon:—

44 eqs. Carbon	3300·00	59·23	59·85
26 ... Hydrogen	325·00	5·83	5·85
2 ... Nitrogen	354·00	6·55	
7 ... Oxygen	700·00	12·66	
1 ... Phosphoric acid	892·28	15·73	
1 ... Phosphate of strychnine	5571·28	100·00	

It is evident from these numbers that the phosphate of strychnine analysed by Regnault is a common phosphate, corresponding to the phosphate of soda with 1 equiv. of fixed base.

Besides this, Dr. A. T. Thomson† relates an analysis of phosphate of morphine by Dr. Gilbert, from which however no conclusion relative to the composition of this salt can be deduced, the analysis being incomplete.

It being a matter of indifference whether the base which I took for experiment was a natural alkaloid or one prepared artificially in the laboratory, I selected aniline, deeming it especially suited to my purpose, as this base generally forms with acids readily crystallizable compounds.

I. COMPOUNDS OF TRIBASIC PHOSPHORIC ACID WITH ANILINE.

1. *Phosphate with 2 equivs. of Aniline and 1 equiv. of Water.*

On adding aniline in excess to a strong solution of tribasic phosphoric acid, the whole instantly solidified to a white crystalline mass, which was drained, pressed, dissolved in a large quantity of boiling dilute alcohol, and filtered through a warm funnel; on cooling, the whole became a mass of crystals; after pressing these between folds of bibulous paper, I finally dried them on a warm porous tile.

When dry, this salt appears as beautiful flesh-coloured nacreous plates, which might be readily taken for thionurate of ammonia, quite inodorous, slightly acid to test paper. They are very soluble in æther and water, sparingly soluble in cold

* *Handwörterbuch der Chemie*, article 'Organic Bases,' vol. i. p. 70.

† *Pharm. Journal*, vol. ii. p. 500, 'On the Preparation, Characters, and Composition of the Nitrate, Phosphate, Tartrates and Hydriodate of Morphia,' by Anthony Todd Thomson, M.D., F.L.S.

alcohol, but very soluble in hot, so that upon cooling the whole liquid becomes solid. This salt cannot be dried at 100°C . (212°F .), because at this temperature it gives off aniline, assuming a red colour. It melts at a gentle heat, and upon raising the temperature gives off its aniline and leaves metaphosphoric acid.

Analysis.

When burnt with oxide of copper—

I. 0.419 grm. of the substance gave 0.774 grm. of carbonic acid and 0.227 grm. of water.

II. 0.646 grm. of the substance gave 1.183 grm. of carbonic acid and 0.356 grm. of water.

III. 1 grm. neutralized with ammonia and precipitated with nitrate of silver, gave 1.461 grm. of tribasic phosphate of silver.

These numbers correspond with the following per-cents:—

	I.	II.	III.
Carbon	50.38	49.94	
Hydrogen	6.01	6.19	
Phosphoric acid . . .	...	...	24.86

These determinations lead to the following formula,

as is seen by the following:—

24 eqs. Carbon	1800.00	50.57
17 ... Hydrogen	212.50	5.97
2 ... Nitrogen	354.10	9.97
3 ... Oxygen	300.00	8.42
1 ... Phosphoric acid . .	892.28	25.07
1 ... Phosphate of aniline	3558.88	100.00

Therefore the salt corresponds to the common phosphate of soda,

and also to an ammonia salt of the same constitution.

It is anhydrous, like this ammonia salt; but, unlike these salts, possesses, as before remarked, an acid reaction, like all the other salts of aniline, this base being incapable of destroying the properties of an acid.

2. Phosphate with 1 equiv. of Aniline and 2 equivs. of Water.

This compound is obtained by adding tribasic phosphoric acid to the salt mentioned before until it ceases to produce a precipitate with chloride of barium, and concentrating in the water-bath. In the course of a few hours the salt crystallizes in beautiful silky needles; these are to be washed with æther and dried on a warm tile.

When dry the salt is quite white, but by exposure to the

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air becomes rose-red; it is very soluble in æther, alcohol, and water; in the latter with decomposition, the common phosphate being produced.

Analysis.

When burnt with oxide of copper—

I. 0.456 grm. of the substance gave 0.633 grm. of carbonic acid and 0.223 grm. of water.

II. 0.403 grm. neutralized with ammonia and precipitated with nitrate of silver, gave 0.880 grm. of tribasic phosphate of silver.

These numbers correspond to the following per-cents.:—

	I.	II.
Carbon	37.86	
Hydrogen	5.44	
Phosphoric acid	...	37.12

These determinations lead to the formula

as is seen by the following:—

12 eqs. Carbon	900.00	37.59	37.86
10 ... Hydrogen	125.00	5.22	5.44
1 ... Nitrogen	177.05	7.39	
3 ... Oxygen	300.00	12.54	
1 ... Phosphoric acid	892.28	37.26	37.12
1 ... Phosphate of aniline	2394.33	100.00	

This salt corresponds to the biphosphate of soda,

Mitscherlich has analysed an ammonia compound of the same constitution.

I did not succeed in forming a phosphate in which the three equivalents of water in the hydrate are replaced by three equivalents of aniline. On adding aniline in excess to an alcoholic solution of the common phosphate, the base did not combine, and the common phosphate remained. I also tried to produce it by decomposing the phosphate with three equivalents of soda by oxalate of aniline; aniline however was instantly set free in the form of oily globules, and the common phosphate was produced with oxalate of soda.

I have not been more successful in endeavouring to prepare phosphates, into which aniline enters beside fixed bases. I have tried to obtain a salt corresponding to phosphorus salt,

by dissolving aniline in a solution of phosphate of soda with one equivalent of fixed base. The crystals, however, which

were formed did not contain soda, and were similar in appearance to the salt first-described. Similar results were obtained by neutralizing the acid phosphate of aniline with carbonate of soda. The salt produced did likewise not contain soda, the common phosphate appearing to be produced.

II. PYROPHOSPHATE OF ANILINE.

There are two pyrophosphates of aniline, acid and neutral, which are always formed together when aniline is added in excess to pyrophosphoric acid. The precipitate produced by addition of aniline to pyrophosphoric acid is gelatinous, and becomes quite hard when exposed to the air.

Several combustions showed me that the compound obtained in this way consists of a mixture of the neutral and the acid pyrophosphate. I have not yet been able to obtain the neutral salt in a state of purity, but I found that by keeping the pyrophosphoric acid in great excess, the acid salt may be procured. The best way of forming it is to add aniline to rather concentrated pyrophosphoric acid (obtained by decomposing pyrophosphate of lead by hydrosulphuric acid), when the acid salt is precipitated along with the neutral compound; the mixture is then to be heated until the whole is dissolved, an excess of acid added, and the solution evaporated in the water-bath; upon cooling, the whole solidifies to a mass of beautiful white needles, which are to be pressed in bibulous paper, washed with æther, and finally dried *in vacuo*. This salt appears as white silky needles, very similar to the common basic sulphate of quinine; they are very acid, soluble in water, and almost insoluble in alcohol and æther; the crystals and their aqueous solution, like all other aniline salts, become red when exposed to the air.

Analysis.

When burnt with oxide of copper—

I. 0.223 grm. of the substance gave 0.333 grm. of carbonic acid and 0.117 grm. of water.

II. 0.269 grm. of the substance gave 0.389 grm. of carbonic acid and 0.132 grm. of water.

III. 0.350 grm. of substance, neutralized by ammonia and precipitated by nitrate of silver, gave 0.578 grm. of pyrophosphate of silver.

These numbers correspond to the following per-cents. :—

	I.	II.	III.
Carbon . . .	39.00	39.43	
Hydrogen . . .	5.68	5.45	
Phosphoric acid ...	...	...	38.85

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which lead to the formula

as is seen by the following:—

12 eqs.	Carbon	900·00	39·44	39·22
9 ...	Hydrogen	112·50	4·93	5·56
1 ...	Nitrogen	177·01	7·75	
2 ...	Oxygen	200·00	8·77	
1 ...	Phosphoric acid	892·28	39·11	38·85
1 ...	Pyrophosphate of aniline	2281·79	100·00	

This salt corresponds to the acid pyrophosphate of soda,

analysed by Professor Graham.

An analogous salt of ammonia is not known, pyrophosphate of ammonia existing only in solution, which, according to Graham's experiments, yields on evaporation crystals of the common phosphate of ammonia, with 2 equivalents of the volatile alkali and 1 equivalent of water.

III. METAPHOSPHATE OF ANILINE.

I obtained this salt by adding a great excess of aniline to a very strong solution of metaphosphoric acid (glacial acid perfectly pure), or by adding metaphosphoric acid to a solution of aniline in alcohol or æther; in both cases the salt precipitates, as a gelatinous white mass; this is to be placed on a filter and well-washed with æther, until the excess of aniline is removed and no smell of this body perceived, pressed and dried over sulphuric acid *in vacuo*.

When dry the salt appears as an amorphous white mass, which changes rose-red in the air, becoming glutinous. It is acid to litmus paper, soluble in water, and almost insoluble in alcohol and æther.

Its solution dissolves metaphosphate of silver, which property belongs also to metaphosphate of soda; upon boiling, it changes red, and partly reduces the silver salt. When an aqueous solution is boiled for a long time it is transformed into common phosphate of aniline.

Analysis.

When burnt with oxide of copper—

I. 0·664 grm. of the substance gave 0·976 grm. of carbonic acid and 0·264 grm. of water.

II. 0·994 grm. of the substance, precipitated by acetate of

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lead, and the precipitate treated with sulphuric acid, gave 2·617 grms. of sulphate of lead.

III. I also determined the acid by precipitating with acetate of lead in great excess and boiling for a long time; the metaphosphate of lead is completely changed into the tribasic salt. This is a very advantageous method of determining metaphosphoric acid. 0·5785 grm. of the substance gave 1·3485 grm. of tribasic phosphate of lead.

These numbers correspond to the following per cents. :—

	I.	II.	III.
Carbon	41·33		
Hydrogen	4·55		
Phosphoric acid	...	41·24	40·98

These analyses lead to the formula

as is seen by the following :—

12 eqs. Carbon	900·00	41·48	41·33
8 ... Hydrogen	100·00	4·62	4·55
1 ... Nitrogen	177·01	8·11	
1 ... Oxygen	100·00	4·62	
1 ... Phosphoric acid	892·28	41·17	41·11
1 ... Metaphosphate of aniline	2169·29	100·00	

This salt is analogous to Prof. Graham's metaphosphate of soda,

which, according to the experiments of this chemist, likewise becomes viscid on evaporation, and never presents the slightest trace of crystallization.

The corresponding metaphosphate of ammonia is only known in solution. On evaporation this salt assimilates 1 equivalent of water, passing into the common phosphate with 1 equivalent of ammonia and 2 equivalents of water.

The experiments which I have described prove that there exist the following series of phosphates of aniline :—

Phosphates	$\left\{ \begin{array}{l} 2(\text{HO, C}_{12}\text{H}_7\text{N}) \text{ HO, PO}_5. \\ \text{HO, C}_{12}\text{H}_7\text{N, 2HO, PO}_5. \end{array} \right.$
Pyrophosphate . .	$\text{HO, C}_{12}\text{H}_7\text{N, HO, PO}_5.$
Metaphosphate . .	$\text{HO, C}_{12}\text{H}_7\text{N, PO}_5.$

This series embraces compounds corresponding to all the combinations of soda with phosphoric acid, except the phosphate with 3 equivalents of soda, and the pyrophosphate with 2 equivalents of fixed base.

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The aniline salt, corresponding to the latter, however exists, but could as yet not be obtained in a state of purity.

All the compounds of aniline with phosphoric acid are anhydrous, like the other salts of this base which have been examined by Professor Hofmann. In this respect they differ from the corresponding soda salts, which nearly all contain a larger or smaller amount of water of crystallization. The two ammonia salts of phosphoric acid which we know, are however likewise anhydrous.

From the results of the preceding investigation we may conclude that the organic bases comport themselves also with polybasic acids like mineral oxides. I intend, however, to analyse the phosphates of some other organic alkaloids, particularly of those which occur in nature, and are frequently employed in medicine.