

VII. *Note on the constitution of the phosphates of the Organic Alkalies.* By THOMAS ANDERSON, M.D., *Lecturer on Chemistry, Edinburgh.*

The following observations were made a considerable time since, with the view of clearing up the apparent anomaly in the results obtained by Regnault* in the analysis of the phosphate of strychnine, which he inferred to consist of single equivalents of phosphoric acid and strychnine, without any basic water, except the atom required by the organic base. As this result was entirely incompatible with the known constitution of the inorganic phosphates, it appeared to me desirable to ascertain its correctness; and it was my intention to have further extended the inquiry to the complete investigation of the phosphates of the organic alkalis, but subjects of more interest having intervened, the analyses were laid aside until I should have leisure for extending and completing them, and they had almost escaped my memory, when my attention was recalled to them by the publication of a paper upon the constitution of the phosphates of aniline, by Mr. Nicholson.† At the conclusion of that paper, the author having stated his intention of further pursuing the subject, and investigating the phosphates of the other alkaloids, I again laid my analyses aside, in order that he might have the opportunity of completing what he had begun. As, however, more than a year and a half have now elapsed since Mr. Nicholson's paper was read to the Chemical Society, without the appearance of any further researches by that gentleman, I have resolved to publish my analyses, as a small addition to our knowledge of these salts.

Phosphate of strychnine with one equivalent of strychnine.—This salt is readily obtained by digesting a moderately dilute solution of tribasic phosphoric acid upon strychnine at a gentle heat, so long as it is freely dissolved. On allowing the solution to cool, the salt is leposited in groups of long radiated needles with truncated extre-

* Annales de Chimie et de Physique, vol. 68, p. 150.

† Memoirs of the Chemical Society of London, Part 19, p. 227.

mities, which are easily obtained half an inch long, even from very small quantities of the solution. These crystals are acid to test-paper, and like all the salts of strychnine, excessively bitter to the taste. They dissolve in five or six times their weight of cold water, and in a much smaller quantity of hot. The analysis gave the following results.

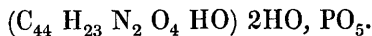
I. 0.3228 grm. dried at 260° gave: 0.699 grm. carbonic acid, and 0.1735 grm. water.

II. 0.4535 grm. dried at 260° gave: 0.9765 grm. carbonic acid, and 0.2435 grm. water.

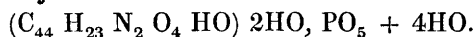
Which correspond with the following numbers per cent. :

	Experiment.		Calculation.		
	I.	II.			
Carbon	59.05	58.72	59.27	C_{44}	3300.0
Hydrogen . . .	5.97	5.96	5.84	H_{26}	325.0
Nitrogen . . .	"	"	6.28	N_2	350.0
Oxygen	"	"	12.58	O_7	700.0
Phosphoric acid .	"	"	16.03	PO_5	892.3
			100.00		5567.3

The formula of the salt is therefore :



0.7516 grammes of crystallized phosphate of strychnine, heated to 260° , lost 0.0598 = 7.95 per cent, corresponding to 4 equivalents of water, the calculated result for which gives 7.42 per cent, and the formula of the crystallized salt is :

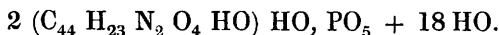


Phosphate of strychnine with two equivalents of strychnine.—If a solution of the salt just described be digested for a long time with an excess of strychnia in fine powder, an additional equivalent of the base is dissolved, and a new salt produced, which is deposited in crystals as the solution cools. In order to obtain it, however, very long continued digestion is necessary, and I have never succeeded in entirely converting the former salt into the latter, a considerable quantity of the acid salt always remaining in the solution. The separation of the two compounds is readily effected by two or three crystallizations, the acid salt being more soluble than that containing two equivalents of base. The latter is deposited from its solutions in the form of rectangular tables, often of considerable size, and sometimes so thin as to be beautifully iridescent. It is not acid to test-paper. The following are the results of the analysis :

0.2798 grm. dried at 260° gave: 0.6805 grm. carbonic acid, and 0.1649 grm. water.

Experiment.		Calculation.		
Carbon	66.31	66.64	C_{88}	6600.0
Hydrogen	6.54	6.18	H_{49}	612.5
Nitrogen	„	7.06	N_4	700.0
Oxygen	„	11.10	O_{11}	1100.0
Phosphoric acid	„	9.02	PO_5	892.3
		100.00		9904.8

0.795 grammes, of the salt dried at 212° , at which temperature the whole of its water of crystallization is expelled, lost $0.143 = 17.6$ per cent, corresponding exactly to 18 HO, the calculated result for which is likewise 17.6 per cent. These analyses give for the formula of the crystallized salt:



The foregoing analyses sufficiently prove that the phosphates of strychnine agree in constitution with the inorganic salts of the acid, and enable us to explain the source of error in Regnault's analysis. He obtained for his phosphate of strychnine:

Carbon	59.85
Hydrogen	5.85

in which result the excess of carbon is no doubt due to his having analysed the acid phosphate mixed with a small quantity of the last described salt, which owing to the long continued digestion necessary for its production in quantity, might easily escape detection unless actually sought for.

I endeavoured to prepare a double phosphate of strychnine and soda, by digesting strychnine in a solution of acid phosphate of soda; but did not succeed in obtaining it.

Phosphate of brucine with two equivalents of brucine.—When tri-basic phosphoric acid is digested upon brucine, rapid solution takes place; and on concentrating and cooling the solution, the salt in question is deposited, in short thick prisms, which have in general a somewhat yellowish colour. The salt is moderately soluble in cold water, and in all proportions in hot. It is neutral to test-paper. The crystals contain a large quantity of water of crystallization, which they lose by efflorescence in the air. When suddenly heated to 212° , they melt in their water, and then solidify into a resinous-looking mass, from which it is difficult to expel the remainder of the water.

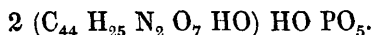
It is advisable, therefore, to remove the greater part of the water over sulphuric acid, and then to complete the drying at 212° .

The analysis gave the following results :

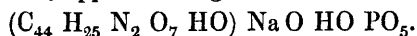
0.3545 grm. dried at 212° gave : 0.8065 grm. carbonic acid, and 0.208 grm. water.

Experiment.		Calculation.		
Carbon	62.05	62.53	C_{88}	6600.0
Hydrogen	6.51	6.27	H_{53}	662.5
Nitrogen	„	6.63	N_4	700.0
Oxygen	„	16.12	O_{17}	1700.0
Phosphoric acid	„	8.45	PO_5	892.3
		100.00		10554.8

corresponding to the formula :



A double phosphate of brucine and soda is readily prepared by digesting brucine with acid phosphate of soda. It crystallizes in short opaque prisms. I was unable to obtain it perfectly pure, but the analysis gave results, approximating to the formula :



Phosphate of quinine with three equivalents of quinine.—Quinine dissolves with great rapidity in warm phosphoric acid, and on cooling, the fluid becomes a solid mass of minute needle-shaped crystals. If the solution be more dilute, it deposits the salt in the form of radiated tufts of silky needles, which are exceedingly thin and soft, and matt together into a mass as they become dry. The salt is perfectly neutral to test-paper. Analysis gave the following results :

0.334 grm. dried at 212° gave : 0.7575 grm. carbonic acid, and 0.205 grm. water.

Experiment.		Calculation.		
Carbon	61.85	61.60	C_{60}	4500.0
Hydrogen	6.81	6.68	H_{39}	487.5
Nitrogen	„	7.18	N_3	525.0
Oxygen	„	12.32	O_9	900.0
Phosphoric acid	„	12.22	PO_5	892.3
		100.00		7304.8

The formula of the dry salt is therefore :



0.548 grm. of the crystallized salt heated to 250° , lost $0.0415 = 7.57$ per cent ; 0.4775 grm. heated to 250° , lost $0.0375 = 7.85$ per

cent ; six equivalents of water of crystallization correspond to .517 per cent, which gives for the crystallized salt the formula :



On another occasion I obtained a salt, the characters of which did not materially differ from those above described, but which lost by a heat of 250° , 15.3 per cent of water ; this agrees with 12 equivalents of water, the calculation for which gives 15.6 per cent. It is probable, therefore, that two different hydrates of this salt exist.

The analyses of these salts are sufficient to establish in a satisfactory manner the general constitution of the phosphates of the organic alkalis, and to show that they agree with the inorganic salts of that acid as well as with the phosphates of aniline described by Nicholson. They contain, however, water of crystallization, which is absent in the phosphates of the latter base ; and in this respect its salts correspond exactly with those of ammonia, while the phosphates of the fixed organic alkalis are more closely analogous to those of the inorganic bases. This peculiarity adds one to the numerous points of relationship subsisting among the volatile bases, and seems at the same time to point to some peculiarity of constitution distinguishing them from the non-volatile members of the class, which may perhaps be of more importance than it at first sight appears. It has always been considered that the organic bases formed an extremely well-marked natural family, agreeing perfectly in their functions and constitution ; but this opinion has been arrived at principally from the observation of their general properties, and scarcely anything has been done in the way of minutely examining their compounds with the view of classifying them, or ascertaining the individual peculiarities of their constitution. The most minute attention has been paid to the examination of the salts of every new acid with the inorganic bases, and their constitution established with very great care, but the discoverer of a new organic base generally contents himself with the analysis of the platinum compound required to determine its atomic weight, and a few observations, sometimes very loose, on the characters of its other salts. It is true that the rarity of many of these substances and the difficulty and expense of obtaining them in sufficient quantity, almost preclude the possibility of a complete investigation ; I apprehend, however, that if the same care which has been bestowed upon the salts with the view of characterizing their acid, were extended to them in relation to their basic constituent, it would afford an important means of classification, and even of indirectly determining the nature of their constitution.

The possibility of this is illustrated by the analyses detailed

above; for it so happens, that the bases whose salts I have examined, may be considered as representing three different classes, according to the number of equivalents of the alkaloid which unite with phosphoric acid to form what may be called its normal salt. Thus, if three portions of phosphoric acid be taken and digested under similar circumstances with quinine, brucine, and strychnine, three, two, and one equivalent of the respective bases will be dissolved. Quinine, therefore, which replaces at once three equivalents of basic water, may be compared to oxide of lead, or the oxides of the heavy metals generally. Brucine may represent the inorganic alkalis which replace two equivalents in their normal compound, while strychnine, which under ordinary circumstances replaces only a single equivalent of water, belongs to a class which has no analogue among the series of inorganic bases.

Feb. 7, 1848.

The President in the chair.

Messrs. T. A. Malone, and J. B. Edwards, were duly elected members of the Society.

The following papers were read :