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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I. *On Hypophosphites.*

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FOR nearly all the facts concerning hypophosphorous acid and its salts, we are indebted to the investigations of Heinrich Rose published in 1827. This celebrated chemist not only determined the composition of the salts and the amount of water belonging to their constitution, but, with regard to the principal purpose of his researches, the gaseous combinations of phosphorus and hydrogen, he also studied the products of decomposition of hypophosphites by heat.

In 1842 Wurtz published a series of analyses of hypophosphites, confirming the fact that two atoms of water belong to their chemical constitution, but the principal object of his papers was to explain his hypothetical views on the constitution of all the acids of phosphorus.

There is no doubt that the history of phosphorus has made essential progress, since the important discoveries of Thomas Graham have elucidated the modifications of phosphoric acid, for it must be remembered that pyro- and meta-phosphoric acids were unknown at the time when H. Rose studied the action of nitric acid and of heat on hypophosphites. It therefore seemed necessary to repeat and extend the former experiments, but before I give the results of my own researches, it may be useful to call attention to the actual state of our knowledge in this part of the science.

According to H. Rose, hypophosphites are changed by nitric acid into *acid* phosphates; and as far as analyses of the products were made, it was evident that *metaphosphates* were formed.

All hypophosphites are decomposed by heat. The products are a phosphate, phosphoretted hydrogen, and water. The phosphate has the oxygen-ratio 2 : 5, and is therefore what we should now designate as a *pyrophosphate*. H. Rose supposed that half of the phosphorus remained in the phosphate, the other half being disengaged in the form of phosphoretted hydrogen. Thus hypophosphite of barium gives—

$$2H_4BaP_2O_4 = Ba_2P_2O_7 + 2H_3P + H_2O.$$

It must, however, be observed that the process of decomposition was determined by numerical experiments of H. Rose only for certain hypophosphites (Ba, Sr, Ca); for the rest it was assumed to take place in like manner. But the nickel and cobalt salts do not follow the general rule: they give hydrogen, phosphoretted hydrogen, and a black residue insoluble in acids. Rose found it to be a phosphate so constituted that we should now call it a mixture of pyro- and metaphosphate.

The phosphoretted hydrogen evolved by the hypophosphites of potassium, barium, strontium, calcium, magnesium, manganese, and lead is, according to H. Rose, self-inflammable; but the zinc, cadmium, nickel, and cobalt salts yield a gas which is not self-inflammable.

My own experiments relate to the hypophosphites of barium, strontium, calcium, magnesium, zinc, manganese, cadmium, lead, cobalt, and nickel, and certain others not hitherto described, viz., those of sodium, thallium, lithium, cerium, and uranium. Their physical properties, crystalline forms, water of crystallisation, volatility at comparatively low temperatures, and principally their mode of decomposition by the action of heat, have been the objects of study.

Hypophosphite of Sodium.

Very small undeterminable crystals, deliquescent in the air, easily soluble, containing 1 mol. of water: $H_2NaPO_2 + aq$. Dried at 200° C., the salt is anhydrous. At a higher temperature it evolves spontaneously inflammable phosphoretted hydrogen, and melts to a white porous mass, containing $Na : P = 5 : 3$ atoms, or

$$Na_5P_3O_{10} = \left\{ \begin{matrix} Na_4P_2O_7 \\ NaPO_3. \end{matrix} \right\}.$$

Hence it follows that—

$$5H_2NaPO_2 = Na_5P_3O_{10} + 2H_3P + 2H_2.$$

and that water cannot appear among the products of decomposition.

Hypophosphite of Thallium.

A solution, prepared with the barium salt and thallium sulphate, yields, after evaporation, small colourless crystals, belonging to the rhombic system, combinations of a rhombic octahedron, $o_{+} = a : b : c$, the prism $p = a : b : \infty c$, and the face $b = b : \infty a : \infty c$.

$$a : b : c = 0{\cdot}786 : 1 : 0{\cdot}805.$$

		Calculated.	Observed.
o 2A	=	121° 18′	121° 0′
2B	=	102° 50′	103° 0′
2C	=	105° 0′	—
$p : p$	=	—	× 103° 40′
b	=	118° 10′	—
o	=	—	× 142° 30′
$o : b$	=	119° 21′	—

The crystals are prismatic. They melt at 150°, but do not lose any essential amount of water.

H_2TlPO_2.

				Calculated.	Found.
2H	=	2	=	0·74	—
Tl	=	204	=	75·84	74·30
P	=	31	=	11·52	11·86
2O	=	32	=	11·90	—
		269		100·	

The mode of decomposition by heat is the same as in the case of the sodium salt; the white residue = 94·60 C., containing 6·73 P (6·9 found), is likewise—

$$Tl_5P_3O_{10} = \left\{ \begin{array}{l} Tl_4P_2O_7 \\ TlPO_3. \end{array} \right\}$$

Hypophosphite of Lithium.

Prepared in a similar manner; the solution yields very small crystals of the monoclinic system, showing the faces—

$q = b : c : \infty a$ $\qquad a = a : \infty b : \infty c.$

$r' = a' : c : \infty b$ $\qquad c = c : \infty a : \infty b.$

$$a : b : c = 0{\cdot}623 : 1 : 1{\cdot}952$$

$$o = 79° \; 52'$$

		Calculated.	Observed.
$q : q$	=	—	× 55° 0′
c	=	117° 30′	117° 22′
a	=	94° 40′	—
$a : c$	=	—	× 100° 8′
r'	=	136° 12′	136° 5′
$c : r'$	=	—	× 123° 40′
$q : r'$	=	91° 28′	—

These crystals are prismatic by predominance of the faces a, c, r' of the vertical zone. They are colourless and transparent, but deliquescent in moist air, and easily soluble.

$$H_2LiPO_2 \cdot + \text{aq.}$$

		Calculated.		Found.
2H	=	2	= 2·22	—
Li	=	7	= 7·77	7·04
P	=	31	= 34·44	34·09
2O	=	32	= 35·57	—
aq.	=	18	= 20·00	21·50
		90	100·	

Dried at 200°, the salt is anhydrous. When heated, it gives phosphoretted hydrogen and hydrogen, and leaves a white fusible residue (76·3 per cent.).

$$Li_9P_5O_{17} = \left\{ \begin{matrix} 2Li_4P_2O_7 \\ LiPO_3. \end{matrix} \right\}$$

containing

	Containing.	Found.
Li	12·86	12·74
P..........	31·63	31·74
O..........	55·51	—
	100·	

Hypophosphite of lithium is decomposed by heat in the following manner:—

$$9H_2LiPO_2 = Li_9P_5O_{17} + 4H_3P + 2H_2 + H_2O.$$

Hypophosphite of Ammonium.

This salt forms rhombic crystals, which are combinations of an octahedron with the faces *a* and *b*.

	Measured.	Calculated.
o { 2A =	—	× 146° 20′
2B =	63° 0′	—
2C =	128° 36′	—
o : *a* =	—	× 148° 30′
b =	106° 50′	107° 0′

Thin plates by the faces *b*; fracture easily obtainable in the direction of *a*.

$$a : b : c = 0·339 : 1 : 0·665$$

Deliquescent in the air.

I found 37·5 per cent. of phosphorus, while the formula $H_2Am_2PO_2$ requires—

$$\begin{array}{rcrcr} 2H & = & 2 & = & 2{\cdot}41 \\ Am & = & 18 & = & 21{\cdot}69 \\ P & = & 31 & = & 37{\cdot}35 \\ 2O & = & 32 & = & 38{\cdot}55 \\ \hline & & 83 & & 100{\cdot} \end{array}$$

Under the influence of heat decomposition takes place, ammonia and phosphoretted hydrogen being evolved (the latter is for the most part not spontaneously inflammable), and a glassy mass of phosphoric acid remaining.

As I found that 100 parts of the salt give 55·2 of residue containing 20·16 phosphorus, it seems that the residue is formed by—

$$\left\{ \begin{array}{c} H_4P_2O_7 \\ 2H\,PO_3 \end{array} \right\}$$

because that supposition would require 57·67 per cent of residue = 21·34 P.

$$7H_2AmPO_2 = H_6P_4O_{13} + H_2O + 7NH_3 + 3PH_3 + 2H_2.$$

Hypophosphite of Barium.

The methods of preparing this salt are well known, but the crystals are very rarely well formed. They belong to the monoclinic system, and show combinations of the faces—

$$\frac{o}{2} = a : b : \tfrac{1}{2}c \qquad p = a : b : \infty c \qquad a = a : \infty b : \infty c$$

$$\frac{o'}{2} = a' : b : \tfrac{1}{2}c \qquad q = b : c : \infty a \qquad c = c : \infty a : \infty b$$

$$s = \tfrac{1}{2}a : b : c \qquad r = a : c : \infty b$$

$$r' = a' : c : \infty b$$

$$\frac{r'}{2} = 2a' : c : \infty b$$

$$a : b : c = 1{\cdot}575 : 1 : 2{\cdot}00$$

$$o = 79^\circ\ 40'$$

	Calculated.	Observed.
$p : p =$	65° 40′	—
$c =$	95° 35′	—
$q : q =$	—	× 53° 40′
$a =$	94° 39′	94° 30′
$a : c =$	—	× 100° 20′
$r =$	—	× 145° 50′
$r' =$	137° 57′	137° 30′

	Calculated.	Observed.
$c : r =$	134° 30′	134° 15′
$r' =$	121° 43′	122° 30′
$\frac{r'}{2} =$	144° 49′	145° 8′
$p : r =$	116° 39′	116° 30′
$r' =$	113° 44′	—
$q : r =$	108° 27′	109° 15′ appr.
$r' =$	103° 44′	104° 20′
$s : s =$	111° 32′	112° 0′
$a =$	141° 2′	140° 55′
$c =$	114° 35′	114° 42′
$q =$	133° 37′	133° 10′

The crystals are prisms *a*, *c*, *r*, *r′*, terminated by *q* and *s*, the faces *p*, $o\frac{1}{4}$, $o'\frac{1}{2}$ being extremely small. They are colourless and transparent, unalterable in air and at temperatures under 100°.

My own experiments agree with those of Wurtz with regard to the composition of the salt, which contains 1 molecule of water.

$$H_4BaP_2O_4 + aq.$$

			Found.
4H =	4 =	1·40	—
Ba =	137 =	48·07	48·01
2P =	62 =	21·75	22·56
4O =	64 =	22·47	—
aq. =	18 =	6·31	6·28
	285	100·	

100 parts treated with nitric acid yielded 103·5 metaphosphate of barium, BaP_2O_6.

When the anhydrous salt is heated in closed vessels, it becomes reddish, gives off inflammable phosphoretted hydrogen, yields a small quantity of yellow phosphorus, and leaves a residue weighing 87·0—87·4 per cent. Hydrochloric acid dissolves it, leaving only a certain quantity of red phosphorus. The composition of the whole was indicated by several analyses, one of which gave—

Phosphorus, free	1·50 =	—
"	12·41 =	14·45
Barium	50·97 =	59·34
Oxygen	22·52 =	26·21
	87·40	100·

Such is the composition of a substance hitherto considered as a pyrophosphate. But the difference, though not great, is evident. In pyrophosphate Ba : P = 1 : 1 atom; 59·34 Ba would then require 13·43 P, while the proportion of the two elements actually found is 13 : 14.

Another test for the assumption that the phosphate cannot be pure pyrophosphate is to be found in its quantity.

$H_4BaP_2O_4$ would give 83 per cent. $Ba'_2P_2O_7$, whereas the experiments have given 85 per cent., or a little more (without the unmixed free phosphorus).

It may therefore be stated that the substance, generated by ignition of hypophosphite of barium is—

$$Ba_{13}P_{14}O_{48} = \left\{ \begin{matrix} 6Ba_2P_2O_7 \\ BaP_2O_6 \end{matrix} \right\}$$

or 6 mol. of pyrophosphate and 1 mol. of metaphosphate. 100 parts of the anhydrous salt should then give 85·9 of these phosphates, and 100 parts of them should contain—

P	14·55
Ba	59·73
O	25·72
	100·

agreeing well with the results of analysis.

Hypophosphite of barium then gives by the action of heat—

$$13H_4BaP_2O_4 = Ba_{13}P_{14}O_{48} + 12H_3P + 4H_2 + 4H_2O.$$

As a part of phosphorus appears in the free state, it is evident that the proportion of free hydrogen will be greater. The water produced being equal to 2 per cent. of the salt, it would be nearly impossible to determine it in a satisfactory manner.

We shall see in the course of these researches, that pure pyrophosphate is not produced by any hypophosphite, but the barium salt yields when heated a residue which approximates closely thereto. It will therefore easily be understood that H. Rose 45 years ago was led to erroneous conclusions on this point, by not extending his quantitative experiments on the nature of the phosphates formed by ignition of hypophosphites to a greater number of salts.

Hypophosphite of Strontium.

By evaporating a solution of carbonate in free hypophosphorous acid, white crystalline crusts are obtained, much less soluble than the barium salt. They contain $H_4SrP_2O_4$ + aq., and give off 7·64 per cent. of water at 200°.

100 parts of the anhydrous salt, decomposed by heat, gave 88·9 of a residue containing 39·32 strontium, 16·4 phosphorus in combination and 3·06 in the free state. Supposing the atomic ratio of Sr : P to be 7 : 8, the substance would be—

$$Sr_7P_8O_{27} = \left\{ \begin{matrix} 3Sr_2P_2O_7 \\ SrP_2O_6 \end{matrix} \right\}$$

and the process of decomposition—

$$7H_4SrP_2O_4 = Sr_7P_8O_{27} + 6H_3P + 4H_2 + H_2O.$$

Hypophosphite of Calcium.

According to Wurtz, the crystals of this salt are anhydrous, and I myself have obtained the same result. No loss at 200°; Ca = 23·75, P = 36·55 per cent., corresponding with the formula $H_4CaP_2O_4$.

The system of crystallisation is monoclinic; observed faces—

$o' = a' : b : c$ $\qquad a = a : \infty b : \infty c$
$s' = 3a' : b : c$ $\qquad b = b : \infty a : \infty c$
$3p = 3a : b : \infty c$ $\qquad c = c : \infty a : \infty b$
$r' = a' : c : \infty b$

$$a : b : c = 0{\cdot}8693 : 1 : 1{\cdot}200$$
$$o = 75^\circ\ 12'$$

	Calculated.	Observed.	
		Rammelsberg.	Schabus.
$o' : o' =$		× 103° 40′	103° 56′
$s' : s' =$	80° 52′	—	—
$3p : 3p =$	43° 16′	—	—
$a : c =$	—	× 103° 40′	—
$r' =$	139° 20′	—	—
$o' : a =$	—	× 126° 25′	126° 35′
$c =$	110° 1′	—	—
$s' : a =$	97° 44′	99° 30′	99° 37′
$c =$	125° 24′	125° 50′	—
$o' =$	151° 3′	152° 30′	—

The crystals become tabular by the extension of face *a;* they are transparent and flexible, and undergo no change on exposure to the air.

Their behaviour when heated is like that of the strontium salt; they gave 79·35—79·8 per cent. phosphates, and 4·4 of free phosphorus. The phosphates contained Ca 29·22—29·43, and P 25·79—26·04; they are consequently—

$$Ca_7P_8O_{27} = \left\{ \begin{matrix} 3Ca_2P_2O_7 \\ CaP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Magnesium.

Very fine regular octahedrons, with the faces of the cube, containing 6 mol. of water, $H_4MgP_2O_4 + 6aq.$, according to the experiments of H. Rose, Wurtz, and my own.

After drying at 200°, the salt yields, when heated, a gas which is for the most part not spontaneously inflammable. The white residue becomes reddish on cooling, and dissolves easily in acids, while a small portion of phosphorus is separated. Experiment gave 4·2 P and 80·7 phosphates = Mg 16·15, P 22·63. Hence we may calculate for the phosphates—

$$Mg_5P_6O_{20} = \left\{ \begin{matrix} 2Mg_2P_2O_7 \\ MgP_2O_6 \end{matrix} \right\}$$

and the process will be—

$$5H_4MgP_2O_4 = Mg_5P_6O_{20} + 4H_3P + 4H_2.$$

Hypophosphite of Zinc.

Isomorphous with the former, it has the composition $H_4ZnP_2O_4 + 6aq.$, as Wurtz has determined by analysis.

Decomposed by heat, the anhydrous salt leaves 85·38 per cent. = Zn 33·86, P 18·94, O 32·58, besides 0·88 free phosphorus, or the same phosphates as the magnesium salt—

$$Zn_5P_6O_{20} = \left\{ \begin{matrix} 2Zn_2P_2O_7 \\ ZnP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Manganese.

Very small reddish crystals, the form of which I could not determine; easily soluble; containing, according to Wurtz, 8·86 per cent. of water (9·85 in my own experiment), and therefore $H_4MnP_2O_4 + aq.$

On heating the anhydrous salt a gas evolved, which for the most does not take fire on coming in contact with the air. The white residue becomes reddish on cooling, contains 2·82 of free phosphorus and 81·07 of phosphates = Mn 29·73, P 20·14, O 31·20; it is therefore like the former—

$$Mn_5P_6O_{20} = \left\{ \begin{matrix} 2Mn_2P_2O_7 \\ MnP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Cerium.

By decomposing the barium salt with sulphate of cerium, white crystalline crusts are obtained, difficultly soluble in water. Analysis gave Ce 39·22, P 26·43, aq. 4·81, corresponding to the formula, $3H_4CeP_2O_4 + 2aq.$

The products of decomposition by heat were 2·87 free phosphorus and 84·95 phosphates = Ce 41·44, P 16·07, which agrees with—

$$Ce_7P_8O_{27} = \left\{ \begin{array}{c} 3Ce_2P_4O_7 \\ CeP_2O_6 \end{array} \right\}$$

like the strontium and calcium salts.

Hypophosphite of Cadmium.

This salt is very much like the cerium or strontium salt, but contains no water of crystallisation. It gives a greyish or reddish residue = 0·34 phosphorus, and 86·5 phosphates = Cd 46·28 and P 14·30, or like the former, 3 mol. of pyrophosphate and 1 mol. of metaphosphate of cadmium.

Hypophosphite of Lead.

The lead salt forms thin splendent scales, dissolves with difficulty in water, is anhydrous, and, according to H. Rose, contains $H_4PbP_2O_4$.

The product of decomposition appears white, and contains no free phosphorus. I obtained 89·48 per cent. = Pb 60·56 and P 10·18, or

$$Pb_9P_{10}O_{34} = \left\{ \begin{array}{c} 4Pb_2P_2O_7 \\ PbP_2O_6 \end{array} \right\}$$

Hence the process must be

$$9H_4PbP_8O_4 = Pb_9P_{10}O_{34} + 8H_3P + 4H_2 + 2H_2O.$$

Wurtz has stated that the salt is changed by an excess of oxide of lead into phosphite, believed by H. Rose to be a basic salt.

Hypophosphite of Cobalt.

Very fine crystals, brownish, regular octahedrons, isomorphous with the magnesium and zinc salt, containing 6 mol. of water. Now Wurtz has determined by analysis, and I have also found, that 36·2 per cent. of water goes off at 120°—130°. If the temperature rises to 150°, decomposition begins, the salt becomes black, and the evolved gas does not for the most take fire spontaneously in the air. From the anhydrous salt 91·7 per cent. of residue were obtained.

This substance treated with strong nitric acid, is oxidized, and after evaporation its weight is augmented by 12·9 per cent. Hence it is evident that the whole is a mixture of phosphate and *phosphide* of cobalt, containing Co 34·04 P 29·95, and O 36·01. The atomic ratio of Co : P is therefore 3 : 5 and Co : O = 1 : 4, as in hypophosphite, and I suppose the substance to be

$$Co_3P_5O_{12}, \text{ or } \left\{ \begin{array}{c} 2CoP_2O_6 \\ CoP \end{array} \right\}$$

and the process

$$3H_4CoP_2O_4 = Co_3P_5O_{12} + H_3P + H_9.$$

H. Rose, in determining only the amount of cobalt in the residue, supposed it to be a mixture of pyro- and metaphosphate, coloured by black phosphorus; but from my own experiments I am convinced that such an admission does not agree with the behaviour of the substance and its composition.

Hypophosphite of Nickel.

Green crystals of the same form, combined with the faces of the cube; their isomorphism, and the analyses made by Wurtz and by myself, establish the formula, $H_4NiP_2O_4 + 6$ aq. At 100° the water is driven off; at 140° decomposition takes place; no inflammable gas is evolved and a black residue = 92·3 per cent. remains. As I found that this salt is exactly like the cobalt salt, and contains Ni 33·49, P 30·88, and O 35·63, it is evidently of the same nature, *i.e.*, $\left\{\begin{array}{c} 2NiP_2O_6 \\ NiP \end{array}\right.$.

Hypophosphite of Uranium.

When the yellow precipitate of uranium-nitrate by ammonia is digested with free hypophosphorous acid, it is changed into a yellow crystalline salt, very difficultly soluble in water.

100 parts gave 39 parts of water, at temperatures of 100°—200°. By treatment with nitric acid, 102·4 of metaphosphate were obtained, proved by analysis to be UPO_4; therefore the hypophosphite is $H_4(U_2O_2)P_2O_4 +$ aq., containing like the other salts, the radical uranyl, U_2O_2, and $U : O = 1 : 3$, while in the foregoing salts the atomic ratio $P : O$ is always $1 : 4$.

For this reason the uranyl hyposulphite differs essentially from the other hypophosphites in its decomposition by heat. No phosphorus is evolved, only hydrogen being set free; the uranyl salt is changed into a uranous salt, and the remaining product contains $U : P : O = 1 : 1 : 3$, like the hypophosphite itself. The process of decomposition, or the disengagement of hydrogen, is accompanied by a detonation, and the residue is a very porous mass of greenish colour. It dissolves in nitric acid, by which it is oxidized. I found U 61·37 and P 13·74 per cent., or UPO_3, and hence suppose the whole to be $\left\{\begin{array}{c} 3U_2P_2O_7 \\ UP_2O_6 \\ U_2P \end{array}\right\}$, or a mixture of pyro-phosphate, metaphosphate, and phosphide of uranium.

$$H_4(U_2O_2)P_2O_4 = 2UPO_3 + 2H_2.$$

The product of oxidation of UPO_3 by nitric acid is uranyl metaphosphate, $UPO_4 = (U_2O_2)P_2O_6$.

The results of my experiments on hypophosphites are in general the following:—These salts crystallise anhydrous (Tl, Ca, Cd, Pb), or, combined with water, the amount of which is 1 mol. (Na, Li, Ba, Sr, Mn, U), or 6 mol. (Mg, Zn, Ni, Co).

All are decomposed by heat.

1. The ordinary manner is that *pyrophosphate and metaphosphate* are formed, but the relative quantities of the two vary from 1 : 1 mol. (Na, Tl) to 2 : 1 mol. (Mg, Zn, Mn), 3·1 mol. (Sr, Ca, Ce, Cd), 4 : 1 mol. (Pb), and 6 : 1 mol. (Ba).

2. *Metaphosphate and phosphide* are formed. (The nickel and cobalt salts.)

3. *Pyrophosphate, metaphosphate, and phosphide* remain. (The uranyl salt.)

It is now easy to understand the difference between my results and those of H. Rose. This celebrated chemist had directed his attention principally to the nature of the phosphoretted hydrogen produced by these salts; his analytical researches on the remaining products were incomplete, and he had not studied those of the alkali-salts, which would have shown him that they are not at all pure pyrophosphates.

The gaseous products of the decomposition of hypophosphites being always a mixture of hydrogen and phosphoretted hydrogen, the inflammability of the gas is of no importance, and seems to vary according to circumstances. I also believe that the separation of phosphorus is due to the process itself, and does not depend on the decomposition of phosphoretted hydrogen, for I observed very often that phosphorus appears at the beginning of the process, while the temperature is not sufficient for the decomposition of phosphoretted hydrogen.

Phosphorous and hypophosphorous acid, phosphites and hypophosphites, are very much alike, notwithstanding that an essential difference exists in the products of their decomposition by heat. Phosphites give pure pyrophosphates, or a mixture of those salts with phosphides (Co, Pb, Mn, Zn), in consequence of the ratio of $R'' : H = 1 : 2$ or $1 : 1$. Phosphites leave no phosphorus: therefore in the products, $R'' : P = 1 : 1$, as in the original salts. They also give only hydrogen, while hypophosphites give hydrogen and phosphoretted hydrogen, the uranyl salt being the only one which resembles the phosphites in this respect.

The whole of the oxygen of phosphites is contained in the newly formed pyrophosphate, consequently water is never set free. The same takes place only in those hypophosphites which give

$$\left\{\begin{matrix} R'_4P_2O_7 \\ R'PO_3 \end{matrix}\right\} \text{ or } \left\{\begin{matrix} 2R''_2P_2O_7 \\ R''P_2O_6 \end{matrix}\right\}$$

or in the salts of Co, Ni, U, which yield phosphates and phosphides. In the other cases a certain portion of the oxygen is required to form a relatively small quantity of water.