[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF PENNSYLVANIA]

The Alkali Metal Phosphides. II. Certain Chemical Properties of Tetrasodium Diphosphide[1,2]

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Tetrasodium diphosphide forms a diammonate, stable at room temperature, which undergoes decomposition when heated evolving hydrogen and ammonia. When treated with water the substance hydrolyzes forming phosphine, hydrogen and a non-volatile residue containing phosphorus. It undergoes reduction in liquid ammonia when ammonium bromide is added to a solution containing both the diphosphide and sodium metal. Reaction takes place according to the equation: $Na_4P_2 + 2Na + 4NH_4Br = 2NaPH_2 + 4NaBr + 4NH_3$. The formation of the dihydrophosphide ion is made evident by its conversion to methylphosphine when the resulting solution is treated with methyl iodide. The reactions of tetrasodium diphosphide with salts of copper, silver and lead have also been studied in liquid ammonia.

I. Introduction

In the preceding paper of this series[3] a method was described for preparing certain of the alkali metal phosphides by treating the metals with white phosphorus in liquid ammonia at its boiling point. The sodium compound having the highest metal to phosphorus ratio was, empirically, Na_2P; the present paper is concerned with certain of the chemical properties of this compound. In particular, data presented herewith indicates that the compound is dimeric and that it may be considered formally a salt of the pseudo-acid, biphosphine,[4] H_4P_2.

II. Reduction of Tetrasodium Diphosphide

Although tetrasodium diphosphide in liquid ammonia is unaffected by dissolved metal,[3] it undergoes reduction when an ammonium salt is added to a solution containing both the diphosphide and sodium metal. Reduction occurs in the sense of the following ionic equation, where e^- is the solvated electron

$$P_2^{-4} + 2e^- + 4NH_4^+ = 2PH_2^- + 4NH_3 \qquad (1)$$

The formation of the dihydrophosphide ion is made evident on treating solutions resulting from (1) with additional ammonium bromide, phosphorus being evolved largely as phosphine according to the equation

$$PH_2^- + NH_4^+ = PH_3 + NH_3 \qquad (2)$$

or, if solutions from (1) are treated with methyl iodide, methylphosphine is formed as shown by the equation

$$PH_2^- + CH_3I = CH_3PH_2 + I^- \qquad (3)$$

Seemingly, this is the first example in which the proton facilitates the reduction of an inorganic compound in liquid ammonia although such reductions occur fairly commonly in the case of organic compounds.[5]

Experimental

1. **Reduction of Tetrasodium Diphosphide.**—The sodium salt was prepared as described previously[3] and sodium was added to the solution to yield a free metal to salt ratio of two moles to one; then finely divided ammonium bromide was introduced slowly from a weighed addition tube.[6] As the reaction neared completion the solution became lighter blue in color and was tinged with green; finally, there was an abrupt change to light yellow marking the completion of the reduction. The addition tube was then weighed and the amount of ammonium bromide consumed in the reaction was determined by difference. The results of four such experiments are presented in Table I.

TABLE I

REDUCTION OF TETRASODIUM DIPHOSPHIDE

Expt. no.	Free Na	Millimoles Na_4P_2	NH_4Br	Mol. ratio, NH_4Br/Na_4P_2
56	1.52_8	0.763_8	3.035	3.97
58	1.48_9	$.744_3$	3.011	4.05
61	1.48_1	$.740_8$	2.960	4.00
62	3.64_3	1.821	7.430	4.08

It is evident that the data in Table I support the reaction as represented by Eq. (1). There was no side reaction involving the production of molecular hydrogen. The nature of the reaction product, PH_2^-, as shown in Eq. (1) was established by treating solutions from the expts. given in Table I with additional ammonium bromide or with methyl iodide as explained below.

2. **Preparation of Phosphine.**—The solutions obtained after completing Expts. (56) and (58) (Table I) were treated with excess ammonium bromide. Gases which evolved were passed through water to remove ammonia and then were drawn through a trap cooled with liquid air by means of a Toepler pump. A relatively small amount of noncondensable gas (1–2 ml., S.T.P.) was isolated which probably came from the water. The condensable fraction was passed over moist phosphorus pentoxide to remove residual ammonia and water and was characterized by standard procedures.

The following results were obtained in the case of Expt. (56): ml., S.T.P., 20.3; g., 0.0308; mol. wt. found, 34.0, calcd. for PH_3, 34.0; yield, 59%. The phosphorus content of the residue was determined using the procedure described previously[3]: g. $Mg_2P_2O_7$, 0.0262; mmole P, 0.237 or 15%; P unaccounted for, 0.368 mmole or 25%. Substantially the same results were obtained in the case of Expt. (58). Apparently the reaction proceeds fairly quantitatively according to Eq. (2); the phosphorus unaccounted for undoubtedly represents losses attending the isolation of the phosphine.

3. **Preparation of Methylphosphine.**—After completing Expts. (61) and (62) of Table I, ammonia was evaporated and toluene was pumped off at room temperature. Methyl iodide, 20% in excess of the amount called for by Eq. (3) was condensed on the dry product cooled with liquid air. Next, approximately 15 g. of ammonia was frozen in the reaction vessel and the system was exhausted to a high vacuum. The reaction vessel was closed off and the liquid air was replaced with a bath of liquid ammonia. The solution was allowed to stand for several hours to ensure complete reaction of excess methyl iodide with the ammonia.

The bulk of ammonia was separated from the methylphosphine by absorption in sodium iodide cooled to 0°. Re-

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(1) Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Detroit, Michigan, April, 1950.

(2) This paper is based on research supported by the Office of Naval Research under Contract N8onr-74200.

(3) E. C. Evers, THIS JOURNAL, **73**, 2038 (1951).

(4) This hydride has been referred to variously as hydrogen hemiphosphide, dihydrogen phosphide or liquid phosphine, but the name biphosphine would seem more suitable; the arsenic analog, for example, is called biarsine. In the case of the alkali metal derivatives of phosphine, it is suggested that the anions, PH_2^{-1} and PH^{-2}, be called the dihydro- and monohydrophosphide ions, respectively.

(5) G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

(6) C. A. Kraus and E. D. Carney, THIS JOURNAL, **56**, 765 (1934).

sidual ammonia was removed by passing the gas through absorption tubes filled with anhydrous magnesium perchlorate. The gaseous product was weighed and characterized and residual material in the reaction vessel was analyzed for phosphorus. The following results were obtained. Expt. (6): *Product*, g., 0.0431; ml., S.T.P., 20.2; mol. wt. found, 47.8, calcd. for CH_3PH_2, 48.0; yield 62%. When the gas was passed over moist phosphorus pentoxide to test for traces of ammonia, it was practically quantitatively absorbed. *Residue*, g. $Mg_2P_2O_7$, 0.0082; mmole P, 0.04. Expt. (62): *Product*, g., 0.1075; ml. S.T.P., 50.3; mol. wt. found, 47.9; yield 62%.

In the case of Expt. (61) the reaction vessel was weighed before and after the completed reaction. The weight of residue was 1.269 g.; assuming complete conversion to methylphosphine the calcd. wt. of residue was 1.274 g. Judging from this result and the analysis for residual phosphorus, the conversion of phosphorus to methylphosphine was essentially quantitative. As with phosphine, the low yield of methylphosphine may well be attributed to losses attending its isolation.

4. **Vapor Pressure of Methylphosphine.**—The methylphosphine produced in Expt. (62) was fractionated in a "Stock-type" high vacuum apparatus. The vapor pressure of the purified material was determined as a function of temperature; when treated by the method of least squares these data led to the equation

$$\log_{10} P(\text{mm}). = -1158/T + 7.402 \qquad (4)$$

The b.p. (extrapolated) was −17.1° as compared with a value of −14° reported by Hofmann[7]; ΔH (vap.) was 5300 cal./mole and Trouton's constant, 20.7 cal./mole/deg.

Five pressure measurements covering the range of vapor volumes of from 4 to 20 ml. were made at each temperature. The variation in pressure between the extremes in vapor volumes was approximately 2%, being higher at the smaller volumes. Pressures were read to the nearest 0.1 mm. by means of a cathetometer; temperatures were measured to the nearest 0.25° using a calibrated copper–constantan thermocouple. Constant temperature baths were prepared by partially freezing various substances. Average values for the experimental vapor pressures are given in Table II; included are pressures computed by means of Eq. (4).

TABLE II

VAPOR PRESSURE OF METHYLPHOSPHINE

Temp., A.	189.0	194.9	209.6	228.8	237.5	250.3
P (mm.) exptl.	19.3	28.7	73.2	213.7	337.8	605.1
P (mm.) calcd.	18.8	28.8	75.3	219.3	335.7	597.0

5. **Reaction of Tetrasodium Diphosphide with Ammonium Bromide.**—When a solution of the diphosphide in liquid ammonia was treated directly with ammonium bromide a faint but perceptible change in color from orange-yellow to yellow occurred after the addition of approximately two equivalents of bromide. Since the exact point of color change was somewhat difficult to judge visually, there was a tendency to add more than the required amount of ammonium bromide; in four experiments, the mole ratio of added ammonium bromide to diphosphide was 2.26, 2.26, 2.16 and 2.28, respectively. It was noted further that phosphine was not evolved until this end-point was passed. For example, in an experiment in which two equivalents of ammonium bromide was added, 4.2% of the phosphorus was recovered as phosphine when the solvent was evaporated. But what was particularly striking, and this has direct bearing on the elucidation of the reduction process, when somewhat less than two equivalents of sodium was added to a solution prepared as above the blue color of free metal persisted on standing overnight.

When more than two equivalents of ammonium bromide was added to a solution of the diphosphide phosphine was evolved immediately. With four or more equivalents the yield of phosphine ranged from 40 to 50%; evaporation of the solvent left a reddish-black residue which could be redissolved in liquid ammonia forming a red colored solution. Entirely analogous results were obtained using water in place of ammonium bromide, but the yield of phosphine was higher (60%) and quite reproducible. Permanent gases were not produced in these reactions.

Discussion

From the results given above it would seem apparent that a hydride is formed, which is unstable in liquid ammonia and disproportionates yielding phosphine as the volatile product, when a solution of the sodium compound in liquid ammonia is treated with four or more equivalents of ammonium bromide or water. Furthermore, it would seem apparent that the addition of protons to the diphosphide anion takes place step-wise in view of the color change exhibited by the metal phosphide solutions on the addition of two equivalents of ammonium bromide, the small loss of phosphorus as phosphine which attends this addition, and the apparent stability of the resulting solutions toward the reducing action of dissolved metal. These results may be accounted for by the successive reactions

$$P_2^{-4} + 2NH_4^+ = HPPH^{-2} + 2NH_3 \qquad (5)$$

$$HPPH^{-2} + 2NH_4^+ = H_4P_2 + 2NH_3 \qquad (6)$$

followed by the disproportionation of the hydride, biphosphine.

In support of the above hypothesis we have prepared biphosphine and have found it to decompose rapidly in liquid ammonia yielding phosphine and a reddish colored solution from which a black solid was obtained on evaporating the solvent.[8] Qualitatively, these results parallel those obtained on treating the sodium salt with an excess of ammonium bromide or water. Moreover, the yield of phosphine (60%) was the same as that obtained on treating the sodium salt with water in liquid ammonia. Consequently, there seems little doubt that biphosphine is the end-product of the reaction of the diphosphide ion with protons.

Although several alternative mechanisms may be offered to account for the course of the reduction reaction it seems fairly evident from the data in Table I that direct reduction is not effected by "nascent" hydrogen, which could arise through reaction of ammonium ions with metal, since we should then expect reduction to take place according to the equation

$$P_2^{-4} + 2NH_4^+ + 2e^- = 2PH^{-2} + 2NH_3 \qquad (7)$$

Furthermore, these data, together with the results discussed above, serve to establish with reasonable certainty that more than two protons must be added to the diphosphide ion before the electrons have complete access to the P–P bond; otherwise, we should again expect reaction to occur in the sense of Eq. (7). Experimentally, it was observed that when ammonium bromide was added to a solution containing two moles of sodium per mole of diphosphide the blue color due to free metal was plainly evident until exactly *four equivalents of ammonium bromide had been added.* Evidently the

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[7] A. W. Hofmann, *Ber.*, **4**, 605 (1871).

[8] Unpublished observations. This residue appears to be the black "salt," $H_2P_6 \cdot xNH_3$, described by A. Stock and co-workers (*Ber.*, **42**, 2853 (1909)), which was obtained together with phosphine when the solid hydride, H_6P_{12}, was treated with liquid ammonia. The results of more extended investigations with the various phosphorus hydrides will be made available shortly.

stability of the intermediate ion, $HPPH^{-2}$, prevents reaction in the sense of Eq. (7).

In light of the above discussion the most reasonable course open for reduction seems through stepwise conversion to biphosphine[9] followed by reduction and bond rupture according to the equation

$$H_2PPH_2 + 2e^- = 2PH_2^- \qquad (8)$$

III. Certain Other Chemical Properties of Tetrasodium Diphosphide

1. **Decomposition of the Solvate.**[10]—Tetrasodium diphosphide precipitates as the diammonate when ammonia is evaporated. The solvated ammonia is held very strongly and cannot be removed at room temperature by continued suction with a mechanical pump. On heating, the solvate decomposes yielding both hydrogen and ammonia. Decomposition becomes apparent somewhat above room temperature and at 150° both hydrogen and ammonia are evolved fairly rapidly; after the rate becomes inappreciable at this temperature heating to 375° produces small additional amounts of the two gases.[11]

After preparing the alkali metal phosphide, ammonia was evaporated and toluene was removed by suction at room temperature. The material lost weight extremely slowly *in vacuo* attesting to the high stability of the solvate. The product was analyzed for nitrogen using the Kjeldahl method with the following results. Expt. (19), mmoles Na_4P_2, 1.647; meq. NH_3 found, 3.22; NH_3/Na_4P_2, 1.95. Expt. (20), 1.518; 2.90; 1.91, respectively. From these data it is evident that the solvate has the formula, $Na_4P_2 \cdot 2NH_3$.

Gaseous products from the thermal decomposition were collected over mercury in an eudiometer tube. Condensable gas was largely ammonia as shown by its molecular weight and the fact that it was practically quantitatively absorbed by moist phosphorus pentoxide; non-condensable gas was hydrogen. The data averaged over four experiments follow; the spread in the data is indicated by the quantities in parentheses: mmole Na_4P_2, 0.933; non-cond. gas, ml. S.T.P., 20.4; mol. wt., 2.86; cond. gas, ml. S.T.P., 22.7; mol. wt., 18.6. Mol. gas/mol. Na_4P_2: non-cond., 1.00 (0.9–1.2); cond., 1.10 (0.9–1.3); total, 2.10 (1.8–2.3). From these results it is seen that hydrogen and ammonia were evolved in roughly equal molar amounts and that the total quantity of gas collected was approximately two moles per mole of diphosphide. These results imply that (1) one mole of solvated ammonia reacts with one mole of diphosphide liberating one mole of hydrogen and leaving a residual NH group, and (2) the solvate contains two molecules of ammonia in agreement with direct analysis.

In a further experiment a sample of the sodium compound was heated to 375° in an atmosphere of ammonia with the expectation that ammonolysis might proceed somewhat further. Although some additional reaction was realized the results were not greatly different than those given above. The following results were obtained; in addition, the residue was analyzed for nitrogen: mmole Na_4P_2, 0.59; ml. H_2, S.T.P., 18.5; mg. atoms N in residue, 0.79; mol. H_2/mol. Na_4P_2, 1.40; atoms N/mol. Na_4P_2, 1.34. Evidently, one atom of nitrogen remains in the residue per mol. of hydrogen produced, thus confirming (1) above.

2. **Hydrolysis of Tetrasodium Diphosphide.**[10]—The dried solvate reacts violently with water evolving both phosphine and hydrogen. In the experiments as conducted the proportion of each gas and the total amount produced varied from one experiment to the next. Seemingly, the course of reaction depends on the rate of addition of water, the temperature and other factors.

In carrying out the hydrolysis the reaction vessel was cooled with an ice-bath and air-free water was admitted drop-wise *in vacuo* through a dropping funnel attached to the top of the reaction vessel by means of a ground glass joint. The results of two typical experiments follow: (1) mmoles Na_4P_2, 1.145; mmoles H_2, 1.895, mol. wt., 2.95; mmole PH_3, 0.973; mol. wt., 33.5; mmoles P in residue, 1.28. (2) Mmoles Na_4P_2, 1.14; H_2, 1.21; PH_3, 1.59; P in residue, 0.63. It was noted that solutions from hydrolysis were colored a blood red, reminiscent of those obtained when biphosphine is dissolved in liquid ammonia; a reddish colored solid also was formed. On standing overnight the solutions decolorized and small additional amounts of gases were produced.

3. **Heavy Metal Derivatives.**—A copper derivative having the empirical composition CuP was obtained on treating a liquid ammonia solution of tetrasodium diphosphide with copper nitrate. However, similar reactions with lead or silver salts did not apparently lead to compounds of definite proportions. Although the copper derivative gave some evidence of possessing a crystalline structure, the silver and lead compounds were amorphous to X-radiation, but they often contained free metal. Most of these substances were pyrophoric and consequently manipulations, such as filling tubes for X-ray examination, were carried out in a dry box filled with an inert atmosphere of carbon dioxide or nitrogen.

CuP.—A gelatinous precipitate resembling ferric hydroxide was obtained on adding copper nitrate to a solution of the sodium salt in liquid ammonia. Excess copper nitrate was removed by washing the precipitate with several successive portions of liquid ammonia; phosphorus was not detected in the wash solutions.

The copper to phosphorus ratio was determined without weighing out samples. The compound was put into solution with nitric acid and the copper was precipitated as the sulfide, ignited and weighed as oxide; phosphorus was determined as indicated above. Expt. (1), ratio, Na/P, 1.99. *Anal.* g. CuO, 0.0188; g. $Mg_2P_2O_7$, 0.2784; Cu/P, 0.91. (2) Ratio, Na/P, 2.01. *Anal.* 0.0238; 0.3256; 0.98, respectively. These results confirm ones obtained previously by Smith.[12]

It is evident that copper and phosphorus combine to form a compound of the type CuP, in which copper quantitatively replaces sodium in the diphosphide; a compound having the same empirical formula has reportedly been prepared by reaction of the elements directly.[13]

Reaction with Lead Iodide.—An amorphous, black precipitate was obtained on adding lead iodide to a solution of tetrasodium diphosphide in liquid ammonia[12]; when dry, the substance was extremely pyrophoric. Free lead was found in the product when examined by X-rays, but there was no evidence of other crystalline material. Significantly, it was noted that if an excess of lead iodide was added all at once the solution "flashed" a reddish color before becoming colorless. This observation suggests that the sodium salt first may have reduced a portion of the lead iodide to free lead with the concomitant formation of a red higher phosphide (the higher alkali metal phosphides are colored red[3]); this could account for the presence of the lead in the precipitated material. The lead to phosphorus ratio was not determined.

Reaction with Silver Iodide or Nitrate.—As with lead, a bulky black precipitate was obtained when the sodium salt was treated with silver nitrate or iodide in liquid ammonia. The products obtained with an excess of the silver salt invariably contained free silver; otherwise the products were amorphous to X-radiation. Furthermore, the atom ratios, Ag/P, were always greater than two. Thus, in one experi-

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(9) The step-wise addition of a third proton to the diphosphide ion does not seem very likely since phosphine is evolved immediately when more than two equivalents of ammonium bromide are added to a solution of the sodium compound in liquid ammonia. However, reduction of the intermediate ion might be accomplished by nascent hydrogen and not involve the electron directly.

(10) Data by S. Roggenburg, Jr.

(11) Sodium metal begins to evolve at 375°. It may be noted that C. Legoux (*Compt. rend.*, **207**, 634 (1939)) has obtained Na_2P_5 by the pyrolysis of $NaPH_2$. From this data it is apparent that pyrolysis proceeds step-wise as the temperature is raised. Phosphine is evolved first in accord with the equation $2NaPH_2 = Na_2PH + PH_3$ (a result confirmed by W. O. Haas, M.S. Thesis, University of Chicago, Dec., 1941); then hydrogen is evolved in an amount sufficient to be accounted for by the equation $2Na_2PH = Na_4P_2 + H_2$. Finally, free metal is obtained yielding Na_2P_5 as residue. Legoux did not postulate the existence of Na_4P_2, but it seems probable that this compound was formed as an intermediate and is the substance tetrasodium diphosphide described here.

(12) H. M. Smith, M.S. Thesis, Clark University, 1922.

(13) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y. 1928, p. 835.

ment, using a large excess of silver nitrate, the ratio was 4.70; in a second, using a 100% excess of silver iodide, the ratio was 2.28.[14]

These products appeared entirely stable in air; furthermore, boiling water, concentrated ammonium hydroxide and hot caustic solution were without noticeable affect, but they dissolved readily in dilute nitric acid or in a solution of potassium cyanide in the presence of air.

Free silver was not detected in products prepared by employing an excess of the alkali metal phosphide, and here the Ag/P ratios were lower, being 2.16, 1.72 and 1.72, respectively, in three experiments. In contrast to those products precipitated in the presence of excess silver salt, these substances were pyrophoric and emitted white fumes when exposed to air.[15]

From the above it is apparent that silver salts do not react with tetrasodium diphosphide to form a compound of definite composition and that the Ag/P ratio depends upon the conditions of reaction.

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(14) It may be noted that after standing several months, free silver could no longer be detected in these substances.

(15) Unpublished observations, J. A. Clarke.

PHILADELPHIA 4, PENNA.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, ANALYTICAL DIVISION]

Phosphates of Niobium and Tantalum[1]

BY RICHARD B. HAHN[2]

Niobium and tantalum form stable phosphate salts, which have not been reported previously. These are formed as amorphous, hydrated precipitates when a potassium niobate or a potassium tantalate solution is treated with an excess of phosphoric acid and nitric acid. The hydrated precipitates lose water and become crystalline upon ignition. Data are presented to show that $NbOPO_4$ and $TaOPO_4$ are the most likely formulas for the ignited compounds.

In studying the precipitation of niobium pentoxide from various aqueous solutions, it was observed that large amounts of the phosphate ion are carried down with the niobium pentoxide precipitate. Schoeller and Webb[3] showed that small quantities of phosphoric acid are almost quantitatively coprecipitated with niobium pentoxide. No investigation was made by these workers, however, of the precipitation of niobium pentoxide in the presence of an excess of phosphoric acid.

Preliminary experiments showed that in the presence of an excess of a soluble orthophosphate about one third of the total weight of the precipitate is phosphorus pentoxide which is about equivalent to a one to one mole ratio of P_2O_5 and Nb_2O_5. This quantity of P_2O_5 in the precipitate could hardly be explained by occlusion or adsorption. The possibility of the formation of an insoluble phosphate of niobium was considered. C. W. Blumstrand reported an insoluble precipitate obtained by adding sodium phosphate to an aqueous solution of niobium oxytrichloride.[4,5] However, no data are presented to show the exact composition of the precipitate. Friend states that niobium salts of phosphoric acid are unknown.[6] Further search of the literature showed no report of a niobium phosphate, hence the following investigation was made.

Experimental

Precipitates were prepared by four methods:

(1) A solution of potassium hexaniobate is treated with an excess of phosphoric and nitric acids and digested in a hot water-bath until precipitation is complete (30–60 min.).

(2) Freshly precipitated niobium pentoxide is dissolved in an excess of oxalic acid. This solution is treated with an excess of phosphoric and nitric acids, and heated in a water-bath. The oxalic acid is destroyed by addition of solid potassium bromate. The mixture is then digested until the precipitate settles.

(3) Freshly precipitated niobium pentoxide is dissolved in an excess of hydrofluoric acid. The resulting solution is treated with an excess of phosphoric acid. This solution is made alkaline with ammonium hydroxide. The mixture is then digested until the precipitate settles.

The above precipitates were air-dried and also oven-dried at 120°. The resulting solids still contained 20–40% of water and showed no X-ray diffraction pattern. These precipitates were ignited at 1000°. The resulting solids gave identical, sharp, characteristic, X-ray diffraction patterns which were different from that of niobium pentoxide and phosphoric acid obtained by ignition at the same temperature. The X-ray diffraction data are given in Table III. It is concluded, therefore, that a salt of niobium and phosphoric acid is formed.

(4) Niobium pentoxide is mixed with an excess of 85% phosphoric acid. The mixture is placed in a crucible and ignited at 1000°. The resulting residue gives X-ray diffraction patterns identical with the previously ignited precipitates, although a few faint lines corresponding to the oxide are still observed.

Analysis of the Compound.—Attempts were made to analyze the precipitates by the procedure given by Schoeller and Webb,[11] which consists of a sodium hydroxide fusion followed by extraction of the residue with half-saturated sodium chloride solution. Experiments with radioactive phosphorus tracer showed this method is satisfactory for separating a few milligrams of phosphate ion from niobium or tantalum, but is unsatisfactory for separating larger amounts of phosphate ion. Hence the following method was employed.

A known weight of niobium pentoxide in solution is taken and precipitated as discussed previously. The precipitate is transferred quantitatively to a 50-ml. centrifuge tube, centrifuged and washed with a 1:1 acetone–water mixture until the excess phosphoric acid is eliminated. (Pure

TABLE I

COMPOSITION OF NIOBIUM PHOSPHATE

	Per cent. Nb_2O_5	Per cent. P_2O_5
Niobium phosphate precipitate	65.2 ± 0.2	34.8 ± 0.2
Calculated for $Nb_2O_5 \cdot P_2O_5$	65.19	34.81

TABLE II

COMPOSITION OF TANTALUM PHOSPHATE

	Per cent. Ta_2O_5	Per cent. P_2O_5
Tantalum phosphate precipitate	75.5 ± 0.2	24.5 ± 0.2
Calculated for $Ta_2O_5.P_2O_5$	75.68	24.32

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(1) Presented as a paper at the Southwide Chemical Conference, Atlanta, Ga., October, 1950.

(2) On loan from Wayne University.

(3) H. R. Schoeller and W. H. Webb, *Analyst*, **61**, 585 (1936).

(4) C. W. Blumstrand, *Acta Univ. Lund.*, **1**, 7 (1864).

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, p. 882.

(6) J. N. Friend, "A Textbook of Inorganic Chemistry," Vol. VI, Charles Griffin and Co., Ltd., London, 1929, Part III, p. 5.