THE ALKALI METAL PHOSPHIDES. III. ELECTROLYSIS STUDIES IN LIQUID AMMONIA^{1,2}

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The electrolysis of sodium and potassium dihydrophosphides and of tetrasodium diphosphide has been studied in liquid ammonia. With the former, the anode reaction is given by the equation: $6PH_2^- + 2NH_3 = N_2 + 6PH_3 + 6e^-$, but a more complicated reaction was found to occur in the case of the diphosphide salt. With the latter the ratio of nitrogen evolved to current passed is the same as with the dihydrophosphides, but no large amount of phosphine is produced until electrolysis is approximately 50% completed; then, almost immediately, 50 to 60% of the phosphorus is evolved as phosphine. These results may be accounted for satisfactorily by assuming that the primary anode process involves the oxidation of solvent, namely $8NH_3 = N_2 + 6NH_4^+ + 6e^-$. The protons liberated in this oxidation then become available for reaction with the protophile diphosphide ion, leading in stages to the several species, P_2H^{-3} , $P_2H_2^{-2}$ and $P_2H_3^{-1}$. A chain mechanism, involving the reaction of solvent with the species $P_2H_3^-$, is postulated to account for the high yield of phosphine, at the point of 50% electrolysis.

Introduction

The present paper³ describes the results of further investigations relating to the properties of certain alkali metal phosphides and is concerned specifically with the electrolysis of sodium and potassium dihydrophosphides, MPH₂, and of tetrasodium diphosphide, M₄P₂, in liquid ammonia.

As might be expected, these substances are extremely protophilic. When treated with ammonium bromide in liquid ammonia the dihydrophosphides evolve phosphine quantitatively. But with tetrasodium diphosphide a more complicated reaction ensues in which only part of the phosphorus is evolved as phosphine; and the evolution of phosphine only occurs appreciably after approximately two equivalents of ammonium ion are added per mole of salt.

In an earlier study^{3b} we obtained indirect evidence indicating that protons apparently may add to the diphosphide ion stepwise in liquid ammonia forming partially hydrogenated species and prob-ably eventually biphosphine, H_4P_2 , on complete protonation. However, it was not found practical to carry out a detailed study of this protonation process by treating solutions of the diphosphide with ammonium bromide for at least two reasons: (1) experimentally it was difficult to add small increments of ammonium bromide quantitatively and obtain interpretable results; (2) biphosphine itself was found to decompose in liquid ammonia yielding a substantial part of its phosphorus as phosphine. As a result, it could only be inferred that biphosphine was a likely end-product of the protonation, and that its decomposition was responsible for the evolution of phosphine when the diphosphide salt was treated with an excess of ammonium bromide.

In searching for another attack on the problem it occurred to us that the protonation reaction might be followed effectively by electrolyzing solutions of the salts in liquid ammonia provided the process could be carried out under such conditions that protons together with nitrogen might be produced at the anode, *i.e.*, under conditions involving the oxidation of solvent. In this way protons produced by the oxidation could become available for reaction with the protophilic anions.

A study, such as that outlined above, has been the object of the present investigation and the data secured serve to demonstrate that protonation does in fact take place at the anode under our experimental conditions.

Experimental

1. Apparatus and Procedure.—Electrolyses were carried out at the boiling point of liquid ammonia using a cell similar to that described by Foster and Hooper⁴ with electrodes approximately 2 cm. apart. The anode (1 cm.^2) was of platinum while the cathode (7 cm.^2) was of mercury, which was forced into the cell from a reservoir just prior to electrolysis; the mercury served to absorb alkali metal produced at this electrode. The electrolysis current was maintained at some predetermined constant value ranging between 10 and 20 ma. by means of a suitable variable resistance which was inserted in series with a 120-v. d.c. supply line. The current was measured within an accuracy of $\pm 0.25\%$ by means of a calibrated ammeter, and the product of current and time served to measure the quantity of electricity used in electrolysis.

The alkali metal phosphides were prepared *in situ* using samples of metal ranging in size from 2.5 to 7.5 milliatoms, which were weighed accurately. The dihydrophosphides were prepared by passing a gaseous mixture of ammonia and phosphine through a solution of the appropriate metal in liquid ammonia; tetrasodium diphosphide was prepared according to the method described earlier.³⁸ Electrolyses of the dihydrophosphides were commenced immediately after purging the system of excess phosphine and hydrogen. With tetrasodium diphosphide it was first necessary to remove the mixture of ammonia and toluene which had been introduced during the preparation of the salt; then the diphosphide was redissolved in approximately 75 cc. of liquid ammonia. In all operations strict precautions were observed to prevent the solutions from coming in contact with the atmosphere.

In carrying out the electrolyses, current was permitted to flow until a predetermined ratio of electricity to starting material was reached. With the dihydrophosphides a steady increase in the voltage was necessary in order to maintain a constant current and a full value of 120 v. was needed as the electrolysis approached completion. With the diphosphide, however, the electrolysis current could be maintained constant with but little adjustment of voltage, and the solutions were fairly good conductors even after the passage of a quantity of current equivalent to the sodium content of the salt. With both systems hydrogen commenced to evolve at the cathode when electrolysis was approximately 80% completed. Evolution of gas began immediately at the anode and continued throughout the electrolysis.

⁽¹⁾ This paper is based on research supported by the Office of Naval Research under contracts N8onr-74200 and Nonr-598(00).

⁽²⁾ From a thesis by John M. Finn, Jr., submitted in partial fulfillment of the requirements for the Ph.D. degree, 1953.

⁽³⁾ Previous papers in this series are: (a) E. C. Evers, J. Am. Chem. Soc., **73**, 2038 (1951); (b) E. C. Evers, E. H. Street, Jr., and S. L. Jung, *ibid.*, **73**, 5088 (1951).

⁽⁴⁾ L. S. Foster and G. S. Hooper, ibid., 57, 76 (1935).

After turning off the current substantially all the liquid ammonia, together with gaseous products, was transferred by distillation from the cell into an evacuated flask containing sodium iodide cooled with ice-water. The sodium iodide served to absorb most of the ammonia and caused the gaseous products to concentrate largely in the vapor phase.³⁶ Thereafter residual ammonia was separated from other gases using essentially the procedure of Johnson and Pechukas.⁶ Finally the products were separated into fractions which were condensable and non-condensable by liquid air. These were measured and then characterized as phosphine and nitrogen, respectively, using standard procedures. **2. Results.**—In several experiments the cathode mer-

2. Results.—In several experiments the cathode mercury was analyzed for total sodium to check the effectiveness of the cathode process. The sodium was extracted with hydrochloric acid and the extract was evaporated to dryness in a platinum vessel. Ammonium chloride was sublimed away and the residue of sodium chloride was weighed. Results of two experiments follow: expt. 21: 1.84 millifaradays electricity, 1.85 milliatoms sodium; expt. 22: 1.85, 1.86, respectively. These results also confirmed the effectiveness of the procedure used in measuring current and time. While analyses were not carried out in most cases, it was assumed that the amount of alkali metal deposited was equivalent to the quantity of electricity employed. Without doubt this assumption was justifiable so long as no cathode gassing was observed, and this took place only after electrolysis was 80% or more completed. When hydrogen did evolve it was necessary to apply a correction to the nitrogen value. This was done within the accuracy of our results by measuring the density of the gas mixtures and computing the percentage of nitrogen.

Molecular weight data were employed almost exclusively to identify the liquid air condensable and non-condensable fractions. The following typical data are presented to indicate the reliability of the results. Non-condensable: expt. 6: 1.33 mmoles gas, 37.9 wt. mg., 28.5 mol. wt. found; expt. 13: 0.733, 20.8, 28.4; expt. 16: 0.352, 10.1, 28.7, respectively. Mol. wt. N₂, calcd., 28.0. Condensable: expt. 16: 0.318 mmole gas, 10.8 wt. mg., 33.8 mol. wt. found; expt. 18: 0.411, 14.1, 34.3, respectively; mol. wt. PH₃ calcd., 34.1.

In view of the large amount of data collected and that their primary function was to indicate the course of the anode reaction, it has seemed most expedient to present the significant results graphically as shown in Figs. 1 and 2. Since the samples of starting materials varied considerably in size, it has been convenient in presenting these data to divide the variable on both ordinate and abscissa axes, *i.e.*, the yields of products and quantity of electricity passed, respectively, by the number of gram-atoms of phosphorus employed in making up the several alkali metal phosphides. In effect this places all the results on an equivalent basis.

While it is intended to discuss the significance of these plots in detail in the sections to follow, it seems appropriate here to emphasize an extremely important feature of these results, namely, that the ratio of the yield of nitrogen obtained to current passed was constant within experimental error and independent of the nature of the solute being studied. For example, in the case of tetrasodium diphosphide, a value of 0.165 was found as an average taken over some twenty-one experiments in which the quantity of electricity passed ranged from approximately 25 to 100% of equivalence, based on the quantity of sodium used in the preparation of the salt. The maximum deviation from the mean was 0.012 unit or 7%, and it showed no trend with the extent of electrolysis. In the last five experiments, using perfected techniques, it was 3%. As typical examples we submit the following data: expt. 41: 2.04 millifaradays electricity, 0.338 mmole N₂, 0.166 ratio N₂ to electricity; expt. 42: 3.61, 0.610, 0.169; expt. 43: 3.15, 0.517, 0.164, respectively. The agreement in the case of the dihydrophosphides was even better, being less than 2%. This is brought out in Fig. 1, where the yield of nitrogen plotted against the extent of electrolysis results in a straight line of slope 0.167, which signifies that the ratio of moles of nitrogen formed to faradays of electricity passed is 1:6.

trogen formed to faradays of electricity passed is 1:6. Whereas the production of nitrogen at the anode is evidently independent of the salt type, the yield of phosphine is very much a function of the nature of the anion which is present in solution. In the case of the dihydrophosphides (Fig. 1) we obtain a linear relation on plotting moles of phosphine evolved against faradays of electricity; in fact, the resulting curve has a slope of unity, signifying that one mole of phosphine is obtained per equivalent of electricity. But in the case of solutions of tetrasodium diphosphide, a sigmoidal type of curve results, as shown by Fig. 2; and the curve rises almost vertically when electrolysis is approximately 50% completed, *i.e.*, at a value of unity on the abscissa axis. It may be pointed out that although the yield of phosphorus as phosphine was usually determined directly, in a few cases the residue was analyzed for total phosphorus and the volatilized phosphorus was computed by difference; these data are represented by solid circles in Fig. 2. Such a procedure was usually legitimate since in those cases when both phosphine and residual phosphorus were determined the material balance was entirely satisfactory.

One other point bears emphasis in order that a correct interpretation may be given these data. First of all it must be realized that each datum shown in Figs. 1 and 2 represents a complete and independent experiment with electrolysis carried to the value given by the abscissa before the products were quantitatively removed for analyses. In this connection it was found unnecessary completely to evaporate our solutions after electrolysis in order to obtain quantitative recovery of volatile products. This is significant since it indicates that any reaction which produces phosphine or nitrogen is completed once the electrolysis is stopped. Thus the data do not refer to equilibrium quantities of volatile products but rather to quantities produced in completed reactions. Furthermore, secondary reactions, which conceivably might have also given rise to these products, apparently do not occur as the residues are taken to dryness.

Electrolysis of Alkali Metal Dihydrophosphides

The over-all reaction at the anode during the electrolysis of the alkali metal dihydrophosphides may be represented by the equation

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$$PH_2^- + 2NH_3 = 6PH_3 + N_2 + 6e^-$$
(1)

where six equivalents of electricity serve to liberate one mole of nitrogen and six moles of phosphine. As may be seen by reference to Fig. 1, the experimental data are in good accord with this equation. The solid lines were computed according to the above expression; the points are experimental. As noted above, the slopes of the lines establish the values of the coefficients for phosphine and nitrogen, respectively, in equation (1).

An entirely analogous result has been obtained by Teal and Kraus,⁶ who found, on electrolyzing solutions of sodium germanyl, that the anode reaction could be expressed by the equation

$$6GeH_3^- + 2NH_3 = 6GeH_4 + N_2 + 6e^-$$
 (2)

It is evident that solvent must be involved intimately in these reactions since, effectively, for every six equivalents of electricity passed two moles of solvent are completely stripped of their hydrogen. While the complexity of the processes leading to this end result cannot be underemphasized, this behavior, *i.e.*, the oxidation of solvent, is not unique. In aqueous systems, for example, whenever conditions are favorable (high discharge potential for the anion, low concentration of solute, etc.) electrolysis very often leads to the evolution of oxygen and accumulation of hydrogen ions at the anode. Consequently, in liquid ammonia under suitable circumstances, the evolution of nitrogen is not unexpected.

However, an outstanding feature of the present study, as well as that on sodium germanyl, lies in

(6) G. K. Teal and C. A. Kraus, ibid., 72, 4706 (1950).

⁽⁵⁾ W. C. Johnson and A. Pechukas, J. Am. Chem. Soc., 59, 2065 (1937).



Fig. 1.—Electrolysis of alkali metal dihydrophosphides in liquid ammonia; O, NaPH₂; •, KPH₂. Curve 1, PH₃/P, moles phosphine evolved per gram-atom phosphorus in the alkali metal salt. Q/P, faradays of electricity passed to gram-atoms phosphorus in the alkali metal salt. Curve 2, moles nitrogen evolved to gram-atoms phosphorus in the alkali metal salt. Solid lines computed according to equation (1); points, experimental.

the fact that the anions are converted quantitatively to the corresponding hydrides during electrolysis. How such a transformation can be brought about appears obscure until it is recalled that normally, in the oxidation of ammonia, we should expect protons to be liberated along with nitrogen at the anode. In view of the highly protophilic nature of the PH_2^- and GeH_3^- ions, it seems reasonable to suppose that they should combine with those protons immediately in a secondary reaction forming the respective hydrides. In effect, then, if we are willing to assume that with these systems the primary anode reaction is the oxidation of solvent, we have here a relatively simple means of accounting for the evolution of phosphine or germane. And, in addition, it may be pointed out that this formulation of the problem has proved particularly fruitful in interpreting the results obtained on electrolyzing solutions of tetrasodium diphosphide which will be discussed in the following section.

Admittedly we have no direct experimental evidence for the above mechanism and several alternative schemes leading to the same stoichiometrical end result might be offered to account for the anode products. However, any mechanism calling for the direct discharge of PH_2^- ions seems inferior for our present purposes. As a matter of fact, had this reaction occurred to any appreciable extent, one might have expected some conversion to biphosphine, H_4P_2 . But such a process would have resulted in lower yields of both nitrogen and phosphine than are called for by equation (1)and there is no evidence pointing in this direction. It also seems unlikely that amide ions might be present in sufficiently high concentrations to undergo appreciable direct discharge. The very fact that stable solutions of the alkali metals may be obtained would indicate that the self-ionization of ammonia is practically nil.⁷

(7) The ion product for ammonia is reported to be 1.9×10^{-33} at -50° : V. A. Pleskov and Monoszon, Acta Physicochim., U.S.S.R., 1, 725 (1935).

A more satisfying mechanism for the formation of molecular nitrogen and liberation of protons would seem to be one patterned after that suggested by Eyring, *et al.*,⁸ to account for the overvoltages of hydrogen and oxygen in aqueous systems. As an essential feature of this theory it is proposed that these gases result from a break-down of the solvent itself and are not necessarily formed by the discharge of hydrogen or hydroxyl ions. It seems likely that some such mechanism is operative during the electrolysis of the alkali metal phosphides under our experimental conditions.

Electrolysis of Tetrasodium Diphosphide

Data showing the course of phosphine evolution on electrolyzing solutions of tetrasodium diphosphide are presented graphically in Fig. 2. As in Fig. 1, the ratios, PH_3/P and Q/P, represent the moles of phosphine evolved and the faradays of electricity passed, respectively, both divided by the gram-atoms of phosphorus used in preparing the diphosphide salt.



Fig. 2.—Electrolysis of tetrasodium diphosphide in liquid ammonia: PH_{θ}/P , moles of phosphine evolved per gramatom of phosphorus in the diphosphide; Q/P, the ratio of faradays of electricity passed to gramatoms of phosphorus in the diphosphide: O, data based on phosphine evolved; \bullet , data based on residual analyses.

Obviously the situation here is more complicated than with the dihydrophosphides and there is no simple relation between the yield of phosphine and the extent of electrolysis. But a clue as to what may be occurring is given by the constancy of the production of nitrogen. As noted above, the average ratio of moles of nitrogen produced to equivalents of electricity passed was 0.165. This certainly suggests that we should consider the oxidation of solvent among the primary anode reactions since the equation representing this reaction, namely

$$3NH_3 = N_2 + 6NH_4^+ + 6e^-$$
 (3)

predicts a nitrogen to electricity ratio of 1:6 or 0.167. Then, as in the case of the dihydrophosphides, secondary reactions of protons with solute might account for the evolution of phosphine.

On reference to Fig. 2 it may be noted that very little phosphine was evolved until approximately 50% electrolysis, *i.e.*, up to a value of unity on the abscissa axis. At this point the curve has a vertical segment which can only mean that the addition of

(8) H. Eyring, S. Glasstone and K. J. Laidler, Trans. Electrochem. Soc., 76, 145 (1939).

a few ammonium ions (by electrolysis of solvent) in this region causes the evolution of an exceedingly large number of phosphine molecules. In fact, substantially all the phosphine is evolved at this point. Thereafter, the production of phosphine falls off measurably with additional electrolysis and the curve approaches the horizontal.

The above results may be more readily interpreted by reference to Fig. 3. Here there is plotted what might be termed the "solute composition" versus the extent of electrolysis. The ordinate values, H/P', represent the equivalents of hydrogen introduced by electrolysis minus those evolved as phosphine divided by the gram-atoms of phosphorus remaining in the solution; the axis of abscissas is the same as that employed in preparing Fig. 2.



Fig. 3.—Electrolysis of tetrasodium diphosphide in liquid ammonia; curve for "solute" composition. H/P', gramatoms hydrogen introduced by electrolysis minus that evolved as phosphine over the gram-atoms of phosphorus remaining in solution. Q/P, faradays electricity passed to gram-atoms phosphorus in the alkali metal salt. Dotted line represents composition curve if no phosphorus were evolved as phosphine.

Three distinct regions, marked by breaks in the curve, may be noted in Fig. 3. The first region ranges from zero on the abscissa axis, Q/P, to approximately 0.5; the second includes the region between approximately 0.5 and 1.0; the third extends to 2.0, where electrolysis may be assumed to be complete, based on the number of faradays needed to electrolyze out the sodium ions.

Little or no phosphine evolution occurred for Q/P values between 0 and approximately 0.5, *i.e.*, before electrolysis was about 25% complete. This we interpret as being due to the absorption of protons by the diphosphide ion, forming the species $P_{\pm}H^{-3}$ according to the equation

$$P_2^{-4} + NH_4^+ = P_2H^{-3} + NH_3$$
 (4)

If phosphine were not evolved, the composition curve would follow the dotted line. However, after a Q/P value of approximately 0.5 some phosphine is produced, the curve bends somewhat toward the abscissa axis and the experimental points fall under the dotted line. Between a Q/Pvalue of 0.5 and 1.0 it seems reasonable to propose that the principal reaction is one between protons liberated at the anode and protophilic P_2H^{-3} ions which leads to the species, $P_2H_2^{-2}$, according to the equation

$$P_2 H^{-3} + N H_4^{+} = P_2 H_2^{-2} + N H_3$$
 (5)

The existence of a dihydrodiphosphide ion also seems reasonable on the basis of certain chemical studies reported previously^{3b} and the species appears to be stable in liquid ammonia solution. To summarize the chemical evidence: (1) When two equivalents of ammonium bromide are added to solutions of tetrasodium diphosphide there is a perceptible change in color and very little phosphine is evolved. (2) If less than an equivalent of sodium metal is added to the above solution the blue color of free metal persists after many hours standing and no gas is evolved. This attests to the absorption of protons by the protophilic diphosphide ions and to the non-reducibility of the resulting product. Thus, evidence presented in (1) and (2) suggests that reaction between ammonium and diphosphide ions has proceeded to the stage indicated by equation (5) above.

In light of the evidence presented above we are led to conclude that the ion, $P_2H_2^{-2}$, exists and is stable in liquid ammonia, and that the evolution of phosphine in region 2 must result from a side reaction in which solvent may be involved. Undoubtedly, in this region there is competition for protons between the species P_2H^{-3} and $P_2H_2^{-2}$ and it does not seem unlikely that the latter may in part be converted to a more highly protonated species, which may either decompose directly or react with solvent evolving phosphine, perhaps by some such mechanism as is discussed below.

In region 3 there is direct evidence that solvent enters into reaction with one or more of the hydrogenated diphosphide species. As noted above, in the neighborhood of unity on the abscissa axis, the composition curve drops extremely rapidly from an ordinate value of approximately 0.6 to a value of -0.6. Negative values for the ordinate signify that more hydrogen has been evolved as phosphine than was introduced as protons by electrolysis. This can only mean that, in addition to anodic oxidation of solvent, there has been chemical attack of solvent. Furthermore, since this rapid drop in the curve occurs over such a small range of Q/Pvalues, this extensive production of phosphine in some way must have been initiated by the anodic processes, probably through the introduction of protons. Though we refrain from offering a concrete mechanism for this process, we should like to propose a tentative explanation—and we feel its validity may be tested by further experiment—as pointed out below.

Referring back to Fig. 2, it is to be noted that after the rapid break in the curve, the PH₃/P values increase gradually and then level off at approximately 0.58 as electrolysis is continued, indicating that after approximately 50% electrolysis little or no additional phosphine is liberated and that most of the protons produced at the anode thereafter remain in solution as such or otherwise enter into reaction. At 100% electrolysis, then, roughly 58% of the phosphorus has been volatilized as phosphine. Since this value is not far removed from that obtained by the direct decomposition of biphosphine in liquid ammonia,⁹ it seems likely that biphosphine may be involved as an endproduct in the protonation process. At any rate, if we may assume this to be true, we have a tenta-

(9) Values ranging between 60 and 63% have been obtained; unpublished observations, E. H. Street, Jr., this Laboratory. tive explanation for the form of the curve in the neighborhood of the point of 50% electrolysis, as explained below.

It would appear in the first place that the protoncatalyzed reaction is necessarily of the chain type, *i.e.*, a species produced by the absorption of protons initiates a reaction with solvent and is regenerated; and the chain-breaking step in which phosphine is produced is the decomposition of some other species, say biphosphine, which is one of the products of the chain reaction. Since it appears unlikely that either the $P_2H_2^{-2}$ ion or biphosphine undergoes reaction with the solvent¹⁰ we are forced to attribute the catalytic activity to an intermediate species which logically may be formed by further protonation of the $P_2H_2^{-2}$ ion, namely, $P_2H_3^{-1}$. In order for reaction to occur with solvent the $P_2H_3^{-1}$ ion appears to be considerably more protophilic than its precursors. We suggest that reaction with solvent occurs according to the equation

$$P_2H_3^- + NH_3 = P_2H_4 + NH_2^-$$
(6)

Then, to establish the chain, biphosphine reacts with the dihydrophosphide ion, which is present in considerable quantity at the break-point in the curve, according to the equation

$$P_2H_4 + P_2H_2^{-2} = 2P_2H_3^{-1}$$
(7)

Hence, by the addition of very few protons we may have an extensive reaction with solvent. The chain-breaking step then involves the somewhat slower decomposition of biphosphine leading to the evolution of phosphine. It would seem possible that the above mechanism might be verified by an attempt to determine whether amide ions are produced in the region of 50% electrolysis. But in any event, this research seems to demonstrate quite well that the diphosphide ion adds protons stepwise and is converted into partially hydrogenated species at the anode, and it suggests that the

(10) The solid residue from the decomposition of biphosphine in liquid aumonia contains nitrogen. This may be substantially removed as aumonia by pumping and heating; consequently, solvent does not appear to be involved chemically; unpublished observation, this Laboratory. electrolytic method might be generally useful in investigating the behavior of protophilic anions.

In conclusion it is of interest to note that the mechanism postulated above, involving as it does the species $P_2H_3^{-}$, serves to augment certain of our previous deductions regarding the properties of the diphosphide ion which were based on chemical evidence.^{3b} For example, as noted in the introduction, when solutions of the diphosphide are treated with an equivalent amount or more of ammonium bromide, phosphine is evolved much as in the electrolytic method. Undoubtedly in this case the reaction yields biphosphine by a stepwise process, but, probably, solvent is not involved since here the $P_2H_3^-$ ion would have protons available in a much more active form, namely, as ammonium ions. Furthermore, it provides a fairly satisfactory explanation for the course of the reaction whereby diphosphide ions may be reduced to dihydrophosphide ions. To accomplish this a solution containing tetrasodium diphosphide and free sodium is treated with four equivalents of ammonium bromide^{3b}; reaction then occurs according to the equation

$$P_2^{-4} + 2e^- + 4NH_4^+ = 2PH_2^- + 4NH_3$$
 (8)

Since a solution of the diphosphide salt containing two equivalents of metal was shown to be stable toward reduction, it was suggested that protonation probably proceeded stepwise through the stage $P_2H_2^{-2}$ to biphosphine before the P-P bond was subject to attack by the solvated electron. In light of the present research, it would seem that, under conditions leading to reaction according to equation (8), the species, $P_2H_3^{-}$, because of its extremely protophilic character, might have only a transitory existence; consequently, conversion from $P_2H_2^{-2}$ to P_2H_4 occurs immediately as ammonium bromide is added and the latter then undergoes attack by the solvated electron.¹¹

(11) Even though unstable in liquid ammonia, biphosphine may be quantitatively converted by sodium to the dihydrophosphide salt under suitable conditions; unpublished observations, E. H. Street, Jr., this Laboratory.