From $E_{f,\,CN^-} = -592$ mv., $E_0 = 612$ mv., $d_4 = 8.2 \times 10^3$, μa./M, cyanide = 0.1 M and $f_{CN^-} = 1.0$, K_4 was calculated from equation 8 as $10^{40.1}$. This can be considered good agreement with the $K_4 = 10^{40.6}$, obtained when mercuric cyanide was assumed to be complexed as $Hg(CN)_4^{--}$ at the surface of the drop.

It was thought necessary to test the polarograms for polarographic reversibility since the arguments above are based upon this condition. In order to do this, anodic waves of cyanide were obtained in basic solutions. As can be seen in Table III, the analyses of the anodic waves were the same as analogous cathodic waves. The system can therefore be said to be polarographically reversible.

Another usually important criterion for reversibility is the attainment of a single continuous polarogram for a mixed anodic and cathodic wave. It can be shown that with the type of electrode phenomena that we have observed this behavior is not to be expected.

In an equimolar solution of cyanide and mercuric cyanide most of the cyanide is complexed by the mercuric cyanide. The cathodic portion of the polarogram should start with a dependency on the reduction of $Hg(CN)_3^-$, with the reduction of $Hg(CN)_4^{--}$ taking over quite early. On the other hand, since the activity of the mercuric ion is decreased by the presence of mercuric cyanide, the anodic portion should start with a dependency upon $Hg(CN)_3^-$, with the reduction of mercuric cyanide taking over quite early.

The cathodic portion would be mainly dependent upon the reduction of $Hg(CN)_4^{--}$ and the anodic portion upon the oxidation of mercury to mercuric cyanide. One should not expect to obtain a straight line over the anodic and cathodic portions from any plot of E_{de} *vs.* log $(i_d - i)/i^n$. When this experiment was tried, the polarogram looked like a single continuous wave, but, as expected, no log plot gave a straight line with the proper slope over the anodic–cathodic portion.

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CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Lower Hydrides of Phosphorus. II. The Decomposition of Biphosphine in Liquid Ammonia[1,2]

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Biphosphine decomposes in liquid ammonia to lose phosphine, leaving a black residue of variable composition containing phosphorus, hydrogen and solvent. Products are obtained whose P/H ratio varies from 3.05 to 4.81 and whose NH_3/H ratio varies from 0.09 to 0.92. Similar substances are formed on treating phosphorus with ethylamine. The constitution of these substances is discussed in relation to solid hydrides obtained when biphosphine is decomposed *in vacuo* and in the presence of moisture.

In our previous communication,[3] we described the decomposition of biphosphine at room temperature under anhydrous conditions. Decomposition *in vacuo* proceeded with the elimination of phosphine, forming orange-yellow solids whose ultimate compositions appear to lie in the neighborhood of $P_{2.25}H$, (P_9H_4). With moisture present the products contained larger proportions of hydrogen; materials obtained in a variety of ways have reported compositions averaging around P_2H.[3-5] These preparations left small amounts of non-volatile residue on strong heating *in vacuo*.

Another class of hydrides has been prepared by treating solid hydrides[6,7] or white phosphorus[6] with a variety of amine solvents. Stock[4a] found that phosphine was eliminated and reddish colored solutions were formed when P_2H was treated with liquid ammonia. The substance $P_{4.5}H$, (P_9H_2), which was reportedly obtained by the thermal decomposition of P_2H under the proper conditions,[4a] likewise dissolved, but without the evolution of phosphine. In all cases black substances were obtained by evaporating the solvent, whose compositions averaged around $P_{4.5}H$ and which contained up to one molecule of ammonia. A small amount of non-volatile residue remained on strong heating *in vacuo*. This appeared to be P_3N_5.[6a] Products obtained by the direct action of liquid ammonia on phosphorus were similar. Although comprehensive quantitative data have been reported only in the case of products obtained from ammonia, it seems likely that other nitrogen bases also yield similar products.

In view of the thermal instability of biphosphine

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[1] Taken in part from a Thesis by Evan H. Street, Jr., presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[2] This research was supported in part by the Office of Naval Research under Contracts Nonr-598(00) and N8onr-74200. Reproduction in whole or in part is permitted for any purpose of the United States Government. Presented before the Inorganic Division of The American Chemical Society, 132nd National Meeting, New York, September, 1957.

[3] E. C. Evers and E. H. Street, Jr., THIS JOURNAL, **78**, 5726 (1956).

[4] (a) A. Stock, W. Bottcher and W. Lenger, *Ber.*, **42**, 2839, 2847, 2853 (1905); (b) R. Schenck and E. Buck, *ibid.*, **37**, 915 (1904).

[5] The molecular formula $P_{12}H_6$ was proposed by R. Schenck and E. Buck, *ibid.*, **37**, 915 (1904), as a result of cryoscopic measurements in molten phosphorus.

[6] R. Schenck, *ibid.*, **36**, 979, 4202 (1903).

[7] (a) A. Stock, *ibid.*, **36**, 1120 (1903); (b) A. Stock and O. Johannsen, *ibid.*, **41**, 1593 (1908); (c) H. Krebs, *Z. anorg. Chem.*, **266**, 175 (1951); *Angew. Chem.*, **64**, 293 (1952).

and the results obtained when its solid decomposition products were treated with liquid ammonia, it seemed of interest to investigate the action of ammonia on biphosphine itself. This seemed particularly important in view of the apparent differences observed between the course of the decomposition of biphosphine in the presence of moisture and under strictly anhydrous conditions. We were particularly interested in determining whether decomposition might not stop at some intermediate stage, say $P_{2.25}H$, rather than proceed further to $P_{4.5}H$.

Preliminary investigations also have been carried out on the reaction of white phosphorus and ethylamine. This base provided a most suitable medium for such a study since phosphorus is readily soluble, allowing the reaction to proceed homogeneously at room temperature.

Experimental

Biphosphine was prepared by treating commercial calcium phosphide with water and was purified according to the procedure described previously.[3] Ammonia was dried by refluxing over sodium. Manipulations were carried out using standard vacuum techniques.

1. **Treatment of H_4P_2 with Liquid Ammonia.**—Measured quantities of biphosphine were taken from the storage system either by distilling directly into the reaction vessel and weighing it or by condensing a known volume of vapor into the vessel. A large excess of ammonia (20 to 30 cc.) was then frozen on top of the biphosphine, and the vessel was isolated and maintained at the boiling temperature of liquid ammonia until the reaction was completed.

Biphosphine is only slightly soluble in, and is more dense than, liquid ammonia. The ammonia phase gradually acquires a yellow, then a red-orange and finally a deep violet color, and the biphosphine phase finally disappears after about 24 hr. The color of this solution is characteristic of those reported by Stock[4] on dissolving the solid hydrides.

Phosphine is evolved during the dissolution of the biphosphine. In order to separate this from the relatively large volume of liquid ammonia, the latter was largely absorbed by distilling onto sodium iodide cooled to 0°, the phosphine concentrating in the gas phase. Residual ammonia was removed by passing the gas through absorption tubes filled with anhydrous magnesium perchlorate. The phosphine was frozen in a detachable trap and weighed directly or measured volumetrically as a gas in a calibrated part of the system. Vapor density measurements were made in order to check the purity of the product.

The black residue remaining after evaporation of the ammonia could be redissolved on adding fresh solvent. However, the red product obtained after heating the residue to 200° and pumping was insoluble in ammonia. This latter procedure served to remove most of the ammonia initially present. Treatment of the black residue with mineral acid also converted it to a reddish colored substance; further treatment with excess ammonium hydroxide solution then restored the original black appearance.

Several methods were investigated in an attempt to establish the compositions of the black residues: (1) The phosphine which evolved was measured. (2) The residue was analyzed for phosphorus using the magnesium ammonium phosphate method.[8] An analysis of the residue for phosphorus was often employed as a check on method 1. (3) The black material was degraded thermally and the vapors were passed over hot copper gauze.[3] Phosphorus was retained by the copper and the hydrogen and ammonia were collected and determined separately. The copper phosphide was weighed to determine phosphorus. (4) The black product was weighed and these data were used to compute the ammonia content of the residue.

In theory, analyses by method 1 should have been adequate to establish the P/H ratio in the residue. In practice, however, the quantitative separation of phosphine from the large amount of solvent proved troublesome. But when an analysis was also made for residual phosphorus (method 2) and a material balance was obtained, we were inclined to place considerable confidence in the results. Experiments in which we have the most comprehensive data are presented in Table I. The compositions of the residues were calculated from the per cent. phosphorus evolved as phosphine. These are given in column 6. In those experiments where the residues were weighed, the ammonia contents were calculated with the results given in column 7.

TABLE I

THE DECOMPOSITION OF BIPHOSPHINE IN LIQUID AMMONIA

Expt. no.	Wt. H_4P_2, g.	P, % Evolved as PH_3	Residue by anal.	Wt. residue, g.	Ratio P/H	NH_3/H
1	1.1997	63.20	36.40	0.4198	3.67	0.16
2	0.0935	62.00	40.30	....	3.05	..
3	.1283	62.78	37.56	....	3.25	..
4	.0324	64.05	...	0.0122	4.59	0.92
5	.6957	63.26	37.00	.2451	3.46	.09
6	1.4589	63.57	...	.5243	3.93	.31
7	1.2940	63.49	...	.4602	3.76	.20

The data recorded in Table I indicate considerable variation in the composition of the products. The average value for the P/H ratio was 3.66. This value leads to the composition $P_9H_{2.50}$, which is to be compared with the value P_9H_2 reportedly obtained by Stock, *et al.*,[4a,5] who employed solid hydrides in their study. Variations in the ammonia content are more apparent. While in part this may be due to inaccuracies in weighing, we have found the ammonia content to be very much a function of experimental conditions, *e.g.*, the time of pumping after removing solvent, the temperature and the efficiency of evacuation. For example, the product in expt. 6 was pumped and weighed after time intervals of 15 min., 1 hr. and 2 hr. The loss in weight then led to the ratios of moles ammonia to hydrogen of 0.31, 0.14 and 0.15, respectively.

In the case of expt. 1, when the product was heated for 1 hr. at 100°, 0.37 mmole of condensable gas was recovered. After heating at 130° for several hours an additional 0.15 mmole was obtained. The molecular weight of the combined gases was 16.8; calculated for NH_3, 17.0. The composition of the residue was now calculated to be $P_{3.67}H(NH_3)_{0.008}$. It is apparent that ammonia was substantially removed by this treatment. The residue was colored a deep red rather than black. Heating above 200° caused the evolution of hydrogen (non-condensable gas), but quantitative data are lacking.

2. **Analysis by Thermal Degradation.**[3]—The product from expt. 6 was allowed to stand in an evacuated vessel for 114 days. Condensable gas was formed, but unfortunately this was lost due to a mishap. Assuming the gas to be ammonia the loss in product weight led to the composition $P_{3.93}H(NH_3)_{0.05}$; if the gas were phosphine, the calculated composition would be $P_{4.54}H(NH_3)_{0.16}$.

Two analyses were made of the material. In the first, 0.2102 g. of sample led to the recovery of 0.123 mmole of NH_3, 0.746 mmole of H_2 and 1.2 mg. of non-volatile residue (P_3N_5).[6a] Some phosphorus diffused through the copper screening without reaction, so its weight was calculated by difference. Correcting for nitrogen (as NH_3) and phosphorus in the residue, the calculated composition was $P_{4.81}H(NH_3)_{0.12}$. In the second sample weighing 0.2342 g., there were recovered 0.806 mmole of H_2, 0.119 NH_3 and 7.366 P, leaving 0.9 mg. residue. The recovery was 98.94%. In this experiment the calculated composition was $P_{4.84}H(NH_3)_{0.10}$. From these results, which are in excellent agreement, it would appear that phosphine was evolved, together with ammonia, during the long period of standing *in vacuo*.

3. **Reaction of Phosphorus with Ethylamine.**—White phosphorus (5–15 mmoles) was transferred to a weighed reaction vessel containing distilled water. The inlet tube was sealed and the water evaporated under vacuum. The vessel was weighed, reattached to the vacuum system by a ground joint, and about 30 cc. of dry ethylamine was condensed on the phosphorus. This was frozen with liquid air and the vessel was evacuated thoroughly; then it was sealed off below the inlet stopcock. The vessel was provided with a break-off tube for re-entry and reattachment to the vacuum system.

At room temperature the liquid assumed a reddish color within an hour and became an opaque black-red within 4 hr.

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

In order to ensure complete reaction, the solutions were allowed to stand for periods ranging from one to six months. A black deposit formed on the walls of the vessel.

On opening the vessel the amine was allowed to evaporate through a column of water. No gaseous products were isolated. The black residue turned red when treated with 10% HCl, and amine was detected in the aqueous phase. The black color of the product was restored on treating with aqueous ammonium hydroxide.

A number of preparations were analyzed for their nitrogen content by digesting the material with 10% HCl, then analyzing filtrate and residue for amine, using the Kjeldahl method.

TABLE II

ANALYSES OF BLACK PRODUCTS OBTAINED ON TREATING WHITE PHOSPHORUS WITH ETHYLAMINE

Time of pumping	P, mmoles	Meq. amine		Mol. amine per atom P
		Filtrate	Residue	
15 min.	8.41	1.93	..	0.23
15 min.	12.49	1.89	..	.15
25 hr.	14.45	1.24	..	.086
72 hr.	6.94	0.30	0.07	.053
168 hr.	5.07	0.18	0.11	.057

From the above data it may be seen that a fairly large proportion of the amine present in the black products may be removed by pumping. Continued suction yields a substance containing about one-half molecule of amine per nine atoms phosphorus. This result is very similar to that obtained by Stock in liquid ammonia. It is of interest to note that treatment with acid under the above conditions did not entirely remove nitrogen from the compound. The residual nitrogen was not determined in the first three experiments, but it probably was relatively small judging by the last two experiments.

The product obtained after 72 hr. of pumping (Table II) was analyzed by the pyrolysis method. A sample weighing 0.2323 g. produced 0.587 mmole of H_2, 0.307 mmoles of amine and 6.824 matoms of P. The non-volatile residue weighed 1.8 mg.; recovery, 98.24%. Neglecting the residue, the calculated composition is $P_{5.81}H(C_2H_5NH_2)_{0.26}$. The phosphorus content was distinctly higher than in those products formed by the decomposition of biphosphine in ammonia.

Discussion

Early investigations on the solids obtained when biphosphine was decomposed thermally were concerned mainly with establishing the existence of compounds of definite proportions. It is probably fortuitous that very nearly stoichiometric combinations were obtained under various conditions on allowing biphosphine to decompose thermally. There is little evidence, chemical or otherwise, favoring the existence of solid hydrides as discrete chemical entities.

Royen[9,10] was the first to question the existence of stoichiometric solid hydrides. In the case of $P_{12}H_6$ an inspection of published data indicated a random distribution of the atomic P/H ratios about P_2H, which seemed to lie outside of analytical error. Thus, values reported by Schenck[4b] and by Stock[4a] ranged from $P_{2.45}H$ to $P_{1.89}H$; and Royen,[10] using Stock's wet method of preparation, obtained values ranging from $P_{2.36}H$ to $P_{2.06}H$. In a lengthy argument, Royen concluded that these solids are "sorption compounds" of phosphine on amorphous phosphorus. We would rather look upon these substances as non-stoichiometric compounds of hydrogen and phosphorus, with hydrogen and sometimes other groups occupying orbitals on phosphorus which might otherwise be used to bond phosphorus to phosphorus.

When biphosphine decomposes *in vacuo* at room temperature, the mobile liquid gradually becomes sirupy, turns yellow, then solidifies. Evidently condensation continues until a polymerized immobile mass is produced, and the elimination of hydrogen as phosphine ceases when active centers such as PH_2 and PH are so far apart that suitable collisions become infrequent. Heating causes the system to become more labile; hence at any particular temperature, phosphine is produced until suitable contacts again become infrequent. Finally we approach a temperature at which the P–H bond itself becomes unstable; hydrogen is produced and we are left with pure phosphorus.

We might next inquire why decomposition does not proceed as far in the presence of moisture. It seems reasonable to propose here that condensation is blocked by the incorporation of water or its fragments in positions which might otherwise be occupied by reactive groups such as PH_2. For example, products obtained in the presence of moisture have been found to contain between 1 and 2% of material which was non-volatile *in vacuo* on strong heating.[3,4] It has been assumed that this residue was caused by air oxidation, but we have found about 1% non-volatile material in hydrides which we prepared from biphosphine in the presence of moisture with air completely excluded.[3] This residue could have resulted only from a reaction involving water. Preparations made by decomposing biphospine *in vacuo* always sublimed cleanly, leaving no residue.

Hydrides prepared by Stock's method and containing more hydrogen than P_9H_2 lose phosphine when treated with liquid ammonia. In all cases black solids are obtained which contain about 18 mole % hydrogen in addition to solvent. Stock[7] found the compositions to average somewhere around $P_9H_2 \cdot xNH_3$, where x reflects the treatment accorded the product after removing solvent. On the average, using P_2H_4, we obtained products of about the same composition. While the results do not point to any particular stoichiometry for the system, it is clear that the hydrogen content is reduced to a low, and more or less constant, value.

Why decomposition proceeds farther in ammonia than in the presence of moisture (or *in vacuo*) is still a moot question. Royen proposes that the less volatile, more basic ammonia displaces phosphine absorbed on the surface of the colloidally dispersed solid hydride; internally absorbed phosphine is not displaced. However, it is doubtful whether this reasoning may be applied to the case of biphosphine. Decomposition here would seem to proceed homogeneously—that is to say there is no *a priori* opportunity for phosphine to be absorbed on (and in) a solid matrix from which it may later be displaced by ammonia. We would suggest that phosphine is evolved in these cases, proceeding to compositions close to P_9H_2, because dissolution creates additional opportunities for more favorable contacts between active groups; in effect this is like heating. It does not appear that any substantial amount of the solvent is bonded in chemically in this process, say as PNH_2 or PNH groups, since solvent may be virtually completely

(9) P. Royen and R. Hill, *Z. anorg. allgem. Chem.*, **229**, 97 (1936).

(10) P. Royen, *ibid.*, **229**, 369 (1936).

removed by mild heating or by treatment with acids; and the red hydride (effectively P_9H_2) may be resolvated, apparently reversibly, by treatment with liquid ammonia. On strong heating, these products, like those obtained in the presence of moisture, do not volatilize completely. We found about 1% non-volatile material in our preparations, suggesting that ammonia unites chemically with the products to about the same extent as does water. On this basis we would venture to suggest that decomposition would be much like that observed in the presence of moisture were it not for the fact that ammonia dissolves the hydrides. Thus the loss of phosphine from substances such as P_2H will be largely intramolecular, and decomposition of biphosphine proceeds to the level dictated by intramolecular blocking and the availability of active groups within a polymeric unit.

Closely related in chemical properties and composition to the above products are those black substances obtained when white phosphorus is treated with amine solvents.[4a,6] For example, on treating phosphorus with ethylamine we obtained a substance which analyzed as $P_{5.8}H(C_2H_5NH_2)_{0.28}$. Evidently the hydrogen is derived from the solvent, although no other products were isolated in our experiments. On heating, or on treating with the aqueous hydrochloric acid, most of the nitrogen was removed as amine and the substances turned orange-red in color. Strong heating *in vacuo* left about 2% non-volatile material.

It is a well-established fact that when white phosphorus is converted to the amorphous form in solution, the resulting solids contain variable amounts of solvent.[6c,7a,11,12] H. Krebs[6c] has pointed out that it is to be expected that solvent will be attacked during the conversion of phosphorus from the white to amorphous form. When the P–P bonds in the P_4 molecule are broken, the free radicals so formed will either combine with solvent or form intramolecular P–P bonds with more favorable bond angles, leading eventually to an insoluble amorphous variety. The conversion of white to red phosphorus is also subject to catalysis, *e.g.*, with iodine or sulfur.[13] Here the catalyst is used up as reaction proceeds and becomes incorporated in the final product. Krebs[7a] has shown that a variety of amines also catalyze the conversion. As in ammonia, and in our experiments with ethylamine, black substances are formed which contain solvent. These solids, which are largely phosphorus but which contain other elements or solvent, are termed "copolymers" by Krebs.

However, we feel the situation, at least with respect to the constitution of the black substances formed with amine solvents, is more subtle than envisioned by Krebs or by Royen. In the first place our experiments with phosphorus in ethylamine, as well as those by Stock in ammonia, indicate unequivocally that more hydrogen is present in the product than could possibly have resulted simply by the incorporation of solvent. This is contrary to the copolymer theory of Krebs and would seem to be difficult to interpret in terms of the absorption theory of Royen. Secondly, the solvent may (for the most part) be reversibly extracted by acid and replaced by redissolving without apparently materially affecting the hydrogen content.[4] Such behavior strongly suggests an acidic behavior on the part of the hydride. In this connection it has been shown that the polyhydrides conduct electricity in liquid ammonia.[14] The most obvious conclusion here is that we have salt formation, a property which is brought out by contact with strongly basic solvents. This would argue for the direct bonding of hydrogen to a polyphosphide substrate. The concept that all hydrogen is present as phosphine hydrogen seems rather forced.[10]

Apparently the end result is the same whether one treats biphosphine or white phosphorus with ammonia or amines. In either case the phosphorus attempts to revert to the thermodynamically stable amorphous form. In the case of biphosphine the conversion is blocked by the presence of bonded hydrogens when the latter are too far apart for elimination as phosphine. A small amount of solvent also seems to be bonded in chemically. White phosphorus appears to attack the solvent as conversion proceeds, with the result that some hydrogen, together with a small amount of solvent, becomes incorporated into the phosphorus structurally. These groups then prevent further conversion to the red form.

PHILADELPHIA, PENNSYLVANIA

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(11) A. Stock, H. Schroder and E. Stamm, *Ber.*, **45**, 1514 (1912).

(12) R. Schenk, *ibid.*, **36**, 979 (1903).

(13) T. W. DeWitt and S. Skolnik, THIS JOURNAL, **68**, 2305 (1946).

(14) P. Royen, *Z. anorg. allgem. Chem.*, **235**, 324 (1938). The molecular weights of solid hydrides in ammonia were found to range between 2640 and 2880.