is thus attributed to the over-all asymmetry due to the p^3-bonds. With increasing electronegativity of the substituent atoms, this asymmetry appears to be counterbalanced by the "abortive bond" resulting from the increasing s-character of the hybrid. Finally, the "abortive bond" seems to overpower the real bonds to again cause an increase in shielding for PF_3 as compared to PBr_3.

The smaller chemical shifts found for the quadruply connected phosphorus atoms are probably due in great part to variations in the distribution of π-bonds among the four σ-bonds. The observed action of electron-donating substituents in causing less shielding of the phosphorus nucleus is thus explained by the action of these substituents in shifting π-bonds within the σ-bonded sp^3-hybrid structure so as to upset the electronic symmetry of the system. It appears that the variations from one individual compound to another in interatomic distances, as discussed in Paper I of this series, are reflected in the minor variations noted in nuclear magnetic resonance shifts. Since the purpose of Papers I and II is to establish broad generalities, peculiarities in the bonding in specific compounds are not elaborated upon here.

The large positive shifts due to more than four atoms connected to the phosphorus are probably attributable to the change in hybridization, with use of d-orbitals in the σ-bond base structure, and the similar shifts for bent bonds must be attributed to the poor overlapping of the orbitals and the resulting change in p-shell symmetry.

Acknowledgment.—The authors are indebted to the several individuals, designated in the Appendix, who generously donated many of the samples, and to Mr. John R. Parks of the Inorganic Chemicals Division of Monsanto for a number of helpful discussions.

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

The Lower Hydrides of Phosphorus. I. The Thermal Decomposition of Biphosphine[1]

BY E. CHARLES EVERS AND EVAN H. STREET, JR.[2]

RECEIVED JUNE 4, 1956

At room temperature under strictly anhydrous conditions biphosphine decomposes in a sealed system eliminating phosphine to form a yellow solid hydride which corresponds closely in composition to P_9H_4. Yellow products having a higher H/P ratio appear to contain biphosphine. There is no evidence for the formation of Stock's $P_{12}H_6$ under these conditions.[6] But when biphosphine is decomposed in the presence of moisture substances are formed which correspond closely to $P_{12}H_6$. On heating it would appear that non-stoichiometric solid hydrides of practically any composition below P_9H_4 may be realized by employing the proper decomposition schedules. Vapor pressure and molecular weight data are recorded for biphosphine.

Introduction

Apart from some very early observations[3] four lower hydrides of phosphorus of apparently definite composition have been reported in the literature. One, biphosphine, H_4P_2, is a clear, water-white liquid, which has been characterized fairly well physically.[4,5] The other three are yellow to red colored solids which have been represented by the empirical formulas P_2H, P_9H_2 and P_5H_2, respectively.

The yellow solid hydride, P_2H, has been studied fairly extensively by Stock, *et al.*[6] It is said to be formed during the decomposition of metallic phosphides by water and in other reactions yielding phosphine or biphosphine or by thermally decomposing biphosphine. . According to Schenck and Buck,[7] the molecular weight in molten yellow phosphorus corresponds to the molecular formula, $P_{12}H_6$.

The substance P_9H_2, a red solid, was first reported by Stock and co-workers,[6] who obtained it by the thermal decomposition of P_2H in the temperature range from 100 to 220°.

Finally, the substance P_5H_2 was reportedly obtained by Hackspill[8] on hydrolysis of alkali metal phosphides of the type M_2P_5. Hackspill also reported that a solid having the composition H_2P_5 could be prepared by heating Stock's[6] P_2H to 80°. Therefore he questioned the existence of P_2H, stating that Stock's result might be explained by the presence of biphosphine stabilized by adsorption on P_5H_2.

More recently Royen and Hill[4] and Royen[9] have repeated certain of the earlier investigations on these substances and have cast some doubt as to the existence of the solid hydrides as true chemical entities. Their investigations indicated that solids of variable composition, amorphous to X-rays, were formed when biphosphine was decomposed thermally under various conditions. . They also reported that substances of similar composition and properties could be formed by the direct reaction of white phosphorus and phosphine, and concluded that the solid forms were "absorbates" of phosphine on an allotropic modification of phosphorus.

Our present investigation was undertaken primarily in an attempt to resolve the question of the stoichiometry of products obtained by decomposing biphosphine thermally. We were particularly concerned with the reliability of certain previous data

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(1) This research was supported in part by the Office of Naval Research under Contract Nonr-598(00). Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Taken from a Thesis by Evan H. Street, Jr., presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

(3) J. W. Mellor. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1923, p. 802.

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

(5) Recent molecular structure studies have been carried out by E. R. Nixon, *J. Chem. Phys.*, in press.

(6) A. Stock, W. Böttcher and W. Langer, *Ber.*, **42**, 2630, 2847, 2853 (1909).

(7) R. Schenck and E. Buck, *ibid.*, **37**, 915 (1904).

(8) L. Hackspill, *Compt. rend.*, **156**, 1466 (1913).

(9) P. Royen, *Z. anorg. allgem. Chem.*, **229**, 112 (1936).

and the conclusions drawn from them in view of the small quantities of material examined and the magnitude of the errors which might be associated with the *modus operandi*.[4] Actually our results probably will serve to add to the confusion since, at room temperature, our data indicate that the solid obtained at the end-point of decomposition approaches the stoichiometry, P_9H_4. There is no indication that decomposition stops at P_2H, or at other intermediate compositions.

Experimental

1. **Preparation and Purification of Biphosphine.**—Several methods of preparing biphosphine are recorded in the literature, including the reaction of white phosphorus with solutions of strong bases or the neutral hydrolysis of various metallic phosphides. We attempted to prepare biphosphine by treating white phosphorus with concentrated potassium hydroxide solution, employing nitrogen as a sweep gas. But the yields were low and we abandoned this method for quantity preparations.

Finally, the neutral hydrolysis of commercial calcium phosphide was selected as a preparative reaction. The reaction was carried out in a 500-cc. flask fitted with a dropping funnel and connected through a series of four traps to a vacuum pump. About 200 g. of phosphide was placed in the reaction vessel, the dropping funnel was attached and the whole system evacuated thoroughly. The first trap was cooled with liquid ammonia to retain unreacted water. The next two traps were cooled with a Dry Ice–isopropyl alcohol slush to condense most of the biphosphine. The first trap was surrounded with liquid air to freeze out phosphine. The reaction vessel itself was surrounded with an ice-bath to minimize the decomposition of unstable biphosphine as formed. Mercury blow-off tubes were provided immediately after the reaction vessel and at the end of the system of traps. These served the dual purposes of compensating for possible pressure surges in the system and providing means for safely purging the system of phosphine after the reaction was completed. Since considerable quantities of hydrogen were produced in the reaction it was necessary to pump on the system continuously, in order to effect rapid removal of hydrides from the reaction zone. If this was not done a considerable amount of biphosphine decomposed in the reaction vessel.

After the addition of 40–50 cc. of water from the dropping funnel, the run was terminated, the material in the fourth trap was surrounded by Dry Ice and the proper stopcocks were manipulated to connect it with the mercury blow-off so that the phosphine might distil away. Residual material in the last three traps was then distilled into a storage vessel. The traps were cooled with liquid ammonia and the storage vessel was cooled with liquid air during this operation. The storage vessel was subsequently removed and attached to an independent system for further purification of the biphosphine. The product was stored at Dry-Ice temperatures. The yield of biphosphine amounted to about 10 g.

The crude material at −78° consisted of water-white liquid and small amounts of a white solid. The latter was not removed by distillation through phosphorus pentoxide, and melted at about −34° in contact with the liquid phase. Therefore it was not water. Solid and liquid were finally separated by subjecting the mixture to careful fractional condensation *in vacuo*. The mixture was cooled to −63°; the fractionation train consisted of four traps cooled to −78, −93, −130 and −185°, respectively. After distillation the white solid was found largely concentrated in the first trap; some was found in the next trap cooled to −78°. The next two traps contained roughly equal quantities of clear liquid biphosphine. Both fractions possessed identical vapor pressure behavior. All subsequent measurements were carried out with these fractions or on material purified by this method. The liquid air trap contained a small amount of phosphine and biphosphine which had passed through the train.

Several samples of the white solid were analyzed for hydrogen and phosphorus by the method described below, but we cannot be certain they were entirely free of biphosphine. The atom ratios H/P were 1.968, 1.980 and 1.922, respectively. These correspond very closely to H_4P_2, being, respectively, $P_2H_{3.936}$, $P_2H_{3.844}$. It is felt that this material represents a new, volatile, solid hydride, and not a modification of biphosphine. All analyses of the latter gave values somewhat below 2. The same material was formed during the preparation of deuterobiphosphine; but it appeared to be somewhat more stable than its hydrogen analog. Both substances turned yellow and eliminated phosphine on warming to room temperature. No further investigation was made of these products.

2. **Stability and Vapor Pressure Measurements.**—Previous data on the vapor pressure of biphosphine were obtained by Royen and Hill[4]; it seemed appropriate to repeat these measurements as a check on the purity of our products. However, at all temperatures above −78° we were faced with the annoying problem of accounting for excess pressure resulting from the decomposition of biphosphine into phosphine and lower hydrides. Our procedure, finally, was to isolate freshly distilled material in the measuring system, allow sufficient time to establish thermal equilibrium, flash off the vapor phase to remove phosphine and then plot pressure as a function of time. Two processes were assumed to contribute to the increase of pressure with time. The first was the warming of the liquid back to the equilibrium temperature after having been cooled by vaporization due to the removal of the forerun. The second was the decomposition of biphosphine into phosphine and lower hydrides. Plots of vapor pressure as a function of time revealed significant plateaus in the region beginning approximately 4 minutes after termination of the forerun distillation and extending for various times, depending on temperature; then the pressure increased regularly with time. At higher temperatures the plateau was distinctly shorter but was still observable at 0° for 5 or 6 minutes. We have recorded the value reached after about 4 minutes as the equilibrium vapor pressure, but are aware of the uncertainties involved. It is not impossible for example that these pressures might even be too low; if decomposition had proceeded to any extent solid decomposition products dissolved in the biphosphine and would lower its vapor pressure. Vapor pressures were recorded to the nearest 0.1 mm. using a mercury manometer in conjunction with a cathetometer; temperatures were held constant to within ±0.2°.

Our data, together with those recorded by Royen and Hill, are shown on a log P (mm.) *vs.* $1/T$ plot in Fig. 1; also included are measurements on D_4P_2, which was prepared in connection with spectroscopic studies being carried out by another group in the laboratory.[5] These data lie on the same curve within experimental error, but the measurements were not carried to the higher temperatures. The solid line in Fig. 1 represents a least-square treatment of all the data, and is given by the equation, log P (mm.) = $-1498/T + 7.330$. This leads to a latent heat of vaporization of 6889 cal./mole, 63.5° for the extrapolated boiling point and 20.46 for Trouton's constant. These values are to be compared with 6728, 66.7° and 19.79, respectively, obtained

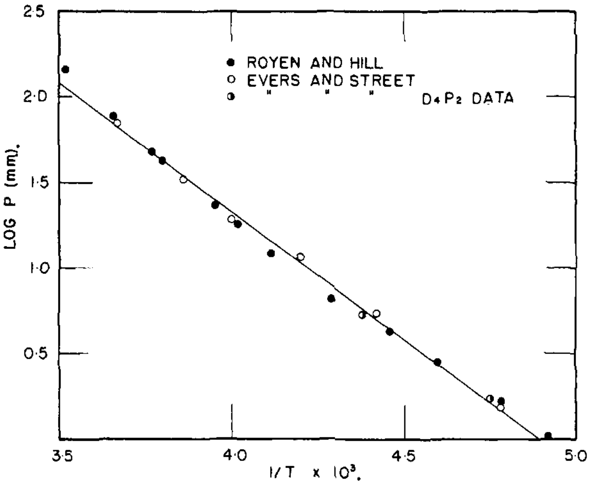

Fig. 1.—Vapor pressure of biphosphine; log p (mm.) *vs.* $1/T \times 10^3$.

using only our data, or to 6945, 62.6° and 20.68, respectively, obtained on treating Royen and Hill's data by the method of least squares. We are unable to justify the values, 7890, 51.7° and 24.2, respectively, reported by the latter, unless they placed more confidence on pressures recorded at the higher temperatures, which we consider more uncertain due to the decomposition of biphosphine. In fact, they concluded there was appreciable association in liquid biphosphine as a consequence of the high value found for Trouton's constant. This conclusion seems unwarranted.

3. Vapor Density Measurements.—At several temperatures, vapor density measurements were made in conjunction with the vapor pressure measurements reported above. The vapor was isolated in a volume calibrated section of the system bearing a manometer; then it was frozen with liquid air into a weighed molecular weight bulb. The bulb was removed and reweighed. Molecular weight data are recorded in Table I. Also recorded are the temperatures of the liquid biphosphine and the corresponding vapor pressures at which molecular weight measurements were made.

TABLE I

VAPOR DENSITY OF P_2H_4

Temp., °C.	Mol. wt.	Vap. pres. (mm.)
−33.5	67.08	10.0
−22.1	67.09	20.4
−14.2	66.34	32.5
−14.0	66.95	33.0
0.0	66.47	73.0

As may be seen from Table I, the average measured molecular weight (66.75) exceeds theory (65.99) by about 1%, but there appears to be no significant trend of values with changing pressure. There is however a slight decrease with increasing pressure, which might be attributed to contamination by phosphine, but we feel the maximum deviation is within experimental error. If measurable association were to occur, we would certainly expect the molecular weight to increase with increasing pressure. Royen and Hill report this type of trend as a result of three measurements in the temperature range from −35 to −8°. They obtained molecular weights of 66.15, 66.30 and 67.05, respectively, and found that the monomeric weight was obtained on extrapolation to zero pressure. We have been unable to duplicate these results; the best we can report is that the hydride is monomeric within our experimental error.

4. Analysis of Biphosphine.—An analysis of the hydrogen and phosphorus content of the various hydrides was carried out employing a method described by Stock, *et al.*[6] This consisted of passing the hydride across weighed rolls of pure copper screening, heated to 250–300°. Phosphorus was retained by the copper in the form of phosphide and the samples could be weighed in air. The hydrogen released in the reaction was pumped into an eudiometer tube, where its volume and pressure were measured. In some experiments the purity of the hydrogen was checked by ascertaining that no gas was condensed on cycling it through a trap cooled with liquid air; after it was oxidized by repeated passages over hot copper oxide it was shown that all material was condensable. In a few experiments the water so produced was absorbed by phosphorus pentoxide and weighed. The weight and volume measurements checked within 0.1%.

In order to calibrate the method the first analyses were carried out using phosphine; the method was then applied to biphosphine and later to the lower hydrides described below. Since only hydrogen to phosphine ratios were desired it was unnecessary to accurately determine the quantity of hydride being analyzed although this was done in several instances with solid materials. The results of determinations on phosphine and biphosphine follow. In three determinations employing phosphine the H/P ratios were, respectively, 3.058, 3.063 and 2.981; average, 3.031. This result was 1% higher than theory, but was considered satisfactory, since only approximately 1.5 millimoles of material was employed. In four determinations using biphosphine, the ratios were 2.053, 2.036, 2.013 and 2.030, respectively; average 2.033. This result was also approximately 1% higher than theory. It would seem that a trend to slightly high values is peculiar to the method.

5. Decomposition of Biphosphine.—For the most part the decomposition of biphosphine was studied at room temperature. Samples of material weighing from 0.5 to 2.0 g. were sealed into weighed flasks approximately 250 cc. in volume. These were fitted with capillary tubes for reentry into the vacuum system after completion of an experiment. With most samples, the liquid phase turned noticeably yellow within the first day of standing, then it became very viscous and gradually solidified. After long standing the solid became increasingly orange in color. Also, the entire inner surface of the bulb became coated with a thin yellow-orange deposit. One sample proved extraordinarily stable. The liquid phase remained colorless and mobile for three days before the characteristic decomposition became noticeable.

After appropriate periods of standing the flasks were reattached to the vacuum system, the contents were frozen with liquid air and the flasks were re-entered by cracking the capillary with a tube opener. All samples were tested for non-condensable gas, but none was found. The liquid air was then replaced by a Dry Ice bath which permitted the phosphine to vaporize, but retained any undecomposed biphosphine. The phosphine was transferred into a volume-calibrated manometer system and its pressure and temperature were determined. The Dry-Ice bath was then removed from the decomposition vessel, the tube was closed off from the vacuum system by means of a stopcock and it was allowed to warm to room temperature. If decomposition had not been completed, any additional phosphine was removed periodically until no more was evolved after standing for 24 hours or more. It was noted (with the exception of experiment 6, Table II) that an additional rapid decomposition always took place after opening the tubes to the vacuum system and removing phosphine. This was true even with samples which had been sealed up for six months. That this actually was decomposition and not merely an evolution of absorbed phosphine was established definitely, since the walls of the reaction vessels and exposed tubing, which connected into the vacuum apparatus, invariably became coated over with a yellow-orange deposit on standing overnight. Unquestionably biphosphine was evolved and it decomposed on contact with the glass vessel. It would appear as if a certain amount of biphosphine were stabilized by absorption in the solid residue, and that removing phosphine permitted it to diffuse more readily into the gas phase.

The composition of the residue was usually determined by a material balance, from a knowledge of the amount of

TABLE II

DECOMPOSITION OF BIPHOSPHINE AT ROOM TEMPERATURE

Expt.	Wt. H_4P_2, g.	Dec. time, days	Residue composition, H_x As $P_{12}H_x$	As P_9H_x
1[a]	1.294	8	10.28	7.72
		9	6.00	4.50
2	1.187	56	6.33	4.75
		57	5.35	4.01
3	1.699	24	6.00	4.50
		25	5.40	4.05
4[b]	1.968	18	9.48	7.12
		19	9.40	7.05
		21	7.87	5.90
		22	7.32	5.48
		22.5	5.80	4.35
		23	5.60	4.20
5	1.408	212	6.22	4.67
		213	6.00	4.50
		217	5 73	4.30
		218	5.45	4.09
6	0.499	222	5.25	3.94

[a] After the ninth day phosphine was still being evolved but the decomposition was not followed. In all other experiments no evolution of phosphine was detected after standing 24 hours following the final reading given in the table. [b] An analysis was attempted of the residue after 23 days, but it inflamed on contact with air.

sample introduced and the quantity of phosphine which was generated. In some instances the residue was analyzed directly employing the procedure described above; in others, the loss in weight was used to calculate the quantity of phosphine evolved. All methods checked excellently. The experimental results are given in Table II. The residue compositions are expressed as $P_{12}H_x$ and P_9H_x, respectively, for convenience in presenting the discussion which follows.

To illustrate the procedure employed in the decomposition experiments and to demonstrate the precision of our analytical methods experiment no. 2 of Table II will be followed through in detail. A sample of biphosphine weighing 1.1873 g. (17.992 mmoles) was collected in a decomposition bulb as described above. After 56 days at room temperature the bulb was reattached to the vacuum system and the phosphine was removed; 21.440 mmoles of phosphine was obtained, leading to a calculated residual composition of $P_{12}H_{6.331}$. On standing overnight at room temperature, the new sections of exposed tubing became coated over with a yellow solid. The following day, additional phosphine was removed, bringing the total up to 21.895 mmoles. The residue composition was now calculated to be $P_{12}H_{5.352}$ or $P_9H_{4.014}$. No further phosphine was evolved overnight. The decomposition bulb was sealed off the system and weighed. The weight loss was 744.0 mg.; the calculated weight loss based on the amount of phosphine evolved was 743.4 mg. These values agree to within 0.1%. The decomposition bulb was broken open and 199.5 mg. of yellow residue was weighed into a quartz boat. This was volatilized through heated copper as described above. From it, 1.405 mmoles of hydrogen and 6.314 milliatoms of phosphorus were obtained. These data give a P/H ratio of 2.245 which corresponds to $P_{12}H_{5.345}$ or $P_9H_{4.009}$, values which are within 0.1% of those based on the measured volume of evolved phosphine. The weight of the silica boat remained unchanged after the run, so all the yellow hydride had been volatilized. A check on the weight recovery showed that 195.6 mg. of phosphorus and 2.8 mg. of hydrogen were obtained. This gave a total weight of 198.4 mg., or a 99.45% recovery, based on the amount of solid employed in the analysis.

It might be pointed out that whenever the P/H ratios were approximately 9/4, the samples were stable in air, but if they were lower, the solid samples were apt to inflame in air. We attribute the inflammability to absorbed undecomposed biphosphine.

6. **Decomposition of Biphosphine in the Presence of Moisture.**—In his investigations on the preparation of solid yellow hydride Stock[6] carried out his decomposition in the presence of moisture and passed biphosphine through some substance having a large surface area, such as calcium chloride. He then removed the salt by washing with water. Under these conditions, air-stable preparations were obtained having P/H ratios fairly close to two, but usually less than two.

We analyzed two samples of yellow hydride which were recovered from the apparatus employed in the preparation of biphosphine. This material had been formed in contact with water in the first trap of the preparative apparatus. Like material prepared by Stock these substances were stable in air. Analyses gave H/P ratios of 0.494 and 0.481, respectively; there was some non-volatile residue. These data lead to the formulas $P_{12}H_{5.93}$ and $P_{12}H_{5.77}$, respectively, which are entirely comparable with data reported by Stock. It would appear that water, in some way, stabilizes substances of compositions approaching $P_{12}H_6$.

In another experiment we removed some yellow hydride which had formed in our fractionation apparatus. This was obtained from carefully purified biphosphine which had been thoroughly dried and fractionated. An analysis of this material gave a H/P ratio of 0.447 or $P_9H_{4.02}$. This result is consistent with those obtained by decompositions in sealed tubes. The material was stable in air.

7. **Decomposition of Biphosphine at Higher Temperatures.**—By heating biphosphine, or the yellow solid obtained at room temperature, to higher temperatures, phosphine is eliminated and products are obtained having lower H/P ratios. Hackspill[8] reports that P_5H_2 is obtained on heating Stock's yellow $P_{12}H_6$[6] to 80°; Stock[6] obtained P_9H_2 by heating $P_{12}H_6$ to 220°.

We have made no extensive investigation of the effect of heating but, qualitatively, with increasing temperatures, the substances take on a deeper reddish color, eliminate phosphine, finally melt and completely volatilize. Presumably the material which volatilizes after melting is phosphorus.

In one instance we attempted to volatilize a product (expt. 5, Table II) whose composition closely corresponded to P_9H_4. This was attempted in high vacuum at 160°. No visible sublimation occurred in two hours time, but phosphine was eliminated. An analysis of the residue gave a P/H ratio corresponding to $P_9H_{3.02}$. In a second experiment we attempted to volatilize a product whose composition corresponded closely to $P_{12}H_6$ using the same procedure. It may be pointed out, however, that the $P_{12}H_6$ used in this experiment was obtained by decomposing H_4P_2 in the presence of water vapor as described in Section 6, above. It was perfectly stable in air and did not appear to be contaminated with H_4P_2. Again we obtained no sublimation and the residue was analyzed as $P_9H_{2.92}$. Both results are close to P_3H, but this does not imply the existence of a compound of definite proportions. Rather, we are inclined to believe that, depending on conditions, one can produce substances of practically any composition.

Discussion

The decomposition of biphosphine in sealed tubes has been followed at room temperature for periods as long as 222 days. The colorless fluid first acquires a yellow color, then becomes viscous and finally solidifies to a yellow solid. As the decomposition proceeds, the solid takes on an orange hue; the color intensifies, becoming almost reddish, if the sample is heated.

The rate of decomposition, with evolution of phosphine, appears to depend on several factors. Among these are purity, cleanliness of the equipment and the amount of surface area exposed. The use of large contact areas to effect rapid decomposition has been described previously[4,6] and we concur in this observation. In this connection, it was noted that decomposition proceeded much more rapidly once our bulbs were reattached to the vacuum system and the phosphine removed. Removing phosphine apparently permitted occluded biphosphine to diffuse more rapidly into the gas phase, where it could decompose on contact with the walls of the container. Also, the operations of alternately cooling and heating could serve to fracture the solid and release biphosphine. This suggests that biphosphine might be stabilized by absorption in the solid matrix.

We are convinced that so long as samples undergo decomposition at room temperature the active species is biphosphine, unless some unknown volatile hydride is responsible for the elimination of phosphine. We base this conclusion on the following qualitative observations: (1) the container walls and connecting tubing became coated over with a film of yellow solid until decomposition ceased; (2) the solids inflamed spontaneously in air so long as phosphine was evolved in measurable quantity. We do not believe that yellow solids prepared as above are "absorbates" of phosphine on a yellow form of phosphorus as has been suggested.[4,9]

An inspection of Table II will show that no detectable amounts of phosphine were evolved after the residue compositions approached the stoichiometry, P_9H_4. For example, when decomposition was allowed to proceed to what appeared to be completion, residues were obtained in four experiments having the composition P_9H_x, where x equaled 4.01, 4.05, 4.09 and 3.94, respectively. Also a sample of yellow solid resulting from biphosphine which had decomposed in our purification train, analyzed as $P_9H_{4.02}$. We are not prepared to state unambiguously that our products represent true chemical entities, although our results suggest this to be the case.

It is a fact that materials containing more or less hydrogen are readily obtainable by adjusting the temperature and time of decomposition and other conditions. Stock[6] reported that P_2H was formed at room temperature, and this was formulated $P_{12}H_6$, as a result of Schenck's molecular weight determinations[7]; but as may be seen in Table II, our decompositions proceeded smoothly through this combination. When decompositions were carried out in sealed tubes it was apparent that residues analyzing as $P_{12}H_6$ contained substantial quantities of undecomposed biphosphine. But when we decomposed biphosphine in the presence of water vapor, as did Stock, we obtained air-stable samples whose compositions in two cases were $P_{12}H_{5.93}$ and $P_{12}H_{5.77}$, respectively. These results are entirely comparable with data reported by Stock. There is no question but that moisture in some way stabilizes substances whose composition averages somewhere near $P_{12}H_6$.

Hackspill[8] reported that the substance P_5H_2 may be obtained on heating Stock's $P_{12}H_6$[6,7] to 80°, and considered Stock's hydride to be P_5H_2 containing absorbed H_4P_2. Although we are inclined to doubt this interpretation, we fully believe that such a composition might be realized under proper conditions. In terms of our representation, Hackspill's compound may be written $P_9H_{3.6}$. This is not far removed from our substance, P_9H_4; but the difference is well outside our experimental error, so that we may state without hesitation that our decompositions at room temperature did not proceed to the level demanded by Hackspill's formulation.

When we heated yellow hydride samples in high vacuum for two hours at 160° we obtained substances corresponding to $P_9H_{3.02}$ and $P_9H_{2.92}$, respectively, in two experiments. Again we are inclined to believe it was fortuitous that substances were formed which corresponded closely to P_3H. By altering conditions slightly we could probably alter the P/H ratio.

Finally, it was reported by Stock that the red hydride, P_9H_2, could be obtained by heating $P_{12}H_6$ up to 220°. Again this seems perfectly reasonable. In the case of substances of about this composition there exists a considerable body of chemical evidence pointing to their existence as compounds of definite proportions.[6,10] We shall have more to say regarding the chemistry of these substances in our next paper.

In conclusion we feel that yellow hydrides prepared by decomposing biphosphine at room temperature contain absorbed, undecomposed biphosphine if the H/P ratio exceeds 4/9. When the ratio is close to 4/9 the elimination of phosphine becomes undetectable, and the substances are stable in air. A continuous elimination of hydrogen as phosphine appears possible on heating, yielding substances of variable composition depending on conditions. The decomposition of biphosphine in the presence of water vapor apparently follows a somewhat different course. Moisture seems to stabilize compositions in the neighborhood of $P_{12}H_6$.

PHILADELPHIA, PENNSYLVANIA

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[10] R. Schenck, *Ber.*, **36**, 979, 4204 (1903).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Chlorination of Arsenic(III) Fluoride[1]

BY HOWARD M. DESS, ROBERT W. PARRY AND GUIDO L. VIDALE

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The oxidation of arsenic(III) fluoride by chlorine is dependent upon the water content of the system. In an anhydrous system no reaction occurs. In the presence of a small amount of water impure tetrachloroarsenic(V) hexafluoroarsenate is obtained. The properties of this compound and methods for its purification are described. In the presence of an excess of water arsenic(III) fluoride is converted quantitatively by chlorine to arsenic acid. In systems of intermediate water content both reactions occur simultaneously. Nitrogen(III) chloride reacts with arsenic(III) fluoride to give tetrachloroarsenic(V) hexafluoroarsenate. The experimental results are discussed.

The early data[2] on the oxidation of arsenic(III) fluoride (AsF_3) by the halogens were either inconclusive or contrary to expected periodic relationships. For example, a reaction was reported with bromine but not with chlorine. If anything, the reverse might have been anticipated. Early studies in this Laboratory revealed that on certain occasions liquid AsF_3 was oxidized by chlorine to give impure tetrachloroarsenic(V) hexafluoroarsenate ($[AsCl_4][AsF_6]$), a compound which was described independently by Kolditz[3] concurrent with the completion of this work. On other occasions no solid product could be obtained. The foregoing anomalies have been correlated with the water content of the AsF_3. Not only the speed but the course of the reaction is dependent upon the amount of water present. Results on the chlorination process are summarized in this paper.

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[1] Abstracted from a thesis submitted on February 9, 1955, to the Horace H. Rackham School of Graduate Studies of the University of Michigan by Howard M. Dess, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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