U.D.C. 541.441

Phosphorus Hydrides

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The chemistry of phosphorus hydrides has assumed considerable importance—phosphine is the starting material for the synthesis of numerous organophosphorus compounds and fire resistant polymers; in recent years phosphorus hydrides have begun to be used in the semiconductor industry for the preparation of metal phosphides with a high degree of purity. The range of applications of phosphorus hydrides has increased in connection with the synthesis of a new class of complex compounds.

The review deals with the physical and chemical properties of the phosphorus hydrides investigated. The methods of synthesis of phosphorus hydrides, particularly phosphine, are examined. The applications of phosphine in industry are discussed. The bibliography comprises 141 references.

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Phosphorus forms the following compounds with hydrogen: PH_3—gaseous hydrogen phosphide (phosphine)[1]; P_2H_4—liquid hydrogen phosphide (diphosphine, biphosphine[1], hydrogen hemiphosphide), and solid hydrogen phosphides [1-5] which include compounds with the empirical formulae $P_{12}H_6$, P_7H_2, P_9H_2, and $(PH)_x$. There is no doubt about the structural formulae of the first two compounds, but no single view exists concerning the structure of the solid hydrides.

1. HYDROGEN PHOSPHIDE (PHOSPHINE)

a. Physical Properties

Phosphine is a colourless gas with an unpleasant smell, sparingly soluble in water (26 volumes of the gas in 100 volumes of water) and readily soluble in carbon disulphide, benzene, cyclohexanol, ether, and other solvents [1-3]. Some of the physical properties of phosphine [2,3] are listed in Table 1. Phosphine has been investigated by infrared, microwave, NMR, and Raman spectroscopy and mass spectrometry [2].

The structure of the phosphine molecule has been established on the basis of infrared and microwave spectra[2]. The molecule has the form of a trigonal pyramid with the phosphorus atom at the apex and has low polarity (dipole moment 0.55 D). All three hydrogen atoms in the molecule are equivalent, with the P–H distance 1.419 Å the height of the pyramid 0.70 Å, and the H–P–H angle 93.7°. [2,3]

The density and compressibility of phosphine have been thoroughly investigated to determine the atomic weight of phosphorus. These data have established that the molecular weight of phosphine is 34.000. Accurate determinations of the density and the compressibility made it possible to establish the deviation of phosphine from ideal gas laws and to derive an equation of state for phosphine vapour [2]. The physical constants of liquid phosphine show [2] that there is some molecular association in the liquid state but that the degree of association is much less than in water.

Comparison with the hydrides of the adjacent elements in the Periodic Table shows that phosphine forms few hydrogen bonds or none at all.

The surface tension of phosphine at −100°C is [2] 22 dyn cm^{-1}. In the solid state phosphine exists in four modifications with transition temperatures of −185.06°, −223.75°, and −242.87°C. Over a short temperature range near the absolute zero the supercooled form has an anomalously high heat capacity. The solution of phosphine in liquid ammonia conducts electricity. When the solution is electrolysed, elemental phosphorus is deposited at the anode[4,5]. Evidently ammonia forms a salt-like compound with phosphine having the probable formula $NH_4^+(PH_2)^-$.

Table 1. Physical properties of phosphine (PH_3).

B.p., °C	Q_{vap}, kcal mole^{-1}	Trouton's constant	ρ, g cm^{-3}	M.p., °C	Q_f, kcal mole^{-1}	$t_{crit.}$, °C	$P_{crit.}$, atm	Q_{form}, kcal mole^{-1}
−87.8	3.49	18.8	1.529	−133.8	0.27	+51	64	+2.29

Phosphine is extremely poisonous and must be handled with care—it is a poison which acts predominantly on the nervous system and interferes with metabolism. The maximum permissible concentration of phosphine in industrial buildings amounts to [6] 0.1 mg m^{-3}.

b. Chemical Properties

When phosphine is heated in the absence of air, it dissociates:

$$4\,PH_{3(gas)} \rightleftarrows P_{4(gas)} + 6H_{2(gas)}.$$

The thermal dissociation of phosphine was investigated in detail by Ipat'ev [7-9] and Frost [10]. At a high temperature the equilibrium is displaced to the right but at low temperatures the gas is quite stable.

The reaction of phosphine with oxygen is a branched-chain process resembling the oxidation of white phosphorus [2,11,12]. Studies on the mechanism of the combustion of phosphine were begun by van de Stadt [12] and the problem was elucidated in detail by Semenov [11].

In air phosphine burns with formation of phosphorus pentoxide:

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O.$$

On considerable rarefaction and particularly in the presence of water vapour, slow oxidation without inflammation, accompanied by the formation of phosphorus acids, may take place [13]:

$$2PH_3 + 3O_2 \rightarrow 2H_3PO_3,$$
$$PH_3 + O_2 \rightarrow HPO_2 + H_2.$$

It has been suggested [14] that the first stage of the slow oxidation is the formation of phosphine oxide PH_3O. However, the latter could not be obtained by direct oxidation of phosphine with nitrobenzene or trimethylamine oxide [10]. The attempt to synthesise phosphine oxide by reducing phosphorus oxychloride and oxybromide with metal hydrides (LiH, $LiBH_4$) in ether at low temperatures was unsuccessful; phosphine oxide was not isolated probably because of its high reactivity, the tendency to polymerise with the elimination of water, and thermal instability at temperatures in excess of $-115°C$.

Since it is a branched chain reaction, the oxidation of phosphine has upper and lower critical pressure limits. Inert gases decrease the lower limit, preventing diffusion to the walls of the vessel, if the pressure of the inert gas is less than that of phosphine or oxygen. Irradiation with ultraviolet light reduces the limiting oxygen pressure [2] through phosphines' forming a substance (possibly atomic hydrogen) which affects the chain reaction. The upper limiting pressure of oxygen in the oxidation of phosphine is independent of the dimensions of the reaction vessel, decreasing somewhat in the presence of an inert gas.

The solution of phosphine in water has virtually no acid or basic properties; however, phosphine hydrate probably does exist. Phosphine dissolved in water gradually decomposes into hydrogen, phosphorus, and a solid phosphorus hydride.

With acids, phosphine forms phosphonium salts. Phosphonium halides can be obtained by the reaction of phosphine with hydrogen halides and the sulphate and perchlorate by the reaction with sulphuric and perchloric acid. The reaction with hydriodic acid can be represented by the equation

$$PH_3 + HI \rightarrow PH_4I.$$

In water these compounds hydrolyse almost completely with formation of phosphine, the hydrogen ion, and the halide ion.

Phosphine is a more powerful reducing agent than ammonia; it reacts spontaneously with chlorine at room temperature, forming phosphorus chlorides and hydrogen chloride, and with fused sulphur it forms hydrogen sulphide. Hydrogen sulphide and phosphine also interact (much more slowly than phosphine and sulphur), hydrogen and phosphorus sulphides being formed [2]. Reaction between phosphine and phosphorus trihalides leads to the formation (together with other products) of elemental phosphorus and the hydrogen halide:

$$PCl_3 + PH_3 \rightarrow 2P + 3HCl.$$

The reaction with pentahalides yields the trihalide and the hydrogen halide:

$$3PCl_5 + PH_3 \rightarrow 4PCl_3 + 3HCl.$$

As a reducing agent, phosphine reacts with many oxidising agents [2]: for example, it reduces metal ions to the free metal:

$$PH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3PO_3,$$

oxides to the phosphides [15]:

$$In_2O_3 + 2PH_3 \rightarrow 2InP + 3H_2O,$$

and iodine to iodides [2]:

$$PH_3 + 3I_2 + 3H_2O \rightarrow H_3PO_3 + 6HI.$$

The reactions of phosphine with silver nitrate, iodine, potassium permanganate, etc. are used for its quantitative determination. The phosphine molecule has a free electron pair at the phosphorus atom and exhibits electron-donor properties, so that phosphine, like ammonia, shows at least some tendency to form complexes with electron-acceptor molecules. For example, phosphine forms complexes of the type $P_2Hg_3.3HgCl_2$ with mercuric chloride [2], $PH_3.BF_3$ and $PH_3.2BF_3$ with boron trifluoride, $2PH_3.B_2H_6$ with diborane, and $[V(CO)_4PH_2]_2$ with vanadium hexacarbonyl [16].

Phosphine reacts with many organic compounds and this leads to the possibility of synthesising compounds with a phosphorus–carbon bond which cannot be prepared in other ways.

The interaction of phosphine with organic compounds takes place stepwise with formation of mono-, di-, and tri-substituted phosphines and sometimes quaternary phosphonium compounds in the presence of strong inorganic acids. The reaction of phosphine with aldehydes and ketones has been thoroughly investigated [17–18]. In the presence of a strong acid this reaction takes place according to the following general equation:

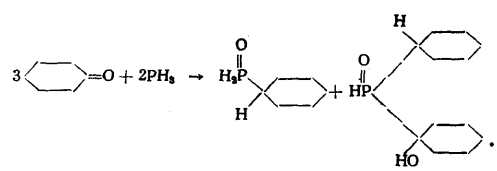
$$PH_3 \xrightarrow{>C=O} >C(OH)-PH_2 \xrightarrow{>C=O} (>C-OH)_2PH \xrightarrow{>C=O}$$

$$(>C-OH)_3P \xrightarrow{>C=O,HX} (>C-OH)_4PX.$$

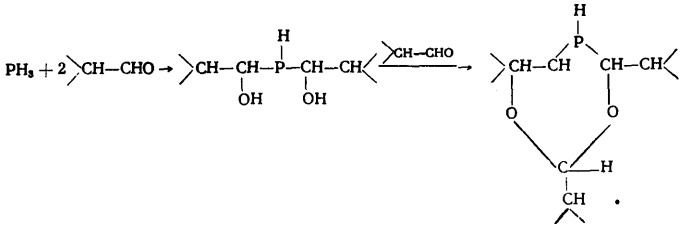
With aliphatic aldehydes, a mixture of mono-, di-, and tri-substituted phosphines and quaternary phosphonium salts is obtained, while aliphatic ketones and aromatic aldehydes yield mono-, and di-substituted phosphines [19,20], which isomerise to phosphine oxides. A classical example of the reaction of phosphine with aldehydes is the reaction of phosphine with formaldehyde in aqueous solution in the presence of hydrochloric acid discovered by Hofmann [23]. The reaction yields tetra(hydroxymethyl)phosphonium chloride—the starting material for the synthesis of many compounds, including fire-resistant polymers [24,25]. Soborovskii and coworkers [26,27] later showed that the reaction of phosphine with formaldehyde can take place also in the absence of a catalyst under a pressure of 150–300 mmHg. Under pressure paraformaldehyde reacts with phosphine [26,27] forming tri(hydroxymethyl)phosphine. With acetone, isopropoxyisopropylphosphine is obtained:

$$2CH_3COCH_3 + PH_3 \rightarrow (CH_3)_2CH-\overset{O}{\overset{\|}{P}}-C(OH)(CH_3)_2$$

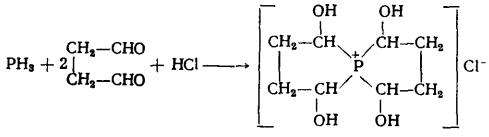
while the reaction with cyclohexane gives a mixture of cyclohexylphosphine oxide and cyclohexyl-1-hydroxycyclohexylphosphine oxide [19,20]



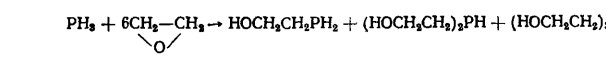
The condensation of phosphine with α-substituted aldehydes stops at the stage involving the formation of a disubstituted product[21], which is converted in the presence of an excess of the aldehyde into a heterocyclic compound:



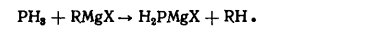
Phosphine reacts with dialdehydes, forming a spiro-ring compound[19,20]:



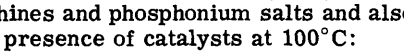
but the rings are only five- and six-membered; glyoxal gives rise to a product with a linear structure; the reaction with epoxy-compounds gives low yields of a mixture of mono-, di-, and tri-substituted phosphines; for example, the reaction with epoxyethane takes place as follows[21,24,28]:



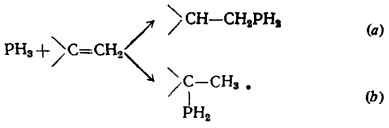
With organomagnesium compounds phosphine forms monosubstituted analogues of the Grignard reagent[21] with high reactivity:



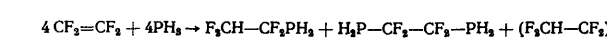
Phosphine adds to olefinic compounds in the presence of strong acids[29,31] with formation of mono-, di-, and trisubstituted phosphines and phosphonium salts and also to 1-olefins[32] in the presence of catalysts at 100°C:



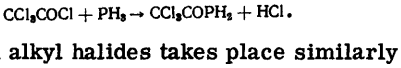
In a radical mechanism the phosphorus atom adds to the terminal carbon atom (*a*) and in an ionic mechanism to the middle carbon atom (*b*):



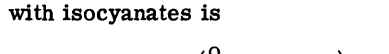
With tetrafluoroethylene, a mixture of products is formed[31]:



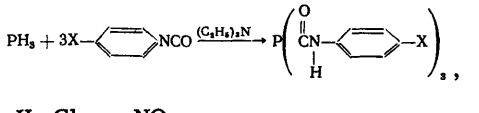
Phosphine reacts with organic acid chlorides to form a mixture of mono-, di-, and tri-substituted products[31]:



The reaction with alkyl halides takes place similarly[21]:



while the reaction with isocyanates is



where X = H, Cl, or NO_2.

2. DIPHOSPHINE

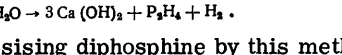
Diphosphine is a colourless highly refractive liquid, which ignites spontaneously in air at room temperature (the principal physical properties are listed in Table 2) and is insoluble in water; alcohol and turpentine appear to dissolve diphosphine (P_2H_4), but the solution is very unstable and rapidly decomposes in the presence of the catalysts: hydrogen chloride, charcoal, pumice[2]. Diphosphine is sparingly soluble in liquid ammonia, and the solutions are unstable and readily decompose. Evers and Street[33,34] stated that diphosphine decomposes on storage into phosphine and solid phosphorus hydrides of composition P_9H_2 and P_5H_2, which decompose further to elemental phosphorus. When diphosphine is stored above 0°C or in the presence of hydrochloric acid, it gradually turns yellow owing to the precipitation of solid phosphorus hydrides†. The structure of the diphosphine molecule was established by NMR:[35]



Table 2. Physical properties of diphosphine (P_2H_4).

B.p., °C	Q_{vap}, kcal mole^{-1}	Trouton's constant	ρ, g cm^{-3}	M.p., °C
56	6.89	21	(1.02—1.007)	—99

Diphosphine is a powerful reducing agent, largely resembling hydrazine in its chemical properties. Its reactions have been scarcely investigated. Gattermann and Hausknecht[36] unsuccessfully attempted to obtain compounds of diphosphine with aldehydes and ketones. Diphosphine was obtained in a mixture with phosphine for the first time in 1945 by Thenard[37,38], who allowed calcium phosphide to react with water:



The possibility of synthesising diphosphine by this method was suggested long ago by Leverriers[39,40]. Subsequently this reaction was the sole preparative method for synthesising diphosphine[36,41]. According to the recommendations of Gattermann and Hausknecht[36], diphosphine is synthesised as follows.. The apparatus consists of a round-bottomed flask connected to a receiver via a cooling coil. The receiver is immersed in a cooling mixture. Water is poured into the flask and the apparatus is thoroughly flushed with hydrogen. The water is heated to 60°C and calcium phosphide is added in pea-sized lumps at 150–200 g h^{-1}. Diphosphine begins to collect in the cooled receiver after approximately 15 minutes.

Recently, reports have been published[42-44] on the preparation of liquid triphosphine (P_3H_5) by the decomposition of phosphine in a reactor consisting of two concentric tubes, the temperature of the inner tube being 65°, and that of the outer 63°C, and on its preparation by the hydrolysis of calcium and magnesium phosphides in the presence of arsenides and germanides with heating under a high pressure[42,43].

P_3H_5 was identified by mass-spectroscopy and gas-chromatography (on kieselguhr with silicone oil).

†Recently a new phosphorus hydride P_2H_2 was prepared by the pyrolysis of diphosphine[140].

3. SOLID PHOSPHORUS HYDRIDES

The most familiar solid phosphorus hydride, $P_{12}H_6$, is a pale yellow powder stable in air, insoluble in water and organic solvents, and soluble in diphosphine and fused yellow phosphorus. Its density, determined for a suspension in a mixture of chloroform and bromoform, is 1.83 g cm^{-3} at 19°C.[2] The product decomposes rapidly in the light, ignites spontaneously at 200°C, and vaporises without change only in a high vacuum.

The solid hydride $P_{12}H_6$ was obtained for the first time in 1827 by Rose[45,46]. When diphosphine was passed through an aqueous solution of hydrochloric acid, Rose observed the precipitation of a solid yellow compound. Later this method was employed by Thenard[37,38] and Schenk[47]. Schenk prepared $P_{12}H_6$ by the reaction of calcium phosphide with water followed by treatment of the gas evolved with hydrochloric acid. The yield of the solid hydride was very low—about 3 g per kilogramme of calcium phosphide. Gattermann[36] improved somewhat the experimental technique but even in his synthesis the yield of $P_{12}H_6$ does not exceed 8 g per kilogramme of calcium phosphide. Up to the present time, this is the only method suitable for preparative purposes.

Other methods of synthesising the solid phosphorus hydride have been reported. Jolibois[48] stated that the solid hydride $P_{12}H_6$ may be obtained by the decomposition of zinc phosphide with hydrochloric acid. Later it was suggested that the hydride be obtained by the decomposition of aluminium phosphide with dry hydrogen chloride[2] or by the reaction of white phosphorus with potassium hydroxide in glycerol[49,50]. Rüdorf[51] suggested a synthesis of $P_{12}H_6$ from phosphorus iodide and water, in which the product is obtained in a low yield, and Besson[52] and Stock[53] proposed syntheses in which phosphine is passed through phosphorus trichloride or tribromide, but the method failed in practice.

Stock et al.[54] reported that the yellow phosphorus hydride $P_{12}H_6$ eliminates PH_3 on heating and is converted into the orange-red solid hydride P_9H_2. The same substance is obtained when liquid ammonia is allowed to react with $P_{12}H_6$,[33,54] the reaction being accompanied by the evolution of phosphine.

Hackspiel[55] showed that the solid hydride to which Thenard assigned the formula $P_{12}H_6$ in fact has the formula P_5H_2. This compound has acid properties and can form metal phosphides. In a vacuum P_5H_2 evolves pure phosphine.

Recently Weiberg and Müller-Schiedmayer[56] reported the preparation of a new phosphorus hydride with the formula $(PH)_x$ by the reduction of phosphorus halides and oxyhalides with lithium and aluminium hydrides in ethereal solution at low temperatures. The yield of this hydride can reach 90% in the reduction of phosphorus dibromide with lithium hydride at 30°C. It is a brown solid stable at room temperature. On heating to 400°C in a vacuum, it decomposes:

$$3(PH)_x \rightarrow 2xP + xPH_3.$$

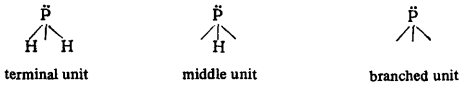
It exhibits weak basic properties, similar to those of trimethylamine, and is a powerful reducing agent—for example, on heating it reduces sulphuric acid to hydrogen sulphide. It is oxidised to phosphoric acid by strong oxidising agents such as hydrogen peroxide or sodium hypochlorite.

When yellow phosphorus is reduced electrochemically at a lead cathode[57], vigorous absorption of hydrogen without evolution of gaseous phosphorus-containing products is observed during the initial period. It is suggested[57] that the first stage of the reduction is the formation of the hypothetical hydride P_4H_4 by the reaction

$$P_4 \xrightarrow{4H^+,4e^-} P_4H_4.$$

This conclusion is based on the study of the variation of the concentration of yellow phosphorus during the electrolysis, but the hydride of the above composition was not isolated.

There exist various views concerning the structures of solid phosphorus hydrides. Royen[42,43] suggested that solid phosphorus hydrides are products of the sorption of PH_3 by one of the forms of yellow phosphorus. According to another view, solid phosphorus hydrides are macromolecular substances resembling in many respects organic plastics and phosphate glasses, which have the general formula P_nH_{n+2} and consist of three of the structural units shown below.



Diphosphine consists of two terminal units linked together. Triphosphone P_3H_5 consists of one middle and two terminal units. The hydride $(PH)_x$ consists only of middle units. There is probably a state of equilibrium between the groups, for example:

$$2\rangle PH \rightleftarrows -PH_2 + \rangle P.$$

The hydrides in which the molar H/P ratio is less than unity must contain branched elements in their structure; these compounds are probably analogous to three-dimensional polymers and this is why they cannot be dissolved in any solvent without breakdown of the molecule.

4. APPLICATIONS OF PHOSPHORUS HYDRIDES

Of the known phosphorus hydrides, only phosphine has practical importance. So far no applications have been found for the other hydrides. The possibility of the spontaneous ignition of phosphine constitutes a great risk in experiments with this material. For this reason, much attention has been devoted to the problem of the spontaneous ignition and stabilisation of phosphine. The spontaneous ignition temperature of pure phosphine in the presence of air is 140°C,[1] but when the gas contains a very small admixture of diphosphine (1 : 500), it ignites spontaneously in air even at −40°C.[1,2] The problem of the spontaneous ignition of phosphine has attracted attention for a long time. Ter-Gazaryan[58] believed that the most effective method for the purification of the gas from traces of other phosphorus hydrides and hydrogen is repeated liquefaction and fractional distillation of the liquid. However, later studies showed that the capacity of phosphine for spontaneous ignition can be suppressed by simpler means. Trautz[59] showed that the gas mixed with hydrogen and alcohol vapour does not ignite spontaneously. Graham[60,61], who studied the conversion from the inflammable to the non-inflammable form of the gas, established that, to achieve this conversion, it is sufficient to keep the gas under water containing air. The conversion can be achieved with the aid of a cork stopper or a lump of gypsum containing air in its pores. If the walls of the vessel are wetted with concentrated phosphoric, sulphuric, and arsenic acids, the conversion takes 2–3 min. Mercurous oxide acts most rapidly, while potassium hydroxide requires several hours for this purpose. Metallic potassium and its amalgam (one part of potassium in 350 000

parts of mercury) suppress the inflammability in several minutes. Johnson[62] recommends that alumina dehydrated at a low temperature be used as the drying agent for the preparation of non-inflammable phosphine. Thenard[37,38] and Amato[63] showed that phosphine loses the capacity for spontaneous ignition in air if it is treated with concentrated hydrochloric acid or stored in a glass vessel in sunlight. Under these conditions the diphosphine in the gas decomposes. Dilution of phosphine with an inert gas can also be used[64].

Until recently phosphine had only limited applications. Thus it was used to combat plant pests[65] and rodents[66], for the preparation of a layer of phosphides of metals resistant to mechanical, thermal, and chemical action, for the preparation of rare-metal phosphides used in semiconductor engineering, and for the preparation of phosphide bronzes used in machine engineering[66]. At present phosphine is attracting much attention in connection with possible new applications. For example, it has been found that phosphorus obtained by the thermal decomposition of its hydrides[67] has high purity and may be used as a semiconductor. The possibility of its military applications has also been noted[67a].

There exist wide possibilities for the application of phosphine in the synthesis of organophosphorus compounds, in particular the preparation of tetra(hydroxymethyl)phosphonium chloride—an intermediate in the manufacture of fire-resistant polymers[22,24,25], the preparation of extracting agents for rare metals, plasticisers for plastics[19,20], etc.

5. METHODS OF PREPARATION OF PHOSPHINE

Since there is a much greater variety of data on phosphine compared with the other hydrides, the methods of its preparation are discussed separately.

a. Synthesis from Metal Phosphides

Phosphine can be obtained by the action of water or dilute acid on alkali and alkaline earth metal phosphides. For example, Hugot[68] obtained phosphine by the action of water or dilute acids on sodium trihydrophosphide:

$$Na_3H_3P_2 + 3H_2O \rightarrow 2PH_3 + 3NaOH,$$

or

$$Na_3H_3P_2 + 3HCl \rightarrow 2PH_3 + 3NaCl,$$

or by heating this substance to 100°C at a reduced pressure. As the temperature is increased, more hydrogen and less phosphine is obtained.

A number of workers recommend that phosphine be obtained by the action of water or a dilute acid on calcium phosphide[35-38,69]. Moissan[70] was the first to obtain phosphine from calcium phosphide and water:

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2.$$

As already mentioned, diphosphine is obtained as a side product in this process.

The gas produced by the action of water on technical calcium phosphide contains considerable amounts (up to 30%) of diphosphine and hydrogen. Phosphine can be synthesised by the action of water and hydrochloric acid on a specially prepared mixture of calcium and aluminium phosphides and on the phosphides of iron, magnesium, and aluminium[71].

The reaction of aluminium phosphide[49,50] with water takes place with evolution of much heat and is difficult to control. Kuznetsov and coworkers[72,73] showed that phosphine can be synthesised by the decomposition of water on aluminium phosphide suspended in an inert liquid; it is stated that the decomposition of aluminium phosphide suspended in organic solvents (methanol, ethanol, acetone, etc.) takes place comparatively smoothly and is easier to control. The decomposition of zinc phosphide with dilute acids (hydrochloric and sulphuric acids) has been thoroughly studied:

$$Zn_3P_2 + 6HCl \rightarrow 2PH_3 + 3ZnCl_2.$$

This reaction is most often used for the synthesis of phosphine[3]. The methods of preparation of phosphine discussed above have certain disadvantages[74-78]: contamination of the gas, expense, and the formation of waste—spent solutions and sludge.

b. Synthesis from Other Phosphorus Compounds

Hofmann[41] attempted to prepare pure phosphine by the decomposition of phosphonium iodide with water or potassium hydroxide solution, but it was found that the resulting gas contains also diphosphine and may ignite spontaneously in air:

$$PH_4I + KOH \rightarrow PH_3 + KI + H_2O.$$

Berzelius and Lüpke[79-81] obtained gaseous phosphine by the reduction of phosphites or a mixture of phosphite and hypophosphite with iron or zinc. An American patent[82] states that, when phosphites and hypophosphites are heated to 300–400°C, phosphine is obtained in yields of 18 and 46% respectively. Thorpe and Tutton[83] obtained phosphine by the action of dilute hydrochloric acid on the amide of phosphorous acid.

Phosphine can be synthesised by heating lower oxygen-containing phosphorus acids, for example hypophosphorous and phosphorous acids[45,46]:

$$2H_3PO_2 \rightarrow PH_3 + H_3PO_4,$$
$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4,$$

but in this reaction only 50 and 25% of phosphorus respectively is usefully employed. It has been reported that phosphine is obtained when atomic hydrogen is allowed to react with lower phosphorus acids[84], the reactions including cathodic reduction[85], thermal decomposition of lower phosphorus hydrides[86], particularly at a reduced pressure, for example:

$$15P_2H_4 \rightarrow 18PH_3 + P_{12}H_6,$$
$$P_{12}H_6 \rightarrow 2PH_3 + 10P,$$

and also in acid and alkaline hydrolysis of phosphorus sulphides (yield 3–5%).[2]

Gutmann[87] reported that, when phosphorus halides are reduced with hydrogen in the gas phase in a gas-discharge tube, phosphine is formed together with red phosphorus.

Paddock, Wiberg, and Müller-Schiedmanyer[14,56,88,89] investigated the hydrogenation of phosphorus halides and oxyhalides with metal hydrides in ethyl ether. They showed that, together with phosphine, the reaction products may contain the solid hydride to which the formula $(PH)_x$ was attributed:

$$PX_3 \xrightarrow[-3X^-]{+3H^+} \begin{cases} PH_3 & \text{(a)} \\ (PH)_x + H_2 & \text{(b)} \end{cases}.$$

By choosing appropriate conditions, the reaction can be driven along pathway (a) or (b). In the synthesis of phosphine it is best to employ as low a temperature as possible. The maximum yield of phosphine (85%) was achieved in the reduction of phosphorus trichloride at −115°C with aluminium hydride and in the reduction of $POCl_3$ at −115°C with lithium tetrahydroaluminate.

The reduction of phosphorus pentahalides [88] with metal hydrides at temperatures between −80° and −100°C led to the formation of a equimolar mixture of phosphine and hydrogen. It has been noted [90] that phosphine (and other hydrides of Group V elements of the Periodic System) can be obtained by the reduction with lithium hydride of phosphorus halides at temperatures in the range 150–250°C. Lithium hydride is mixed with an inert powder (quartz, sodium chloride, etc.) in an inert gas, the halide vapour in an evaporator being supplied to the fluidised bed from below.

c. Synthesis from Elemental Phosphorus

Chemical methods. Phosphine may be obtained by the reaction of phosphorus with hydrogen, but only in a small yield. Rötgers [91] was the first to report the formation of phosphine by the reaction of incandescent red phosphorus with hydrogen. Dolique [92] did not confirm these data. He observed the formation of only traces of phosphine at 400°C. The use of decomposition and hydrogenation catalysts (activated charcoal, kieselguhr, pumice, nickel, copper, and iron) had no effect on the results.

Ipat'ev, Nikolaev, and Frost [7–10] observed the formation of phosphine on heating yellow phosphorus with hydrogen in a sealed tube at 360°C; the yield did not exceed 2%. Langmuir [93,94] obtained phosphine by the reaction of phosphorus with atomic hydrogen, formed from molecular hydrogen by heating the latter in the presence of platinum, palladium, or tungsten to 1100°C at a pressure of 0.001–0.2 mmHg. The synthesis of phosphine by the action on phosphorus of hydrogen activated in an electric discharge or by high-energy radiation has been patented [95].

A number of methods of the synthesis of phosphine are based on the reduction of yellow phosphorus with hydrogen at the instant of precipitation. The experiments of Vournasos [96] constituted one of the first studies based on this principle. By heating a mixture of sodium formate and red phosphorus, he obtained a spontaneously inflammable gas. Probably in this gas the hydrogen formed in the decomposition of formate reacted with the phosphorus:

$$6\,HCOONa \rightarrow 6\,H + 3Na_2C_2O_4,$$
$$2\,P + 6H \rightarrow 2PH_3.$$

Yellow phosphorus is reduced by the hydrogen evolved when zinc reacts with a concentrated solution of alkali. The reaction begins about 60°C. Brössler [97] obtained phosphine by adding yellow phosphorus to dilute sulphuric acid. Vitali [98] established that the presence of mercuric chloride in the acid retards the formation of phosphine.

Dusart [84] and Davy [99] believe that only traces of phosphine can be obtained by this procedure, while Dumas [100] altogether rejects the possibility of the formation of phosphine in this reaction. Oppenheim [101] obtained phosphine by heating red phosphorus with concentrated hydrochloric acid in a sealed tube to 600°C; when hydriodic acid is used, the same effect is achieved on heating to 160°C. Oppenheim heated phosphorus with glacial phosphoric acid in a sealed tube at 200°C, which led to the formation of hypophosphorous acid and this was subsequently converted into phosphine and phosphoric acid. Weyl [102] obtained phosphine by the action of hydrogen peroxide on red phosphorus. It has been stated [103] that phosphine is formed when ammonia and sodamide and also a mixture of sulphuric and phosphoric acids are allowed to react with yellow phosphorus.

Palmer [104–107] suggested that phosphine be obtained by the action of zinc and cadmium amalgams in acid solutions on yellow phosphorus. The yield of phosphine reaches 90%, but the apparatus and technology of the synthesis are very complex; furthermore, apparatus for the preparation of the amalgams is necessary.

In much later patents [108–110], it was stated that phosphine can be synthesised by heating white phosphorus with water vapour in the presence of phosphorus pentoxide:

$$8P + 12H_2O \rightarrow 3H_3PO_4 + 5PH_3.$$

The content of phosphine in the gas reaches 94–99 vol.% (yield 62.5%). Condensed phosphates are produced in addition to phosphine. For a successful reaction, it is recommended that finely ground red phosphorus containing up to 4% of white phosphorus be used. Because of the highly corrosive nature of the medium, the process is carried out in a graphite or quartz reactor. In the absence of phosphorus pentoxide the reaction of phosphorus with water is possible only under a pressure of 50 atm and in the presence of catalysts [111,112].

Phosphine is known to form [113] in small amounts in the industrial preparation of yellow phosphorus by the thermal reduction of phosphorites in electric furnaces as a result of the partial reduction of the elemental phosphorus. The phosphine content in the furnace gases amount to 1 vol.%.

Phosphine was obtained for the first time by Gengembre [114] in 1773 and independently by Kirwan [115] in 1789 by boiling a concentrated solution of potassium hydroxide with yellow phosphorus. Rose [45,46], who made a detailed study of this reaction, found that the gas is evolved at a temperature as low as 15°C. The phosphine obtained by this method contains a considerable amount of diphosphine. The main reaction may be represented by the equation

$$4P + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3,$$

and the side reaction by

$$6P + 4KOH + 4H_2O \rightarrow 4KH_2PO_2 + P_2H_4.$$

The diphosphine produced decomposes partially with formation of a solid phosphorus hydride:

$$15\,P_2H_4 \rightarrow P_{12}H_6 + 18PH_3.$$

A considerable amount of hydrogen is produced together with phosphine. According to the data of Dumas [99] [Davy ? or Dumas [100] ? (Ed. of Translation)] and Hofmann [41], it is difficult to obtain phosphine containing less than 55–60% of hydrogen. Hydrogen is formed by the reaction

$$4P + 5KOH + 3H_2O \rightarrow PH_3 + 2H_2 + KH_2PO_2 + 2K_2HPO_3.$$

When calcium hydroxide is used, the hydrogen content of the gas is 89–90%. It is stated in patents [116–118] that, when an alcoholic solution of alkali (more than 70% of alcohol) is used, 95% of the theoretical yield of phosphine is obtained.

Phosphorus is hydrogenated by the organism phihothion [119].

All the methods of preparation of phosphine from elemental phosphorus enumerated above give relatively low yields of the product with considerable amounts of impurities. The possibility of synthesising phosphine by the electrochemical reduction of yellow phosphorus must be regarded as more promising.

Electrochemical Synthesis

The preparation of phosphine with the aid of an electric current was first reported by Grove [120] in 1863. He passed an electric current through moist phosphorus in order to fuse it and observed the formation of phosphine.

Blumenberg [65] asserted that phosphine can be obtained like arsine by the cathodic reduction of phosphorus salts and oxides. However, this has still not been confirmed. Subsequently it was stated in a French patent [105] that, in the preparation of hypophosphorous acid by the anodic oxidation of yellow phosphorus (or phosphorus alloys—for example ferrphosphorus), phosphine is formed at the cathode, probably as a result of the reduction of hypophosphorous acid. This was also reported by Baudler [85], but the process conditions were not given. Somewhat later, West German, British, and United States patents appeared [74,121,122], in which it is suggested that phosphine be obtained by the cathodic reduction of yellow phosphorus in aqueous solutions of salts and acids on metals with a high hydrogen overvoltage, for example, lead, zinc, mercury, etc. Aqueous solutions of hydrochloric, sulphuric, phosphoric, and acetic acids and their salts were used as the catholyte. To prevent the oxidation of phosphorus and its reduction products, the cathodic compartment was separated from the anodic compartment by a diaphragm. Since the solubility of phosphorus in aqueous solutions is very low, the solution was stirred mechanically (or magnetically) to emulsify the phosphorus. Price and Gordon [74,121,122] assert that, under these conditions, fused phosphorus rises vertically along the cathode like liquid in a wick ("wick effect"), wetting its entire surface. Platinum, lead, lead dioxide, lead–arsenic alloy, graphite, and stainless steel have been used as anode materials. The maximum yield of phosphine was observed in a solution of orthophosphoric acid (4 M) at mercury and zinc cathodes and amounted to 87%.

It is stated in patents [121,122] that the yield of phosphine falls with time and, in order to improve the yield, it is recommended that salts of certain metals (lead, barium, calcium, zinc, etc.) be added to the catholyte. The temperature is kept above the melting point of phosphorus (44°C) and below the boiling point of the solution (below 110°C) and the current density is maintained in the range 150–400 A m^{-2}. The authors do not describe the optimum conditions.

Recently a large number of patents have been published [75-78,123-132], describing various versions of the electrochemical method for the preparation of phosphine and its further development. The process conditions and the yields of phosphine are given in Table 3, which shows that comparatively concentrated aqueous solutions, mainly of phosphoric acid, are most often employed as the electrolyte. Only in one case was the employment of an aqueous sodium chloride solution described [74] and it was noted that sodium hypophosphite was formed together with phosphine.

In all cases the electrolysis is carried out at elevated temperatures (between 50° and 120°C). Usually comparatively low current densities are stated (in the range 50–300 A m^{-2}). Ceramics, tantalum, titanium, rubber, and polyethylene are employed as constructional materials for the electrolysers. Judging from later patents [129-132], the electrochemical preparation of phosphine has encountered considerable difficulties in attempts to achieve a continuous process. It appears that the most serious are the following: rapid loss of reducing activity by the cathode; the adhesion of phosphorus to the surface of the cathode leading to an increase of voltage in the electrolyser; contamination of the electrolyte; blocking of diaphragm pores. The aim of the improvements to the process described in the patents is to eliminate the phenomena listed above.

In order to stabilise the activity of the electrode, it is suggested that bismuth, cadmium, and mercury salts be added to the electrolyte, whereby the yield of phosphine can be raised to 92–92%. In one patent [75] it is recommended that the electrolysis be carried out in the presence of lead ions which are generated by a periodic replacement of the

Table 3. Effect of electrolysis conditions on the yield of phosphine.

Cathode material	Anode material	Diaphragm material	Electrolyte	Current, A	Current density, A m^{-2}	Voltage, V	Yield of phosphine, %	Duration of expt.	t, °C	Gas flow rate, ml min^{-1}	Remarks	References
Wood's alloy	graphite	porous glass	sat. NaCl soln.	1	220	18	50	—	80	8	5% of sodium hypophosphite formed in catholyte	74
Wood's alloy	graphite	porous glass	40% H_3PO_4 soln.	1	—	7	92.5	—	85	7.3		126
Pb	Pb, Pt, PbO_2	ceramic, glass, resin	40% H_3PO_4 soln.	0.5	60—200	2.9—3.4	80—90	1 day	75—85		pre-electrolysis, addition of bismuth salts	73, 121, 122, 75, 76
Pb	Pt	ceramic	18% H_3PO_4 soln.	3	—	18.7	60	—	85	17.9		124
Pb	PbO_2	resin	ethanol with phosphorus	0.2—1	—	13—46	42.5	—	65			123
Pb	graphite	alundum covered by glass fabric	6—10% HCl 0.05% Pb	—	—	4	70—85	—	50		40-50% of cathode gas passed into catholyte	131
Pb	graphite	porcelain	6% HCl 0.05% Pb	—	258	—	90—95	—	85		cathode has 1.59 x 1.59 ribs 3.18 mm deep	132
Pb–Bi or Sn–Bi alloy	Pt, Sn	ceramic	40% H_3PO_4 soln.	0.5	260	0.9	90	6 days	74		alternate replacement of platinum anode by tin anode	75
Ni(77%)–Cu(4.8%)–Cr(1.5%)–Fe(14.9%) alloy	Pt	ceramic	40% H_3PO_4 soln.	0.5	—	2—3	85	16 days	95		4 ml of 10% lead acetate soln. added	75
Hg	Fe, Pt, Pb, graphite	glass, alundum	18–40% H_3PO_4 soln.	0.5—5	—	6—10	80—95	30 h	69—90		cadmium added to catholyte	73, 121, 122, 77, 125, 126
Hg	graphite	none	40% H_3PO_4 soln.	3	—	10	70	—	85			127
Zn	Fe	glass	4 M H_3PO_4 soln.	—	80—300	—	83.1	—	—			73, 121, 122

platinum anode by a lead anode. This modification increases the stable yield of phosphine to about 85%.

In all the examples quoted it is noted that, after prolonged operation, loose spongy deposits are formed on the cathode, which increase the electrical resistance of the electrolyser and, since part of them crumble away, they contaminate the phosphorus present in the solution. A special design of the electrolyser has been described[78], in which the cathode is located above the anode. According to the authors of the patent[78], in this case deposits are formed on the upper side of the electrode and do not hinder the passage of current. A special device has been described with the aid of which it is possible to remove continuously part of the catholyte and phosphorus to free them from contamination. Finally, an unusual form of cathode is recommended. The cathode should have ribs, projections, and channels. It is not clear from the patent data how a cathode of this shape prevents the formation of loose deposits.

To achieve the best contact between the electrode and phosphorus, the cathode should either touch the layer of fused phosphorus at the bottom of the electrolyser, or the phosphorus should be introduced in amounts such that its thickness on the cathode does not exceed 0.7 mm.

To prevent the blocking of the pores of the diaphragm, it is recommended that the latter be covered by a layer of polyethylene or another material which is not wetted by phosphorus[129,130]—fibreglass, plastics, graphite, etc. In one patent[77] it is suggested that the level of the anolyte be maintained above that of the catholyte, whereupon hydrostatic pressure will prevent the adhesion of phosphorus to the diaphragm.

One of the methods for reducing the adhesion of phosphorus consists in the introduction into the electrolyte of hydrocarbons, hydrogen, or cathode gas containing hydrogen[131]. On dissolving in phosphorus, these substances reduce its viscosity and hence the possibility of its adhesion to the diaphragm and to the walls of the electrolyte. A noteworthy application of a catholyte mixed with organic solvents in different proportions has been described[123]. It is asserted that in this case the cathode gas does not contain phosphorus hydrides other than PH_3.

Various improvements in the electrolyser design (for example, use of a carbon cathode, when there is no need for a diaphragm) are proposed in patents[125-128]. However, despite these improvements, optimum conditions for the electrochemical synthesis of phosphine have probably still not been found.

Recently studies were made[57-133] to determine favourable conditions for the electrochemical preparation of phosphine in aqueous solutions. It was established that the optimum conditions are as follows: current density of the order of 1800–2000 A m^{-2}, temperature 75–85°C, and a zinc cathode in solutions of 40% phosphoric acid. Under these conditions the current yield of phosphine (and the yield with respect to the phosphorus employed) reaches 65%. In contrast to the data of other patents[74-78,121-132], it is then unnecessary to use special devices for the circulation and purification of the catholyte and phosphorus, for coating the diaphragm, etc.

The mechanism of the electrochemical reduction of phosphorus has been investigated in fair detail for the mercury cathode[134,135]. It was established that phosphorus in aqueous ethanol solutions is reduced by mechanism with addition of twelve electrons per molecule:

$$P_4 + 12H^+ + 12e^- \rightarrow 4PH_3 .$$

In aprotic media the process takes place by the addition of two electrons with formation of an anion and subsequent protonation of the latter[136]. The study of the reduction at a pendant mercury drop showed[135] the intermediate formation of a chemisorbed P_4Hg_X complex and in this respect the electrochemical reduction of phosphorus is analogous to the reduction of sulphur. Electrochemical reduction of phosphorus at a lead cathode is complicated by the formation of an intermediate phosphorus hydride[57].

A method for the preparation of phosphine and other volatile hydrides (silicon, boron, etc. hydrides) has been described recently[67,137-139]. The essential feature of the process is the electrolysis of fused lithium chloride, the lithium formed at the cathode reacting with the hydrogen supplied to the cathodic compartment forming lithium hydride; the latter passes to a separate chamber, where it reacts with phosphorus trichloride:

$$3\,LiH + PCl_3 \rightarrow PH_3 + 3\,LiCl .$$

The process is carried out at a temperature such that the phosphine formed is thermally stable. The chlorine evolved at the anode is used to prepare fresh portions of phosphorus trichloride. The design of the electrolyser provides for the elimination of contact between the phosphorus trichloride and the alkali metal to avoid the formation of free phosphorus.

A cell design has been developed for periodic and continuous operation. The anodic and cathodic compartments are separated either mechanically or a zone of "frozen melt" is set up in the middle. The anode and cathode are both made of graphite. This may be regarded as a method for the indirect chemical preparation of phosphine.

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It follows from the foregoing that phosphine has already found practical applications and that their range is being continuously extended. In this connection the development of rational methods for the preparation of phosphine on an industrial scale is assuming increasing importance. Comparison of the various methods for the synthesis of phosphine shows that the only procedure which has found practical application hitherto, despite its disadvantages, is the decomposition of metal phosphides. Although it is being tested under experimental industrial conditions[141], the synthesis of phosphine by the reaction of phosphorus with steam is scarcely likely to prove economical in view of the considerable consumption of phosphorus in the formation of phosphorus acids.

The most promising is the electrochemical method but its application has encountered certain difficulties, which, judging from the literature data, have not been resolved.

The chemistry of other phosphorus hydrides has been hardly investigated and probably the time is now ripe for systematic research in this field.

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