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# Phosphorus Nitrides

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The literature data on the methods of preparation, structures, and properties of phosphorus nitrides PN, poly(phosphorus nitrides) (PN), ($P_3N_5$), etc., poly(phosphorus oxynitride) (NPO), and its thio-analogue (NPS) are surveyed and their practical applications, in particular as unique starting materials, formed as a result of the direct binding of molecular nitrogen, in the manufacture of phosphorus-nitrogen fertilisers are examined.
The bibliography includes 169 references.

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## I. INTRODUCTION

More than 100 years have elapsed since the first synthesis of phosphorus nitrides[1], but fairly complete and reliable data on their structures and properties have been obtained only recently. This can be explained by the specific features of the high-temperature synthesis of such systems, the wide variety of their polymeric forms, and the difficulty of studying them. Nevertheless the possibility of extensive practical applications of phosphorus nitrides continues to attract the attention of specialists in various branches of chemistry, physics, engineering, and agriculture. Systematic research in this field was carried out at the beginning of the century in Germany, in the 1930's in France, and after the war in the USA.[1] Studies on poly(phosphorus nitrides) have developed recently to a considerable degree in the Soviet Union.

Unfortunately the review literature on phosphorus nitrides[1-4] does not describe adequately the advances in the study of their structures, properties, and reactivities. In Allcock's book[5], wholly devoted to phosphorus–nitrogen systems, there are no data whatever on these compounds. All these factors make it useful to publish the present review, which covers the classical research and the entire modern literature published up to January 1976 known to the authors.

## II. THE SYNTHESIS, PROPERTIES, AND ELECTRONIC STRUCTURE OF THE PN MOLECULE

### 1. Synthesis

Monomolecular phosphorus nitride, detected spectroscopically for the first time by Curry and Herzberg[6], is stable in the vapour state at temperatures between approximately 450° and approximately 800°C. At lower temperatures, PN is deposited on the walls of the vessels in the form of an amorphous polymer, while at higher temperatures it decomposes into the elements[7-10].

The free energies of the gas-phase formation of PN molecules via the reactions

$$P_2 + N_2 = 2PN\ , \quad (1)$$
$$2P + N_2 = 2PN\ , \quad (2)$$
$$P_4 + 2N_2 = 4PN \quad (3)$$

are respectively 12, −97, and 68 kcal mole$^{-1}$ at 298 K and 3, −53, and −3 kcal mole$^{-1}$ at 2000 K according to calculations[11]. Thus phosphorus nitride is formed comparatively readily only when nitrogen interacts with atomic phosphorus [reaction (2)]. Low temperatures are optimum for the occurrence of this reaction, but $P_2$ molecules dissociate above 2500–3000 K†. The synthesis of PN from $P_2$ and $N_2$ requires a large expenditure of energy. The formation of phosphorus nitride via reaction (3) is even less likely, particularly since $P_4$ dissociates into diatomic phosphorus about 1500°C.[12,13]

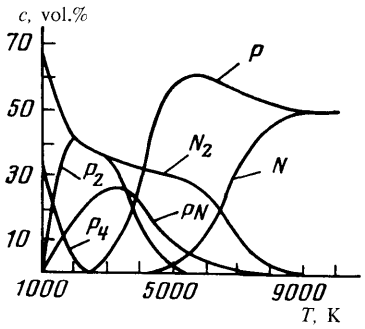
The equilibrium composition of the homogeneous phase incorporating P, $P_2$, $P_4$, N, $N_2$, and PN (see Figure) was calculated by Krasnokutskii and coworkers[13,14] (see also Vil'k et al.[12]). It was shown that, in the temperature range 1000–10 000 K and pressures in the range 0.1–1000 atm and for $N_2 : P_2$ ratios of 1–4, there is a possibility of direct synthesis of PN from $P_2$ and $N_2$. The concentration of PN at 1000 atm and 5000 K reaches 33.8%. The optimum conditions for the synthesis are as follows: temperature 2500–3000 K, pressure 1–10 atm, and a nitrogen : phosphorus ratio of 2. Under these conditions, the PN concentration is 20.5% and the energy consumed is 0.177 kW h mole$^{-1}$.[13,14] A further increase of temperature leads to the decomposition of phosphorus nitride. According to calculations, the temperature of the greatest thermal stability of phosphorus nitride is related to pressure in the system by the expression

$$T_{stab} = 3.236p^{0.06295} \cdot 10^3 \pm 20\ \text{K}\ . \quad (4)$$

†The temperature range 3200–3250 K corresponds to the maximum proportion of phosphorus nitride formed by reaction (2).[12]

An increase of pressure in the system to 1000 atm leads to an increase of the PN concentration in the gas only by a factor of 1.4, so that it is pointless to employ such a pressure in the synthesis of phosphorus nitrides[13,14].

Ginderich[15] carried out a careful experimental study on the thermodynamics of the formation of PN molecules. He investigated the equilibrium in the vapour phase over the UP–BN system. The enthalpies of reactions (1) and (2) were determined mass-spectrometrically. The values of $\Delta H^{\circ}_{298}$ obtained are respectively 47.6 and −65.3 kcal mole$^{-1}$.




The calculated equilibrium composition of the P–N system at a pressure of 1 atm and for nitrogen : phosphorus = 1.

The kinetics and equilibria in the reactions involving the synthesis and decomposition of PN molecules below 905°C were investigated by Huffman et al.[9] The equilibrium constant in the synthesis of PN from diatomic molecules [reaction (1)] was found to be 0.01 at 900°C and 0.2 at 2000°C. The heat of formation of PN via reaction (1) is −14 kcal mole$^{-1}$. The activation energy for reaction (1) was calculated as approximately 31 kcal mole$^{-1}$ from the above value and from the observed activation energy for the decomposition of the PN molecule into $P_2$ and $N_2$. Having compared this value with the dissociation energies of $N_2$ and $P_2$, the authors[9] concluded that N and P atoms are not involved in the formation of the activated complex in the synthesis of phosphorus nitride. However, the activation energy, corrected using Ginderich's data[15] (approximately 47 kcal mole$^{-1}$), shows that this conclusion is not adequately justified. The hypothesis that the rate of formation of PN is not the factor responsible for the low yield of phosphorus nitride also appears to be premature.

Fedorov and coworkers[13,16] investigated the kinetics of the synthesis of PN in the temperature range 3000–7000 K. By numerical integration on a computer of the system of differential equations corresponding to chain, molecular, atomic, and overall mechanisms, they showed that a satisfactory agreement between calculated and experimental parameters is obtained only for the interaction between atoms:

$$P + N + M \rightarrow PN + M \qquad (5)$$

where M is a third body—an atom or molecule (or the reactor wall). The reaction

$$P_2 + M \rightarrow P + P + M \qquad (6)$$

does not affect the yield of PN, which can be explained by the high rate of decomposition of the molecules of the initial phosphorus. Thus the nitrogen content in the product and the rate of formation of the latter are determined solely by reaction (5), whose rate constant is $1.25 \times 10^9$ litre$^2$ mole$^{-2}$ s$^{-1}$ under these conditions.

The efficiency of the synthesis of PN molecules from the elements may be increased by using an electric discharge or catalysts to initiate the dissociation of the parent molecule. The interaction of the nitrogen atoms, obtained by exposing the $N_2$ molecule to a microwave discharge, with $P_4$ molecules in the temperature range 100–400° has been investigated by Khanna et al.[17] According to these authors, the upper limit to the rate constant for the second-order reaction

$$P_4 + N \xrightarrow{k} [P_4N] \begin{cases} \longrightarrow (P_xN_y) + P \\ \xrightarrow{[N]} P_4 + N_2 \end{cases} \qquad (7)$$

is approximately $5 \times 10^{12}$ cm$^3$ mole$^{-1}$ s$^{-1}$.

The mechanism of the formation of phosphorus nitride molecules in a low-temperature plasma has been analysed by Mel'nik et al.,[18] who showed that the synthesis of PN should proceed via a complex mechanism involving a series of competing stages. This chain process is initiated by the formation of phosphorus atoms from $P_4$ and $P_2$ molecules and also by the formation of $P_3$ radicals.

The dependence of the rate of synthesis of PN molecules from the elements in a glow discharge on the potential $u$, the discharge current $i$, and the pressure $p$ in a closed reactor was studied by Millers and coworkers[19]. Mathematical treatment of experimental data showed that there are maxima in the rate of absorption of nitrogen as a function of pressure, the optimum values of which are 0.08–0.1 and 0.03–0.06 mmHg. There is a linear relation between the rate of reaction and the discharge current. The change in the mass of nitrogen in the reactor, characterising the reaction dynamics, is described by the equation

$$dm = -miK(p, i, u)dt, \qquad (8)$$

where $K(p) = ce^{\alpha/p}$ and $c$ and $\alpha$ are constants for the given $i$ and $u$. The same workers investigated the interaction of phosphorus and nitrogen in a glow discharge for different methods of supplying nitrogen to the reactor[19] (see also the Addendum to this review).

## 2. Physical Constants, Electronic Structures, and Properties

The upper limit to the dissociation energy of the PN molecule (7.8 eV) has been determined by the Birge–Sponer linear extrapolation of the observed energies of the vibrational levels in the ground state[6,7]. A detailed study of the electronic spectra of this molecule led to $D_0^0$ = 6.3 eV (obtained by extrapolation of the energy of the vibrational levels of the lowest excited state $A^1\Pi$). It has been noted[7] that the relatively small number of the identified vibrational levels (10 out of the 95 possible levels in the ground state and 9 out of the 76 possible levels in the excited state) may be the cause of the possible error in the determination of the dissociation energy from spectroscopic data. The study of the equilibrium in an equiatomic mixture of nitrogen and phosphorus at temperatures in the range 895–905°C led to $D_0^0$ = 7.1 eV.[9] A somewhat higher value (7.57 eV) was obtained by Vu and Karlson[20]

in a study of the evaporation of $P_3N_5$, but their investigation has been criticised[15,21]. The value of $D_0^0$ obtained from the analysis of the thermodynamics of the evaporation of phosphorus nitride is 7.0 eV.[21] However, the most reliable dissociation energy has been found by Ginderich[15]. The dissociation energies of the $P_2$ and PN molecules which he calculated are listed in Table 1.

Table 1. Comparative characteristics of the $N_2$, PN, and $P_2$ molecules.

| Parameter | $N_2$ | PN | $P_2$ | References |
|---|---|---|---|---|
| $E_{dis}$ (exp.), eV | 9.90 | 6.43 | 5.08 | 15, 31 |
| Interatomic distance, Å | 1.094 | 1.49085 | 1.894 | 7, 22, 48 |
| Vibration frequency, $cm^{-1}$ | 2359.61 | 1337.24 | 780.43 | 7, 48 |
| Ionisation potential, eV | 15.8 | 11.85 | 10.2* | 20, 31, 40 |
| Energy of corresponding single bond, kcal | 38 | 70 | 50 | 51 |
| Population of 3*d* orbital, el.units | 0.06 | 0.12 | 0.17 | 32, 35, 37 |
| $\Delta E$**, eV | 2.58 | — | 2.53 | 32, 35, 37 |
| $E^b$***, eV | 5.27 | 1.80 | 0.06 | |
| Additional molecular correlation energy, eV | 4.63 | 4.63 | 5.02 | |

*Value obtained by the LCAO-MO SCF method[37].
**The decrease of the total energy following the inclusion of 3*d* orbitals in the calculation.
***$E^b$ are the dissociation energies of the molecules obtained by quantum-chemical calculations.

The rotational spectrum of the PN molecule in the microwave range was studied recently[22]. Measurements were made of the frequencies of five lines of the quadrupolar hyperfine structure corresponding to the rotational transitions in the ground and first excited states; using literature data, the effective rotational, centrifugal distortion, and vibrational-rotational interaction constants were calculated from them. The calculated interatomic distance agrees well with the value found earlier from the analysis of the vibrational spectrum (Table 1). The millimeter and submillimeter regions of the rotational spectrum of phosphorus nitride have been studied[23].

The potential curves for the ground and first excited states of phosphorus nitrides were calculated using Lippincot's three-parameter function[24]. The dissociation energies obtained for the above two states are 6.3 and 4.0 eV (the dissociation energies of the $P_2$ molecule in the corresponding $X^1\Sigma^+_g$ and $B^1\Sigma^+_u$ states are 5.1 and 2.2 eV). Witchel[25] calculated the internuclear distance in the $A^1\Pi$ state of the PN molecule (1.5466 Å). Szoke[26] used a semiempirical method for the derivation of the potential energy function for the PN molecule as well as $P_2$ and $N_2$. It was shown that the Rydberg–Klein–Rees potential, obtained from the known spectroscopic constants and extrapolated with the aid of the Rydberg and Lippincot potentials, agrees with the experimental data over a wide range of internuclear distances.

Sankaraharayanan[27,28] calculated the Frank–Condon factors for certain bands of the $A^1\Pi - X^1\Sigma^+$ system, the electron transition moment for interatomic distances in the range 1.426–1.630 Å, and the relative probabilities of the transitions, which made it possible to explain the characteristic features of the vibronic spectrum of the PN molecule. Silver and Moller[29] showed that the values of the Frank–Condon factors obtained from the relative band intensities in the resonance fluorescence spectrum agree well with the theoretical values. The same workers used the Hanle effect to determine the lifetime of the $A^1\Pi$ state of the PN molecule as 230 ± 70 ms.[29]

The thermodynamic functions of the PN molecule in the temperature range 273–15 000 K have been calibrated by Potter and Di Stefano[30] (see also Ref. 31). The results of two non-empirical calculations for the ground ($^1\Sigma^+$) state of the PN molecule by the LCAO-MO SCF method have been published[32,34]. A calculation similar to the calculation by the Hartree–Fock method has been carried out by McLean and Yoshimine[32]. The basis set included 25 σ and 13 π Slater-type functions proportional to $e^{-\zeta r}$, where ζ is a parameter usually referred to as the exponent in quantum-chemical literature. Boyd and Lipscomb[34] used the minimum basis set of Slater-type functions and, in the case of the phosphorus atom, took into account the 3*d* functions, whose exponents were varied. The electronic configuration of the PN molecule obtained by *ab initio* calculations, namely ... $5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4$, is analogous to that calculated for the $^1\Sigma^+_g$ states of the $N_2$ and $P_2$ molecules[35–37]‡. The contribution of the atomic orbitals of phosphorus to the upper occupied molecular orbitals of PN is fairly large, which is the reason for the smaller ionisation potential of the PN molecule compared with that of $N_2$ (Table 1).[32,39]§

Table 1 presents the dissociation energies of the $N_2$, PN, and $P_2$ molecules obtained from the most accurate of the published non-empirical calculations. These values differ from the experimental energies by the additional molecular correlation energy, equal to the difference between the correlation energies for the above molecules and for their constituent atoms[41]. The additional molecular correlation energies found in this way are virtually identical for the $N_2$ and PN molecules and differ slightly from the value for the $P_2$ molecule, which is probably too high. This may be caused, on the one hand, by the similarity of the correlation energies of the electrons in the inner shells of the molecules and their constituent atoms and, on the other, by the similarity of the bonds in these diatomic molecules.

A clear idea about the characteristics of the distribution of electron density in PN, $P_2$, and $N_2$ is provided by the full and difference maps of charge density. The formation of the above diatomic orbitals leads to an increase of electron density in the region between the nuclei along the molecular axis and to a decrease in density at the nuclei and in the direction away from the molecular axis[34,42,43]. The concentration of electronic charge in the internuclear region together with the overlapping of the atomic orbitals is known to play an important role in bond formation. The relative decrease in the density of the electron cloud in the internuclear region is responsible for the decreased stability of the above diatomic orbitals in the sequence $N_2 > PN > P_2$. This is caused by the presence in the phosphorus atoms of additional inner filled shells and by the lower capacity of the phosphorus valence orbitals for *sp* hybridisation compared with the corresponding valence orbitals of the nitrogen atom[37,39]. Analysis of the difference maps characterising the distribution of the π and σ

‡The agreement between the calculated and experimental molecular orbital energies for the $N_2$ and PN molecules has been analysed[38,39].

§According to Wu and Fehlner's data[40], the photoelectron spectrum of PN has two distinct maxima at 11.85 and 12.52 eV, which may be attributed to the σ and π levels.

electron densities, shows that the contribution of $\pi$ electrons towards bonding diminishes in the sequence $N_2 > PN > P_2$. Analysis of the overlap populations leads to an analogous conclusion[36,39,42,44].

The inclusion in the calculation of $3d$ orbitals, which play the role of polarising terms in the above three molecules, leads to an increase of electron density in the bonding region[42,45]. The population of the $3d$ orbitals increases when nitrogen atoms are replaced by phosphorus atoms. The changes in the total energies, occurring when the $3d$ orbitals are included in the calculations for the $P_2$ and $N_2$ molecules, are in their turn virtually identical (Table 1). According to Boyd's data[42], the change in the exponent of the $3d$ atomic orbitals from 1.0 to 1.5 (the optimum values for non-empirical calculations with an unbalanced basis set) leads to an increase of the overall overlap population, which diminishes somewhat on further contraction of the $3d$ orbitals. The optimum value of the $\sigma$-bonding component of the overlap population also corresponds to the optimum value of the exponent, since the $\pi$-bonding component diminishes monotonically with decrease in the size of the $3d$ orbitals. The overlap population of the $d^{\sigma}$ phosphorus orbitals with the corresponding nitrogen orbitals increases monotonically under these conditions, the overlap population of the phosphorus $d^{\pi}$ orbitals diminishes, and the kinetic energy of the electrons and the sum of the molecular orbital energies increase[42].

The heteroatomic PN molecule has a dipole moment, which has been measured (2.75 D) by Raymonda and Klemperer[46] from the electrical resonance spectrum in a molecular beam. They also described the dependence of the dipole moment and the quadrupole interaction constant on the vibrational state of the molecule. The dipole moment is due to a redistribution of electron density in the PN molecule compared with the "non-interacting" atoms. Using his method for subdividing space into regions corresponding to atoms and the results of a non-empirical calculation[32], Politzer[47] calculated the effective charges $\Delta q$ of the P and N atoms (0.25 and $-0.25$ a.u. respectively) and the distances from the centres of the positive and negative charges to the centre of the interatomic distance (0.715 and 0.768 Å). The centre of the negative atomic charge is beyond the nuclei, owing to the presence of the lone electron pair at the nitrogen atom. Politzer's calculated effective atomic charges are somewhat smaller than the values obtained by the LCAO-MO SCF method in terms of the CNDO/2 valence approximation[49] with and without allowance for the $3d$ functions of the phosphorus atom¶ ($|\Delta q| = 0.35$ and 0.45 a.u. respectively[39,45]).

As already mentioned, the phosphorus nitride molecule is stable over a narrow temperature range. The simplest derivatives of PN, the great structural variety of which has frequently led to some confusion in the interpretation of experimental data[1], are also extremely labile. In this situation, it is necessary to employ, together with physicochemical data, the results of quantum-chemical calculations of various characteristics of such systems, and also to calculate the potential surfaces for the chemical reactions. A logical investigation of the relation between the electronic structure and properties of phosphorus nitride and its derivatives is being carried out by one of the authors of the review[39,45,52,53].

¶The exponents of the $3d$ orbitals were assumed to be 1.6, in agreement with the value optimised by Boyd[42].

A fragment of the potential surface for the protonation of the PN molecule has been calculated[45] by the CNDO/2 method. It was found that the minimum total energy corresponds to a nearly linear geometry of the cation with the proton attached to the nitrogen atom. In the $(HNP)^+$ cation, the polarity of the H–N bond is low as a result of the acceptance by the proton of electrons from the $s$ orbital of the nitrogen atom and the $p^{\pi}$ orbital of the phosphorus atom. The overall population of the $3d$ orbitals in the cation, calculated by the CNDO/2 method, hardly changes relative to the PN molecule and there is only a redistribution of electron density between the $d^{\pi}$ and $d^{\sigma}$ orbitals.

The characteristic features of the electronic structures of the $H_2NP$ and $H_4NP$ isomers have been analysed[52] and the relation between the electronic structure and properties of aminophosphine $H_2NPH_2$ has been examined theoretically in detail[53–56].

## III. METHODS OF PREPARATION AND PROPERTIES OF POLY(PHOSPHORUS NITRIDES) (PN), $(P_3N_5)$, ETC.

A common feature of the PN and $P_2$ molecules is the formation of polymers with different structures, which is not characteristic of nitrogen. Aggregation leads to the formation of new $\sigma$ bonds (two additional bonds per diatomic molecule), the sums of the energies of which for PN and $P_2$ are greater than the dissociation energies of the diatomic molecules by approximately 62 and 33 kcal respectively, while in the case of $N_2$ the sum is smaller by 114 kcal (Table 1). Thus the ability of phosphorus nitride to form stable polymeric systems should be more pronounced than that of phosphorus.

Polymeric compounds of nitrogen and phosphorus, whose composition corresponds to the formulae $(P_3N_5)$, $(P_4N_6)$, and (PN), have been described. Variable-composition compounds with nitrogen : phosphorus ratios in the range 0.9–1.7 are also possible[1].

### 1. The Synthesis and Properties of (PN)

Poly(phosphorus nitride) (PN) was obtained for the first time[57] by exposing a mixture of nitrogen and white phosphorus vapours under a pressure of 200 mmHg to a silent electric discharge at a potential of 4000–15 000 V. It was noted that at pressures less than 200 mmHg, red phosphorus, which limits the reaction, is formed simultaneously with (PN). The action of a silent electric discharge on a mixture of nitrogen and phosphorus vapour has also been investigated in other studies[58,59]. Mourey and Wetroff[10] obtained (PN) by passing nitrogen and phosphorus vapours (at an overall pressure of 1 atm) through an electric arc maintained between tungsten electrodes by a potential of several thousands of volts. Poly(phosphorus nitride) is also formed when nitrogen atoms interact with phosphine,

$$N + PH_3 = PH_2 + HN,$$
$$PH_2 + N = PN + H_2,$$

in the temperature range 80–290°C,[60] when a high-frequency discharge is passed through a mixture of nitrogen and phosphorus trichloride[29], when phosphorus trichloride interacts with ammonia at −78°C,[61] in the reaction of triphosphonitrile chloride with sodium[62,63], etc.

At room temperature, (PN) is a stable yellow (possibly owing to contamination with phosphorus) amorphous powder, which is insoluble in water, liquid ammonia, and the

usual organic solvents[64,65]. The polymer sublimes without leaving a residue[9,62] and condenses below 500°C. It dissolves readily, but more slowly than $(P_3N_5)$ in hot sulphuric acid with formation of phosphoric acid, ammonium sulphate, and sulphur dioxide[65]. It is readily oxidised by peroxides and sodium nitrate[62]. Above 500°C, it reacts with chlorine to form the trimeric phosphonitrile chloride contaminated with phosphorus pentachloride[66-68] and it also reacts with atomic nitrogen[69] and ammonia[9] to form $(P_3N_5)$.

## 2. The Synthesis of $(P_3N_5)$

A solid substance with a composition $(P_3N_5)$ was obtained for the first time by Briegleb and Genther[70] in 1862 by the reaction of magnesium nitride with phosphorus pentachloride:

$$5Mg_3N_2 + 6PCl_5 = 2P_3N_5 + 15MgCl_2 .$$

Both Briegleb and Genther[70] and later investigators (Schneider[71] and Stock and Grunberg[72]) were unable to isolate in a pure form the phosphorus nitride obtained in this way; the product was also contaminated with a small amount of magnesium and chlorine. Nor could a pure product be obtained by the reaction of $NH_3$ with $(NPCl_2)_3$.[73] A fairly effective method for the preparation of pure $(P_3N_5)$, based on the reaction of phosphorus pentasulphide with ammonia, was developed at the beginning of the present century by Stock and Hoffman[74]:

$$40NH_3 + 3P_2S_5 = 2P_3N_5 + 15(NH_4)_2S .$$

The phosphorus nitride produced in this reaction consists of an extremely porous mass[59].

The method of synthesising phosphorus nitrides by heating phospham ($PN_2H$) at 400–700°C has become very common. This reaction was discovered by Besson[75] in 1892. Phospham is usually obtained by the prolonged heating of the products of the reaction of ammonia with phosphorus pentachloride and by heating to 800°C tri- and tetra-phosphonitrile chlorides[4], diamidotetrachlorophosphorus nitride[76], and hexa-aminophosphonitrile chloride[4].

Thermodynamic calculation of the equilibrium composition of the P–N system in the temperature range 1000–10 000 K, in the pressure range 0.1–1000 atm, and for N : P ratios of 1–4, 12, and 24 showed[13,14] that the synthesis of the poly(phosphorus nitride) $(P_3N_5)$ via the reaction

$$3PN(gas) + N_2 = (P_3N_5) \qquad (9)$$

at high temperatures can be extremely effective. At atmospheric pressure below 1100 K, virtually the entire PN is converted into $(P_3N_5)$. An increase of pressure makes it possible to condense the nitride at higher temperatures. It has been noted that the highest yield is obtained when nitrogen interacts with phosphorus in the high-temperature homogeneous region with subsequent quenching of the reaction products at a temperature below 1100 K. On quenching to room temperature, the maximum yield of $(P_3N_5)$ corresponds to the maximum concentration of PN obtained in the homogeneous region (2500–3500 K). The minimum energy expenditure (3.26 kW h $kg^{-1}$ at 2500 K, 1 atm, and N : P = 2) corresponds to the same conditions. By increasing the pressure, it is possible to increase the content of the nitride in the product to 48 wt.% (for N : P = 1), but this entails an increase of the energy expenditure to 4–5 kW h $kg^{-1}$. On raising the N : P ratio, one can obtain a $(P_3N_5)$ concentration in the product up to 61 wt.%, but the energy expenditure then increases to 4.3 kW h $kg^{-1}$.[13,14]

A study of the synthesis of $(P_3N_5)$ in a flow-type arc reactor showed that the maximum yield of the product is reached at temperatures greatly exceeding that of the maximum thermal stability of PN, whence it was concluded that the process proceeds under non-equilibrium conditions[14].

The synthesis of $(P_3N_5)$ in the presence of an incandescent tungsten wire is also a non-equilibrium process. The rate-limiting stage in the formation of solid phosphorus nitride from $P_2$ and $N_2$ molecules at temperatures in the range 1720–2127 K is the catalytic dissociation of $P_2$ into atoms[9]. This follows from the similarity of the activation energy for this reaction (approximately 59 kcal at approximately 1800 K) to the dissociation energy of $P_2$ and also from the observed relation between the rate constant for the formation of phosphorus nitride $k$ and the concentration of $P_2$:

$$d c_{P_2}/d t = k c_{P_2}^{1/2} .$$

The process probably includes a stage in which $P_2$ is adsorbed on the surface of the tungsten wire, phosphorus atoms are removed from the surface, and then react with nitrogen in the gas phase†. It is apparently possible to explain in this way the deviation of the composition of the solid product formed under experimental conditions (N : P = 1.03–1.19) from the equimolecular composition of the initial gaseous mixture.

According to the authors[9], the reaction of a phosphorus atom with an $N_2$ molecule leads to the formation of the complex PNN, which may react with another phosphorus atom. The resulting groups probably combine to form the polymer (PN) or continue to grow, colliding alternately with nitrogen and phosphorus molecules until the molecular N : P ratio reaches the highest possible value (as in $P_3N_5$).

## 3. The Structure and Properties of Poly(phosphorus nitrides)

The synthesis usually yields the amorphous phosphorus nitride $(P_3N_5)$, which may be converted into a crystalline form by heating in a stream of nitrogen or ammonia above 800°C.[69] The study of the crystal structures of phosphorus nitrides is of considerable interest because of their potential wide variety and structural similarity to the corresponding modifications of phosphorus, from which the structures of phosphorus nitrides may be formally derived by a regular (or stochastic) replacement of phosphorus atom by nitrogen atoms[2]. However, bearing in mind the high thermal stability of phosphorus nitrides with a regular structure and also the sequence of the energies of the single and multiple NN, NP, and PP bonds (Table 1), one may assume *a priori* that such compounds cannot contain fragments with single and multiple NN bonds as well as the –P=P– and –P=N– linkages. Thus the principal structural element in phosphorus nitrides must be the single P–N bond and the multiple $\rangle$P=N– bond. We may note that the average bond energy (68.3 kcal) calculated from the energy of formation of the amorphous (PN)[77] is virtually identical with the energy of the P–N bond in $(Me_2N)_3P$[50] (Table 1). Crystalline phosphorus nitrides

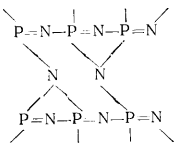
† Tungsten nitrides and phosphides are not formed at these temperatures[1].

are obtained in the form of powders, which are stable up to 700°C; on subsequent heating to the melting point or sintering, the powders may decompose or their structure may change[78-80].

X-Ray diffraction analysis showed[81] that ($P_3N_5$) crystallises in the hexagonal system with formation of spherulites 2–5 μm in size. A tetragonal modification, formed when phosphorus oxynitride is acted upon by ammonia, has also been detected[82,83]. The crystals of this modification have dimensions of approximately 30 μm. By treating the tetragonal modification with ammonia, it is possible to obtain the hexagonal modification. The converse transition cannot be achieved[84]:

$$(P_3N_5)\ \text{(tetragon.)} \xrightarrow[850^\circ C]{NH_3} (P_3N_5)\ \text{(hexagon.)} \xrightleftharpoons{NH_3+O_2}$$
$$\rightleftarrows (NPO) \xrightleftharpoons[O_2+NH_3]{NH_3\ \text{slow}} (P_3N_5)\ \text{(tetragon.)}$$

On the basis of the analysis of the infrared spectra, Steger[85] suggested that amorphous ($P_3N_5$) has a three-dimensional structure:



Judging from infrared spectroscopic data, the hexagonal modification of ($P_3N_5$) has an analogous but more ordered structure in which the phosphorus atom forms four σ bonds and one π (*pd*) bond with the neighbouring nitrogen atoms[84]. The infrared spectrum of the tetragonal modification has no band with $\nu_{max} = 1260\ cm^{-1}$, which may be attributed to the antisymmetric vibrations of the $\geq P=N-$ linkages[5]; this is regarded[84] as evidence for the presence in such systems of five P–N bonds. This band is also absent from the infrared spectrum of the crystalline modification of ($P_3N_5$) obtained from the hexagonal modification on treatment with ammonia at 500°C and approximately 40 atm.[86] The X-ray diffraction pattern of this modification differs from that of the tetragonal modification identified by Millers and coworkers[82].

Under the usual conditions, the phosphorus nitrides ($P_3N_5$) are white or yellowish highly stable substances, which are insoluble in water and organic solvents and are resistant to the action of dilute nitric and hydrochloric acids and alkalis[59,65]. ($P_3N_5$) can be dried in air at 120°C without risk of decomposition, which begins above 700°C at the normal pressure.

The evaporation of ($P_3N_5$) at 690–950°C has been investigated[20]. A combination of mass-spectrometric measurements with a study of the overall rate of diffusion of the preparation was employed. Under the conditions of congruent evaporation and for equal ionisation cross-sections of the PN and $P_2$ molecules, the partial pressures of $N_2$, PN, and $P_2$, corresponding to the overall reaction (8) at 970–1270 K, were determined. Owing to a number of methodological inadequacies and the lack of identification of the test substance, the thermodynamic characteristics for the evaporation process obtained in the above study involve large systematic errors. Thus the calculated dissociation energy of PN is appreciably higher than the value in Table 1. In order to determine the ratios of the partial pressures of PN, $P_2$, and $N_2$, Gordienko et al.[21] used a thermodynamic method of calculation. They analysed the temperature variation of the equilibrium constants for the reactions expressed in terms of the mass-spectrometric currents corresponding to the vapour components. Analysis of the mass spectra obtained at 950–1100 K and for an ionisation energy of approximately 30 eV showed that the evaporation of the hexagonal and tetragonal modifications of ($P_3N_5$) corresponds to the consecutive occurrence of reaction (9) and the reverse reaction (1). The mechanism of the evaporation of the two modifications is the same. However, the strength of the chemical bonds in the tetragonal modification is greater than in the hexagonal modification, which is confirmed by the higher heats of evaporation (111.0 and 105.1 kcal $mole^{-1}$ respectively) and the higher heats of formation (352.4 and 339.5 kcal $mole^{-1}$ respectively).

On heating in a stream of nitrogen, phosphorus nitride ($P_3N_5$) decomposes into elemental nitrogen and phosphorus; in a stream of hydrogen, phosphorus and ammonia are formed[59,64,65] and in a stream of air one obtains a residue consisting of $P_2O_5$.[59] Like (PN), phosphorus nitrides of the type ($P_3N_5$) can be chlorinated at 700°C with formation of triphosphonitrile chlorides[68]; on interaction with fluorine or nitrogen trifluoride, they give rise to the trimers and tetramers of phosphonitrile fluorides[87]. On heating in a sealed tube, nitric acid decomposes ($P_3N_5$) quantitatively. The ease of decomposition of phosphorus nitride by hot concentrated sulphuric acid has been used by Postnikov and Kuz'min[59] in chemical analyses. Phosphorus nitrides are also decomposed on fusion with alkalis and alkali metal salts. Heating of phosphorus nitride with lead, arsenic, antimony, etc. oxides leads to the liberation of the corresponding elements in a free state[59]. When ($P_3N_5$) interacts with fused magnesium, the phosphonitrile amide $PN(NMg)_2$ is formed; the analogous reaction with calcium begins at 200°C.[88]

The action of water on phosphorus nitrides has been studied in detail[1,59,89,90]. When ($P_3N_5$) is heated with water it does not dissolve at all and does not decompose. On treatment with steam at 150°C, the period during which amorphous phosphorus nitrides are 50% hydrolysed is about 55 h. Subsequent heating increases the rate of decomposition. Above 250°C under pressure, quantitative hydrolysis takes place in 2–3 h in accordance with the equations

$$PN + 3H_2O = (NH_4)H_2PO_4,$$
$$P_3N_5 + 12H_2O = 2(NH_4)_2HPO_4 + (NH_4)H_2PO_4,$$

amorphous phosphorus nitride (PN) hydrolysing more slowly at the same temperatures than ($P_3N_5$). The activation energy for the hydrolysis of ($P_3N_5$) is about 30 kcal $mole^{-1}$.[1]

The poly(phosphorus nitride) ($P_4N_6$) is an intermediate in the reaction of phosphorus trichloride with ammonia:

$$PCl_3 \xrightarrow{+NH_3} P(NH_2)_3 \xrightarrow[500-600^\circ]{-NH_3,H_2} (P_4N_6) \xrightarrow[750^\circ]{-N_2} (PN).$$

It is a yellowish substance which ignites spontaneously in air and is hydrolysed by water more readily than (PN).[89,91] Analysis of the hydrolysis products showed that the ratio of phosphorus(V) and phosphorus(III) in this compound is three and that ($P_4N_6$) is not a simple mixture of the phosphorus nitrides ($P_3N_5$) and (PN).[3] By allowing phosphorus trichloride to react with sodium azide, Grudmann and Ratz[92] obtained a coloured substance, which is hexa-azidophosphonitrile $[PN(N_3)_2]_3$. Phosphorus azides $P(N_3)_3$ as well as $OP(N_3)_3$ are exceptionally unstable and explosive[4].

## IV. METHODS OF PREPARATION AND PROPERTIES OF POLY(PHOSPHORUS OXYNITRIDE) (NPO) AND ITS THIO-ANALOGUE (NPS)

The NPO and NPS molecules have not been identified, but, bearing in mind the somewhat greater affinity of phosphorus for oxygen and sulphur[50], the results of the studies of the infrared spectra of the corresponding monomeric forms, as well as data on the structure and properties of poly(phosphonitrile halides) ($Hal_2PN$) (Allcock[5]) and nitrous oxide, these molecules presumably have a linear geometry with a two-coordinated phosphorus atom. These structures are preferred owing to the greater capacity for involvement in bonding of the 3*d* orbitals of the atoms of elements in the Third Period compared to the corresponding elements in the Second Period[93].

Poly(phosphorus oxynitride) (NPO), obtained for the first time by Gerhardt in 1846[1], exists in amorphous and crystalline forms, like the phosphorus nitride ($P_3N_5$). Amorphous (NPO) is obtained by heating phosphoric acid triamide $OP(NH_2)_3$ *in vacuo*[94] or by the reaction of phosphonitrile chlorides with metal oxides[95].‡ A detailed study of the first reaction has been carried out recently[96, 97]. Analysis of the infrared spectra of the condensation products showed that the P=N–P group is apparently formed as a result of the elimination of an $NH_3$ molecule with formation of the P–NH–P group and its subsequent rearrangement to P=N–P. Thus the formation of (NPO) from $OP(NH_2)_3$ can be represented by the following scheme:

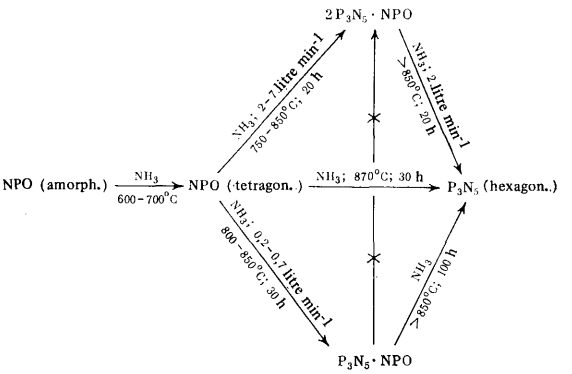
$$OP(NH_2)_3 \xrightarrow[\sim 100^\circ]{-NH_3} (NH_2)_2P(O)\text{—}NH\text{—}P(O)(NH_2)_2 \xrightarrow[\sim 300^\circ]{-NH_3} \rightarrow H_2N\text{—}[NP(O)\text{—}NH]_n\text{—}N \xrightarrow{450\text{–}500^\circ} (NPO).$$

The white poly(phosphorus oxynitride) formed has a coarsely porous structure and a relatively small specific surface[98]. This white substance melts above 1000° with formation of black vitreous bodies, which exist in three and more forms. Under normal conditions, (NPO) is insoluble in water and the usual solvents[98]. On heating, atmospheric water causes the dissociation of the PN bond with subsequent substitution of the $NH_2$ groups by OH via a tautomeric rearrangement[96,97]. The final product of the hydrolysis of (NPO) at 175°C is $(NH_4)H_2PO_4$. Poly(phosphorus oxynitride) is resistant to the action of dilute acids and alkalis, but readily decomposes on fusion with alkalis, forming ammonia and alkali metal phosphates. It reacts with concentrated sulphuric acid to form ammonium phosphate[98]: at 800°C, it reacts with chlorine and gives rise to $POCl_3$ and traces of phosphonitrile chlorides[68]. Above 550°C, it is appreciably volatile, losing approximately 55% of its weight in 4 h.[96]

When it is pressed under a pressure of 140 atm at 800°C, (NPO) is converted into a ceramic, which is not very resistant to hydrolysis[99]. The preparation of crystalline (NPO) has been described[100]. Poly(phosphorus oxynitride) crystallises in the tetragonal system[83].

The results of mass-spectrometric studies on the composition of the vapour of crystalline (NPO), formed on evaporation *in vacuo* (0.2 mmHg) at 905–1225 K, have been published[101]. A method analogous to that employed in the study[21] of the evaporation of ($P_3N_5$) was used and it was found that (NPO) vaporises without change in the composition of the solid phase. The $N^+$, $N_2^+$, $PN^+$, $P_2^+$, $P_4^+$, and $P_4O_{6-10}^+$ ions were detected in the spectra, the principal vapour components being $N_2$, PN, $P_2$, and $P_4O_{10}$.

The conversion of poly(phosphorus oxynitride) into ($P_3N_5$) on treatment with ammonia has been investigated in detail[102,103]. When X-ray-amorphous (NPO) interacts with ammonia, different products are obtained depending on the temperature, the ammonia flow rate, and the duration of heating: crystalline (NPO); a crystalline phase with the empirical formula ($P_3N_5$.NPO); the crystalline phase ($2P_3N_5$.NPO), which was not described previously. The overall interaction of amorphous (NPO) can be represented by the following scheme:




Phosphorus thionitride (NPS) is obtained by the ammonolysis of phosphorus pentasulphide[74,104,105]:

$$P_4S_{10} + 4NH_4Cl \rightarrow 4(NPS) + 6H_2S + 4HCl.$$

The yield of product after heating for 2 h at approximately 300°C reaches 85%. (NPS) is a grey insoluble diamagnetic substance, which decomposes at approximately 600°C. It reacts with hydrogen at 450°C to form ammonia, hydrogen sulphide, and phosphine. The reaction with chlorine proceeds in accordance with the equation

$$2(NPS) + 3Cl_2 \rightarrow 2(Cl_2PN) + S_2Cl_2,$$

the product being phosphonitrile chlorides having different molecular weights[105]. The reaction with dry hydrogen chloride at 350°C involves the mechanism

$$(NPS) + 4HCl \rightarrow NH_4Cl + SPCl_3.$$

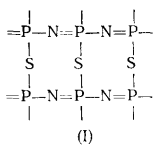
The adduct ($AlCl_3$.NPS), which is stable up to approximately 700°C, is formed when phosphorus thionitride reacts with aluminium chloride at 350°C.[105]

The sulphur in (NPS) may be substituted by oxygen under comparatively mild conditions, for example on boiling with water for a short time.[1]

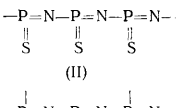
On the basis of infrared spectroscopic data, Steger[85] suggested that the most probable structure of phosphorus oxynitride is one containing phosphonitrile and phosphate chains. This type of structure is preferred also in view of the considerable difference (approximately 80 kcal) between the sum of the energies of two P–O bonds and the energy of the P=O bond. On the other hand, the difference between the energies of two P–S bonds and the P=S bond is only 12 kcal.[50] Thus, together with structure (I) analogous to that proposed for (NPO), non-cross-linked or

‡ There is also an indication that (NPO) may be formed during the simultaneous oxidation of nitrogen and phosphorus in a low-temperature plasma[18].

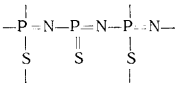
partly cross-linked structures (II) and (III) are possible for phosphorus thionitride:



(I)



(II) NPS



(III)

## V. ELECTROPHYSICAL PROPERTIES OF PHOSPHORUS NITRIDES

As already mentioned, it is quite appropriate to attempt to draw analogies when one considers the characteristic features of the structures and properties of various modifications of phosphorus, phosphorus nitrides, and their derivatives.

Orthorhombic black phosphorus is known to be a semiconductor[106]; the electrical conductivity of polycrystalline black phosphorus is a maximum at 40 K.[107] At very high pressures and low temperatures, phosphorus acquires the properties of a superconductor[108,109].

The presence of a large number of electrons capable of being delocalised in phosphorus nitrides is apparently the reason why the specific conductances of phosphorus oxynitride and nitride show an exponential temperature dependence, which is characteristic of semiconducting materials[79]§. In the temperature range 286–800 K, the specific conductances of the substances investigated decrease in the sequence

$$(P_3N_5)^{cr} > (NPO)^{cr} > (NPO)^{am} .$$

The electrical d.c. resistances of phosphorus thionitride have been investigated[111] in the range 20–120°C. At 20°C, the specific conductance of (NPS) is $1.5 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$, exceeding by several orders of magnitude the specific conductances of the cyclic phosphazenes $(X_2PN)_3$, which are $10^{-11}$–$10^{-13}\ \Omega^{-1}\ cm^{-1}$. According to the authors[111], the greater number of conjugated bonds and $\pi$ electrons in phosphorus thionitrides [see Structures (I)–(III)] compared with phosphazenes should be responsible for the mainly electronic nature of the conduction, which is ohmic at an electric field strength of 500–1000 V $cm^{-1}$. It was noted, that in the temperature range employed, the energy gap $E\sigma$ is virtually constant at 0.82 eV. The conductivity of (NPS) and $E\sigma$ are appreciably influenced by the applied pressure. For pressures of 100, 300, 500, and 1000 atm at 20°C, the resistivities are $9.3 \times 10^9$, $1.4 \times 10^9$, $6.9 \times 10^8$, and $4.7 \times 10^8\ \Omega$ cm respectively and the values of $E\sigma$ vary in the range 0.04–1.80 eV.[111]

The extension of the temperature range in the measurement of the conductivities of phosphorus nitrides towards lower values is of considerable interest. We may recall here the metallic conduction in the (NS) polymer at liquid helium temperatures and its superconducting properties at 0.3 K.[112–115]

Poly(phosphorus selenonitride) (NPSe), which has not so far been synthesised, may possess interesting electrophysical properties.

§ Powders pressed into discs, clamped in an evacuated cell, were investigated. The excess of $p$ electrons is apparently responsible also for the weak photoluminescence of (NPO).[110]

## VI. PRACTICAL APPLICATIONS AND INDUSTRIAL SYNTHESIS OF PHOSPHORUS NITRIDES

### 1. Applications of Phosphorus Nitrides

Phosphorus nitrides are already used in engineering. It has been shown that $(P_3N_5)$ is an active diffusant when a silicon surface is saturated with phosphorus[116]. The possibility of employing $(P_3N_5)$ in the manufacture of semiconductors is also indicated in a patent[117]. Like (NPO), poly(phosphorus nitride) is a more convenient gas absorber than red phosphorus in the manufacture of incandescent lamps and similar apparatus[118,119]. Cellulose articles containing 10% $(P_3N_5)$ or 12% (NPO) are resistant to spontaneous inflammation and combustion and the addition of phosphorus nitride does not impair the mechanical properties of articles[120].

Further study of the binding (by reaction with phosphorus) of molecular nitrogen in the poly(phosphorus nitrides) $(P_3N_5)$ and (PN), which constitute an extremely attractive ballast-free starting material for the preparation of phosphorus–nitrogen fertilisers[59]¶, is of undoubted interest. The need for such research has become particularly urgent recently owing to a number of economic and technological causes. Among these, mention should be made of the increasing requirement for fertilisers† due to the growing world population, the reduced yield of grain crops per unit weight of fertilisers[127,129], the increasing price of fertilisers, and also the increasing cost of agricultural production (per unit weight of fertilisers)[130–134], the disproportion in the manufacture and consumption of individual components of fertilisers in developed and under-developed countries[127], etc.

The hydrolysis of phosphorus nitrides results in the formation of ammonium phosphates, which are widely used in the manufacture of fertilisers (including complex, solid, and liquid fertilisers), animal feed‡, and for technical purposes[126,134–136]. Ammonium phosphates are obtained by the reaction of ammonia with phosphoric acids or phosphorus pentoxide, formed when elemental phosphorus is combusted[126,137–139]. The desirability of employing phosphorus itself in the manufacture of phosphorus-containing compounds increases from year to year in view of the increasing development of the electrothermal manufacture of phosphorus. This is due to the gradual exhaustion of phosphate ores with a high $(P_2O_5)$ content, the increasingly stringent requirements for the purity of

¶ The direct employment of $(P_3N_5)$ as a fertiliser in a pure form is hardly possible in view of its resistance to different reagents under the usual conditions. Allison[121] introduced $(P_3N_5)$ into soil under the required conditions in order to convert nitrogen into a nitrate form. Since this conversion was not observed, he concluded that $(P_3N_5)$ as such cannot serve as a satisfactory fertiliser. Other workers[122,123], who investigated the decomposition of $(P_3N_5)$ in heated soil, later arrived at a similar conclusion. A systematic study of the possible employment of different compounds with PN bonds as fertilisers has been carried out[124,125] (see also Mattinghley and Taligudden[126]).

† During the last 15 years, the world requirement for combined nitrogen increased by 400% and for phosphorus by 150%[127] (see also Kodama[130]).

‡ The production of chemical additives to animal feed in the USSR will reach 5 million tonnes in 1980.[128]

the products§, and the possibility, in principle, of a fairly complete extraction of secondary components from slags in electrothermal manufacturing processes: fluorine, lanthanides[140,141], etc. The preparation of ammonium phosphates by the hydrolysis of phosphorus nitrides, which are formed directly from nitrogen and phosphorus, will reduce the cost of phosphoric¶, sulphuric, and nitric acids, which are used in the manufacture of phosphorus-containing fertilisers[138,142], and also of ammonia†.

An undoubted advantage of this method of synthesis is the absence of waste, which is important for the protection of the environment, the transportability of phosphorus nitrides, and also the possibility of preparing from them various compositions with nutrient substances.

The use of phosphorus nitrides as the starting materials for the preparation of phosphonitrile halides[66-68] and their derivatives, which have recently found extensive practical applications[5,145-147] in catalysis, etc., is no less promising.

## 2. Industrial Synthesis

The methods of obtaining phosphorus nitrides on an industrial scale were already outlined before the war. Miner[148] patented a method for the large-scale synthesis of (PN) based on the reaction of phosphorus halides with metal nitrides. However, the direct synthesis from the elements is more promising. It is recommended that ($P_3N_5$) be obtained by the direct reaction of nitrogen and phosphorus at a pressure of 1000 atm at 850 K.[149,150] An approximately analogous method has been proposed in a patent[151]. Quite recently Krasnokutskii and coworkers[13,152] investigated the interaction of nitrogen with gaseous phosphorus in a flow-type electric arc reactor. Nitrogen was passed to the electric arc chamber of the reactor where it was heated to a temperature of approximately 6500–7000 K, emerging from the anode-nozzle in the form of a jet, into which phosphorus vapour heated to 600°C was introduced. It was found that the content of bound nitrogen increases with the space velocity of the gases and the enthalpy of nitrogen, reaching approximately 25% by weight for the optimum volume of the reaction chamber, contact time (approximately $10^{-3}$ s), and temperature (3000–4500 K). The experimentally obtainable maximum contents of bound nitrogen are close to the amount in the P–N system found by thermodynamic calculation for the experimental conditions[14,152]. Kinetic studies are essential for a more complete description of the specific features of the given process.

The efficiency of the high-temperature method of manufacture of phosphorus nitrides follows from a comparison of the energy expenditures characterising various thermal processes in which molecular nitrogen is combined (Table 2).[152]

**Table 2.** Energy expenditure in manufacturing processes[138].

| Method of binding atmospheric nitrogen | Maximum product concentration, vol.% | Minimum energy expenditure per tonne of bound nitrogen, $10^3$ kW h |
|---|---|---|
| Formation of nitrogen oxides | 8 | 27.9 |
| Formation of dicyanogen | 59 | 17.2 |
| Simultaneous formation of hydrogen cyanide and acetylene | 11 | 10.6 |
| Formation of phosphorus nitride | 50* | 7.6 |

*Weight percentages.

Methods involving the combined initiation of this reaction (high temperature, discharge, irradiation) as well as catalytic processes are no less promising. Urbain[153,154] suggested that nitrogen and phosphorus vapours be compressed over a catalyst consisting of aluminium, titanium, magnesium, and bauxite in the presence of traces of cobalt, aluminium, and potassium oxides above 900°C. A scheme for an industrial apparatus, in which phosphorus nitride is manufactured on a scale consistent with the synthesis of fertilisers, has been proposed in a patent[155]. The recommended process includes the thermal generation of phosphorus vapour, the reaction of which with molecular nitrogen is initiated by an electric discharge.

The importance of plasmas has recently greatly increased in chemical engineering[156,157]. In the synthesis of phosphorus nitrides, plasmas may be used not only to initiate the reaction between nitrogen and phosphorus molecules but also to obtain elemental phosphorus from phosphorus-containing ores[157,158].

A decrease of the intrinsic cost of the manufacture of phosphorus nitride would be possible if the gases from phosphorus furnaces containing 14% of phosphorus and 86% of carbon monoxide were used instead of pure phosphorus[158]. This would permit the elimination of the stages involving the condensation of phosphorus and its consequent evaporation. The corresponding thermodynamic analysis showed that the quasi-equilibrium composition of the $N_2$–P–CO system hardly differs from the composition of the $N_2$–P system presented in Fig. 1. In the temperature range 1000–4000 K, only P, $P_2$, $N_2$, CO, and PN are present in the system in large amounts. The maximum concentration of PN in the mixture reaches approximately 7 vol.%. It was noted that the concentrations of polyatomic phosphorus and nitrogen oxides may be neglected in the above temperature range[158].

Vinokurov et al.[159] made a thermodynamic analysis[158] of the possibility of obtaining phosphorus nitrides (as well as phosphorus and iron) from ferrophosphorus, which is a waste product in high-temperature electrothermal manufacture. The highest yield of phosphorus nitride (22 wt.%) in the nitrogen plasma is ensured at a temperature of 3300 K and for the ratio nitrogen : ferrophosphorus = 1 : 1. The highest concentration of PN in the gas phase (26%) should be reached for the ratio ferrophosphorus : nitrogen = 8 : 1 at 3300 K.

§In the course of the current 5-year plan in the USSR, it is planned to obtain mineral fertilisers containing not less than 40% of nutrient substances[128].

¶According to Greek's data[143], 80% of the phosphoric acid obtained in industry is used to synthesise phosphorus fertilisers.

†Synthetic ammonia serves at the present time as the starting material for the synthesis of the majority of products containing bound nitrogen. The manufacture of ammonia has reached a high degree of technical sophistication. However, its manufacture may require a large capital expenditure and expensive materials, and, furthermore is based on a hydrocarbon starting material[144], the availability of which is limited.

Presumably further experimental and theoretical research will lead to the development of an effective industrial method for the synthesis of phosphorus nitrides and will give rise to further prospects for their employment in various branches of science and engineering. On the other hand, the study of phosphorus nitrides and their derivatives will permit a deeper understanding of their general properties and will make it possible to discover differences between the structures, properties, and reactivities of compounds with single and multiple NN, NP, and PP bonds.

## ADDENDUM

Mention should be made of the following data published during the preparation of the review for printing. One of the principal disadvantages of the high-temperature methods of synthesis of phosphorus nitrides is the use of the readily inflammable and toxic white phosphorus, some of which remains in the reaction product. The application of ion bombardment for the evaporation of phosphorus makes it possible to avoid the heating of the apparatus under laboratory conditions[160]. The resulting amorphous nitride contains no white phosphorus, which makes it possible to open the reactor and carry out experiments with the product in air.

Table 3. The effective charge on the phosphorus atoms in poly(phosphorus nitride) $(P_3N_5)$*.

| $\Delta q^P$, e.u. | | | |
|---|---|---|---|
| *A* | *B* | *C* | *D* |
| 1.65 | 0.63 | 1.08 | 1.1 |

*Method of calculation: *A*) from the estimate of the total number of electrons removed from the orbitals of the phosphorus atom[166]; *B*) from the change in the effective charge in a sphere with a radius equal to the covalent radius of phosphorus[167]; *C*) from the empirical relation[168]

$$\Delta q = 0.813\sqrt[4]{E_b^{2p} - 130.1};$$

*D*) by a method based on the combination of the Boron–Haber cycle with Kapustinskii's lattice equation[168].

A simple method was proposed recently for the preparation of (NPO).[161,162] The one-stage synthesis includes the interaction of concentrated phosphoric acid, pyrophosphoric acid, $P_4O_{10}$, and ammonium phosphates or urea with melamine, guanamines, and trialkyl($C_{1-3}$)-1,3,5-triazines at 500–750°C.

A convenient method for the synthesis of $P(N_3)_3$, $PO(N_3)_3$, and $P(N_3)_5$ as well as a detailed study of the structures of these compounds by vibrational and NMR spectroscopy were published by Volgnandt and Schmidt[163]. According to Pelavin et al.,[164] the interaction of phosphorus pentafluoride with an excess of sodium azide in acetonitrile at −20°C can be represented schematically as follows:

$$PCl_5 + 10NaN_3 \begin{cases} \nearrow P(N_3)_5 + 5NaCl + 5NaN_3 \\ \searrow NaP(N_3)_6 + 5NaCl + 4NaN_3 \end{cases}.$$

The hexa-azidophosphate anion hydrolyses in accordance with the equation

$$P(N_3)_6^- + 2H_2O \rightarrow PO_2(N_3)_2^- + 4HN_3 .$$

A number of attempts have been made to determine the effective charge of phosphorus $\Delta q$ in $(P_3N_5)$ from the binding energies, obtained from X-ray photo electron spectra, of the 2*p* electrons of phosphorus ($E_b^{2p}$) in $(P_3N_5)$ and red phosphorus (133.2 and 130.1 eV respectively—Table 3). Naturally the employment of different models in calculations gives rise to a different significance and different values of the calculated effective charges.

Veprek and Koos[169] showed that a dielectric constant of $(P_3N_5)$ varies linearly with temperature in the range 77–525 K. Phase transformations were not observed in the temperature range 300–765 K, but the structure of $(P_3N_5)$ synthesised from the elements in an ultrahigh frequency discharge depends on the precipitation temperature. At a precipitation temperature of 265°C, it is amorphous, while at higher temperatures a crystalline product is obtained. The dielectric strength of $(P_3N_5)$ is $0.9 \times 10^7$ W $cm^{-1}$.

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