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Reactivity of Trivalent Phosphorus Derivatives

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The review deals with the most important features of phosphorus(III) derivatives, which determine their chemical properties. These are the biphilicity of the phosphorus atoms due to the presence of a free electron pair and unfilled *d* orbitals and the ambidentate properties of phosphorus(III) derivatives determined by the specific contribution of both nucleophilic elements (O, N, S) and elements with vacant *d* orbitals (Si, Sn) directly linked to the phosphorus atom. Certain limits and characteristics of this contribution have been elucidated and the mechanism of the relevant reactions has been discussed.
The last section deals with the specificity of the behaviour of phosphorus(III) compounds with a phosphorus-halogen bond. The significant role of the *d* orbitals of the phosphorus atom in its chemical reactivity is discussed.
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I. INTRODUCTION

Considerable advances in the practical applications of organophosphorus derivatives and the important role of phosphorus compounds in vital processes are responsible for the considerable interest in the chemistry of these compounds. During the last 15–20 years the preparative chemistry of organophosphorus compounds has been considerably developed and an enormous amount of experimental data have accumulated, systematic and general accounts of which have been published in numerous reviews and monographs. Theoretical studies have also been pursued, but the theoretical approach to problems of the reaction mechanism and reactivity of organophosphorus compounds proved to be more difficult, particularly for phosphorus(III) derivatives, and the results obtained have been less significant compared with advances in classical organic chemistry.

This review was undertaken to examine the chemical properties of phosphorus(III) derivatives. It does not give an exhaustive compilation of studies on definite types of reaction but an attempt is made to establish certain relations which determine the chemical behaviour of phosphorus(III) derivatives in reactions. Hudson, Kirby, and others partially dealt with some of these problems in their monographs or reviews. Other problems have been formulated in a definitive form only very recently.

II. THE CONCEPT OF "BIPHILICITY" FOR PHOSPHORUS(III) DERIVATIVES

Phosphorus(III) compounds are very reactive and can enter into a wide variety of reactions. The phosphorus atom can behave either as a nucleophilic or an electrophilic centre. There are also a number of reactions in which the nucleophilic and the electrophilic properties of phosphorus are shown simultaneously.

Thus the nucleophilic properties of phosphines are well known[1,2]:

$$R_3P + R'I \rightarrow R_3\overset{+}{P}R'\overset{-}{I},$$

but in the presence of powerful nucleophilic agents phosphines are also capable of substitution reactions[3]:

$$R_2P{-}R + Na \rightarrow R_2PNa + NaR.$$

A dual reactivity is characteristic also of many other phosphorus(III) compounds, for example[4,5]:

$$(RO)_3P + R'I \rightarrow [(RO)_3\overset{+}{P}R']\overset{-}{I} \rightarrow (RO)_2P(O)R' + RI,$$
$$(RO)_3P + nR'MgI \rightarrow (RO)_{3-n}PR'_n + nROMgI.$$

The capacity of phosphorus(III) compounds to behave both as electron donors and electron-acceptors has been reflected also in the formation of complexes. Kirby[6] concluded that tertiary phosphines can behave as electron-donating species (as a result of the free electron pair of the phosphorus atom) in complex-formation reactions with metal cations, forming complexes similar to those which metals form with amines. The stability of the phosphine complexes is lower than that of the corresponding amine complexes.

However, the formation of complexes with cations such as Ag^+, Pt^{2+}, and certain others takes place via the interaction of their *d* electrons with the vacant *d* orbitals of the phosphorus atom. This is confirmed by the finding[7] that the introduction of strong electron-accepting groups into the phosphine molecule, for example CF_3, entails an increase in the stability of the complex with Pt^{2+} and by the fact that phosphorus trichloride can be displaced from the complex $Ni(PCl_3)_4$ by phosphorus tribromide or trifluoride but not by triphenylphosphine[8].

The dependence of the electron-donating or electron-accepting capacity of phosphorus(III) compounds on the substituents at the phosphorus atom has been clearly revealed by the stability of the complexes formed. Thus the stability of phosphorus(III) complexes with boranes (substances with markedly electron-accepting properties) increases in the series[9]

$$R_3P > (>N)_3P > (RO)_3P >> PCl_3.$$

The introduction of electron-accepting substituents, for example, halogens, sharply reduces the electron density at the phosphorus atom, with a corresponding

increase of the capacity of such compounds to behave as electron acceptors. Phosphorus(III) halides form complexes with electron donors such as amines[10,11], phosphines[12], and arsines[13]. Phosphorus-containing ligands can be arranged in the following sequence in terms of the stability of the complexes which they form[14]:

$$PCl_3 > PBr_3 >> RPCl_2 >>> R_3PCl\ .$$

Evidently the stability of the two types of phosphorus(III) complexes described above varies with the type of substituent in the opposite sense.

There are many examples of reactions in which phosphorus(III) compounds can behave as nucleophilic or electrophilic agents depending on the type of substituent or the second reactant. Such dual reactivity is one of the specific features of phosphorus(III) atoms. It can be explained by a combination of two factors: the presence at the phosphorus atom of both a free electron pair and vacant *d* orbitals. A characteristic feature of the phosphorus atom is that the participation of its *d* orbitals in the formation of new bonds requires a considerable positive charge, under the influence of which the levels of the *d* orbitals are lowered and their participation in the formation of new bonds becomes energetically favourable[15]. The origin of the positive charge at the phosphorus atom is apparently insignificant. It can be induced by electron-accepting substituents in the initial phosphorus(III) compounds or it can arise as a result of attack of an electrophilic agent on the phosphorus atom.

The presence of vacant *d* orbitals determines the capacity of phosphorus(III) compounds to behave as electron acceptors. The specificity of such involvement of *d* orbitals of the phosphorus atom is clearly illustrated by an example such as the hydrolysis of halogeno-derivatives of nitrogen and phosphorus[16]:

$$NCl_3 + H_2O \rightarrow NH_3 + HOCl,$$

$$PCl_3 + H_2O \rightarrow (HO)_2\overset{\overset{O}{\|}}{\underset{H}{P}} + HCl\ .$$

In 1962 Syrkin[17] formulated the following postulate: "All outer electrons and all outer orbitals participate in the simultaneous general lowering of the energy of the molecule formed". The application of this principle in the discussion of the reactivity of phosphorus(III) compounds can explain many important features of their behaviour in numerous reactions. Indeed all reactions of phosphorus(III) derivatives involving an increase in valence are based on the participation of both the free electron pair and the vacant *d* orbitals. One of the best investigated examples of this reaction is the Arbuzov rearrangement:

$$R-\ddot{O}-\underset{\underset{R'}{|}}{P}:+CH_2Hal \rightarrow [R-O-\overset{+}{\underset{\underset{R'}{|}}{P}}-CH_2]\,\bar{H}al \rightarrow R-Hal + O=\underset{\underset{R'}{|}}{P}-CH_2R'.$$

Within the framework of the electronic theory, this reaction may be described as follows. The process begins with the nucleophilic attack of the free electron pair of the phosphorus atom on the electrophilic carbon atom by an S_N2 bimolecular substitution mechanism. The positive charge at the phosphorus atom in the quasiphosphonium cation thus produced makes its *d* orbitals available for reaction. This increases the degree of interaction of the *p* electrons of the oxygen atom with the *d* orbitals of the phosphorus atom and leads to the formation of a new π bond. Probably this process may involve an intermediate stage with formation of an oxonium cation and subsequent elimination of a carbonium cation:

$$R-\ddot{O}-\overset{+}{P}< \longrightarrow R-\overset{+}{O}=P< \longrightarrow R^+ + O=P<\ .$$

Analysis of extensive experimental data shows that the decomposition of the intermediate quasiphosphonium salt probably takes place by a unimolecular mechanism[18-21]. Moreover, depending on the environment of the phosphorus atom, processes involving a nucleophilic transfer of the electron pair of the phosphorus atom and the interaction of the oxygen *p* electrons with the *d* orbitals in the course of the Arbuzov rearrangement can occur either at different times or synchronously:

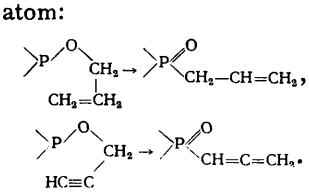
$$R-\ddot{O}-P: \quad CH_2-Hal \longrightarrow [R\cdots O=P\cdots CH_2\cdots Hal] \longrightarrow R^+ + O=P-CH_2- + Hal^-.$$

Theoretical examination of the possibility of the participation of the phosphorus *d* orbitals in the formation of additional bonds showed that the formation of fairly strong bonds via the *d* orbitals is possible only when the electron density at the phosphorus atom is reduced[15]. This in fact is the reason for the occurrence of two types of reactions, leading to an increase of the valence of trivalent phosphorus.

For compounds where the substituents can increase the electron density at the phosphorus atom, the rate-limiting process is the nucleophilic attack by the free electron pair on the electrophilic centre of the second reactant. When the free electron pair is transferred, the electron density at the phosphorus atom is reduced synchronously and conditions are created for the formation of additional σ and π bonds via the *d* orbitals, as shown above for Arbuzov rearrangement. This is satisfactorily consistent with data on the oxidation of phosphorus(III) derivatives by oxygen, peroxides, and peracids[22] and also on their interaction with sulphur[23]. For derivatives where the trivalent phosphorus atom has a reduced electron density, the rate-limiting process is the interaction of the reaction centre having an enhanced electron density with the vacant *d* orbitals of phosphorus. An example of such interaction is that of phosphorus trichloride with amine *N*-oxides[2] and sulphoxides[25]. In this case the process begins with nucleophilic attack by oxygen on the vacant *d* orbitals of the phosphorus atom:

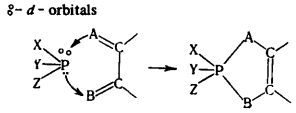
$$R_3N \rightarrow O + PCl_3 \rightarrow R_3\overset{+}{N}-O-\bar{P}Cl_3 \rightarrow R_3N + O=PCl_3\ .$$

In this connection the intramolecular rearrangement of the allyl and propargyl esters of acids derived from trivalent phosphorus, investigated in detail by Pudovik et al[26], is also of interest. The authors suggest that the process begins by attack by the free electron pair of the phosphorus atom on the unsaturated centre. However, in this case there is a possibility of a primary interaction between the π electrons of the olefin and the vacant *d* orbitals of the phosphorus atom:



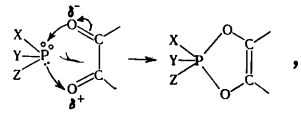
As a result of a synchronous cyclic electron transfer, phosphite is also converted into phosphonate in this case. The concept of the simultaneous utilisation of the free electron pair and the vacant *d* orbitals accounts also for

the possibility of the participation of various acids derived from trivalent phosphorus in reactions with diketones, $\alpha\beta$-unsaturated carbonyl compounds, and diene hydrocarbons:



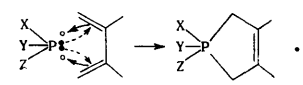
Depending on the electron density of the phosphorus atom, the rate-limiting step in this reaction can be either the transfer of the free electron pair of the phosphorus atom to the electrophilic centre or, conversely, the nucleophilic interaction of the conjugated system with the *d* orbitals of the phosphorus atom [27].

In reactions of $\alpha\beta$-dicarbonyl compounds with esters, ester-amides, and amides of acids derived from phosphorus(III), the nucleophilic properties of which have been revealed in a number of interactions, the rate-limiting process is most likely nucleophilic attack by the free electron pair of the phosphorus atom on the electrophilic centre of the conjugated system and conversely:



where X, Y, Z = OR or NR_2. The electrophilic behaviour of phosphorus in various acid chlorides derived from phosphorus(III) suggests that in this case the rate-limiting process is the interaction of the vacant *d* orbitals of phosphorus with the π-electrons of the conjugated system.

Arbuzov and coworkers and also Petrov and Razumova showed that the reactivity of dienes in interactions with trivalent phosphorus compounds increases in the sequence dimethylbutadiene < isoprene < butadiene < piperylene [28-33]. The ease of the interaction of phosphorus(III) acid derivatives of the type RPX_2 and R_2PX with diene systems increases in the sequence where R has the following significance: NCS < Cl < SR < F < OR < NR_2. [34,35] All these findings convincingly demonstrate that in these cases the rate-limiting step is the interaction of the π-electrons of the diene system with the vacant *d* orbitals of the phosphorus atom followed by the involvement of the free electron pair in the formation of a pentacovalent adduct:



Therefore all the factors favouring an increase in the electron-donating capacity of the conjugated diene and reducing the electron density of the phosphorus atom tend to increase the rate of such processes.

Heteroconjugated systems, which are readily polarised or already have both nucleophilic and electrophilic centres, are capable of interacting at a fairly high rate with any derivatives of phosphorus(III) acids. Depending on the type of the substituents at the phosphorus atom, the rate-limiting step may be the interaction of the free electron pair with an electrophilic centre, or of the π electrons of the heteroconjugated systems with the vacant *d* orbitals [36,37]. It is quite logical to postulate that the interaction in the system (X, Y, Z,)P: +A = C−C = B involves synchronous formation of the P−A and P−B bonds (at least for the *cis*-form of the conjugated system), since any transition, having once begun, induces the next. By the term "synchronous" we imply that the structures $\rangle\bar{P}-A-C-C-\bar{B}$ and $\bar{A}-C=C-B-\overset{+}{P}\langle$ are not formed as kinetically independent species or there is no minimum corresponding to them in the energy diagram for the reaction. Such treatment is not of course correct in all cases. Thus it is known [38] that in the interaction of phosphorous triamide with benzil the dipolar form is fairly stable and one cannot of course exclude the possibility that in certain cases it can exist also as a kinetically independent structure, particularly since the contribution of the *trans*-forms of the conjugated systems to the formation of pentacovalent adducts has not so far been accurately established. However, one must always distinguish whether the P−A or the P−B bond is formed faster, i.e. whether the process begins with nucleophilic attack by the free electron pair of phosphorus or with the interaction of the vacant *d* orbitals with the π electrons of the conjugated system—one of these processes will be rate-limiting for the reaction as a whole.

Kirby and Warren (Ref. 6, p. 22) suggested the term biphilicity for the capacity of the trivalent phosphorous atom to donate both an electron pair and *d* orbitals in a single process involving the formation of a new compound and defined it as follows: "A biphilic compound can donate electrons to the substrate to form a σ bond and also to accept electrons at the same centre, which results in the formation of a second σ or π bond".

The definition of "biphilicity" as the capacity of the same reaction centre (in this case the phosphorous atom) to function consecutively or synchronously as an electron donor or acceptor in an interaction with another reactant, involving the formation of two new bonds, differs fundamentally from concepts such as ambidentate properties, dual reactivity, and amphoteric properties; as a concept defining the properties of the reaction centre, it merits recognition.

III. AMBIDENTATE PROPERTIES OF PHOSPHORUS(III) DERIVATIVES (DUAL REACTIVITY)

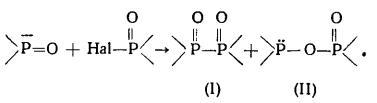
In an estimation of the nucleophilic properties of phosphorus(III) derivatives account must also be taken of the fact that many of these have two nucleophilic centres. Phosphorus(III) compounds with substituents of the type $R\ddot{\underset{\cdot\cdot}{S}}$, $R\ddot{\underset{\cdot\cdot}{O}}$, and $R_2\ddot{N}$ may be included among systems of this kind. Although the ambidentate nature of many phosphorus(III) compounds has been known for a long time and was demonstrated for the first time by A.E. and B.A. Arbuzov [39,40] in 1932 in the interaction of dialkyl phosphite salts with phosphorus-containing acid chlorides and by Kabachnik [41] and Michaelis [42] in the interaction of thiophosphites [phosphorothi-ites] with alkyl halides, these data have not been reviewed systematically and have been inadequately taken into account in the assessment of the occurrence of particular processes with participation of esters, thioesters, and amides of acids derived from phosphorus(III).

Two mesomeric forms, $\rangle\bar{P}=O \leftrightarrow \rangle\ddot{P}-\bar{O}$, are possible for an anion of the type $\rangle\bar{P}=O$. Depending on the type of substituents at the phosphorus atom, the reaction conditions, and the second reactant, the nucleophilic centre can be either the oxygen or the phosphorus atom.

In the interaction with alkyl halides and carboxylic acid halides[40] and in reactions involving addition to an activated C=C double bond, a carbonyl group, and a C=N bond,[44] the phosphorus atom behaves as the nucleophilic centre in the anion

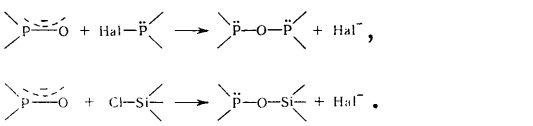


In the reaction of dialkyl phosphite salts with phosphorus(V) chlorides[45] both possible reaction products are formed, the yield of product (I) reaching 90%:

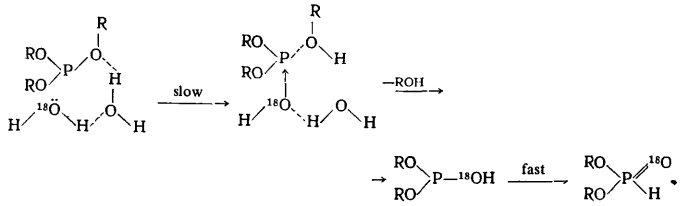


(I) (II)

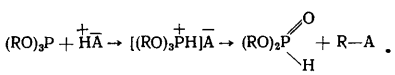
However, in reactions with phosphorus(III) acid chlorides[46] or with chlorosilanes[47-49] the oxygen atom behaves as the nucleophilic centre and trivalent phosphorus compounds are formed preferentially:



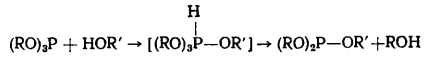
Until recently it was believed that esters of phosphinous and phosphorous acids interact in all reactions with electrophilic reagents with participation of the free electron pair of the phosphorus atom. Aksnes and Aksnes[50], who investigated the kinetics of the neutral hydrolysis of phosphites by water with labelled oxygen and analysed the hydrolysis products by infrared spectroscopy, showed that the alkoxy-radical is exchanged for the hydroxy-group with labelled oxygen. On this basis, they concluded that the oxygen of the ester group is protonated in an intermediate stage and the hydrolysis is described by the equation



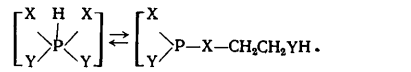
It is now generally accepted that the hydrolysis of phosphites in an acid medium[51] involves the protonation of the phosphorus atom in the phosphite with subsequent decomposition of the intermediate complex to dialkylphosphorous acid:



Transesterification of phosphorus(III) acids is analogous to neutral hydrolysis in many of its details. By analogy with the acid hydrolysis of phosphites, some workers believe[52-54] that in this case the phosphorus atom is also protonated and the breakdown of the intermediate complex is accompanied by the exchange of the alkoxy-groups:

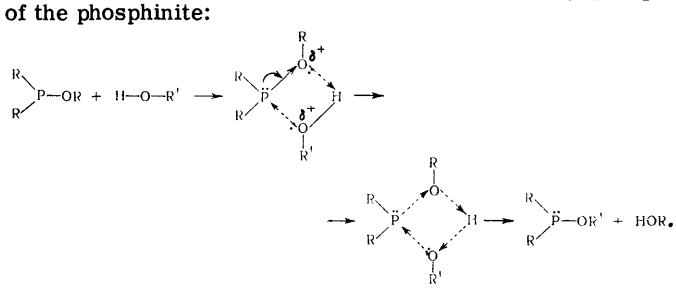


Grechkin and also Burgada and coworkers[55-58] showed that the transesterification of the esters and amides of trivalent phosphorus acids with ethanolamine or glycol involves the formation of a pentacovalent product with a spiro-structure and, what is most interesting, there is a possibility of an interconversion of the pentacovalent and trivalent forms:



The isolation of the pentacovalent spiro-product with a phosphorus–hydrogen bond and the demonstration of the interconversions of the trivalent and pentacovalent forms constitutes unquestionable proof of the possible occurrence of transesterification with participation of the free electron pair of the phosphorus atom.

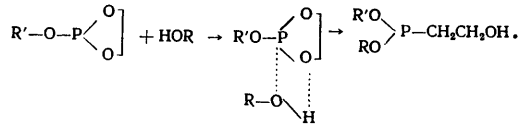
In a study of the kinetics of the transesterification of phosphinic and phosphinous acids with alcohols of different structures, Pudovik and Evstaf'ev showed that the rate of transesterification varies with the pK of the alcohol in the opposite sense for trivalent and pentavalent phosphorus acid esters[59-62]. The rate of transesterification of pentavalent phosphorus acid esters, which is a nucleophilic substitution reaction at the tetrahedral phosphorus atom, falls with increase of the acid properties and with decrease of the basic properties of the alcohol. For trivalent phosphorus acid esters, the opposite relation holds. This enabled the authors to suggest that, like neutral hydrolysis, the transesterification involves the initial protonation of the oxygen atom of the alkoxy-group of the phosphinite:



The formation of an 'onium' oxygen atom gives rise to a change in both the bonding pair and in the type of $d-p$ interaction of the oxygen–phosphorus bond. This leads to a reduced electron density at the phosphorus atom and gives rise to the possibility of a nucleophilic interaction between the free electrons of the oxygen atom of the alcohol and the vacant d orbitals of the phosphorus atom. Such cyclic synchronous electron transfer results in the formation of a "new" phosphinite and a "new" alcohol molecule.

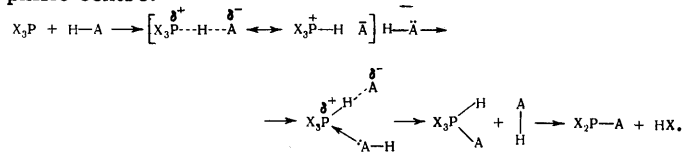
Although these data are apparently in conflict with the results of Grechkin and Burgada, the two sets are in fact complementary rather than mutually exclusive. It may be supposed that, while the initial reversible transition involving the protonation of the phosphorus atom is most likely to be determined by steric factors, in transesterification with alcohols the conditions for thermodynamic equilibrium constitute the decisive factor.

The possibility of the protonation of oxygen is confirmed by data[63] on the transesterification of a cyclic phosphite with alcohols:



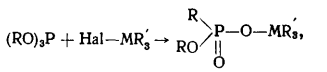
In conclusion it should be noted, however, that, in reactions between phosphorus(III) compounds and substances containing a mobile hydrogen atom, the species responsible

for the reaction may not be the trivalent phosphorus compound itself but its complex with a proton donor HA, in which the phosphorus atom behaves as the reactive electrophilic centre:



The ambidentate properties of trivalent phosphorus acid esters have been reflected also in the formation of complexes with a number of elements. The formation of a copper(I) complex was suggested by A. E. Arbuzov[64] as a typical reaction of phosphorus(III) acid esters. Later investigations[65,66] permitted a more detailed study of the metal–phosphorus bond formed.

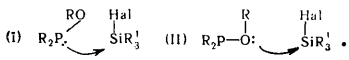
A number of investigators showed that interaction of phosphorus(III) acid esters with halogeno-compounds of silicon and tin takes place according to the equation[67–71]:



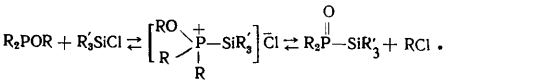
where M = Si or Sn.

Malatesta[68] suggested that the reaction with alkyl halides initially involves the isomerisation of trialkyl phosphite to alkyl phosphonate, which gives rise to the final product by reacting with the halogeno-derivatives of silicon and tin.

However, Pudovik and Muratova[72] showed that esters of dialkylphosphinous acid can react with halogeno-derivatives of silicon and tin to form stable intermediate complexes. They believe that the complexes are formed as a result of a donor–acceptor interaction between the free electron pair of the phosphorus or oxygen atom and the vacant *d* orbitals of the silicon or tin atom:

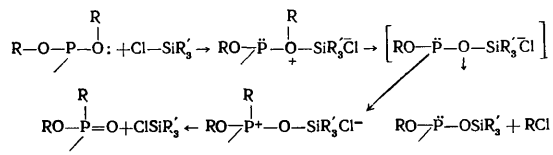


If the complex formation involves the participation of the free electron pair of the phosphorus atom and the vacant *d* orbitals of silicon or tin, then the available date on the behaviour of compounds of this kind would lead to the expectation that the breakdown of this complex would result either in the initial materials or compounds with a phosphorus–silicon bond:



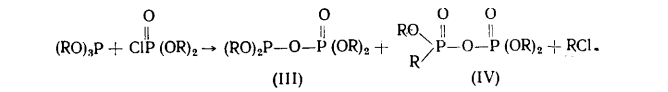
Alkylation of the phosphorus atom is quite unlikely, since this would involve the interaction of the carbonium ion formed with the positively charged phosphorus atom.

On the other hand, if the complex is formed as a result of a donor–acceptor interaction between the free electron pair of the oxygen atom in the alkoxy-radical of the phosphinite and the vacant *d* orbitals of the silicon or tin atom, then the remaining free electron pair of phosphorus in the intermediate complex would interact with the resulting carbonium ion with formation of a phosphorus–carbon bond:

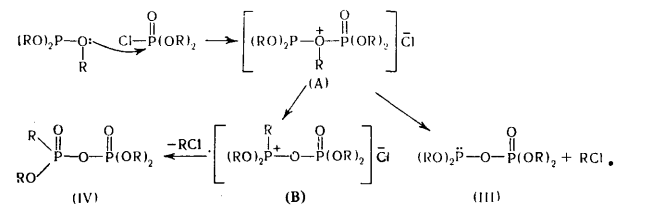


In such donor–acceptor interaction the carbonium ion formed can interact also with the halide anion, as a result of which a phosphorus(III) compound of the type $\rangle\ddot{P}-O-SiR_3$ is formed.

The formation of such a compound has been reported[48], confirming the validity of the mechanism discussed above. It may be supposed that a similar mechanism obtains also in the reaction of triethyl phosphite with a phosphorochloridate ester[45,73,74]:



The authors do not discuss the possible pathways in the formation of subphosphoric acid esters (III), while the formation of compound (IV) is accounted for by the isomerisation of (III) under the influence of the alkyl halide formed. However, the specificity of the structure of the product formed suggests that in this case also the participation of the oxygen atom of the alkoxy-group of the phosphite as a nucleophilic species in the primary step of the interaction is most likely:

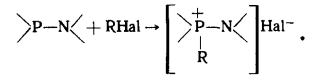


The carbonium ion R^+ is eliminated from the intermediate complex A and interacts with the free electron pair of the trivalent phosphorus atom, which leads to the formation of a quasiphosphonium salt B, or with the chloride ion to form an alkyl halide and compound (III). The decomposition of the salt B yields the product (IV).

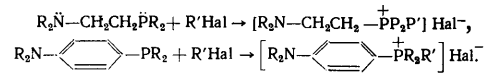
It is noteworthy that the examination of the ambidentate properties of trivalent phosphorus acid esters is made very difficult by the fact that few data characterising their behaviour with different reagents are available; the data on the structure of the products formed are not in most cases sufficient to arrive at a conclusion concerning the participation of the phosphorus or oxygen atom in the initial reaction steps, since the structure of the final products may not depend on the mode of attack.

The opposite behaviour is observed for compounds with the bond $\rangle\ddot{P}-\ddot{N}\langle$ or $\rangle\ddot{P}-\ddot{S}$—for the vast majority of reactions, the structure of the final product permits a fairly reliable conclusion concerning the participation of the free electron pair of a particular atom in the initial reaction steps. This has been shown in greatest detail for the amides and amido-esters of trivalent phosphorus acids.

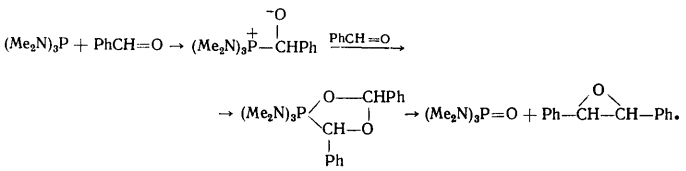
There exists also the view that in trivalent phosphorus acid amides the nucleophilic properties of the nitrogen atoms are reduced and those of the phosphorus atom are enhanced. This is attributed to the occurrence of intense $d-p$ interaction[75]. However, only a few reactions of the amido-esters and amides of phosphorus(III) acids take place with participation of the free electron pair of the phosphorus atom, for example reactions with alkyl halides[76,77]:



It is interesting to note that the formation of phosphonium salts is observed for both β-aminoethylphosphine[78] and for *p*-aminophenylphosphines[79]:

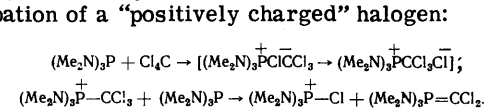


To account for the formation of an epoxide in the interaction of phosphorous triamides with aldehydes, Mark suggested the following reaction mechanism[80]:

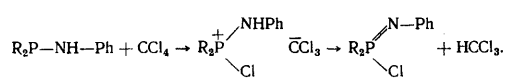


The phosphorus atom behaves as a nucleophilic centre in this reaction. The mechanism is confirmed by measurements of phosphorus-31 chemical shifts and the changes in the PMR spectra of the reaction mixtures.

Hudson and coworkers[81-83] also believe that the phosphorus atom behaves as a nucleophilic centre in the interaction of phosphorous triamides with carbon tetrachloride, which they believe to involve a mechanism with participation of a "positively charged" halogen:

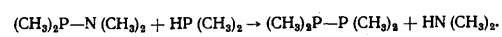


According to their data, in the interaction of *N*-phenyl diphenylphosphinous amide with carbon tetrachloride proton exchange in the ion pair formed leads to the formation of a phosphinimine and chloroform:



The interaction of phosphorus(III) compounds having a P–N bond with hydrogen halides[84-86] differs fundamentally in the reaction products from the analogous reactions of phosphites:

The formation of acid halides with retention of the valence of phosphorus shows that the nitrogen atom behaves as a nucleophilic centre. The interaction of aminophosphines with secondary phosphines takes place similarly[87]:



The appreciably greater basicity of the nitrogen atom compared with phosphorus is indicated by the interaction of dialkyl-(α-aminomethyl)phosphine with secondary phosphines[88]:

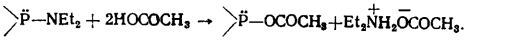


These data and also the fact that the valence of phosphorus remains unchanged suggest that the phenolysis, alcoholysis, and amidolysis reactions of phosphorus(III) acid amides take place with participation of the free electron pair of the nitrogen atom[89-93].

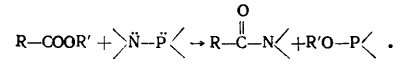
The study of the reactions of alcohols with phosphorous tri(dialkyl amides) showed that the dialkylamine hydrochloride present as an impurity in the triamide has a considerable influence on the rate of the process[94]. The influence of impurities on the rate and also on the mode of reaction has been demonstrated for the interaction of phosphorous triamides with phenolic Mannich bases[95-97].

It is noteworthy that virtually all the reactions investigated with amido-esters and amides of trivalent phosphorus acids were carried out in the presence of appreciable amounts of amine hydrochlorides as impurities. Such acid impurities may lead to the formation either of an activated complex or a phosphonium salt, which probably accelerates the transesterification. This hinders the interpretation of the interaction between trivalent phosphorus acid amides and compounds with a mobile hydrogen atom as a reaction involving the initial protonation of the nitrogen atom.

The complexity of this problem is not restricted to the effects of impurities. In the reactions of trivalent phosphorus acetamides with compounds having a mobile hydrogen atom an activated complex may be formed initially and then react with a second reactant molecule having a mobile hydrogen atom. It is quite likely that the interaction of the amides with hydrogen halides and acetic acid takes place in this way[43,48,49]:

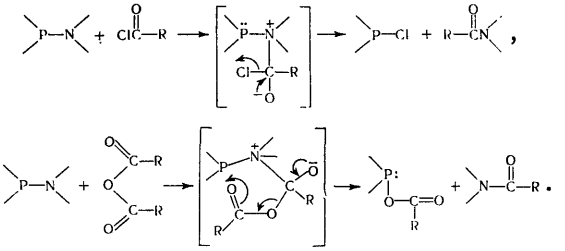


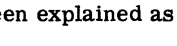
An interesting example of catalysis by compounds with a "hydrogen atom" is the interaction of trivalent phosphorous acid amides with carboxylic acid esters[89]:

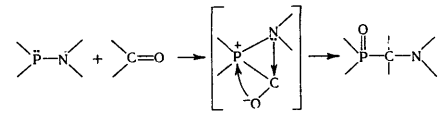


These reactions hardly occur with benzoate and acetate esters. However, phenylacetamide and malonamide are formed in high yields.

The examples of reactions of trivalent phosphorus acetamides with compounds containing a carbonyl group quoted below show that here too the nitrogen atom is the nucleophilic centre: these are reactions with carboxylic acid halides[100-102] and anhydrides[103-106]:

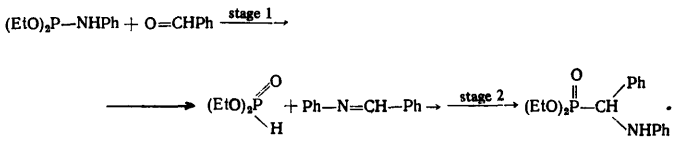


The main products of the reactions of trivalent phosphorus acid amides with aldehydes and ketones are derivatives with the group , [107-110] the formation of which has been explained as follows:

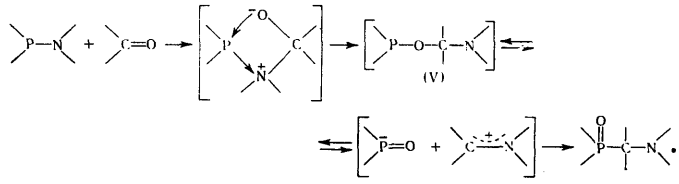


However, Hudson showed[111] that in the reaction between diethyl *N*-phenylphosphoramidite and benzaldehyde,

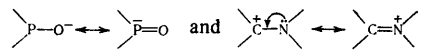
diethylphosphorous acid and the corresponding Schiff base may be isolated as the main products in the initial period:



This was confirmed by following the reaction by infrared spectroscopy and kinetic measurements. As a result, Hudson proposed the following mechanism for the interaction of trivalent phosphorus acid amides with aldehydes:

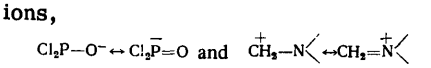


Hudson explains the possibility of the rearrangement of the intermediate compound (V) by the high stability of the ion formed on its decomposition:

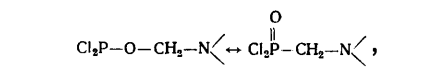


This hypothesis does not contradict the literature data on the dependence of the stability of phosphites on their structure. Thus attempts to obtain phosphites by the interaction of trivalent phosphorus acid chlorides with hydroxymethyl derivatives of various kinds[112-115] always resulted in the formation of the corresponding phosphonates and not esters of phosphorus(III) acids.

Even earlier than Hudson, the idea of resonance-stabilised ions,

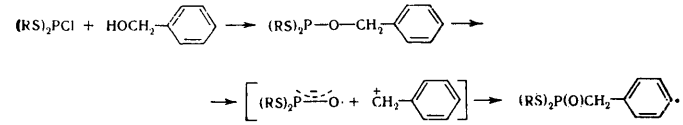


was employed by Rumpf[116] to explain the rearrangement

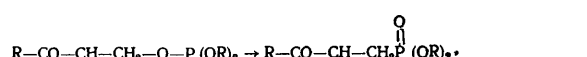


which takes place readily in the interaction between trivalent phosphorus and hydroxymethylamides.

Similar reactions were observed by A. E. Arbuzov and Nikonorov[117] between dialkyl phosphorochloridodithi-ite and benzyl alcohol:

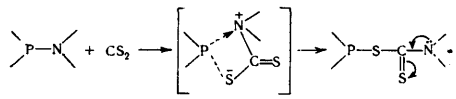


The capacity of phosphites for thermal rearrangement to phosphonates was demonstrated by Rizpolozhenskii and Mukhametov in the reaction with a γ-oxoalkoxy-radical[118]:

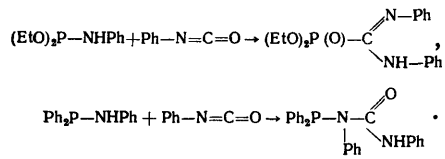


B. A. Arbuzov and coworkers[119] believe that the rearrangement of the phosphite $R-CONHCH_2OP(OR)_2$ to the phosphonate $R-CONHCH_2-P(O)(OR)_2$ can occur also in the interaction of hydroxymethylamides with triethyl phosphite.

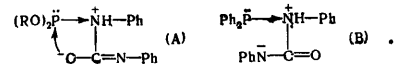
The study of the reactions of phosphoramidites and aminophosphines with carbon disulphide, carbon dioxide, and isocyanates confirms the validity of Hudson's reaction mechanism. Thus in the reaction of carbon disulphide[120] or carbon dioxide[121] with trivalent phosphorus acid amides the process stops at the stage involving the formation of a new phosphorus(III) derivative, the stability of which can probably be explained by the conjugation in the thioamide group:



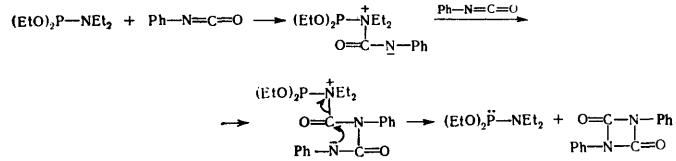
Interesting features of the rearrangement in the intermediate complex were observed in the study of the reaction of diethyl *N*-phenyl phosphoramidite and diphenylphosphinous anilide with isocyanates[122,123]:



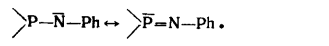
The authors explained the difference by the fact that in the intermediate complex A the alkoxy-groups make the phosphorus atom selective with respect to oxygen as a nucleophilic centre, while phenyl groups favour the interaction with the less powerful nucleophilic centre—the nitrogen atom (intermediate complex B):



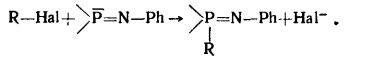
Finally, in contrast to dialkyl *N*-phenylphosphoramidite, dialkyl *NN*-diethylphosphoramidite causes only the dimerisation of the isocyanate:



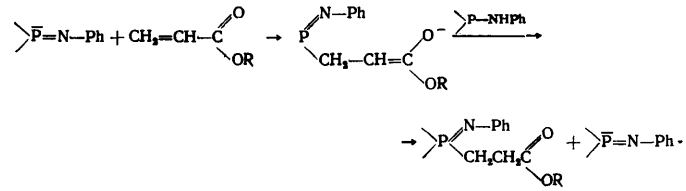
Kabachnik and Gilyarov suggested that, like dialkylphosphorous acids, *N*-phenylphosphoramidites can exist in two tautomeric forms[124] and found that the anion formed after the elimination of a proton from the aniline-nitrogen constitutes an ambidentate system like the anion of dialkylphosphorous acid:



In reactions with alkyl halides the phosphorus atom is the nucleophilic centre in this anion:



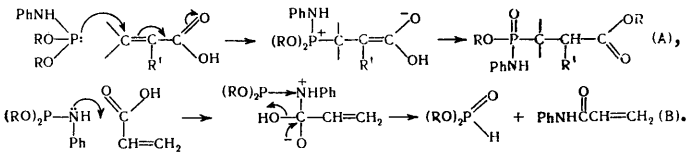
In the reaction of *N*-phenylphosphoramidites with $\alpha\beta$-conjugated systems in the presence of basic catalysts[125], the electrophilic centre is also attacked by the phosphorus atom:



N-phenylphosphoramidites react with Schiff bases similarly[126,127]:

$$(C_2H_5O)_2P{-}NHPh + PhCH{=}NPh \rightarrow (C_2H_5O)_2P{-}\underset{\displaystyle NPh}{\underset{|}{C}}HPh{-}NHPh\,.$$

N-Phenylphosphoramidite reacts somewhat differently[128] with $\alpha\beta$-unsaturated carboxylic acids. In this case the ambidentate properties of both reactants are revealed: either the free electron pair of the phosphorus atom reacts with the electrophilic terminal carbon atom of the conjugated C=C double bond (pathway A) or the free electron pair of the nitrogen atom attacks the carbonyl carbon atom of the unsaturated acid (pathway B):



The second pathway begins to predominate when the steric hindrance at the terminal C=C bond increases. Thus the interaction of *N*-phenylphosphoramidite with cinnamic acid leads to the formation of diethyl phosphite and cinnamic acid anilide only.

Compounds with the bond $\rangle\ddot{P}{-}SR$ have been investigated in less detail than other types of phosphorus(III) compounds and their chemical behaviour is not known as completely as that of compounds with the $\rangle\ddot{P}{-}\ddot{N}\langle$ bond. It has been established that the thioesters of trivalent phosphorus acids are oxidised by hydrogen peroxide and peracids with formation of compounds having the $\rangle P{=}O$ group and combine with sulphur to form compounds containing the $\rangle P{=}S$ group[129,130]. Interaction of the thioesters with alkyl halides leads to products other than those obtained in the reactions of alkyl halides with esters, ester-amides, and amides of acids with phosphorus(III). The esters of dialkyl-, alkyl-, and diaryl-phosphinothious acids react with alkyl halides only via the free electron pair at the phosphorus atom[131,132]:

$$\begin{matrix} R' \\ R'' \end{matrix}\!\!\rangle P{-}SR + R'''{-}Hal \rightarrow \left[\begin{matrix} R' \\ R'' \end{matrix}\!\!\rangle \overset{+}{P}{-}\begin{matrix} R''' \\ SR \end{matrix}\right] \bar{H}al \rightarrow \begin{matrix} R' \\ R'' \end{matrix}\!\!\rangle \underset{\displaystyle S}{\underset{\|}{P}}{-}R''' + R{-}Hal\,.$$

The interaction of esters of alkyl- and phenyl- phosphonodithious acids with alkyl halides also leads to the alkylation of the phosphorus atom[133,134]. The instability and the capacity for intermolecular rearrangement to phosphonothioates characteristic of the esters of phenylphosphonodithious acid should be noted[131]. Mixed *O*, *S*-esters of phosphorous acid interact in two ways: both the phosphorus and the sulphur atoms behave as nucleophilic centres[135-137]:

$$(RO)_2P{-}SR' + R''{-}Hal \begin{cases} \rightarrow \left[(RO)_2\overset{+}{P}\begin{matrix} R'' \\ SR' \end{matrix}\right] \bar{H}al \rightarrow RO{-}\underset{\displaystyle O}{\underset{\|}{P}}\begin{matrix} R'' \\ SR' \end{matrix} + R{-}Hal \\ \rightarrow \left[(RO)_2P{-}\underset{\displaystyle R''}{\overset{+}{S}}{-}R'\right] \bar{H}al \rightarrow (RO)_2P{-}Hal + R'{-}S{-}R'' \end{cases}$$

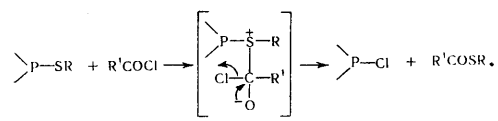
Phosphorotrithioites react with alkyl halides only via the sulphur atom[41]:

$$(RS)_3P + 3P'{-}Hal \rightarrow \left[(RS)_2P{-}\underset{\displaystyle R}{\overset{+}{S}}R\right] \bar{H}al \rightarrow (RS)_2P{-}Hal + RSR'.$$

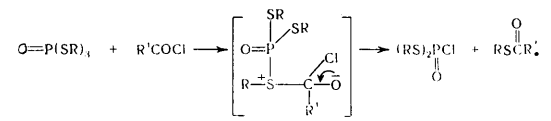
Triphenyl phosphorotrithioites reacts similarly with alkyl halides[138]. However, it is striking that, in contrast to triphenyl phosphite, its intermediate product cannot be isolated:

$$(PhS)_3P + 3CH_3I \rightarrow 3\,PhSCH_3 + PI_3\,.$$

The nucleophilic interaction of phosphorus(III) thioesters with an unsaturated electrophilic carbon centre has been investigated only in reactions with acid halides. It was shown[137,139,140] that in phosphorotrithioites and in alkyl-(aryl)-phosphonothioites and -phosphonodithioites the nucleophilic centre is the sulphur atom:



It is remarkable that even in the molecule of phosphorotrithiolic acid the sulphur atoms can participate in reactions with carboxylic acid halides:



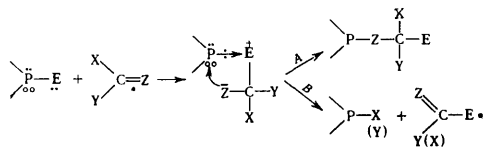
One of the most interesting problems which follow from the examination of the above experimental data is the discovery of the factors which control the selectivity in ambidentate phosphorus–element systems. Although the available experimental data do not provide an exhaustive solution of the problem in many of its aspects, certain relations are revealed quite clearly.

In the first place a fairly sharp difference in selectivity when the P–E system reacts with an electrophilic centre at a saturated and an unsaturated carbon atom is striking. While in the first case the phosphorus atom behaves as the nucleophilic centre of the system, in the second case attack by the free electron pair of the second element (particularly nitrogen and sulphur) is most typical.

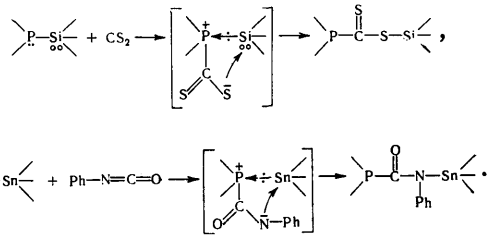
If the phosphorus atom is the nucleophilic centre, a quasi-phosphonium complex is formed and the final product is always a derivative of tetracoordinate phosphorus, which depends on the nature of the substituent. On the other hand, when the nucleophilic centre is not the phosphorus atom but another element (O, S, N) directly linked to it, the structure of the final product as a rule indicates a number of rearrangements of the reaction complex formed initially. The specificity of the properties of the phosphorus atom—the presence of both a free electron pair and vacant *d* orbitals—is responsible for the possibility of rearrangements of this kind.

Indeed, when E behaves as the nucleophilic centre in the reaction of the system P–E (E = O, N, or S) with an unsaturated electrophilic carbon atom, an intermediate reaction complex is formed. The reduction of electron density at the atom (the formation of a positive charge) is compensated both by a shift of the binding electron pair of the P ÷ E bond and a change in the type of $d-p$ interaction (it disappears). An increase in electron density at the Z atom may be compensated by interaction with the vacant *d* orbitals of the phosphorus atom, which becomes possible only after the reduction of electron density of the

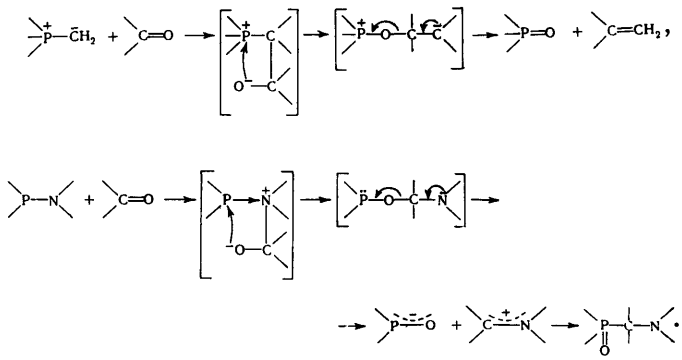
latter due to the shift of the binding electron pair of the P–E bond in the initial nucleophilic attack by E:



Further reaction of the intermediate reaction complex is determined mainly by the nature of the substituents X and Y. If they are electron-donating, then pathway A will predominate via the stabilisation of the intermediate complex. Electron-accepting substituents X and Y (X = Cl or Br) most often lead to the stabilisation of the intermediate complex via pathway B. This explanation is confirmed both by the experimental data described above and the results obtained in the study of the interaction of compounds of the type $R_3Si-PPh_2$ and $R_3Sn-PPh_2$ with carbon disulphide, isocyanates, and many other electrophilic agents[141-144]. Tin and silicon have only vacant *d* orbitals. Therefore in their compounds with trivalent phosphorus the latter is the only nucleophilic centre and their interaction with an unsaturated electrophilic centre leads to a situation opposite to that described above:



It is striking that the mechanism discussed is essentially analogous to the mechanism proposed to account for the Wittig reaction[145]:



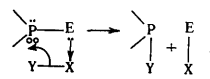
Examination of a wide range of examples of the ambidentate behaviour of derivatives of acids with phosphorus(III) shows that the nucleophilic properties of E in the system P–E diminish in the sequence S > N > O. There is no doubt that this problem is directly linked to the nature of the *d–p* interaction in the P–E system. The changes in nucleophilic properties in the series O, N, and S should be reflected appreciably also in the type of interaction between phosphorus(III) derivatives and heteroconjugated systems. The first studies on these lines, by Pudovik and coworkers[146], led to the discovery of the characteristic features of the behaviour of these systems.

Apparently the concept of the ambidentate properties of phosphorus(III) compounds can significantly facilitate the theoretical analysis of the possible reaction mechanisms in the reaction system and can give a fairly correct indication of the structure of the final reaction products. Therefore it is both urgent and necessary that attention be drawn to the assessment of the ambidentate property as a real property of phosphorus(III) derivatives.

IV. SUBSTITUTION REACTIONS AND CHARACTERISTICS OF SYSTEMS WITH A PHOSPHORUS–HALOGEN BOND IN A SERIES OF PHOSPHORUS(III) DERIVATIVES

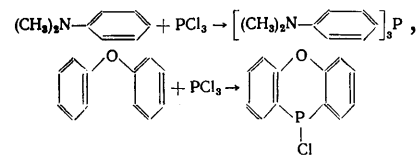
Substitution reactions are most common for phosphorus(III) compounds. They are characteristic of both primary and secondary phosphines as well as the amides, esters, and halides of acids containing phosphorus(III). They frequently take place at very high rates.

Substitution reactions in phosphorus(III) compounds in which the electron density at the phosphorus atom is enhanced and it behaves as a typical nucleophilic centre were analysed in detail in the previous section. A reduced electron density at the phosphorus atom, as a necessary condition for the interaction between a nucleophilic agent and a *d* orbital of phosphorus, arises via the primary attack by the free electron pair of E on the electrophilic centre of the second reactant:



A second type of substitution reaction involves the usual nucleophilic substitution at the phosphorus atom as an electrophilic centre. The introduction of a chlorine (bromine or iodine) atom into any derivative of phosphorus(III) is known to reduce sharply its nucleophilic properties. For example, even powerful nucleophilic agents such as Alk_3P and $(\rangle N)_3P$ can react with only the most reactive compounds after the replacement of the alkyl or amino-group by chlorine[147-150], while $RPCl_2$ and $\rangle NPCl_2$ are incapable of alkylation by alkyl halides. The nucleophilic properties of PCl_3 are not revealed in any reaction and the study of PCl_3 complexes have shown that the phosphorus atom exhibits distinct electron-accepting properties[11-14].

Substitution reactions are most typical for trivalent phosphorus acid chlorides. These reactions take place extremely readily with the majority of the usual nucleophilic agents: alcohols[151], mercaptans[152], phenols[153], and amines[154]. It is noteworthy that the ease of reaction of phosphorus(III) acid chlorides and compounds of the type P–E (where E = N, O, or S) varies in the opposite sense as a function of the nucleophilic properties of the nucleophilic agent. Similar reactions take place with activated benzene derivatives[155,156] (with formation of a P–C bond).



or compounds having a mobile H–C bond, such as acetoacetic ester, the product containing an enol ester bond[157]:

$$(EtO)_2PCl + CH_3C(=O)-CH(H)-COOEt \xrightarrow[-B\cdot HCl]{+:B} (EtO)_2P-O-C(CH_3)=CH-COOEt.$$

Many substitution reactions, which are of the exchange type in a wider sense than the usual nucleophilic substitution, are known at present. Frequently these reactions constitute the first step in multistage processes leading to the formation of phosphorus(V) derivatives. In many cases these stages can be separated. Thus, while formals do not react with phosphorus(III) derivatives without a catalyst, in its presence the reaction takes place readily[158]:

$$\rangle P-Cl + H_2C(OR)_2 \xrightarrow{ZnCl_2} \rangle P-OR + ClCH_2OR \rightarrow \rangle P(=O)-CH_2OR + RCl.$$

The replacement in the formal of even one alkoxy-group by an amino-group leads to a sharp increase of the rate of reaction:

$$\rangle P-Cl + \rangle N-CH_2OR \rightarrow \rangle P-OR + Cl^-[CH_2=\overset{+}{N}\langle] \rightarrow \rangle P(=O)-CH_2N\langle + R-Cl.$$

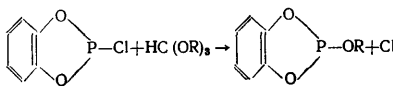
The reactions with di(dialkylamino)methane take place even more readily[159]:

$$RO-PCl + (\rangle N)_2CH_2 \rightarrow RO-P-N\langle + Cl^-[CH_2=\overset{+}{N}\langle] \rightarrow \rangle P(=O)-CH_2-N\langle + RCl.$$

In the orthoesters of carboxylic acid the replacement of an alkoxy-group does not require any catalyst, unlike formals[160–163]:

$$R_nPCl_{3-n} + HC(OR')_3 \rightarrow R_nP(OR')_{3-n} + ClCH(OR')_2 \rightarrow R_n(R'O)_{3-n}P(=O)-CH(OR')_2 + R'Cl.$$

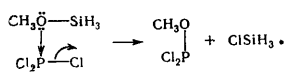
These reactions can be carried out in stages until the substitution of the last halogen at the phosphorus atom. However, in the case of pyrocatecholphosphorous acid chloride [phenylene phosphorochloridite] the reaction ceases after the exchange of one alkoxy-group[162,163]:



It is remarkable that $Si(OR)_4$ does not undergo a similar interaction with PCl_3 under mild conditions. However, the reaction with PBr_3 and PI_3 takes place vigorously with formation of an alkyl halide and resinous products of unknown structure[164]. The reaction between alkoxytrimethylsilane and PCl_3 takes place in stages[165]. While in the system $(H_3Si)_2O + PCl_3$ no interaction is observed, when there is even only one methoxy-group at the silicon atom the reaction takes place according to the mechanism[166]

$$H_3SiOCH_3 + PCl_3 \rightarrow H_3SiCl + CH_3OPCl_2.$$

The author suggests that the initial stage includes the formation of a four-centre transition complex and the decisive factor is the electron-donating capacity of the oxygen in the Si–O bond:



In agreement with this, the exchange reactions of compounds containing an amino-group (which has more pronounced electron-donating properties) and an Si–N bond take place more readily and proceed to higher degrees of substitution[167,168]:

$$R_2N-Si(CH_3)_3 + PCl_3 \xrightarrow[3:1]{1:1} R_2N-PCl_2 \;(R_2N)_2PCl + ClSi(CH_3)_3 \;(R_2N)_3P$$

$PhPCl_2$, Ph_2PCl_2, and $O-PCl_3$ react in exactly the same way. This reaction is typical not only for phosphorus(III) halides but also for halogeno-derivatives of sulphur: S_2Cl_2, $SOCl_2$, RSO_2Cl.[169] Probably many other reactions also involve the same mechanism[170,171]:

$$PCl_3 + PhS-Sn(CH_3)_3 \rightarrow ClSn(CH_3)_3 + (PhS)_3P,$$

$$R_3SnCH_2COOR' + PCl_3 \rightarrow Cl_2PCH_2COOR' \;ClP(CH_2COOR')_2 + R_3SnCl \;P(CH_2COOR')_3$$

However, with analogous α-ketone or aldehyde derivatives the mode of reaction depends on the substituent at the phosphorus atom[172]:

$$R_3SnCH_2COCH_3 + (RO)_nPCl_{3-n} \rightarrow (RO)_nP(O-C(CH_3)=CH_2)_{3-n} + R_3SnCl$$

and at the same time

$$R_3SnCH_2COCH_3 + Alk_2PCl \rightarrow Alk_2P-CH_2C(=O)CH_3 + R_3SnCl.$$

A difference between phosphorochlorodites[173–175] and phosphites[176] is observed also in reactions with α-(halogenomercuri)carbonyl compounds:

$$(RO)_nPCl_{3-n} + ClHgCH_2COR' \rightarrow (RO)_nP(OC(R')=CH_2)_{3-n},$$

where $n = 1 - 2$ and $R' = H$ or CH_3, and

$$(EtO)_3P + ClHgCH_2CH=O \rightarrow (EtO)_2POCH=CH_2 + EtCl.$$

There is also a wide variety of reactions of halogeno-derivatives of phosphorus(III) with other derivatives of trivalent and quinquevalent phosphorus. These are primarily disproportionation reactions in the series of phosphorus(III) derivatives, a typical feature of which is the formation of equilibrium systems[177–180]:

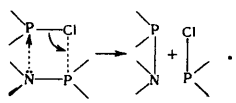
$$PhPCl_2 \rightarrow Ph_2PCl + RCl_3,$$

$$PCl_3 + P(OEt)_3 \rightleftarrows ClP(OEt)_2 + Cl_2POEt,$$

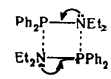
$$PCl_3 + P(OPh)_3 \rightleftarrows ClP(OPh)_2 + Cl_2POPh,$$

$$PCl_3 + P(NR_2)_3 \rightleftarrows ClP(NR_2)_2 + Cl_2PNR_2,$$

and many others[181–183]. The rate of reaction increases in the sequence $Ph < PhO < AlkO > R_2N$. All these findings suggest that the exchange reactions involve a cyclic mechanism:



Moreover, the capacity of phosphorus(III) derivatives for such cyclic interactions may be the cause of the formation of relatively stable association complexes. Recently Evdakov and coworkers[184] showed that the rate of oxidation of dialkylaminodiphenylphosphine without solvent or in polar solvents is relatively low, but increases sharply in non-polar solvents. They explain the relatively low capacity of this compound for oxidation in a free state by the formation of association complexes:



In a non-polar solvent this substance is present in the form of "free" molecules more available for chemical interaction with other reactants.

While the exchange reactions in the series of acid halides derived from phosphorous acid do not lead to a change in the valence of phosphorus, the reactions of halogenophosphines have a mechanism involving the Arbuzov rearrangement[185]:

$$Ph_2PCl + (RO)_nPPh_{3-n} \rightarrow Ph_2P{-}\overset{\overset{O}{\|}}{P}(OR)_{n-1}(Ph)_{3-n} + RCl$$

or

$$PhPCl_2 + P(OR)_3 \rightarrow PhP(\overset{\overset{O}{\|}}{O})(OR)_2 \xrightarrow{P(OR)_3} (RO)_2P(\overset{\overset{O}{\|}}{O})P(\overset{\overset{O}{\|}}{O})(OR)_2 .$$

While the reaction between a secondary phosphine and a halogeno-derivative of trivalent phosphorus takes place according to the equation[186]

$$\rangle P{-}H + Hal{-}P\langle \rightarrow \rangle P{-}P\langle + HHal,$$

in the case of tertiary phosphines the reaction takes place in quite a different way[187]:

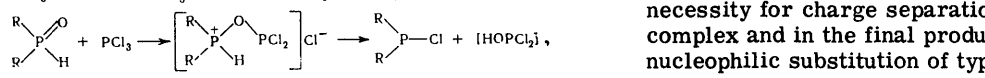
$$(C_4H_9)_3P + PhPCl_2 \rightarrow (C_4H_9)_3PCl_2 + (PhP)_4 ,$$
$$(C_4H_9)_3P + Ph_2PCl \rightarrow (C_4H_9)_3PCl_2 + Ph_2P{-}PPh_2 .$$

Substitution reactions can take place with phosphorus(V) derivatives as nucleophilic agents and the nature of the nucleophilic centre may be various[188–192]:

$$(RO)_2\dot{P}{=}\bar{O} + ClP(OR)_2 \longrightarrow (RO)_2P{-}O{-}P(OR)_2 + \bar{C}l ,$$

$$(RO)_2P(\overset{\overset{O}{\|}}{O})^- + ClP(OR)_2 \longrightarrow (RO)_2P(O){-}O{-}P(OR)_2 + \bar{C}l ,$$

$$[Ph_3P{=}CHR \longleftrightarrow Ph_3\overset{+}{P}{-}\bar{C}HR] + ClPPh_2 \longrightarrow [Ph_3\overset{+}{P}{-}CHR{-}\ddot{P}Ph_2]\bar{C}l ,$$



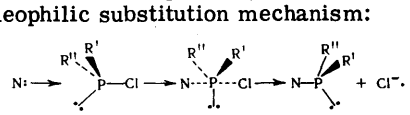


The fact that in the last two reactions[191,192] the decisive factor is the nucleophilic properties of the oxygen atom in the P = O group and not a tautomeric equilibrium between the quinquevalent and trivalent forms of phosphorus is confirmed by the finding that[193]

$$SiHal_4 + nO{=}PPh_3 \rightarrow Hal_{4-n}Si\{[-O{-}\overset{+}{P}Ph_3]\bar{C}l\}_n \quad (n = 2, 4).$$

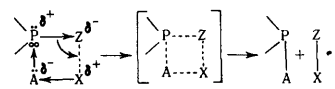
This structure of the adducts was based on infrared spectroscopic and conductimetric data.

The examples of substitution or exchange reactions with participation of a phosphorus–halogen bond quoted above fall far short of exhausting the available literature data. Nevertheless they are extremely typical and are adequate for the discussion of certain problems of the mechanism of those reactions. With the usual nucleophilic agents, substitution reactions at an electrophilic phosphorus atom can take place via a classical S_N2 bimolecular nucleophilic substitution mechanism:



However, so far there are no quantitative data in the literature concerning the true mechanism of the substitution reaction or the elucidation of the role and contribution of the phosphorus *d* orbitals in this mechanism. Nevertheless, the numerous examples quoted, mainly of exchange reactions, can be very readily explained qualitatively if one takes into account the significant contribution of the *d* orbitals of the trivalent phosphorus atom as an electrophilic centre in the substitution reactions. The involvement of the *d* orbitals should alter significantly the type of reaction as a whole.

In the nucleophilic attack by the second reactant on the phosphorus atom a free electron pair of the nucleophilic agent is transferred to the *d* orbitals of the phosphorus atom. According to quantum-chemical concepts, such interaction can be favourable only in the presence of a reduced electron density at the phosphorus atom[15]. Therefore, with increasing electronegativity of the substituent or the number of substituents at the phosphorus atom, its positive charge increases also, which facilitates, owing to the energy factor, the participation of the phosphorus *d* orbitals in the nucleophilic substitution reaction. The involvement of the *d* orbitals of the phosphorus atom makes possible electron transfer via a four-centre cyclic mechanism:



In those cases where the group Z can be readily eliminated in the form of an anion and the process is facilitated by its additional interaction with the electrophilic centre of the second reactant (X = H, $-Si\langle$, etc.), a process of this kind takes place without a change in the valence of the phosphorus atom, i.e. a substitution reaction occurs. Therefore the group Z need not necessarily be eliminated in the form of an anion, since the possibility of a synchronous cyclic electron transfer eliminates the necessity for charge separation both in the transition complex and in the final product, in contrast to classical nucleophilic substitution of type S_N1 or S_N2.

Thus the primary interaction between the electrons of the nucleophilic agent and *d* orbitals of the phosphorus atom leads in the first instants essentially to an increase of coordination and of the valence of the phosphorus atom, but cyclic electron transfer can reduce them both in the final reaction product. Such stabilisation is not the only one possible. One of the other pathways may be a further increase of the valence with retention or increase of the degree of coordination of the phosphorus atom in the final reaction products—these are examples of the reactions mentioned above in which the phosphorus atom exhibits biphilic properties.

The examples of substitution reactions quoted above for the series of phosphorus(III) derivatives reveal a considerable role of the phosphorus *d* orbitals in chemical reactions. Even a purely qualitative hypothesis of this kind can serve as a firm basis for the understanding of the behaviour of phosphorus as a biphilic reagent in an even greater range of chemical reactions.

To estimate the role and contribution of the *d* orbitals of phosphorus in any of its reactions, it is necessary to know at least its relative electron density. On the other hand, a knowledge of this quantity is necessary for the estimation of the nucleophilic properties of the free electron pair of the phosphorus atom. Depending on the nature of the substituent, the charge at the phosphorus atom may change due to the inductive effect of the added group and its capacity for conjugation with the phosphorus *d* orbitals. It is interesting that the π-electron systems of substituents are incapable of $p-\pi$ conjugation with the unshared electron pair of phosphorus, which is explained

by the enhanced *s*-character of the pair[194]. The determination of the contribution of conjugation with the *d* orbitals to the overall electron density at the phosphorus atom as well as the determination of the latter are undoubtedly some of the most difficult and urgent problems in the chemistry of phosphorus(III) derivatives.

The attempts by Van Wazer and coworkers[195,196] to determine the conjugation effect for phosphorus(III) derivatives by comparing the calculated ^{31}P chemical shifts with the experimental values cannot be regarded as satisfactory because their conclusions concerning the electron density at the phosphorus atom are difficult to reconcile with the chemical properties of the corresponding derivatives. Moreover, the theoretical principles of the calculation of the ^{31}P chemical shifts have been seriously criticised[197]. Thus it might have been expected that dialkylchlorophosphine should be more nucleophilic than trialkyl phosphites. However, the former is much less reactive in classical substitution reactions with alkyl halides[147-149]. On the other hand, the phosphine is incomparably more reactive than phosphites in substitution reactions where the phosphorus atom exhibits its biphilic properties.

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Explanations without internal contradictions are at present possible for only a few reactions of trivalent phosphorus. We have attempted to assess on the basis of the chemical properties of phosphorus(III) derivatives the role of the free electron pair and the *d* orbitals of the phosphorus atom and the effect of substituents and their nature in various reactions. In view of the complexity and the controversial nature of the problems discussed, the specific views expressed cannot be regarded as definitive. The principal aim of the present review was to reveal the many-sided nature of the reaction mechanisms of trivalent phosphorus and to draw attention to the most important problems.

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