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The Structure and Reactivity of Phosphorus Pentachloride

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Data are presented on the reactions of phosphorus pentachloride with compounds containing oxa- and oxy-groups (ethers, acetals, oxetans, tetrahydrofuran, 1,3-dioxans, dioxolans, dihydropyrans, and alcohols). The structure of phosphorus pentachloride in various solvents and its influence on the course of reactions are considered. The mechanisms proposed for the reactions under discussion are analysed.
The bibliography includes 119 references.

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I. INTRODUCTION

Interest in methods of synthesis of organophosphorus compounds containing a phosphorus–carbon bond is due to the practical importance of phosphonates and phosphinates and the development of theoretical ideas concerning the cause of the redistribution of old and the formation of new bonds.

The possibilities of phosphorylation with phosphorus pentachloride have been greatly expanded in recent years in connection with the use in this reaction of many ethers and a wide variety of oxa-compounds. A common feature of the latter reactions is that they proceed via a stage involving the formation of an α-halogeno-ether, which is capable of undergoing further dehydrochlorination. Definite advances have been achieved in the interpretation of the mechanisms of the interaction of phosphorus pentachloride with nucleophiles.

The history of the development of studies on the reactions of phosphorus pentachloride is described in Kabachnik's review[1] and has been supplemented by Pudovik and Khairullin[2].

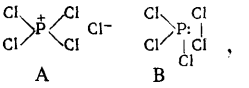
Thus the character of this review differs somewhat from that of the above publications and, apart from the description of syntheses, includes data on the structure of phosphorus pentachloride and the proposed mechanisms.

II. THE STRUCTURE OF PHOSPHORUS PENTACHLORIDE

In many cases the phosphorus atom is capable of expanding its valence shell, probably by employing vacant 3*d* orbitals. It is believed that the problem of the degree of involvement of *d* orbitals in σ and π bonds should be solved separately for each specific instance[3]. The hybridisation of *s* and *p* orbitals with *d* orbitals leads to several geometrical shapes which are determined by different angular functions of the *d* orbitals[4]. One of the possible forms is a bipyramidal dsp^3-hybrid structure[5].

Studies on phosphorus pentachloride in the vapour state by electron diffraction[6,7] indicate a trigonal bipyramid. Phosphorus pentachloride molecules in the liquid phase have a similar structure, which has been confirmed by conductimetric and Raman spectroscopic studies[8]. The spectra proved to be characteristic of molecules with a trigonal bipyramidal structure[9-11]. The bipyramidal sp^3d-hybrid structure is believed to be energetically the most favourable[5] for derivatives of five-coordinated phosphorus and has been confirmed by the existence of many covalent compounds in which the phosphorus atom is linked to five ligands: PF_5, PF_3Cl_2, PCl_5, $P(OC_6H_5)_5$, and $P(C_6H_5)_5$.[12-15]

However, the involvement of *d* orbitals in the formation of bonds is not indisputable and the problem still remains controversial. The ionisation potential of the *s* electron in the free atom is ~19 eV.[5] Calculations have shown that the energy evolved on formation of five P–Cl bonds is less than the excitation energy required for the transfer of 3*s* electrons to the 3*d* level[16]. Pauling[17] suggested that PX_5 molecules are stabilised by means of five resonance structures[17] of type A and six structures of type B:



A B

The Cl–Cl bond in structure B is longer than the usual bond and its formation does not entail an appreciable decrease of molecular energy. According to Pauling's hypothesis, the five atoms in structure A are linked as a result of the hybridisation of the 3*s* and 3*p* orbitals and as a result of the electrostatic attractions between the P^+ ion and the single negative charge distributed between the five electronegative atoms. The energetic feasibility of the structure was demonstrated by Hudson[18] in relation to the formation of phosphorus pentachloride:

$$\ddot{P}Cl_3 \xrightarrow{-e} Cl_3P^+ \xrightarrow[-D_{P-Cl}]{Cl^\cdot} Cl_4\dot{P} \xrightarrow[-E_{Cl}]{e;+Cl^\cdot} \dot{P}Cl_4\bar{Cl} \rightarrow Cl_4\dot{P} \ldots Cl^- ,$$

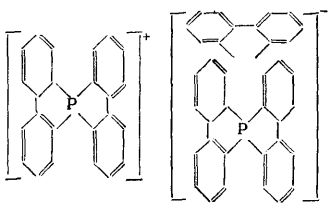
where D_{P-Cl} is the dissociation energy and E_{Cl} the electrostatic interaction energy.

If it is assumed that 3*d* orbitals are involved in the formation of bonds in five-coordinated phosphorus compounds, then the formation of derivatives of six-coordinated phosphorus is also possible. This high valance is manifested in the PF_6^- and PCl_6^- ions corresponding to sp^3d^2 hybridisation[19,20]. Comparison of non-empirical calculations led Bochvar et al.[21] to the conclusion that the invocation of *d* orbitals in order to account for the electrophilic properties of phosphorus and the structure of its compound is not necessary. The authors believe that the bonds with axial ligands can be formed with participation of the p_z orbital of phosphorus and the atomic orbitals of the ligands, so that the hypothesis of the expansion of the valence shell of the phosphorus atom and of the existence

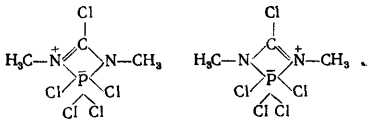
of its sp^3d and sp^3d^2 valence states is not essential to account for the structure of phosphorus pentachloride and the PX_6^- anion. However, the conclusions in the above study[21] are not categorical; for this reason, we think it permissible to assume the involvement of d orbitals in bond formation.

The salt-like structure of phosphorus pentachloride has been confirmed by X-ray diffraction and by the determination of transport numbers in phosphorus pentachloride solutions in nitrobenzene[22,23]. According to ^{31}P NMR data, phosphorus pentachloride exists in the vapour state in a pentacovalent form (the chemical shift is +80 p.p.m.)[24]; in conformity with the ionisation hypothesis, two signals occur in a polar solvent: −91 p.p.m., which has been attributed to the $\overset{+}{P}Cl_4$ cation, and +281 p.p.m., attributed to the $\overset{-}{P}Cl_6$ anion. The phosphorus atom in the cation exists in the sp^3-hybrid state and the cation has a tetrahedral geometrical structure; the anion is a tetragonal bipyramid, which corresponds to sp^3d^2-hybridisation. The existence of tetrachlorophosphonium cations has been observed not only in the crystal lattice of phosphorus pentachloride but also in salt-like complexes, which have been examined by Horing and Baum[25] and studied in connection with ion transport in a nitrobenzene solution in the presence of aluminium trichloride and iron(III) chloride.[26,27] X-Ray diffraction analysis of crystalline compounds having the general composition $PCl_5.NbCl_5$ and $PCl_5.TaCl_5$, which showed that these compounds have heteropolar structures and consist of the $\overset{+}{P}Cl_4$ cation and the $NbCl_6$ and $TaCl_6$ anions respectively, led to the conclusion that the phosphorus is present in an ionic state[28].

The existence of phosphorus as a cation and an anion has been confirmed by an interesting reaction of phosphorus pentachloride with 2,2-dilithiobiphenyl and by a study of the resulting crystalline 'onium complex; the complex includes two phosphorus atoms with chemical shifts of −26.5 p.p.m. and +186.5 p.p.m.,[29] which corresponds to the structure:



X-Ray diffraction and ^1H and ^{31}P NMR spectra showed that the structure of the crystalline product [obtained by reaction of N,N'-dimethylchloroformamidine hydrochloride with PCl_5, $C_3H_6Cl_5N_2P$ (Ed. of translation)] with phosphorus in the six-coordinated state[30] may be represented by the formula



Thus, depending on the conditions, the phosphorus atom in PCl_5 may exist in both pentacovalent and ionic states. The nature of the structure is determined by external factors: the phase state, the type of solvent, and temperature. Thus it is believed that PCl_5 dissolved in carbon tetrachloride exists in a dimeric form while in methylene chloride it is monomeric[30-32]. It has been found[33] that PCl_5 in carbon tetrachloride is monomeric, the distortion being caused by the formation of associated species with the solvent. Analogous studies have been made for phosphorus halides R_nPX_{5-n} by NMR in solvents of different polarity and it has been concluded that these compounds have a pentacovalent structure in non-polar solvents[34]. The tendency to retain the pentacovalent structure falls in the sequence of substituents F > Cl > Br > I. Finally mention should be made also of the proposed structure (of the molecular complex type) of $PCl_3.Cl_2$, which is quite capable of existing under certain conditions: it has been detected for halides at a reduced temperature, but it is as a rule unstable on heating to room temperature[35-37].

Definite information about the structure of phosphorus halides is provided by nuclear quadrupole resonance (NQR). The ^{35}Cl NQR spectra of crystalline phosphorus pentachloride contain two groups of signals, which are similar within each group[37]. The NQR spectral frequencies quoted in the Table for phosphorus halides indicate the chemical non-equivalence of the chlorine atoms linked to phosphorus, which may be attributed to the non-equivalence of the axial and equatorial positions in the bipyramid[38]. The most bulky substituents occupy the equatorial positions, but this is probably not a general rule: thus the trichloromethyl groups is in the axial position. It is noteworthy that the structure of phosphorus pentabromide has not aroused controversy and is treated as ionic: $P\overset{+}{B}r_4\overset{-}{B}r$.[40] Phosphorus pentafluoride is treated as a pentacovalent compound[41].

The NQR spectra of phosphorus halides.

Compound	Transition frequency, MHz			Refs.
	$_{eq}P-Cl$	$_{ax}P-Cl$	C—Cl	
PCl_5	33,753; 33,753; 33,753	29,278; 29,245	—	38
$C_6H_5PCl_4$	33,446; 33,582	25,610; 25,512	—	38
CCl_3PCl_4	31,952; 29,458	28,250	39,689; 39,609; 39,749	39

III. PHOSPHORYLATION BY PHOSPHORUS PENTACHLORIDE OF COMPOUNDS WITHOUT MULTIPLE BONDS

1. Phosphorylation of Ethers

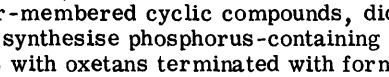
Reactions of these types have been discovered and investigated recently and are not included in the reviews quoted above. A series of studies on phosphorylation by phosphorus pentachloride was stimulated by the investigation of Petrov et al.[42], who demonstrated the possibility of the phosphorylation of ethers, and suggested that the reaction proceeds via a stage involving the formation of an α-halogeno-ether, which gives rise to a multiple bond on dehydrochlorination:

$$ROCH_2CH_3 + PCl_5 \xrightarrow{-HCl} [ROCHClCH_3 \xrightarrow{-HCl} ROCH{=}CH_2] + 2PCl_5 \rightarrow$$
$$\rightarrow [ROCHClCH_2PCl_3]^+PCl_6^- \xrightarrow{SO_2} ROCH{=}CHP(O)Cl_2 + POCl_3 + SOCl_2 + HCl.$$

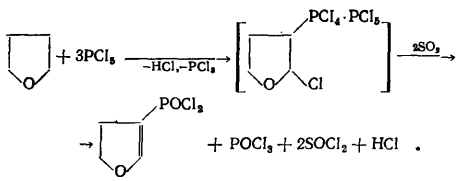
This was confirmed by a study of the reactions of phosphorus pentachloride with α-halogeno-ethers, which led to the isolation of the corresponding phosphonates[42-44].

2. Phosphorylation of Cyclic Oxa- and Dioxa-compounds

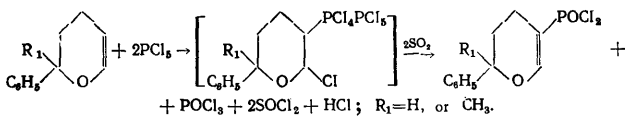
These reactions, which were carried out for the first time with four-membered cyclic compounds, did not make it possible to synthesise phosphorus-containing products. The reactions with oxetans terminated with formation of di-(γ-chloropropyl) ethers:



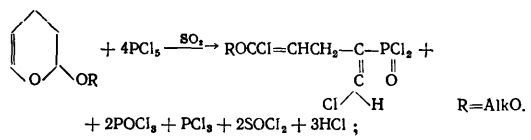
The reactions with tetrahydrofuran led to the synthesis of a phosphorylated product[45]:



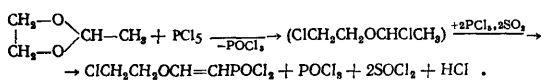
The reactions with dihydropyrans were also of the usual type:



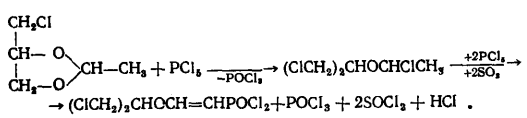
However, with R=AlkO the process occurred in such a way that the oxygen of the pyran ring was involved in the reaction, which was accompanied by consecutive chlorination and dehydrochlorination processes[46]:



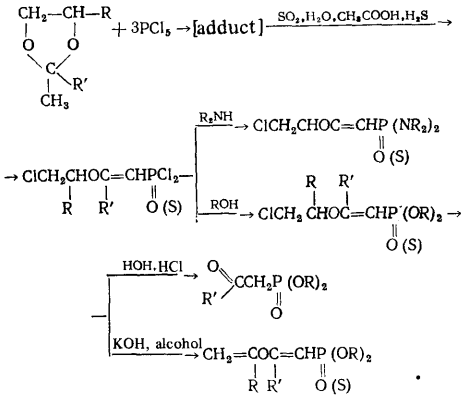
The first reactions with 4-methyl-1,3-dioxolan did not allow the isolation of products with a phosphorus–carbon bond[44]. On the other hand, a wide variety of derivatives of dioxolans and dioxans, containing substituents in the 2-position, led to phosphonates, confirming the general mechanism[47,48]:



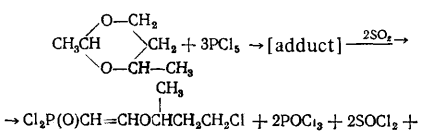
The properties of β-chloroethoxyvinyldichlorophosphonic acid agreed with data for the product synthesised by the reaction of β-chloroethyl vinyl ether with phosphorus pentachloride[49]. The characteristics of this reaction confirm its electrophilic mechanism. Electropositive substituents in the 2- and 4-positions facilitate the process appreciably and increase the yield of the final phosphonate[50]. An electron withdrawing substituent in the 4-position lowers the rate of the process and makes it possible to isolate the intermediate α-halogeno ether[51]:



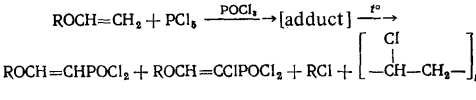
When the product is decomposed by hydrogen sulphide, derivatives of phosphonothioic acids are obtained. Thus the possibilities associated with these reactions can be described schematically as follows:



Derivatives of 1,3-dioxan containing an alkyl substituent in the 2-position react similarly with phosphorus pentachloride[52]:

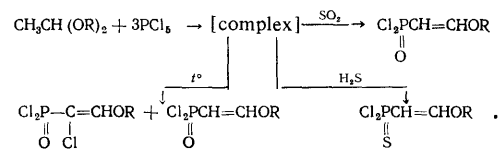


In contrast to adducts with vinyl ethers, complexes with the above dioxolans and dioxans lead to the formation of phosphonates on heating[53]. This is caused by the phosphoryl chloride formed in the initial stages:



3. Phosphorylation of Acetals, Mercaptals, Hemiacetals, and Hemimercaptals

Oxa- and hydroxy-derivatives of hydrocarbons have been phosphorylated by phosphorus pentachloride[55]. The authors demonstrated the error of the earlier views[56] concerning the retention of the acetal group in the reaction and proposed the following mechanism for the phosphorylation of acetals:



They suggest that β-alkoxyvinylphosphonic dichloride and β-alkoxyvinylphosphonothioic dichloride are formed via an α-chloro-ether, as suggested previously[41]. The formation of β-alkoxy-α-chlorovinylphosphonic dichloride was explained by the occurrence of consecutive reactions: chlorination of the multiple bond of β-alkoxyvinylphosphonic dichloride and dehydrochlorination on heating during distillation. It was shown subsequently that ketals and acetals react with phosphorus pentachloride[57]. Bromoacetals do not enter into this reaction, most probably

owing to the difficulty of the dehydrochlorination of the $\alpha\beta$-dihalogeno-ethers. Nor was it possible to isolate a phosphonate in the reaction with ethoxyacetal.

The reaction of acrolein acetals, which have two nucleophilic centres (the multiple bond and the acetal group) is interesting[58]. Studies on the structure of the final product, which is 1-chloro-3-ethoxyprop-2-enylphosphonic dichloride (the dichloride of 1-chloro methyl-2-ethoxy-vinylphosphonic acid) suggested the following reaction mechanism:

$$CH_2{=}CHCH(OEt)_2 \xrightarrow{PCl_5} CH_2{=}CHCHOEt \xrightarrow{\text{isomerisation}} \underset{Cl}{|}$$

$$\rightarrow ClCH_2CH{=}CHOEt \xrightarrow{2PCl_5} \left[\begin{array}{c} Cl \\ | \\ Cl_3PCH{-}CHOEt \\ | \\ CH_2Cl \end{array}\right]^{+} PCl_6^{-} \rightarrow Cl_2P(O){-}C(CH_2Cl){=}CHOEt .$$

The reaction can be carried out with hemiacetals and hemimercaptals without their isolation and involves in essence the treatment with phosphorus pentachloride of mixtures of the alcohol (mercaptan) and aldehyde.[59] The yield of phosphonic dichlorides was, however, very low.

Phosphorus-containing unsaturated peroxides were obtained by the reaction of phosphorus pentachloride with acetals, acetates, and allyl ethers of α-hydroxyalkyl t-butyl peroxides[60]. It is of interest that the peroxy-group is preserved in this reaction:

$$(CH_3)_3COO\diagdown\!\!\diagup CHCH_2R + PCl_5 \rightarrow [\text{complex}] \xrightarrow{SO_2} (CH_3)_3COOCH{=}C(R){-}PCl_2(O) .$$
$$R'O\diagup\!\!\diagdown$$

Many tertiary alcohols and their derivatives (ethers and esters) proved to be capable of being phosphorylated by phosphorus pentachloride under mild conditions[61,62]. The substitution of the hydroxy-group by chlorine proved to be a competing reaction under these conditions. It is suggested that in both cases the process begins with electrophilic attack by phosphorus pentachloride on the nucleophilic oxygen of the hydroxy- or ether group. This results in the formation of an olefin via a carbonium ion and complex (I). The decomposition of complex (I) into phosphoryl chloride and hydrogen chloride tends to increase the content of butyl chloride; a decrease of temperature lowers the rate of decomposition of the complex and promotes *C*-phosphorylation:

$$(CH_3)_3COH \xrightarrow{PCl_5} \underset{CH_3}{\overset{CH_3}{\diagdown\!\!\diagup}}C^{+}{-}CH_3 + [HOPCl_4] + Cl^{-} \quad (I)$$

$$\downarrow -HCl$$

$$Cl_2P(O)CH_2{-}C(CH_3)_2 \xleftarrow[a]{PCl_5,\ SO_2} CH_2{=}C(CH_3)_2 \xrightarrow[b]{HCl} (CH_3)_3CCl .$$

The phosphorylation of methyl phenyl ketone has been observed by Dogadina et al.[63], while Fokin et al.[64] showed that this possibility also exists for aliphatic ketones. It has been noted that 2-chloroalkenylphosphorus chlorides are formed in very small amounts. The reaction leads to the synthesis mainly of chloro-derivatives by the mechanism:

$$RC(O)CH_3 + PCl_5 \rightarrow RCCl_2CH_3 \xrightarrow{-HCl} RCCl{=}CH_2 \xrightarrow[-HCl]{+PCl_5}$$
$$\rightarrow RCCl{=}CHPCl_4 \xrightarrow{-PCl_3} RCCl{=}CHCl .$$

Methyl vinyl ketone reacted via the 1,4-addition mechanism, as in the phosphorylation of dienes[65]:

$$CH_3{-}C(O){-}CH{=}CH_2 + 3PCl_5 \rightarrow [\text{complex}] \xrightarrow{SO_2} Cl_2P(O){-}O{-}C(CH_3){=}CH{-}CH_2Cl .$$

4. Phosphorylation of Esters

The reactions of phosphorus pentachloride with esters have been investigated in detail[66,67]. Analysis of the yields of products as a function of the reaction of the complex led the authors to the quite justified conclusion that the reaction proceeds via the addition of phosphorus pentachloride to the carbonyl group of the ester and that the adduct gradually decomposes to the $\alpha\alpha'$-dichloro-ether (III), which is dehydrochlorinated under the reaction conditions to the unsaturated α-chloro-ether (IV). This product undergoes further phosphorylation, similar to that of di-(α-chloroethyl) ether, by phosphorus pentachloride[68]:

$$RCH_2C(O)OR' + 2PCl_5 \rightarrow \left|\begin{array}{c} Cl \\ | \\ RCH_2C(OR')OPCl_3 \end{array}\right| \overline{P}Cl_6 \rightarrow$$

$$\rightarrow \underset{(III)}{RCH_2CCl_2OR'} \xrightarrow[-HCl]{} \underset{(IV)}{RCH{=}CClOR'} \xrightarrow{PCl_5} \left[\begin{array}{c} Cl_3\overset{+}{P}CHCCl_2OR' \\ | \\ R \end{array}\right] \overline{P}Cl_6 \rightarrow$$

$$\xrightarrow{SO_2} \underset{(II)}{Cl_2P(O){-}C(Cl){=}C(OR){-}R} + \underset{(I)}{Cl_2P(O){-}CHCl{-}C(O)Cl{-}R} .$$

Phosphorylation by phosphorus pentachloride is not restricted to the examples indicated above. It was found that dialkyl sulphides[69] also react with phosphorus pentachloride. The reaction has its characteristic features, because it gives rise to two types of phosphonic dichlorides as a function of temperature:

$$R{-}S{-}CH{=}CHPCl_2(O) \quad \text{or} \quad R{-}S{-}C(Cl){=}CHPCl_2(O) .$$

The formation of β-alkylthio-β-chlorovinylphosphonic dichloride was noted for the first time[70].

The synthetic possibilities of the reactions with phosphorus pentachloride are very extensive and have been confirmed by the latest communications[71,72] concerning the reduction of phosphorus pentachloride–olefin adducts by reaction with silanes containing one or several Si–H bonds. The dichlorophosphines evolved under these conditions serve as the starting materials for the synthesis of a whole series of products.

The results of recent years examined above demonstrate the exceptional reactivity of phosphorus pentachloride and the wide scope of its use for the synthesis of phosphonates, which have found practical applications[73].

IV. THE MECHANISMS OF THE REACTIONS OF PHOSPHORUS PENTACHLORIDE

1. The Chlorination Reactions

Consideration of the chemical properties of phosphorus pentachloride suggests that it is an electrophile. This has been strikingly demonstrated by its reactions with alcohols, water, and organic acids. In relation to tertiary amines, phosphorus pentachloride exhibits the properties of a Lewis acid and yields salt-like adducts[74]. Acid properties are also shown in the reaction of phosphorus pentachloride with various derivatives of four-coordinated phosphorus containing the phosphoryl group and the reaction then involves the latter[75,76]:

$$PCl_5 + R_3P{=}O \rightarrow [Cl_5\overline{P}{-}O{-}\overset{+}{P}R_3] .$$

The five-coordinated derivatives of phosphorus are hard Lewis acids and form stable six-coordinated neutral complexes [77]. It is believed [78] that phosphorus pentachloride forms a negative ion even on reaction with hydrogen chloride:

$$PCl_5 + HCl \rightleftarrows H^+PCl_6^- .$$

The weakening of acid properties in the series of halides leads to a gradual substitution of the halogen by hydrocarbon groups [79,80]:

$$RPX_4 > R_2PX_3 > R_3PX_2; X=F, \text{ or } Cl.$$

The pentahalides exhibit basic properties much more rarely. In these reactions they are converted into structures with a lower coordination [number]. Such processes include the above examples of reactions with aluminium chloride and iron(III) chloride. The following mechanism has been proposed in an interesting communication [75]:

$$F_3B \cdot NH_2CH_3 + 2PCl_5 \rightarrow CH_3N\langle \overset{+}{P}Cl_3 \atop \overset{-}{B}Cl_3 + PF_3Cl_2 + 2HCl .$$

The lack of broad and specific studies on the reaction stages and of data on the structure of phosphorus pentachloride at the instant of the reaction precludes a unique representation of the mechanisms of reactions with its participation.

The mechanism of the interaction of phosphorus pentachloride with ketones has been deduced [81] on the hypothesis that it reacts in an ionic form and undergoes a series of successive transformations:

$$2PCl_5 \rightleftarrows \overset{+}{P}Cl_4\overset{-}{P}Cl_6 , \quad (1)$$

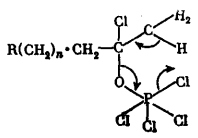
$$RCOCH_3 + \overset{+}{P}Cl_4 \rightleftarrows \left[R\overset{+}{C}CH_3 \atop OPCl_4\right] , \quad (2)$$

$$R\overset{+}{C}(OPCl_4)-CH_3 + Cl^- \rightarrow \left[R-\overset{Cl}{\overset{|}{C}}(OPCl_4)-CH_3\right] , \quad (3)$$

$$RC(OPCl_4)-CH_3 \xrightarrow{a} RC(Cl)=CH_2 + POCl_3 + HCl$$
$$RC(OPCl_4)-CH_3 \xrightarrow{b} R\overset{+}{C}(Cl)-CH_3 + POCl_3 + Cl^- , \quad (4)$$

$$\left[R-\overset{+}{C}(Cl)-CH_3\right] + Cl^- \rightarrow RCCl_2CH_3 . \quad (5)$$

The reaction begins with electrophilic attack on the carbonyl oxygen. The stage involving the formation of the chloro-olefin can, however, be represented, as in a later study [82], by a six-membered cyclic intermediate:



The different results obtained in the interaction of ketones with phosphorus pentachloride, using different solvents, were explained [83] by the different forms in which phosphorus pentachloride can exist: dimeric or monomeric. Depending on this factor, mechanisms were proposed for the reaction with benzylidenedeoxybenzoin.

The influence of the solvent on the mechanism of the reaction with ketones was noted also in subsequent investigations.

Together with these mechanisms, the possible radical chlorination of benzene homologues [84] via the mechanism

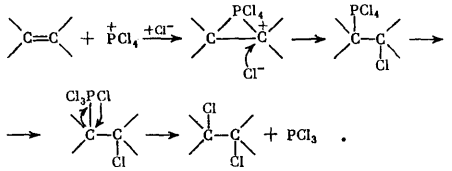
$$PCl_5 \rightleftarrows PCl_3 + Cl_2; \quad Cl_2 \rightleftarrows 2Cl\cdot$$

or

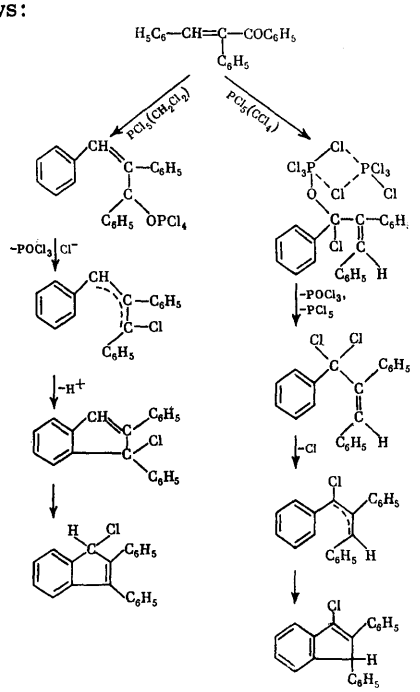
$$PCl_5 + R\cdot \rightarrow RCl + \cdot PCl_4; \; PCl_4 + RH \rightarrow R + HPCl_4; \; HPCl_4 \rightarrow PCl_3 + HCl$$

when a catalyst is present, has been reported.

The following competing ionic mechanism has been put forward [84]:



The mechanism of the interaction of benzylidenedeoxybenzoin with phosphorus pentachloride in CCl_4 and CH_2Cl_2 is as follows:



It is believed [85] that catalysts of reactions involving chlorination by phosphorus pentachloride is due to its ability to be coordinated to a chlorine molecule, which favours the homolysis of the Cl–Cl bond:

$$PCl_5 + Cl_2 \rightleftarrows \left[Cl_4PCl_2\right]Cl \rightleftarrows \dot{P}Cl_4 + Cl_2 + \dot{C}l \; (\text{or } Cl_3^{\cdot}) .$$

Disregarding the numerous communications where the chlorinating activity of phosphorus pentachloride is reported [86], we shall examine the existing views on the mechanisms of its interaction with various types of hydrocarbons, which results in the formation of the phosphorus–carbon bond. Since studies on the phosphorylation by phosphorus pentachloride of compounds containing a multiple bond have already been described in other reviews [1,2], we shall examine below studies concerning the process mechanism.

2. The Phosphorylation Reactions

The most systematic studies, carried out by Bergman and Bondi[87], showed that the addition of phosphorus pentachloride occurs readily in reactions with asymmetrically substituted ethylene derivatives and leads to the formation of products whose hydrolysis gives rise to unsaturated phosphonic acids and the following mechanism was proposed:

$$RCH{=}CH_2 + PCl_5 \rightarrow RCHClCH_2PCl_4 \xrightarrow[-5HCl]{3H_2O} RCHCHP(=O)(OH)_2 .$$

The authors[87] did not isolate the intermediate, but noted that high yields require at least a twofold excess of phosphorus pentachloride.

Later studies[88,89] showed that the addition of phosphorus pentachloride to a multiple bond takes place in such a way that the $\overset{+}{P}Cl_4$ group adds to the most hydrogenated carbon atom, while the chlorine atom adds to the least hydrogenated carbon atom. The addition products can be regarded as binary compounds with phosphorus pentachloride:

$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHClCH_2PCl_4 \cdot PCl_5 .$$

It has been suggested[90] that the reaction of phosphorus pentachloride with unsaturated hydrocarbons may proceed without the formation of β-chlorophosphonic acid derivatives via an ionic mechanism:

$$RCH{=}CH_2 + {}^{+}PCl_4 \rightarrow R\overset{+}{C}HCH_2PCl_4 \xrightarrow{-HCl} RCH{=}C\overset{+}{H}PCl_3 \xrightarrow{+PCl_5} RCH{=}C\overset{+}{H}PCl_3\bar{P}Cl_6 .$$

The formation of the intermediate addition product $ArCHClCH_2.PCl_4$ is believed to be unlikely[90]. In the reaction with styrene the structure $C_6H_5CH{=}C\overset{+}{H}P\bar{C}l_3\bar{P}Cl_6$ is attributed to the complex, which takes into account its ability to interact with sulphur dioxide, styrene, and red phosphorus. These reactions are regarded as confirmation of the structure of the complex.

Grechkin and Kalabina[91] treat the above reaction as electrophilic substitution of hydrogen. They suggest that the reaction begins with the formation of a π-complex of the olefin and the $\overset{+}{P}Cl_4$ cation, which is stabilised after the elimination of hydrogen chloride. The resulting cation can react, according to the authors, with a Cl^- ion, whereby it is converted into alkenyltetrachlorophosphorane, or with a PCl_6^- ion, giving rise to a salt-like product. The mechanism is outwardly similar to that described by Fedorova and Kirsanov[90]:

$$RCH{=}CH_2 + \overset{+}{P}Cl_4 \rightarrow [RCHCH_2PCl_4]^+ \xrightarrow{-HCl} RCH{=}C\overset{+}{H}PCl_3 \rightleftarrows RCH{=}C\overset{+}{H}P\bar{C}l_6$$

$$\xrightarrow{Cl^-} RCH{=}CHPCl_4 \xrightarrow{PCl_5} RCH{=}C\overset{+}{H}PCl_3\bar{P}Cl_6 .$$

These mechanisms take into account the fact that, in the interaction with styrene or vinyl ethers[92], the addition of the phosphorus pentachloride–chlorine fragment to the multiple bond is not observed.

The authors concluded[90,91] that an electrophilic substitution mechanism operates solely on the grounds that no-one has isolated β-chloro-β-phenylethylphosphonate on phosphorylating styrene and that the reaction always leads to a compound with a multiple bond—styrylphosphonic dichloride (this also applies to the products of the interaction of phosphorus pentachloride with vinyl ethers). However, this cannot be regarded as proof of the mechanism, because the proton in the α-position relative to the phosphoryl group is known to be highly mobile, which was noted for the first time by Kabachnik[93,94]. As regards vinyl ethers, we may note the enhancement of the mobility of chlorine under the influence of the alkoxy-group. The elimination of hydrogen chloride from a series of α-halogeno-ethers is known to occur under very mild conditions[95]. In the intermediate phosphorylation products these substituents act in concert, leading to the formation of phosphonates containing a multiple bond. The halogenation of β-alkoxyvinylphosphonic dichlorides may serve as a model[96-98]:

$$\begin{matrix} R' \\ | \\ ROC{=}CHPOCl_2 \end{matrix} + Hal_2 \rightarrow \left[\begin{matrix} Hal & Hal \\ | & | \\ ROC{-}CHPOCl_2 \end{matrix} \right] \xrightarrow[-HHal]{t^\circ} \begin{matrix} R' & Hal \\ | & | \\ ROC{=}CPOCl_2 \end{matrix} .$$

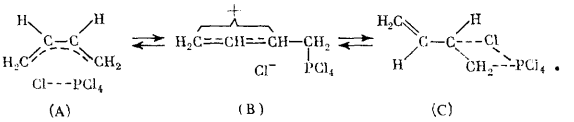
The phosphorylation of aliphatic olefins leads correspondingly to products without a multiple bond[99]:

$$RCH{=}CH_2 + PCl_5 \rightarrow [\text{adduct}] \xrightarrow[-SOCl_2]{SO_2} RCHClCH_2POCl_2$$

$$RCH{=}CHPOCl_2 + Br_2 \rightarrow RCHBrCHBrPOCl_2 .$$

In a series of studies[100,102] on the phosphorylation of diene and acetylene derivatives by phosphorus pentachloride carried out in recent years a molecular reaction mechanism is postulated. It is believed that, in the reaction of phosphorus pentachloride with unsaturated hydrocarbons, several mechanisms may operate, differing in the degree of charge separation in the transition state and in the lifetime of the polarised structure, which leads, depending on the initial hydrocarbons, to the formation of products whose structure is determined by the process kinetics (acetylenes) or thermodynamics (dienes).

On the grounds of stereochemical considerations, the transition state in the reaction with dienes is believed to be highly polar and to incorporate the covalent structures A and C and structure B with separated charges:

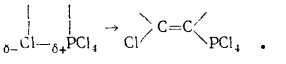


(A) (B) (C)

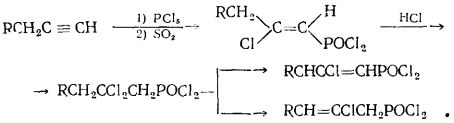
In the case of dienes the transition state is closer to the polarised structure B and this is sufficient for the occurrence of a rearrangement and the formation of thermodynamically more favourable isomers.

The stereospecific *cis*-addition to an isolated triple or double bond is believed[103] to be a confirmation of the addition of the phosphorus pentachloride molecule in a pentacovalent form.

The nature of the influence of substituents at the multiple bond on the mode of addition of the phosphorus fragment shows unambiguously that the addition process has an electrophilic mechanism and probably proceeds via a four-membered cyclic transition state:



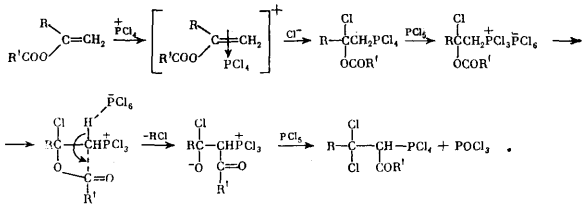
The possibility of a prototropic rearrangement in the reaction with acetylenic derivatives, leading to 2-chloroalk-2-enylphosphonic acids, has been examined[104]: however, other workers[105] reject the possibility of isomerisation, particularly since a prototropic rearrangement takes place in the presence of bases[106]. Bearing this in mind, Meisters and Swan[104] believe that the alk-2-enyl isomer is formed as a result of the addition-elimination of a further hydrogen chloride molecule:



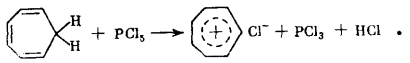
The results of the latest studies by Rybkina et al.[107] support a molecular mechanism of addition to multiple bonds. In their studies on the phosphorylation of olefins in different aprotic solvents the authors showed that in polar solvents, promoting the existence of phosphorus pentachloride in the form of an ionic dimer, the yields of the reaction products are a minimum, while in non-polar solvents, where phosphorus pentachloride exists in a molecular form, they are a maximum.

Finally, in connection with the discussion of the mechanisms of the phosphorylation reactions of ethers, acetals and cyclic oxa- and dioxa-compounds, we shall consider briefly studies where the dehydrogenating activity of phosphorus pentachloride was noted. This pathway was observed for the first time in the reaction of α-benzylstilbene with phosphorus pentachloride, which resulted in ring closure and the formation of 2,3-diphenylindene.[87,107]

In a study of the phosphorylation of esters containing a multiple bond by phosphorus pentachloride, Lutsenko and coworkers[109-114] included a deprotonation stage in the process mechanism:



Phosphorus pentachloride behaves similarly in the reaction with cycloheptatriene, which results in the formation of tropylium chloride, phosphorus pentachloride being reduced to the trichloride[115]:



In conclusion we shall consider the role of the formation of a complex by phosphorus pentachloride with an electrophile and nucleophilic centres: oxygen or a multiple bond. The transformations of the adducts of phosphorus pentachloride with vinyl ethers[54], styrene derivatives, and α-alkoxystyrene[116,117] may be regarded as an indirect confirmation of the formation of molecular donor–acceptor complexes by phosphorus pentachloride:

$$C_6H_5CH{=}CH_2 + PCl_5 \xrightarrow{t^\circ} C_6H_5CH{=}CClPCl_2 + 2HCl\ ;$$

$$C_6H_5C(OR){=}CH_2 + PCl_5 \xrightarrow{t^\circ} C_6H_5CCl{=}CH_2 + POCl_3\ ;$$

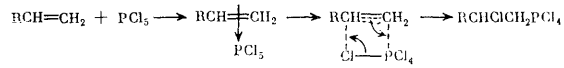
$$ROCH{=}CH_2 + PCl_5 \rightarrow [\text{adduct}] \xrightarrow{t^\circ} \text{chlorinated products};$$

$$2ROCH{=}CH_2 + PCl_5 \xrightarrow{POCl_3} [\text{adduct}] \xrightarrow{t^\circ}$$

$$\rightarrow ROCH{=}CHPOCl_2 + POCl_3 + RCl + [CH(Cl){-}CH_2{-}]_n + HCl\ .$$

Phosphorus-containing substances are formed only in those cases where it is possible to postulate the coordination of phosphorus pentachloride to a multiple bond (styrene). α-Alkoxystyrene and vinyl ethers react with phosphorus pentachloride to form only chlorination products, possibly owing to the formation of a complex involving the coordination of the alkoxy-group to an oxygen atom. The introduction of phosphoryl chloride into the reaction mixture in the process involving vinyl ethers promotes the formation of phosphorus-containing vinyl ethers.

The data examined suggest that the interaction of phosphorus pentachloride with olefins involves the following probable stages: (a) the formation of a donor–acceptor complex; (b) electrophilic addition of fragments of phosphorus pentachloride (Cl and PCl_4) to the double bond:



During the preparation of the review for the press, new original reports were published. Studies on keten[118] showed that phosphorus pentachloride interacts with it to form a phosphorus–carbon bond. The possibility of the simultaneous formation of bonds with two carbon atoms has been illustrated[119] in relation to the reaction with bis(α-chloromethylvinyl) sulphide.

In conclusion we may note that the preparative possibilities of phosphorus pentachloride in the syntheses of compounds with a phosphorus–carbon bond continue to expand. Among carbon-containing compounds, studies are being made not only on compounds with a multiple bond but also on those which are capable of forming multiple bonds under the influence of phosphorus pentachloride. It would be premature to express any definite view concerning the mechanism. The reactions with phosphorus pentachloride are complex and probably have a whole range of different mechanisms. It appears essential to investigate in greater detail the individual stages of the reactions, in the first place complex formation, and to elucidate the role of the third agent—sulphur dioxide, hydrogen sulphide, etc.

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