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# STRUCTURE AND PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS

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## I. INTRODUCTION

The interest in organophosphorus compounds which has grown in recent years is explained by the considerable broadening of their field of use. Much attention has been paid to establishing the relation between the structure and properties of organophosphorus compounds, which is important, in particular, for solving the problems associated with the production of materials with specified properties.

Hammett's constant[1] is now widely used as a quantitative or semiquantitative characteristic of the structural features of organic compounds which determine their chemical and physical properties; it has been shown that the effect of *meta*- and *para*-substituents in the benzene ring on the rate constant or equilibrium constant of a reaction is expressed by the equation:

$$\log K - \log K_0 = \sigma\rho, \quad (1)$$

where $K$ and $K_0$ are the rate or equilibrium constants of the reactions with the substituted and unsubstituted molecules respectively, $\sigma$ is a constant characterising the polar effect of the substituent (the inductive effect and the conjugative effect), and $\rho$ a constant characterising the reaction type and conditions.

Jaffé[2] has given evidence of the wide use of Hammett's equation; his review has values of $\sigma$ and $\rho$ for ~ 42 000 rate and equilibrium constants for 3180 reactions, which include addition, substitution, esterification, polymerisation, and copolymerisation. Eqn. (1) is satisfied with an accuracy of ±15% by experimentally measured rate or equilibrium constants of the reactions. This shows that although Hammett's equation does not give accurate results, it is sufficiently reliable for a first approximation.

Hammett's equation is applicable for benzene derivatives but inadequate for alkyl compounds. Furthermore, the constants $\sigma$ are not always independent of the nature of the reaction. These constants reflect the polarisability of the bonds under the influence of the inductive effect and the conjugative effect, but it is known[3] that in the transition state the conjugative effect can vary according to the reaction type. Eqn.(1) does not take into account steric factors.

In this connection, Taft[4] proposed the empirical equation:

$$\log K - \log K_0 = \sigma^*\rho + E_s\delta + \psi^*, \quad (2)$$

for esterification, hydrolysis, alcoholysis, and various other exchange reactions, where $K$ and $K_0$ are the rate or equilibrium constants for the substituted molecules and the molecules with the standard substituent $CH_3$, $\sigma^*$ is the polarity constant of the substituent, $E$ a constant characterising the steric effect of the substituent with respect to the $CH_3$ group (the standard), $\psi$ a constant characterising the conjugative effect arising as a result of the interaction of the substituent and the reaction centre, and $\rho$ and $\sigma$ are constants which characterise the reaction type and conditions. This equation can eliminate the defects mentioned to some extent.

For hydrolysis, the polarity constant of the substituent is calculated by the formula:

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{K}{K_0}\right)_B - \log\left(\frac{K}{K_0}\right)_A\right], \quad (3)$$

where $(K/K_0)_B$ and $(K/K_0)_A$ are ratios of the constants of the reactions of alkaline and acid hydrolysis (under the conditions: the same ester, solvent, identical temperature), and 1/2.48 is a coefficient relating all the quantities to the Hammett scale.

It has been shown[3] that the Hammett and Taft equations are applicable to tautomeric equilibria and also to a series of exchange reactions, substitutions, and additions involving certain organophosphorus compounds. In addition to the quantitative and semiquantitative characteristics of the influence of the structural features of organophosphorus compounds on their reactivity and physical properties, there are works which characterise this effect without using empirical equations and constants.

In this article an attempt is made to review and systematise the available material on the study of the relation between the structure and the physical, and chemical properties of organophosphorus compounds.

## II. REACTIVITY OF ORGANOPHOSPHORUS COMPOUNDS

### 1. Substitution, Addition, Hydrolysis, and Isomerisation; Tautomeric Equilibrium

A series of investigators[5-10] has established a relationship between the Hammett and Taft constants and rate constants of the reactions of certain organophosphorus compounds.

A relation has been found between the dissociation constant and the basicity index $pK_a$ of phosphines and the Taft constants[11] $\Sigma\sigma^*$ characterising the polarity of the substituents $\Sigma\sigma^* pK_a = -\log K_a$, where $K_a$ is the dissociation constant of the acid. This dependence is reflected in Tables

1 and 2, which show that the basicity of the phosphines decreases with increase in the polarity, so that there is consequently also a decrease in their reactivity in substitutions and additions. There are departures from the general rule, for example, for $(C_2H_5)_3P$ $\Sigma\sigma^* = -0.3$, $pK_a = 8.69$; and for $(^iC_4H_9)_3P$ $\Sigma\sigma^* = -0.375$, $pK_a = 7.97$.

The possibility of using the Taft constant for the reaction of phosphines with alkyl halides has been demonstrated[12]:

$$RR'R''P + C_2H_5I \xrightarrow[\text{acetone, } 35^\circ]{K_2} RR'R''C_2H_5P^+ + I^-.$$

With increase in the polarity in the alkylphosphine series, their reactivity increases in the following order:

$$C_2H_5P(CH_3)_2 > (C_2H_5)_2PCH_3 > (CH_3)_3P > (C_2H_5)_3P;$$

trimethylphosphine is anomalous. As a rule there is a decrease in the rate constant of this reaction with increase in the polarity, according to the equation

$$\log 10^5 K = 1.939 - 0.767\sigma^*. \quad (4)$$

In this it is assumed that other factors (steric and conjugative) have little effect on the rate constants of phosphine reactions[12].

In a study[13] of substitution at phosphorus(V) it was noted that nucleophilic substitution at phosphorus depends on the relative magnitude of the polarity and polarisability of the phosphorus compound (the $-\overset{|}{\underset{|}{P}}=O$ group has a marked influence) and on the relative magnitudes of these properties of the nucleophilic reagent.

The polarisability of the phosphoryl group is greater than that of the carbonyl, and therefore a greater inductive effect is possible in phosphorus compounds than for their carbon analogues. Allowance must be made for the possibility of the double bond in phosphorus compounds being formed with *s*, *p*, and *d* orbitals[14], whereas in carbon compounds a double bond is formed by electrons of *s* and *p* orbitals.

A nucleophilic substitution which has been studied more fully is the hydrolysis of organophosphorus compounds, which is catalysed by both hydrogen and hydroxide ions[5].

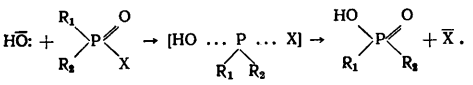
TABLE 1. Equations relating basicity and the Taft constant $\Sigma\sigma^*$ of alkyl- and aryl-phosphines[11].

| Compound | Equation | Compound | Equation |
|---|---|---|---|
| Phosphines: | | Amines: | |
| tertiary | $pK_a = 7.85 - 2.67\ \Sigma\sigma^*$ | tertiary | $pK_a = 9.61 - 3.3\ \Sigma\sigma^*$ |
| secondary | $pK_a = 5.13 - 2.61\ \Sigma\sigma^*$ | secondary | $pK_a = 12.13 - 3.23\ \Sigma\sigma^*$ |
| primary | $pK_a = 2.46 - 2.64\ \Sigma\sigma^*$ | primary | $pK_a = 13.23 - 3.14\ \Sigma\sigma^*$ |

TABLE 2. Values of $pK_a$ and $\Sigma\sigma^*$ for various phosphines[11].

| Compound | $\Sigma\sigma^*$ | $pK_a$ | Compound | $\Sigma\sigma^*$ | $pK_a$ |
|---|---|---|---|---|---|
| Tertiary phosphines: | | | | | |
| $(CH_3)_3P$ | 0.00 | 8.65 | Secondary phosphines: | | |
| $C_2H_5P(CH_3)_2$ | −0.10 | 8.62 | $(C_2H_5)_2PH$ | 1.69 | 0.03 |
| $(C_2H_5)_2PCH_3$ | −0.20 | 8.62 | $(CNC_2H_4)_2PH$ | 2.09 | 0.41 |
| $(C_2H_5)_3P$ | −0.30 | 8.69 | | | |
| $(^iC_4H_9)_3P$ | −0.375 | 7.97 | | | |
| $(C_2H_5)_2PC_6H_5$ | +0.40 | 6.25 | | | |
| $(C_6H_5)_3P$ | +1.8 | 2.75 | Primary phosphines: | | |
| | | | $^nC_6H_{17}PH_2$ | 0.85 | 0.43 |
| | | | $PH_3$ | 1.47 | 14 |

The most extensive investigation has concerned alkaline hydrolysis, for which the following scheme has been proposed:



The effect of the nature of the substituents on hydrolysis rate was studied[6]; replacement of alkyl by alkoxy usually leads to a decrease in hydrolysis rate.

Kabachnik[3] examined the data on the alkaline hydrolysis of alkyl alkylphosphonofluoridates and on the alcoholic solvolysis of dialkyl phosphorochloridates, using the constant $\sigma$ (Figs. 1 and 2). Some breakdown in the proportionality between Hammett's constants and the reaction rate is possible because there are two opposing effects. On the one hand the increase in the charge on the phosphorus accelerates the reaction, and on the other this increases the increment of the energy of conjugation of the P–O bond, which leads to a decrease in reactivity[7]. Therefore replacement of an ethoxy-group by a phenoxy-group causes an increase in the hydrolysis rate. pH has a very strong influence on the rate of reaction; thus, the reactivity of monoalkyl phosphates is greatly increased at pH 1–5.[8] In acid media the rate of hydrolysis increases with the polarity of the substituent, and in alkaline, hydrolysis is possible at the C≡N bond as well as at the C–O–P bond[9].

As well as the polarity constants of the substituents, their steric characteristics must also be taken into account. Thus the steric hindrance of the substituent $CH_3NHCH_2CH_2-$ is less than that of the substituent $(C_2H_5)_2NCH_2CH_2-$ by a factor[4] of ~ 3.5.

The reaction rate also depends on the solvent. For example, as the basicity of the solvent is increased the P–X bond energy decreases, but simultaneously there is an increase in the steric hindrance (Table 3).

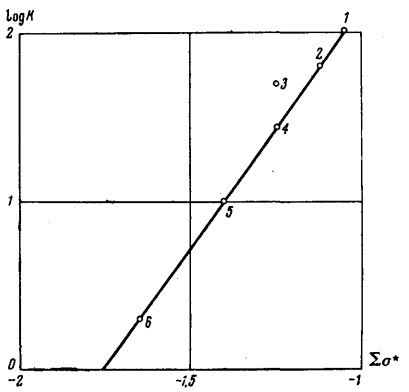



Fig. 1. Dependence of $\log K_1$ on $\Sigma\sigma^*$ for the alkaline hydrolysis of esters of alkylphosphonofluoridic acids:
1) $CH_3P(O)(OCH_3)F$;
2) $CH_3P(O)(OC_2H_5)F$;
3) $CH_3P(O)(OC_3H_7)F$;
4) $CH_3P(O)(O^iC_3H_7)F$;
5) $C_2H_5P(O)(O^iC_3H_7)F$;
6) $C_3H_7P(O)(O^iC_3H_7)F$.

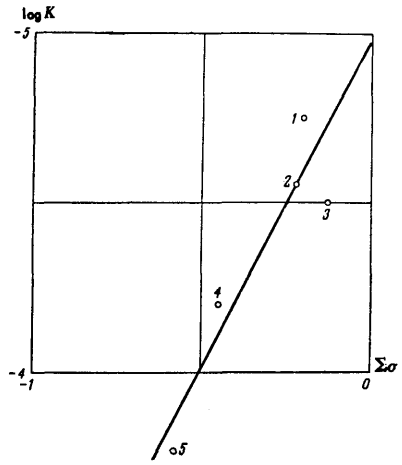


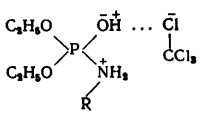

Fig. 2. Dependence of $\log K_1$ on $\Sigma\sigma$ for the solvolysis of dialkyl phosphorochloridates by alcohol:
1) $(CH_3O)_2POCl$; 2) $(C_6H_5CH_2O)_2POCl$;
3) $(C_6H_5O)_2POCl$; 4) $(C_2H_5O)_2POCl$;
5) $(^iC_3H_7O)_2POCl$.

TABLE 3. Dependence of the rate constants for the hydrolysis of acid chlorides of phosphonic acids ($10^3 K$) on the nature of the solvent[7].

| Solvent | $\sigma^*$ of substituent at OH group | $10^3K$ at 25°*** | $E_{act}$* | log A** |
|---|---|---|---|---|
| H—(OH) | 0.49 | 128 | 8.5 | 5.37 |
| $CH_3$—(OH) | 0.00 | 10.3 | 8.0 | 3.88 |
| $C_2H_5$—(OH) | —0.10 | 5.7 | 7.3 | 3.07 |

* Energy of activation.
** Activity constant of the solvent.
*** The last entry in this column should be 5.07 according to the original; log A is really the log of the Arrhenius factor, PZ (Ed. of Translation).

In several instances the solvent has quite a strong influence on the reactivity of phosphorus-containing compounds, which is explained by the formation of an intermediate compound, for example, in the reaction of phosphites with amines in the presence of polyhalides[10]:



The replacement of $CCl_4$ by $CCl_3Br$ or $CNCCl_3$ increases the reactivity of phosphorus-containing compounds of phosphites [*sic* (Ed. of Translation)].

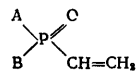
In addition to the hydrolysis and solvolysis of various phosphorus-containing compounds, there have been investigations of the alkaline cleavage of phosphonium salts, the protolysis of phosphorus acids, and of benzylation[15-17]; Hammett's equation is applicable to all these reactions.

Several papers[18-24] have established a correlation between the dissociation constants of phosphonic acids or their derivatives and the Hammett constants. A linear relation between $\sigma$ and $pK_a$ is obtained for aromatic phosphonic acids[18,19]. The Taft constants were also determined for the reaction of hydroxamic acids with phosphonofluoridates[20-24].

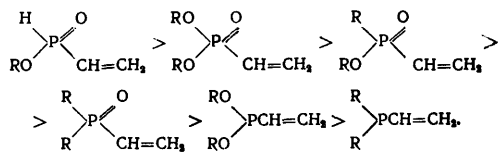
Since the tautomeric equilibrium constant in the selected medium equals the ratio of the ionisation constants of the tautomeric forms, which, in turn, can be calculated by Hammett's equation[1,3], the equilibrium position is mainly determined by the magnitude of Hammett's constant, characterising the nature of the substituent. Kabachnik showed the applicability of Hammett's equation to the tautomeric equilibrium of phosphorus thio-acids[22-24]:

$$(RO)_2P(S)OH \rightleftarrows (RO)_2P(O)SH,$$
$$R(RO)P(S)OH \rightleftarrows R(RO)P(O)SH, \text{ etc.}$$

Study of the bromination of unsaturated phosphorus-containing compounds and their addition to secondary amines shows that Hammett's equation is also applicable to these reactions[3,25]. As the value of $\Sigma\sigma$ of the substituents is reduced, the reactivity of the vinyl group in compounds of the type



also decreases. For such compounds, and also for analogous compounds of phosphorus(III), a series of decreasing reactivity of the vinyl group has been compiled[25]:



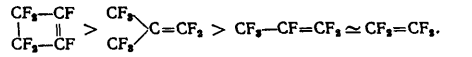
For the first four compounds of this series (R = $-C_4H_9$), $\Sigma\sigma$ is respectively -0.411, -0.822, -1.370, and -2.438.

In addition to those mentioned there are several investigations which establish a qualitative relation between the reaction rate and the structure of the reactants. Thus, the addition of phosphines to unsaturated compounds of the styrene type has been studied[26,27]. Phosphines are chain carriers in polymerisation:

$$RPH + CH_2{=}CHX \rightarrow RPHCH_2{-}\dot{C}HX + RPH_2 \rightarrow RPHCH_2CH_2X + R\dot{P}H,$$

where $R\dot{P}H$ is the chain carrier.

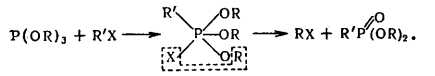
For the addition of phosphines to the vinyl group the substituent R in the phosphines can be arranged in the following series of decreasing activity[27]: bis-(2-cyanoethyl) > > 2-cyanoethyl > phenyl > octyl. The addition of phosphorus-containing compounds to unsaturated bonds of a monomer depends on the structure of the monomer containing this bond. Thus the activity of perfluoroalkenes in the reaction with triethyl phosphite falls in the sequence[28]:



Many investigators[29-46] have evaluated the reactivity or the activity of a compound by the yield of the main product and the time of reaction.

In particular it has been noted that the Arbuzov rearrangement proceeds more rapidly and with a greater yield the more electronegative and the smaller the radical in the alkyl

halide [37-45]. Thus, rearrangement does not occur with 9-chloroanthracene but does with 9-chloroacridine [43]. Polymerisation proceeds through intermediate addition products [33]:



Radicals entering into the composition of phosphite esters also affect the isomerisation rate: the rate is greater with radicals of small dimension and high electronegativity. According to their influence on reaction rate, the groups attached to phosphorus can be arranged in the series [32,33]: Alk > Ar > AlkO and $CH_3O > C_2H_5O > C_3H_7O > C_4H_9O$.

Other conditions being equal, the rate of isomerisation of phosphite esters depends on the halogen of the alkyl halide [33,46]. The reaction under the action of alkyl iodides is more rapid than that with the chlorides; bromides occupy an intermediate position.

Thus, for several exchange reactions, substitutions, additions, isomerisations, and tautomeric equilibria of phosphorus-containing compounds the Taft constants can be used for the quantitative or qualitative characterisation of the reactivity of the reactants.

## 2. Polymerisation, Copolymerisation, and Telomerisation

The applicability of Hammett's equation has been shown for the polymerisation and copolymerisation of common organic compounds, but such investigations of the polymerisation of phosphorus-containing monomers have not been made [47,48].

The polymerisation and copolymerisation of phosphorus-containing unsaturated compounds of various structures has been studied without using Hammett's and Taft's constants. Toy and Cooper [49] give the comparative characteristics of phosphorus-containing monomers for activity in polymerisation, by the example of diallyl alkylphosphonates, where we will quote the R in $RP(O)(OCH_2CH{=}CH_2)_2$:

$$C_6H_5{\simeq}H > C_6H_5CH_3 \simeq C_6H_5O \simeq (CH_3)_2C{=}CH_2 \gg C_6H_5CH{=}CH > > CH_3 \simeq C_2H_5 > {}^iC_3H_7 \simeq C_8H_{17} \gg C_2H_5O \simeq (CH_3)_2N.$$

Kamai and Kukhtin [50] gave the following series:

$$C_6H_5 > RC(=O) > ROC(=O) > ROCCH_3(=O) > CCl_3 > CH_3 > C_2H_5.$$

Kennedy and coworkers [51] supplemented and corrected these two series for allyl alkylphosphonates, and gave this series for the activity:

$$CCl_3 \simeq CCl_2{=}CHO \gg H \gg CH_2{=}CHCH_2O \simeq OCH_3 \simeq C_2H_5OCCH_3(=O) > > CH_3{=}CHCH_2 \gg OH \simeq N(CH_3)_2 \simeq CH[N(C_2H_5)_2]CH{=}CH_2. \quad (I)$$

The series of compounds $A_3P{=}O$, $(AO)_2P(O)OH$, $(AO)_2P(O)N(CH_3)_2$, $(AO)_2P(O)CH(NEt_2).CH:CH_2$, and $(AO)_3P$ (A = allyl group) do not form solid polymers, and the last three of this series even inhibit polymerisation.

These series suggest that the greater the electronegativity and the smaller the substituent at the phosphorus atom in the allyl esters, the more readily polymerisation takes place.

When there is little interaction between the $\pi$ electrons of the allyl group and the P=O bond, for example, in the compounds $(CH_2{=}CHCH_2)_3PO$ and $(CH_2{=}CHCH_2)_2P(O)OH$, the ability to polymerise is negligible [51] These results have been repeatedly confirmed [52-61], but several results have been obtained which do not correspond with the empirical series [50,51,53,54]. This is because the polymerisation rate can be strongly depressed by impurities in the monomers [51,53,54]. The presence of even insignificant amounts of triallyl phosphite completely inhibits polymerisation [51].

Upson, Kabachnik, Gefter, and many other investigators [62-78] have studied the ability of phosphorus compounds with a vinyl group to polymerise. Unlike allyl esters — whose activity in the presence of three double bonds (three allyl groups) in polymerisation is small — the analogous vinyl esters readily form solid vitreous polymers [62].

Vinyl esters with one double bond either do not polymerise at all, or form viscous liquids or gelatinous polymers, depending on the substituents at the phosphorus atom.

The preparation and polymerisation of derivatives of vinylphosphonic acids have been studied [65-77]; usually, the larger the aliphatic radical in the ester group, the lower the molecular weight of the polymers obtained but the greater the yield of phosphorus-containing polymer [66]. Fig. 3 shows the results of the polymerisation of vinylphosphonic esters of various structures.

The polymerisation of unsaturated derivatives of phosphorus acids has formed the subject of many papers. Polymers have been obtained from $(HOCH_2)_4PR$, where R is the residue of an unsaturated acid (methacrylic or acrylic), from various phosphorus-containing dienes, vinylphosphine oxides [74-76], etc. Vinylphosphine oxides polymerise very badly, which some investigators attribute to the large steric hindrance [76]. Products of higher molecular weight are obtained from monovinylphosphine oxides on irradiation with X-rays [76].

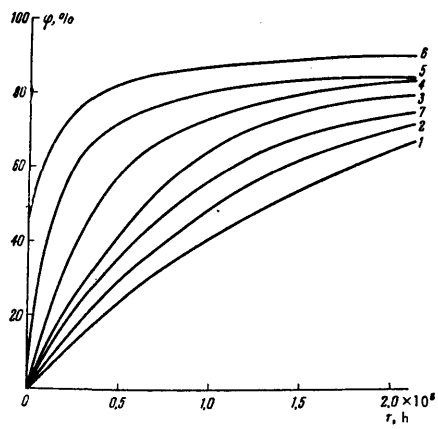



Fig. 3. [Polymerisation of vinyl phosphonic esters of various structures (Ed. of Translation).]* Dependence of the yield of polymer $\varphi$ on the duration of the reaction: 1) ethyl and isopropyl esters; 2) n-propyl ester; 3) methyl ester; 4) n-butyl and isopentyl esters; 5) n-hexyl ester; 6) n-heptyl ester; 7) isobutyl ester.

* Since $2 \times 10^5$ h is about 20 years it is likely that the time scale should be $10^{-5}$ t where t is in seconds (Ed. of Translation).

There is considerable interest in the study of the relation between the structure of phosphorus-containing monomers and their activity in copolymerisation [79-100]. The copolymerisation of styrene and diethyl vinylphosphonate has been studied. Arcus and Matthews [98] found the constants for the copolymerisation to be $r_1 = 3.25$; $r_2 = 0$.

The copolymerisation of acrylonitrile and esters of vinylphosphonates has also been studied [66]; Table 4 shows that the activity of the esters increases with decrease in the polarity and increase in the length of the ester residue: the polarity of the methyl, ethyl, isobutyl, and n-butyl radicals are respectively $\sigma_1 = 0.00$, $\sigma_2 = -0.100$, $\sigma_3 = -0.125$, $\sigma_4 = -0.130$.

The copolymerisation of acid chlorides of unsaturated phosphorus acids with vinyl monomers [80,90], of vinyl monomers with unsaturated phosphorus-containing polyesters, and of phosphorus-containing monomers with unsaturated polyesters [89-95] has been studied.

Polymers can be obtained by addition of phosphines to the double bond of a polyester or monomer. Phosphonates can be used instead of the phosphines [80,101]. The rate of this copolymerisation depends on the initiation conditions [80,101]. A high activation energy ensures sources of free radicals or conditions which guarantee the formation of free radicals. In several instances, for example, in the copolymerisation of styrene with a phosphorus-containing polyester, an accelerator of the reaction (here, isocyanates) is used to increase the rate of reaction [102]. The copolymerisation of *p*-xylylenes with phosphorus trichloride gave thermostable polymers [103,104].

The telomerisation of unsaturated phosphorus-containing compounds has been studied [105-107]. It has been established that trialkyl phosphites can undergo the Arbuzov rearrangement under the action of $\alpha\beta$-unsaturated aldehydes and acids. It is suggested that in the case of the acids telomerisation is possible, the reaction proceeding thus:

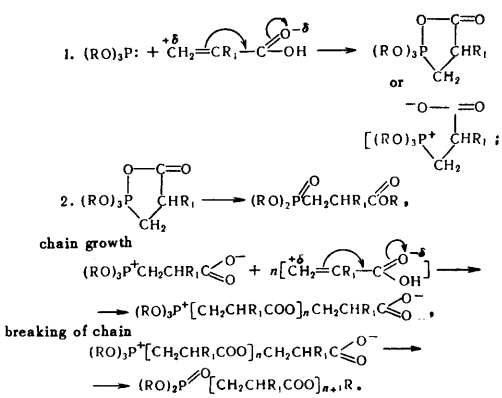
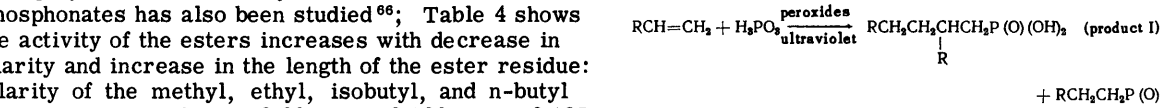


TABLE 4. Copolymerisation of vinylphosphonate esters with acrylonitrile [66].

| Ester | $\sigma^*$ of substituent in RO | $E_s$ of substituent in RO | Composition of initial mixture, % | | Yield of copolymer, % | Composition of copolymer, % | |
|---|---|---|---|---|---|---|---|
| | | | acrylonitrile | ester | | acrylonitrile | ester |
| Methyl | 0.00 | 0.00 | 50 | 50 | 18 | 86.5 | 13.5 |
| Ethyl | −0.10 | −0.07 | 55.7 | 44.3 | 33.3 | 82.4 | 17.6 |
| Isobutyl | −0.125 | −0.93 | 58.5 | 41.5 | 25.6 | 78.7 | 21.3 |
| n-Butyl | −0.130 | −0.39 | 50 | 50 | 37.3 | 63.1 | 36.9 |

The authors of this investigation suggest that during the reaction an intermediate dipolar ion is formed and further reaction can proceed in two directions: the Arbuzov rearrangement or telomerisation [106].

Telomers can be formed in the reaction of alkenes with phosphorus acid:



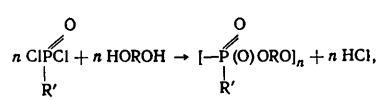
The percentage yield in this reaction depends on the structure of the alkene and is determined by the nature of the radical [107]:

| R | Yield of I | Yield of II | Total yield |
|---|---|---|---|
| $^nC_4H_9$ | 8 | 23 | 31 |
| $C_6H_{11}$ | 9 | 20 | 29 |
| $^nC_8H_{17}$ | 6 | 18 | 24 |

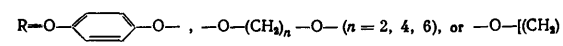
From the above, it is evident that as the size of the substituent is increased, the total yield of the products diminishes. Hence, for polymerisation, copolymerisation, and some telomerisations we can compile series for the influence of the substituents on the rate of reaction or the activities of the reagents. The substituents are arranged according to their electronegativity and dimensions.

## 3. Polycondensation

Of the polycondensation phosphorus-containing resins, the best known are the phoryl resins of type $[OArOP(O)(OR)]_n$, which were obtained earlier [108] from phosphoryl chloride and polyhydric phenols. Subsequently analogous resins were made in which alkyl (or aryl) is attached directly to a phosphorus atom, from acid chlorides of phosphorus acids and polyhydric phenols or other compounds containing two or three hydroxyl groups. For example [110]:



where R′ is $CH_3$, and



In such a reaction the components are rapidly exhausted — after 4 h, 95% of the reactants have been consumed.

In carrying out polycondensations under ordinary conditions using methyl-, chloromethyl-, or phenyl-phosphonic dichlorides and hydroquinone as reagents, the reaction was less complete when the phenylphosphonic dichloride was used, which may be due to a steric effect of the substituent on the reaction rate. The degree of completion of the reaction also falls with an increase in the length of the alkyl group up to heptyl [111]. When the acid dichlorides react with glycols, especially with glycols having from 2 to 4 carbon atoms, cyclic esters are formed, which sensibly reduces the yield of polyester [111,112]. The reaction conditions, especially temperature and duration, have a marked effect on the rate of polycondensation (Figs. 4 and 5) [109-111].

By carrying out the polycondensation at high temperature or on heating in a vacuum, polymers could be obtained from dichloroethyl alkyl- and aryl-phosphonates, and also

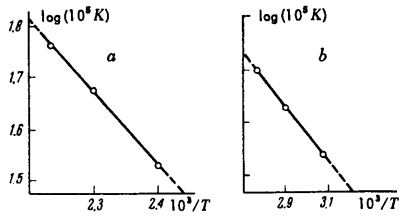



Fig. 4. Temperature dependence of the rate constants of the reaction of methylphosphonyl dichloride with: *a*) hydroquinone; *b*) diethylene glycol.

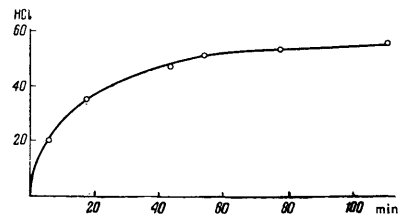



Fig. 5. Rate of liberation of HCl with time in the reaction of phenylphosphonyl dichloride with hydroquinone at 91°, with $MgCl_2$ catalyst. [The graph appears to give the total HCl liberated with time rather than the rate of liberation of HCl with time (Ed. of Translation).]

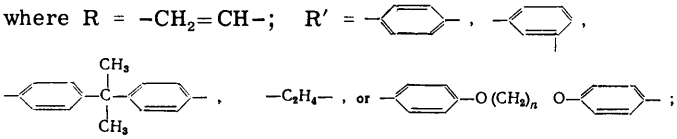
from phosphorus esters of the type $ClCH_2C_6H_4P(OR)_2$.[113-115] In investigating the polycondensation of di-2-chloroethyl methylphosphonate it was noted that an increase in the duration of the reaction brings about an increase in the yield of products of low molecular weight. It was also found that the yield of the polymer depends on the nature of the substituent and the temperature of the reaction. During the reaction[114,115]:

$$n\,ClCH_2C_6H_4P(OR)_2 \rightarrow -[-CH_2PC_6H_4CH_2-]_n- + RCl,$$
(O above P; OR below P)

the alkyl halide is released and the reaction mechanism is similar to that of the Arbuzov isomerisation.

Resins of type $-[-(R)P(O)OR'O-]_n-$ can be obtained by polymerisation[91,93-95,116,117]:

$$n\,RP(OR'')_2 + n\,HOR'OH \rightarrow -[-(R)P(O)OR'O]_n + R''OH,$$
(O above P)

where R = $-CH_2=CH-$; R′ = 

R′ = $C_2H_5$ or $C_6H_5$.

This reaction is carried out in the presence of catalysts — magnesium chloride or zinc acetate — at temperatures up to 250°. The reaction rate is greater with diphenyl vinylphosphonate than with the diethyl ester, but the yield of polyester is rather greater in the reaction of diphenyl vinylphosphonate with hydroquinone and diphenylpolypropane than with resorcinol. A change in the structure of the dihydroxy-compound has very little effect on the yield of polymer[91].

Ethylenepolyphosphites $[O(CH_2)_mOP(OH)]_n$ were obtained by poly(ester interchange), and polyesterification was used to give poly(phosphorus esters), polymers based on $(RCH_2)_2P(O)CH_2OCH_2CH(OH)R'$ [117,118] and various others. However, the activity of the monomers in these reactions in relation to their substituents has still not been studied.

There is considerable interest in studying the reaction of di(alkoxycarbonylaryl)phosphine oxides† with various diamines and hydroxy-compounds, and also in making polyphosphonamides[119-124]. The latter can be obtained thus:

$$C_6H_5P(O)(NH_2)_2 \xrightarrow{-NH_3} -(-P(O)(C_6H_5)-NH-)_n-$$

The structure of the polymer depends on the reaction temperature. Thus up to 275° polymers are obtained with molecular weight averaging from 300 to 400, which is explained by the formation of a cyclic dimer or trimer; above 300° polymers of higher molecular weight are obtained. Below 200° polycondensation products are not formed[122]. Polymers with P–N-type bonds

$$-[-P(O)(C_6H_5)N(CH_3)-]_n-,\quad -[-P(O)(NH_2)-NH-]_n-,\quad -[-P(O)(C_6H_5)-NHCONH-]_n-,\quad -[-P(O)(C_6H_5)-NHCSNH-]_n-$$

were obtained respectively from substituted phenylphosphonium diamines, $POCl_3$ and $NH_3$, phenylphosphonic diamides, and urea or thiourea[122-124]. Similar polymers can be obtained from nitrogenous compounds and phosphorus-containing acid dichlorides. Various polymers have been obtained using these acids and tetrahydroxymethylphosphonium derivatives[125-136].

## III. PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS

### 1. Low-Molecular-Weight Compounds

Physical properties are known to be related to the chemical ones, since both depend on the structure of the compound. And since reactivity can be evaluated by empirical quantities which quantitatively or semiquantitatively characterise the structural features of the compound, then it is natural for these quantities and the physical properties to show a relationship[137-141].

Thus, for organophosphorus compounds there is a quantitative relation between the displacement of the $-P(O)-$ bond frequency ($\gamma_{PO}$) and the Taft constants $\Sigma\sigma^*$, which can be expressed by the equation[137]:

$$\gamma_{PO} = 16.8\Sigma\sigma^* + 1198. \qquad (5)$$

Usually the values of $\gamma_{PO}$ calculated by Eqn. (5) and found experimentally agree or are very close. The value of

† For example $(MeO_2C.C_6H_4)_2P(O)Et$ (Ed. of Translation).

$\gamma_{PO}$ increases with the polarity of the substituent in phosphorus(V) compounds. As the steric hindrance increases it becomes necessary to introduce a correction into the value of $E_S$. Subsequent work has shown a linear relation between the absorption frequency of various bonds and the total inductive effect of the substituent groups[141].

In studying the nuclear quadrupolar resonance spectra of phosphorus compounds, in particular phosphoryl chloride and phosphorus trichloride, it is found that conjugation can be transmitted through the phosphorus(V) atoms. Furthermore, a relation has been reported between the electronegativity of the substituent and the resonance frequencies for the compounds $RP(O)Cl_2$.[142]

A relation is observed between the Taft constants and such physical properties as boiling and melting points, refractive indices, and density.

Table 5 shows the Taft constants and data on some physical properties of various organophosphorus compounds. Usually the melting or boiling points and refractive indices of these compounds increase with the polarity ($\sigma^*$) and with a decrease in steric hindrance $E$.

A change in the radical of the ester group at the phosphorus atom leads to the reverse dependence between polarity, the steric factors of the substituent, and the physical properties, which is characteristic for aliphatic radicals. Table 6 shows such results for phosphonic esters and phosphorodichloridates, together with the corresponding Taft constants and the physical properties of phosphoric acid derivatives containing aryl radicals in the ester group. In this case there is a linear relation between the polarity of the radical and the boiling point of the compound[143-150].

The relation between the nature of the substituent and the physical properties of the compound has been studied by other investigators[150-153] also. Despite individual exceptions it can be concluded that there is a connection between the nature of the substituent, which is characterised by the empirical quantities, and the physical properties of organophosphorus compounds containing this substituent.

TABLE 5. Taft constants for substituents of a series of phosphorus-containing compounds and their physical properties[108].

| Compound | $\sigma^*$ | $E_S$ | Boiling point, °C/mmHg | Melting point, °C | Refractive index |
|---|---|---|---|---|---|
| $RP(O)(OR')_2$ | | | | | |
| R: | | | | | |
| $C_2H_5$ | −0.10 | −0.07 | 53/30 | | 1.422 |
| $C_6H_5CH_2$ | +0.215 | −0.38 | 88—90/3 | | 1.503 |
| $C_6H_5$ | +0.60 | | 100/5 | | 1.513 |
| $ArPCl_2$ | | | | | |
| $p$-$CH_3C_6H_4$ | +0.6 | | 109—110/11 | | |
| $p$-$ClC_6H_4$ | +1.00 | | 132—133/20 | | |
| $m$-$ClC_6H_4$ | +1.04 | | 124—125/18 | | |
| $p$-$CNC_6H_4$ | +1.228 | | 127—128/4.5 | | |
| $ArP(O)(OH)H$ | | | | | |
| $m$-$ClC_6H_4$ | 1.04 | | | 90.9—91.5 | |
| $p$-$CNC_6H_4$ | 1.23 | | | 166—167 | |
| $ArP(O)(OH)_2$ | | | | | |
| $p$-$Cl(CH_2)_2C_6H_4$ | 0.985 | | | 137 | |
| $CH_2$-$CHC_6H_4$ | 1.00 | | | 173—174 | |
| $R(OH)P(O)CH_2CH_2CH(NH_2)COH$ | | | | | |
| $C_2H_5$ | −0.1 | −0.07 | | 185—187 | |
| $C_6H_5$ | +0.6 | | | 237 | |
| $RP(O)Cl_2$ | | | | | |
| 1) $ClCH_2$ | 1.05 | −0.24 | 77—78/10 | | 1.4978 |
| 2) $CH_3CCl_2$ | $\sigma_1^* < \sigma_2^*$ | | | 147—150 | |
| $C_5H_{11}$ | −0.17 | −0.4 | 64—69/2 | | 1.4694 |
| $C_6H_5$ | 0.6 | | 104/4 | | 1.5581 |
| 3) $C_6H_5CH_2$ | 0.215 | −0.38 | 130/2 | 57.5 | |
| 4) $C_6H_5CHCl$ | $\sigma_3^* < \sigma_4^*$ | | 124/2 | 61 | 1.566 |
| $p$-$CH_3OC_6H_4$ | 0.5 | | 173/12 | | |
| $p$-$CH_3C_6H_4$ | 0.6 | | 142/11 | | |
| $RP(O)(ArCOOH)_2$ | | | | | |
| $CH_3$ | 0.00 | | | 285 | |
| $C_2H_5$ | −0.10 | | | 265 | |
| $C_6H_5$ | 0.6 | | | 304—310 | |

TABLE 6. Taft constants for substituents in the ester group of a series of phosphorus-containing compounds and their physical properties[108,144-146].

| Compound | $\sigma^*$ | $E_S$ | Boiling point, °C/mmHg | Refractive index |
|---|---|---|---|---|
| $CH_3P(O)(OR)(OR')$ | | | | |
| $R'=C_6H_5$ | −0.10 | −0.07 | 82—83/25 | 1.4265 |
| $C_3H_7$ | −0.115 | −0.36 | 79/8 | 1.422 |
| $C_4H_9$ | −0.13 | −0.39 | 96/3.5 | 1.43 |
| $CH_3C(O)P(O)(OR)(OR')$ | | | | |
| $R'=C_2H_5$ | −0.10 | −0.07 | 76.5/2 | 1.435 |
| $C_3H_7$ | −0.115 | −0.36 | 67/1 | 1.436 |
| $ROP(O)Cl_2$ | | | | |
| $CH_3$ | 0.00 | 0.00 | 49 | |
| $C_2H_5$ | −0.10 | −0.07 | 58 | |
| $C_3H_7$ | −0.115 | −0.36 | 72 | |
| $C_4H_9$ | −0.13 | −0.39 | 84 | |
| $C_6H_5$ | +0.6 | — | 104/2 | 1.522 |
| $p$-$ClC_6H_4$ | 1.00 | — | 130/7 | 1.538 |
| 2,4,6-$Cl_3C_6H_2$ | 1.54 | — | 75 * | |
| 2,4,6-$(CH_3)Cl_2C_6H_2$ | 1.14 | — | 57 * | |

* Melting point, °C.

## 2. High-Molecular-Weight Compounds Obtained by Polymerisation

It is known that the presence in the polymer of a certain percentage of phosphorus brings about the appearance of self-extinguishing properties[49]. Thus, as the phosphorus content of poly(vinyl alcohol) fibres is increased, the flame resistance‡ of the fibre increases and the strength decreases. Table 7 gives data on the phosphorylation of poly(vinyl alcohol) fibres[154]. However, the flame resistance and the other physical properties of polymers depend not only on the phosphorus concentration but also on the nature of the substituent at the phosphorus atom. The structure of the polymers is determined by the structure of the monomers from which they are obtained. Therefore there is a definite correlation between certain physical properties of the monomer and of the polymer. For example, there is a relation between the thermal stability of the monomer and the flame resistance of the polymer[49]. With an increase in the former there is an increase in the latter. The flame resistance of polymeric phosphonates is greater than that of

TABLE 7. Comparison of the physical properties and phosphorus concentration of various fibres[154].

| Fibre | P in fibre, % | Strength, r.km* | Elongation, % | Flame resistance | Colour |
|---|---|---|---|---|---|
| Ordinary | — | 21.6 | 39 | burns | pale yellow |
| Phosphorylated | 1.94 | 16.1 | 43 | burns 1 s, does not smoulder | yellow |
| Phosphorylated | 6.02 | 14.7 | 67 | does not burn, does not smoulder | dark brick red |

* *Sic*; presumably an error. In the U.K., fibre strengths are normally expressed in g per denier (Ed. of Translation).

‡ Toy and Cooper's terminology.

polymeric phosphates (Table 8), mainly due to the greater stability of the P–C bond compared with that of the P–O–C bond[49,54].

Table 8 shows that the flame resistance of polymeric aromatic phosphonates is better than that of aliphatic ones despite a lower phosphorus content. Furthermore, such physical properties as melting point[57,59], softening point[66], and glass point[66] vary with the structure of the polymers. It has been noted that the glass points of polymers obtained on the basis of vinylphosphonate esters falls with increase in the length of the n-alkyl radical, but increases slightly with branching of the alkyl radical[66,68].

Fig. 6 shows the glass points of polymers obtained from vinylphosphonate esters as a function of the number of carbon atoms in the alkyl radical chain. The increase in the glass point can evidently be explained by an increase in the polarity of the radicals as the number of carbon atoms in the chain is reduced: $\sigma^*_{CH_3} = 0.00$, $\sigma^*_{C_2H_5} = -0.10$, $\sigma^*_{C_3H_7} = -0.115$, $\sigma^*_{C_4H_9} = -0.130$. Polymers are known which are obtained from methylphosphonic and vinylphosphonic dichlorides and diethylene glycol. Polyesters were obtained by polycondensations and were then polymerised at the vinyl groups. The softening point of these polymers increases with the concentration of vinyl groups in the polyester. Copolymers based on vinylphosphonic esters and various monomers, for example, acrylonitrile, have been obtained; their glass temperatures lie between 90° and 100°,[66] owing to the presence of the second component (acrylonitrile) in the copolymer.

Of the copolymers obtained from polybutyleneglycol fumarate and allyl phosphonates those with composition close to azeotropic have the best mechanical and dielectric properties[93,94]. The composition of the copolymers approximates to azeotropic in the region of relatively high polyester : monomer molar ratios (10 : 1).[92-95]

The thermal stability of the allyl alkylphosphonate copolymers depends on the alkyl group and on the ratio of the components in the reacting mass[108]. The relation between the polar§ factor of the substituent in the vinyl monomer and the softening point of the copolymer is shown in Table 9. In the copolymerisation of unsaturated phosphorus-containing polyesters with vinyl monomers[94] both the nature of the polyester and the vinyl monomer greatly influence the properties of the copolymer obtained. There is a sharp increase in the softening point when the polyester is obtained from an unsaturated phosphorus-containing acid and aromatic dihydroxy-compounds. However, when there is alternation in the polyester of aromatic bridges or groupings of the type $-Ar(CH_3)C(CH_3)Ar-$ it is necessary to allow for the steric factor of the substituent[80].

TABLE 8. Structure and flame resistance of phosphorus-containing polymers[49].

| Monomer | Flame resistance of polymer | Phosphorus in polymer, % |
|---|---|---|
| $C_6H_5P(O)(OCH_2CH=CH_2)_2$ | good | 13 |
| $CH_3P(O)(OCH_2CH=CH_2)_2$ | good | 17.6 |
| $i\text{-}C_4H_7P(O)(OCH_2CH=CH_2)_2$ | satisfactory | 14.4 |
| $P(O)(OCH_2CH=CH_2)_3$ | bad (burns) | 14.2 |
| $HP(O)(OCH_2CH=CH_2)_2$ | very bad (burns) | 19.2 |

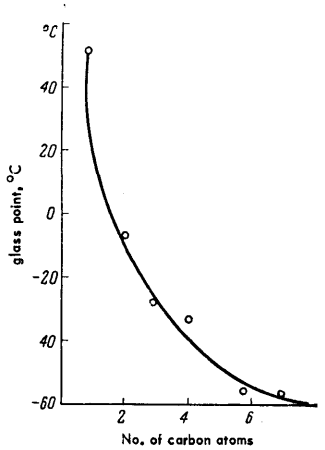



Fig. 6. Dependence of the glass point on the number of carbon atoms in the chain of the alkyl radical.

## 3. High-Molecular-Weight Compounds Obtained by Polycondensation

Attempts have been made to make a comparative appraisal of the dependence of polymer properties on structure for certain phosphorus-containing polymers obtained by polycondensations. Many investigators note[108,121,150,151,154,157,158] that replacement of a P–C bond by P–O–C in a side radical at a phosphorus atom leads to the formation of polymers with a lower softening point (Fig. 7). The physical properties of the polymer are greatly influenced not only by the structure of the phosphonic and phosphoric acid derivatives, but also by that of the dihydroxy-compounds which participate in the polyesterification. The introduction of aromatic structures in place of aliphatic in the polymer chain sharply increases the glass point[156].

From what has been said earlier it is evident that the Taft equation is applicable to the hydrolysis and alcoholysis of phosphoric compounds, and these are the back reactions to polyesterification. It is known that the molecular weight of the polymer depends on the reaction rate, and the properties of the polymer (softening and melting points) are

TABLE 9. Softening point of copolymers of vinylphosphate esters and some vinyl-containing monomers, and their Taft constants[4,108].

| Monomers | Proportion, % | $\sigma^*_R$ | $\sigma'_R$ | Softening point, °C | Reaction conditions |
|---|---|---|---|---|---|
| $(C_2H_5O)_2P(O)OCH=CH_2$ | 63.4 | | | | |
| $CH_2=CHR$ | 36.6 | | | | |
| $R=C_6H_5$ | | 0.6 | 0.1 | 68 | $N_2$, 4.93% $Bz_2O_2$, 80°, 42 h |
| $(C_2H_5O)_2P(O)OCH=CH_2$ | 64 | | | | |
| $CH_2=CHR$ | 36 | | | | |
| $R=CH_2OC(=O)$ | | 2.00 | 0.35 | 110 | $N_2$, 5% $Bz_2O_2$, 80°, 42 h |
| $(C_2H_5O)_2P(O)OCH=CH_2$ | 77 | | | | |
| $CH_2=CHR$ | 23 | | | | |
| $R=N\equiv C$ | | 1.95 | 0.6 | 210—220 | $N_2$, 6% $Bz_2O_2$, 80°, 42 h |

§ $\sigma'$ is the conjugation factor in $\sigma$ values, which characterises the interaction between the substituents and the reaction centre (Taft's terminology for $\sigma'$ is the resonance constituent of $\sigma$).

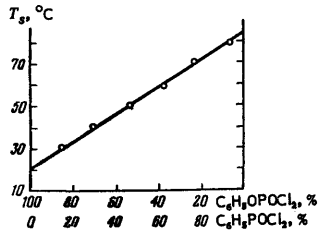



Fig.7. Softening points of mixed polyesters obtained from $C_6H_5POCl_2$, $C_6H_5OPOCl_2$, and hydroquinone.

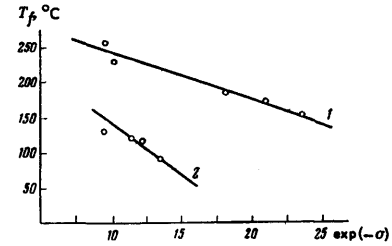
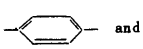
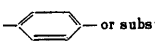


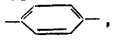

Fig.8. Dependence of the melting points of polymers with three P–C bonds on the constants $10\exp(-\sigma)$:
1) polyamides; 2) polyesters.

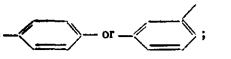
related to the molecular weight[162-163]. Therefore a relation between the Taft constants σ or $10\exp(-\sigma)$ and certain properties of polycondensation polymers is possible. Such a dependence can be traced by the example of phoryl resins, polymers with a lateral P–C bond, polymers with a P–N bond (polyureas and polyurethanes), and polymers with three P–C bonds (polyesters and polyamides)[103-112,115,125,151,153,160,161].

The conditions under which the reaction is performed have a great effect on the properties of the polymers; therefore they are best considered in groups of polymeric compounds obtained under almost identical conditions:

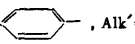
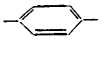
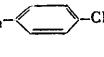
$-[-P(O)(OAr')OArO-]_n-$, where Ar =  and Ar′ is substituted phenyl;

$-[-P(O)(Alk)OArO-]_n-$, where Ar =  or substituted *p*-phenylene and Alk = $CH_3$, $C_6H_5$, $(CH_3)_2N$;

$-[-P(O)(Alk)NHC(=O)NHArNH-]_n-$ and $[P(O)(Alk)NHC(=O)Ar'O-]_n-$, where Ar = ,

Alk = $C_2H_5$, Ar′ =  or ;

$[P(O)(Alk)ArC(=O)OAlk'O]_n$, where Alk = $CH_3$, $C_2H_5$, $C_6H_5$, Ar = , Alk′ = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$;

$[P(O)(Alk)ArC(=O)NHAlk'NH]_n$, where Alk = $C_2H_5$, $C_6H_5$, Ar = , Alk′ = $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-(CH_2-)_{10}$, , $-CH_2-$$-CH_2-$.

Figs. 8 and 9 give data on the melting and softening points of various polymers as functions of $10\exp(-\sigma)$ and $\exp[-(\Sigma\sigma + \Sigma E_S)]$ respectively, and show that for most of the substituents in the phosphorus-containing component or in the phosphorus-free component an increase in σ and a decrease in $10\exp(-\sigma)$ for the substituents corresponds to increases in the softening and melting points.

The term Σσ was calculated, using the additivity principle, from published data[1-4]. The phosphorus-containing polyamides are distinguished by higher melting points than the polyesters, but polyamides from aromatic diamines have higher melting points than polyamides from aliphatic diamines. The effect of parity on the properties of phosphorus-containing polyamides is retained in the aliphatic series. Furthermore, the change in melting and softening points is more gradual for polyesters and polyamides than for polyurethanes and polyureas. The melting and softening points for the series of phosphorus-containing polymers are greater when the functional groups are in the *para*-position. The softening point increases with the polarity and with a decrease in the steric factor of the substituent.

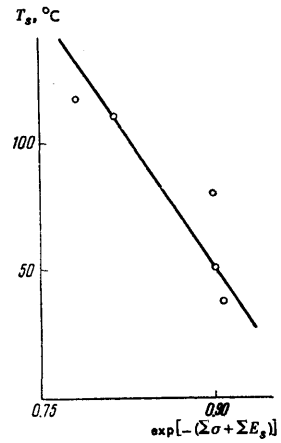



Fig.9. Dependence of the softening point of certain phoryl resins on the constant $\exp[-(\Sigma\sigma + \Sigma E_S)]$.

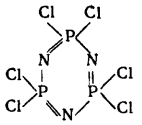
From the above it is evident that there is a relation between the Taft constants and certain properties of polymers, when the reaction proceeds under ordinary conditions. This has been confirmed repeatedly[164-166].

## IV. PROPERTIES OF INORGANIC AND ORGANO-ELEMENTAL PHOSPHORUS-CONTAINING COMPOUNDS

Dichlorophosphazene, from which thermally stable and fire-resistant polymers are now produced, corresponds to a series of polymers of general formula $(PNCl_2)_x$, where $x$ = 3, 4, 5, 6, 7, etc. The methods of preparing halogenophosphazenes and their derivatives have been described in many papers and reviews[167-184]; rather fewer works have been devoted to the structure of the halogenophosphazenes and their derivatives[176,184-191].

The cyclic structure of phosphazenes is retained in many reactions in which the chlorine atoms are replaced by other electronegative groups. However, such reactions relate mainly to trimeric and tetrameric chlorides (halides), since the higher polymers, for example, a mixture of composition $(PNCl_2)_{8-n}$ [where $n$ may be large (Ed. of Translation)],

are comparatively inert. Chlorophosphazenes are less reactive in hydrolysis than acid chlorides. The lower chlorophosphazenes have a cyclic structure which ensures that the compound has a high stability:

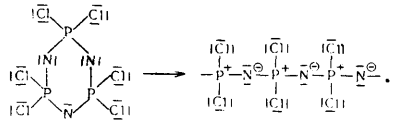


The chlorine and phosphorus atoms are situated in planes perpendicular to the $P_3N_3$ ring, which is planar in both the trimer and tetramer [176].

To study the structure, the frequencies of the bending vibrations of the P–N bonds were measured. The electronegativity of the substituent greatly affects the frequency of these vibrations (it increases with the electronegativity). With the cyclic halogenophosphazenes there is the possibility of using *d* orbitals for the formation of $\pi$ bonds [175], since the phosphorus atom has five electrons for four bonds formed from $sp^3$ hybrid orbitals, and a *d* orbital is left for the formation of a $\pi$ bond. In this, the *p* orbital and the *d* orbital have different symmetry and for maximal overlap must alternate in sign:



With an increase in the fractional positive charge on the phosphorus its reactivity towards nucleophilic reagents is increased. Steric effects must also be considered. Thus the inter- and intra-molecular forces of interaction of large chlorine atoms have a marked effect on stability [176,184,186]. Consequently, the stability and reactivity of halogenophosphazenes and their derivatives are determined by the polar and steric factors of the substituent at the phosphorus atom. It is also known that phosphorus(V) derivatives having a group of low electronegativity form cyclic halogenophosphazenes (polymers) with difficulty. The polymerisation of halogenophosphazenes usually proceeds with cleavage of the ring:



Oily halogenophosphazenes have a linear structure. Such a chain consists on the average of ten $-N-PCl_2-$ groups,

and at their ends are $-N=PCl_3$ or $-\overset{|}{\underset{|}{P}}=NH$ groups.

The linear polymers based on chlorophosphazenes are unstable to moisture. The replacement of chlorine by a radical increases the moisture resistance slightly [178–185], the increase being greater the more electronegative the radical. Polymers obtained from halogenophosphazenes have high thermal stability (up to 350–500°).

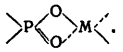
There have been some interesting studies of phosphinoborines and polymers based on them. Trimeric dialkylphosphinoborine has been studied in greater detail. The tetramers and high polymers which have been obtained are unstable and difficult to investigate. Phosphinoborines are hydrolysed by water only under very drastic conditions [192–195]. The reason for the chemical inertness lies in the nature of the covalent bond, which includes the 3*d* orbital of phosphorus [194]. The stability is also determined by the steric effects of the alkyl groups. Thus in the homologous series of alkylphosphinoborines — with substituents at boron of $(CH_3)_3P$, $(C_2H_5)_3P$, and $^i(C_3H_7)_3P$ — the stability falls to zero on account of the increasing steric hindrance and decreasing polarity of the substituents at the phosphorus atom [195]. Other investigators have also confirmed these facts [195–199].

Phosphorus- and silicon-containing polymers are also of interest [200–210]. They are obtained in the modification of hydroxyl derivatives of trimeric chlorophosphazene with chlorosilanes, in the reaction of phosphoric anhydrides or esters with derivatives of silanols, of phosphines with unsaturated silicon-containing compounds [200–202], and by other methods. Comparative data on the properties of monomers containing silicon and phosphorus are available. For example, it is noted that the more polar the substituent between silicon and phosphorus, the higher the melting point of the compound [205].

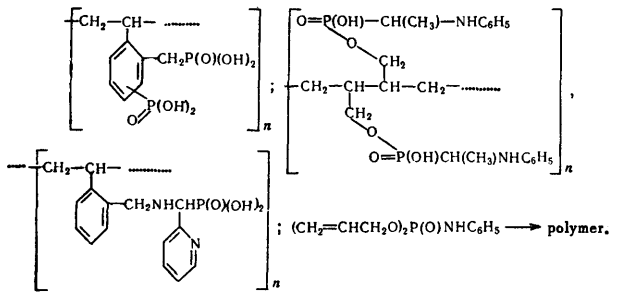
Polymers have been prepared containing phosphorus and selenium, titanium and phosphorus, tin and phosphorus, phosphorus and aluminium, and other neighbouring elements [211–214], but their properties have not yet been studied sufficiently.

The influence of the structure of phosphorus-containing monomers and polymers on salt formation and complex formation and on the properties of the compounds obtained has been studied [215–218]. Salt formation can be illustrated by the formation of salts of phenylphosphonic acid at definite pH in the medium [215].

Complex formation can proceed with monomers and polymers in the presence of $>PO(OH)$ groups, with the formation of monomeric or polymeric chelate complexes [216–218]. Thus, Kennard and his coworkers phosphorylated chloromethylated styrene cross-linked with divinylbenzene. The product forms with metal ions the four-dimensional chelate ring:



Analogous resins are obtained on the basis of allyl phosphates:



Resins of this type are used to separate copper, iron, and nickel ions, and partly for the separation of gold, palladium, and uranium ions. The activity of the resin in saltion to the metal ions changes in the following order:

$$Th^{4+} \text{ and } U^{4+} > UO_2^{2+} > Fe^{3+} > \text{rare earths} > H^+ > Cu^{2+} > Ba^{2+}.$$

The products formed as a result of complex formation have high thermal stability and strength [216]. When monomeric

complexes are formed, a change in the frequency of the bending vibrations of the $-\overset{|}{\underset{|}{P}}=O$ bond is possible, because in complex formation the following factors may affect the P–O bond. An increase in the charge on the metal ion and a decrease in its radius increase the deformation of the $P^+-O^-$ bond. At the same time, on account of the shift of electrons from the *p* orbital to the *d* orbital a decrease in the back-bonding (Cotton's terminology) of $O^--P^+$ is possible, and together with this a reduction in the bond deformation. A shift of the $d\pi$ electrons of the metal to the *p* orbital of oxygen, from which the electrons are displaced to the vacant *d* orbital of phosphorus, makes possible an increase in the bending vibration frequency of the P–O bond[218].

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The available published information on the effect of the structure of phosphorus-containing compounds on their reactivity and physical properties have been collected in this article, using, where possible, quantitative and semiquantitative characteristics (the Hammett and Taft constants). It should be noted that the published data on this subject are far from adequate and their use is hindered by the variety of conditions under which they were obtained. The authors hope, however, that this material will be of use in solving the problems of the production of phosphorus-containing compounds of desired properties.


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