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Gorky State University

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TRANSESTERIFICATION OF PHOSPHITES AND PHOSPHONITES WITH MONOHYDRIC AND POLYHYDRIC ALCOHOLS AND PHENOLS

K.A. Petrov and R.G. Gol'tsova

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I. INTRODUCTION

Twenty years ago the chemistry of the organic compounds of phosphorus entered a period of vigorous development. About a hundred years were required, after the first organophosphorus compounds had been prepared, for sufficient experimental results to accumulate and for the theoretical and practical value of certain compounds to be assessed, which determined the further development of this branch of organic chemistry. The most important work, which provided a foundation for further investigations, was undertaken by Michaelis, Arbuzov, and their many students.

At the present time the practical application of organophosphorus compounds is being continually extended. Because of their high thermal and chemical stability they are successfully employed as plasticisers for synthetic resins, on which they confer non-flammability, resistance to frost[1-3], and sometimes stability towards radiation[4]. The use of organic compounds of phosphorus as extractants[5,6] and flotation agents[7] is no less valuable. Substances containing phosphorus have proved to be valuable additives for lubricating oils, giving to the latter durability and several other desirable properties[8]. Polymers and oligomers containing phosphorus are used for the manufacture of ion-exchange resins, surface-active agents, adhesives, glasses with unique optical properties, etc.[9]

A large number of physiologically active substances of practical interest have been found among organophosphorus compounds. The chemistry of phosphorus occupies a primary place in the number and variety of pesticides. The products Thiophos, Chlorophos, Carbophos, Octamethyl, Butaphos, Ragor, Systoxes, etc. have received wide publicity, and are used in large quantities in agriculture.

Organophosphorus poisons, discovered during recent decades, are more toxic than all hitherto known poisons, and in this respect approach the most virulent compounds of vegetable and animal origin.

Organophosphorus compounds are used also as drugs, e.g. in the treatment of glaucoma (Phosarbin, Armin, Fosfakol)[10], tumours (TEPA, Thio-TEPA, DIPIN, etc.)[11,12], and cardiovascular diseases (hydrazides and amides of thiophosphates)[13]. Natural substances containing phosphorus — nucleic acids, phosphatides, coenzymes, glycopyrophosphates, and many others — are extremely important for the vital activity of organisms[14].

The organophosphorus compounds which find practical use or which are of importance in biochemical processes are mainly esters and amide–esters of phosphoric, phosphorothioic, and pyrophosphoric acids, derivatives of alkylphosphonic acids, and phosphine oxides. It is essentially the chemistry of phosphates and pyrophosphates which is of concern to industry and biochemistry. The importance of phosphates, phosphorothioates, and pyrophosphates is determined not only by their usefulness but also by their availability.

A common feature of several methods of obtaining these compounds is the use of acid and normal phosphorous esters as intermediates in their synthesis. Thus various phosphates are obtained by oxidising phosphites by the addition of sulphur to them, chlorination, reaction with sulphur chlorides, disulphides, thiocyanates, sulphenyl chlorides, chloramines, etc. The alkylation of sodium phosphites by Michaelis' method and of normal phosphites by Arbozov's method or the addition of dialkyl phosphites to unsaturated compounds, etc. yields phosphonates.

Thus phosphites, while being of intrinsic value in their use as such, possess high reactivity, and are therefore

key materials for the preparation of various organic compounds of phosphorus. However, the synthesis of phosphites by the reaction of alcohols with phosphorus trichloride often gives poor yields of the desired products, and sometimes leads to negative results, especially in the preparation of esters containing acid-labile groups. A good method for the synthesis of esters is transesterification, which is widely known in organic chemistry. Its application to the chemistry of carboxylic esters has especially varied aspects, and it has been studied in detail in the preparation of these compounds. The reaction occurs under comparatively mild conditions, is not accompanied by the liberation of corrosive products, and gives good yields of the required materials, so that it is often employed in the preparation of vitamins[15], proteins[16-18], lipids[19,20], and other labile compounds[21,22]. Alcoholysis of esters of dibasic and polybasic acids with glycols and polyols is employed for the synthesis of polymeric compounds[23]. For example, lavsan (Terylene) is obtained by the interaction of dimethyl terephthalate with ethylene glycol.

Study of transesterification has shown that, as a rule, the alkoxy-group of the ester is replaced by an alcohol radical of higher molecular weight. In some cases this does not apply: esters formed by phenols, glycol, glycerol, and some other hydroxy-compounds having enhanced acidic properties are transesterified by simple alcohols[21,24-26]. The presence of a double bond in the $\alpha\beta$-position to the alkoxycarbonyl group of the initial ester hinders transesterification[21,27,28], while the presence of electrophilic groups (phenyl, acetyl, acetoxyl, carboxyl, nitrile, carbonyl) favours alcoholysis[21,29-34]. Transesterification is accelerated by the addition of mineral acids[33,35], sodium alkoxides[36-39], and in isolated cases pyrophoric lead[40], oxides of magnesium and lead, and acetates of cadmium, zinc, and cobalt or a mixture of the oxides and acetates of these metals[41].

Esters of boric[42], silicic[43-46], titanic[47-49], antimonous[50], arsenious[51,52], and phosphoric acids also undergo transesterification, but considerably less work has been done on these reactions.

II. TRANSESTERIFICATION OF NORMAL PHOSPHITES

Esters of acids containing tervalent phosphorus readily undergo transesterification, which involves all or only some of the ester groups depending on the conditions, the structure of the initial reactants, and especially the proportions of the latter. In the former case symmetrical esters are produced, and in the latter mixed esters:

$$(RO)_3P + 3R'OH \longrightarrow (R'O)_3P,$$
$$(RO)_3P + 2R'OH \longrightarrow (R'O)_2POR,$$
$$(RO)_3P + R'OH \longrightarrow (RO)_2POR'.$$

The most detailed study of the reaction has been made on the alcoholysis of triethyl phosphite.

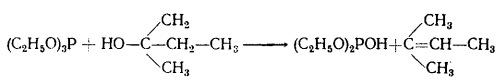
The exhaustive transesterification of triethyl phosphite was first studied by Arbuzov and Vinogradova: with a phosphite : alcohol molar ratio close to 1 : 3–4 in the presence of orthophosphoric acid, they obtained 30–50% yields of trihexyl, trioctyl, trinonyl, trihexadecyl, and tricyclohexyl phosphites[53]. The relatively low yield of products of complete transesterification is explained by the formation, with the above relative proportions of the reactants, of considerable quantities of mixed phosphites. This was subsequently confirmed by other investigators, who conducted the reaction in the presence of sodium alkoxides[54]. Even with a phosphite : alcohol ratio exceeding 1 : 5, unsymmetrical phosphites were detected among the reaction products[53-56]. With a ratio of 2 : 1 the reaction can be halted[55] at the first stage, i.e. at the formation mainly of monosubstituted products.

The mixed phosphites $(RO)_2POR'$ which are thus formed can react with another alcohol to form phosphites containing three different alkoxy-groups[54]:

$$(RO)_2POR' + HOR'' \longrightarrow (RO)(R'O)(R''O)P.$$

Derivatives of the lower alcohols are unstable and readily disproportionate on distillation. Mixed esters containing residues of higher alcohols are more stable to disproportionation: butyl dihexyl phosphite remains practically unchanged on distillation[54].

The character of the transesterification is greatly influenced by the structure of the initial alcohol. Whereas the alcoholysis of trialkyl phosphites by primary and secondary alcohols proceeds normally, diethyl hydrogen phosphite and 2-methylbut-2-ene have been isolated from the reaction between triethyl phosphite and t-pentyl alcohol[55]:

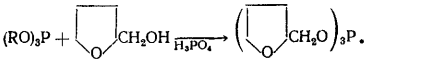


It was not established whether initial partial transesterification to diethyl isopentyl phosphite was followed by decomposition of the latter into the alkene and diethyl hydrogen phosphite, or whether the initial alcohol was dehydrated and the initial phosphite hydrolysed.

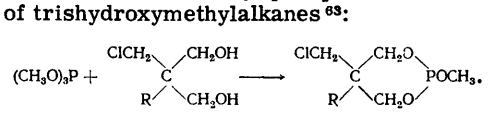
Alcoholysis by alcohols containing electronegative substituents (2,2,2-trichloroethanol, 2,2,2-trifluoroethanol) is extremely sluggish: with the latter alcohol only 4% of the monotransesterification product can be isolated[55]. This process goes considerably better with 2-alkylthioethanols, which possess less acidic hydroxyls[57-59]:

$$(RO)_3P + HOCH_2CH_2SR' \longrightarrow (RO)_2POCH_2CH_2SR',$$

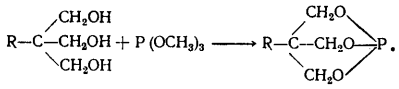
while with tetrahydrofurfuryl alcohol the product of complete transesterification is obtained in good yield[60]:



Trialkyl phosphites are transesterified not only by monohydric but also by polyhydric alcohols. However, few relevant data are available, and these are not soundly based. For example, it has been suggested that the use of glycol yields polyesters[61,62], although the conditions of the synthesis are not cited, and no evidence is given for the structure of the products. It is quite possible that in this case cyclic phosphites were obtained, as in the transesterification of trimethyl phosphite with monochlorohydrins of trishydroxymethylalkanes[63]:

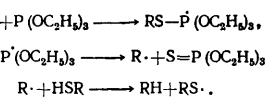


Trialkyl phosphites react with trishydroxymethylalkanes themselves to form products of complete transesterification — bridged cyclic phosphites — which it is difficult to prepare by other methods[63]:

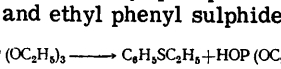


Phosphites are not transesterified by thiols, with which they interact to form hydrocarbons and phosphorothionates[64-66]:

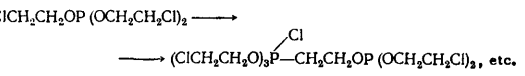
The reaction is catalysed by free radicals, and probably proceeds by a radical mechanism:



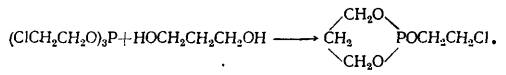
Benzenethiol reacts with triethyl phosphite to form diethyl hydrogen phosphite and ethyl phenyl sulphide[65]:



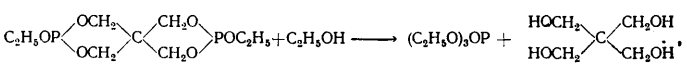
Phosphites of more complicated structure are also capable of undergoing transesterification. It has been stated that tris-2-chloroethyl phosphite can be completely transesterified more readily than triethyl phosphite with 2-ethylhexanol and benzyl alcohol even in the absence of a catalyst[62,67], but concrete data on the yields of the final products of alcoholysis are lacking. It was reported[67] that transesterification was accompanied by alkylation of the tris-2-chloroethyl phosphite with formation of a mixture of difficultly separable products:



Reaction of tris-2-chloroethyl phosphite with propane-1,3-diol leads to the formation of a cyclic phosphite[68]:



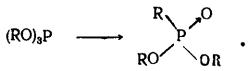
Another example of the alcoholysis of a complex phosphite is the transesterification of the dicyclic ester formed by pentaerythritol with two molecules of ethyl dihydrogen phosphite



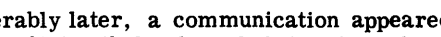
which also occurs under milder conditions than with simple phosphites[69].

The transesterification of triaryl phosphites has been studied mainly on the reactions of triphenyl phosphite with monohydric alcohols, glycols, and polyhydric phenols. This reaction also occurs in stages, but under milder conditions than with trialkyl phosphites.

The earliest data on the possibility of transesterifying esters of acids containing phosphorus were obtained in 1917 by Milobendzki and Szulgin using triphenyl phosphite[70]. These workers first tried to transesterify triphenyl phosphite with methanol and propanol by heating in glass tubes, but obtained negative results: under the experimental conditions the trialkyl phosphites formed isomerised into alkylphosphonates:



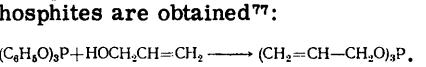
The complete transesterification product could be obtained only by using the alkoxides instead of the alcohols[70]:



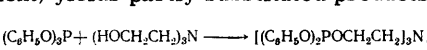
Considerably later, a communication appeared on the preparation of trimethyl and triethyl phosphites by complete transesterification of triaryl phosphites with alcohols[71]. It was remarked that the reaction goes smoothly in the presence of calcium or lead oxide, or sodium phenoxides or alkoxides. According to results obtained by the present Reviewers, the transesterification of triaryl phosphites with methanol and ethanol yields a difficultly separable mixture of products[72]. Satisfactory (60–99%) yields of the complete transesterification products are achieved only by using alcohols containing six or more carbon atoms and 2-naphthol.

The partial transesterification of triaryl phosphites has been studied more thoroughly[73-76]. Alkyl diaryl phosphites have been obtained by the reaction of triphenyl and tritolyl phosphites with butanol, octanol, hexadecanol, and cyclohexanol in equimolecular proportions. Mixed phosphites containing higher alkyl radicals, e.g. hexadecyl, have found application as antioxidants for lubricating oils[73,74].

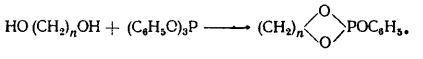
Triaryl phosphites are readily transesterified by various substituted alcohols, the completeness of the transesterification being found to depend on the proportions of the reactants. When allyl and 2-methylallyl alcohols are used with a phosphite : alcohol ratio close to 1 : 6, trialkenyl phosphites are obtained[77]:



At lower concentrations of the alcohol mixed alkenyl aryl phosphites are observed in the reaction products. Alcoholysis of triaryl phosphites (one mole) with aminoalkanols (one equivalent) yields partly substituted products[78]:

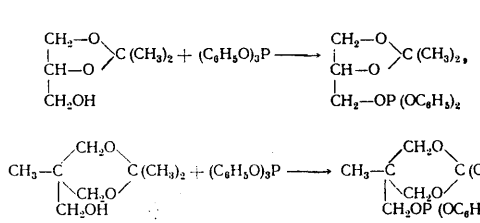


Triphenyl phosphite reacts with glycols to form cyclic phosphites[79]:



With glycols in which the hydroxyls were well separated ($n > 5$) polymeric products were formed, but were not characterised.

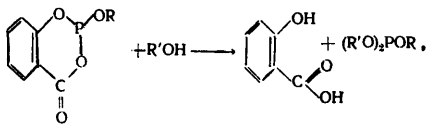
Transesterification of triphenyl phosphite with the isopropylidene derivatives of glycerol and metriol in equimolecular proportions gives high yields of the isopropylidenedioxyalkyl diphenyl phosphite, only one ester group of the phosphite being transesterified[80]:



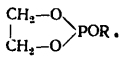
Reaction of triphenyl phosphite with cellulose at 130–135° yields a phosphorylated cellulose containing up to 5–6% of phosphorus[81].

When dihydric and trihydric phenols are used in this reaction, good yields are obtained of cross-linked or branched poly(arylene phosphites)[82]. The phenolic components used were quinol, 2,2-diphenylpropane-*pp'*-diol, and benzene-1,2,4-triol. Phenolysis occurred quite readily, and was accompanied by separation of almost the theoretical quantity of phenol. The presence of catalysts has little influence on the transesterification or the quality of the polymers. Poly(arylene phosphites) of network structure form an infusible, stable vitreous mass, which is insoluble in organic solvents.

Alkyl salicyloyl phosphites react with alcohols to form a mixed trialkyl phosphite and salicylic acid[83]:



The first stage probably involves cleavage of the anhydride link with formation of an *o*-dialkoxyphosphino-oxybenzoic acid, after which the aromatic radical of the phosphorous ester undergoes transesterification. The reaction goes vigorously with ethanol, isopentyl alcohol, and ethylene glycol, with formation in the last case of a cyclic ester



III. TRANSESTERIFICATION OF ACID PHOSPHITES

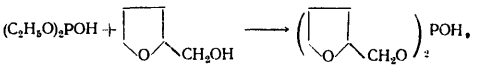
Dialkyl and diaryl phosphites, like normal phosphites, are transesterified by monohydric alcohols, glycols, and polyhydric phenols. The reaction occurs in stages (complete and partial), and can be terminated at the formation of unsymmetrical phosphites.

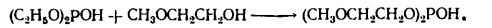
The complete transesterification of dialkyl phosphites was used for the first time by Arbuzov and Vinogradova for the synthesis of higher dialkyl phosphites[43]. With a phosphite : alcohol molar ratio of 1 : 2 in the presence of orthophosphoric acid they obtained symmetrical dialkyl phosphites mixed with considerable quantities of unsymmetrical phosphites, resulting from partial alcoholysis.

Interaction of dialkyl phosphites with cyclohexanol, benzyl alcohol, octan-2-ol, and ethylene glycol gave a complex mixture, from which pure substances could not be isolated. It was later found that the formation of transesterification products is accelerated in the presence of alkaline catalysts and an increased molar ratio of alcohol to phosphite[84–86]. With a phosphite : alcohol ratio of 1 : 3 in the presence of sodium ethoxide, symmetrical dialkyl phosphites were obtained in yields of 70–90%.[83]

The complete transesterification of dialkyl phosphites by aliphatic alcohols goes smoothly in xylene (with yields up to 85%) and in the absence of a catalyst[87]. Bis-2-ethylhexyl and bis-2-chloroethyl phosphites have been obtained in this way; in the presence of orthophosphoric acid without a solvent the yield of the latter is only 43%.[88]

Transesterification of diethyl phosphite with tetrahydrofurfuryl alcohol and 2-methoxyethanol in the presence of sodium gave the complete substitution products in yields of 44%[89] and 60.5%:[88]



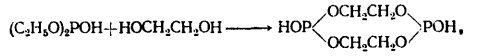


When diethyl phosphite was treated with β-hydroxypropionitrile in proportions of 1 : 3 in the presence of phosphoric acid, a 30% yield of the product of complete transesterification was obtained[88]. The reaction of phosphorus trichloride with β-hydroxypropionitrile results in a complex mixture of products, which it is almost impossible to separate[90].

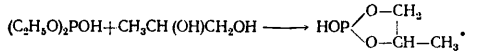
Complete replacement of alkoxy-groups has been reported in the transesterification of simple dialkyl phosphites with alcohols containing ethylenic and acetylenic bonds[91]. The reaction of bis-2-chloroethyl phosphite with 2-ethylhexan-1-ol occurs similarly[67]. Alcoholysis of dialkyl phosphites occurs more readily the more strongly electrophilic the substituents in their ester groups. Thus diethyl phosphite is transesterified by decanol at 160–170°, bis-2-chloroethyl phosphite at 140–150°, and bis-2-fluoroethyl phosphite at 120–130°.[88] With equimolecular proportions of the reactants in the presence of orthophosphoric acid or sodium ethoxide, or in the absence of a catalyst, mixed dialkyl phosphites are formed in yields of 24–45%.[43,85,92]

Unsymmetrical phosphites can be used to obtain various unsymmetrical esters of phosphoric and phosphonic acids[93], individual representatives of which possess physiological activity.

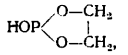
The transesterification of dialkyl phosphites with glycols is of great interest. Several papers have been published on the reactions of diethyl hydrogen phosphite with ethylene glycol, but results obtained by different investigators are mutually contradictory. It has been reported[68] that in the presence of sodium a bisphosphite containing a ten-membered ring is obtained:



while with other glycols, in particular propane-1,2-diol, a phosphite containing a five-membered ring is formed:

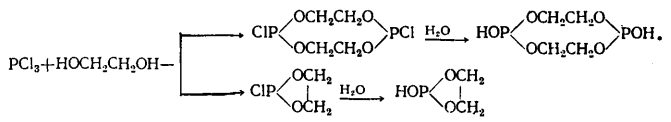


Several other papers suggest that the transesterification of dialkyl phosphites with glycols, mainly ethylene glycol (under similar conditions), yields polymeric products[94–96]. In no case, however, is any evidence given for the structure of the substances which are formed. Nevertheless, we cannot exclude the formation, in the transesterification of diethyl phosphite with a glycol, of a linear bisphosphite — the partial transesterification product $C_2H_5OP(OH).OCH_2CH_2OP(OH)OC_2H_5$ — and the five-membered cyclic phosphite



which are similar in composition to the ten-membered cyclic bisphosphite. The linear bisphosphite is unknown;

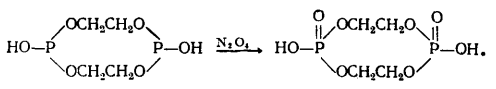
cyclic mono- and bis-phosphites have previously been obtained from the same starting materials under analogous conditions[97-103], and their structures have also not been proved:



It has subsequently been shown, as a result of a detailed study of this reaction[104], that, with equimolecular proportions of diethyl phosphite and glycol in the presence of sodium at 135–140° (200 mm) a substance is obtained which distils almost completely under vacuum. Elementary analysis and molecular weight determination† show it to correspond to a ten-membered cyclic bisphosphite.

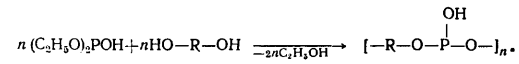
The same product is obtained by the action of ethylene glycol on bis-2-chloroethyl phosphite.

On oxidation with nitrogen dioxide the cyclic bisphosphite is converted into the corresponding bisphosphate, which can be titrated as a dibasic acid:



Polyesters containing two or three residues of the starting materials are formed when diethyl phosphite is transesterified with di-, tetra, and hexa-ethylene glycols, propylene glycol, butane-1,3-diol, butane-1,4-diol, but-2-yne-1,4-diol, and bis-2-hydroxyethylamine[96].

Polyphosphites of high molecular weight are readily formed by the reaction of diethyl phosphite and other simple dialkyl phosphites with glycols which either possess spatially isolated hydroxyls or are unstable in conformations with adjacent hydroxyls[105,106]:



Positive results were obtained with the following glycols — pentane-1,5-diol, hexane-1,6-diol, diethylene glycol, triethylene glycol, diethanols, pentafluoropentane-1,5-diol, 1,4:3,6-dianhydrosorbitol, *p*-bishydroxymethylbenzene, and 2,2-bischloromethylpropane-1,3-diol — but polyphosphites could not be obtained with 1,4-diols, dehydration of the glycol probably occurring in this case with the formation of tetrahydrofuran.

Polyphosphites were synthesised by heating an equimolecular mixture of the reactants with a catalytic quantity of metallic sodium in a stream of an inert gas at 130–150°,

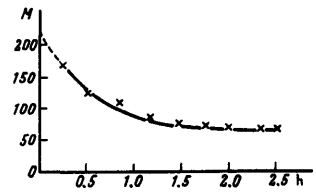


Fig. 1. Dependence of molecular weight *M* of diethylene bisphosphite on time of storage of the solution .

first at atmospheric pressure and then at reduced pressure (200 mm). Reaction was complete in 5–6 h. It is considerably more difficult to transesterify phosphites with 1,4:3,6-dianhydrosorbitol and pentafluoropentane-1,5-diol. This is probably due in the first case to the use of a secondary alcohol, and in the second case to the fact that the glycol is considerably more acidic than the other diols. Better results are obtained in the transesterification of bis-2-chloroethyl phosphite.

The polyphosphites obtained are thick liquids or vitreous materials, faintly yellowish, and soluble in most polar organic solvents; polyphosphites containing a heteroatom in the alkylene radicals are soluble in water. An exception to this rule is provided by the polyphosphite obtained from *p*-bishydroxymethylbenzene, which dissolves in no known solvent. This polymer is distinguished also by high thermal stability: under conditions of prolonged heating it begins to change only at 300–500° (Fig. 2).

The linear polyphosphites had molecular weights of $23-150 \times 10^3$ determined by light scattering.

As the excess of glycol in the reaction mixture is increased, polymers of lower specific viscosity are formed on transesterification. The regular fall in viscosity of the products is probably due to the formation of oligomers under the given conditions.

Thus the transesterification of dialkyl phosphites with glycols is a convenient method of synthesising polyphosphites. From the point of view of practical application, however, the method has the disadvantage that many glycols are still relatively difficult to obtain. It is therefore of interest to use the readily accessible polyols — glycerol and pentaerythritol[106,107].

The molecular weights of the polyphosphites obtained do not usually exceed 1000–1500, probably owing to contamination of the polyesters with cyclic phosphites of the polyols. On prolonged storage and heating, the cyclic esters are converted into polymeric compounds, since the specific viscosities of the solutions are greatly increased.

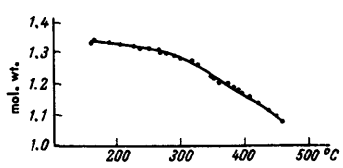
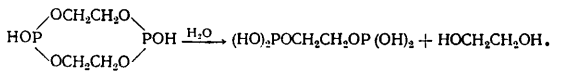


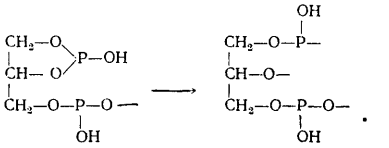
Fig. 2. Thermal stability of poly-(*p*-xylylene phosphite).

† The molecular weight was determined cryoscopically in water. Its value depends on the time of storage of the solution, the maximum of 220 (found by extrapolation) falling to 60 and then remaining unchanged for a long time (Fig. 1). This is probably explained by hydrolysis of the cyclic bisphosphite:



Titration of the hydrolysis product showed that a dibasic acid had been formed.

Thus the product obtained from glycerol and diethyl phosphite, for example, having a specific viscosity of 0.36, has almost double this viscosity after storage for 2 months; after heating at 175–180° for 10 h the viscosity rises to 0.50, and for 20 h to 0.74.



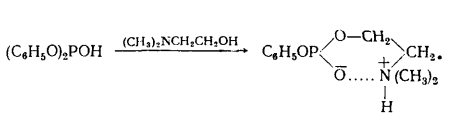
Transesterification of diethyl phosphite with cellulose in the presence of sodium at 160–165° yields a cellulose phosphite containing up to 6.4% of phosphorus [81].

Poly(arylene phosphites) have been obtained by the transesterification of dialkyl phosphites with dihydric phenols [106,108–110].

The transesterification of diaryl phosphites has been studied only with diphenyl phosphite, which is almost quantitatively transesterified by butyl, isopentyl, hexyl, octyl, nonyl, and decyl alcohols even at 100° without the phenol being distilled off from the reaction mixture during the process [111,112]. The duration of the reaction depends on the molecular weight of the alcohol used, normally varying over the range 4–10 h. The synthesis goes smoothly both in the presence and in the absence of a catalyst (sodium). Yields of the products of complete transesterification are 90–95%. It is noteworthy, however, that our own experiments under the conditions described have not given positive results.

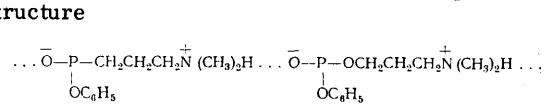
Diphenyl phosphite reacts readily with substituted alcohols [111]. The reactions with 2-chloroethanol and ethyl glycollate, for example, gave the complete transesterification products in yields of 93% and 94% respectively.

Diphenyl phosphite is also readily transesterified by aminoalcohols. When equimolecular quantities of diphenyl phosphite and dimethylaminoethanol are mixed, for example, heat is evolved, and one mole of phenol separates; the crystalline product is formed in almost quantitative yield. The substance is soluble in water and is readily oxidised. In view of this, and also the results of elementary analysis, the compound may be assumed to be an internal salt of dimethylaminoethyl phenyl hydrogen phosphite:

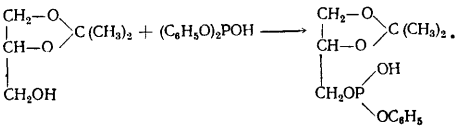


Diethylhydroxyethylmethylammonium iodide reacts with greater difficulty.

Alcoholysis of diphenyl phosphite with dimethylaminopropanol under similar conditions yields a thick oil, which does not crystallise on prolonged standing. The product is soluble in certain polar organic solvents, e.g. in *p*-cresol. Its molecular weight (determined cryoscopically in this solvent) is 4000. The structure of the polymer was not elucidated. By analogy with the product of the transesterification of diphenyl phosphite with dimethylaminoethanol, we may assume that in this case the polymer has the structure

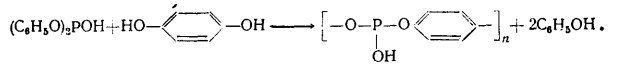


Alcoholysis of diphenyl phosphite with isopropylidene derivatives of glycerol and metriol gives good yields of the isopropylidenedioxyalkyl phenyl hydrogen phosphites [80]:



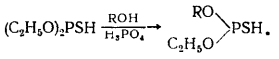
Cross-linked polyphosphites have been obtained by the transesterification of diphenyl phosphite with α-methyl-, *N*-phenyl-, and α-propyl-glucosides [113].

Reaction of diphenyl phosphite with quinol yields a poly(arylene phosphite) [82]:



The poly(arylene hydrogen phosphite) is unstable to hydrolysis whether in neutral, acid, or alkaline medium.

Diethyl phosphorothioite is transesterified by alcohols with considerably greater difficulty than are dialkyl (or diaryl) phosphites: in this case only 32–39% yields of the partial substitution products are obtained [114]:



IV. TRANSESTERIFICATION OF PHOSPHONITES

Few papers have been published on the transesterification of normal esters of alkylphosphonous acids. The complete transesterification of diethyl butylphosphonite with butanol in the presence of metallic sodium occurs more readily than in the case of phosphites [115]. Transesterification of simple phosphonites with substituted alcohols containing electrophilic groups takes place under more severe conditions [88], the yields of the complete transesterification products being considerably diminished. Thus diethyl phenylphosphonite is transesterified by ethyl glycollate, tetrahydrofurfuryl alcohol, and furfuryl alcohol in the presence of sodium to give yields of 40.7%, 61.5%, and 19.2% respectively. In the absence of catalysts the alcoholysis of phosphonites results in the formation of mixtures of complete and partial transesterification products [58,116]. Unsymmetrical phosphonites, obtained by the transesterification of phosphonous esters with 2-alkylthioethanols, have been used for the synthesis of Systoxes [58,117].

The polytransesterification of dimethyl and diethyl phenylphosphonites and diethyl ethylphosphonite with equimolecular quantities of various glycols has been investigated [118]. The rate and the degree of completion of the reaction decrease in the sequence ethylene, diethylene, and tetraethylene glycols. The reaction was found to involve the intermediate formation of cyclic phosphonous esters.

The transesterification of diethyl phenylphosphonite with glycerol and pentaerythritol has been studied [107] with various relative proportions of the reactants and under various temperature conditions. The best results were obtained at 140°. The polymers obtained were thick, viscous liquids or vitreous masses, yellow or light brown in colour, insoluble in water but soluble in benzene and dichloroethane; many of the polyesters were soluble in

ethanol and dimethylformamide. Bis-2-chloroethyl phenylphosphonite shows a great tendency to transesterification [119], undergoing the reaction even at 30–40°.

Phenyl esters of alkyl(or aryl)phosphonous acids react readily [72]:

$$RP(OC_6H_5)_2 \xrightarrow{R'OH} RP(OR')_2,$$

the yields of the complete transesterification products being 78–84%. Diphenyl methyl- and phenyl-phosphonites have been successfully employed for the phosphorylation of various nucleotides [120] and glucosides [113], mixed esters being obtained in the first case, and network polyphosphonites in the second case.

The transesterification of aromatic esters of phosphonous acids with dihydric and trihydric phenols yields poly(arylene phosphonites) [82]:

$$RP(OC_6H_5)_2 + HOR'OH \xrightarrow[-C_6H_5OH]{} \left[\begin{array}{c} -P-OR'O- \\ | \\ R \end{array}\right]_n,$$

where R = CH_3, C_6H_5 and R′ = C_6H_4, $C_6H_4.C_6H_4$, $C_6H_4.C(CH_3)_2.C_6H_4$. Diphenyl methyl- and phenyl-phosphonites have been used as the phosphorus-containing components, and quinol, biphenyl-*pp*′-diol, and 2,2-diphenylpropane-*pp*′-diol as the phenolic components. Phenolysis was accomplished quite readily, and was accompanied by the separation of almost the theoretical quantity of phenol. The yields of polyphosphonites were close to quantitative.

Hardly any work has been done on the transesterification of dialkylphosphinous esters. There is only the statement that the alcoholysis of propyl dipropylphosphinite with β-hydroxypropionitrile, 2-hydroxyethanol, and furfuryl alcohol in the presence of sodium gives the complete transesterification products in yields of 44.3%, 28.4%, and 36.3% respectively [88].

A detailed study has been made of the transesterification of acid esters of methylphosphonous acid. The dependence of the reaction on the temperature conditions, the relative proportions of the reactants, and the catalyst has been investigated with the interaction of ethyl hydrogen methylphosphonite and hexan-1-ol as example [121]:

$$CH_3P(OH)(OC_2H_5) + C_6H_{13}OH \longrightarrow CH_3P(OH)(OC_6H_{13}) + C_2H_5OH.$$

The best results are obtained with equimolecular proportions of the reactants in the presence of metallic sodium as catalyst at 150–160°. The temperature can be somewhat lower if the process is conducted in a slight vacuum, but the yield of phosphonite is then diminished. A definite though smaller catalytic effect is also shown by zinc borate; zinc chloride, orthophosphoric acid, and aluminium chloride impede transesterification.

The transesterification of phosphonites takes place more readily the lower the molecular weight of the alkoxy-residue. Under optimum conditions (after 5 h) the yields obtained with hexan-1-ol were respectively 71.5% and 44.4% for methyl and isopropyl methylphosphonites. Methyl methylphosphonite (yield 64.3%) constitutes an exception to this rule, for it partly decomposes under the reaction conditions.

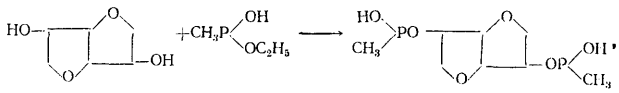
Transesterification occurs more readily with primary alcohols, and less readily with secondary alcohols [121]. Attempts to effect alcoholysis with tertiary alcohols (in the case of 1,1-dimethylpentan-1-ol) were unsuccessful.

Investigation of the transesterification of ethyl hydrogen methylphosphonite with alcohols containing functional groups has shown that the yield of ester depends substantially on the nature of the substituent and on its position in the alcohol molecule: the more electrophilic the substituent and the closer it is to the carbon atom attached to the hydroxyl the more difficult is it to effect transesterification [88]. Thus 2-chloroethanol reacts with greater difficulty (yield 45%) than does 3-chloropropanol (60%), furfuryl alcohol (10%) reacts less readily than does tetrahydrofurfuryl alcohol (69.7%), etc. Ethyl hydrogen methylphosphonite readily undergoes alcoholysis with 2-methoxyethanol and aminoethanol, the yields of the transesterification products being 70% and 100% respectively.

Ethyl hydrogen methylphosphonite reacts smoothly with glycols to give good yields of bismethylphosphonites [122], e.g.

$$CH_3P(OH)(OC_2H_5) + HOCH_2CH_2OH \longrightarrow CH_3(HO)POCH_2CH_2OP(OH)CH_3.$$

A similar reaction occurs with 1,4:3,6-dianhydromannitol:



as also with 1,2:3,4-di-isopropylidenegalactose [123]. Transesterification of ethyl hydrogen methylphosphonite with 1,4:3,6-dianhydrosorbitol occurs under more severe conditions, and yields only the monophosphonite of dianhydrosorbitol. When isopropylidene derivatives of glycerol and metriol are used in this reaction, the isopropylidenedioxyalkyl phosphonites are formed in high yields [80].

It has not proved possible to transesterify an acid ester of methylphosphonous acid with ethylene glycol to involve only one of the hydroxyls: in all cases, even with a large excess of the glycol present, only the bisphosphonite is formed [122].

The bisphosphonites obtained are thick liquids or else solids, which can be distilled without decomposition only in a high vacuum. They are sparingly soluble in most of the usual solvents; the simplest of them are soluble in water and in alcohol [124].

A phosphorylated cellulose having a high phosphorus content (up to 19.1%) has been obtained by transesterifying methyl and ethyl hydrogen methylphosphonites with cellulose, while a phosphorylated polysaccharide containing up to 23% of phosphorus has been obtained with inulin [81].

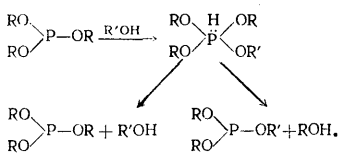
Diethyl methylphosphonodithioite reacts with both primary and secondary alcohols to form methylphosphonous esters [125]:

$$CH_3P(SC_2H_5)_2 + 2ROH \longrightarrow CH_3P(OR)_2 + 2C_2H_5SH.$$

The yield of phosphonites did not exceed 25–50%, being lower than in the transesterification of acid phosphonous esters. The probable reason is that the thiol liberated in the reaction and its oxidation product (disulphide) interact with the phosphonite to form a complicated mixture of compounds.

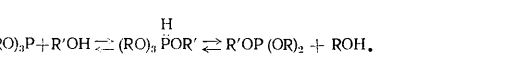
V. MECHAMISM OF THE TRANSESTERIFICATION OF ESTERS OF ACIDS FORMED BY TERVALENT PHOSPHORUS

No detailed study has been made of the mechanism by which esters of acids containing tervalent phosphorus are transesterified. The mechanism is assumed[55,121] to involve alternating addition of a proton to the phosphorus atom with addition of an alkoxide anion to the phosphonium cation and elimination of alcohol from the intermediate product containing quinquevalent phosphorus to form either the original or a different phosphite or phosphonite:



Indirect evidence for the formation of an intermediate addition product is provided by data on the mechanism of the Arbuzov reaction and its various modifications, and also by experimental results on the alcoholysis of esters of tervalent phosphorus acids.

The primary step in the reaction is necessary but insufficient to achieve transesterification of the phosphite (or phosphonite). As shown above, the adduct can break down in two ways. An equilibrium is established in the alcoholysis of any phosphite with any alcohol:



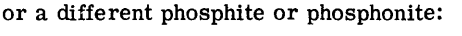
Transesterification will take place if the equilibrium is displaced to the right, i.e. if an alkoxyl (or phenol residue) of the original phosphite — not the alkoxyl of the alcohol taken for the transesterification — splits off from the adduct. Thus the second step in the reaction — cleavage of the addition product — plays the decisive part in the process of transesterification, and probably determines not only the direction but also the rate of the reaction.

Which alcohol will be eliminated from the intermediate product depends directly on the electrophilic character of the alkoxy(or phenoxy)-groups involved. It is obvious that the more electrophilic an alkoxyl the more preferentially will it be eliminated together with a proton in the form of the "more acidic" alcohol. Hence it is desirable, in the preparation of phosphites by transesterification, for the alkoxy-groups in the original phosphite to be more electrophilic than the alkoxyl of the alcohols used in the reaction.

The above arguments are consistent with data obtained for the transesterification of diethyl, bis-2-chloroethyl, bis-2-fluoroethyl, and diphenyl phosphites with decanol, of diethyl phosphite with β-hydroxypropionitrile, 2-chloroethanol, and 2-methoxyethanol, of ethyl hydrogen methylphosphonite with aminoethanol, 2-methoxyethanol, β-hydroxypropionitrile, 3-chloropropanol, etc.

The transesterification equilibrium can be shifted to the right by distilling off the alcohol which is liberated. This procedure is widely used to prepare various phosphites when the liberated alcohol boils at a lower temperature than the original alcohol.

Another possible mechanism consists in attack on the oxygen atom by an alkyl cation (formed by heterolytic cleavage of the alcohol) with simultaneous liberation of the alkyl cation of the original ester[55]:



However, this reaction is only of secondary importance, since transesterification with the two optically active butan-2-ols and with optically active neopentanol yields phosphites which on hydrolysis give alcohols having 75% and 100% respectively of the original optical activity. If only the second type of reaction had taken place, hydrolysis of the products of transesterification should have produced optically inactive alcohols.

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NEW THEORIES OF THE CHEMICAL NATURE OF LUMINESCENCE CENTRES IN ZINC SULPHIDE PHOSPHORS

A.M. Gurvich

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I. INTRODUCTION

The chemistry of sulphide phosphors of the ZnS type is an important and very interesting area of solid state chemistry†. Because of their high luminescence efficiency under a variety of excitation conditions, and of the unusually wide range of their properties, crystal phosphors of this class have found extensive technical applications in television tubes, radar screens, oscilloscopes, electron--optical converters, X-ray screens, electroluminescent panels, electron microscopes, dosimeters and detectors of different types of radiation, etc. Cadmium sulphide crystals, which belong to the same class of materials, are among the most sensitive photoconductors.

The influence of very small traces of impurities on these two properties of crystalline sulphides — luminescence and photoconductivity — was recognised at the turn of the century. The efficiency with which the absorbed radiant energy is transformed into visible light (of spectral composition determined by the nature of an impurity, termed the activator) suggested that energy transfer takes place from the sites where energy is absorbed to the sites where the activator is located. This gave rise to the theory that the luminescence centres are special groupings where the act of light emission occurs. The ability of ZnS and CdS crystals to transmit the absorbed energy with high efficiency to the luminescence centres accounts for their high luminescence yield, their high photoconductivity, and the extreme sensitivity of phosphors of this class to a number of impurities, which can effect the optical properties of these phosphors even at a concentration of 10^{-6}–10^{-8} gramme per gramme of the sulphide.

Elucidation of the nature of the luminescence centres and of the relationship between the optical properties of phosphors and the structure of these centres, being one aspect of the more general problem of establishing the relation between the atomic–molecular structure and the properties of materials, is the key problem in luminescence and is of great importance in the general development of solid state chemistry and physics. Yet the first serious studies in this field began only towards the end of the 1940's, when research on the kinetics of luminescence and on the accompanying internal photoeffect provided, on the basis of the band model of solids, a fairly orderly picture of the physical effects involves in the luminescence of zinc sulphide luminous compositions. The work done in the last 15–20 years and still in progress has significantly changed our ideas on the nature of the luminescence centres and on the processes by which they are formed, and has made it clear that the solution of the problem lies in the domain of chemistry to a much greater extent than had originally been realised. Many difficulties still remain to be overcome, in particular those associated with the extreme sensitivity of the optical properties of zinc sulphide phosphors to various impurities present at a concentration level which defies analytical control with the required degree of precision, and also with our inadequate knowledge of the nature of structural defects and of the role played by these defects in the formation of sulphide phosphors. The situation is made worse by the abundant literature and by the close interplay of chemistry and physics: as a result, authors attempting to interpret their

† Luminescent crystals of zinc sulphide were prepared for the first time 100 years ago by Sidot, in Sainte-Clare Deville's laboratory.