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Electrochemical syntheses based on elemental phosphorus and phosphorous acid esters

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Abstract. The literature data on the electrochemical synthesis of phosphorous acid and phosphoric acid esters from elemental phosphorus are surveyed. The possible mechanisms of the electrode processes are discussed. The procedures for the employment of electrolysis in the preparation of various derivatives of phosphorous acid esters are examined. The bibliography includes 63 references.

I. Introduction

The syntheses of phosphorus-containing compounds based on elemental phosphorus have become important because they make it possible to reduce significantly the amount of industrial waste compared with the classical methods employing phosphorus chlorides. The review of Dorfman et al.[1] published in 1993 contains information about the chemical methods for the syntheses of phosphorus-containing compounds from elemental phosphorus, but electrochemical methods are not considered although numerous studies demonstrating that this aspect is promising have been published during the last decade. It has been established that phosphorus exhibits an electrochemical activity in both anodic and cathodic processes. This make it possible to obtain various phosphorus-containing compounds in a single stage and under mild conditions. Electrochemical methods have been used successfully also for the syntheses of various phosphorous acid esters. Although in many cases the details of the mechanisms of the electrode processes occurring remain obscure, the synthetic possibilities of the electrochemical methods are evident. The aim of the present review is to survey the experimental data which have accumulated hitherto in this field.

II. Syntheses based on the anodic oxidation of phosphorus

It has been found that in alkaline and acid solutions white phosphorus gives rise to a distinct oxidation wave at a carbon paste anode at a potential of 1.08 V.[2] According to coulometric measurements, between 12 and 16 electrons are consumed in the oxidation of a phosphorus molecule in acid solutions. On these grounds, it is concluded that the anodic oxidation of phosphorus results in the formation of a mixture phosphoric and phosphorous acids. In an alkaline medium, the process is complicated by the oxidation of PH_3 — the product of the interaction of phosphorus with water.

The development of a process for the preparation of phosphorous acid by oxidising a suspension of white phosphorus in the presence of hydrogen halide solutions constitutes an interesting attempt at the practical employment of the anodic oxidation of phosphorus.[3] The best yield of phosphorous acid is attained in the presence of hydriodic acid. Hydrobromic acid yielded somewhat poorer results. It is postulated that the anodic process includes several stages: the generation of the free halogen, the interaction of the latter with phosphorus, and finally the hydrolysis by water of the phosphorus trihalide formed in the second stage to phosohorous acid.

$$3Hal^- \longrightarrow 3Hal^{\bullet} + 3e,$$
$$P + 3Hal^{\bullet} \longrightarrow PHal_3,$$
$$PHal_3 + 3H_2O \longrightarrow H_3PO_3 + 3HHal,$$
$$P + 3H_2O \longrightarrow H_3PO_3 + 3H^+ + 3e.$$

The hydrogen halide is not consumed in the process but acts as a homogeneous catalyst. It is recommended that a two-phase electrolyte, constituting a mixture of water and benzene, be employed.

This method makes it possible to obtain only relatively dilute solutions of phosphorous acid, since the accumulation of the acid during electrolysis leads to its partial oxidation to phosphoric acid. Furthermore, the phosphorous acid formed contains a small admixture of the hydrogen halide, the complete elimination of which is difficult.

The direct synthesis of phosphoric acid is of much greater interest. The possibility, in principle, of obtaining phosphoric acid esters by electrolysing suspensions of red phosphorus in an aliphatic alcohol was first demonstrated by Varshavskii et al.[4] The electrolysis was carried out in a diaphragm-free electrolyser with an anode and cathode made of graphite. During electrolysis, the solution containing a suspension of red phosphorus in a aliphatic alcohol was saturated with dry hydrogen chloride. It was noted that the change in current density in the range from 400 to 1000 A m^{-2} and at temperatures from 20 to 50 °C hardly affects the yield of trialkyl phosphates. It is suggested that the overall anodic oxidation process proceeds in accordance with the equation

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$$P + HCl + 4ROH \xrightarrow{5F} (RO)_3PO + 2.5H_2 + RCl.$$

However, the amount of alkyl chloride isolated proved to be much smaller than might have been expected from the above equation. The following phosphoric acid esters have been obtained by this method:

Ester	$(MeO)_3PO$	$(EtO)_3PO$	$(BuO)_3PO$	$(C_5H_{11}O)_3PO$
Yield (%)	77.5	55.0	88.3	83.1

Subsequently, the direct synthesis of alkyl phosphates was investigated at a greater depth. The reports that other transfer catalysts have been used instead of hydrogen chloride merits attention. Thus the employment of copper(II) chloride as the transfer catalyst has been described.[5]

It was shown that $CuCl_2$ oxidises white phosphorus:

$$P_4 + 16ROH + 20CuCl_2 \longrightarrow 4(RO)_3PO + 20CuCl + 4RCl + 16HCl.$$

The anodic process reduces to the regeneration of $CuCl_2$ by the oxidation of copper(I) chloride. The introduction of HCl lowers the yield of trialkyl phosphate and promotes the formation of a dialkyl phosphite. The electrolysis is carried out in an electrolyser with a diaphragm and, in order to increase the solubility of phosphorus, toluene–alcohol mixtures and not pure alcohol are used. Under optimum conditions [current density $(2-6) \times 10^{-3}$ A cm^{-2}, $CuCl_2 : P_4 \geqslant 20$], the yield of alkyl phosphates is nearly quantitative. One cannot rule out the possibility of the formation in this process of copper phosphide as an intermediate, since it has been reported that triethyl phosphate has been obtained in a high yield by the anodic dissolution of copper phosphide in ethyl alcohol.[6]

The anodic oxidation of a suspension of white phosphorus in an acetonitrile–alcohol mixture in the presence of tetrabutylammonium iodide as the supporting electrolyte has been studied in detail.[7–10]

Interesting studies have been carried out by Romakhin et al.,[10] who followed the changes in the outward appearance of the catholyte. It was noted that, soon after the current has been switched on, the state of the white phosphorus changes. It is converted into a dark-yellow deposit with a high phosphorus content, which is insoluble in organic solvents. It is postulated that oligomeric structures are formed in this stage, decomposing in the course of electrolysis (Fig. 1).

This accounts for the low rate of formation of monomeric phosphorus-containing products at the beginning of the electrolysis, the rate increasing significantly towards the end of the process.

It has been found that, under the conditions of diaphragm electrolysis, alkyl phosphates are formed only in an insignificant yield and the presence of trialkyl phosphites was also detected.

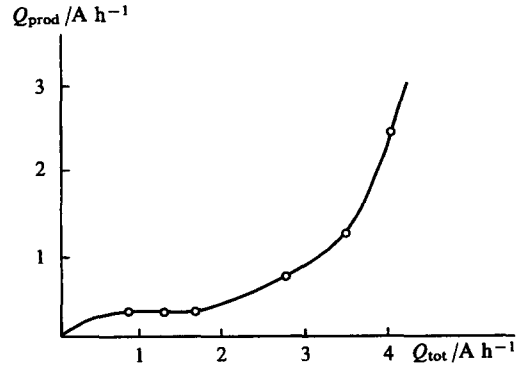


Figure 1. Dependence of the amount of electricity (Q_{prod}) consumed in the formation of triethyl phosphite on the total amount of electricity (Q_{tot}) in the electrolysis of a suspension of phosphorus in acetonitrile in the presence of ethanol.[10]

The diaphragm-free electrolysis,[8] where the trialkyl phosphate is formed with participation of both the cathodic and anodic reactions, proved to be more effective.

After the theoretical amount of electricity has been passed, more than 95% of the phosphorus taken is converted into monomeric products. In the electrolysis of a suspension of white phosphorus in the aliphatic alcohol–acetonitrile–tetrabutylammonium iodide system, dialkyl alkylphosphonates $(RO)_2P(O)R$ and dialkyl phosphites $(RO)_2P(O)H$ are formed in addition to trialkyl phosphates. The yield of the former depends significantly on the electrolysis conditions, particularly on the presence of moisture.[11] Unfortunately, the mechanism of this reaction is not discussed in the above study.[11] Thus, in the electrolysis of a suspension of white phosphorus in the presence of ethanol at 18–25 °C and a current density of 5 A cm^{-2}, the following dependence of the yield of the electrolysis products on the water content in the reaction mass was obtaned:

$H_2O : P_4$ (in moles)	Yield (%)	
	$(EtO)_3PO$	$(EtO)_2P(O)H$
In the absence of water	81.1	8.9
0.255	73.0	13.8
0.328	70.1	18.8
1.000	72.5	27.0
3.125	50.1	17.4

Thus an increase in the water content lowers appreciably the yield of trialkyl phosphate. In the absence of water, the electrolysis of white phosphorus in the alcohol–acetonitrile–tetrabutylammonium iodide system is accompanied by the formation of a mixture of phosphoric acid esters,[8] the yield of which varies as a function of the nature of the alcohol.

Alcohol	Yield with respect to phosphorus (%)		
	$(RO)_3PO$	$(RO)_2P(O)H$	$(RO)_2P(O)R$
MeOH	70	11	3
EtOH	69	9	14
BuOH	66	7	15

The yields quoted were not obtained under optimum conditions and can be improved when the process is optimised.

The employment of tetraalkylammonium iodides as the supporting electrolytes has the advantage that the alkyl iodide formed during electrolysis is reduced at the cathode, affording the corresponding hydrocarbon and generating the supporting electrolyte at the same time. Ultimately, the overall process scheme may by formulated as follows:

$$P_4 + 16ROH \xrightarrow{20F} 4(RO)_3PO + 4RH + 6H_2.$$

This method is inapplicable to the synthesis of triaryl phosphates, because phenol and its derivatives interact with phosphorus under these conditions, giving rise to a mixture of triaryl phosphates and triaryl phosphites.[12]

Alcohol	Yield with respect to phosphorus (%)	
	$(ArO)_3PO$	$(ArO)_3P$
PhOH	20	46
o-MeC_6H_4OH	32	38
p-ClC_6H_4OH	32	11

The process is accompanied by the passivation of the anode. The addition of pyridine eliminates the passivation, but in this case the main product of the elecrolysis becomes the triaryl phosphite. Thus in the presence of pyridine the yield of $P(OPh)_3$ increases to 78%, whilst that of $(PhO)_3PO$ remains 20%.

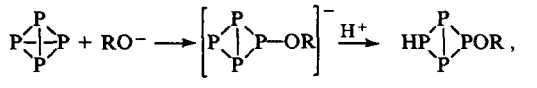
The question of the mechanism of the formation of trialkyl phosphates in the electrolysis of a suspension of phosphorus in the

presence of an aliphatic alcohol and a halide salt merits separate consideration.

According to Budnikova et al.,[11] the first step in the electrochemical process is the reduction of an alcohol molecule at the cathode and the formation of alkoxide ions.[9]

$$ROH + e \longrightarrow RO^- + \tfrac{1}{2}H_2.$$

The P–P bond in the phosphorus molecule is ruptured by the alkoxide ions generated at the cathode (in the presence of a large excess of phosphorus, there is a possibility of the formation of polymeric structures) and the resulting ROP_4^- anion is protonated and subsequently interacts with the alkyl hypoidite generated at the anode:

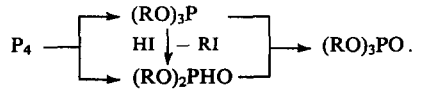


$$I^- \longrightarrow I^{\cdot} + e,$$

$$2I^{\cdot} + ROH \longrightarrow HI + ROI,$$

$$(RO)P_4H \xrightarrow[-HI]{ROI} (RO)P_4(OR).$$

Subsequent alkoxylation ultimately leads to a full phosphorous acid ester, which is oxidised to an alkyl phosphate at the anode. On the basis of the above considerations, a mechanism has been proposed for the possible processes occurring during electrolysis in a single-solution electrolyser of alcoholic solutions of tetrabutylammonium iodide in the presence of white phosphorus:[11]



In the case of phenols, a triaryl phosphite is formed in the first stage of the electrolysis. It reacts with the iodide and phenol generated at the anode, affording a pentaphenoxyphosphorane; the latter is partly converted into a triaryl phosphate at the anode:[12]

$$(PhO)_3P \xrightarrow{I_2} (PhO)_3PI_2 \xrightarrow[-HI]{2PhOH} (PhO)_5P \longrightarrow (PhO)_3PO.$$

The above data demonstrate that the electrolysis of a suspension of phosphorus in aliphatic alcohols (when halide salts are used as the supporting electrolyte) may be regarded as a way of obtaining phosphoric acid esters, bypassing the stage involving the formation of phosphorus halides. In the study of the formation of alkyl phosphates, the cathodic activation of white phosphorus and the possibility of the anodic oxidation of phosphites to phosphates were observed. These two possibilities merit independent consideration.

III. Cathodic activation of phosphorus

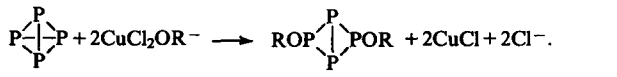
As already mentioned, the electrochemical synthesis of trialkyl phosphates from white phosphorus may be achieved with a satisfactory yield only in an electrolyser without a diaphragm, i.e. the cathodic process plays in this case a significant role, inducing the activation of phosphorus molecules.

The formation of active phosphorus species in chemical processes has been frequently discussed in the literature. For example, in a study of the reactions of elemental phosphorus with electrophiles in a highly basic medium, it was suggested that the P–P bond is ruptured by the base:[13]

$$P_n + OH^- \longrightarrow P_{n-1}^- + POH.$$

Phosphorus is also activated by amines.[14] Thus in the presence of triethylamine, white phosphorus reacts with epoxyethane.

The high reactivity of red phosphorus in the presence of copper halides has also been explained by the dissociation of the P–P bond:[15]

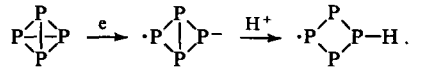


We shall now consider the possible paths leading to the activation of white phosohorus molecules in cathodic processes.

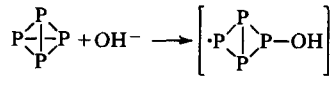
White phosphorus is known to be electrochemically active and gives a wave in the region of -1.90 V.[16] The process involves the transfer of 12 electrons to the P_4 molecule and the final reduction product is phosphine.[17,18] However, in a study of the electrochemical reduction of a suspension of white phosphorus in 50% acetic acid (with addition of potassium acetate in order to increase the electrical conductivity), it was noted that part of the phosphorus (12.3%) in the cathodic compartment is converted into phosphorus acids. Thus, phosphorous, hypophosphorous, and orthophosphoric acids were detected among the reaction products in proportions of 45:55:5 by weight.[19] Particular experiments demonstrated that white phosphorus does not react with the catholyte.

Another interesting fact was observed in the electrochemical reduction of a suspension of withe phosphorus in an acid solution at a lead cathode.[20] In the first instants of the electrolysis, gaseous products are hardly evolved at the cathode (Fig. 2), the joint evolution of hydrogen and phosphite being observed only after some time. The yield of phosphine increases sharply, exceeding 100% relative to the amount of electricity passed through the system. As phosphorus is consumed, the yield of hydrogen increases and reaches the theoretical value. This experiment demonstrated that involatile phosphorus compounds are formed initially and are converted during electrolysis into phosphine.

There are different views on the nature of the active phosphorus species formed initially at the cathode. The formation of partly hydrogenated phosphorus molecules, arising in the course of its reduction, appears most probable. For example,



Another path, involving the generation of nucleophilic species in the cathodic compartment, is also possible. For example,



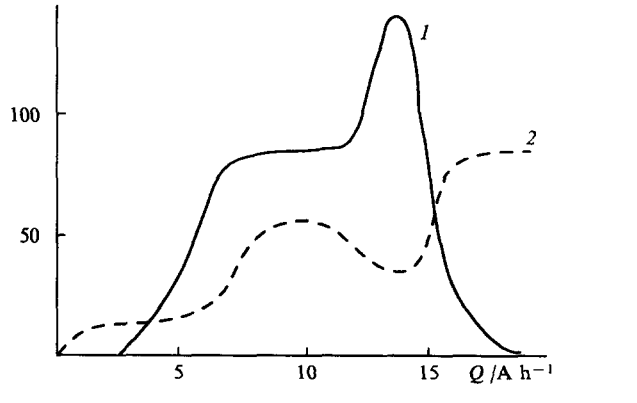
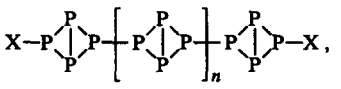


Figure 2. The formation of phosphine (*1*) and hydrogen (*2*) in the electrolysis of a suspension of phosphorus in sulfuric acid solution.[20]

The radical species produced in both cases can give rise, in the presence of an excess of phosphorus, to polymeric structures of the type



where X = H or OH. Such structures are usually formed in the first stage of the electrolysis.

The example of the reduction of phosphorus at a lead cathode described above agrees well with the first mechanism, according to which higher phosphorus hydrides are formed initially, whereas the formation of phosphorus acids in the cathodic compartment would be more logically explained on the basis of the second mechanism. This mechanism also demonstrates the role of the cathodic process in the synthesis of trialkyl phosphates. One may postulate that the mechanism of the activation of phosphorus depends on the electrolysis conditions and principally on the material on the cathode. On metals with a high hydrogen overpotential, the reduction of P_4 and the formation of lower phosphorus hydrides (the first mechanism) are more likely, whereas on metals with a low hydrogen overpotential the activation of phosphorus by the nucleophile generated at the cathode is more probable. In particular, in the preparation of trialkyl phosphates, phosphorus is activated by the alkoxide ions formed at the cathode.

The electrochemical activation of phosphorus molecules may be used for various synthetic purposes. For example, the possibility of obtaining phosphites by the electrolysis of a suspension of red phosphorus in an aqueous solution of ethylenediamine has been demonstrated.[21] The phosphite is formed in the cathodic compartment of the electrolyser, the yield with respect to the red phosphorus taken amoung to ~40%. Under the same conditions but in the absence of ethylenediamine, the only product of the reduction of red phosphorus is phosphine.[22] Since phosphorus does not react chemically in a aqueous solution of ethylenediamine, it remains to postulate that phosphites are formed as a result of the interaction of electrochemically activated phosphorus molecules with water. When this process is carried out in an electrolyser with a platinum anode but without a diaphragm, the yield of the phosphite increases slightly.[23] This shows that the phosphite is formed exclusively from cathodically activated phosphorus.

The formation of organophosphorus compounds in the electrolysis of suspensions of white phosphorus in aprotic solvents in the presence of alkyl halides[24,25] and unsaturated compounds[26] can apparently be also accounted for by the cathodic activation of phosphorus. In all cases, the formation of the corresponding phosphines was observed. For example, the electrolysis of a suspension of white phosphorus in acetonitrile in the presence of styrene afforded a series of compounds, the main one being the monosubstituted phosphine $PhCH_2CH_2PH_2$ (26%). The other reaction products were the di- and tri-substituted phosphines $(PhCH_2CH_2)_2PH$ (0.5%) and $P(PhCH_2CH_2)_3$ (2.5%) and also the diphosphine $[(PhCH_2CH_2)_2P]_2$ (1.0%).[26]

In the presence of alkyl halides, tertiary phosphines are formed preferentially, reacting with the excess alkyl halide to form quaternary phosphonium salts:

$$3RI + P \xrightarrow[-3I^-]{3e} R_3P \xrightarrow{RI} (R_4P)I.$$

IV. Anodic oxidation of phosphrous acid and electrochemical syntheses based on it

Free phosphorous acid in 0.5 N H_2SO_4 gives rise to a distinct oxidation wave at a potential of + 0.52 V relative to the saturated calomel electrode (s. c. e.) at a palladium electrode.[27] It is suggested that under these conditions phosphorous acid is oxidised via a catalytic dehydrogenation mechanism:[28]

$$H_3PO_3 + Pd \rightleftharpoons H_2PO_3 + Pd(H),$$

$$Pd(H) \rightleftharpoons H^+ + Pd + e,$$

$$2H_2PO_3 + H_2O \rightleftharpoons H_3PO_4 + H_3PO_3.$$

Orthophosphoric acid is the product of the oxidation of phosphorus acid. At a platinum anode in an alkaline medium, the oxidation taken place with a current yield of ~40%.[29,30] The addition of potassium iodide to the solution increase the yield of orthophosphoric acid to 66%.[31] At a graphite anode in the presence of 0.5 N HCl, phosphorous acid is oxidised fairly effectively, but this requires the passage of 180% of electricity relative to the theoretical amount, whereupon phosphorous acid is almost fully oxidised (97%).

In an alkaline solution, the oxidation takes place effectively even at a nickel anode, but a fully defined ratio of disodium hydrogen phosohite and sodium hydroxide is then necessary. The optimum ratio disodium hydrogen phosphite : sodium hydroxide = 1.6 : 1.0 makes it possible to attain a degree of oxidation of 99% with a current yield of 43%. The process can be carried out also in a diaphragm-free electrolyser, since the losses in reduction do not exceed 1% – 3%.[32]

The sodium salts of phosphorous acid are polarographically active. Thus sodium dihydrogen phosphite has a reduction wave with $E_{1/2} = -0.605$ V ($n = 0.4$), wherease disodium hydrogen phosphite has one with $E_{1/2} = -0.42$ V ($n = 0.7$).[33] Unfortunately the nature of these waves has not been discussed.[33]

In an aqueous solution, the product of the electrochemical reduction of phosphorous acid is phosphonous acid:[34]

$$H_3PO_3 + 2H^+ + 2e \longrightarrow H_3PO_2 + H_2O.$$

The formation of phosphine has also been observed.[32]

Electrochemical synthesis based on acid phosphite esters merits separate consideration. The characteristic features of their electrochemical behaviour are determined by the equilibrium

$$(RO)_2POH \rightleftharpoons (RO)_2P(O)H,$$

which is almost fully displaced towards four-coordinate phosphorus.

In the accessible range of potentials, dialkylphosphorous acids are not oxidised,[35] but in aprotic media they give rise to a reduction wave at transition metal cathodes.[36] Thus, in acetonitrile in the presence of quaternary ammonium salts as supporting electrolytes, dimethyl phosphites have the following reduction potentials (in V) at different cathodic materials:

Phosphine	Pt	Ni	Fe	Cu
$(MeO)_2P(O)H$	1.88	1.88	1.90	2.00
$(EtO)_2P(O)H$	1.89	–	2.06	2.04

It is suggested that the cathodic process leads to the formation of anions, since the evolution of hydrogen is observed at the cathode:

$$(RO_2)P(O)H + e \longrightarrow [(RO)_2PO]^- + \tfrac{1}{2}H_2.$$

Four-coordination of the phosphorus atom in the anion is indicated by the finding that diaphragm-free electrolysis with a soluble anode leads to dialkyl phosphite salts with a metal–phosphorus bond.[36] In this case, the anodic process consists in the dissolution of the anode material and its transition to an ionic state:

$$M \longrightarrow M^{n+} + ne.$$

The interaction of the phosphite anions generated at the cathode with the metal cations leads to the formation of salts:[36,37]

$$n[(RO)_2PO]^- + M^{n+} \longrightarrow [(RO)_2PO]_nM.$$

The formation of the corresponding platinum salt has been described in a study[37] where a platinum electrode was employed.

In aqueous solutions of alkali metal halides, dialkyl phosphites are oxidised to dialkyl phosphates at a graphite anode:[38,39]

$$(RO)_2P(O)H \xrightarrow{H_2O} (RO)_2P(O)OH + 2e + 2H^+.$$

The oxidation is carried out at a current density not exceeding 0.01 A cm^{-2} and a temperature of 30–35 °C. The yield of phosphates is 75%–80%. In the electrolysis of lower dialkyl phosphites (Alk = C_1–C_3), the process is accompanied by partial hydrolysis with formation of monoalkylphosphoric acids.

In the electrolysis of an aqueous solution of dialkylphosphorous acid with an aluminium anode, aluminium alkyl phosphate was obtained in a yield of 90%–95%:[40]

$$3(RO)_2P(O)H + Al + 3H_2O \xrightarrow{5F} \left[RO\overset{H}{\underset{O}{P}}O \right]_3 Al + 3ROH + 1.5H_2.$$

This process was used as a basis for the industrial preparation of the Russian-produced systemic fungicide EFAL'-50.[41] The technological scheme is significantly simplified as a result of the employment of a diaphragm-free electrolyser fitted with aluminium elctrodes. The electrolysis is carried out with an alternating current at a frequency of 50 Hz.[42]

The aluminuum salt can be obtained similarly from methylphosphonic acid.[43]

The electrolysis of dialkyl phosphites in a nonaqueous medium using an insoluble graphite anode leads to a complex mixture of products, more than 60% of which comprises tetraalkyl pyrophosphate $(RO)_2P(O)OP(O)(OR)_2$.[44] The mechanism of its fromation is not clear. It has been suggested that, since hydriodic acid is used as supporting electrolyte, the acyl iodide formed at the anode reacts with water, giving rise to a dialkyl phosphate; the latter reacts with a second acyl iodide molecule:[45]

$$(RO)_2\overset{\overset{O}{\|}}{P}I \xrightarrow{H_2O} (RO)_2\overset{\overset{O}{\|}}{P}OH + HI,$$

$$(RO)_2\overset{\overset{O}{\|}}{P}OH + (RO)_2\overset{\overset{O}{\|}}{P}I \longrightarrow (RO)_2\overset{\overset{O}{\|}}{P}O\overset{\overset{O}{\|}}{P}(OR)_2 + HI.$$

However, from our point of view this mechanism is unlikely, since the use of even thoroughly dried acetonitrile does not lower the yield of pyrophosphate. A similar reaction occurs in the electrolysis of acetonitrile solutions of alkyl alkylphosphonates, leading to the formation of dialkyl dialkylpyrophosphonates (RO)RP(O)OP(O)R(OR).[44] Data on the electrosynthesis of pyrophosphates and pyrophosphonates from phosphorous acid esters are presented below (the mechanism of this reaction has not been investigated):

$(RO)_2\overset{\overset{O}{\|}}{P}O\overset{\overset{O}{\|}}{P}(OR)_2$

R	Et	Pr^n	Bu^n
Yield /10^3 mol A^{-1} h^{-1}	12.2	11.1	11.0

(RO)MePOPMe(OR)

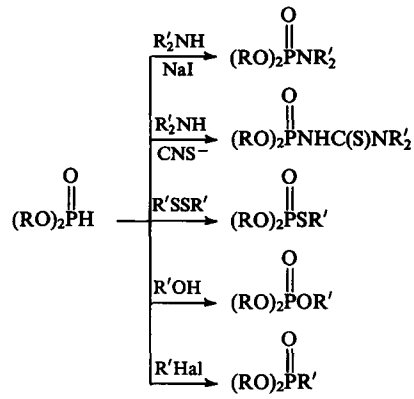
R	Et	Pr	Pr^i	Bu	Bu^i	n-C_5H_{11}	iso-C_5H_{11}
Yield/10^3 mol A^{-1} h^{-1}	12.3	8.8	11.6	7.9	10.4	6.3	10.1

(RO)EtPOPEt(OR)

R	iso-C_3H_7	iso-C_4H_9
Yield /10^3 mol A^{-1} h^{-1}	11.2	10.2

Although, as already mentioned, the acid phosphite esters themselves do not undergo anodic oxidation, they react readily with the halogens generated at the anode, forming reactive acyl halides. This reaction has been used successfully for the synthesis of compounds with P–N, P–S, and P–O bonds. The possibility of the electrochemical formation of the P–C bond was later demonstrated.

The overall mechanism of the electrochemical phosphorylation reactions of organic compounds can be represented as follows:



We shall examine these reactions in greater detail.

1. Synthesis of amidophosphates

The formation of amidophosphates in a high yield has been noted in the electrolysis of acetonitrile solutions of dialkyl phosphites containing an alkali metal iodide as the supporting electrolyte to which a secondary amine has been added. The process is carried out in a diaphragm-free electrolyser with platinum electrodes. The yields of the amidophosphates as a rule exceed 75%. For example, when dimethyl phosphite was coupled with dipropylamine, the yield of the amidophosphate was 76%, while the yields in the reactions with dibutylamine and morpholine were 83% and 80% respectively.[46]

The most probable reaction path involves the anodic iodination of the phosphite:

$$(RO)_2P(O)H + 2I^- \longrightarrow (RO)_2P(O)I + HI + 2e,$$

$$(RO)_2P(O)I + R'_2NH \longrightarrow (RO)_2P(O)NR'_2 + HI.$$

An alternative path involving the anodic iodination of the amine is also possible:

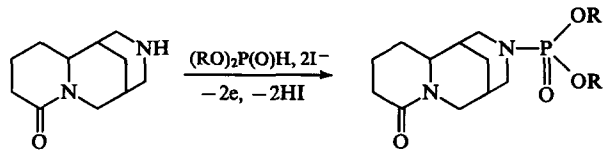
$$R'_2NH + 2I \longrightarrow R'_2NI + 2e.$$

The iodoamine formed as a result of this reaction reacts subsequently with the phosphite:

$$R'_2NI + (RO)_2P(O)H \longrightarrow (RO)_2P(O)NR'_2 + HI.$$

On the basis of voltammetric measurements and quantum-mechanical calculations, preference is given to the first path.[47]

This reaction has been used successfuly for the phosphorylation of various alkaloids. For example, cytisine has been phosphorylated electrochemically:

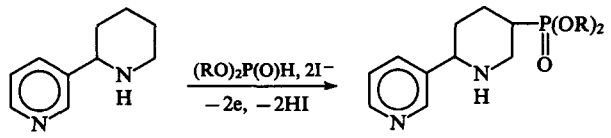


The reaction was carried out in the presence of tetraethylammonium bromide with added free iodine as the supporting electrolyte. The following yields of the phosphorylation products were obtained depending on the nature of R:[48]

R	Me	Et	Pr	Pr^i	Bu^t
Yield (%)	53	84	78	73	70

L-Ephedrine,[49] lupinine,[50] pyrazidol,[51] salsolidine,[52] and anabasine[48,53] have been phosphorylated in 85%–91% yields.

The phosphorylation of anabasine is represented by the following overall equation:



The yield of the phosphorylated product depends on the nature of the group R:

R	Me	Et	Pr^n	Pr^i	Bu^n
Yield (%)	79.0	91.2	86.4	86.0	87.1

In the phosphorylation of quinine, it was established that the hydroxy-group is initially oxidised to the carbonyl group with formation of the corresponding quinone, which is then phosphorylated to the α-hydroxyphosphonate.[54]

As already mentioned, the phosphorylation of amines takes place with iodine as the transfer catalyst. Other halogens proved to be appreciably less effective. Thus the following dependence of the yield of the target product on the nature of the halogen-containing additive has been obtained in the synthesis of the diethylamide of ethylphosphorous acid:[14]

Additive	I_2	NaI	NaBr	NaCl
Yield (%)	94	92	36	4

It is of interst to note that lupinine is most effectively phosphorylated in the presence of crown-ethers to which lithium chloride has been added.[50] The presence of surfactants has apparently a favourable effect on the process.

2. Synthesis of thioamides

If during the electrolysis of acetonitrile solutions of dialkyl phosphites in the presence of secondary amines ammonium thiocyanate is used instead of sodium iodide, the nature of the products changes significantly. The synthesis of *N*-phosphorylated thioamides has been observed. Cyclic voltammetric data and quantum-mechanical calculations have shown that the most probable mechanism for the simplest dimethyl phosphite–dimethylamine system involves the interaction of the phosphite with the iodine thiocyanate formed at the anode:[55]

$$(MeO)_2P(O)H + 2CNS^- \longrightarrow (MeO)_2P(O)NCS + HCNS + 2e.$$

The thiocyanato-derivative obtained as a result of this reaction then reacts with the amine, affording *N*-phosphorylated thioamides:

$$(MeO)_2P(O)NCS + Me_2NH \longrightarrow (MeO)_2P(O)NHC(=S)NMe_2.$$

This reaction has been used successfully for the phosphorylation of ephedrine alkaloids. The corresponding phosphorylated thioamides were obtained in 48%–53% yield. The phosphorylated quinine and lupinine thioamides are formed in approximately the same yield.[56]

3. Synthesis of thiophosphates

The electrochemical generation of the halogens makes it possible to achieve the coupling of dialkylphosphorous acid with disulfides, which results in the formation of compounds with a P–S bond. The following process mechanism has been proposed on the basis of polarisation measurements for the initial components:

$$(RO)_2P(O)H + 2Br^- \longrightarrow (RO)_2P(O)Br + HBr + 2e,$$

$$(RO)_2P(O)Br + R'SSR' \longrightarrow (RO)_2P(O)SR' + R'SBr,$$

$$(RO)_2P(O)H + R'SBr \longrightarrow (RO)_2P(O)SR' + HBr.$$

Best results were obtained in the presence of bromide salts; the reactions with other halides are less successful (see, for example, Torii et al.[45]):

Additive	NaI	NaBr	NaCl
Yield of $(EtO)_2P(O)SPh$ (%)	73	91	59

The coupling of diethyl phosphite with diphenyl disulfide is carried out in an electrolyser without a diaphragm, which maked it possible to obtain coupling products with entirely satisfactory yields. For example, in the coupling of dimethyl phosphite with diphenyl disulfide, dibenzyl disulfide, and bis(ethoxycarbonylmethyl) disulfide, the yields of the coupling products were 61% 71%, and 75% respectively.

4. Synthesis of trialkyl phosphates

The anodic oxidation of dialkyl phosphites in an alcoholic solution in the presence of chloride ions makes it possible to obtain trialkyl phosphates in high yields.[57] It has been suggested that in the first stage the phosphite undergoes anodic chlorination to the acyl chloride, which then reacts with the alcohol, affording the corresponding trialkyl phosphate:

$$(RO)_2P(O)H + 2Cl^- \longrightarrow (RO)_2P(O)Cl + HCl + 2e,$$

$$(RO)_2P(O)Cl + R'OH \longrightarrow (RO)_2P(O)(OR') + HCl.$$

This method made it possible to obtain phosphoric acid esters with various substituents. Although the yield of the esters synthesised in this way is somewhat lower than in the syntheses examined previously, the method is nevertheless preparatively important. Thus, when dimethyl phosphite was coupled with methyl, ethyl, and propyl alcohols, the yields of the corresponding trialkyl phosphates were 46%, 57%, and 63% respectively. The syntheses were carried out using perchloric acid with added lithium chloride as the supporting electrolyte. The anode was made of vitreous carbon and a diaphragm electrolyser was used, although the need for a diaphragm in this process can hardly be justified.

5. Synthsis of phosphonates

The cathodic reduction of dialkyl phosphites in the presence of halogen-containing compounds leads to phosphonates. The mechanism of this process differs singnificantly from those examined above. The primary process is apparently the cathodic reduction of the dialkyl phosphite with formation of the anion $(RO)_2P(O)^-$:[36]

$$(RO)_2P(O)H + 2e \longrightarrow [(RO)_2P(O)]^- + \tfrac{1}{2}H_2.$$

The anion reacts further with the halogen-containing compound:[36]

$$[(RO)_2P(O)]^- + R'Hal \longrightarrow (RO)_2P(O)R' + Hal^-.$$

The electrochemical synthesis of phosphonates was first described by Petrosyan and Niyazymbetov.[58] The process was carried out in a diaphragm electrolyser at a platinum anode in acetonitrile at a current density of 0.003–0.005 A cm^{-2} at 20 °C. A 0.3 M solution of tetraethylammonium bromide was used as the supporting electrolyte.

The starting compounds were dimethyl, diethyl, and diphenyl phosphites as well as methyl and benzyl iodides and chlorides. The yields of the corresponding phosphates were in the range 55%–65%.

An interesting modification of this reaction has been proposed.[58] In it, methylene chloride containing 0.3 M tetraethylammonium bromide and 0.015–0.03 M phosphite (Pt cathode) was used as the catholyte, while the anolyte was a 0.3 M solution of tetraethylammonium bromide in methylene chloride to which

cyclohexene had been added to bind the bromine evolved. The reaction proceeds in accordance with the equation:

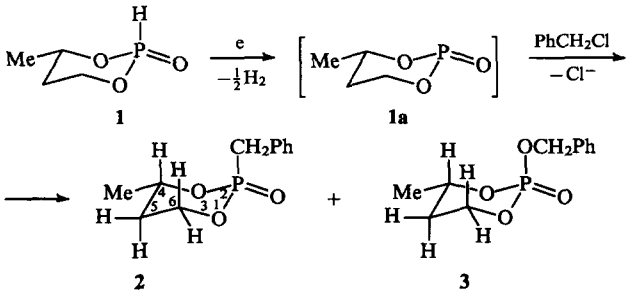
$$(RO)_2P(O)H + CH_2Cl_2 \longrightarrow \underset{\mathbf{A}}{(RO)_2P(O)Me} + \underset{\mathbf{B}}{(RO)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{P}}(OR)_2}$$

R = Me, Et, Ph.

The yields of the products **A** and **B** depend on the amount of electricity passed through the system. Thus, when three Faradays are passed per mole of the phosphite, mainly product **A** is formed, its yield amounting to 75% for dimethyl phosphite, 72% for diethyl phosphite, and 51% for diphenyl phosphite. It was later shown [59] that the alkylation of phosphites in the presence of small amounts of water proceeds more successfully than in the anhydrous solvent. The following composition of the catholyte has been recommended for alkylation: solution containing 2 mmol of the phophite and 3 mmol of the alkyl halide in 25 ml of dimethylformamide containing 4 mmol of tetrabutylammonium as the supporting electrolyte and 4 mmol of water.

For example, the coupling of diethyl phosphite with butyl iodide has been achieved under these conditions in 74% yield, but in the reactions with butyl bormide, benzyl bromide, and benzyl chloride the yields were 49%, 60% and 55% respectively. These data show that compounds containing a sufficiently mobile halogen atom must be used as the coupling component. In other examples, the yields of the phosphonates vary in the range 56% – 58%.

The elctrochemical alkylation of *cis*-2-hydro-4-methyl-2-oxo-1,3,2,-dioxaphosphorinane **1** with equatorially oriented methyl and oxo-groups proceeds strereoselectively and leads to 2-benzyl-4-methyl-2-oxo-1,3,2-dioxaphosphorinane in 60% – 70% yield. [60] Together with the phosphonate **2**, the phosphate **3** was isolated. The mechanism of the formation of the latter has not yet been investigated.



In contrast to dialkyl phosphites, the sodium salts of dialkylphosphorous acids are readily oxidised at a platinum anode in solution in acetonitrile in the presence of sodium perchlorate as the supporting electrolyte: [61]

R in $(RO)_2PONa$	Et	Pr^i	Pr^n	Bu^n
$E_{1/2}$ /V	0.45	0.50	0.63	0.63

It is suggested that the oxidation proceeds in accordance with the equation:

$$(RO)_2PONa \xrightarrow[-e,\,-Na^+]{} [(RO)_2PO^{\cdot}] \xrightarrow[-e]{} [(RO)_2PO]^+.$$

The electrolysis of such a system in the presence of aromatic and heterocyclic compounds leads to the corresponding phosphonates, for example,

$$[(RO)_2PO]^+ + \text{(thiophene)} \longrightarrow (RO)_2P(O)\text{—(thiophene)} + H^+.$$

Apart from thiophene, furan, quinoline, and naphthalene have been introduced into this reaction. The yield of the phosphorylation products varied in the range 25% – 30%, the reaction being accompanied by the formation of a number of side products, such as $(RO)_2P(O)H$, $(RO)_2P(O)R$, and $(RO)_3PO$. [61]

In the presence of secondary amines, amidophoshite diesters were synthesised at the oxidation potential of sodium dialkyl pyrophosphite. [62] It is suggested that the reaction proceeds via the following path:

$$(RO)_2PONa \longrightarrow [(RO)_2PO]^+ + Na^+ + 2e,$$

$$[(RO)_2PO]^+ + (RO)_2PONa \longrightarrow (RO)_2POP(O)(OR)_2 + Na^+,$$

$$(RO)_2POP(O)(OR)_2 + R'_2NH \longrightarrow (RO)_2PNR'_2 + (RO)_2P(O)OH,$$

$$3(RO)_2PONa + R'_2NH \longrightarrow (RO)_2PNR'_2 + (RO)_2P(O)ONa + 2Na^+ + 2e.$$

In the presence of a large excess of the amine in the solution, the following process may occur: [63]

$$[(RO)_2PO]^+ + R'_2NH \longrightarrow (RO)_2P(O)NR'_2.$$

The following amidophosphites have been synthesised electrochemically: $(EtO)_2PNEt_2$, $(BuO)_2PNEt_2$, and $(BuO)_2PNBu_2$ in 30%, 20%, and 32% yields respectively.

* * *

The data presented in this review show that electrolysis can be used successfully for the synthesis of trialkyl phosphates from white and red phosphorus. Data on the catalytic influence of copper halides on the synthesis of alkyl phosphates merit attention. The study of the characteristic features of the formation of trialkyl phosphates demonstrated the possiblity, in principle, of the direct synthesis of phosphites from elemental phosphorus and also the possibility of the electrochemical oxidation of phosphites and dialkyl phosphites to the corresponding phosphates and pyrophosphates. It is noted that electrolysis is a promising procedure for the preparation of various derivatives of dialkyl phosphites.

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