ELECTROCHEMICALLY INDUCED PROCESSES OF FORMATION OF PHOSPHORUS ACID DERIVATIVES.

4. SYNTHESIS OF TRIALKYL PHOSPHATES FROM WHITE PHOSPHORUS

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The products of electrolysis in dipolar aprotic solvents on the background of tetraethylammonium iodide in the presence of white phosphorus are trialkyl phosphite (the primary product after splitting of all the P—P bonds in the phosphoric oligomers) and triaryl phosphate. It was found that the formation of triaryl phosphate from white phosphorus proceeds by way of electrochemical reduction of pentaaroxyphosphorane — an intermediate product of the reaction of triaryl phosphite with iodine and phenol. A strong dependence of the yields and distribution of the products on the composition of the electrolyte has been observed.

Keywords: white phosphorus, electrosynthesis, triaryl phosphate.

The electrosynthesis based on white phosphorus and aliphatic alcohols makes it possible to obtain various esters of phosphorus acids, depending on the reaction conditions. The use of other reagents, which potentially could take part in the functionalization of white phosphorus is of particular interest from the point of view both of the extension of the synthetic possibilities of the electrosynthesis of organophosphorus compounds (OPC) from P_4, and for developing concepts on the reaction mechanism of phosphorus and its oligomers. In this connection, the alcohols of the aromatic series deserve attention.

It is known that phenols, like alcohols, are capable of undergoing reduction on transition metals with the separation of hydrogen and formation of phenolate [1], which under favorable conditions will react with white phosphorus similarly to other nucleophilic reagents, although it is a weaker nucleophile [2]. As has already been reported in [3], the behavior of the phenolate ions differs from the behavior of the alcoholate ions in the reaction with white phosphorus. Attempts to carry out the transformation of white phosphorus into organophosphorus products by using carbon tetrachloride as the electrophilic component have not been successful. It is to be expected that in the combination with iodine, the reactivity of the arylate ions with respect to white phosphorus will be fairly high. Nevertheless, it is very probable that even when the reaction of the arylate ions with P_4 proceeds at an acceptable rate, the subsequent transformations of the organophosphorus intermediates will differ substantially from their behavior in alcoholic media.

The aim of the present work was to study the possibilities of drawing elemental phosphorus into reaction with electrochemically generated products of the cathodic and anodic processes in phenolic solutions of Et_4NI in dipolar aprotic solvents. During the electrolysis of a solution of phenol in acetonitrile on the background of Et_4NI in the presence of an emulsion of white phosphorus, after passing 3 F of electricity per mole of white phosphorus, a mixture of triphenyl phosphite and triphenyl phosphate is formed (Table 1). Thus, some of the phosphorus remains in the form of a solid precipitate of variable composition, which is insoluble in water and in organic solvents, and slowly decomposes in air with the separation of iodine, the precipitate mainly covering the anode. The phosphite $(PhO)_3P$ is probably the first relatively stable intermediate,
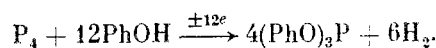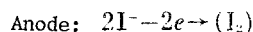
TABLE 1. Products of Electrolysis of Solutions of Phenols in Acetonitrile on the Background to Et_4NI in the Presence of White Phosphorus

ArOH	Products	Yield, %	
		rel. to phosphorus, %	rel. to current, %
C_6H_5OH	$(C_6H_5O)_3P$	46	45
	$(C_6H_5O)_3PO$	20	19
$o\text{-}CH_3C_6H_4OH$	$(o\text{-}CH_3C_6H_4O)_3P$	38	38
	$(o\text{-}CH_3C_6H_4O)_3PO$	32	32
$p\text{-}ClC_6H_4OH$	$(p\text{-}ClC_6H_4O)_3P$	10	10
	$(p\text{-}ClC_6H_4O)_3PO$	52	52

having an importance in itself — it is a product of the reaction of phosphorus with nucleophilic and electrophilic reagents generated on the electrodes after splitting of all the $P-P$ bonds in the phosphoric oligomers:

$$\text{Cathode:} \quad 2PhOH + 2e \rightarrow 2PhO^- + H_2$$

$$\text{Anode:} \quad 2I^- - 2e \rightarrow (I_2)$$

$$P_4 + 12PhOH \xrightarrow{\pm 12e} 4(PhO)_3P + 6H_2.$$

The appearance of phosphate can be most simply explained as being due to the hydrolysis of the unstable iodine derivatives by residual water in the electrolyte [4]:

$$(PhO)_3P + (I_2) \rightarrow (PhO)_3PI_2 \rightarrow (PhO)_3PO.$$

However, the content of the residual water (0.01 M) is too low to be able to ensure the formation of the entire amount of $(PhO)_3PO$, although undoubtedly this path is not to be ruled out. Even the addition of inappreciable amounts of water to the electrolyte $[M(P):M(H_2O) = 1:(0.06-0.1)]$ sharply decreases the conversion of phosphorus into the desired phosphorus acid esters, increases the overvoltage of the anodic process due to the formation on the anode of a nonelectroconducting film of adsorbed phosphorus containing polymeric products (45% phosphorus) and even leads to other reaction end products — only diphenyl phosphite is formed in a yield of ~20% with respect to phosphorus. These passivating processes are always characteristic for given electrolytes during the anodic oxidation of iodide ions, and some authors link them with the formation of I^+ ions on the anode, as primary oxidation products at the electrolysis potentials [5]. It was thereby noted that in phenolic solutions the anodic oxidation process is sometimes completely inhibited [6, 7]. It is probable that the entry of water into the electrolyte from the gaseous phase in amounts required for the reaction should be discounted, since the experiments were carried out n hermetically closed cells and the yield of phosphate was independent of the duration of the process.

Another possible path of formation of trialkyl phosphate is the transformation of triaryl phosphite with the participation of phenol as a source of oxygen. It is known that a direct transformation of triaryl phosphite via the iodine derivative $(PhO)_3PI_2$ and rearrangement of the quasiphosphonium compound $(PhO)_4PI$ into the phosphate does occur, in contrast to the case of aliphatic phosphites. However, by extraction with hot hexane from the reaction mixture in the course of the electrolysis and also by examination of the solid undistillable residue after its treatment, we were able to identify pentaphenoxyphosphorane (P = -85 ppm) and possibly $(PhO)_3PI_2$ (P = 104 ppm), which may be the intermediate products in the transformation of triphenyl phosphite into the phosphate. If the electrolysis with white phosphorus is prolonged, and instead of 3 F/mole of phosphorus, 5.6 F/mole of phosphorus are passed through the electrolyte, the whole phosphite $(PhO)_3P$ is converted into a phosphate, probably as the result of the following reactions:

$$(PhO)_3P \xrightarrow{I_2} (PhO)_3P I_2 \xrightarrow[-2HI]{2PhOH} (PhO)_5P \longrightarrow (PhO)_3PO.$$
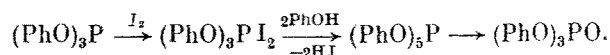
The last stage is here particularly interesting, since virtually no data are available in the literature on the possible paths and conditions of transformations of phosphorane into phosphate. A chemically synthesized phosphite in the course of electrolysis without separation of the cathode and anode spaces is an acetonitrile solution of phenol and Et_4NI is transformed completely into triphenyl phosphate after 2.7 F of electricity per mole of phosphite was passed through. A GLC analysis of the solvent distilled from the reaction mixture showed the presence of benzene in it.
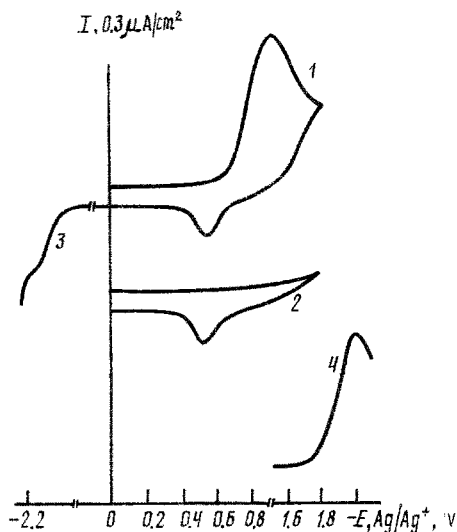
Fig. 1. Voltamperograms in a 0.1 M solution of Et_4NBF_4 in acetonitrile on a stationary platinum electrode: 1) 10^{-3} M $(PhO)_5P$; 2) 10^{-23} M PhONa; 3) 10^{-3} M PhH; 4) 10^{-3} M PhOH.

TABLE 2. Characteristics of Synthesized Compounds

Compound	Bp, °C (p, mm Hg)	δ ^{31}P, ppm
$(C_6H_5O)_3P$	145-147/1	126
$(C_6H_5O)_3PO$	178-180/1	−18
$(o\text{-}CH_3C_6H_4O)_3P$	177-178/1	129
$(o\text{-}CH_3C_6H_4O)_3PO$	210-215/1	−17
$(p\text{-}ClC_6H_4O)_3P$	178-179/1	129
$(p\text{-}ClC_6H_4O)_3PO$	235-236/3	−18

We studied the voltammetric behavior of pentaphenoxyphosphorane obtained by a method described in [8]. Pentaphenoxyphosphorane is irreversibly reduced on a platinum electrode in acetonitrile, giving one two-electron wave (Fig. 1). Since its reduction potentials are less negative than those of phenol, pentaphenoxyphosphorane, formed at the intermediate stages of the process, undergoes in the course of electrolysis cathodic reduction to triphenyl phosphate. On the anodic branch of the voltammetric curve on a stationary platinum electrode, waves corresponding to the oxidation of the phenolate ion and benzene are also observed (Fig. 1). Thus, the general scheme of the reduction of phosphorane can be represented by the following scheme:

$$(PhO)_5P + 2e \xrightarrow{[H+]} (PhO)_3PO + PhH + PhO^-.$$
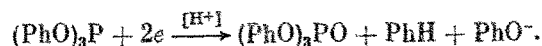
The preparative electrolysis in which pentaphenoxyphosphorane is reduced on a nickel electrode in acetonitrile on the background of Et_4NI in a cell separated by a diaphragm confirms this scheme of the process: after the treatment of the reaction mixture, triphenyl phosphate and benzene were isolated.

A disadvantage of the above-described transformation of white phosphorus into aromatic esters of phosphorus acids in acetonitrile is the incomplete conversion of phosphorus into the desired end products — part of it does not enter the desired reaction, and remains in the form of a polymeric film, which screens the anode during the electrolysis. Bearing in mind the assumption that the passivation of platinum anodes at the first oxidation wave potentials of the iodide ions is caused by the formation of adsorbed I^+ ion, which then reacts with the solution components, it can be seen that the inhibition could possibly be weakened if additives with a higher donor number than acetonitrile are introduced into the solution. This makes it possible to decrease the specific adsorption of cations by increasing the energy of their solvation [9] (iodine is not solvated under these conditions). To verify this expectation, pyridine was used as the additive. It was experimentally shown that in the presence of pyridine (0.04 M) the anodic process is notably facilitated, but in this case the main product is triaryl phosphite (for example, under the conditions listed in Table 1, the yields with respect to phosphorus are: 78% $(PhO)_3P$ and 20% $(PhO)_3PO$.

EXPERIMENTAL

For recording the polarization curves using the preparative electrolysis, a P-5848 potentiostat with a three-electrode cell was used. $Ag/AgNO_3$ (a 0.01 M solution in acetonitrile) was used as the reference electrode. Platinum served as the anode, and nickel−platinum as the cathode. The scanning rate of the potential during the recording of the voltammetric curves was 10 mV/sec.

The ^{31}P NMR spectra were obtained on a nonserially produced apparatus KGU-4 with a frequency of 10.2 MHz relative to 85% phosphoric acid (the positive values of chemical shifts are given in the direction of weak fields). The chromatographic analysis of reaction mixtures and synthesized compounds was carried out on a Chrom-4 gas−liquid chromatograph using helium as the carrier gas and a flame ionization sensor-detector. Glass columns filled with a 5% Silicone SE-30 packing on a chromaton N-AW (0.125-0.160) were used. Acetonitrile was purified by distillation over P_2O_5 with addition of $KMnO_4$. Tetraethylammonium iodide was recrystallized from ethanol and dried in vacuo at 100°C. The phenols were purified by distillation in vacuo. Pentaalkoxyphosphorane was prepared by a method described in [8] (Table 2).

The electrolysis was carried out in a galvanometric regime at a current density of 1-2 mA/cm^2, temperature 50°C, and molar ratio of phenol and phosphorus equal to 30.

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