7. V. A. Koptyug, *Arenonium Ions. Structure and Reactivity* [in Russian], Nauka, Novosibirsk (1983), pp. 12, 13.
8. G. I. Borodkin, E. I. Chernyak, M. M. Shakirov, and V. G. Shubin, *Zh. Org. Khim.*, **22**, No. 2, 330 (1986).
9. L. M. Épshtein, *Usp. Khim.*, **48**, No. 9, 1600 (1979).
10. N. D. Sokolov (ed.), *The Hydrogen Bond* [in Russian], Nauka, Moscow (1981).
11. V. N. Kondrat'ev (ed.), *Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinity* [in Russian], Nauka, Moscow (1974), pp. 77, 78, 336, 337.
12. J. March, *Organic Chemistry* [Russian translation], Vol. 1, Mir, Moscow (1987), p. 113.
13. L. B. Fisher, I. L. Kotlyarevskii, E. S. Domnina, and Z. P. Trotsenko, *Izv. Akad. Nauk, Ser. Khim.*, No. 6, 1090 (1964).
14. A. Gordon and R. Ford, *The Chemist's Companion*, Wiley-Interscience (1973).
15. H. Günther, *NMR Spectroscopy. An Introduction*, Wiley (1980).

ELECTROCHEMICALLY INDUCED PROCESSES IN THE FORMATION OF PHOSPHORUS ACID DERIVATIVES.
# 1. SYNTHESIS OF TRIALKYL PHOSPHATES FROM WHITE PHOSPHORUS

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An electrochemical method, based on the joint action of nucleophilic and electrophilic reagents on P_4, is proposed in order to utilize white phosphorus in the formation of the esters of phosphorus acids. The action of alkoxide ions on white phosphorus in an alcohol medium in the presence of iodine generated at the anode leads to the formation of phosphate esters. A scheme in which the intermediate products are dialkyl and trialkyl phosphites and the side product is dialkyl alkylphosphonate is proposed for the process.

Key words: Phosphate esters, white phosphorus, electrosynthesis.

The problem of direct functionalization of white phosphorus has become more acute in connection with vigorous developments in the chemistry of organophosphorus compounds and with the ecological problems that have arisen in the production of these compounds on an industrial scale. The experimental material which has accumulated at the present time on the synthesis of organophosphorus compounds from elemental phosphorus has mainly been obtained under rigorous thermal conditions for very complex multicomponent systems, in which it is difficult to establish even the approximate mechanism of the process. The greatest progress in this region has been achieved in synthesis paths based on the joint action of nucleophilic and electrophilic reagents on white phosphorus. It is known that the phosphorus atoms in the P_4 tetrahedron exhibit very weak nucleophilic characteristics, and this has been confirmed by quantum-chemical calculations [1]. On account, however, of the strain in the ring and the weakness of the P–P bond, as strong electrophiles, they react readily with various nucleophiles [2]:
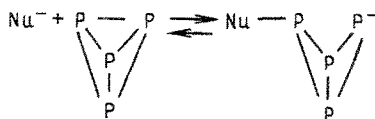
TABLE 1. Products from Electrolysis of Alcohol Solutions in Acetonitrile in the Presence of White Phosphorus [M(P):M(ROH) = 1:20, Q = 5.2 F/mole P]

ROH	T, °C	Product	Yield in P
MeOH	18	$(MeO)_2PHO$	11
		$(MeO)_3PO$	70
		$(MeO)_2P(O)Me$	3
	50	$(MeO)_3PO$	51
		$(MeO)_2P(O)Me$	28
EtOH	20	$(EtO)_2PHO$	9
		$(EtO)_3PO$	69
	56	$(EtO)_3PO$	65
		$(EtO)_2P(O)Et$	14
BuOH	25	$(BuO)_2PHO$	7
		$(BuO)_3PO$	66
	56	$(BuO)_3PO$	60
		$(BuO)_2P(O)Bu$	15

As a strong base and nucleophile, the obtained phosphide anion can be stabilized by reacting with various electrophilic components of the solution (protons, alkyl halides [3], aldehydes [4], acrylonitrile and other α, β-unsaturated compounds [5], disulfides [6], tetrachloromethane [7]). By repeating the attack by the nucleophile and subsequent capture of the phosphide ion by the electrophilic reagent it is possible to obtain various products under mild conditions.

It is clearly expedient to use these theoretical considerations for the design of electrochemical reactions with white phosphorus. An attempt was made to synthesize organophosphorus compounds by combining homogeneous chemical reactions in the volume of the solution with heterogeneous electrochemical reactions taking place at the electrodes. Preliminary results in this direction showed the possibility of converting P_4 into the aliphatic esters of phosphorus acids [8]. Determination of the mechanism of this process, however, requires more comprehensive investigations. The aim of the present work was to study the conditions for successive cleavage of the P—P bonds in the P_4 molecule, the oligomerization and the state of the electrochemically generated nucleophilic components, the relationships governing the subsequent electrochemical and chemical reactions of the initial intermediate products with various nucleophiles (alkoxide, hydroxide, phenolate ions) and anodically generated electrophiles, and the other elementary events of the overall process involved in the synthesis of the organophosphorus compounds from white phosphorus. An important task is undoubtedly the successful choice of pairs of such nucleophile—electrophile reagents for the attainment of a high degree of conversion of the phosphorus into useful products and the creation of conditions of high selectivity.

It is known [9] that at cathodes with a low hydrogen overpotential with tetraalkylammonium salts as indifferent electrolyte the alcohol O—H bond is cleaved with the formation of the alcoholate ion:

$$2ROH+2e^- \rightarrow 2RO^-+H_2.$$
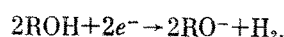
The process takes place at fairly high cathodic potentials ($E_{1/2} \approx -2.2$-2.4 V with reference to Ag/AgNO$_3$, 10^{-2} M). We supposed that it would be possible to use this reaction and the known ability of white phosphorus to react readily with nucleophiles for its functionalization [10], on the assumption that the role of the essential electrophile could be played by the halogen generated at the anode during the oxidation of the halide ions (by analogy with the familiar functionalization of the P—H bond of dialkyl phosphites by the action of iodine as catalyst). Analysis of published data showed that the most effective catalyst for the functionalization of P—H bonds was iodine, although the reasons for this were not quite clear.

In order to select a system that would make it possible to use white phosphorus most fully in the synthesis of organophosphorus compounds we examined several possible alternatives. In the first case the process was conducted in the cathode compartment of an electrolysis cell with a partition, where the white phosphorus in a medium containing iodine as electrophile reacted with the nucleophile (ethoxide ion) generated at the cathode. As a result only an insignificant amount of triethyl phosphate (yield with respect to phosphorus 15%) was isolated after ~10 F of electricity per mole of phosphorus atoms had passed through the electrolyte. This is probably due to the poor solubility of iodine in the alcohol medium and to the occurrence of side reactions involving the iodine and the white phosphorus.

In the second method the process was conducted in the anode compartment of an electrolysis cell with a partition in the presence of sodium ethoxide, previously introduced into the system with the white phosphorus, as nucleophile, and here the cleavage of the phosphorus bonds was initiated by the anodically regenerated electrophilic reagent (iodine). The product yield was increased to 60%. However, although they demonstrate the fundamental possibility of synthesizing the organophosphorus

compounds in this way, both methods are not free from disadvantages, including low yields, the need for the addition of an excess of one of the poorly soluble reagents to the electrolyte, and the occurrence of side reactions. In this connection it seemed possible and promising to combine the two methods, i.e., simultaneous generation of the nucleophilic and electrophilic particles in a nonpartitioned cell during electrolysis.

For detailed investigation we chose absolute alcohol solutions of triethylammonium iodide, in which the white phosphorus was dispersed. When current was passed through the electrolyte, a gradual change was observed in the state of the white phosphorus; it changed into yellow deposits with a high phosphorus content insoluble in organic solvents. As a result of electrolysis (which ended after complete dissolution of the phosphorus oligomers) mixtures of organophosphorus products were obtained (Table 1). Their formation can be explained in the following way. As known, during the action of the alcoholate ion generated at the cathode cleavage of the P−P bond in the phosphorus molecule takes place with the formation of the phosphide anion (1):

$$P_4 + RO^- \longrightarrow$$
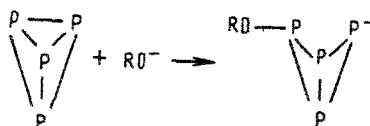
It is possible to propose several paths for the subsequent stabilization of the phosphide anion in a medium containing various electrophilic particles (the initial P_4 molecules, the products from anodic oxidation of I^-, proton donors). As a strong base (the pK_a value of the conjugate acid is 29 [11]), it must be protonated rapidly in the alcohol medium. It is known [12], however, that the molecule of white phosphorus itself reacts readily with various phosphide ions, and account must therefore be taken, particularly at the initial stages of electrolysis, of the fact that reaction concurrent with the protonation process occurs between the cyclic phosphide (1) and the next molecule of white phosphorus with the subsequent formation of polyphosphide chains, which break during protonation at various stages of growth. However, all the P−P bonds in such polyphosphides must be equivalent to a first approximation, and their subsequent cleavage must lead in the final count to the same products, as confirmed by the possibility of the selective production of one compound from white phosphorus [6]. The observed selectivity is probably due to the regioselectivity of attack by the nucleophilic and electrophilic reagents during opening of the cyclic structures.

There is no unambiguous opinion in the literature regarding the nature of the products from the anodic oxidation of the iodide ion at the electrolysis potentials (+0.2-0.3 V with reference to $Ag/AgNO_3$, 10^{-2} M). Equally probable with them may be I_3^-, I_2, and I^+, which themselves enter into equilibrium reactions with each other and with the components of the solution (I^-, the alcohol, and the $P-H$ fragments of the phosphorus oligomers) [13], and it is therefore only possible to consider iodine arbitrarily as a product of the anodic reaction.

The equilibrium $ROH + I_2 \rightleftarrows ROI + HI$ will be shifted to the right under the influence of the cathodically generated alcoholate ions. It can be supposed that under the conditions of a large excess of the alcohol over the indifferent electrolyte the substitution of the proton of the $P-H$ fragment will take place through the action of the iodoether:

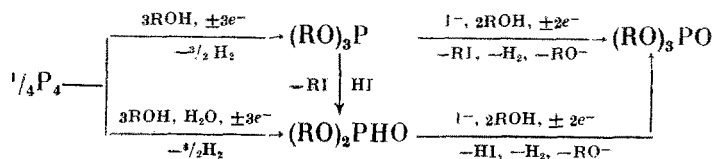$$\xrightarrow[-RO^-]{ROH} \quad \xrightarrow[-HI]{ROI}$$
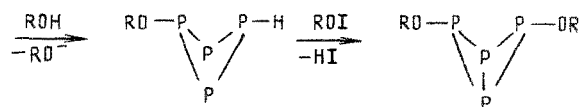
The joint action of the alcoholate ions and the iodoether on the elemental phosphorus will lead to successive cleavage of all the P−P bonds and to the formation of the phosphite $(RO)_3P$, which is clearly unstable under the electrolysis conditions (it cannot be detected) and undergoes further rapid chemical transformations. The fact that the phosphite $(RO)_3P$ is converted finally into the corresponding phosphate under the conditions of electrolysis of the alcohol solution of tetraethylammonium iodide in a cell without a partition was confirmed in independent experiments.

The products with the phosphoryl group $\,{>}P{=}O$ can probably be formed directly during decomposition of the oligomeric forms of phosphorus, and the residual water and the alcohol (which is more probable under the conditions of a large excess) can participate in their formation. More favorable conditions for the appearance of such phosphoryl groups in the oligomers can be

created at the later stages of the cleavage of the tetrahedra as a result of decrease in the strain of the rings. As yet, however, it is difficult to choose one or the other path.

On the basis of the data in Table 1 it is possible to present a general scheme for the possible processes that occur during electrolysis without separation of the anode and cathode compartments in alcohol solutions of tetraethylammonium iodide in the presence of white phosphorus:

$$\frac{1}{4}P_4 \begin{cases} \xrightarrow[-\frac{3}{2}H_2]{3ROH, \pm 3e^-} (RO)_3P \xrightarrow[-RI, -H_2, -RO^-]{I^-, 2ROH, \pm 2e^-} (RO)_3PO \\ \quad -RI \Big\downarrow HI \quad \uparrow \\ \xrightarrow[-\frac{5}{2}H_2]{3ROH, H_2O, \pm 3e^-} (RO)_2PHO \xrightarrow[-HI, -H_2, -RO^-]{I^-, 2ROH, \pm 2e^-} \end{cases}$$

The transformation of trialkyl phosphite into the corresponding phosphate is an Arbuzov rearrangement of the quasi-phosphonium compound and has been described for similar conditions, e.g., in [14]:

$$(RO)_3P \xrightarrow{I_2} (RO)_3PI_2 \xrightarrow[-HI]{ROH} (RO)_4\overset{+}{P}\overset{-}{I} \xrightarrow[-RI]{} (RO)_3PO.$$
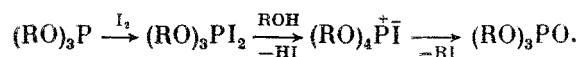
Dialkylphosphorous acid can be formed not only by acid cleavage of the trialkyl phosphite as a result of local oxidation of the electrolyte close to the anode but also direct from the white phosphorus through the residual water.

The dialkyl phosphite itself is capable of being converted in the course of electrolysis into the corresponding phosphate according to the following reaction, analogous with the functionalization of the $\diagdown$P—H bond described above:

$$(RO)_2PHO \xrightarrow[-HI]{ROI} (RO)_3PO.$$
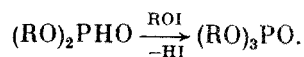
The quantitative transformation of $(RO)_2PHO$ into the phosphate was confirmed in an independent experiment under analogous conditions of electrolysis after the passage of 2.5 F/mole of electricity through the electrolyte.

Thus, several processes, directed at the final formation of the trialkyl phosphate, occur simultaneously in the system. Increase of the temperature and the presence of the alcoholate ions favor the rearrangement of the $(RO)_3P$ under the influence of the alkyl iodide, formed at the intermediate stages of the process, into the dialkyl alkylphosphonate according to the Arbuzov reaction:

$$(RO)_3P \xrightarrow{RI} (RO)_2P(O)R.$$
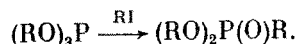
The formation of the alkyl iodide as a side product during the production of the phosphate should lead to substantial consumption of the indifferent electrolyte, but this is not observed. Analysis of the distilled solvent by GLC showed only trace quantities of RI. This result can be explained by the fact that the alkyl iodide is reduced at the cathode more readily than the alcohol in the course of electrolysis, and the indifferent electrolyte is thus regenerated. This version is confirmed by the presence of hexane in the electrolyte in the case of the initial hexyl alcohol.

The overall scheme for the formation of the trialkyl phosphate from the alcohol and white phosphorus can be written finally in the following form:

$$P_4 + 16ROH \xrightarrow{\pm 20e^-} 4(RO)_3PO + 4RH + 6H_2.$$
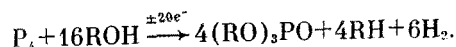
EXPERIMENTAL

To record the polarization curves with preparative electrolysis we used a P-5848 potentiostat with a three-electrode cell. The reference electrode was $Ag/AgNO_3$ with a 10^{-2} M solution in acetonitrile. The anode was platinum, and the cathode was steel. A cellulose diaphragm was used in the experiments with separate anode and cathode compartments.

The ^{31}P NMR spectra were obtained on a KGU-4 instrument at 10.2 MHz with reference to 85% phosphoric acid. Chromatographic analysis of the reaction mixtures and of the synthesized compounds was conducted on a Chrom-4 gas—liquid chromatograph with helium as carrier gas and with a flame-ionization detector. Glass columns with 5% of silicone SE-30 on Chromaton N-AW (0.125-0.160 mm) were used.

TABLE 2. Characteristics of the Synthesized Compounds

Compound	bp, °C (p, mm Hg)	n_D^{20}	$\delta\ ^{31}P$, ppm
(MeO)$_3$PO	56–57(2)	1.3968	–3
(MeO)$_2$PHO	49–50(5)	1.3990	8
(MeO)$_2$P(O)Me	44–45(2)	1.4099	31
(EtO)$_3$PO	69–70(2)	1.4060	0
(EtO)$_2$PHO	45–46(3)	1.4078	8
(EtO)$_2$P(O)Et	55–56(2)	1.4165	32
(BuO)$_3$PO	117–118(2)	1.4320	–3
(BuO)$_2$PHO	82–83(2)	1.4338	8
(BuO)$_2$P(O)Bu	98–99(2)	1.4405	30

The acetonitrile was purified by distillation over phosphorus pentoxide with the addition of potassium permanganate. The indifferent salts were recrystallized from ethanol and dried at 100°C under vacuum. The alcohols were boiled for 5 h with a reflux condenser over freshly calcined barium oxide and were then redistilled.

The reagents used as markers in GLC were the commercial reagents of chemical purity and were purified either by distillation or by recrystallization from hexane to constant physical constants.

The electrolysis was conducted at a constant current density of 1-2 mA/cm^2. At the end of electrolysis the excess of the alcohol and the solvent were distilled from the electrolyte, the indifferent salt was filtered off, and the residue was distilled under vacuum. The characteristics of the electrolysis products are given in Table 2.

LITERATURE CITED

1. F. Fluck, C. M. E. Pavlidou, and R. Janoshek, *Phosphorus and Sulfur,* **6**, No. 3, 469 (1979).
2. Ch. Brown, R. F. Hudson, and G. A. Wartew, *Phosphorus and Sulfur,* **5**, No. 3, 67 (1978).
3. M. M. Rauhut and A. M. Semsel, *J. Org. Chem.,* **28**, No. 2, 471 (1963).
4. L. Maier, *Z. Anorg. Allg. Chem.,* **394**, 117 (1972).
5. M. M. Rauhut, R. Bernheimer, and A. M. Semsel, *J. Org. Chem.,* **28**, 478 (1963).
6. Ch. Wu, *J. Am. Chem. Soc.,* **87**, No. 11, 2522 (1965).
7. Ch. Brown, R. F. Hudson, and G. A. Wartew, *J. Chem. Soc. Chem. Commun.,* No. 1, 7 (1978).
8. A. S. Romakhin, I. M. Zaripov, Yu. G. Budnikova, et al., *Élektrokhimiya,* **25**, No. 6, 780 (1989).
9. A. V. Bukhtiyarov, V. N. Gol'shin, and O. V. Kuz'min, *Zh. Obshch. Khim.,* **56**, No. 6, 1356 (1986).
10. Ch. Brown, R. F. Hudson, and G. A. Wartew, *Phosphorus and Sulfur,* **6**, No. 3, 481 (1979).
11. G. A. Lemann, Proceedings of Sixth Conference on *"Chemistry and application of organophosphorus compounds,"* Naukova Dumka, Kiev (1981), p. 194.
12. A. Schidpeter, *Nova Acta Leopoldina Neue Folge,* **59**, 69 (1985).
13. T. Shono, Y. Matsumura, and J. Hayashi, *Tetrahedron Lett.,* No. 2, 165 (1979).
14. A. W. Frank and Ch. F. Baranauckas, *J. Org. Chem.,* **31**, No. 3, 872 (1966).