ELECTROCHEMICALLY INDUCED PROCESSES IN THE FORMATION OF PHOSPHORUS ACID DERIVATIVES.

2. THE ROLE OF POLYMERIZATION PROCESSES IN THE ELECTROSYNTHESIS OF THE ESTERS OF PHOSPHORUS ACIDS FROM WHITE PHOSPHORUS

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The mechanism of the electrosynthesis of phosphate esters from white phosphorus was investigated. It was shown that the reaction takes place by two paths, i.e., monomeric (with the participation of dissolved phosphorus) and polymeric (with the participation of phosphorus on the surface of an emulsion drop). It was established that in an alcohol solution of tetraethylammonium iodide the main part of the final product is formed through an intermediate polymeric compound. It was noticed that by studying the dynamics of the accumulation of the dissolved product during electrolysis it is possible to trace the mechanism of reaction of the phosphorus at the individual stages of the process.

***Key words:** Phosphate esters, white phosphorus, electrosynthesis.*

During examination of the mechanism of the electrosynthesis of phosphate esters from white phosphorus in the previous communication [1] the phosphorus polymerization stage was not considered for reasons of simplicity, although it is known [2] that this stage is an insuperable obstacle in the synthesis of organophosphorus compounds. The experimental material accumulated by various authors makes it possible to speak of the complex nature of the polymerization stage, which depends on the conditions of the synthesis. The transformation of white phosphorus into the final products in the general case has heterogeneous character, due to the low solubility of P_4 and its oligomeric forms in the investigated reaction media, as a result of which the phosphorus is present in the form of separate phase. The nucleophilic reagent reacts with the white phosphorus on the surface of a phosphorus drop, and this in turn favors polymerization. It is impossible to rule out the probability of reaction of the phosphide anion in various directions, including the formation of three-dimensional "cross-linked" structures, significantly less reactive and involved in further transformation under more drastic conditions. However, on account of the difficulty of isolation and identification of these phosphorus oligomers such researches either were not conducted or the data from them were fairly superficial. The solid dark precipitates with a large phosphorus content, formed with an excess of phosphorus in reaction with the disulfides [3], and the unidentified phosphorus-containing side products in many other cases [4, 5] show a tendency for polymerization of the phosphorus in reductive cleavage reactions. For instance, the action of sodium naphthalide on P_4 in dimethoxyethane can lead to the formation of P_7^{3-}, P_{19}^{3-}, P_{26}^{4-}, P_{16}^{2-}, and other forms of phosphorus, which are unstable at ~20°C and are capable of rearranging and decomposing. During nucleophilic cleavage of the phosphorus by the action of $LiPH_2$ a product containing the P_5^- anion was also isolated [6]. Earlier attempts to establish the structure of the intermediate phosphorus oligomers formed during the action of nucleophiles of the PhLi and BuLi type on P_4 [2] showed that these polyphosphides probably have a cross-linked structure.

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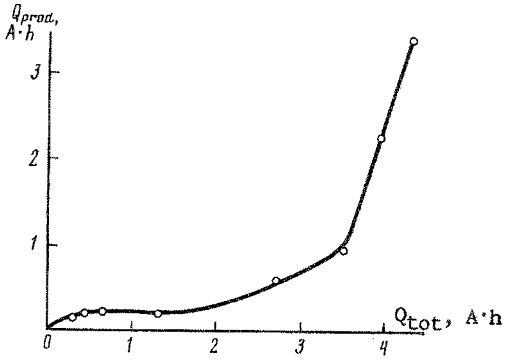


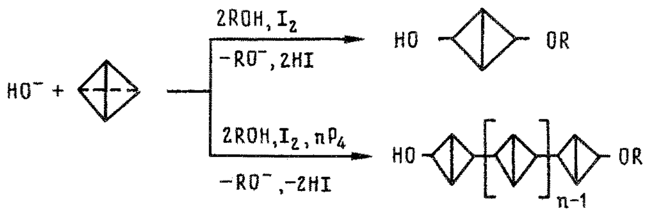
Fig. 1. Dependence of the total amount of electricity Q_{prod} used in the formation of the monomeric phosphorus-containing products on the total amount of electricity Q_{tot} used at a given time during the electrolysis of an emulsion of white phosphorus in hexyl alcohol against tetraethylammonium iodide as indifferent electrolyte.

Subsequent researches revealed the even more complicated nature of the reactions that take place after the initial action of nucleophilic reagents on the phosphorus molecule [7] and include subsequent disproportionation and elimination of polyphosphide residues from the destroyed assemblies [6, 7]. These processes are determined by the reaction conditions, i.e., by the reactivity of the nucleophilic and electrophilic components of the system, the concentration of the phosphorus, etc. [7]. The choice of conditions in a number of cases makes it possible to secure the final selective formation of products from all the intermediate oligomeric forms of phosphorus. It is possible that the direction of the polymerization of P_4 is affected by its phase state (liquid or solid), the presence of impurities, and other factors.

Thus, from the standpoint of the mechanism of the transformation of P_4 the polymerization stage merits more detailed study to control the polymerization process and to suppress it when necessary.

The aim of the present work was to study the dynamics of the accumulation of the monomeric phosphorus-containing products and the effectiveness of using electricity on the whole transformation of P_4 in an electrochemical cell.

White phosphorus is practically insoluble in polar solvents and exists in the electrolyte at $t > 44°C$ in the form of an emulsion. Therefore, although the nucleophilic and electrophilic reagents are generated simultaneously, the protonation stage may be preceded by attack on other molecules of white phosphorus. The charged nucleophile attacks the surface phosphorus atom of the P_4 molecule, and the phosphide anion is surrounded by other molecules of white phosphorus inside or on the surface of the phosphorus drop. This moment is probably the key point in the understanding of the paths for the stabilization of the initially formed phosphide anions and the whole mechanism of the involvement of white phosphorus in the reaction under the investigated conditions:



If 5 F of electricity per mole of P is used in the process, both paths (monomeric and polymeric) should lead under the favorable conditions described in the previous communication [1] to one and the same products.

In order to investigate the paths of involvement of white phosphorus in the synthesis reaction it is necessary to determine the relationship between the amount of monomeric products formed and the amount of electricity passed through the electrolyte at the various stages of the process. In spite of the difficulties in direct analysis of the intermediate forms of phosphorus, these data will probably make it possible to obtain additional information in favor of one or the other mechanism. A preliminary examination of such a relationship shows that in the simplest case it should have a linear form; the amount of the soluble products increases from zero to limiting values after passage of all the required amount of electricity; if the reaction

TABLE 1. Amount of Monomeric Phosphorus-Containing Products during the Electrolysis of an Emulsion of P_4 ($R = C_6H_{13}$), mole·10^4

Q, A·h	$(RO)_3PO$	$(RO)_2P(O)R$	$(RO)_2PHO$
0.330	1.52	–	11.5
0.434	8.8	–	5.97
0.683	11.4	0.97	3.5
1.300	12.7	0.97	2.6
2.730	37.8	13.20	1.32
3.460	52.0	32.30	–
3.890	140.0	68.0	–
4.330	197.0	110.0	–

takes place through the polymeric forms of phosphorus, the soluble products should not be formed at the initial stages on account of polymerization. In the general case the dynamics of the accumulation of the electrosynthesis products can be more complicated. The results from experiments with various amounts of electricity passed through the electrolyte are given in Fig. 1 and in Table 1.

Table 1 gives the molar quantities of the three main monomeric products (trihexyl phosphate, dihexyl hexylphosphonate, and dihexyl phosphite), found in the electrolyte during electrolysis of an emulsion of white phosphorus (0.0323 mole of P). Under the described conditions, as seen from the presented data, up to 95% of the taken phosphorus can be converted into the phosphate and phosphonate with a certain overconsumption of electricity. The curve drawn in Fig. 1 characterizes the total amount of electricity Q_{prod} used at a given moment of time on the formation of the monomeric phosphorus-containing products in relation to the total amount of electricity Q passed through the electrolyte at this moment of time. If the formation of the monomeric products took place according to the equations:

$$\tfrac{1}{4}P_4+3ROH+H_2O \xrightarrow{\pm 5e^-} (RO)_3PO+\tfrac{5}{2}H_2$$

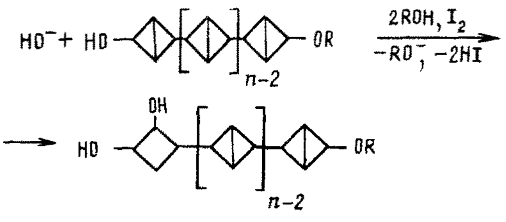
$$\tfrac{1}{4}P_4+3ROH \xrightarrow[RI]{\pm 3e^-} (RO)_2P(O)R+\tfrac{3}{2}H_2$$

$$\tfrac{1}{4}P_4+2ROH+H_2O \xrightarrow{\pm 3e^-} (RO)_2PHO+\tfrac{3}{2}H_2,$$

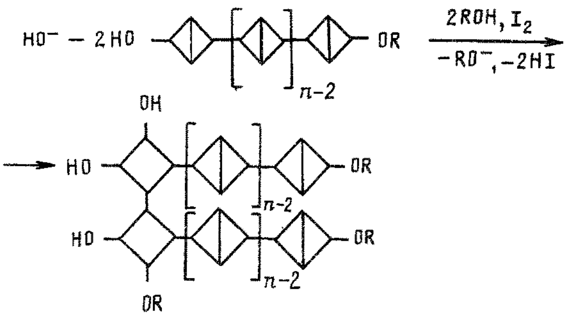
a linear relationship with a slope equal to the current yield would be observed against the coordinates Q_{prod} and Q_{tot}. Since the experimental relationship is nonlinear (Fig. 1), the synthesis takes place in a more complicated manner. It can be supposed that at the beginning of the process the synthesis of the esters of the phosphorus acids takes place in two directions; one part of the phosphorus is present in the electrolyte in the form of an emulsion, while the second is in the dissolved state.

The polymerization is a second-order reaction, and its rate in liquid phosphorus is much higher than its rate in solution. The dissolved phosphorus is therefore transformed into the products, by-passing the polymerization stage. At the beginning of electrosynthesis the contribution from the polymeric form to the formation of the products is insignificant. One way of suppressing the polymerization processes may be to use dissolved phosphorus in the experiments and also to reduce the working current density.

The constancy of the molar quantity of the dissolved synthesis products at the section up to 1.5 A·h of electricity indicates that electricity is used on the transformation of the polymeric form of phosphorus without the formation of soluble products according to the following scheme:



It is also impossible to exclude "cross-linking" of the linear macromolecules with each other:



It is, however, difficult to obtain information about the structure of the polymeric form. The accumulation of the liquid products in the electrolyte at the section between 1.5 and 3.5 A·h is probably due to the fact that together with the transformations of the polymer not leading to the final products the P–P bonds are cleaved at the ends of the polymer and fixed trialkyl phosphate and dialkyl alkylphosphonate are formed.

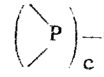
The abrupt increase of the curve after 3.5 A·h may be due to the fact that at this moment the polymer is completely saturated with organic fragments and no bonds whose cleavage would not lead to the formation of the detected products remain within it.

The slope of the tangents to the curve of the various sections reflects to "effectiveness" of the electrochemical process $\Delta Q_{prod}/\Delta Q_{tot}$, i.e., the current yield. At the initial stages of electrolysis (up to 0.5 A·h), where the dissolved phosphorus reacts, the current yield amounts to 40%, and this is then followed by a sharp decrease – electricity is used on the polymerization processes. On the section of the curve between 1.5 and 3.5 A·h the current yields are again increased to ~33% on account of destruction of the polymeric structures. After 3.5 A·h the "effectiveness" of the process is greatly increased to 330%. This supports the arguments given above about the formation of the phosphates at the last stages of electrolysis from the polymeric forms of phosphorus functionalized to a large degree by the alkoxy groups. The phosphonate product from rearrangement of the trialkyl phosphite is formed at a finite rate in competition with the fast transformation of the latter into the phosphate, and the "effectiveness" of its accumulation in the electrolyte is not therefore so high.

The dialkyl phosphite is present in the electrolyte only at the initial stages of electrolysis and is probably formed mainly with participation of the residual water.

It should be noted that even under the most favorable conditions for the synthesis of the organophosphorus compounds, where all the intermediate polymeric structures can be destroyed and complete conversion of the P_4 into the soluble products can be realized, the reaction of the phosphorus is fairly complicated in nature.

The obtained preliminary results show that in certain cases, e.g., with a reduction in the protogenic activity of the medium, it is not possible to bring all the phosphorus completely into the desired reaction, and part of it remains in the polymeric form, the structure of which must probably differ from the forms that are smoothly converted into the liquid products.

The suggestion about the participation of nucleophilic particles of the  type in the cleavage of the P–P bonds in this case is directly confirmed by the heterogeneous nature of the transformation of the phosphorus into pyrophosphates.

It was found that the nature of the solvent also has an effect on the polymerization stage. Thus, in DMFA, for example, the fraction of phosphorus converted into the final products through the polymeric form is appreciably smaller, and the dynamics of the accumulation of the final products consequently differ from those described above. The impossibility of producing the pyrophosphates in DMFA, glyme, and other solvents is probably also due to the transformation paths of the phosphorus and to the structure of its intermediate forms. Another example is the reaction of P_4 in a secondary amine medium in acetonitrile, where the phosphorus is almost completely polymerized at the initial stages of electrolysis, while in DMFA under the same conditions the polymer is not formed at all and the emulsion of phosphorus quickly changes into a red solution of phosphorus oligomers. It is clear that the facts presented above require a more detailed study.

EXPERIMENTAL

The apparatus and conditions of electrosynthesis were similar to those used in [1]. The yields of the synthesized compounds were determined by GLC. The assignment of the chromatographic peaks was made by comparison of their retention times with the retention times of standard industrial samples. The quantitative treatment of the chromatograms was realized by the internal standard method, for which tripropyl phosphate was used. The internal standard was added to the electrolyte after electrolysis before treatment of the reaction mixture. The treatment was similar to that described in [1].

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