

Electrochemical synthesis of phosphorus esters from white phosphorus in the presence of copper complexes and ethanol

Yu. H. Budnikova,^{a*} A. G. Kafiyatullina,^a O. G. Sinyashin,^a and R. R. Abdreimova^b

^aA. E. Arbutov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.

Fax: +7 (843 2) 75 2253. E-mail: yulia@iopc.knc.ru

^bInstitute of Organic Catalysis and Electrochemistry,

142 ul. Kunaeva, 480100 Alma-Ata, Kazakhstan.

E-mail: abdreimioce@nursat.kz

In the presence of white phosphorus the redox potentials of the copper ions change and the potential of the reduction wave of $\text{Cu}^{\text{I}}/\text{Cu}^0$ shifts noticeably toward more positive values. The $\text{Cu}^{\text{I}}-\text{P}_4$ complex is characterized by a lower value of the electrochemical gap, that is, higher polarizability and reactivity compared to those of the free Cu^{I} cation. Phosphorus esters can be synthesized from P_4 and ethanol. The latter is in the composition of the copper(II) complexes, which act as a catalyst-charge mediator.

Key words: catalysis, electrochemistry, copper complexes, white phosphorus, phosphorus esters.

Since copper(II) is characterized by high complex-forming ability and its salts and complexes are highly soluble in organic solvents and can be regenerated by oxygen, copper(II) complexes are widely used in catalysis,^{1–8} including the synthesis of organophosphorus compounds from white phosphorus.^{2–7} At the same time, only few electrochemical syntheses involving copper catalysts have been studied.⁸

It is known^{2–4} that the reaction of white phosphorus with an ethanol solution of the copper(II) acido complexes under oxygen affords trialkyl phosphates and dialkyl phosphites. The phosphorus-containing compounds are formed in the step of copper(II) reduction to copper(I) by white phosphorus, and oxygen acts as an oxidizing agent to recover copper(II). Under aerobic conditions this reaction requires additional precautions. Water, which is produced by the oxidation of Cu^{I} with dioxygen, provokes a side reaction, the oxidative hydroxylation of P_4 to phosphoric acid, decreasing the yield of the organophosphorus products.^{2–4}

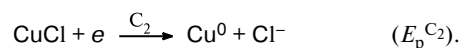
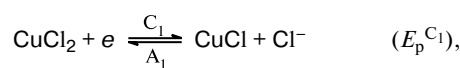
We suggested that the oxidation of Cu^{I} to Cu^{II} in this process can be carried out electrochemically. An important advantage of the electrochemical regeneration of the catalyst could be an enhancement of the yield of the target products due to elimination of side reactions.

This work is aimed at studying by cyclic voltammetry and preparative electrolysis the electrochemical behavior of the copper(II) salts and complexes in the absence and presence of P_4 , their role in the electrocatalytic synthesis

of phosphorus esters from white phosphorus, and the mechanism of these reactions.

Results and Discussion

Voltammetric studies. The published data on the electrochemical behavior of the copper salts and complexes concern with different conditions and methods and are incomplete.^{9–15} In this work, using cyclic voltammetry (CV) on a stationary glass-carbon (GC) electrode, we studied chemical transformations of copper(II) chloride in the presence and absence of white phosphorus in aprotic (MeCN, DMF), proton-donor (EtOH), and mixed media (aprotic solvents with EtOH additives) in an argon flow. The obtained data are presented in Figs. 1–6. The reduction of CuCl_2 in the chosen solvents proceeds in two steps consuming one electron per the formula unit of CuCl_2 at each peak potential and can be described by the following scheme:



The first reversible peak has the anodic component (A_1) of Cu^{I} oxidation (see Figs. 1, 2, and 4–6) related to the cathodic process (C_1), and the second peak is irreversible in most cases (except for a MeCN–EtOH mix-

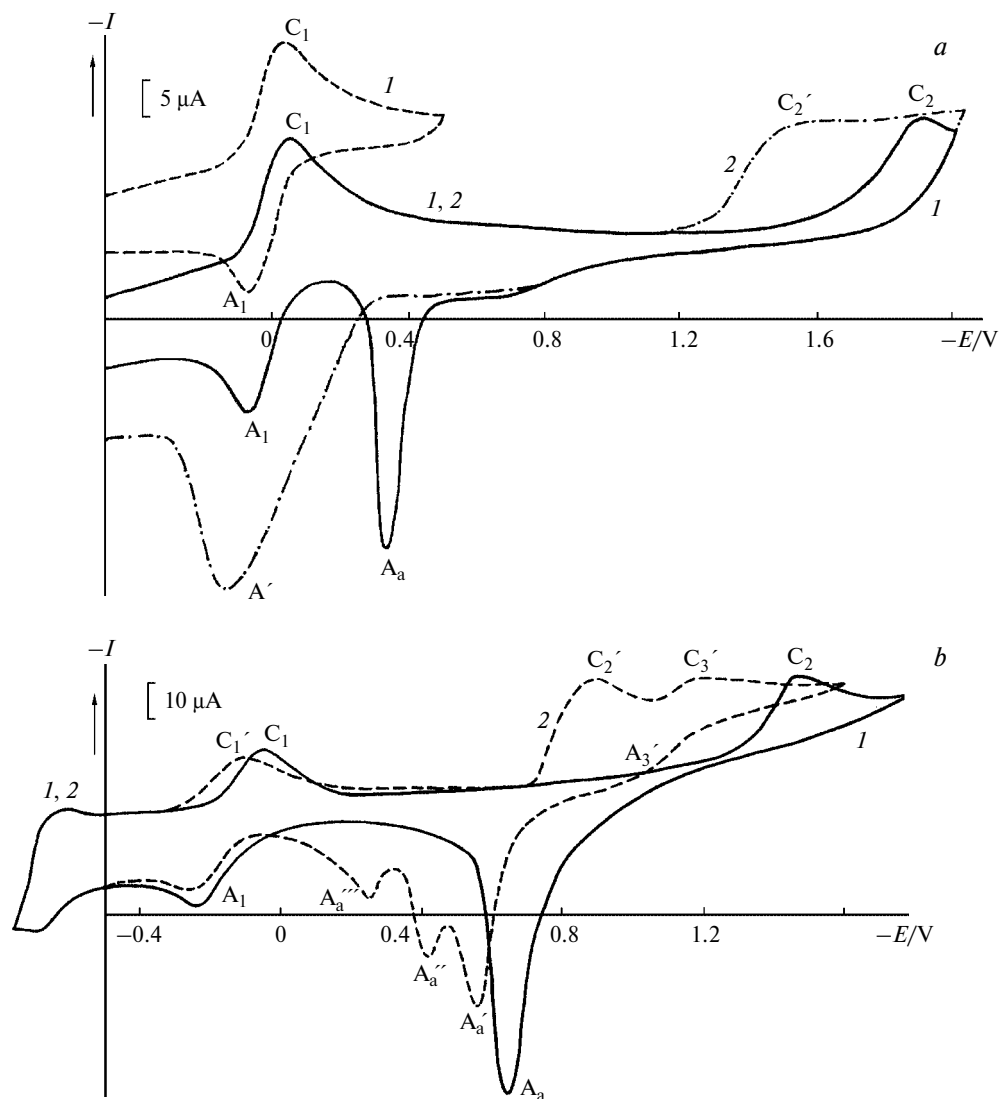


Fig. 1. CV curves for solutions of CuCl_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) in DMF (a) and in MeCN (b) in the absence (1) and presence (2) of white phosphorus ($1.5 \cdot 10^{-2} \text{ mol L}^{-1}$).

ture, where a series of close reversible cathodic peaks of reduction, most likely, of different copper(I) ethoxides are observed) (see Fig. 2, b). A great difference between the potentials of the first and second cathodic processes is probably due to the high thermodynamic stability of Cu^{I} in these systems, particularly in the aprotic medium (see Fig. 1). The reverse scan beginning from the more negative potential than $E_p^{C_2}$ results in the oxidation peaks of electrodeposited copper. A symmetrical shape of the peaks without a diffusional tail indicates their adsorption nature.

The oxidation peak of halide ions in solutions of CuCl_2 corresponds to oxidation and lies in the anodic potential region (approximately +1.0 V in DMF).

The gradual addition of white phosphorus (as a saturated solution in benzene) to a solution of CuCl_2 changes the shape of the CV curves, which is related, most likely,

to both complex formation and other chemical reactions. In aprotic media and at a low content of EtOH, the potential of CuCl_2 reduction somewhat shifts in the anodic direction, but the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ peak remains reversible. Insignificant changes in the CV curves in these solutions upon the addition of P_4 can be explained by either the low rate of formation of the corresponding complexes and their low stability or a comparable stability of the complexes formed by both components of the redox pair. Probably, the Cu^{I} complex is stable in a solution under these conditions. Therefore, the peak of its reduction (C_2^{I}) is observed at a more negative potential $E_p^{C_2}$, which can be explained by binding of Cu^{I} to form the complex with phosphorus $\text{Cu}^{\text{I}}(\text{P}_4)_n$. It is known¹⁶ that the electrochemical redox potentials reflect, to some approximation, the energies of HOMO and LUMO of compounds even when

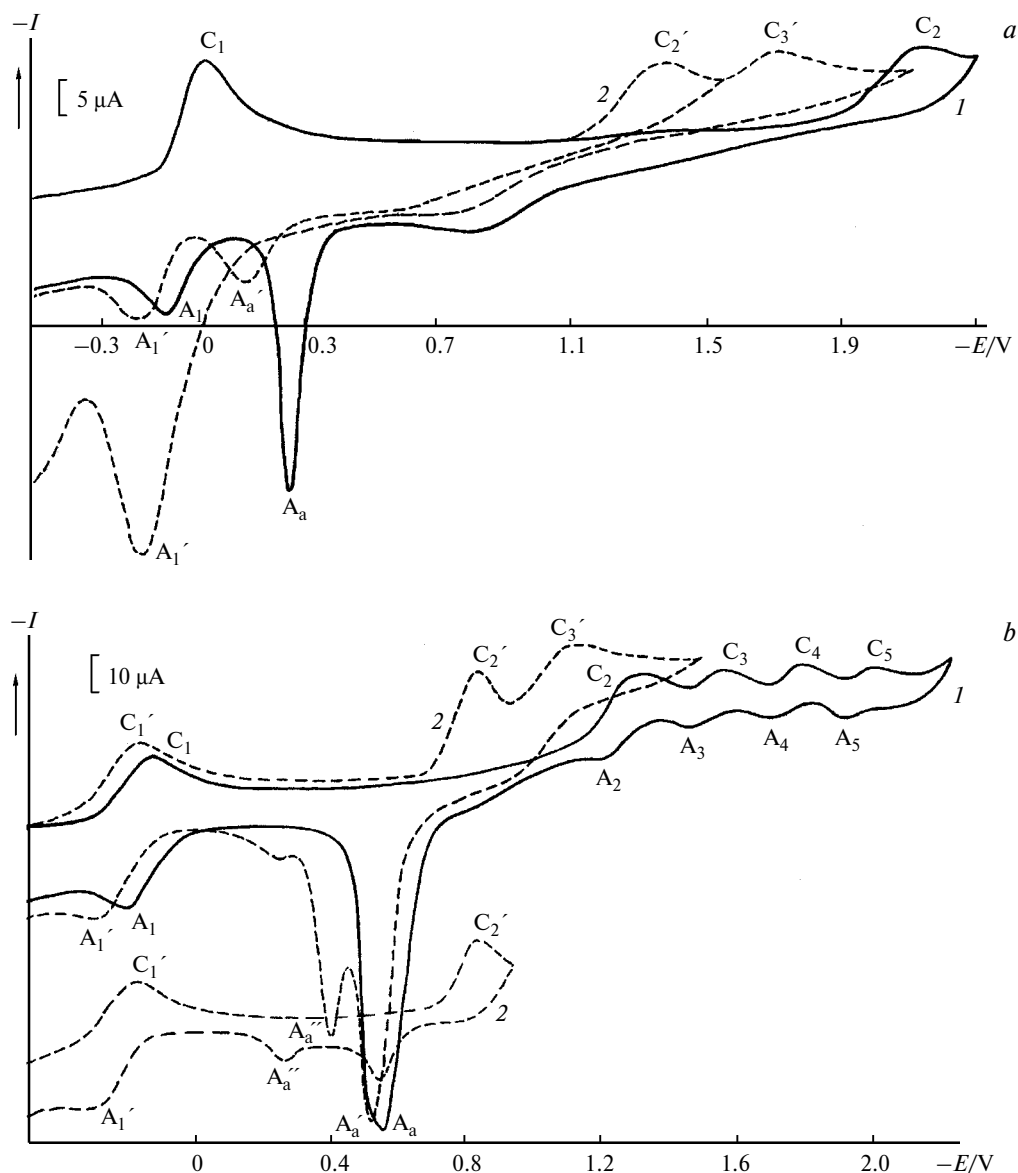


Fig. 2. CV curves for solutions of CuCl_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) in DMF (a) and in MeCN (b) with EtOH additives ($2 \cdot 10^{-2} \text{ mol L}^{-1}$) in the absence (1) and presence (2) of white phosphorus ($1.5 \cdot 10^{-2} \text{ mol L}^{-1}$).

the processes are thermodynamically irreversible. Complex formation changes these energies and shifts E_p . π -Acceptor ligands (2,2'-bipyridine, phosphine, and phosphites) shift E_p of the reduction of the complexes toward less negative potentials thus facilitating reduction.¹⁷ Anodic scan results in a large peak of oxidation of copper phosphides ($E_p^A \approx -0.1 \text{ V}$ in DMF and -0.3 V in EtOH). The heights of the $I_p^{C_1}$ and $I_p^{C_2}$ peaks remain unchanged, indicating the absence of a noticeable chemical reaction between Cu^{II} and P_4 under these conditions. Only in the presence of great excess EtOH (when it is the only solvent), a more complicated, changing in time pattern is observed (see Fig. 6). Several minutes after phosphorus was added to a solution of CuCl_2 in EtOH (against LiClO_4

or Bu_4NBF_4), the voltammogram exhibits a slight shift of the $E_p^{C_1}$ and $E_p^{C_2}$ potentials with the retention of reversibility of the first peak. However, after 30 min, in the same solution (under argon) the heights of reduction peaks (C_1^{II} and C_2^{II}) decrease simultaneously, *i.e.*, the concentrations of Cu^{II} and Cu^{I} in a solution decrease (the current is proportional to the concentration of the species). Therefore, it is improbable that Cu^{II} oxidizes P_4 and transforms into Cu^{I} . It is most likely that copper polyphosphides, which are electrochemically inactive in the accessible cathodic region of potentials, are formed in the solution. The solution becomes brown with time, and a brown precipitate is gradually formed. After some time, the C_1^{II} and C_2^{II} peaks disappear, and both the initial

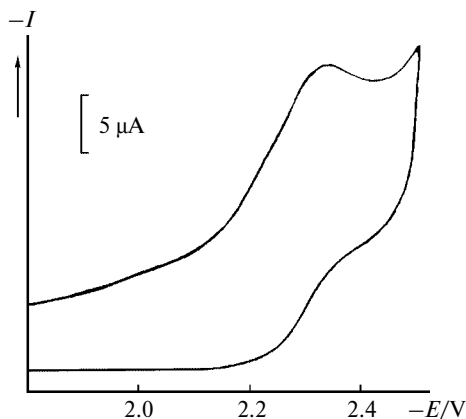


Fig. 3. CV curves for solution of white phosphorus ($1 \cdot 10^{-2} \text{ mol L}^{-1}$) in MeCN with a benzene additive (10 vol.%) against $0.1 \text{ M Et}_4\text{NBF}_4$.

Cu^{II} ions and Cu^{I} ions are absent from the solution (see Fig. 4), whereas the peak of excess phosphorus is observed at its standard potential of -2.35 V (see Fig. 3). The observed influence of the EtOH concentration on the reaction of Cu^{II} with phosphorus (Table 1) suggests that EtOH is the third reactant in this reaction, and the phosphorus-containing intermediate products contain the EtO groups.

Unlike the known catalytic oxidative alkoxylation of P_4 in the presence of oxygen,^{2–4} in this work we used the electrochemical regeneration of Cu^{II} . In this method, Cu^{I} should be oxidized on the anode either through a mediator (for example, Cl_2 formed by the oxidation of the Cl^- ions) or immediately on the anode through a heterogeneous reaction (in the absence of the Cl^- ions in a solution).

The potential of the beginning of oxidation of the components of the $\text{CuCl}_2\text{--P}_4\text{--EtOH}$ system is close to the oxidation potential of Cl^- . When the synthesis is carried out in an undivided electrochemical cell, EtOH can be reduced on the cathode, and either Cl^- or copper polyphosphides can be oxidized on the anode (at low concentrations of EtOH or in its absence, the CV curves contain a pronounced diffuse anodic peak at low anodic potentials ($+0.2\text{--}+0.3 \text{ V}$)). This peak (A^1) appears due to the superposition of several peaks of oxidation of the copper phosphides with close oxidation potentials. Although the main potential of the broad peak is close to the oxidation potential of Cu^{I} (A^1), its shape is more complicated (great currents and peak widths).

We studied the electrochemical behavior of the copper(II) complexes with 2,2'-bipyridine (bpy) in the absence and presence of P_4 to stabilize the copper ions

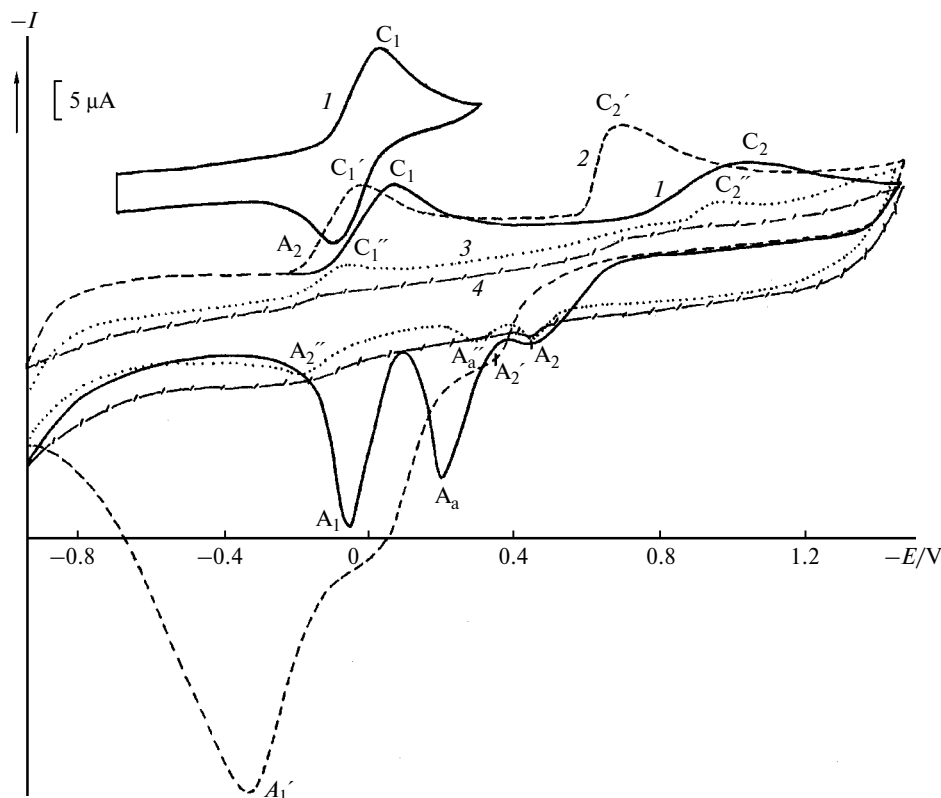


Fig. 4. CV curves for solutions of CuCl_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) in EtOH against 0.1 M LiClO_4 in the absence (1) and presence (2–4) of white phosphorus: 2, $5 \cdot 10^{-3} \text{ mol L}^{-1}$, immediately after addition; 3, the same after 0.5 h; and 4, 1 h after addition of P_4 ($1 \cdot 10^{-2} \text{ mol L}^{-1}$).

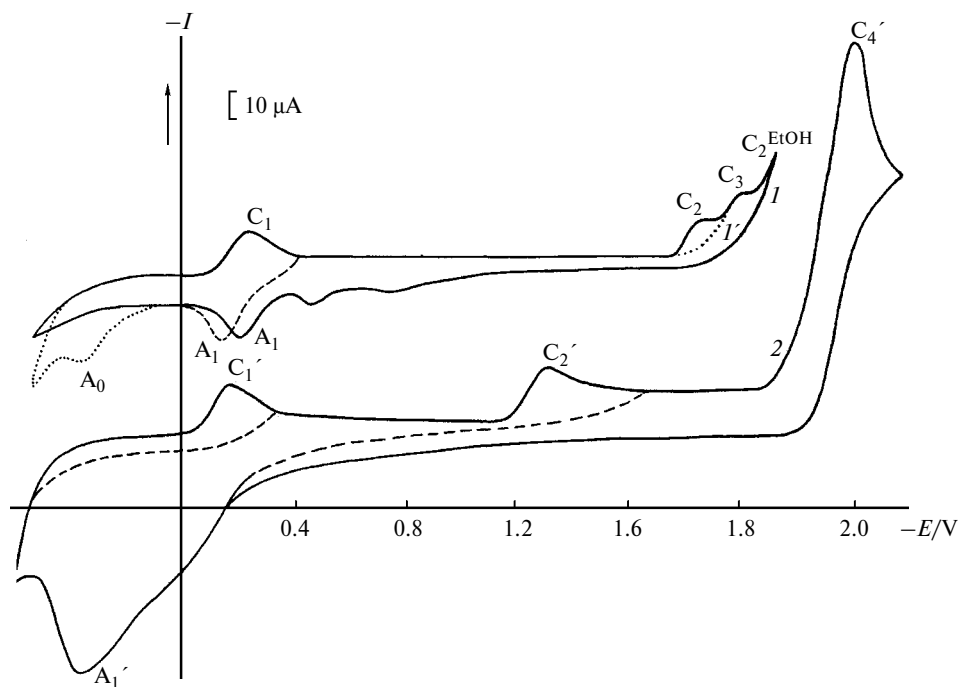


Fig. 5. CV curves for solutions of CuCl_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) + bpy ($1.5 \cdot 10^{-2} \text{ mol L}^{-1}$) in DMF (I) and a DMF–EtOH mixture ($2 \cdot 10^{-2} \text{ mol L}^{-1}$) (I') in the absence (I, I') and presence (2) of white phosphorus ($1 \cdot 10^{-2} \text{ mol L}^{-1}$).

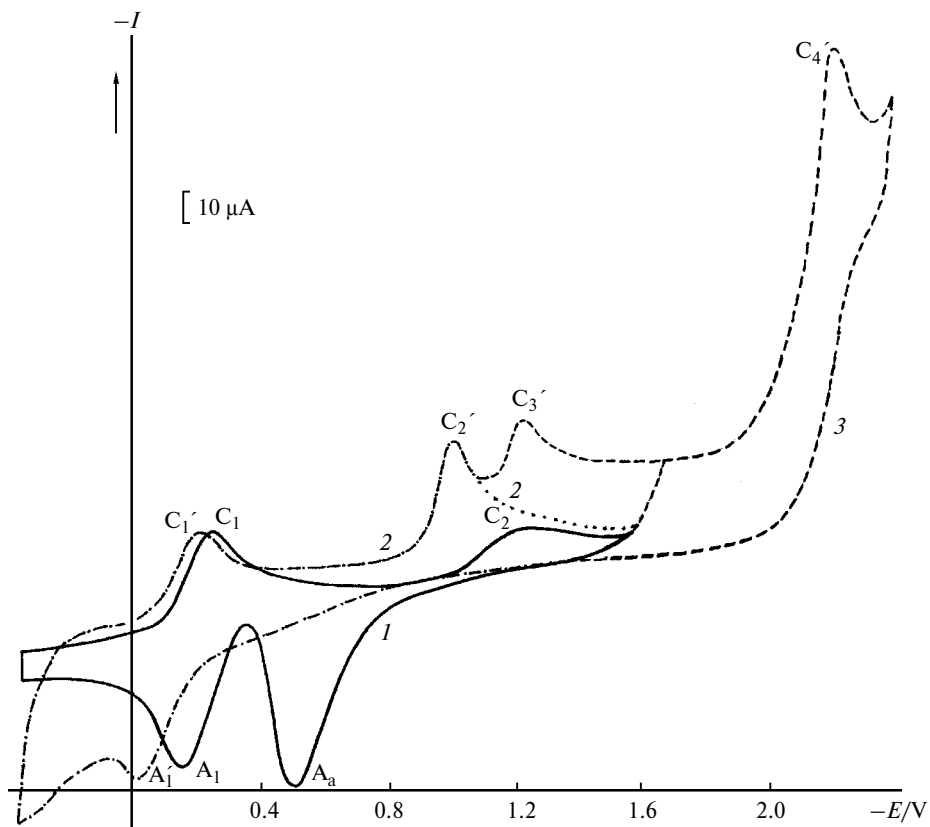


Fig. 6. CV curves for solutions of CuCl_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) + bpy ($1.5 \cdot 10^{-2} \text{ mol L}^{-1}$) in MeCN (I) in the absence (I) and presence of phosphorus in concentrations of $5 \cdot 10^{-3}$ (2) and $1.5 \cdot 10^{-2} \text{ mol L}^{-1}$ (3).

Table 1. Yields of the products of electrolysis of solutions of P_4 in EtOH, DMF–EtOH, and MeCN–EtOH in the presence of $CuCl_2bpy_3$ in the undivided cell

Product	Yield (%)		
	EtOH	DMF–EtOH	MeCN–EtOH
$(EtO)_2P(O)Et^*$	17.5	5.4	15.5
$(EtO)_2PHO^*$	16.0	15.3	29.5
$(EtO)_3PO^*$	28.5	79.3	55.0
Sum of products**	62	90	81

* The yield calculated per P is presented.

** The total yield is presented.

and intermediates by complex formation. The $CuCl_2bpy_3$ complex is characterized by two cathodic peaks in a solution of MeCN and by three cathodic peaks in DMF. The addition of bpy to a solution of $CuCl_2$ in DMF or MeCN remarkably shifts the peaks of the Cu^{II}/Cu^I redox system to the cathodic direction with retention of their reversibility (see Figs. 5 and 6). A great difference in the $E_p^{C_1}$ and $E_p^{C_2}$ potentials gives evidence for a high thermodynamic stability of Cu^I in a DMF solution and a lower stability in MeCN. Minor EtOH additives (with respect to the main solvent) to the electrolyte ($CuCl_2 : EtOH = 1 : 4$) have almost no effect on the shape of the CV curves. The changes concern the C_2 and C_3 peaks in DMF (they join), and a new irreversible oxidation peak (approximately +0.35 V), which does not coincide with the peak of Cl^- oxidation, appears in all cases. The transformation of $Cu^{II}L_3$ into Cu^IL_2 is reversible, and the transformation of Cu^IL_2 into Cu^0L_2 is irreversible. The addition of phosphorus only insignificantly shifts the C_1 peak to the anodic region in MeCN and exerts no effect on its position in DMF. In the presence of phosphorus, the first C_1 wave is reversible in MeCN and irreversible in DMF. It is most likely that the fast chemical reaction of Cu^I with P_4 occurs in the latter case. The addition of P_4 to the copper complex does not substantially change the heights of the C_1 and C_2 peaks (or $C_2 + C_3$). This indicates the absence of a fast chemical reaction of $CuCl_2bpy_3$ with white phosphorus, likely, due to the absence of free coordination sites for P_4 in this complex. It is noteworthy that the peak of reduction of P_4 itself, which is observed at high cathodic potentials ($E_p = -2.35$ V), is much higher than the diffusional peak, *i.e.*, this is rather catalytic peak. The EtOH additives to the $CuCl_2bpy_3$ complex do not remarkably change the shape of the curves in both the absence and presence of white phosphorus.

The shifts of the reduction potential of Cu^I upon phosphorus addition depend on the solvent nature and the presence of the bpy ligand (Table 2). For example, for $CuCl_2bpy_3$ the greatest shift is observed in DMF, and for $CuCl_2$, in MeCN. In a solvent–EtOH mixture, the presence of the ligand has no noticeable effect on the ΔE^{C_2}

Table 2. Change in the reduction potential of Cu^I/Cu^0 (ΔE^{C_2}) in various solvents with white phosphorus additives ($P_4 : Cu^{II} = 3$) in the presence of the $CuCl_2$ and $CuCl_2bpy_3$

Catalyst	$\Delta E^{C_2}/V$			
	DMF	MeCN	DMF–EtOH	MeCN–EtOH
$CuCl_2$	0.41	0.55	0.73	0.51
$CuCl_2bpy_3$	0.61	0.36	0.80	0.36

value. It is likely that the electrochemical gaps, *viz.*, differences between the potentials of reduction and oxidation of a species $G = E^A - E^C$ (V), can most correctly be used instead of particular reduction potentials for the estimation of the reactivity of species.¹⁸ The electrochemical gap characterizes the polarizability and donor ability of a complex. The electrochemical gap values for Cu^I ($CuCl$ or $CuClbpy$) in the absence and presence of white phosphorus are presented in Table 3. In most cases, with some exception, $G(Cu^IP_4) < G(Cu^I)$. Thus, Cu^I-P_4 is a more easily polarized ("softer") and, hence, more reactive complex than Cu^I ($CuCl$ or $CuClbpy$) in the absence of P_4 .

An increase in the EtOH concentration in a solution of $CuCl_2bpy_3$ (unlike $CuCl_2$) does not affect the process, and white phosphorus does not react for several days. According to the ^{31}P NMR and CV data, no changes occur in the system.

Thus, the redox properties of the copper complexes change in the presence of white phosphorus, and the reduction potential of Cu^I/Cu^0 shifts strongly toward more positive values. The Cu^I-P_4 complex is characterized by a lower electrochemical gap, *i.e.*, it is more readily polarizable and reactive than the initial Cu^I . The reactivity of the copper ions changes in the presence of the bpy ligand.

Preparative electrolysis. Preparative electrosynthesis of phosphorus esters from white phosphorus and EtOH in the presence of the copper complexes was carried out in an undivided electrochemical cell. The supporting electrolyte was Et_4NBF_4 (0.02 M solution in EtOH or in a mixture of EtOH with an aprotic solvent). Electricity (5 F per P atom) was passed through the electrolyte at 50 °C. The catalyst was $CuCl_2$ or the $CuCl_2-bpy$ complex. After

Table 3. Electrochemical gap for Cu^I ($G = E^A - E^C$) in various solvents in the absence (figures in the numerator) and presence of P_4 (figures in the denominator)

Catalyst	G/V			
	DMF	MeCN	DMF–EtOH	MeCN–EtOH
$CuCl_2$	<u>1.80</u>	<u>1.23</u>	<u>2.01</u>	<u>1.11</u>
	1.33	0.64	1.19	0.50
$CuCl_2bpy_3$	<u>1.43</u>	<u>1.05</u>	<u>1.92</u>	<u>0.93</u>
	0.84	0.99	1.27	1.00

electrolysis, the color of the solution changed from light green to brown. A minor amount of a brown phosphorus-containing precipitate is formed in a solution of EtOH or in an EtOH–MeCN mixture, whereas no precipitate is formed in an EtOH–DMF mixture. In all the cases, triethyl phosphate, diethyl ethylphosphonate, and diethyl phosphite were the reaction products (composition was determined from the integral intensity in the ^{31}P NMR spectrum, see Table 1).

Thus, the most optimal conditions for the synthesis of phosphorus-containing products from P_4 are those with the use of the CuCl_2bpy catalyst in a DMF–EtOH mixture. In this case, phosphorus is completely converted to organic derivatives, among which triethyl phosphite predominates. An increase in the amount of the passed electricity to $\sim 6 F$ makes it possible to transform all the diethyl phosphite into triethyl phosphite. Diethyl ethylphosphonate is the product of rearrangement of triethyl phosphite.

For comparison, we carried out electrooxidation in a divided cell. A saturated solution of white phosphorus in toluene was added to the anolyte containing CuCl_2 in a solution of EtOH. This solution was electrolyzed in the galvanostatic regime at 50°C . At the moment of addition of white phosphorus (0.5 moles of P_4 per mole of CuCl_2) the potential of the anode did not change. After the repeated addition of phosphorus (in the first minutes of electrolysis) to the ratio $\text{P}_4 : \text{CuCl}_2 = 3 : 1$, the color of the solution sharply became brown, a brown precipitate formed, and the anodic potential began to shift gradually

to the anodic region, to the oxidation potential of Cl^- . These observations agree with the results obtained by the CV method: some time after the beginning of electrolysis, the solution contains no copper ions and the cell voltage increases dramatically. The use of, e.g., Et_4NCl as supporting electrolyte maintains the conductivity of the medium. In this case, the anodic oxidation of Cl^- can be used for regeneration of free copper ions in that or another oxidation state, although the phosphorus-containing precipitate remains in the solution even after passing $6 F$ electricity per P atom. The electrolysis products are ethyl phosphorus esters, viz., $(\text{EtO})_3\text{PO}$, $(\text{EtO})_2\text{PHO}$, $(\text{EtO})_2\text{P}(\text{O})\text{OH}$, and others. The electrolyte is acidified. Thus, undivided electrolysis provides the lower yield and selectivity.

As mentioned in the literature,^{2–4} the $\text{Cu}^{\text{II}} : \text{P}_4$ ratio exerts a substantial effect on the rate and selectivity of the oxidative alkoxylation of white phosphorus in the presence of the copper catalysts, and in excess copper salt (molar ratio $\text{Cu}^{\text{II}} : \text{P}_4 = 15\text{--}20$) P_4 can rapidly be transformed into triethyl phosphate without intermediate formation of insoluble copper polyphosphides or Cu^0 . We carried out the chemical reduction of CuCl_2 by white phosphorus ($\text{CuCl}_2 : \text{P}_4 = 20$) in EtOH in an argon atmosphere at $55\text{--}60^\circ\text{C}$. The primary emerald color of the solution became light green within 1 h but no precipitate was formed.

According to the ^{31}P NMR spectroscopic data, the resulting solution contains triethyl phosphate bound to the copper ions (6 ppm). The CV data showed that the

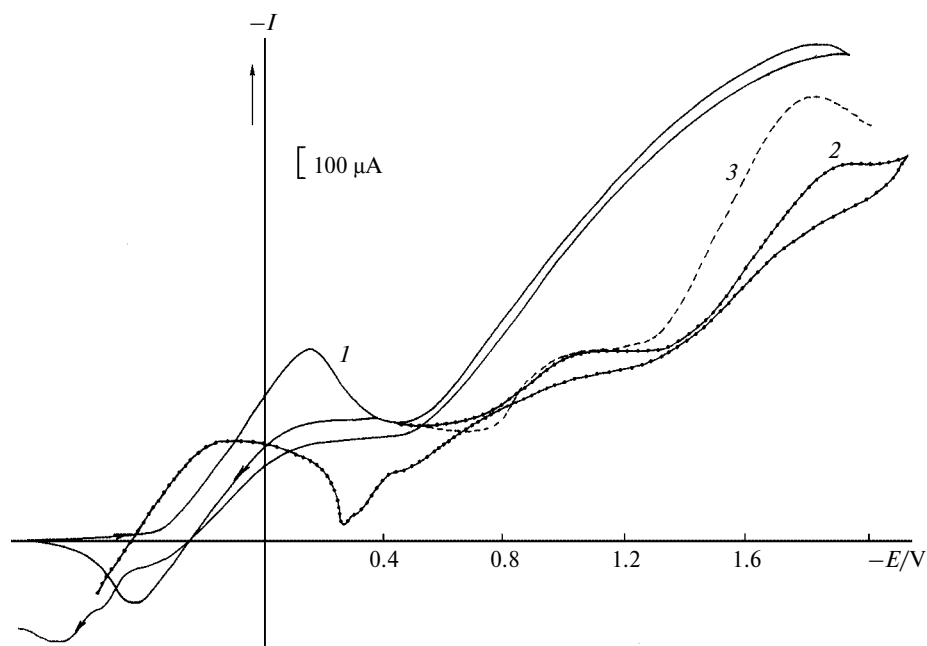


Fig. 7. CV curves in EtOH against $0.1 M \text{Et}_4\text{NBF}_4$ after the reaction (1 h) of CuCl_2 (0.2 mol L^{-1}) with P_4 dissolved in toluene: 1, $\text{CuCl}_2 : \text{P}_4 = 20$ immediately after the reaction at 60°C (the color of the solution changed from emerald to light green); 2, under the same conditions after cleaning of the electrode; and 3, $\text{CuCl}_2 : \text{P}_4 = 10$ (a brown solution).

Cu^{II} concentration decreased and Cu^{I} appeared (the second peak increased over the first peak), although Cu^{I} exists in a solution, most likely, in different forms, because it is characterized by two rather one peaks (Fig. 7). However, since under these conditions all copper compounds exist in a solution, Cu^{I} can electrochemically be oxidized to Cu^{II} . Then P_4 can be added again, Cu^{II} can be reduced to Cu^{I} , and the electrochemical oxidation of Cu^{I} can be repeated to accumulate $(\text{RO})_3\text{PO}$ in the solution. However, when the process is performed in an undivided cell, much smaller excess copper chloride and a higher concentration of phosphorus can be used to obtain higher yields of the product based on the solution volume at a much higher rate of the process.

The addition of triethyl phosphate to a solution of CuCl_2 in EtOH shifts the potentials of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}/\text{Cu}^0$ peaks to the cathodic region (to -0.16 V). The formation of the Cu^{II} complex with $(\text{EtO})_3\text{PO}$ that formed explains the above-mentioned cathodic shift of the equilibrium potential of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ pair approximately by the same value after the reaction ceased in the $\text{CuCl}_2\text{—EtOH—P}_4\text{—arene—O}_2$ system.

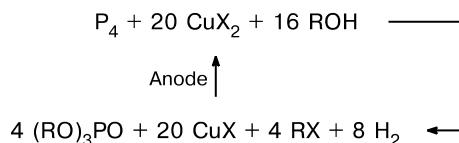
It is of interest to reveal routes of intermediate transformation of the copper complexes.



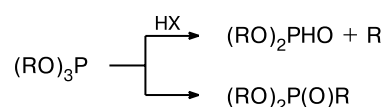
It has previously been asserted^{2–4} that at $\text{CuCl}_2 : \text{P}_4 = 1\text{—}12$ the Cu^{II} atoms are reduced by tetraphosphorus to Cu^0 avoiding formation of copper-phosphorus intermediates, and at greater excess CuCl_2 ($\text{Cu}^{\text{II}} : \text{P}_4 \geq 20$), they are reduced to Cu^{I} . The $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ reaction is confirmed by the results of our experiments on the synthesis of trialkyl phosphate from P_4 and the CV data for the oxidized and reduced copper species (see above). However, our experiments at $\text{Cu}^{\text{II}} : \text{P}_4 < 10\text{—}12$ gave insoluble copper polysulfides instead of Cu^0 . It can be assumed that Cu^0 forms a complex with the P_4 ligand. However, similar M^0L complexes ($\text{M} = \text{Ni}, \text{Co}, \text{Cu}$; $\text{L} = \text{bpy}, \text{PPh}_3$, and others) are reduced in the accessible potential region ahead of the ligand.¹⁷ Our CV study did not detect the Cu^0P_4 complex in a solution likely because of its low stability.

In further experiments, we replaced copper(II) chloride by acetate, which, as can be assumed, can more easily be reduced to elemental copper with white phosphorus. The CV data showed that the reaction of $\text{Cu}(\text{AcO})_2$ with P_4 (in a ratio of 10 : 1) in EtOH against Et_4NBF_4 results in the disappearance of the copper(II) ions. A black precipitate containing copper and phosphorus is formed in a solution, which contradicts the assumption^{2–4} on the reduction of Cu^{II} to Cu^0 with white phosphorus. The reaction products contained $(\text{EtO})_3\text{PO}$ and $(\text{EtO})_2\text{PHO}$. The height of the peak corresponding to Cu^{I} increases in the CV curves. The elemental composition of the precipitate formed is close to $\text{Et}_4\text{N}^+\text{Cu}_2\text{P}^- \cdot 2\text{H}_2\text{O}$.

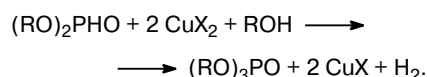
Based on analysis of the published data^{2–4} and our experimental results, we can assume that under optimal conditions the oxidative alkoxylation of P_4 in the presence of the Cu^{II} salts and complexes (CuX_2) includes two main reactions: homogeneous reduction of CuX_2 with white phosphorus, which affords phosphorus esters and electrochemical oxidation of CuX on the anode.



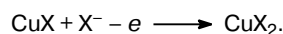
Trialkyl phosphite undergoes dealkylation to dialkyl phosphite and isomerization to alkyl phosphonate.



Trialkyl phosphate is formed due to the homogeneous oxidative alkoxylation of dialkyl phosphite in the presence of CuX_2 .¹⁹



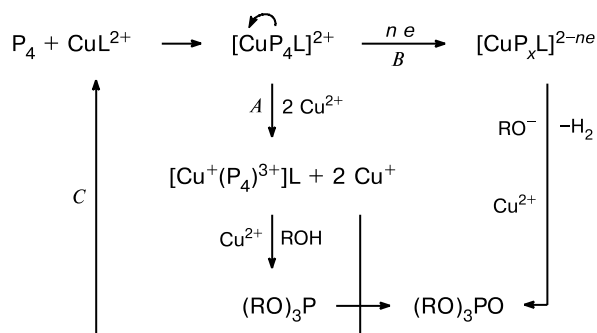
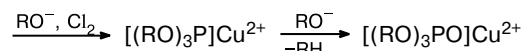
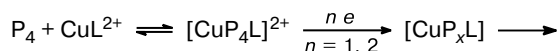
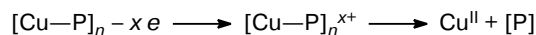
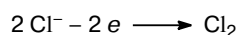
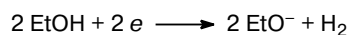
The electrochemical reduction of CuX on the anode closes the catalytic cycle



In the case of electrosynthesis involving the CuCl_2bpy complex instead of CuCl_2 , the direct oxidation of white phosphorus with copper(II) does not occur, and the process proceeds, likely, through other several steps. In these systems, the copper complexes with white phosphorus and EtOH are reduced on the cathode in the initial steps of electrolysis ($E^{\text{C}} = -1.8\text{—}2.0$ V during electrolysis), and the chloride ions and copper-phosphorus complexes are oxidized on the anode. The main routes of the reaction of phosphorus are presented in Scheme 1.

Electrosynthesis using CuCl_2 as catalyst has several disadvantages. Considerable excess CuCl_2 ($\text{CuCl}_2 : \text{P}_4 = 20$) is needed for the selective transformation of white phosphorus into liquid products, predominantly $(\text{RO})_3\text{PO}$. In fact, the copper(II) salt acts as an oxidizing agent rather than catalyst. The regeneration of CuCl_2 by the electrooxidation of Cu^{I} is limited by the slow chemical transformation of Cu^{II} into Cu^{I} , so that electrosynthesis should be carried out at a low current density and with a low efficiency. The reaction occurs differently, depending on the $\text{Cu} : \text{P}_4$ ratio. When excess copper or its high concentration is present in a solution,

Scheme 1



L = bpy

A. Homogeneous oxidation. B. Electrochemical reduction on electrode. C. Electrochemical oxidation on electrode.

phosphorus is homogeneously oxidized with copper(II) *via* route A, and Cu^{I} that formed is oxidized on the anode. At low concentrations of the copper salt, the reaction of phosphorus either occurs slowly if at all, and at the electrolysis potentials (-1.8 V, all copper-phosphorus complexes and intermediates are reduced on the cathode) the complex is reduced to transform the tetrahedral phosphorus *via* route B.

The use of CuCl_2bpy as catalyst makes it possible to perform electrosynthesis more efficiently. The copper complex is used in catalytic amounts, white phosphorus is taken in great excess, and now the process rate is not determined by the rate of Cu^{I} formation. The active intermediates are generated at more positive (on the anode) and, correspondingly, more negative potentials (on the cathode), so that this results in the individual step (generation of the reactant on the electrode and volume chemical reaction) rate-balanced transformation of white phosphorus. In this case, the mechanism of electrosynthesis is more complicated and requires a special study. However, this approach seems to be most promising.

Thus, in our experiments, we found the dependence of the redox properties of the copper catalysts in the absence or presence of white phosphorus and showed that

the phosphorus acid derivatives can be prepared by electrosynthesis from P_4 in the presence of the copper(II) compounds, which act as the catalyst and charge transfer agent.

Experimental

CV curves were recorded on a GC electrode 1.5 mm in diameter. A silver electrode, *i.e.*, a 0.01 M solution of Ag/AgNO_3 in MeCN, served as reference electrode. A Pt wire 1 mm in diameter was used as auxiliary electrode. Measurements were carried out in a cell with the temperature maintained at 25°C in an argon atmosphere. CV curves were detected using a PI-50-1 potentiostat, a PR-8 programmer, and a two-coordinate recorder at a potential sweep of 50 mV s^{-1} . The supporting salts were Et_4NBF_4 , Bu_4NBF_4 , and LiClO_4 .

Preparative electrolysis was carried out using a B5-49 dc source in a thermostatted (at 50°C) three-electrode 40-mL cell in EtOH or its mixture (1 : 3) with DMF or MeCN under argon. The electrolyte was magnetically stirred. In experiments on undivided electrolysis, a Pt cylinder with a working surface of 40 cm^2 was used as cathode, and a coaxial Pt rod with a working surface of 15 cm^2 served as anode. In experiments with a divided cell, a butter-paper diaphragm was used, the same Pt cylinder was used as anode, and a GC plate with a surface of 8 cm^2 served as cathode. The catholyte was a saturated solution of Et_4NBF_4 in EtOH. White phosphorus was introduced into the catholyte in the solid state or as a saturated solution of P_4 in C_6H_6 .

The ^{31}P NMR spectra were recorded on a Bruker CXP-100 spectrometer with a working frequency of 36.5 Hz relatively to the external standard (85% H_3PO_4) with positive downfield chemical shifts.

Undivided electrolysis at the ratio Cu : P_4 = 0.25. An undivided cell was loaded with EtOH (10 mL), DMF or MeCN (30 mL), CuCl_2 (0.1 g, 0.74 mmol), bpy (0.12 g, 0.77 mmol), white phosphorus (0.372 g, 3 mmol), and Et_4NBF_4 as supporting salt to a concentration of $1 \cdot 10^{-2} \text{ mol L}^{-1}$. In pure EtOH electrolysis was carried out under the same conditions. The solution was heated under argon to 50°C . Electricity (1.61 A h, 5 F electricity per P atom) was passed through the electrolyte in the galvanostatic regime at a current of 200 mA. The potentials to -1.8 V on the cathode and to $+1.7$ V on the anode were maintained during electrolysis. In a DMF solution the reaction occurs without formation of the heterogeneous phase, and a minor amount of a dark brown unstable in air phosphorus-containing precipitate with the phosphine odor appears in MeCN and EtOH. After electrolysis, excess solvent was distilled off from the electrolyte, the supporting salt was precipitated with diethyl ether, and the etheric extract was concentrated by evaporation and distilled *in vacuo*. The physical and spectroscopic characteristics of the synthesized phosphorus esters, *viz.*, $(\text{EtO})_3\text{PO}$, $(\text{EtO})_2\text{P}(\text{O})\text{Et}$, and $(\text{EtO})_2\text{PHO}$, correspond to the published data. The yields of the products are presented in Table 1.

Divided electrolysis at the ratio Cu : P_4 = 1. The anodic area of a divided cell was loaded with EtOH (30 mL), CuCl_2 (0.0537 g, 0.4 mmol), and a saturated solution of white phosphorus in benzene (1.6 mL, 0.4 mmol). A saturated solution of Et_4NBF_4

in EtOH was in the cathodic area. The solution was heated under argon to 50 °C. After passing 200 mA h electricity (<1/3 of the amount obtained based on 5 F per P atom) at the anodic potential from +1.0 to +1.26 V, the cell voltage increases dramatically (from 16 to 75 V), because the copper ions are separated from the solution within a brown precipitate and the solution becomes nonconducting. The absence of the copper ions in the solution is confirmed by the CV data. The addition of the supporting electrolyte does not change the situation. Thus, it is impossible to continue electrolysis under these conditions because the solution contains no anodic depolarizer.

Divided electrolysis at the ratio Cu : P₄ = 20. The anodic area of the divided cell was loaded with EtOH (30 mL), CuCl₂ (0.268 g, 2 mmol), and a saturated solution of white phosphorus in benzene (4 mL, 0.1 mmol). A saturated solution of Et₄NBF₄ in EtOH was in the cathodic area. The solution was stirred under argon at 50 °C for ~1 h. The color of the solution changed from saturated green to brown but the solution remained homogeneous. The CV curves demonstrated a decrease in the height of the Cu^{II}/Cu^I peak and an increase in the height of the more cathodic peak (presumably, Cu^I). According to the ³¹P NMR spectroscopic data, (EtO)₃PO is selectively formed under these conditions. The anodic oxidation of Cu^I was carried out at a current of 200 mA and a potential of +0.2 V (5 F per initial phosphorus atom or 1 F per initial Cu^{II} salt). Then the procedure on loading and consumption of phosphorus was repeated thus accumulating triethyl phosphate in the solution.

Reaction of copper(II) acetate with white phosphorus in an ethanol medium at the ratios Cu : P₄ = 20 and 10. A saturated solution of white phosphorus (0.2 mL, 0.05 mmol) in benzene was added to a solution of Cu(AcO)₂·H₂O (0.2 g, 1 mmol) in EtOH (10 mL), so that the initial molar ratio Cu^{II} : P₄ was 20. In order to record the CV curves, Et₄NBF₄ (5·10⁻² mol L⁻¹) was added. The solution was stirred for 1 h at ~20 °C, due to which its color changed from blue to brown. After the repeated addition of a saturated solution of white phosphorus in benzene (0.2 mL, 0.05 mmol), the Cu : P₄ molar ratio in the solution became equal to 10. The solution was stirred with the added second portion of P₄ for 2 h, and a black precipitate was formed. Heating of the solution to 50 °C accelerates the process, so that the reaction ceases within 20 min. The precipitate was filtered off and washed with diethyl ether. The elemental composition of the precipitate corresponds to the formula C₈H₂₄Cu₂NPO or Et₄N⁺Cu₂P⁻·2H₂O. Found (%): C, 33.3; H, 6.9; Cu, 44.1; N, 4.9; P, 10.8. Calculated (%): C, 29.63; H, 7.40; Cu, 39.20; N, 4.32; P, 9.57. The products of phosphorus transformation are (EtO)₃PO and (EtO)₂PHO with the total yield to 30%.

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