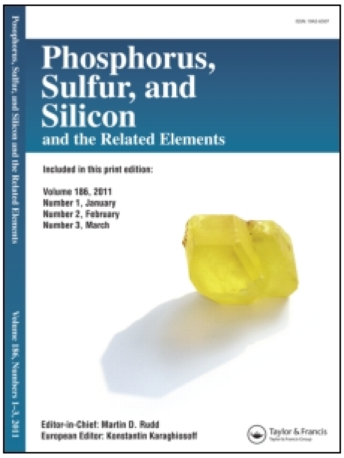

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Electrochemical Functionalization of White Phosphorus

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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.

Keywords: white phosphorus; electrosynthesis; metallocomplexe catalysis

INRODUCTION

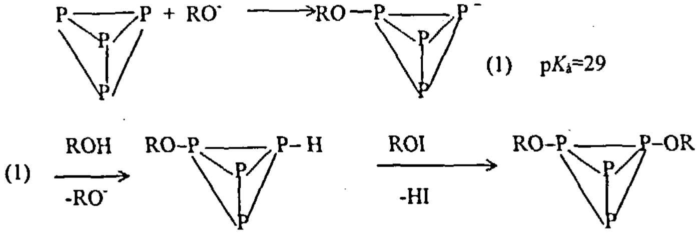
The problem of direct functionalization of white phosphorus has become more acute in connection with vigorous developments of the chemistry of organophosphorus compounds and with the ecological problems that have arised in the production of these compounds on an industrial scale. An attempt was made to synthesize organophosphorus compounds by combining homogeneous chemical reactions in the volume of the solution with heterogeneous electrochemical reactions taking place at the electrodes. 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 relationships governing the subsequent electrochemical and chemical reactions of the initial intermediate products with various nucleophiles (alkoxide, hydroxide, phenolate, amide ions, nickelorganic compounds) and anodically generated electrophiles.

RESULTS AND DISCUSSION

It is known that at a cathode with a low hydrogen overvoltage with tetraalkylammonium salts as supporting electrolytes, the alcohol O-H bond is cleaved at the formation of alcoholate ion:

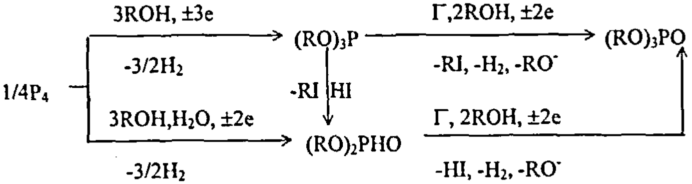
$$2ROH + 2e \rightarrow 2RO^- + H_2\uparrow, \qquad E_{1/2} \approx -2.2 \div -2.4V \text{ (ref. Ag/AgNO}_3\text{, }10^{-2}\text{l)}$$

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, 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. During the action of the alcoholate ion generated at the cathode, a cleavage of P-P bond in the phosphorus molecule takes place with the formation of a phosphide anion:



The joint action of the alcoholate ions and iodoether on the elemental phosphorus will lead to successive cleavage of all P-P bonds and to formation of the phosphite $(RO)_3P$ which is clearly unstable under the electrolysis conditions and undergoes further rapid chemical transformations.

On the basis of the data in Table 1 it is possible to present a general scheme for plausible processes:



The overall scheme for trialkyl phosphate formation from alcohol and white phosphorus can be written finally follows:

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

On electrolysis of alcohol or phenol solutions of tetraalkylammonium in the presence of white phosphorus, complete esters of phosphorus acids are formed. The opening of the strained P_4 ring and formation of the whole product occurs as a result of sequential attack of nucleophilic and electrophilic components, formed respectively at the cathode and anode in an unseparated electrochemical cell. The yields with respect to phosphorus are: 95% $(BuO)_3PO$, 78% $(PhO)_3P$ or 80% $(PhO)_3PO$.

We were able to identify pentaphenoxyphosphorane and $(PhO)_3PI_2$ which may be the intermediates:

$$(PhO)_3P \xrightarrow[HJ]{I_2} (PhO)_3PJ_2 \xrightarrow{2PhOH} (PhO)_5P \longrightarrow (PhO)_5PO$$

We have shown that pentaphenoxyphosphorane is irreversibly reduced at the platinum electrode in acetonitrile to triphenyl phosphate by one two-electron wave at less negative potentials than phenol:

$$(PhO)_5P + 2e \xrightarrow{[H^+]} (PhO)_3PO + PhH + PhO^-$$

Either triarylphosphite as a main product with pyridine additive or triarylphosphate with 75-94% yields can be obtained from white phosphorus varying conditions of the electrolysis.

We propose that under the action of the cathode-generated amide anion the P-P bonds splitting occurs followed by substitution of the hydrogen of the P-H bonds in phosphorus oligomers first by iodine and then by amido group. Hence, as a result of the main reaction, phosphorous triamide is formed.

$$P_4 + 12R_2NH \xrightarrow{\pm 12e} 4(R_2N)_3P + 6H_2$$

Conversion of the latter to phosphate takes place presumably due to hydrolysis of unstable iodine derivatives by residual water in the electrolyte and during a treatment of reaction mixture.

$$(R_2N)_3P + J_2 \longrightarrow (R_2N)_3PJ_2 \xrightarrow{H_2O} (R_2N)_3PO$$

The general scheme of the process is given below.

$$P_4 + 12R_2NH + 4H_2O \xrightarrow{\pm 20e} 4(R_2N)_3PO + 10H_2$$

Another way to convert the unstable $(R_2N)_3P$ to the final products can be performed, for instance, by addition of carbon disulfide to the the electrolyte. It will act as a sulfur source, ensuring conversion of $(R_2N)_3P$ to $(R_2N)_3P{=}S$, thioformamide being a by-product. The phosphorous triamide reacts with thiocarbamate, yielding triamidothiophosphate. The general scheme of the process is as follows:

$$P_4 + 16R_2NH + 4CS_2 \xrightarrow{\pm 20e} 4(R_2N)_3PS + 4R_2NC(S)H + 6H_2\uparrow$$

In all instances given above, the product of iodide ion oxidation acts as an electrophile generated at an anode. In a search for other routes we studied anode-generated reagents of radical-cation type namely , triarylamine ($Ar_3N^{+\cdot}$) and phenothiazine ($PT^{+\cdot}$). Electrolysis of alcohol solutions of PT in the presence of white phosphorus results in a mixture of dialkyl phosphite (the main product) and trialkylphosphate but the overall conversion of phosphorus was somewhat lower in comparison to the electrolyte containing iodide ions.

We have suggested that white phosphorus can be involved in a reaction leading to phosphorus cage disruption and P-C bonds formation in conditions where the reagent is generating continuously in situ in reaction medium in the presence of P_4. With this in mind we have selected Ni(0) complexes of bipy generated electrochemically from Ni(II). They yield organonickel compounds reacting fast with organic halides.

The results of our experiments have shown that arylation or alkylation of white phosphorus in the presence of electrochemically generated Ni(0) complexes and halides RX can be carried out.

Cathode: $Ni(II)L_3 + 2e \rightleftarrows Ni(0)L_2 + L$, L=bipy, E = -1.68V

Anode: $Al - 3e \longrightarrow Al^{3+}$

$$P_4 + RX \xrightarrow[-X^-]{Ni(0)L_2} >P\text{–}R$$

Thus, electrolysis can be used successfully to obtain a large variety of compounds with P-O, P-N, P-C and P-S bonds from white phosphorus and above all, electrochemical methods allow to control this complicated process resulting in high selectivity in some instances. Besides, electrochemistry allows to study mechanisms of white phosphorus reacting, to calculate the constants of separate stages of the process, to find kinetic and thermodynamic regularities. All the above can be used as a basis for consideration of these processes of white phosphorus functionalization at the technological level.