

ELECTROCHEMICAL FUNCTIONING OF WHITE PHOSPHORUS AS NOVEL WAY TO EFFICIENT ORGANOPHOSPHORUS COMPOUNDS PREPARATION

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A longstanding aim of electrochemical research has been to develop a clean, selective method for carrying out organic synthesis. The renaissance of electrochemistry has come with the general realization of its ubiquity.

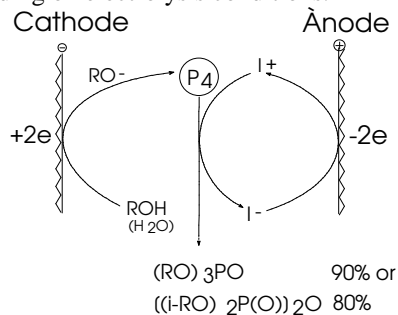
The interest to direct synthesis of organophosphorus compounds from white phosphorus, escaping the traditional stages of its chlorination, is connected to the increase of the requirements of ecological safety and low-waste production and is also caused by a number of advantages compared to common chemical methods:

- mild conditions of the process (normal pressure and temperature);
- a possibility to carry out the reaction in practically closed system with minimum amount of cyclically regenerated reagents;
- high environmental safety of synthesis, especially in comparison with the traditional procedures of organophosphorus chemistry.

It is necessary to mention that the use of electrochemical methods provides a unique opportunity to study the reaction mechanisms of elemental phosphorus with various reagents generated on electrodes along with the solution of synthesis problems.

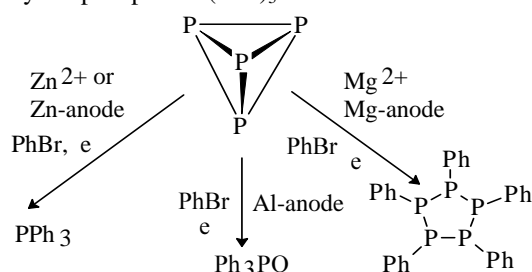
This report is devoted to consideration of electrochemical methods for synthesis of the most significant types of industrially important OPC.

The most promising approach involving a joint action of nucleophilic and electrophilic reagents on the white phosphorus was the basis for electro-synthesis of esters of phosphorus acid. The consecutive repetition of the stages of nucleophile attack on phosphorus and phosphide anion capture by electrophilic agent allows to obtain various organophosphorus products under mild conditions. Combining the advantages of usual homogeneous chemistry in solution and electrochemistry, when the reagents (both nucleophiles and electrophiles) are generated on electrodes directly in the reactions system, we succeeded in gaining high conversion of white phosphorus to desired products and choosing conditions of high selectivity of the process. The joint action of alkoxy anion and halide on the white phosphorus molecules results in various derivatives of phosphorus acids (phosphates, pyrophosphates, phosphites), depending on electrolysis conditions.



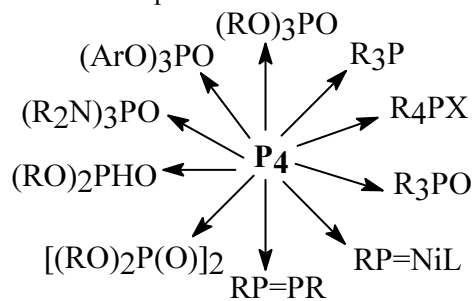
Electrochemical generation of alkoxy or amide anions on cathode and iodine on anode in the presence of white phosphorus offers a novel approach to synthesis of the appropriate esters or amides of phosphorus acids under mild conditions. But this electrochemical method is unsuitable to prepare compounds with the phosphorus-carbon bond, which are the most important in phosphorus chemistry. In this connection, a supposition was expressed about the possibility of selective obtaining some organophosphorus compounds with the phosphorus-carbon bond from white phosphorus under conditions of metallocomplex catalysis using electrochemical methods.

We supposed that white phosphorus can be involved to the reaction with alkyl and aryl halides under conditions of cyclic regeneration of metallocomplex catalyst on electrode. In fact, we showed, for the first time, a possible formation of tertiary phosphines and their oxides from white phosphorus and alkyl or aryl halides in the presence of electrochemically generated catalysts, complexes of zero-valent nickel. The essential influence of the sacrificial anode on the nature and the yield of the target products of electrochemical phosphorylation of organic halides by white phosphorus was shown. Zinc anode yield to three-coordinated phosphorus - triorganylphosphines, aluminium anode - triorganylphosphine oxides, and the magnesium anode promotes the transformation of white phosphorus into cyclic phosphines (PhP)₅.



Thus, we showed, for the first time, a possibility of high-selective electrochemical alkylation and arylation of white phosphorus under conditions of metallocomplex catalysis. Phosphinidenes are the phosphorous analogues of carbenes, nitrenes and silenes and present the class of low-ligated phosphorus compounds. Although terminal phosphinidene complexes are receiving an increasing amount of attention, well characterized examples remain relatively rare. We have obtained phosphinidene nickel complexes $RP=NiL$ from P_4 for the first time.

It should be marked that electrochemical methods not only allow to carry out these processes under mild conditions with high rate but to control them achieving a high selectivity in many cases. It is obvious that optimization of the methods for electrochemical functionalization of white phosphorus is a basis for realization of these processes on an industrial scale.



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