

Diaphragmless Electrosynthesis of Diphenylphosphate

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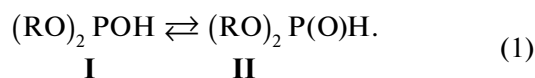
Abstract—The process of mediated diaphragmless electrosynthesis (platinum anode, nickel cathode) of diphenylphosphate from diphenylphosphite with alkali metal halides (KI, LiBr) used as the mediator is studied in water-organic (acetonitrile, benzene) medium. It is found that after passing 2 F per mole of diphenylphosphite through the electrolyte, two phosphorus-containing compounds are detected in the reaction mixture: original diphenylphosphite and target diphenylphosphate. The highest content of diphenylphosphate is observed when the electrosynthesis is carried out in the water-acetonitrile-benzene mixture. It is found that the excess of protons in the electrolyte accelerates the hydrolysis of original diphenylphosphite.

Keywords: diphenylphosphite, diaphragmless electrosynthesis, diphenylphosphate, mediator, potassium iodide, lithium bromide, platinum anode, nickel cathode

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INTRODUCTION

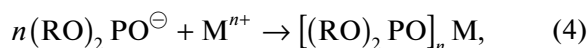
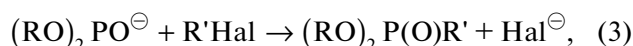
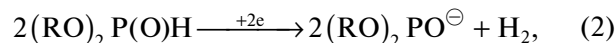
Dialkylphosphites are capable of tautomeric transition from the phosphite form **I** with three-valent phosphorus to the phosphonate form **II** with four-coordinated phosphorus (Eq. (1)).



The possibility of the equilibrium shift from one form to another depending on experimental conditions makes it possible to widely use dialkylphosphites in synthesis [1]. The latter fact together with the high lability of the phosphorus-hydrogen bond in tautomeric form **II** are the reasons for studying the electrochemical properties of $(\text{RO})_2\text{P(O)H}$. It was shown that in syntheses of various compounds, dialkylphosphites can be used both in cathodic [2–4] and in anodic reactions [5–13].

The cathodic reactions are based on the ability of $(\text{RO})_2\text{P(O)H}$ to be reduced on electrodes of transition metals (Pt, Ni, Fe, Cu) with the evolution of gaseous hydrogen and the formation of active dialkylphosphite anions (Eq. (2)) [2]. Thus, by the cathodic generation of phosphite anions in the presence of alkylhalides, a series of alkylphosphonates were produced (Eq. (3)) [3]. The use of diaphragmless electrolyzers with solu-

ble anodes made it possible to obtain salts of dialkylphosphorous acids (Eq. (4)) [4].



R = Me, Et, Ph; R' = Me, PhCH₂; Hal = Cl, I; M = anodically soluble metal

It is well known that dialkylphosphites are not oxidized on the platinum electrode in the conventionally used region of anodic potentials (0.0–2.4 V vs. Ag/Ag⁺ reference electrode (0.1 M solution in CH₃CN)) [14]; hence, to carry out an anodic syntheses involving $(\text{RO})_2\text{P(O)H}$, the indirect oxidation was used. The following three methods were used. (1) The synthesis of active substituted phosphates (by preliminary anodic generation of free halogens or dithiocyanogens (Eq. (5)) which react later with nucleophiles (water, alcohols, amines, thiols, disulfides). These reactions are described in detail in a review [5]. (2) Preliminary transition of dialkylphosphite to the phosphite form **I** by treating it with an alkali metal followed by electro-oxidation of $(\text{RO})_2\text{POM}$ salts (Eq. (6)). Arylphosphonates [6, 7], pyrophosphites [8], styrylphosphonates [9], hypophosphates [10], and alkylphosphonates were synthesized by the latter method [11]. (3) The