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Catalytic Synthesis of Organophosphorus Compounds from Inorganic Derivatives of Low Valence Phosphorus

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Abstract

A variety of new reactions of inorganic compounds of elemental and low valence phosphorus (phosphine, white phosphorus, sodium hypophosphite) with various organic substrates (alcohols, olefins, quinones) catalysed by different transition metal (Pd^{II}, Hg^{II}, Pt^{II}, Pt^{IV}, Ag^{I}, Fe^{III}, Cu^{II}) salts leading to the formation of valuable organophosphorus derivatives (trialkylphosphates, dialkylphosphites, trialkylphoshinoxides, phosphonium salts) are reviewed. The principal features of the oxidative phosphorylation reactions which are of great practical importance are described. The mechanisms of the catalytic oxidative P-O and P-C coupling of phosphine, white phosphorus and hypophosphite with alcohols, olefins and quinones are considered. It has been shown that this catalytic protocol allows to provide a highly selective conversion of relatively inexpensive feedstocks to desirable higher added-value products.

Introduction

During the second part of this century, the chemistry of phosphorus compounds has evolved considerably into one of the cornerstones of chemistry and biochemistry. Few other branches of chemistry have a greater influence on chemistry, biology and material scienses and offer greater potential for addressing the future needs and opportunities in far-reaching areas of science and engineering. Phosphorus compounds are industrially important in several areas of commercial interest and are producing in megatons amount as fertilisers, pesticides, detergents, additives for lubricants, metal extractors in nuclear industry, flame-retardant additives for plastic materials *etc*. Moreover, they play a key role in living processes being essential not only for the hereditary processes, but also for the growth, development and maintenance of living organisms. Nowadays the chemistry of organophosphorus compounds is therefore rivalling the chemistry of carbon in most of its aspects and in the foreseeable perspectives.

The industrial manufacturing of organophosphorus compounds usually involves multistep processes conducted under harsh reaction conditions and based largely on the substitutive P-O, P-C coupling of the high-valent phosphorus derivatives (PCl_3, PCl_5, $POCl_3$) with an organic substrates. The emission of a large amount of hydrogen chloride accompanies these reactions with consequent serious environmental and corrosion problems. In this connection, the elaboration of new environmentally acceptable processes for the syntheses of organophosphorus compounds becomes an urgent task. These increased environmental and commercial interests have prompted us to investigate “chlorine free” protocols for the direct conversion of a various low-valent phosphorus-containing compounds (including elemental (white and red) phosphorus and such a waste from phosphorus industry as an effluent phosphine- and phosphorus contating gases, dilute phosphorus sludges, metal phosphides) into useful derivatives which are alternative to the presently used procedures based on phosphorus chlorides.

Prior to our investigations summarized in the review [1], the catalytic activation of the above phosphorylating agents has been unknown. We have reported there that a different copper salts are capable of mediating under mild reaction conditions the reactions of (i) the oxidative P-O coupling of white and red phosphorus, phosphine, zinc and copper phosphides with alcohols to give di- and trialkylphosphates

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*corresponding author. E-mail: adm@orgcat.academ.alma-ata.su and dialkylphosphites, (ii) the oxidative P-N coupling of white phosphorus and phosphine with amines to give triamidophosphazoalkanes, (iii) the oxidative P-C coupling of white phosphorus and phosphine to nitriles to give tri(cyanomethyl)phoshazoalkyls and tri(cyanomethyl)phoshine, respectively.

During consequent investigations we have found that a variety of transition metal salts, apart of copper, can catalyze the same or a new reactions of inorganic compounds of elemental or low-valent phosphorus. We report here a review of our last experimental results concerning the oxidative P-O and P-C coupling of phosphine, white phosphorus and hypophosphite with alcohols, olefins and quinones.

Experimental

The kinetics, mechanism, the main and intermediate products of the reactions have been studied by the methods of volumometry, redox-potentiometry, inhibition of free radicals, GC, ^{31}P NMR -, IR -, UV-, EPR-spectroscopy, chemical modelling, orbital symmetry, quantum chemistry (CNDO, MWG , PMO) [1].

All starting materials (organic substrates, solvents, phosphorylating agents, catalysts, additives) and gases (O_2, Ar) were purified and dried by the usual methods. The PH_3 reactions were carried out in an isothermal assembly composed of a gas-flow reactor, a flowmeter for measuring a gas flow velocity, and 20 L gas-meter for recording the volume of gases passed through the reactor. A PH_3-Ar gas mixture, diluted with respect to phosphine (< 3%), was employed in the reactions. The kinetics of the P_4 and NaH_2PO_2 reactions were studied on a volumetric installation consisting of the same reactor connected with a gasometric oxygen buretts for measurement of O_2 absorbed. The reactions were conducted at the partial pressure of O_2 equal $(0\text{-}6)\times10^4$ Pa under nonstationary conditions in which kinetic control was ensured until P_4 or NaH_2PO_2 have been completely consumed.

The glass 150 mL reactor was equipped with the reactants charge and sampling tubes, and potentiometric unit comprised of platinum and calomel half-cells. The kinetical regime of the reactions has been achieved at the rigorious shaking of the reactor with frequency about 250-300 swingings per minute.

The kinetic and potentiometric studies were performed as follows. The phosphine (PH_3-Ar gas mixture), white phosphorus (the arene solution of P_4) or sodium hypophosphite (the solid NaH_2PO_2) were added into reactor and mixed with catalytic solution. In the course of the reactions, the rate of PH_3 (or O_2) absorption, the amount of PH_3 (or O_2) absorbed and the redox potential of the catalytic system were continuously measured, a product sample was periodically taken and subjected to GC and NMR analysis.

The quantitative monitoring of trialkylphosphates and dialkylphosphites has been performed with a modern Chrompack 9002 gas chromatograph supplied with a computer programs and capillary column CIPSIL19 CB (25 m, ∅ 25 mm). The products concentration has been determined with respect of internal standard (pentadecane). Trialkylphoshinoxides and phosphonium salts were identified by ^{31}P NMR spectroscopy with WP-80 (Bruker) instrument at 20°C. The chemical shifts were reported in ppm downfield from an external reference (85% H_3PO_4) and compared with an available information.

Results and discussion

1. Oxidative P-O and P-C coupling of PH_3 with alcohols, quinones and olefines

The low-polar PH_3 molecule is active in homolytic reactions but extremely inert in a heterolytic organic reactions of the electrophylic or nucleophylic association and substitution [2,3].

We have discovered that the mixed solutions of ROH-Py (alcohol-pyridine), $C_6H_4O_2$-$C_4H_8O_2$ (1,4benzoquinone-dioxane), RCH=CH_2-$C_6H_4O_2$-$C_4H_8O_2$ (olefins-1,4benzoquinone-dioxane), RCH=CH_2-$C_6H_4O_2$-ROH (olefins-1,4benzoquinone-alcohol), containing $PdCI_2$, $HgCI_2$, Na_2PtCI_6, Na_2PtCI_4 or $AgNO_3$, rapidly and selectively oxidize even trace (< 10^{-2} % vol.) amount of PH_3 with formation of products of the oxidative P-O and P-C-coupling in dependence on the nature of metal and substrates [4-8].

New reactions (1-6) proceed under mild conditions at 40-90°C with rather high velocity (120 h^{-1}) and selectivity (90-100%). Trialkylphosphates (1,2), trialkylphoshinoxides (3,4,6), phosphonium salts (5) have been obtained as products.

$$PH_3 + 8AgNO_3 + 4ROH \rightarrow (RO)_3PO + 7HNO_2 + RNO_2 + 8Ag \qquad (1)$$

$$PH_3 + 4PtCI_4 + 4ROH \rightarrow (RO)_3PO + RCI + 7HCI + 4PtCI_2 \qquad (2)$$

$$4PtCl_2 + 5RCH_2OH \rightarrow (HOCHR)_3PO + (RCH_2)_2O + 8HCl + 4Pt \qquad (3)$$

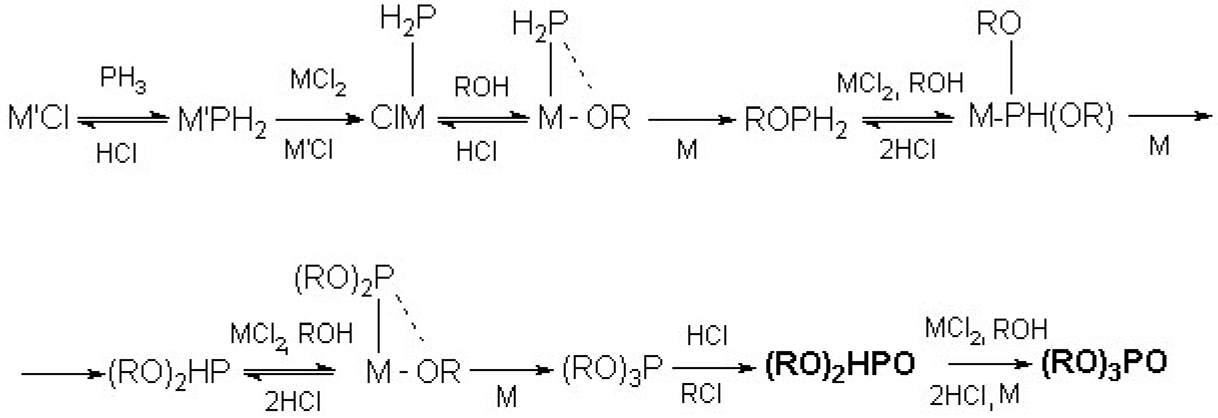
$$PH_3 + 4PdCl_2 + 5RCH_2OH \rightarrow (HOCHR)_3PO + (RCH_2)_2O + 8HCl + 4Pd \qquad (4)$$

$$PH_3 + 4C_6H_4O_2 + HCl \xrightarrow{HgCl_2,PdCl_2} (HOC_6H_4O)_4PCl \qquad (5)$$

$$PH_3 + 3R''C_2H_3 + 4C_6H_4O_2 + 3HCl + H_2O \xrightarrow{HgCl_2,PdCl_2} (R''ClC_2H_3)_4PO + 4C_6H_4(OH)_2 \qquad (6)$$

R = Me, Et, Bu, i-Bu, Am, i-Am;
R′ = i-Pr, C_6H_{11}, $PhCH_2$;
R″ = Bu, C_6H_{13}, Ph.

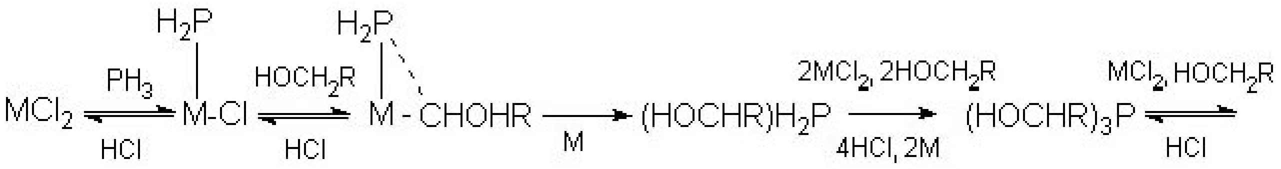
The reduced metals were recycled by the mixture of O_2-HNO_2 (1), or $NaBrO_3$ (2), $C_6H_4O_2$ (3,4). It has been established that the PH_3 ligand is dissociated with formation of phosphide and an equivalent amount of acid inside coordination sphere of a high-valent transition metal ion. The subsequent reactions of the metalphosphide depend on the nature of cenrtal atom and substrate. Alkoxyde RO^--ion formed from alcohols in coordination sphere of $PtCI_4$ (MCI_2) give with phosphide-ion a products of P-O and P-N-coupling as a result of the even reduction of the central atom. The interaction of MCl_2 with PH_3 happens only in the presence of $PtCI_2$ (M’CI). The coordinatively saturated ions of metals do not react with PH_3. The mechanism of the oxidative P-O-coupling of PH_3 with alcohols in the presence of $PtCI_4$ includes the following main stages:



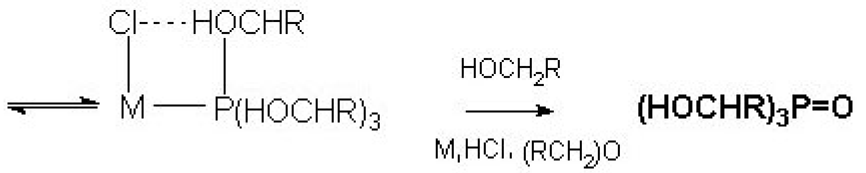
$$M'Cl \underset{HCl}{\overset{PH_3}{\rightleftarrows}} M'PH_2 \xrightarrow[M'Cl]{MCl_2} \overset{H_2P}{\underset{}{\overset{|}{ClM}}} \underset{HCl}{\overset{ROH}{\rightleftarrows}} \overset{H_2P}{\overset{|}{M}}\text{-}OR \xrightarrow[M]{} ROPH_2 \underset{2HCl}{\overset{MCl_2,\ ROH}{\rightleftarrows}} \overset{RO}{\overset{|}{M}}\text{-}PH(OR) \xrightarrow[M]{}$$

$$\longrightarrow (RO)_2HP \underset{2HCl}{\overset{MCl_2,\ ROH}{\rightleftarrows}} \overset{(RO)_2P}{\overset{|}{M}}\text{-}OR \xrightarrow[M]{} (RO)_3P \xrightarrow[RCl]{HCl} \mathbf{(RO)_2HPO} \xrightarrow[2HCl,\ M]{MCl_2,\ ROH} \mathbf{(RO)_3PO} \qquad (7)$$

The hydroxyalkyl-ions $HOCHR^-$ formed in the internal sphere of $PdCI_2$, $HgCI_2$, $PtCI_2$ (MCI_2) give with phosphide-ion a product of the oxidative P-C-coupling which is stimulated by the synchronous even demetallation of the intermediate complex.

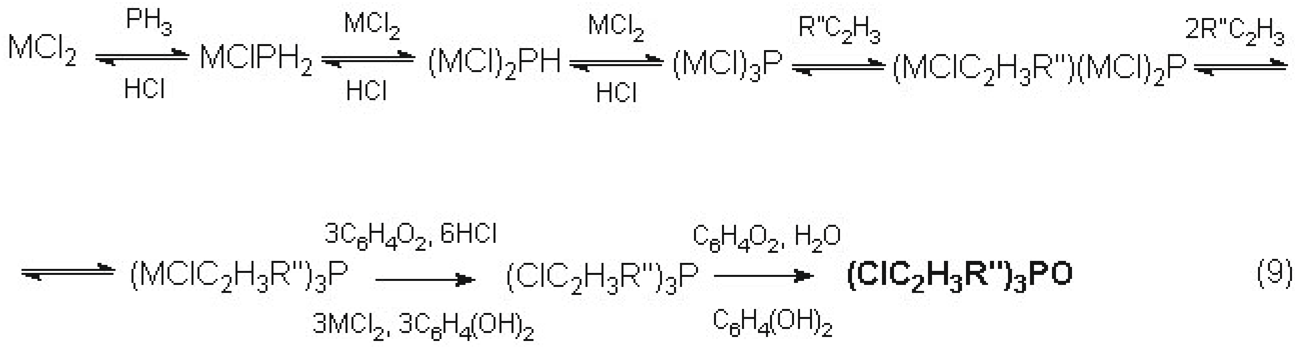


$$MCl_2 \underset{HCl}{\overset{PH_3}{\rightleftarrows}} \overset{H_2P}{\overset{|}{M}}\text{-}Cl \underset{HCl}{\overset{HOCH_2R}{\rightleftarrows}} \overset{H_2P}{\overset{|}{M}}\text{-}CHOHR \xrightarrow[M]{} (HOCHR)H_2P \xrightarrow[4HCl,\ 2M]{2MCl_2,\ 2HOCH_2R} (HOCHR)_3P \underset{HCl}{\overset{MCl_2,\ HOCH_2R}{\rightleftarrows}}$$



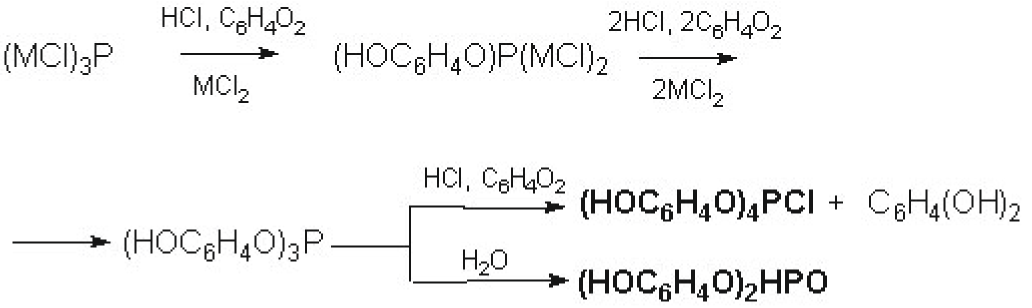
(8)

The oxidative P-C-coupling of PH_3 with olefins takes place as a result of phosphidometallation of olefins followed by the redox demetallation of organometallic ligand under influence of oxidant ($C_6H_4O_2$).



(9)

The tetra(hydroxyaryloxy)phosphonium chloride is received as a result of interaction of Hg(II)- and Pd(II)-phosphides with 1,4 benzoquinone $C_6H_4O_2$ (5). The impurity of H_2O (4-6 %) promotes the formation of di(hydroxyaryl)phosphite:



(10)

2. Oxidative P-O coupling of white phosphorus to alcohols

Non-polar molecule of white phosphorus (P_4) is not prone to undergo heterolytic reactions [9]. We have before discovered the fast and selective reactions of the direct oxidative alkoxylation of white phosphorus to trialkyl phosphates at 30-80°C in an alcohol-arene solutions of Cu(II) salts [1].

With the aim to find another effective catalysts, we have tested a Fe(III) salts which are widely used as a reversible catalysts of the oxidation of a variety of organic and inorganic substances by molecular oxygen. It has been found [10] that P_4 reacts with O_2 in the alcohol-toluene solutions of the FeX_3 at 70-90°C to yield trialkyl phosphates $(RO)_3PO$ (60-90%) as indicated in the following general reaction:

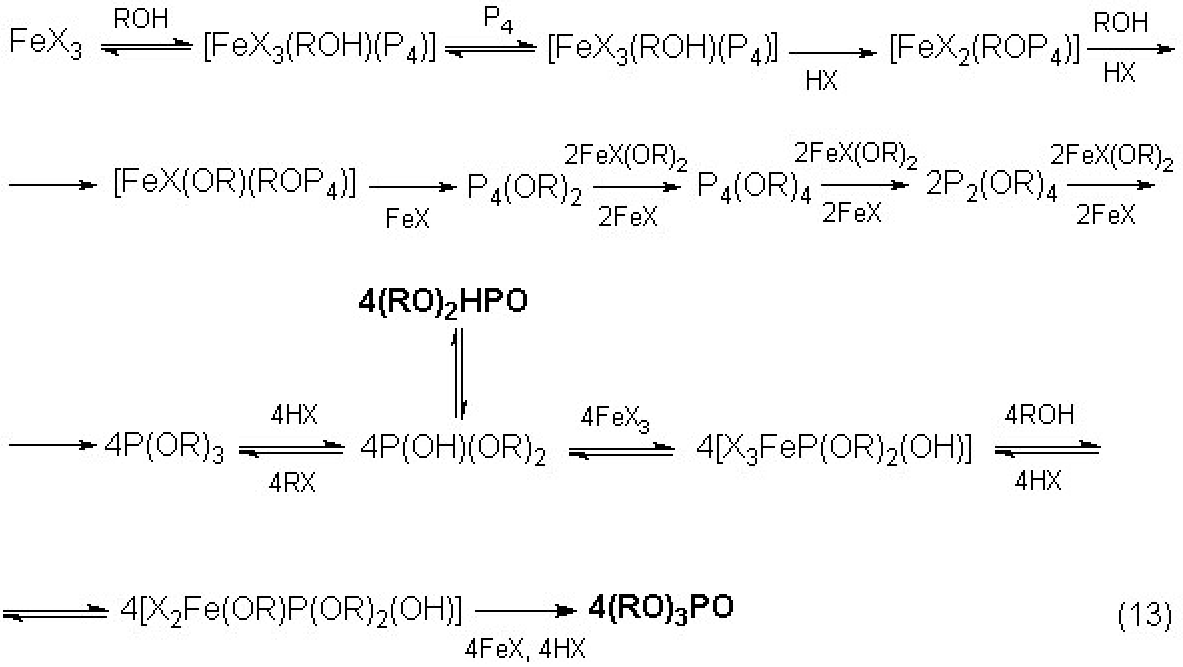
$$P_4 + 5O_2 + 12ROH \rightarrow (RO)_3PO + 6H_2O \qquad (11)$$

R = Bu, i-Bu, Am, i-Am;
X = Cl, Br; NO_3.

In dependence on the reaction temperature the major product $(RO)_3PO$ is accompanied with some amount of dialkylphosphites $(RO)_2HPO$ (10-40%). Experimental results obtained indicate that the reaction (11) proceeds *via* the step redox mechanism. The innerspheric reduction of Fe(III) by P_4 with formation of trialkylphosphate and FeX takes place in the first key stage:

$$P_4 + 10FeX_3 + 16ROH \rightarrow (RO)_3PO + 10FeX + 4RX + 16HX \qquad (12)$$

Twenty-electron conversion of P_4 into $(RO)_3PO$ icludes 10 irreversible two-electron redox reactions and a number of the complexation stages:



(13)

Inside the initial intermediate the insertion of P_4 into the Fe-O bond with formation of the monoalkoxytetraphosphine $P_4(OR)^-$ anion takes place. Reductive coupling of $P_4(OR)^-$ and RO^- anions with liberation of a cyclic dialkoxytetraphosphine $P_4(OR)_2$ and FeX proceeds during the rate-controlling stage. The reaction is realized owing to a rather big (0.508 V) difference between redox potentials of transitions $Fe^{3+} \rightarrow Fe^+$ and $P_4 \rightarrow P_4^{2+}$ and the high (335 kJ/mol) energy of the formed P-O bond in comparison with broken P-P bond (201 kJ/mol) of P_4.

The following oxidative alkoxylation of $P_4(OR)_2$ and another intermediate organophosphorus derivatives (a cyclic $P_4(OR)_4$, a linear $P_2(OR)_4$) to $P(OR)_3$ proceeds similarly, but faster. Trialkylphosphite $P(OR)_3$ undergoes dealkylation to dialkylphosphite $(RO)_2HPO$ followed by catalytic oxidative alkoxylation of the latter into trialkylphosphate $(RO)_3PO$. The FeX formed is immediately oxidized by FeX_3 to FeX_2 (15). Oxidation of FeX_2 by O_2 (16) gives the catalyst back into the catalytic cycle:

$$FeX + FeX_3 \rightarrow 2FeX_2 \qquad (14)$$

$$4FeX_2 + O_2 + 4HX \rightarrow 4FeX_3 + 2H_2O \qquad (15)$$

3. Oxidative P-O coupling of NaH_2PO_2 with alcohols

Sodium hypophosphite is a perspective phosphorylation agent but its organic reactions are still poorly inverstigated. We have first established that sodium hypophosphite in alcohol solutions of CuX_2 can be oxidized up to dialkylphosphites and trialkylphosphates at 50-80°C [11].

$$NaH_2PO_2 + 2CuX_2 + 2ROH \rightarrow (RO)_2HPO + 2CuX + HX + NaX + H_2O \quad (16)$$

$$NaH_2PO_2 + 4CuX_2 + 3ROH \rightarrow (RO)_3PO + 4CuX + 3HX + NaX + H_2O \quad (17)$$

R = Et, Bu, Am.
X = CI, Br, NO_3, CH_3CO_2.

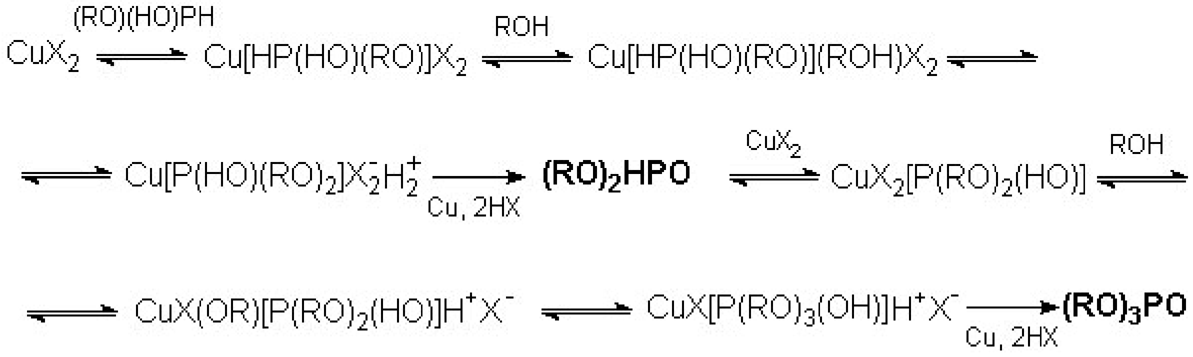
The reactions (16,17) rate is increased with magnification of concentration of reactants and catalyst, with temperature and acidity of alcohol. In the presence of halide-ions (CI^-, Br^-) the reaction proceeds faster than the presence of the oxygen-containing ligands ($CH_3CO_2^-$, NO_3^-). The activity of the $CH_3CO_2^-$, NO_3^- ligands is strongly increased in the presence of an acid. The total yield of organophosphorus compounds also depends on the nature of the catalyst ligand, being increased in a sequence: $CI^- \leq NO_3^- < Br^- < CH_3CO_2^-$.

Based on the obtained experimental kinetic, potentiometric, GC and ^{31}P NMR results, we offered the following mechanism of the synthesis of organophosphorus compounds from NaH_2PO_2, which is converted into more reactive hypophosphoric acid or alkylhypophosphite in the alcohol solutions:

$$NaH_2PO_2 + ROH \Leftrightarrow (HO)H_2PO + NaOR \quad (18)$$

$$(HO)H_2PO + ROH \Leftrightarrow (RO)(HO)PH + H_2O \quad (19)$$

The key stages of the reaction are the formation of alkylhypophosphite- and alcohol-alkylhypophosphite complexes of CuX_2:



(20)

The two-electron transfer redox decomposition of the $Cu[P(HO)(RO)_2]X_2^-H_2^+$ complex with formation of dialkylphosphite and Cu(0) takes place in the rate-limiting stage.

The further oxidation of $(RO)_2HPO$ to $(RO)_3PO$ *via* the stages of complexation with CuX2 and redox collapse of the complex has no influence on the reaction rate.

The formed Cu is oxidized by CuX_2 up to CuX followed by the reoxidation of the latter by oxygen back to CuX_2:

$$Cu + CuX_2 \Leftrightarrow 2CuX \qquad (21)$$

$$4CuX + O_2 + 4HX \rightarrow 4CuX_2 + 2H_2O \qquad (22)$$

Conclusion

The using of the transition metal catalysts allows to synthesize a valuable organophosphorus derivatives directly from phosphine, white phosphorus and hypophosphite. This catalytic protocol incorporates into the catalytic cycle all the advantages proper of a homogeneous catalytic reaction, i. e. the possibility to provide a highly selective conversion of relatively inexpensive feedstocks to desirable higher added-value products.

Acknowledgement

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