

Copper (II) Mediated Oxidative Alkoxylation of White Phosphorus. Communication 1.

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Abstract

White phosphorus has been oxidized by copper (II) acetylacetonate, halides or carboxylates in aliphatic alcohols to yield dialkyl phosphates and trialkyl phosphates under inert atmosphere and mild reaction conditions. Trialkyl phosphite has been observed as unstable organophosphorus intermediate, which is being converted into the main reaction products. In the case of methanolic solutions, the derivatives of two step acidolysis of dimethyl phosphite, monomethyl phosphite and phosphorous acid, have been additionally detected among the reaction products. The influence of the copper (II) oxidants on the kinetics of accumulation and transmutation of organophosphorus products has been explored. The order of oxidative ability of the copper (II) compounds has been established. The major steps of the reaction including (i) the coordination of white phosphorus and alcohol to metal ion and (ii) the redox decomposition of this intermediate complex accompanied by reducing elimination of elementary copper and formation of organophosphorus product have been also suggested.

Introduction

White phosphorus (P_4) is the most reactive allotrope of elementary phosphorus due to the strain of the P_4 -tetrahedron bond angles. In contrast with the inertness exhibited by the red and black allotropes of the element, white phosphorus is easily oxidized by oxygen, sulphur and halogens to give the phosphorus oxides, sulphides and halides. The P_4 suspension capable to dislodge the elementary metals from the aqueous solutions of the copper, silver or lead salts [1]. The reaction velocity is considerably increased at using the P_4 solutions in organic solvents. The stirring of the P_4 dissolved in the mixture of C_6H_6/CCl_4 solvents with aqueous solution of $CuSO_4$ under inert atmosphere at 40-60°C readily gives a gray sediment consisting of the copper salts of phosphorous and phosphoric acids together with elementary copper [2]. The reduction of Cu (II) compounds by P_4 in alcoholic solutions has not yet properly investigated, only its theoretical modeling has been described in a series

of dedicated papers [3, 4]. The CNDO calculations of the model intermediate complexes ($X = Cl, Br, OH$; $L = H_2O, CH_3OH, NH_3$; $m \leq 3$) suggest that molecules of P_4 and alcohol are in coordination sphere of Cu(II) ion towards the P-O coupling with each other irrespectively on the nature of the X and L ligands [3, 4].

Recently, we have experimentally confirmed the formation of the esters of phosphorous and phosphoric acids in the reaction of P_4 with copper (II) compounds in aliphatic alcohols under inert atmosphere.

The present work was undertaken to explore the kinetics of the organophosphorus products accumulation and transmutation during reaction and to propose the mechanism of the oxidative alkoxylation of white phosphorus in the presence of Cu (II) compounds under argon. Special attention will be focused to identification of intermediate organophosphorus products during reaction.

Experimental

Anhydrous condition was a major requirement for the oxidative alkoxylation of P_4 to prevent the

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competitive side reaction of the oxidative hydroxylation of white phosphorus [2]. Alcohols (methanol, *n*-butanol) and solvents (benzene, toluene) were purified and dried by the usual methods [5]. Argon was dried under CaCl₂. The copper (II) compounds were dried by heating at 80°C up to constant mass. The solid P₄ was weighted in a beaker under water, rinsed with ethanol and benzene at room temperature and then dissolved in dried benzene or toluene at 45–50°C. The concentration of P₄ in the solution was determined by iodometric titration [6].

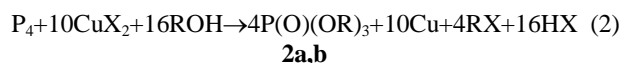
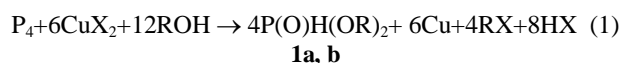
The reactions were carried out in a glass “jacket” reactor equipped with a dropping funnel, a sampling tube and connected to a thermostat to control the reaction temperature and to a burette filled by argon. The alcohol and CuX₂ were added to the reactor in this order and the resulting solution was thoroughly purged with argon during 10–15 min. Then, an aliquot of the stock’s arene solution of P₄ (1–2 mL, 0.16–0.27 mmol) was added through the dropping funnel into the reaction solution. The resulting solution volume was about 10–20 mL. The reactor was rigorously shaken with frequency about 250–300 swinging per minute. Accumulation of organophosphorus products was monitored by periodically withdrawing solution samples and checking their composition by GC analysis on a Chrompack 9002 chromatograph (CIPSIL19 CB column) with respect to a pure samples (the appropriate trialkyl phosphates, tri- and dialkyl phosphites). The yield of phosphorus esters was calculated with respect of P₄ amount taken in the reaction. For selected experiments, ³¹P NMR spectra of the reaction products were recorded on a Bruker AC-200 NMR spectrometer at 25°C using C₆D₆ as a solvent. In order to eliminate the species of paramagnetic CuX₂ salts, solid Na₂SO₃ (3 to 10 g) was added to crude reaction solutions and the resulting suspension was stirred overnight. The chemical shifts (δ) are reported in ppm relative to 85% H₃PO₄ with downfield shifts taken as positive. Coupling constants (*J*) are reported in hertz.

Caution. White phosphorus is flammable, extremely poisonous and volatile and particular care must be taken in handling it.

Results and discussion

The intensive stirring of the alcoholic solution of Cu(II) acetylacetonate, carboxylates or halides

(CuX₂) with white phosphorus dissolved in an arene at 40–70°C and the [CuX₂]/[P₄] molar ratio, equal 10, under inert atmosphere is accompanied by a rapid color change from green (or brown in the case of CuBr₂) to brownish-black with formation of some insoluble material which caused the formation of a turbid solution. The progress of the reaction was monitored by GC at prescribed time intervals (5–10 min). Irrespectively on the alcohol and oxidant used, the oxidative alkoxylation of P₄ mediated by Cu(II) compounds gives a mixture of dialkyl phosphites 1a,b and trialkyl phosphates 2a,b according to the following general reactions:



X = Cl, Br, CH₃CO₂, C₃H₇CO₂, acac

a: R = *n*Bu; b: R = Me

The kinetics of organophosphorus products accumulation (the yield vs. time) for the oxidative coupling of P₄ with *n*-butanol in the presence of CuX₂ oxidants is shown at Fig. 1–3. The major product dibutyl phosphite P(O)H(OBu)₂ 1a, the minor product tributyl phosphate P(O)(OBu)₃ 2a and unstable organophosphorus intermediate tributyl phosphite P(OBu)₃ were usually identified during the reaction. In addition, a trace amount (1–2%) of monobutyl phosphite P(O)H(OH)(OBu) 3a is sometimes observed.

The products formed behave differently in terms of accumulation kinetics. In contrast to phosphate 2a, which is, slowly but steadily, accumulated in the reaction solution, the intermediate P(OBu)₃ passes a maximum before disappearing at 30–50 min because of transmutation to main organophosphorus products (see the proposed reaction mechanism illustrated hereinbelow in Fig. 5). In dependence on the reaction conditions, the phosphite 1a may accumulate or go through some maximum. Decreasing of the 1a content in the reaction end is explained by its oxidative alkoxylation to trialkyl phosphate 2a mediated by CuX₂ [7].

In the presence of copper acetate, the phosphite 1a (28%) and phosphate 2a (33%) were detected in the reaction solution in 60 min (Fig. 1a and Table, entry 1). The intermediate tributyl phosphite disappears at 50 min (Fig. 1a).

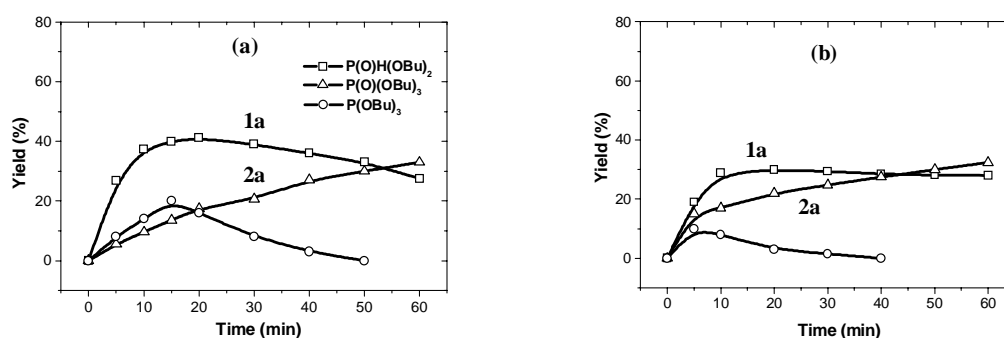


Fig. 1. Dependence of the products yield on the reaction time for the oxidative alkoxylation of white phosphorus mediated by copper carboxylates at following conditions: oxidant $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ (a), $\text{Cu}(\text{C}_3\text{H}_7\text{CO}_2)_2$ (b) 2.7 mmol, P_4 0.27 mmol; BuOH 18 mL, toluene 2 mL, 60°C ; argon.

A bulky brownish-black sediment formed includes Cu and Cu(I) species such as cuprous phosphides [8] and $[\text{CuXP}(\text{OR})_3]$, $[\text{Cu}_2\text{X}_2\text{P}(\text{OR})_3]$ complexes [9]. The Cu(I) derivatives are appeared as a result of oxidation of elementary copper formed in the reactions (1, 2) by CuX_2 :



The reaction (3) is a converse one with disproportionation of CuX . The close results were obtained at using the copper butyrate (Fig. 1b and Table, entry 2). The oxidative alkoxylation of P_4 is also mediated by stearate $\text{Cu}(\text{C}_{17}\text{H}_{35}\text{CO}_2)_2$, however, GC analysis of organophosphorus products in this case was complicated due to liberation and solidification of stearic acid.

Table

Copper (II) oxidants screening for oxidative alcoholysis of white phosphorus under argon ^a

Entry	Oxidant	T ($^\circ\text{C}$)	Time (min)	1a,b ^b (%)	2a,b ^b (%)
1	$\text{Cu}(\text{CH}_3\text{CO}_2)_2$	60	60	28	33
2	$\text{Cu}(\text{C}_3\text{H}_7\text{CO}_2)_2$	60	60	28	32
3	CuCl_2	60	120	54	28
4	CuBr_2	60	60	68	25
5	CuBr_2	50	90	57	37
6	$\text{Cu}(\text{acac})_2$	60	60	80	15
7	$\text{Cu}(\text{acac})_2$	70	40	79	21
8	CuCl_2	40	60	25	13
9	CuCl_2	50	60	7	41

^a Reaction conditions: P_4 , 0.27 mmol; CuX_2 , 2.7 mmol; BuOH, 18 ml; toluene, 2 ml (entries 1-7). P_4 , 0.16 mmol; CuCl_2 , 1.6 mmol; MeOH, 9 ml; benzene, 1 ml (entries 8, 9).

^b Based on GC results. 1a = $\text{P}(\text{O})\text{H}(\text{OBu})_2$, 2a = $\text{P}(\text{O})(\text{OBu})_3$; 1b = $\text{P}(\text{O})\text{H}(\text{OMe})_2$, 2b = $\text{P}(\text{O})(\text{OMe})_3$.

Copper (II) halides exhibit more oxidative ability as compared with carboxylates. In the presence of CuCl_2 , the amount of insoluble material is decreased whereas content of 1a and 2a in liquid phase is reached 54 and 28%, respectively (Fig. 2a and Table, entry 3). A small amount of intermediate tributyl phosphite was identified in the solution till 60 min.

The reaction velocity (estimated as the total products yield per 1 min) is about twice increased at using copper (II) bromide instead of chloride

(Fig. 2b). In this case no intermediate formation of $\text{P}(\text{OBu})_3$ is observed. The oxidation of P_4 by CuBr_2 in *n*-butanol at 60°C yields the phosphite 1a (68%) and phosphate 2a (25%) after 60 min (Table, entry 4). At lower temperature (50°C), the reaction of P_4 with CuBr_2 is decelerated and only 57% of 1a and 37% of 2a are formed in 90 min (Table, entry 5). The effect of temperature was also studied in the systems containing copper (II) acetylacetonate as oxidizing agent for white phosphorus (Fig. 3).

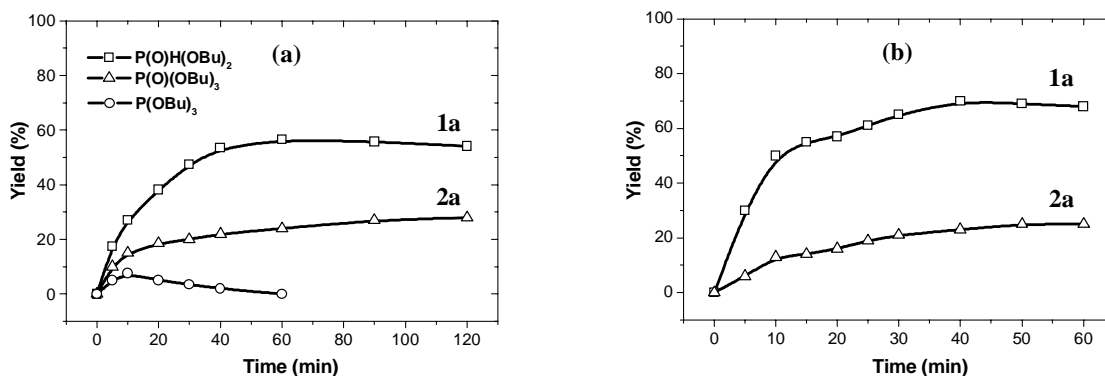


Fig. 2. Dependence of the products yield on the reaction time for the oxidative alkoxylation of white phosphorus mediated by copper halides at following conditions: oxidant CuCl₂ (a), CuBr₂ (b) 2.7 mmol, P₄ 0.27 mmol; BuOH 18 mL, toluene 2 mL, 60°C; argon.

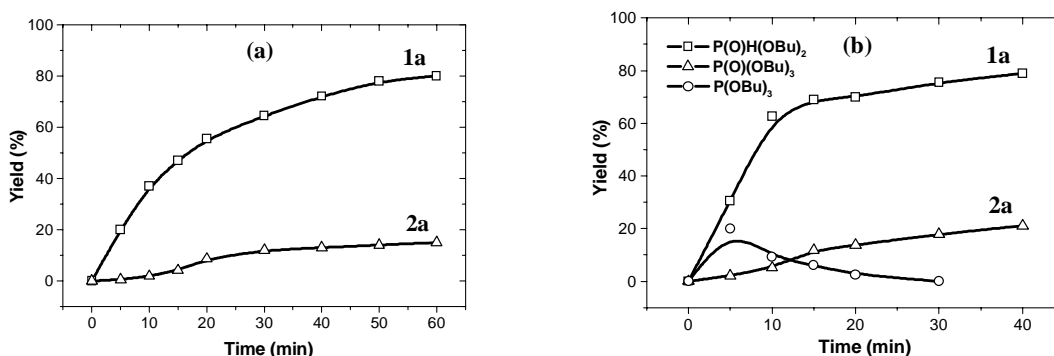


Fig. 3. Dependence of the products yield on the reaction time for the oxidative alkoxylation of white phosphorus mediated by copper acetylacetonate at following conditions: Cu(acac)₂ 2.7 mmol, P₄ 0.27 mmol; BuOH 18 mL, toluene 2 mL, 60 (a) and 70°C (b); argon.

At 60°C, both dibutyl phosphite 1a and tributyl phosphate 2a were gradually accumulated in the reaction solution (Fig. 2a) reaching respectively 80 and 15% yield in 60 min (Table, entry 6). The complete conversion of P₄ in the presence of Cu(acac)₂ giving 1a (79% yield) and 2a (21% yield) is achieved at 70°C in 40 min (Fig. 2b, Table, entry 7). The intermediate tributyl phosphite passes a maximum (20%) at 5 min and then disappears at 30 min. At elevated temperature, the velocity of P(OBu)₃ formation mediated by Cu(acac)₂ is apparently higher than the velocity of its further transformation.

Remarkably, when methanol is used as organic substrate the lowest total yield of appropriate dimethyl phosphite 1b and trimethyl phosphate 2b is obtained (Table, entries 8, 9). To establish the reason of this phenomenon, the ³¹P NMR analysis of the methanolic solutions was performed after reaction. Besides the P(O)H(OMe)₂ 1b (δ 11.9, ¹J_{P-H}

H = 706), P(O)(OMe)₃ 2b (δ 2.0), the spectra additionally contained the chemical shifts of the monomethyl phosphite P(O)H(OH)(OMe) 3b (δ 7.94, ¹J{P-H} = 679) and phosphorous acid P(O)H(OH)₂ (δ 4.1, ¹J_{P-H} = 700) which are formed as a result of stepwise acidolysis of the dimethyl phosphite 1b [10, 11].

The steps to be reasonably included in a putative mechanism accounting for the reduction of CuX₂ by P₄ in alcohol should likely include the coordination of P₄ and ROH to the copper (II) center to give an intermediate η²-P₄ complex (A) with the coordination octahedron around the metal completed by X ligands and solvent (the latter is omitted at the Fig. 4 for simplicity). The CNDO calculations suggest that both P₄ and ROH are activated in coordination sphere of Cu(II) ion building up neat intraligand charge separations that favor their further intramolecular coupling step.

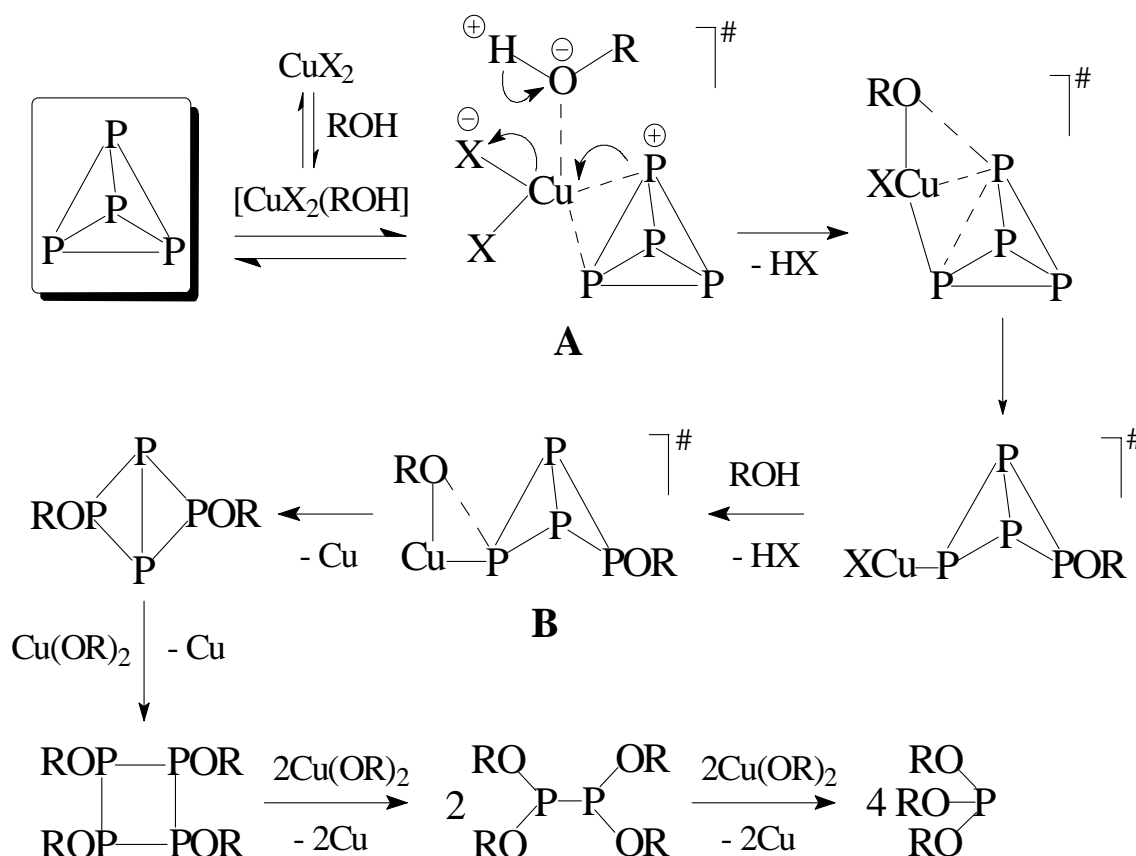


Fig. 4. Proposed mechanism of the oxidative P-O coupling of white phosphorus with alcohol in the coordination sphere of $Cu(II)$ complexes.

Thus, while the tetrahedral P_4 molecule undergoes a severe pyramidal distortion, weakens the P-P bond coordinated to the metal, and accumulates therein a positive charge, the ROH ligand hyperpolarizes at the O-H bond and, with the assistance of the *cis* arranged X ligand, deprotonates converting to an alkoxyde ligand [3, 4]. Once this positive electric and steric situation has been set up, the intramolecular nucleophilic attack of the OR ligand to the closest of the two positively charged P-atoms eventually affords the $P_4(OR)$ ligand. The generation of the second P-OR bond follows from metal coordination and activation of second ROH molecule. The collapse of the intermediate complex **B** takes place by reducing elimination of Cu and intramolecular coupling of OR and $P_4(OR)$ ligands to produce the bicyclic dialkoxy tetraphosphine $P_4(OR)_2$ [12, 13]. If one takes for granted the general view of the oxidative alkoxylation of white phosphorus mediated by copper (II) compounds described hereinbefore, it is straightforward to assume that

the cleavage of the remaining five P-P bonds may occur following a similar stepwise mechanism involving in sequence, (i) the oxidative alkoxylation of $P_4(OR)_2$ by the cupric alkoxyde formed from CuX_2 and alcohol (schematically, as $Cu(OR)_2$) to yield the cyclic tetraalkoxy tetraphosphine $P_4(OR)_4$, (ii) the further cleavage of two P-P bonds of $P_4(OR)_4$ promoted by $Cu(OR)_2$ to give two equivalents of the linear tetraalkoxy diphosphine $P_2(OR)_4$ and, eventually, (iii) the last alkoxylation reaction by $Cu(OR)_2$ promoting the last P-P bond breakage which transforms $P_2(OR)_4$ into intermediate trialkyl phosphite $P(OR)_3$ (Fig. 4).

Only $P(OR)_3$ is revealed by GC and NMR methods while the other proposed cyclic and acyclic organophosphorus intermediates which should form during the oxidative alkoxylation of P_4 were not detected in the reaction solution because of their high kinetic lability. Likely, this is a consequence of the very high rate attributable to the elementary steps of the oxidative alkoxylation

reactions shown in Fig. 4. Such hypothesis may be strongly sustained when one considers that a greater reactivity towards heterolytic activation is developed when the white phosphorus tetrahedron is partially opened [14].

Trialkyl phosphite is rather reactive under the

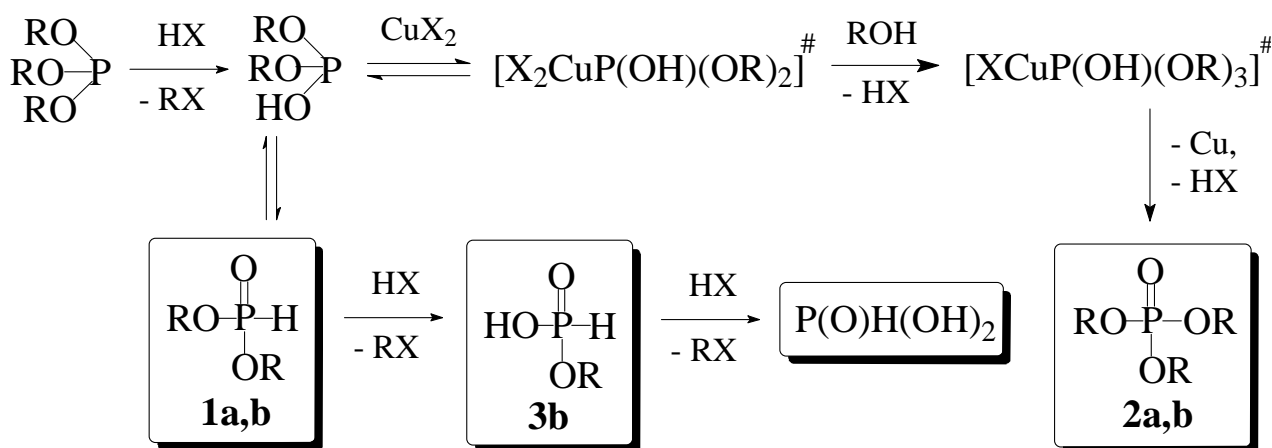


Fig. 5. Proposed mechanism of the trialkyl phosphite transmutation into the main products.

Dealkylation of $P(OR)_3$ by an acid HX generated *in situ* yields dialkylhydroxy phosphite $P(OH)(OR)_2$ which, in turn, may tautomerize to the more thermodynamically stable dialkyl phosphite 1a,b as a result of the conversion of triple-connected to quadruple-connected phosphorus [15]. The $P(OH)(OR)_2$ is a strong nucleophile capable to form complexes with transition metal ions [16]. Thus, complexation of $P(OH)(OR)_2$ to CuX_2 could lead to the formation of the intermediate complex $[X_2CuP(OH)(OR)_2]^\#$. This latter, may react with ROH to give the $[XCuP(OH)(OR)_3]^\#$ complex which is decomposed to Cu, HX and trialkyl phosphate 3. In dependence on the reaction conditions, the methanolic derivative 1b may be dealkylated with HX to monoalkyl phosphite 3b and phosphorous acid. Two step acidolysis of $P(O)H(OMe)_2$ is well documented in the literature [10, 11]. The bulky *n*-butyl P(III) ester is much more stable to acidolysis than methyl one [11]. Therefore, the ^{31}P NMR analysis of the butanolic reaction solutions exhibits the chemical shifts of the dibutyl phosphite, $P(O)H(OBu)_2$ 1a, (δ 8.2, $J_{P-H} = 701$), tributyl phosphate, $P(O)(OBu)_3$ 2a, (δ -0.6), traces of monobutyl phosphite $P(O)H(OH)(OBu)$ 3a, (δ 5.84, $J_{P-H} = 677$) and no phosphorous acid.

At using $Cu(acac)_2$, the acetylacetonone is released as HX in contrast to acids generated from another

reaction conditions and may enter into a string of reactions which account for the formation of every other detected organophosphorus products. The possible reactions related to dealkylation and oxidation of $P(OR)_3$ are outlined in Fig. 5.

copper(II) salts. The $CH_3COCH_2COCH_3$ is a tautomeric mixture of the cetonic (*ca.* 24%) and enolic (*ca.* 76%) forms [17]. The enolic form $CH_3-C(OH)=CH-CO-CH_3$ (pK_a 9) has much weaker acidic properties than HCl, HBr or carboxylic (pK_a *ca.* 5) acids, however it capable to dealkylate $P(OR)_3$ to dialkyl phosphite which is a major product of the oxidative alkoxylation of P_4 mediated by $Cu(acac)_2$.

Noticeably, dialkyl alkylphosphonate $P(O)R(OR)_2$ was not detected among the reaction products, thus indicating that the possible isomerization of $P(OR)_3$ to $P(O)R(OR)_2$ proceeds much slower than its dealkylation to 1a,b and oxidation to 2a,b.

From a thermodynamic viewpoint, the driving forces pushing the system to oxidative P-O coupling of P_4 to ROH are the favorable energy balance between the formation of P-O, P-H, P=O bonds and the loss of the P-P bonds of P_4 (335, 322, 544 and 201 kJ/mol, respectively) and high standard redox potential of the Cu(II)/Cu(0) pair (0.337 V) [18].

Conclusion

White phosphorus may be stoichiometrically oxidized by copper(II) carboxylates,

acetylacetonate or halides in the arene-alcoholic solutions at 40-70°C under an inert atmosphere to give dialkyl phosphites (*ca.* 30-80%) and trialkyl phosphates (*ca.* 15-40%). The study of the kinetics of the products accumulation reveals the unstable intermediate trialkyl phosphite which is being readily converted into the major products. In the case of methanolic solutions, the monomethyl phosphite and phosphorous acid were additionally formed as a result of two step acidolysis of dimethyl phosphite. On the basis of obtained results, the tested copper compounds may be put in the following order in terms of oxidative ability: $\text{Cu}(\text{acac})_2 \geq \text{CuBr}_2 > \text{CuCl}_2 > \text{Cu}(\text{CH}_3\text{CO}_2)_2 \geq \text{Cu}(\text{C}_3\text{H}_7\text{CO}_2)_2$. The oxidative alkoxylation of P_4 mediated by Cu(II) compounds proceeds *via* the coordination of white phosphorus and alcohol to metal ion followed by their activation towards the P-O coupling with each other and decomposition of this intermediate complex accompanied by formation of organophosphorus product. In the course of the reaction under an inert atmosphere, the copper (II) oxidants are stoichiometrically reduced by P_4 to Cu and Cu(I) species which are accumulated in the reaction solution.

Acknowledgement

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