

Copper (II) Catalyzed Oxidative Alkoxylation of White Phosphorus. Communication 2.

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Abstract

White phosphorus has been catalytically oxidized by oxygen in alcoholic solutions of copper (II) acetylacetonate, halides or carboxylates to yield dialkyl phosphites and trialkyl phosphates under 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) catalysts on the kinetics of accumulation and transmutation of organophosphorus products has been explored. It has been found that the Cu(II) compounds take a role of catalysts-electron-carriers from white phosphorus to oxygen. The indispensable molar ratio between catalyst and white phosphorus and the order of catalytic activity for the copper (II) compounds have been established. The major steps of the catalytic reaction including (i) the coordination of white phosphorus and alcohol to metal ion, (ii) the redox decomposition of this intermediate complex accompanied by reducing elimination of elementary copper and formation of organophosphorus product and (iii) the oxidation of the reduced form of catalyst by oxygen have been also suggested.

Introduction

The current technology for the synthesis of phosphorus esters is based on the oxidation of white phosphorus (P_4) by chlorine, followed by phosphorylation of alcohol by the phosphorus chloride. Evolution of the aggressive hydrogen chloride accompanies this latter reaction causing serious environmental problems. The increased commercial and environmental interests have prompted the search for technical protocols for converting white phosphorus into useful derivatives which are alternative to the presently used procedures. The direct oxidation of P_4 by such accessible technical oxidant as oxygen in alcoholic solution leads to the radical chain oxidation of P_4 by O_2 which afford a dense white smoke of phosphorus oxides P_4O_6 , P_4O_{10} and only traces of organophosphorus compounds. To accelerate the desired reaction of the oxidative P-O coupling of P_4

to alcohol, the catalysis by copper (II) compounds has been used [1, 2]. The application of catalysts has allowed to substitute the toxic Cl_2 by harmless O_2 and to prevent the undesirable interaction of white phosphorus with oxygen. Nevertheless, this new catalytic protocol is in an early stage of development, so the rate and sequence of the organophosphorus compounds formation has not yet investigated. This contribution is aimed at expanding further the fundamental knowledge on the catalytic functionalization of white phosphorus. Special attention will be devoted to the kinetics of accumulation of organophosphorus products and to the molar ratio between catalyst and white phosphorus.

Experimental

The dehydration of alcohols, arenes and the copper (II) catalysts, the preparation of P_4 arene solution and the GC analysis of organophosphorus products were accomplished as described in the

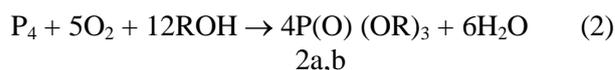
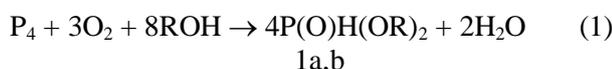
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communication 1 [3]. Oxygen was dried under CaCl_2 . The Cu(II) catalyzed oxidative alkoxylation of white phosphorus was carried out in a glass "jacket" reactor equipped with a dropping funnel, a sampling tube and connected to a thermostat to control the reaction temperature, and to a gasometric burette filled by oxygen for measurement of O_2 consumed. The alcohol and CuX_2 were added to the reactor in this order and the resulting solution was thoroughly purged with oxygen during 10-15 min. Then, an aliquot of the stock's arene solution of P_4 (2-4 mL, 0.18 - 0.62 mmol) was added into the reaction solution through the dropping funnel connected with a glass tube reaching the reactor bottom. The reactions were conducted at partial pressure of oxygen (P_{O_2}) equal 0.6 or 1.0 atm. During experiment, the reaction velocity W_{O_2} (M/min), equal to the mols of O_2 consumed by 1 L of the catalytic solution per 1 min, was continuously measured and the solution sample was periodically taken and subjected to GC analysis.

Caution. White phosphorus is flammable, extremely poisonous and volatile and particular care must be taken in handling it. It is strongly recommended to conduct its reactions under oxygen atmosphere behind shields.

Results and discussion

The intensive stirring of the alcoholic solution of Cu(II) acetylacetonate, carboxylates or halides (CuX_2) with white phosphorus dissolved in an arene at 40-60°C and the $[\text{CuX}_2]/[\text{P}_4]$ molar ratio, equal 5, under oxygen atmosphere is accompanied by a rapid color change from green to brownish-black and by consumption of O_2 by this solution. As soon as O_2 is steadily consumed, the brown sediment eventually dissolves and solution gradually lightens to restore the original green transparent color of the initial catalytic solution. The white smoke of the phosphorus oxides is not observed above catalytic solution. The progress of the reaction was monitored by GC at prescribed time intervals (5-10 min). Irrespectively on the alcohol and catalyst used, the oxidative alkoxylation of P_4 catalyzed by Cu(II) compounds gives a mixture of dialkyl phosphites 1a,b and trialkyl phosphates 2a,b according to the following general reactions:



Blank control experiment, carried out in the absence of catalyst, did not produce organophosphorus derivatives, only dense white smoke of phosphorus oxides were observed in the reactor. The kinetic curve (the velocity vs. time) and kinetics of organophosphorus products accumulation (the yield vs. time) for the oxidative coupling of P_4 with *n*-butanol catalyzed by some CuX_2 catalysts under oxygen atmosphere at 60°C and the $[\text{CuX}_2]/[\text{P}_4]$ molar ratio, equal 5, are shown at Fig. 1, 2. In the presence of CuCl_2 , the kinetic curve passes a maximum ($2,5 \cdot 10^{-3}$ M/min) at 10 min (Fig. 1).

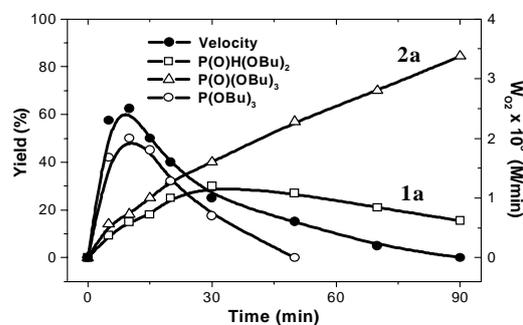


Fig. 1. Dependence of the velocity and products yield on the reaction time for the oxidative alkoxylation of white phosphorus catalyzed by copper dichloride at following conditions: CuCl_2 3.1 mmol, P_4 0.62 mmol; BuOH 16 mL, toluene 4 mL, 60°C; P_{O_2} 0,6 atm.

The yield of dibutyl phosphite 1a also passes a maximum (30% at 30 min) while tributyl phosphate 2a is rapidly accumulated in the catalytic solution. In addition to the main reaction products, GC monitoring of the catalytic reaction reveals the intermediate tributyl phosphite P(OBu)_3 which passes a maximum (50% at 10 min) and disappears at 50 min because of a gradual transmutation into the main products 1a and 2a (see the reaction equations below). The complete P_4 conversion is achieved in 90 min, 1a and 2a are obtained in 16 and 84% yield, respectively (Table, entry 1). As one can see from the entry 1, the experimental molar ratio between O_2 consumed and P_4 introduced in the reaction (O_2/P_4) is close to 5, *i.e.* to the reaction stoichiometry depicted in the equation (2).

The copper(II) acetylacetonate exhibits more catalytic activity in the oxidative alkoxylation of white phosphorus as compared with chloride. The

complete P_4 conversion is achieved in 40 min, the reaction velocity passes a maximum ($8,5 \cdot 10^{-3}$ M/min) at 3 мин (Fig. 2).

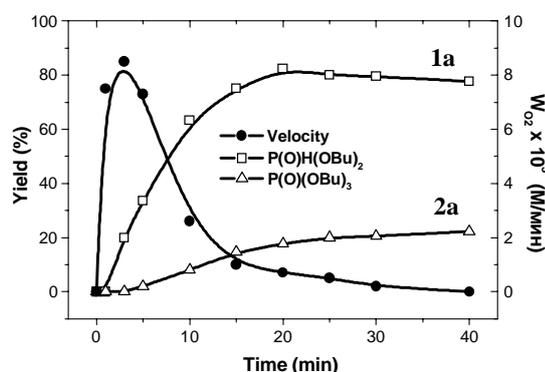


Fig. 2. Dependence of the velocity and products yield on the reaction time for the oxidative alkoxylation of white phosphorus catalyzed by copper acetylacetonate at following conditions: $Cu(acac)_2$ 1.35 mmol, P_4 0.27 mmol; BuOH 12 mL, toluene 3 mL, $60^\circ C$; P_{O_2} 0,6 atm.

During reaction of P_4 with *n*-BuOH and O_2 in the presence of $Cu(acac)_2$, phosphite 1a passes a maximum (81%) at 20 min whereas phosphate 2a is slowly accumulated in the solution. The final product distribution is as follows: 78% yield of dibutyl phosphite 1a and 22% yield of tributyl phosphate 2a (Table, entry 2). The intermediate tributyl phosphite is not detected in the presence of $Cu(acac)_2$. Under these conditions, the rate of $P(OBu)_3$ transmutation is apparently higher than the rate of its formation from P_4 . The experimental

molar ratio O_2/P_4 of the entry 2 is close to stoichiometry of the reaction (1).

In contrast to oxidative ability demonstrated by the copper(II) butyrate and bromide [3], the catalytic activity of $Cu(C_3H_7CO_2)_2$ is higher than one of $CuBr_2$. In the presence of both copper (II) butyrate and bromide, tributyl phosphite 2a is predominantly obtained (Table, entries 3, 4). Copper (II) acetate, butyrate and bromide catalyze the oxidative P-O coupling of P_4 to MeOH at $50^\circ C$ and the molar ratio CuX_2/P_4 , equal 5, to give trimethyl phosphate 2b in a moderate yield (Table, entries 5-7). Dimethyl phosphite 1b is not identified because it is strongly sensitive toward the cleavage by acid and water both generated during the catalytic reaction.

Thus the same products are obtained in the oxidative alkoxylation of P_4 under both inert [3] and oxygen atmosphere, *i.e.* oxygen does not directly react with P_4 and participate in formation of organophosphorus compounds. In both cases, white phosphorus is oxidized by CuX_2 in alcohol to yield organophosphorus products. Our results suggest the following major steps for the catalytic reaction of the oxidative alkoxylation of P_4 : the reduction of CuX_2 by white phosphorus in alcohol, which generates elementary copper together with the intermediate trialkyl phosphite (3), the oxidation of Cu by CuX_2 to CuX (4) and the regeneration of catalyst *via* acidic oxidation of CuX by dissolved oxygen (5).

Table

Copper (II) catalyst screening for oxidative alkoxylation of white phosphorus under oxygen ^a

Entry	Catalyst (mmol)	P_4 (mmol)	ROH (mL)	Arene (mL)	Time (min)	$\frac{O_2}{P_4}$	1a,b (%) ^b	2a,b (%) ^b
1	$CuCl_2$ (3.1)	0.62	16	4	90	4.8	16	84
2	$Cu(acac)_2$ (1.35)	0.27	12	3	40	3.7	78	22
3	$Cu(C_3H_7CO_2)_2$ (1.35)	0.27	7	3	50	4.9	9	91
4	$CuBr_2$ (0.9)	0.18	7	3	100	5.0	3	97
5 ^c	$Cu(CH_3CO_2)_2$ (1.1)	0.22	8	2	50	4,2	-	53
6 ^c	$Cu(C_3H_7CO_2)_2$ (1.1)	0.22	8	2	70	4,0	-	51
7 ^c	$CuBr_2$ (1.1)	0.22	8	2	80	4,5	-	69
8 ^d	$CuCl_2$ (0.7)	0.28	6	4	220	4.1	-	48
9 ^d	$CuCl_2$ (1.4)	0.28	6	4	80	4.3	-	67
10 ^d	$CuCl_2$ (2.8)	0.28	6	4	50	4.7	-	78

^a Reaction conditions: $60^\circ C$; P_{O_2} 0.6 atm; BuOH, toluene (entries 1-4); MeOH, benzene (entries 5-10).

^b GC values based on pure samples. 1a = $P(O)H(OBu)_2$, 2a = $P(O)(OBu)_3$; 1b = $P(O)H(OMe)_2$, 2b = $P(O)(OMe)_3$.

^c $50^\circ C$; P_{O_2} 1 atm. ^d $40^\circ C$; P_{O_2} 1 atm.

receptor. A number of similar processes are known which proceed in the presence of a catalysts-electron-carriers (CEC), such as transition metal compounds or their combinations [5-10]. These redox reactions are based on the reversible reduction / or oxidation of the CEC resulting in the oxidation / or reduction of organic or inorganic substrates. To hasten the reactions, a large amount of CEC is often used. A typical example of such reaction is the industrial process of the ethylene oxidation by O₂ to acetaldehyde in aqueous solution of the combined PdCl₂/CuCl₂ catalytic system, which proceeds *via* the reduction of Pd(II) by ethylene to Pd, accompanied by the acetaldehyde formation, followed by the reoxidation of Pd by Cu(II) and of Cu(I) by O₂ [5]. The PdCl₂/CuCl₂ system behaves as a CEC from ethylene to oxygen. The PdCl₂ concentration in the reaction solution is equal 0.02-0.2 M, while CuCl₂ is usually taken in a large excess (100 mol CuCl₂ per mol PdCl₂) [11]. Although the redox steps sequence above mentioned includes no catalytic reactions from the conventional point of view, the PdCl₂ and CuCl₂ are considered as catalysts and this step sequence – as a catalytic one [5]. The redox catalysis of the oxidative alkoxylation of white phosphorus (1, 2) is realized *via* a sequence of the similar key steps (3-5, 7) where the Cu(II) compounds carry 12 or 20 electrons from white phosphorus to oxygen to yield four molecules of P(III) or P(V) esters, respectively. After finishing the first catalytic cycle, the same catalytic solution can convert the second and following portions of P₄ solution practically with the same rate. As a result, the final molar ratio between initial CuX₂ and total P₄ oxidized may be considerably decreased. A series of preparative scale experiments with CuX₂ as catalyst have been carried out by this manner, the phosphorus esters have been isolated and characterized by NMR spectroscopy [12].

Conclusion

Under oxygen atmosphere, the oxidative alkoxylation of white phosphorus in the presence of copper (II) compounds proceeds in a catalytic fashion yielding the same set of products as under inert atmosphere. The nature of Cu(II) catalysts and alcohols used does not dramatically change the nature of reaction products. In all cases, dialkyl phosphites and trialkyl phosphates are formed, only the ratio of these products changes. Trialkyl phosphate is predominantly obtained in the

presence of copper (II) halides and carboxylates, whereas acetylacetonate promotes the formation of dialkyl phosphite. Trialkyl phosphite is observed as unstable organophosphorus intermediate, which is being converted into the main reaction 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. The catalytic activity of the tested Cu(II) compounds is decreased in the following order: Cu(acac)₂ > Cu(CH₃CO₂)₂ ≥ Cu(C₃H₇CO₂)₂ > CuCl₂ ≥ CuBr₂. The oxidative alkoxylation of white phosphorus in the presence of Cu(II) compounds under argon and oxygen atmosphere proceeds according to an identical mechanism. In both cases, organophosphorus compounds are formed as a result of the activation and P-O coupling of P₄ and ROH in coordination sphere of the copper center. The only difference is that under argon the reduced Cu(I) species are accumulated in the solution while under oxygen atmosphere they are regenerated by O₂ to return Cu(II) compounds back to the catalytic cycle. To avoid the side oxidation of P₄ by O₂, a special condition should be kept in order to white phosphorus transferred its electrons to oxygen through catalyst CuX₂. A rather large amount of catalyst, between 4 and 6 equivalents of catalyst CuX₂ for each P₄, *i. e.* between 1.0 and 1.5 equivalents for each phosphorus atom, is therefore needed for safety and productivity reasons. In fact, the Cu (II) compounds take a role of catalysts-electron-carriers from white phosphorus to oxygen.

Acknowledgement

This work has been in part supported by the ISTC K-1284.2 research grant.

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Received 3 May 2010