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Oxidation of white phosphorus by peroxides in aqueous and alcoholic solutions: mechanistic aspects and catalytic studies

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Abstract

The oxidation of white phosphorus by hydrogen peroxide or different organic peroxides (such as *tert*-butyl hydroperoxide, dibenzoylperoxide, 3-chloroperoxybenzoic acid) has been studied in both aqueous and alcoholic solutions under anaerobic conditions. Depending on the reaction conditions, P(I) (hypophosphorous acid), P(III) [phosphorous acid, mono- and dialkyl (or diaryl) hydrogen phosphonates] and P(V) [phosphoric acid or trialkyl (or triaryl) phosphates] derivatives are produced. The catalytic oxidative P–O coupling of P_4 to water, aliphatic alcohols and phenol under mild reaction conditions is accomplished by using copper(I), copper(II) and vanadium(IV) complexes. Catalytic conversion of white phosphorus with complete efficiency and high selectivity for monoalkyl hydrogen phosphonates (>95%) may be achieved using 3-$ClC_6H_4C(O)OOH$ as oxidant under optimized conditions. An identical radical mechanism is suggested to account for both the stoichiometric and the catalytic oxidative hydroxydation, alkoxydation and phenoxydation of white phosphorus promoted by peroxides in both aqueous biphasic conditions and organic solutions.
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1. Introduction

The search for an ecoefficient catalytic conversion of elemental phosphorus to organophosphorus compounds and phosphorus oxyacids has received increasing attention during the last decade when a large body of research in this area has been motivated by increased emphasis to the reduction of environmental pollution originated from chemical industries [1]. Attempts to develop alternative synthetic methods to produce organophosphorus compounds which avoid the use of the highly polluting white phosphorus chlorination process have moved the first steps following pathways typical of either homogeneous catalysis [1a–k] and electrocatalysis [2]. Worth to be mentioned here are the pioneristic studies by Dorfman et al. describing the catalytic alk(ar)oxydation of white phosphorus (P_4) to give organophosphorus esters, mainly dialkyl hydrogen phosphonates and trialkylphosphates [1b–j] or triphenylphosphite and triphenylphosphate [1e,h,k]. The oxidative P–O coupling of P_4 with aliphatic alcohols and phenol was successfully carried out in aromatic solvents in the presence of Cu(II) [1b–e] and Fe(III) [1e–g] salts as well as of mixed catalyst/cocatalyst systems such as I_2/Fe(III) [1h], Pd(II)/$NaNO_2$, Ru(IV)/$NaNO_2$ [1i], I_2/$NaNO_2$ [1j,k], using oxygen as cheap and environmentally benign oxidant. A few patents originating from these processes have been recently filed [3].

Much less attention has been addressed to test alternative oxidants such as hydrogen peroxide and organic peroxides in spite of the apolar character of the tetrahedral white phosphorus molecule would suggest a strong preference to undergo homolytic reactions initiated by free radicals and UV light [4].

Peroxides are considered simple and universal sources of radical species which are easily generated by homolysis of the O–O peroxo bond. A huge variety of oxidative reactions initiated by inorganic and organic peroxides have been reported [5], and several highly efficient and environmentally appealing

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oxidative catalytic processes have been developed using hydrogen peroxide [6] and organic peroxides [7] as ecobenign and efficient oxidants. Scarce attention has been however focused to the oxidation of white phosphorus by peroxides. The oxidation of P_4 by H_2O_2 in aqueous solution was mentioned in an old paper to be accompanied by phosphorus disproportionation to phosphine and phosphoric acid [8], but these result remains questionable. In a recent paper Trofimov et al. briefly reported on the copper(II) catalyzed oxidation of P_4 by acidic aqueous H_2O_2 in the presence of alcohols (EtOH, *n*-BuOH) [1a]. The reaction gave dialkyl hydrogen phosphonates and trialkyl phosphates in moderate yields. The modest production of organophosphorus products was tentatively attributed to competitive reactions of P_4 with H_2O yielding phosphorus oxyacids. The non-selective oxidation of red phosphorus by aqueous H_2O_2 to yield a mixture of different anions of phosphorus oxyacids and polyacids has been also reported [9]. Finally, the reaction of P_4 with (*tert*-BuO)$_2$, in the presence of different alkenes, has been reported to proceed at 150–160 °C giving poorly characterized $R_xP_4O_2H_2$ organophosphorus compounds [10].

This article sheds some light in this area giving an account of our studies on the stoichiometric and catalytic oxidation of P_4 by organic peroxides in water, aliphatic alcohols and phenol. A few comparative experiments describing the simple oxidative hydroxydation of P_4 promoted by H_2O_2 have been also performed and are here reported. Oxidative tests in aqueous/biphasic and alcoholic solutions in the presence of different organic solvents have been carried out leading predominantly to P(III) derivatives.

2. Experimental

2.1. Materials

Peroxides [H_2O_2, 35% in H_2O, 11.3 M); *tert*-BuOOH, 70% in H_2O, 7.2 M; *tert*-BuOOH, 5–6 M in decane (an averaged value of 5.5 M was taken for stoichiometric calculations); $(C_6H_5CO)_2O_2$ (97%); 3-$ClC_6H_4C(O)OOH$ (57–86%; an averaged value of 72% was taken for stoichiometric calculations), D_2O and C_6D_6 were used as received from Aldrich or Fluka without further purification. Alcohols (MeOH and *n*-BuOH), phenol and organic solvents (benzene, toluene, *n*-hexane, tetrahydrofuran (THF), CCl_4) were purified and dried by the usual methods [11]. The gases (N_2 and Ar) were UPP grade and were dried by passing over a $CaCl_2$ column. The metal catalysts, $CuCl_2$, CuI, Cu(acac)$_2$, Cu(CH_3COO)$_2$, Cu($CH_3CH_2CH_2COO$)$_2$, and VO(acac)$_2$, were dried by prolonged heating under vacuum (acac = acetylacetonate). White phosphorus was mechanically cleaned from oxide layers, washed with THF and dried in a stream of nitrogen. It was then used as a solid or as a stock solution in arene (benzene or toluene). In the latter case, P_4 was weighted in a beaker under water, dipped into three successive beakers containing THF, and then dissolved in benzene or toluene at 45–50 °C. The concentration of P_4 in the arene solution was determined by iodometry [12].

2.2. Caution

White phosphorus is highly flammable, extremely poisonous and volatile and particular care must be taken in handling it and properly dispose its residues.

2.3. Typical reaction procedures

2.3.1. Homogeneous hydroxydation and alkoxydation of white phosphorus

2.3.1.1. Method A. The reactions were performed under an inert atmosphere using Schlenk type techniques and an oil bath to keep the reaction flask at the desired temperature (40–90 °C). Solid P_4 (29.7 mg, 0.24 mmol) divided in small portions, was added under a stream of argon to a degassed 1:1 mixture (2–4 mL) of the substrate (deuterated water or alcohol) and the organic solution of the peroxide in a prepurified solvent (toluene, *n*-hexane, THF, CCl_4). The solution was rapidly heated to the desired temperature under vigorous magnetic stirring which was maintained until the reaction was completed (0.5–4 h). After this time, the crude reaction solution was analyzed by GC/MS, using a constant amount of naphthalene as external standard, and/or $^{31}P\{^1H\}$ NMR spectroscopy, using a constant amount of TPPMS-oxide [TPPMS = $Na^+Ph_2P(3\text{-}SO_3C_6H_4)^-$] as internal standard to allow for the comparative integration of the ^{31}P signals through the different experiments. To estimate the quantity of unreacted P_4 in the organic layer, a known amount of PPh_3O was added to the reaction solution as internal standard.

2.3.1.2. Method B. The reactions of alcohols with dissolved P_4 were also carried out under anaerobic conditions in a glass "jacket" reactor equipped with a dropping funnel and connected to a burette filled with argon and a thermostat to control the reaction temperature. The kinetic reaction regime was reached by shaking the reactor with frequency of about 250–300 swingings/min. The alcohol, the organic peroxide and, for selected experiments, the catalyst [ROH:R′OOR″:Cat = 3500–7300:30–200:1] were added to the reactor in this order and the resulting solution was thoroughly purged with argon during 15 min. Then, an aliquot of a stock arene (toluene or benzene) solution of P_4 (1–2 mL, 0.14–0.27 mmol) was added into the reactor against a brisk argon current through the dropping funnel. The resulting solution volume was about 10–20 mL. The products accumulation and the P_4 consumption were monitored by periodically withdrawing solution samples and checking their composition by GC analysis.

2.3.1.3. Products analysis. ^{31}P NMR spectra of the reaction products formed during the heterogeneous tests were recorded on a Bruker ACP200 or a Varian Gemini g300bb spectrometers at 25 °C, using D_2O or C_6D_6 as solvents. All chemical shifts are reported in ppm (δ) relative to 85% H_3PO_4 with downfield shifts taken as positive. Coupling constants (J) are in Hertz. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The accumulation of organophosphorus products in the homogeneous tests was

monitored and quantified with respect to pure samples of each organophosphorus product by GC analysis using a Chrompack 9002 chromatograph equipped with a flame ionization detector and a 25 m (0.25 mm i.d.) CPSIL 19CB capillary column.

3. Results and discussion

3.1. Oxidation of white phosphorus by peroxides in aqueous biphasic conditions

White phosphorus finely suspended under nitrogen or argon in a vigorously stirred mixture of water and an apolar organic solvent (toluene, THF, CCl_4, *n*-hexane) is easily oxidized by hydrogen peroxide or organic peroxides, such as *tert*-butyl hydroperoxide and dibenzoyl peroxide, to give mixtures of phosphorous $P(O)H(OH)_2$ (**1a**), hypophosphorous $P(O)H_2(OH)$ (**2a**) and phosphoric $P(O)(OH)_3$ (**3a**) acids [13]. Under optimized reaction conditions, the total yield of **1a**, **2a** and **3a** is close to 100% (see Table 1). Depending on the nature of either the peroxide and the solvent, the reaction generally completes in 0.5–2 h at 25–90 °C using a 1:10 molar ratio between white phosphorus and the peroxide.

Under these experimental biphasic conditions, the oxidative hydroxydation of P_4 occurs with phosphorus dissolved in the organic layer and the peroxide distributed in both phases. During the progress of the reaction, the inorganic acids, **1a**–**3a**, which form accumulate exclusively in the aqueous layer. ^{31}P NMR spectroscopy of the aqueous phase, with D_2O in place of H_2O, represents a reliable and fast method to monitor the reaction progress showing the expected signals for the three fully deuterated phosphorus acids due to fast H–D exchange with the solvent. Thus, **1a**–***d*₃** gives a 1:1:1 triplet centered at 5.0 ppm ($^1J_{P-D} = 102.5$), **2a**–***d*₃** appears as a lowfield shifted non-binomial quintet (δ 11.47, $^1J_{P-D} = 85.6$) and **3a**–***d*₃** exhibits a sharp singlet at δ 0.56 in keeping with the lack of any direct P–D bond. Irrespectively of the organic solvent and of the peroxide used as oxidant, phosphorous acid, **1a**, is always the major reaction product with yields ranging between 35 and 76%. The molar ratio between the other two oxyacids (**2a** and **3a**) is generally close to 1:1.

Table 1
Oxidation of white phosphorus by H_2O_2 and organic peroxides under aqueous biphasic conditions[a]

Entry	Oxidant	Conversion % (h)[b]	% **1a**[b]	% **2a**[b]	% **3a**[b]
1	H_2O_2	57 (1)	24	20	13
2[c]	H_2O_2	8 (2)	3	3	2
3[d]	H_2O_2	70 (1)	35	12	23
4	*tert*-BuOOH	100 (0.25)	67	15	18
5[c]	*tert*-BuOOH	100 (0.5)	71	13	16
6[e]	*tert*-BuOOH	63 (0.5)	37	12	14
7[f]	*tert*-BuOOH	100 (0.5)	70	14	16
8[g]	*tert*-BuOOH	100 (1)	66	22	12
9[h]	*tert*-BuOOH	100 (4)	76	11	13
10[i]	*tert*-BuOOH	100 (1)	69	13	18
11[j]	*tert*-BuOOH	25 (2)	20	1	4
12[k]	$(C_6H_5CO)_2O_2$	10 (0.5)	5	3	2
13	$(C_6H_5CO)_2O_2$	100 (0.5)	51	20	29
14[g]	$(C_6H_5CO)_2O_2$	100 (0.5)	52	15	33
15[h]	$(C_6H_5CO)_2O_2$	93 (0.5)	48	18	27
16[i]	$(C_6H_5CO)_2O_2$	88 (0.5)	54	16	18

[a] Reaction conditions: solid P_4, 29.7 mg, 0.24 mmol. Oxidant: H_2O_2 (35 wt% sol, 0.21 mL, 2.4 mmol, 60 °C) (entries 1–3). *tert*-BuOOH 70 wt% sol, 0.33 mL, 2.4 mmol; D_2O, 1 mL; toluene, 1 mL; 60 °C (entries 4–11). $(C_6H_5CO)_2O_2$, 0.6 g, 2.4 mmol; D_2O, 2 mL; toluene, 2 mL; 90 °C (entries 12–16).

[b] Determined by $^{31}P\{^1H\}$ NMR spectroscopy. **1a** = $P(O)H(OH)_2$, **2a** = $P(O)H_2(OH)$, **3a** = $P(O)(OH)_3$.

[c] At 25 °C.

[d] At 90 °C.

[e] *tert*-BuOOH, 0.166 mL, 1.2 mmol at 25 °C.

[f] P_4 dissolved in toluene at 25 °C.

[g] THF, 1 mL (entry 8) or 2 mL (entry 14).

[h] C_6H_{14}, 1 mL (entry 9) or 2 mL (entry 15).

[i] CCl_4, 1 mL (entry 10) or 2 mL (entry 16).

[j] D_2O, 1 mL at 90 °C.

[k] At 60 °C.

Remarkably, at 60 °C an aqueous solution H_2O_2 (35%), produces a mixture of phosphorus oxyacids in moderate yield within 1 h (57%) with practically no selectivity (Table 1, entry 1). The undesired thermal decomposition of H_2O_2 to O_2 and H_2O at elevated temperatures is likely responsible for the modest conversion of P_4 [14]. Lowering the temperature to 25 °C dramatically drops out the efficiency of the P_4-oxidation (Table 1, entry 2) while increasing the temperature up to 90 °C does not considerably grow up the P_4 conversion (Table 1, entry 3) due to the simultaneous raise of the thermal decomposition of H_2O_2. In contrast to a previous report, [8] no evidence for phosphorus disproportionation to PH_3 and $P(O)(OH)_3$ with either H_2O_2 and organic peroxides (see below) was found.

When a commercial 70% aqueous solution of *tert*-BuOOH is used as oxidizing agent, the complete conversion of P_4 in toluene takes place within 15 min at 60 °C (Table 1, entry 4). *tert*-BuOOH proves to be an efficient oxidant towards white phosphorus even at room temperature (Table 1, entry 5). The selectivity in phosphorous acid is significant, but never higher than 76%. As expected, the P_4 conversion considerably reduces by dropping the white phosphorus to peroxide molar ratio to 1:5 (Table 1, entry 6). Similar reaction rates are observed irrespectively from introducing P_4 as a solid or dissolved in arene solution (Table 1, entries 5 and 7).

The best solvent to carry out the P_4 oxidation by *tert*-BuOOH at 60 °C is toluene where the conversion completes in 15 min. A similar conversion requires about 1 h in THF and CCl_4, while in *n*-hexane the reaction completes only after 4 h (Table 1, entries 4 and 8–10). Remarkably, the worse results are obtained when *tert*-BuOOH is used without any additional organic solvent. As an example, the production of P-oxyacids is less than 25% even at 90 °C (**1a**:**2a**:**3a** = 20:1:4) in the absence of organic solvents, *i.e.* when D_2O is added instead of toluene (Table 1, entry 11). In contrast to *tert*-butyl hydroperoxide, which is active in the range 25–60 °C, dibenzoyl peroxide carries out effectively the oxidation of P_4 only at elevated temperature (90 °C), but the selectivity remains poor (Table 1, entries 12–16).

The redox reactions leading to the formation of the phosphorus oxyacids are accompanied by electron transfer from the tetraphosphorus tetrahedron to the peroxide R′OOR″ molecule summing up to 4 [P(I), **2a**], 12 [P(III), **1a**] and 20 [P(V), **3a**]

electrons, respectively. The simple stoichiometries accounting for the P_4 oxidation in each of these processes are given below in Eqs. (1)–(3):

$$P_4 + 12H_2O + 6R'OOR'' \rightarrow \underset{\mathbf{1a}}{4P(O)H(OH)_2} + 6R'OH + 6R''OH \quad (1)$$

$$P_4 + 8H_2O + 2R'OOR'' \rightarrow \underset{\mathbf{2a}}{4P(O)H_2(OH)} + 2R'OH + 2R''OH \quad (2)$$

$$P_4 + 12H_2O + 10R'OOR'' \rightarrow \underset{\mathbf{3a}}{4P(O)(OH)_3} + 6R'OH + 6R''OH + 4R'OR'' \quad (3)$$

R′ = H, R″ = H. R′ = *t*-Bu, R″ = H. R′ = C_6H_5CO, R″ = C_6H_5CO.

The organic species (R′OH, R″OH and R′OR″), *i.e. tert*-butanol, benzoic acid and alkylbenzoates formed from reactions (1)–(3), respectively, were determined by GC–MS analysis, while the quantification of the inorganic phosphorus acids was done by running $^{31}P\{^1H\}$ NMR spectra in the presence of an internal standard (see Section 2).

In conclusion, under aqueous biphasic conditions, H_2O_2 and organic peroxides are able to efficiently oxidize P_4 yielding mixtures of hypophosphorous, phosphorous and phosphoric acids. Hydrogen peroxide is the worse oxidant and the activity of the tested peroxides follows the order: *tert*-BuOOH ≫ $(C_6H_5CO)_2O_2$ ≫ H_2O_2. In simple accordance with their ability to dissolve white phosphorus, the rate of P_4 conversion depends markedly from the solvent following the order: toluene > THF ≅ CCl_4 > hexane ≫ D_2O.

3.2. Oxidation of white phosphorus by organic peroxides in aliphatic and aromatic alcohols

Besides of the aqueous biphasic conditions, the oxidation of solid P_4 by organic peroxides has been studied also in aliphatic and aromatic alcohols. In order to make the reaction system homogeneous, the reaction has been accomplished in the presence of an organic solvent to dissolve white phosphorus (toluene, THF, CCl_4 or *n*-hexane). The identification and quantification of the reaction products (phosphorus esters, phosphorous acid, benzoic and 3-chlorobenzoic acids and their ethers) has been

Table 2
Oxidation of white phosphorus by organic peroxides in aliphatic alcohols or phenol[a]

Entry	Alcohol	Conversion % (h)[b]	%**1b/d**[b]	% **3b/d**[b]	% **4b/d**[b]	% **1a**[b]
1	MeOH	100 (0.5)	18	6	73	3
2[c]	MeOH	100 (1)	19	7	57	17
3[d]	MeOH	64 (1)	21	6	25	12
4[e]	MeOH	90 (1)	20	4	49	17
5[f]	MeOH	100 (1)	19	8	52	21
6[g]	MeOH	100 (1)	15	3	73	9
7[h]	MeOH	100 (1)	8	14	60	19
8[i]	MeOH	90 (2)	10	8	72	–
9[j]	MeOH	100 (2)	16	20	64	–
10[c]	*n*-BuOH	100 (1)	32	7	42	19
11[d]	*n*-BuOH	75 (1)	17	5	38	15
12[e]	*n*-BuOH	97 (1)	44	5	35	13
13[f]	*n*-BuOH	100 (1)	13	2	54	31
14[g]	*n*-BuOH	100 (1)	19	4	49	28
15[h]	*n*-BuOH	100 (1)	17	3	12	68
16	PhOH	92 (2)	84	–	8	–
17[c]	PhOH	14 (2)	11	–	3	–
18[f]	PhOH	90 (2)	75	–	15	–
19[g]	PhOH	87 (2)	86	–	1	–
20[h]	PhOH	89 (2)	81	–	8	–
21[k]	PhOH	89 (2)	74	5	10	–
22[l]	PhOH	79 (4)	32	–	47	–

[a] Reaction conditions: solid P_4, 29.7 mg, 0.24 mmol. *tert*-BuOOH (5.5 M decane sol), 0.44 mL, 2.4 mmol; ROH: R = Me (entries 1–9), 1 mL, 24.7 mmol; R = *n*-Bu (entries 10–15), 1 mL, 10.9 mmol; R = Ph (entries 16–21), 1.0 g, 10 mmol; toluene, 1 mL (entries 1–15) or 2 mL (entries 16–22); 50 °C.

[b] Determined by $^{31}P\{^1H\}$ NMR: **1b** = $P(O)H(OMe)_2$, **3b** = $P(O)(OMe)_3$, **4b** = P(O)H(OH)(OMe); **1c** = $P(O)H(OBu^n)_2$, **3c** = $P(O)(OBu^n)_3$, **4c** = P(O)H(OH)(OBu^n); **1d** = $P(O)H(OPh)_2$, **3d** = $P(O)(OPh)_3$; **4d** = P(O)H(OH)(OPh); **1a** = $P(O)H(OH)_2$.

[c] At 25 °C.

[d] *tert*-BuOOH, 0.11 mL, 0.6 mmol at 25 °C.

[e] *tert*-BuOOH, 0.22 mL, 1.2 mmol at 25 °C.

[f] THF, 1 mL (entries 5 and 13) or 2 mL (entry 18).

[g] *n*-hexane, 1 mL (entries 6 and 14) or 2 mL (entry 19).

[h] CCl_4, 1 mL (entries 7 and 15) or 2 mL (entry 20).

[i] 3-$ClC_6H_4C(O)OOH$, 0.58 g, 2.4 mmol.

[j] 3-$ClC_6H_4C(O)OOH$, 0.58 g, 2.4 mmol; THF, 1 mL.

[k] *tert*-BuOOH, 0.88 mL, 4.8 mmol; *n*-hexane, 2 mL.

[l] 3-$ClC_6H_4C(O)OOH$, 0.58 g, 2.4 mmol at 90 °C.

performed by GC–MS analysis and/or ^{31}P NMR spectroscopy (C_6D_6). The yield of organophosphorus products during the kinetic studies was monitored and quantified by GC analysis.

3.2.1. NMR studies

Table 2 summarizes the results of the P_4 oxidation using *tert*-butyl hydroperoxide or 3-chloroperoxybenzoic acid in aliphatic alcohols such as MeOH and *n*-BuOH or phenol as organic substrates and co-solvents. The major product of the P_4 oxidation by organic peroxides in aliphatic alcohols is monoalkyl hydrogen phosphonate (MAHP) **4b**,**c** (42–72%). Additionally, dialkyl hydrogen phosphonate (DAHP) **1b**,**c** (8–44%), trialkyl phosphate **3b**,**c** (3–20%) and, unexpectedly, phosphorous acid, **1a**, (0–68%) are also detected in the reaction mixture after P_4 oxidation.

In methanolic solutions, the dimethyl hydrogen phosphonate (DMHP), $P(O)H(OMe)_2$, **1b**, (^{31}P NMR: δ 11.9, d, $^1J_{P-H} = 706$), trimethyl phosphate, $P(O)(OMe)_3$, **3b**, (^{31}P NMR: δ 2.0, s), monomethyl hydrogen phosphonate (MMHP), P(O)H(OH)(OMe), **4b**, (^{31}P NMR: δ 7.94, d, $^1J_{P-H} = 679$) and phosphorous acid, $P(O)H(OH)_2$, **1a**, (^{31}P NMR: δ 4.1, d, $^1J_{P-H} = 700$) are observed (Table 2, entries 1–9). The reaction of P_4 with MeOH in the presence of *tert*-butyl hydroperoxide (*tert*-BuOOH/P_4 = 10), results in the complete conversion of P_4 after 0.5 h at 50 °C, while at room temperature the transformation requires *ca.* 1 h to complete (Table 2, entries 1 and 2). Decreasing the *tert*-BuOOH/P_4 ratio to 2.5 and 5 gives lower P_4 conversions (64 and 90%, respectively) (Table 2, entries 3, 4). With *tert*-butyl hydroperoxide, the complete conversion of P_4 is achieved in THF, *n*-hexane and CCl_4 in 1 h, but the higher formation of phosphorous acid (**1a**) is observed in THF (21%) and CCl_4 (19%) (Table 2, entries 5 and 7). Larger differences in P_4-oxidation are found as a function of the peroxides, with conversions ranging from excellent for *tert*-butyl hydroperoxide (Table 2, entries 1 and 5) to modest for 3-chloroperoxybenzoic acid (Table 2, entries 8 and 9). The highest yield of MMHP **4b** (64–72%) is found when 3-chloroperoxybenzoic acid is used as oxidant (Table 2, entries 8 and 9).

The same set of products is obtained after replacing MeOH with *n*-BuOH:dibutyl hydrogen phosphonate (DBHP), $P(O)H(OBu)_2$, **1c**, (^{31}P NMR: δ 8.2, d, $^1J_{P-H} = 701$), tributyl phosphate, $P(O)(OBu)_3$, **3c**, (^{31}P NMR: δ −0.6, s), monobutyl hydrogen phosphonate (MBHP), P(O)H(OH)(OBu), **4c**, (^{31}P NMR: δ 5.84, d, $^1J_{P-H} = 677$) and phosphorous acid, $P(O)H(OH)_2$, **1a**. Like for MeOH, *tert*-butyl hydroperoxide oxidizes P_4 in *n*-BuOH even at room temperature (Table 2, entry 10). Decreasing the peroxide/P_4 ratio to 2.5 and 5 reduces the conversion of P_4 (75 and 97%, respectively) (Table 2, entries 11 and 12). The complete P_4 conversion was obtained in all organic solvents used, while the highest formation of phosphorous acid (**1a**) was found in THF (31%) and CCl_4 (68%) (Table 2, entries 13–15).

Replacing aliphatic alcohols with phenol slows down the reaction. Diphenyl hydrogen phosphonate, $P(O)H(OPh)_2$ (DPHP) **1d**, (^{31}P NMR: δ 0.5, d, $^1J_{P-H} = 749$) and monophenyl hydrogen phosphonate, P(O)H(OH)(OPh) (MPHP) **4d**, (^{31}P NMR: d, δ 2.8, $^1J_{P-H} = 717$) are produced, with **1d** as the major product (Table 2, entries 16–20). Notably, no phosphorous acid, **1a**, is observed irrespectively of the reaction conditions. The conversion of P_4 dramatically decreases from 92 to 14% on lowering the reaction temperature from 50 to 25 °C (Table 2, entries 16 and 17). The solvent does neither affect the overall P_4 conversion nor the products distribution (Table 2, entries 18–20). Increasing the R′OOR″/P_4 ratio up to 20 causes only a small increase of the organophosphorus derivatives yield (overall yield 89%), but small amount (5%) of triphenyl phosphate, $P(O)(OPh)_3$ **3d** (^{31}P NMR: δ −17, s), appears among the products (Table 2, entries 19 and 21). In contrast to the experiments described above carried out in both water and aliphatic alcohols, unreacted P_4 (^{31}P NMR: δ −520.1, s) is present in the reaction mixture even after 4 h at 90 °C (Table 2, entry 22). In the latter experiment the highest amount of **4d** (47%) is produced. The incomplete conversion of P_4 indicates that phenol is a substrate more recalcitrant than alcohols to undergo the oxidative coupling with white phosphorus. A justification for this behavior may be found in the radical mechanism which we propose to account for the present oxidative phosphorylation of alcohols (see below). In such hypothesis, phenol, at variance with aliphatic alcohols, may retard the radical chain reactions being a well-known radical scavenger [15].

3.2.2. Gas-chromatographic studies

In order to collect mechanistic information about the present alkoxydation of P_4 promoted by organic peroxides, we decided to carry out an in-depth investigation of the P_4 oxidation in the presence of *n*-BuOH. Just to summarize our results, white phosphorus dissolved in toluene (0.135 M) quickly reacts with organic peroxides (dibenzoyl peroxide or 3-chloroperoxybenzoic acid) dissolved in *n*-butanol in the temperature range between 40 and 80 °C to yield a mixture of organophosphorus derivatives which was quantitatively analyzed by GC analysis. In keeping with the NMR study illustrated above, the compounds formed were: dibutyl hydrogen phosphonate (DBHP), $P(O)H(OBu)_2$, **1c**, (3–50%) tributylphosphate, $P(O)(OBu)_3$, **3c**, (2–12%) and monobutyl hydrogen phosphonate (MBHP), P(O)H(OH)(OBu), **4c**, (23–79%) [16]. Under optimized reaction conditions, the total yield of **1c**, **3c** and **4c** was 100% (Table 3, entries 1, 3, 5 and 7) with the reaction completing at *ca.* 60 °C within 0.7–1.8 h.

A preliminary test using a stoichiometric R′OOR″/P_4 molar ratio (*i.e.* equal to 6), does not bring about the complete conversion of P_4 (Table 3, entry 2) convincing us to use a higher R′OOR″/P_4 ratio (equal to 10) in the next experiments. Doubling the amount of peroxide (1:20) doubles the reaction rate (Table 3, entries 1 and 3), without practically affecting the product distribution, which suggests a first order dependence of the reaction with respect to peroxide concentration. The oxidation of P_4 by dibenzoyl peroxide in *n*-butanol goes on slowly at 40 °C, but speeds up on increasing the temperature. Rising the temperature from 40 to 60 °C doubles the total yield of the organophosphorus products (Table 3, entries 1 and 4). The highest reaction rate is achieved at 80 °C (Table 3, entry 5). Using 3-$ClC_6H_4C(O)OOH$

Table 3
White phosphorus oxidation by organic peroxides in *n*-butanol[a]

Entry	% Conversion (h)[b]	% **1c**[b]	% **3c**[b]	% **4c**[b]
1	100 (1.8)	36	6	58
2[c]	49 (1.8)	3	4	42
3[d]	100 (0.9)	34	4	60
4[e]	51 (2.7)	16	12	23
5[f]	100 (0.7)	50	2	48
6[g]	52 (1.2)	18	4	30
7	100 (1.5)	16	5	79

[a] Reaction conditions: P_4 (0.135 M solution in toluene), 2 mL, 0.27 mmol; $(C_6H_5CO)_2O_2$, 0.67 g, 2.7 mmol (entries 1–5); 3-$ClC_6H_4C(O)OOH$, 0.65 g, 2.7 mmol (entries 6 and 7); *n*-BuOH, 18 mL; toluene, 2 mL, 60 °C.
[b] GC values are based on standardization with pure samples of the organophosphorus compounds: **1c** = $P(O)H(OBu)_2$, **3c** = $P(O)(OBu)_3$, **4c** = P(O)H(OH)(OBu).
[c] $(C_6H_5CO)_2O_2$, 0.4 g, 1.62 mmol.
[d] $(C_6H_5CO)_2O_2$, 1.3 g, 5.4 mmol.
[e] At 40 °C.
[f] At 80 °C.
[g] At 50 °C.

instead of $(C_6H_5CO)_2O_2$ gives moderate yields of organophosphorus products at 50 °C, but at 60 °C P_4 is completely converted (Table 3, entries 6 and 7).

To intercept possible organophosphorus intermediates formed during the alkoxydation reaction, most of the experiments listed in Table 3 were repeated with GC monitoring by withdrawing aliquots of the reaction solution at regular intervals (5–10 min). Under these conditions, the intermediate formation of tributyl phosphite $P(OBu)_3$ (**5c**) was detected. As an example, the GC monitoring of the reaction carried out under the conditions of entry 4 is shown in Fig. 1.

In contrast to **1c**, **3c** and **4c**, which, slowly but steadily, accumulate in the solution, **5c** goes through a maximum before disappearing after 50 min due to conversion to other organophosphorus products (see the proposed reaction mechanism illustrated in Scheme 1). The stoichiometries of the four

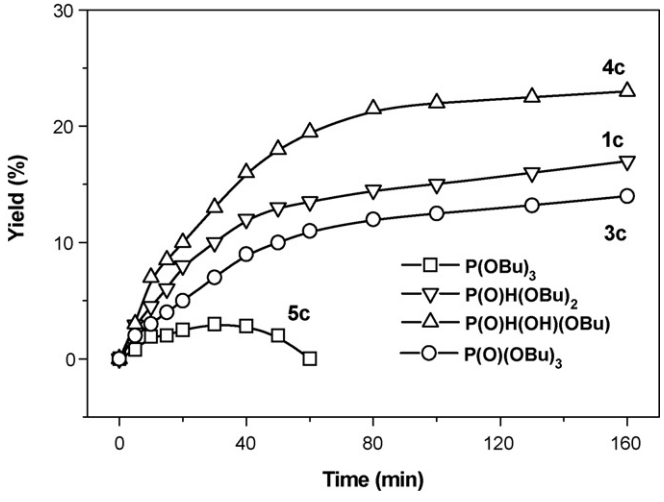


Fig. 1. GC monitoring of the oxidation of P_4 by dibenzoyl peroxide in *n*-BuOH. Reaction conditions (as for entry 4 of Table 3): P_4 (0.135 M in toluene), 2 mL, 0.27 mmol; $(C_6H_5CO)_2O_2$, 0.67 g, 2.7 mmol; *n*-BuOH, 18 mL; toluene, 2 mL, 40 °C.

different processes accounting for the formation of the reaction products resulting from the P_4 oxidation in aliphatic alcohols and phenol are presented below as Eqs. (4)–(7):

$$P_4 + 12ROH + 6R'OOR'' \rightarrow \underset{\mathbf{1b/d}}{4P(O)H(OR)_2} + 4R'OH + 4R''OH + 2R'OR + 2R''OR \quad (4)$$

$$P_4 + 12ROH + 10R'OOR'' \rightarrow \underset{\mathbf{3b/d}}{4P(O)(OR)_3} + 6R'OH + 6R''OH + 4R'OR'' \quad (5)$$

$$P_4 + 12ROH + 6R'OOR'' \rightarrow \underset{\mathbf{4b/d}}{4P(O)H(OH)(OR)} + 2R'OH + 2R''OH + 4R'OR + 4R''OR \quad (6)$$

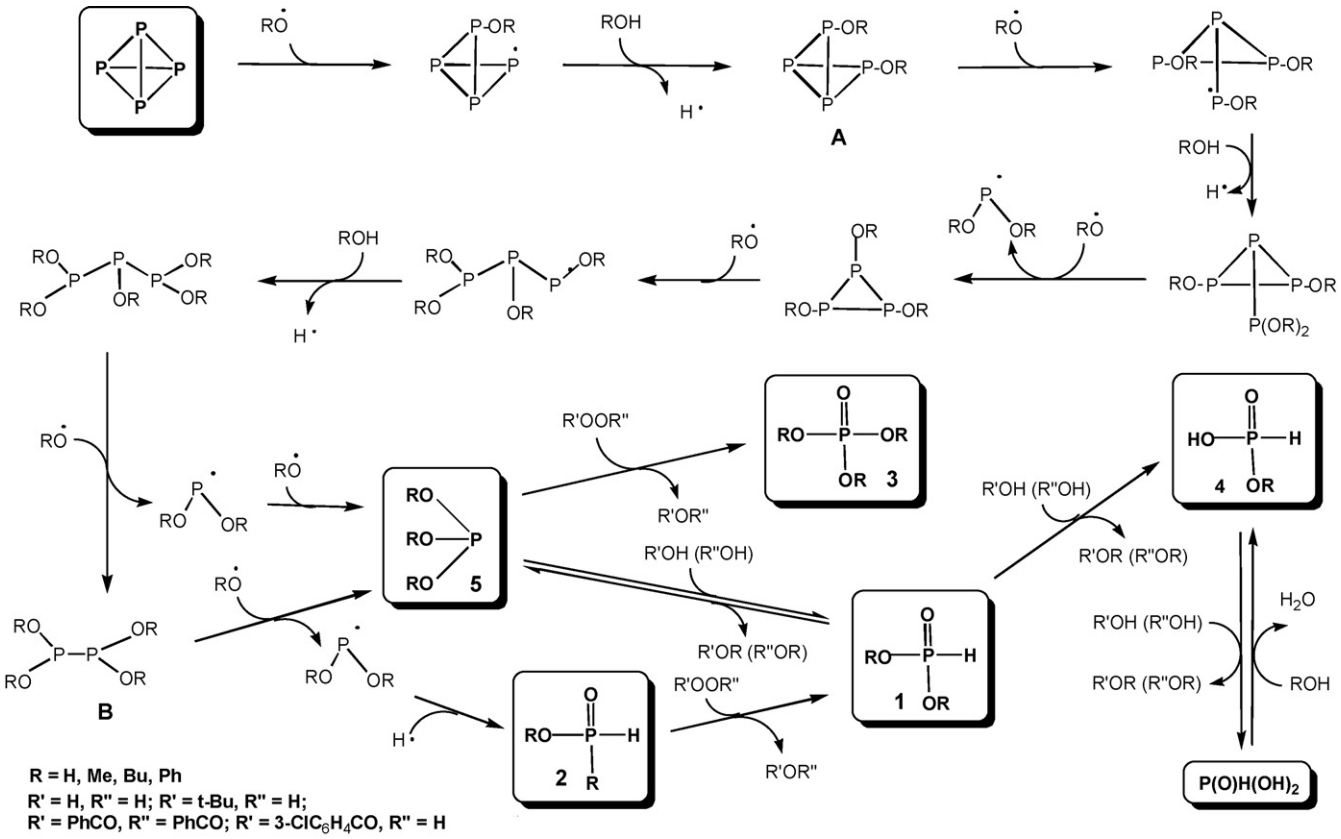
$$P_4 + 12ROH + 6R'OOR'' \rightarrow \underset{\mathbf{5b/d}}{4P(OR)_3} + 6R'OH + 6R''OH \quad (7)$$

R = Me (**b**), Bu (**c**), Ph (**d**). R′ = *t*-Bu, R″ = H. R′ = C_6H_5CO, R″ = C_6H_5CO. R′ = 3-ClC_6H_4CO, R″ =H.

From both ^{31}P NMR and GC studies outlined above, we can safely conclude that organic peroxides are able to efficiently oxidize P_4 in alcoholic solutions giving a variety of organophosphorus compounds such as: **1b/d**, **3b/d**, **4b/d** and **1a**. The intermediate formation of trialk(ar)yl phosphites **5b/d** is observed during the process (Eq. (7)). Likely, products **1b/d**, **3b/d**, **4b/d** and **1a** do not form directly from P_4 (as indicated in the formal stoichiometries in Eqs. (1) and (4)–(6)), but are secondary products resulting from the interaction of **5b/d** with other solution components. Indeed, in the presence of water or weak organic acids (R′OH, R″OH), generated *in situ* from the reactions listed above, **5b/d** may be rapidly dealkylated to give DAHP (**1b/d**). Dialkyl hydrogen phosphonate may, in turn, undergo a two-step acidolysis (or hydrolysis) to give monoalkyl hydrogen phosphonates, MAHP, **4b/d** and phosphorous acid **1a** (see the proposed reaction mechanism illustrated in Scheme 1). At variance with DAHP the preparation of MAHP has been poorly investigated [17]. The general methods currently used for the synthesis of MAHP include the esterification of phosphorous acid [4d] or the alkaline hydrolysis of dialkyl hydrogen phosphonates [18].

The unexpected formation of $P(O)H(OH)_2$ (**1a**) in dried alcoholic solutions may be explained through this dealkylation process. Both acidolysis and hydrolysis of DAHP are indeed well documented in the literature [19]. The industrial method for the production of pure phosphorous acid is based on the oxidative alkoxydation of P_4 followed by hydrolysis of P(III) esters [20]. Since the phenyl P(III) esters are much more resistant to hydrolysis or acidolysis than the alkyl ones [4d], the phenylsubstituted DPHP (**1d**) is, at variance with DAHP (**1b/c**), barely dearylated to phenylsubstituted MPHP (**4d**) and does not dearylate to phosphorous acid **1a** (Table 2, entries 16–22).

The activity of the scrutinized organic peroxides to bring about the oxidative P–O coupling of P_4 with aliphatic and



Scheme 1.

aromatic alcohols follows the order: *tert*-BuOOH > $ClC_6H_4C(O)OOH$ > $(C_6H_5CO)_2O_2$. As the effect of solvent is concerning, the rate of P_4 conversion decreases in the order toluene > THF ≅ CCl_4 ≅ *n*-hexane. The dealkylation of DAHP (**1b/d**) to MAHP (**4b/d**) and, then, that of **4b/d** to phosphorous acid (**1a**) are accelerated on increasing the reaction temperature and generally proceed better in THF and CCl_4.

Although tributyl phosphite **5c** forms always in small amount and it has been never identified among the final reaction products, its intermediate formation provides an important mechanistic hint supporting the hypothesis that identical radical mechanisms are responsible for the oxidation of P_4 by peroxides in either water and aliphatic/aromatic alcohols (see below).

3.3. Mechanistic considerations

From the large body of experimental and analytical data collected in our study, it may be argued that the same radical mechanism is governing the oxidative P–O coupling of P_4 to water, aliphatic alcohols and phenol promoted by either H_2O_2 and organic peroxides, R′OOR″. It is conceivable that the molecule of peroxide does not directly interact with P_4, but rather initiates the reaction generating radical species via homolysis of the O–O bonds (Eq. (8)) [5]. Once formed, the R′O• (or R″O•) radicals may easily react with the substrate (ROH; R = H, Me, Bu, Ph) to generate RO• radicals and R′OH (or R″OH) as byproducts (Eqs. (9) and (10)):

$$R'OOR'' \rightarrow R'O^{\bullet} + R''O \quad (8)$$

$$ROH + R'O^{\bullet} \rightarrow RO^{\bullet} + R'OH \quad (9)$$

$$ROH + R''O^{\bullet} \rightarrow RO^{\bullet} + R''OH \quad (10)$$

RO• radicals are powerful oxidants towards organic and inorganic substrates [15a], and it is not unexpected that they can successfully promote the oxidation of elemental phosphorus in alcohols or water [1a,8,9]. A rationale for the whole process is hard to be proposed in the absence of detectable intermediates during the transformation of P_4 in the product mixture of P(I), P(III) and P(V) species. However, we think reasonable, in agreement with previous considerations to explain the stepwise mechanism of the P_4 degradation by radical species [21], to propose the mechanistic picture depicted in Scheme 1 which combines elementary steps of radical chain oxidations with other basic processes. An outline of the process firstly includes the attack of the RO• radical to the P_4 tetrahedron which promotes a first P–P bond homolytic cleavage and results in the formation of a $(P_4OR)^{\bullet}$ radical. Hydrolysis (or alcoholysis) of this species would afford a butterfly $P_4(OR)_2$ type intermediate (**A**) [22]. From now on, a cascade of the same elementary reactions may occur resulting in the progressive disruption of all six P–P bonds originally existing in the P_4 molecule [23] and ending with the generation of the P(I), P(III) and P(V) oxyacids as well as of the P(III) and P(V) organophosphorus

compounds which have been detected by both NMR and/or GC methods (**1**–**5**). Central to the proposed mechanism is the tetraalk(hydr)oxydiphosphine, $P_2(OR)_4$, (**B**) which, upon attack of a further $RO^{\bullet}$ radical, generates equivalent amounts of $P(OR)_3$ (**5**) and of $P(OR)_2^{\bullet}$ radical from which P(I) (**2**) and P(III) (**5**) species may be produced, respectively. In aqueous/biphasic conditions, the tris(hydroxy)phosphine (**5a**) is unstable [18] and spontaneously tautomerizes to form a molecule of phosphorous acid, $P(O)H(OH)_2$ (**1a**) [24]. In contrast, in the presence of alcohol (or phenol), the trisubstituted phosphites (**5b/d**) may be dealk(ar)ylated by the R′OH or R″OH species to afford dialkyl (or diphenyl) hydrogen phosphonates (**1b/d**). In turn, DAHP may be stepwise dealkylated by R′OH or R″OH to give MAHP (**4b/d**) and eventually $P(O)H(OH)_2$ (**1a**). Trialk(phen)yl phosphates (**3b/d**) may be also produced from peroxidic oxidation of trialk(phen)yl phosphites **5b/d** [4c]. The primary esters of phosphinic acid P(O)H(OR)R (**2b/d**) [$\delta \sim 32$ (Me), ~30 (Bu), ~20 (Ph)] may be also produced by recombination of $P(OR)_2^{\bullet}$ and $H^{\bullet}$ radicals. However, these products were never detected in the case of alcohols from either NMR and GC studies, likely, due to their immediate peroxidic oxidation to **1b/d**. Finally, it should be noted that the possible products of **5b/d** isomerisation, *i.e.* the esters of phosphonic acid $P(O)(OR)_2R$[$\delta \sim 32$ (Me), ~31 (Bu), ~11 (Ph)], were not found among the reaction products. Likely, the isomerisation of **5b/d** intermediates proceeds much slower than their dealkylation to **1b/d** or their oxidation to **3b/d**. The possible esterification of **1a** to MAHP **4b/d** is also shown on the Scheme 1.

From a thermodynamic viewpoint, there are two driving forces which sum their effects to make feasible the direct phosphorylation of water and alcohols, *i.e.* (i) the favorable energy balance between the formation of P–O, P–H and P=O bonds (335, 322, 544 kJ/mol, respectively) and the loss of the P–P bonds of P_4 (201 kJ/mol) and (ii) the high standard redox-potential of peroxides (for example, 1.776 V for H_2O_2) [25].

3.4. Transition metal catalyzed oxidation of P_4 by peroxides

The decomposition of peroxides, R′OOR″, is strongly accelerated by a variety of transition metal ions, M^{n+}, such as manganese [26], iron [27], cobalt [28], copper [29], *etc*. [30]. The process results in the M^{n+} to M^{n+1} oxidation with simultaneous decomposition of the R′OOR″ molecule to the radical $R'O^{\bullet}$ and the anion $R''O^{-}$. A secondary reaction of the M^{n+1} ion decomposes a second peroxide molecule to give one $R'OO^{\bullet}$ radical and one R''^{+} cation (*i.e.* a proton or a carbocation depending on the nature of R″). However, this secondary process is much slower than the interaction of the peroxide with the transition metal ion M^{n+}.

In order to verify if transition metal ions are effective in accelerating the radical peroxidic oxidation of white phosphorus, the reaction between white phosphorus, the substrate and the organic peroxide (either dibenzoyl peroxide and 3-chloroperoxybenzoic acid) has been repeated in the presence of metal salts such as CuI, CuX_2 (X = Cl, acac, CH_3COO, C_3H_7COO) and $VO(acac)_2$ (usually, 10 mol% with respect to P_4).

3.4.1. Catalytic oxidation in water (NMR studies)

The oxidation of P_4 by dibenzoyl peroxide, the less reactive peroxide among those investigated in the present study, in aqueous biphasic solutions at 60 °C is considerably accelerated by the presence of catalytic amounts of copper(II) and copper(I) salts such as $Cu(CH_3COO)_2$ and CuI. Vanadium(IV) salts, like $VO(acac)_2$, which are also known to catalyze the peroxidic oxidation of organic substrates [31], show a similar effect (Table 4).

Only 10% P_4 conversion was obtained in a blank test of the P_4 oxidation by dibenzoyl peroxide at 60 °C without any metal promoter (see entry 1 in Table 4 which duplicates entry 12 in Table 1) after 0.5 h. Addition of $Cu(CH_3COO)_2$, CuI or $VO(acac)_2$ (10% molar ratio with respect to P_4) increases the P_4 conversion from four to five times (Table 4, entries 2–4) without significantly affecting both the nature and the distribution of the reaction products (compare Tables 1 and 4). Copper acetate dissolves in the water phase giving a transparent pale-green solution. Upon adding solid P_4, the reaction mixture becomes gradually black during 30 min. In contrast, CuI does not dissolve in water but forms a white-off deposit, which darkens in *ca*. 20 min after addition of solid P_4. Also vanadyl acetylacetonate does not dissolve in water forming a green deposit which does not change the color after addition of solid P_4.

3.4.2. Catalytic oxidation in alcohols (NMR studies)

At 50 °C, without adding any metal promoter, the oxidative coupling between P_4 and MeOH promoted by dibenzoyl peroxide leads in 2 h to 70% conversion of P_4 with yields of **1b**, **3b**, **4b** and **1a** of 22, 8, 35 and 5%, respectively (Table 5, entry 1).

In the presence of copper salts, $Cu(CH_3COO)_2$ or CuI, the complete conversion of P_4 is obtained within 1 h. Remarkably, also the selectivity is significantly affected resulting in the formation of only **1b** and **3b** (Table 5, entries 2 and 3). In both cases, $P(O)H(OMe)_2$ (**1b**) is the most abundant product formed with a quite good 95% selectivity when copper acetate is used as catalyst. $VO(acac)_2$ also doubles the reaction rate and

Table 4
Effect of metal salts on the oxidation of white phosphorus by dibenzoyl peroxide in aqueous biphasic solutions[a]

Entry	Catalyst (mg)	% Conversion (h)[b]	% **1a**[b]	% **2a**[b]	% **3a**[b]
1	–	10 (0.5)	5	3	2
2	$Cu(CH_3CO_2)_2$ (4.4)	50 (0.5)	26	10	14
3	CuI (4.6)	42 (0.5)	23	9	10
4	$VO(acac)_2$ (6.4)	47 (0.5)	24	10	13

[a] Reaction conditions: solid P_4, 29.7 mg, 0.24 mmol; catalyst, 2.4×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.6 g, 2.4 mmol; D_2O, 2 mL; toluene, 2 mL; 60 °C.
[b] Determined by $^{31}P\{^1H\}$ NMR: **1a** = $P(O)H(OH)_2$, **2a** = $P(O)H_2(OH)$, **3a** = $P(O)(OH)_3$.

Table 5
Oxidation of white phosphorus by dibenzoyl peroxide in aliphatic alcohols or phenol in the presence of a metal salt[a]

Entry	Catalyst (mg)	% Conversion (h)[b]	% **1b/d**[b]	% **3b/d**[b]	% **4b/d**[b]	% **1a**[b]
1	–	70 (2)	22	8	35	5
2	$Cu(CH_3COO)_2$ (4.4)	100 (1)	95	5	–	–
3	CuI (4.6)	100 (1)	88	12	–	–
4	$VO(acac)_2$ (6.4)	73 (1)	52	21	–	–
5	–	67 (2)	24	3	26	14
6	$Cu(CH_3COO)_2$ (4.4)	100 (1)	93	7	–	–
7	CuI (4.6)	100 (1)	91	9	–	–
8	$VO(acac)_2$ (6.4)	64 (1)	17	7	33	7
9	–	20 (2)	14	–	6	–
10	$Cu(CH_3COO)_2$ (4.4)	49 (2)	41	–	8	–
11	CuI (4.6)	44 (2)	34	–	10	–
12	$VO(acac)_2$ (6.4)	58 (2)	39	–	19	–

[a] Reaction conditions: solid P_4, 29.7 mg, 0.24 mmol; catalyst, 2.4×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.6 g, 2.4 mmol; ROH: R = Me (entries 1–4), 2 mL, 49.4 mmol; R = *n*-Bu (entries 5–8), 2 mL, 21.8 mmol; R = Ph (entries 9–12), 2 g, 20 mmol; toluene, 2 mL; 50 °C.
[b] Determined by $^{31}P\{^1H\}$ NMR: **1b** = $P(O)H(OMe)_2$, **3b** = $P(O)(OMe)_3$, **4b** = P(O)H(OH)(OMe); **1c** = $P(O)H(OBu)_2$, **3c** = $P(O)(OBu)_3$, **4c** = P(O)H(OH)(OBu); **1d** = $P(O)H(OPh)_2$, **3d** = $P(O)(OPh)_3$, **4d** = P(O)H(OH)(OPh); **1a** = $P(O)H(OH)_2$.

increases the selectivity to **1b** although it does not accomplish the complete P_4 conversion (Table 5, entry 4). Similar good catalytic performances in terms of efficiency and selectivity are also found for the oxidative phosphorylation of *n*-BuOH in the presence of copper salts (Table 5, entries 5–7). In contrast, $VO(acac)_2$ does not completely convert P_4 and is also less selective favoring the dealkylation of DBHP (**1c**) to MBHP (**4c**) and **1a** (Table 5, entry 8).

The blank reaction between P_4 and PhOH in the presence of dibenzoyl peroxide leads to a modest 20% conversion of P_4 to **1d** (14%) and **4d** (6%) in 2 h (Table 5, entry 9). Both copper and vanadium catalysts raise the P_4 conversion up to *ca*. three times with similar **1d** and **4d** products distribution (Table 5, entries 10–12). Irrespectively of the presence of metal salts, MPHP (**4d**) does not dearylate to phosphorous acid **1a** (Table 5, entries 9–12).

Both $Cu(CH_3COO)_2$ and $VO(acac)_2$ readily dissolve in alcohols to give green transparent solutions. After admitting solid P_4 into the reaction vessel, the solution containing $Cu(CH_3COO)_2$ becomes gradually black. When 100% P_4 conversion is achieved (Table 5, entries 2 and 6), the black mixture turns colorless in *ca*. 20–30 min before restoring the initial light-green color. In the case of CuI, the white-off deposit initially formed gradually darkens after adding P_4. When P_4 is converted completely (Table 5, entries 3 and 7), such black solid slowly disappears giving a transparent colorless solution, from which a white-off deposit of CuI again precipitates at the end of the reaction. Finally, the green solution formed upon dissolving $VO(acac)_2$ catalyst, remains practically unchanged during the reaction with white phosphorus. Recycling of the catalyst solution and testing of its activity through a second catalytic run shows that the solution maintains practically unaltered its catalytic efficiency (see below Section 3.4.3).

3.4.3. Catalytic oxidation in alcohols (GC studies)

In the presence of Cu(II) salts, the color of the solution changes to light green as described above [32]. After addition of the P_4 arene solution (benzene or toluene) to the alcoholic solution of CuX_2 and R′OOR″, the initial color becomes immediately pale brown, before turning colorless in 30–40 min. Then, within further 20–40 min stirring the light-green (or yellow) color restores. These neat color changes observed during both NMR and GC studies of the catalytic oxidation of P_4 by organic peroxides are typical of the copper(II) catalyzed oxidation of white phosphorus by dioxygen in alcohols [1b–e] and, therefore, indirectly support the occurrence of a fast reduction of Cu(II) to Cu(0) by P_4, followed by the comproportionation of Cu(0) and Cu(II) to yield Cu(I) which eventually is oxidized back to Cu(II) by the peroxide after consumption of P_4. Table 6 reports the results of the catalytic oxidation of white phosphorus in MeOH (entries 1–3) and *n*-BuOH (entries 4–13) with GC analysis of the organophosphorus derivatives formed by P_4 alkoxydation using dibenzoyl peroxide and 3-chloroperoxybenzoic acid as oxidants. Three different copper(II) salts (chloride, acetylacetonate and butyrate) and vanadyl acetylacetonate were tested as catalysts. They all show positive effects for the oxidation of P_4 by organic peroxides. Inspection of the experimental results listed in Table 6 shows that both the nature and the distribution of the organophosphorus products **1b/c**, **3b/c**, **4b/c** do not significantly depend on the Cu(II) catalyst, but rather on the peroxide used.

The stoichiometric oxidation of P_4 by $(C_6H_5CO)_2O_2$ in MeOH at 50 °C leads after 1 h to 27% conversion of P_4 into DMHP (**1b**) (Table 6, entry 1). In the presence of $CuCl_2$ (10 mol% with respect to P_4) under identical conditions, the conversion of P_4 increases to 94% giving **1b**, **3b** and **4b** with yields of 64, 21 and 9%, respectively (Table 6, entry 2). Reducing the catalyst/P_4 (5 mol%) ratio and keeping unchanged the R′OOR″/P_4 ratio, to 6, slightly affects the overall yield, but not the product distribution (Table 6, entry 3).

In the presence of copper(II) salts (10 mol%), the complete alkoxydation of white phosphorus may be accomplished also at 40 °C providing that a R′OOR″/P_4 ratio, equal to 10 is used (Table 6, entries 4 and 9). The $Cu(acac)_2$ catalyzed oxidation of P_4 by $(C_6H_5CO)_2O_2$ at 40 °C in *n*-BuOH completes after 1.3 h and gives **1c**, **3c** and **4c** (68, 7 and 25%, respectively) (Table 6, entry 4). Without any copper salt, only 51% P_4 conversion was

Table 6
Oxidation of white phosphorus by organic peroxides in methanol and *n*-butanol in the presence of a metal salt[a]

Entry	Catalyst (mg)	% Conversion (h)[b]	% **1b**,**c**[b]	% **3b**,**c**[b]	% **4b**,**c**[b]
1	–	27 (1)	27	–	–
2	$CuCl_2$ (2.2)	94 (1)	64	21	9
3[c]	$CuCl_2$ (2.2)	89 (1)	57	17	15
4[d]	$Cu(acac)_2$ (7.1)	100 (1.3)	68	7	25
5.1[e]	$Cu(acac)_2$ (7.1)	100 (0.7)	61	15	24
5.2[f]	–	100 (1.2)[g]	53	17	30
5.3[f]	–	100 (2.0)[g]	41	18	41
5.4[f]	–	100 (3.0)[g]	36	20	44
6	$CuCl_2$ (3.6)	100 (1)	38	5	57
7[h]	$CuCl_2$ (1.9)	98 (1)	48	9	41
8	$Cu(C_3H_7COO)_2$ (6.4)	100 (1)	52	8	40
9[d]	$Cu(C_3H_7COO)_2$ (6.4)	98 (1.3)	66	6	26
10[i]	$Cu(C_3H_7COO)_2$ (1.3)	100 (1.7)	41	4	55
11[d]	$VO(acac)_2$ (7.2)	73 (2)	41	8	24
12[j]	$Cu(acac)_2$ (7.1)	100 (0.7)	–	–	100
13[k]	$Cu(acac)_2$ (7.1)	100 (1)	23	1	76

[a] Reaction conditions: P_4 (0.16 M solution in benzene), 1 mL, 0.16 mmol; catalyst, 1.6×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.24 g, 0.96 mmol; MeOH, 9 mL; benzene, 1 mL, 50 °C (entries 1–3). P_4 (as 0.135 M solution in toluene), 2 mL, 0.27 mmol; catalyst, 2.7×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.67 g, 2.7 mmol; *n*-BuOH, 18 mL; toluene, 2 mL, 60 °C (entries 4–13).

[b] GC values are based on standardization with pure samples of the organophosphorus compounds: **1b** = P(O)H(OMe)$_2$, **3b** = (O)(OMe)$_3$, **4b** = P(O)H(OH)(OMe); **1c** = P(O)H(OBu)$_2$, **3c** = P(O)(OBu)$_3$, **4c** = P(O)H(OH)(OBu).

[c] P_4 (0.16 M in benzene), 2 mL, 0.32 mmol; $(C_6H_5CO)_2O_2$, 0.48 g, 1.92 mmol; benzene, 2 mL.

[d] At 40 °C.

[e] At 50 °C.

[f] Recycling experiment: P_4 (0.135 M in toluene), 2 mL, 0.27 mmol; $(C_6H_5CO)_2O_2$, 0.67 g, 2.7 mmol.

[g] Reaction time for achieving the total conversion of P_4.

[h] P_4 (0.14 M in toluene), 0.14 mmol; $CuCl_2$, 1.4×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.21 g, 0.84 mmol; *n*-BuOH, 9 mL; toluene, 1 mL, 70 °C.

[i] $Cu(C_3H_7COO)_2$, 5.4×10^{-3} mmol.

[j] 3-$ClC_6H_4C(O)OOH$, 0.65 g, 2.7 mmol at 50 °C.

[k] 3-$ClC_6H_4C(O)OOH$, 0.65 g, 2.7 mmol at 40 °C.

achieved after 2.7 h under similar reaction conditions (Table 3, entry 4). Increasing the temperature to 50 °C does not appreciably affect the distribution of the organophosphorus products but doubles the reaction rate (Table 6, entry 5.1). In an attempt to verify the possibility to recycle the catalyst, at the end of the first catalytic cycle, as indirectly showed by the renovation of the initial light-green color due to regeneration of Cu(II) ion, a second batch of P_4 and $(C_6H_5CO)_2O_2$ were added to the same catalytic solution which maintained unchanged its activity with P_4 conversion in 0.5 h (Table 6, entry 5.2). Then, two further tests with further addition of both P_4 and $(C_6H_5CO)_2O_2$ were run showing complete conversion in 0.8 and 1 h, respectively (Table 6, entries 5.3 and 5.4). Inspection of these entries in Table 6 shows that the yield of **1c** gradually decreases while the amount of **4c** slightly increases on going from the first to the fourth catalytic cycle.

In summary, four portions of P_4 were completely oxidized by the initial catalytic solution within 3 h without practically change the reaction rate. In other words, the catalyst completely maintains unaltered its activity after four cycles and remains still able to convert more aliquots of white phosphorus.

Cu(II) chloride and butyrate (10 mol%) are also efficient in catalyzing the oxidative P–O coupling of P_4 with *n*-BuOH (Table 6, entries 6–9). Rising the temperature to 70 °C allows to convert white phosphorus completely even when the stoichiometric R′OOR″/P_4 ratio (6) is used (Table 6, entry 7). Decreasing the catalyst loading to 2 mol% causes the separation of a brownish-black precipitate of Cu(0) and the complete conversion of P_4 requests much longer time (see Table 6, entries 10 and 8).

$VO(acac)_2$ accelerates the peroxidic oxidation of P_4 in *n*-BuOH at 40 °C (see Table 6, entry 11 and Table 3, entry 4) but shows a lower activity than copper(II) salts. The rate of P_4 oxidation by 3-chloroperoxybenzoic acid in *n*-BuOH is considerably increased in the presence of $Cu(acac)_2$ (compare Table 6, entries 12 and 13 with Table 3, entries 6 and 7). In contrast to dibenzoyl peroxide, the 3-chloroperoxybenzoic acid favors the formation of MAHP **4b/c**. Thus, the ratio (**1c/4c**) is usually >1 when $(C_6H_5CO)_2O_2$ is used, but is <1 with 3-$ClC_6H_4C(O)OOH$. Selective formation of monobutyl hydrogen phosphonate, P(O)H(OH)(OBu) (**4c**), is achieved under mild reaction conditions (entry 12 in Table 6). Obviously, this means that the acidolysis of tributyl phosphite (**5c**) to dibutyl hydrogen phosphonate (**1c**) and its further acidolysis to monobutyl hydrogen phosphonate (**4c**) by 3-chloroperoxybenzoic acid (generated *in situ*) proceeds faster than the direct oxidation of **5c** by 3-$ClC_6H_4C(O)OOH$ to tributyl phosphate (**3c**) under the working reaction conditions (see Scheme 1). The high capability of 3-$ClC_6H_4C(O)OH$ to promote the acidolysis matches the results of entries 8 and 9 in Table 2. According to our experimental data, 3-chloroperoxybenzoic acid is a stronger dealkylating agent as compared with benzoic acid or water.

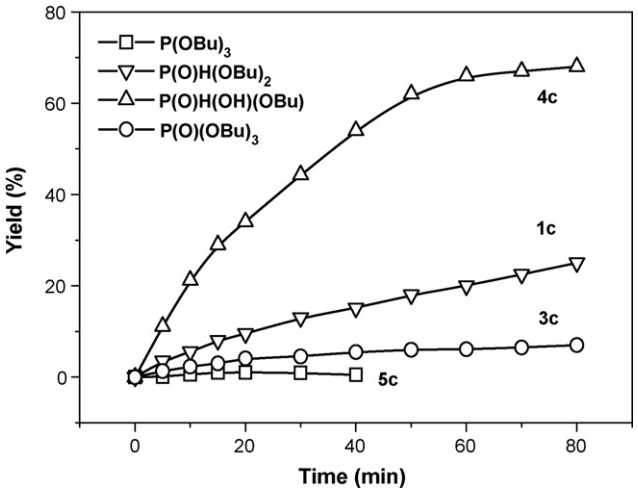


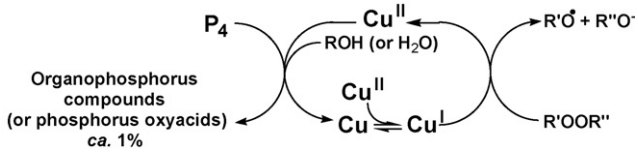
Fig. 2. GC monitoring of the oxidation of P_4 by dibenzoyl peroxide in *n*-BuOH in the presence of copper(II) acetylacetonate. Reaction conditions (as for entry 4 in Table 6): P_4 (0.135 M in toluene), 2 mL, 0.27 mmol; $Cu(acac)_2$, 7.1 mg, 2.7×10^{-2} mmol; $(C_6H_5CO)_2O_2$, 0.67 g, 2.7 mmol; *n*-BuOH, 18 mL; toluene, 2 mL, 40 °C.

Like in the stoichiometric tests described above, GC monitoring of most of the catalytic reactions listed in Table 6 (ROH = *n*-BuOH) were carried out at regular intervals (5–10 min) confirming the ubiquitous formation of small amount of tributyl phosphite (**5c**). As an example, the conversion curves resulting from GC monitoring of the reaction under the conditions of entry 4 are shown in Fig. 2.

Although the conversion curves of both the stoichiometric and catalytic reactions have a similar appearance (compare Figs. 1 and 2), the rates of accumulation of the organophosphorus products **1c**, **3c** and **4c** and the conversion of the intermediate species **5c** are considerably accelerated by the presence of $Cu(acac)_2$ reflecting the catalytic activity of the metal ion. As a matter of fact, a total conversion of 51% is achieved in 160 min without any metal promoter (see Fig. 1), whereas in the catalyzed reaction a similar conversion is reached already in 20 min (Fig. 2), demonstrating a strong speeding up of the P_4-oxidation of about eight times in the presence of $Cu(acac)_2$. In general, depending on both the temperature and the nature of the catalyst, the rates of the P_4 alkoxydation increase between two and eight times.

A sketch of the catalytic copper oxidation of white phosphorus promoted by peroxides in alcohol (or water) is presented in Scheme 2.

It should be emphasized that the active catalytic species which accelerate the decomposition of peroxides are Cu(I) complexes rather than the initial Cu(II) species, The former indeed are generated *in situ* via the fast reduction of Cu(II) to Cu(0) by white phosphorus followed by oxidation of Cu(0) to Cu(I) by Cu(II) salts. Therefore, Scheme 2 well accounts also for the catalytic activity of commercial copper(I) salts (like CuI), which effectively catalyze the oxidation of P_4 by organic peroxides in both aqueous and alcoholic solutions. A similar mechanism is likely responsible for the catalytic activity exhibited by $VO(acac)_2$, which favors the peroxides decomposition being readily oxidized to V(V) species. The further two-electron reduction of vanadium(V) by elemental phosphorus generates a V(III) species, which similarly to V(IV) ion speeds up the decomposition of the peroxide and then accelerates the alk(hydr)oxydation reaction. In this case, the color of the solution remains practically unchanged because both V(V) and V(III) species are green colored. The minor catalytic activity of $VO(acac)_2$ may probably be explained with the slower regeneration of the catalytically active V(III) species, *i.e.* with the slower oxidation of P_4 by V(V) formed which, in contrast to Cu(II), behaves as a strong oxidant only in strong acidic solutions [25].



Scheme 2.

In the case of copper salts, the active Cu(I) catalytic species is generated from the comproportionation of two catalytically inactive forms like Cu(0) and Cu(II) (Scheme 2). However, when a lower loading of CuX_2 (*ca.* 2 mol%) is used, the metal is completely reduced by P_4 to Cu(0) and no CuX_2 remains to reoxidize metallic copper to the catalytically active Cu(I) species. In this case, there is no catalytic boosting of the reaction which does not practically differ from the not catalyzed process (see Table 6, entry 10 and Table 3, entry 1).

The reduction of Cu(II) by P_4 in alcohol (water), shown in Scheme 2, agrees with a heterolytic reaction pathway involving the coordination of both ROH (H_2O) and P_4 to Cu(II), followed by the building of the organophosphorus product (or of the phosphorus oxyacid) while the copper ion is reduced to Cu(0) [1b–e]. Eq. (11) accounts for this chemistry and takes into consideration the capability of P_4 to separate out metallic copper from the solution of its salts [33]:

$$P_4 + 12ROH + 6CuX_2 \rightarrow \underset{\mathbf{1a/d}}{4P(O)H(OR)_2} + 6Cu + 4RX + 8HX \quad (11)$$

However, taking into account the stoichiometry of this heterolytic reaction and the substoichiometric amount of CuX_2 used (5–10% molar ratio), one can envisage that the contribution of this alternative reaction to the synthesis of organophosphorus compounds or phosphorus oxyacids should be very low (*ca.* 1%). Our experimental results therefore show that the oxidation of white phosphorus by organic peroxides in water or alcohols in the presence of catalytic amount of metal ions is almost completely accomplished via the radical pathway (Scheme 1) where the production of $RO^{\bullet}$ radicals is boosted by the low-valent metal ions as highlighted in Scheme 2.

4. Conclusions

The oxidation of white phosphorus by H_2O_2 and organic peroxides in aqueous and alcoholic solutions has been studied

under anaerobic conditions. The reaction results in the formation of a mixture of P(I) (hypophosphorous acid), P(III) (phosphorous acid, mono- and dialkyl hydrogen phosphonates) and P(V) (phosphoric acid or trialkyl phosphates) derivatives which form via oxidative phosphorylation of the substrate (H_2O and alcohol) by P_4.

Depending on both the reaction conditions and the nature of the alcohol, up to three organophosphorus compounds, $P(O)H(OR)_2$, $P(O)H(OH)(OR)$ and $P(O)(OR)_3$, and one phosphorus oxyacid, $P(O)H(OH)_2$, are produced in variable amounts. Generally, the P(III) species are the major products of the reaction whereas the phosphate derivatives are usually produced in limited amount. In the presence of catalytic amounts of Cu(I), Cu(II) or V(IV) complexes, the oxidative alkoxydation and hydroxydation of P_4 promoted by organic peroxides is significantly enhanced with increasing of the reaction rate up to eight times. Noticeably, under optimized reaction conditions, 100% conversion of white phosphorus to organophosphorus products is achieved with high selectivity in P(III) esters (*ca.* 95%). A perusal of the oxidative experiments, carried out with and without a metal catalyst, suggests the following order for the activity of the peroxides, substrates, solvents and catalysts tested in this work: *tert*-BuOOH $\gg$ 3-ClC_6H_4 CO_3H > $(C_6H_5CO)_2O_2 \gg H_2O_2$; H_2O > MeOH > BuOH $\gg$ PhOH; toluene > THF $\cong$ CCl_4 > *n*-hexane $\gg$ D_2O; $Cu(acac)_2 \cong Cu(CH_3COO)_2 \cong Cu(C_3H_7COO)_2 \cong$ CuI > $CuCl_2$ > $VO(acac)_2$.

An identical stepwise radical mechanism has been proposed for enlightening the oxidation of white phosphorus by peroxides in both aqueous biphasic and alcoholic solutions. The catalytic oxidation of P_4 by organic peroxides in alcohols is proposed to proceed with the same mechanism, the only difference being in the preliminary step of peroxide homolysis which is now replaced by the metal assisted reduction of the peroxide to yield the radical initiator. Based on the reaction herein described, a method for the selective catalytic synthesis of monoalkyl hydrogen phosphonates, P(O)H(OH)(OR), may be elaborated. Further studies in our laboratories are in progress to better evaluate the scope of the reaction and to verify whether this process may represent a credible replacement to the known methods for the synthesis of different monoalkyl hydrogen phosphonates based on the hydrolysis of DAHP or esterification of phosphorous acid.

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References

[1] (a) B. Trofimov, B. Timokhin, N. Gusarova, M. Kazantseva, A. Golubin, Phosphorus Sulfur Silicon Rel. Elem. 177 (2002) 2385;
(b) Ya.A. Dorfman, M.M. Aleshkova, G.S. Polimbetova, L.V. Levina, T.V. Petrova, R.R. Abdreimova, D.M. Doroshkevich, Russ. Chem. Rev. 62 (1993) 877;
(c) Ya.A. Dorfman, R.R. Abdreimova, Zh. Obshch. Khim. 63 (1993) 289;
(d) Ya.A. Dorfman, R.R. Abdreimova, D.N. Akbayeva, Kinet. Katal. 36 (1995) 103;
(e) R.R. Abdreimova, F.Kh. Faizova, D.N. Akbayeva, G.S. Polimbetova, S.M. Aibasova, A.K. Borangazieva, M.B. Aliev, Euras. Chem.-Technol. J. 4 (2002) 11;
(f) R.R. Abdreimova, D.N. Akbayeva, F.Kh. Faisova, S.M. Aibasova, Izv. NAS RK 4 (1998) 65;
(g) G.S. Polimbetova, R.R. Abdreimova, F.Kh. Faisova, Euras. Chem.-Technol. J. 2 (2000) 21;
(h) S.M. Aibasova, M.B. Aliev, F.Kh. Faizova, A.K. Dabeeva, G.S. Polimbetova, R.R. Abdreimova, Izv. NAS RK 4 (2003) 41;
(i) R.R. Abdreimova, D.N. Akbayeva, G.S. Polimbetova, A.-M. Caminade, J.-P. Majoral, Phosphorus Sulphur Silicon 156 (2000) 239;
(j) Ya.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova, S.M. Aibasova, D.N. Akbayeva, Kinet. Katal. 37 (1996) 199;
(k) M.B. Aliev, S.M. Aibasova, F.Kh. Faizova, A.K. Borangazieva, G.S. Polimbetova, R.R. Abdreimova, Dokl. NAS RK 3 (2003) 45;
(l) M. Peruzzini, Special. Chem. Mag. (2003) 32;
(m) J.I. Heise, E.D. Sall, M.P. McGrath, International Patent WO 99/43612.
[2] (a) Yu.H. Budnikova, Russ. Chem. Rev. 71 (2002) 111;
(b) Yu.H. Budnikova, A.G. Kafiyatullina, O.G. Sinyashin, R.R. Abdreimova, Russ. Chem. Bull. 52 (2003) 929;
(c) Yu.H. Budnikova, D.I. Tazeev, D.G. Yakhvarov, Russ. Chem. Bull. 52 (2002) 269;
(d) Yu.H. Budnikova, A.G. Kafiyatullina, A.S. Balueva, R.M. Kuznetsov, V.I. Morozov, O.G. Sinyashin, Russ. Chem. Bull. 52 (2003) 2419;
(e) M. Peruzzini, Special. Chem. Mag. 26 (2006) 40.
[3] (a) C. Bianchini, M. Peruzzini, D. Akbayeva, R.R. Abdreimova, G.S. Polimbetova, Italian Patent 2202/2PTIT.;
(b) Ya.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova, D.N. Akbayeva, Kazakh Pre-Patent, 1998, No 6277.;
(c) Ya.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova, D.N. Akbayeva, S.M. Aibasova, Kazakh Pre-Patent, 1998, No 6278.;
(d) Ya.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova, D.N. Akbayeva, Kazakh Pre-Patent, 1998, No 6279.;
(e) Ya.A. Dorfman, R.R. Abdreimova, G.S. Polimbetova, D.N. Akbayeva, Kazakh Pre-Patent, 1998, No 6280.
[4] (a) A.J. Kirby, S.G. Warren, The Organic Chemistry of Phosphorus, Elsevier, Amsterdam, 1967;
(b) L. Maier, Fortschritte der Chemischen Forschung, vol. 19, Springer, Berlin, 1971, p. 1;
(c) A.I. Rakhimov, Sintez fosfororganicheskikh soedineniy. Gomoliticheskie reakztii (Synthesis of organophosphorus compounds. The homolytic reactions), Moscow, RUS Nauka, 1985;
(d) E.E. Nifant'ev, Fosfororganicheskie soedineniya (Organophosphorus compounds), Moscow, RUS, Khimiya, 1996;
(e) A. Romerosa, S. Mañas, Ch. Richter, Spanish patent, ES2209628, 2004.
[5] (a) G. Sosnovsky, Free radical reactions in preparative organic chemistry, NY, 1964;
(b) C.J.M. Stirling, Radicals in Organic Chemistry, Oldbourne Press, London, UK, 1965;
(c) S. Patai, The Chemistry of Peroxides, Wiley, NY, 1983;
(d) R. Noyori, M. Aoki, K. Sato, Chem. Commun. (2003) 1977;
(e) W. Ando, Organic Peroxides, John Wiley & Sons, Chichester, UK, 2002.
[6] (a) R. Neumann, M. Levin-Elad, Appl. Catal. A 122 (1995) 85;
(b) W. Nam, H.J. Han, S.-Y. Oh, Y.J. Lee, M.-H. Choi, S.-Y. Han, C. Kim, S.K. Woo, W. Shin, J. Am. Chem. Soc. 122 (2000) 8677;
(c) C. Venturello, E. Alneri, M. Ricci, J. Org. Chem. 48 (1983) 3831;
(d) C. Venturello, R. D'Aloisio, J. Org. Chem. 53 (1988) 1553;
(e) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, J. Org. Chem. 53 (1988) 3587;
(f) T. Oguchi, T. Ura, Y. Ishii, M. Ogawa, Chem. Lett. 5 (1989) 857;
(g) C. Venturello, M. Gambaro, J. Org. Chem. 56 (1991) 5924;
(h) E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, J. Org. Chem. 63 (1998) 7190;

(i) C.W. Jones, in: J.H. Clark (Ed.), Applications of Hydrogen Peroxide and Derivatives, RSC Clean Technology Monographs, Cambridge, UK, 1999;
(j) J.-E. Bäckvall, Modern Oxidation Methods, Wiley–VCH, Weinheim, D, 2004.

[7] (a) R.A. Sheldon, J.A. Van Doorn, J. Catal. 31 (1973) 427;
(b) A.J. Pearson, Y.S. Chen, S.Y. Hsu, T. Ray, Tetrahedron Lett. 25 (1984) 1235;
(c) G. Strukul, R. Sinigalia, A. Zanardo, F. Pinna, R.A. Michelin, Inorg. Chem. 28 (1989) 554;
(d) R.I. Volnyanskaya, V.M. Mikhal'chuk, T.V. Kryuk, A.N. Nikolaevskii, Ukrain. Khim. Zhurn. 70 (2004) 99;
(e) V.R. Choudhary, D.K. Dumbre, B.S. Uphade, V.S. Narkhede, J. Mol. Catal. A 215 (2004) 129;
(f) T.K. Das, K. Chaudhari, E. Nandanan, A.J. Chandwadkar, A. Sudalai, T. Ravindranathan, S. Sivasanker, Tetrahedron Lett. 38 (1997) 3631;
(g) M.D. Nikalje, A. Sudalai, Tetrahedron 55 (1999) 5903;
(h) Y. Kurusu, J. Inorg. Organomet. Polym. 10 (2000) 127;
(i) M.B. Andrus, Z. Zhou, J. Am. Chem. Soc. 124 (2002) 8806;
(j) M.G. Topuzova, S.V. Kotova, T.M. Kolev, Appl. Catal. A 281 (2005) 157;
(k) Z. Li, C.-J. Li, J. Am. Chem. Soc. 127 (2005) 3672.

[8] T. Weyl, Berlin 39 (1906) 1307.

[9] N. Yoza, S. Ohashi, Bull. Chem. Soc. Jpn. 38 (1965) 1408.

[10] (a) W.E. Garwood, L.A. Hamilton, F.M. Seger, Ind. Eng. Chem. 52 (1960) 401;
(b) W.E. Garwood, L.A. Hamilton, F.M. Seger, US Pat. 2,731,458, 1956.

[11] D.D. Perrin, W.L.F. Armarengo, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1980.

[12] N.N. Postnikov, Termicheskaya fosfornaya kislota. Khimia i tekhnologia (The thermal phosphoric acid. The chemistry and technology), Moscow, Khimiya, 1970.

[13] The use of D_2O as substrate allowed for the immediate quantification of the reaction products by ^{31}P NMR analysis of the reaction solution.

[14] W.C. Schumb, Ch.N. Satterfield, R.L. Wentworth, Hydrogen peroxide, Reinhold Publishing Corporation, 1958.

[15] (a) W.A. Waters, Mechanism of Oxidation of Organic Compounds, Methuen & Co, Ltd./John Wiley & sons Inc., London/New York, 1963;
(b) P. Studt, Petrochemie 29 (1976) 199;
(c) G.A. Razuvaev, P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin, Dokl. Akad. Nauk SSSR 253 (1980) 629;
(d) V.A. Kurbatov, A.N. Ivanova, G.A. Furman, E.T. Denisov, Khim. Fiz. 3 (1984) 1316.

[16] Although $P(O)H(OH)_2$ (**1a**) is likely formed, it could not be detected as the GC detector we used in this study was not appropriate for the detection and the quantification of phosphorous acid **1a**.

[17] (a) Stauffer Chemical Co. Neth. Appl. Patent 6,612,966, 1967, 11 pp.;
(b) C.F. Baranauckas, J.J. Hodan, U.S. Patent 3,331,895, 1967, 5 pp.;
(c) G. Szabo, K. Jakus, G. Szuk, Fr. Demande Patent 2,392,029, 1978, 14 pp.;
(d) C. Craiu, G. Dumitrescu, L. Kurunczi, P. Schulz, R. Vilceanu, Rom. Patent 59,706, 1975, 3 pp.;
(e) P.W. Gann, R.L. Heider, U.S. Patent 2,692,890, 1954.

[18] D.E.C. Corbridge, Phosphorus, an Outline of its Chemistry, Biochemistry and Technology, 5th ed., Elsevier, Amsterdam, 1995.

[19] (a) N.A. Kaslina, L.V. Kriniztkaya, A.V. Kessenikh, T.V. Balashova, Yu.P. Reshetnikov, Zh. Obsh. Chim. 62 (1992) 1531;
(b) H. Fakhraian, A. Mirzaei, Org. Proc. Res. Dev. 8 (2004) 401.

[20] Y. Ma, J.D. Heise, European Patent 1,008,552 A1., publ. 14.06.2000.

[21] (a) A.B. Burg, W. Mahler, A.J. Bilbo, J. Am. Chem. Soc. 70 (1957) 247;
(b) N.K. Bliznyuk, Z.N. Kwasha, A.F. Kolomietz, Z. Obzh. Khim. 37 (1967) 890;
(c) P.Z. Airey, Z. Naturforsch. 243 (1969) 1393.

[22] (a) Ch. Brown, R.F. Hudson, L.A. Wartew, J. Chem. Soc., Chem. Commun. (1978) 7;
(b) L. Riesel, M. Kant, R. Helbing, Z. Anorg. Allg. Chem. 580 (1990) 217.

[23] M. Ehses, A. Romerosa, M. Peruzzini, Top. Curr. Chem. 220 (2002) 107.

[24] For a reverse, ruthenium mediated tautomerization of phosphorous acid to $P(OH)_3$, see D.N. Akbayeva, M. Di Vaira, S. Seniori Costantini, M. Peruzzini, P. Stoppioni, Dalton Trans. (2006) 389.

[25] J.E. Huheey, Inorganic Chemistry. Principles of Structure and Reactivity, Haper & Row, New York, 1985.

[26] (a) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, L. Turkian, J. Mol. Catal. A Chem. 157 (2000) 183;
(b) G.B. Shul'pin, Neftekhimiya 41 (2001) 440;
(c) T.G. Carrell, S. Cohen, G.C. Dismukes, J. Mol. Catal. A Chem. 187 (2002) 3;
(d) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, J. Mol. Catal. A Chem. 186 (2002) 101;
(e) V.R. Choudhary, D.K. Dumbre, V.S. Narkhede, S.K. Jana, Catal. Lett. 86 (2003) 229.

[27] (a) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, J. Mol. Catal. A Chem. 175 (2001) 105;
(b) N. Sehlotho, T. Nyokong, J. Mol. Catal. A Chem. 209 (2004) 51;
(c) W. Nam, S.-Y. Oh, M.H. Lim, M.-H. Choi, S.-Y. Han, G.-J. Jhon, Chem. Commun. 18 (2000) 1787;
(d) S.J. Yang, W. Nam, Inorg. Chem. 37 (1998) 606;
(e) M.B. Meder, B.A. Siggelkow, L.H. Gade, Z. Anorg. Allg. Chem. 630 (2004) 1962.

[28] (a) I.M. Reibel, A.Ya. Sychev, S.I. Timofeeva, Zh. Fiz. Khim. 45 (1971) 366;
(b) E.T. Farinas, C.V. Nguyen, P.K. Mascharak, Inorg. Chim. Acta 263 (1997) 17;
(c) F.A. Chavez, J.A. Briones, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 38 (1999) 1603;
(d) N. Sehlotho, T. Nyokong, J. Mol. Catal. A Chem. 209 (2004) 51;
(e) M. Salavati-Niasari, S.H. Banitaba, J. Mol. Catal. A Chem. 201 (2003) 43;
(f) M. Nowotny, L.N. Pedersen, U. Hanefeld, T. Maschmeyer, Chem. Eur. J. 8 (2002) 3724.

[29] (a) G. Ferguson, A. Nait Ajjou, Tetrahedron Lett. 44 (2003) 9139;
(b) G.B. Shul'pin, J. Gradinaru, Y.N. Kozlov, Org. Biomol. Chem. 1 (2003) 3611;
(c) M. Contel, C. Izuel, M. Laguna, P.R. Villuendas, P.J. Alonso, R.H. Fish, Chem. Eur. J. 9 (2003) 4168;
(d) G. Olason, D.C. Sherrington, React. Funct. Polym. 42 (1999) 163;
(e) C.R. Jacob, S.P. Varkey, P. Ratnasamy, Appl. Catal., A: Gen. 182 (1999) 91;
(f) M. Schulz, R. Kluge, F.G. Gelalcha, Tetrahedron: Asymmetry 9 (1998) 4341.

[30] (a) D.D. Agarwal, R. Jain, P. Sangha, R. Rastogi, Ind. J. Chem., Sect. B 32B (1993) 381;
(b) K. Jitsukawa, K. Kaneda, S. Teranishi, J. Org. Chem. 49 (1984) 199;
(c) D.D. Agarwal, S. Srivastava, P. Chadha, Polyhedron 9 (1990) 487;
(d) R.A. Sheldon, J.A. Van Doorn, J. Catal. 31 (1973) 427.

[31] (a) E. Glotter, M. Zviely, J. Chem. Soc., Perkin Trans. 1 2 (1986) 321;
(b) E. Glotter, M. Zviely, J. Chem. Soc., Perkin Trans. 1 2 (1986) 327;
(c) V. Conte, F. Di Furia, G. Licini, Appl. Catal. A: Gen. 157 (1997) 335;
(d) A. Lattanzi, S. Piccirillo, A. Scettri, Eur. J. Org. Chem. 8 (2005) 1669.

[32] Due to higher dilution of the metal catalyst with respect to the amount used during the NMR studies, a yellow color may be rather observed.

[33] J.R. Van Wazer, Phosphorus and its Compounds, vol. 1, Wiley, NY, 1958.