ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2017, Vol. 91, No. 10, pp. 1873–1876. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © R.R. Abdreimova, D.N. Akbaeva, G.S. Polimbetova, 2017, published in Zhurnal Fizicheskoi Khimii, 2017, Vol. 91, No. 10, pp. 1672–1676.

CHEMICAL KINETICS AND CATALYSIS

Oxidation of White Phosphorus by Peroxides in Water

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Received May 25, 2016

Abstract—A mixture of hypophosphorous, phosphorous, and phosphoric acids is formed during the anaerobic oxidation of white phosphorus by peroxides [ROOH; R = H, 3-ClC_6H_4CO, $(CH_3)_3C$] in water. The rate of reactions grows considerably upon adding nonpolar organic solvents. The activity series of peroxides and solvents are determined experimentally. NMR spectroscopy shows that the main product of the reaction is phosphorous acid, regardless of the nature of the peroxide and solvent. A radical mechanism of oxidation of white phosphorus by peroxides in water is proposed. It is initiated by the homolysis of peroxide with the formation of $HO^•$ radicals that are responsible for the homolytic opening of phosphoric tetrahedrons. Further oxidation and stages of the hydrolysis of intermediate phosphorus-containing compounds yield products of the reaction.

Keywords: phosphorus, oxidation, hydrogen peroxide, hydroperoxide, water, mechanism
DOI: 10.1134/S0036024417100028

INTRODUCTION

The nonpolar tetrahedral molecule of white phosphorus (P_4) is most reactive under conditions of high temperatures, ionizing radiation, UV irradiation, and in the presence of free radical sources; i.e., under conditions where a homolytic reaction mechanism is possible [1–3]. Simple and universal sources of free radicals, which are easily formed during the homolysis of O–O peroxo bonds, are organic and inorganic peroxides. A number of processes using hydrogen peroxide [4–7] and organic peroxides [8–14] as environmentally friendly and effective oxidizing agents have been described recently. Considerably less attention has been devoted to the oxidation of white phosphorus by peroxides. It has been noted that the oxidation of P_4 in aqueous solutions of hydrogen peroxide is accompanied by the disproportionation of phosphorus into phosphine and phosphoric acid [15]. It has also been reported that the reaction between P_4 and (*tert*-BuO$)_2$ and different alkenes at 150–160°C yields a mixture of organophosphorus compounds with the general formula of $R_xP_4O_2H_2$ [16, 17].

The aim of this work was to fill a gap in investigations of the oxidation of white phosphorus by peroxides. Optimum temperature conditions, product composition, and the effect of oxidizing agents and solvents were therefore determined, and a possible mechanism of oxidation of P_4 by hydrogen peroxide and hydroperoxides in water is proposed.

EXPERIMENTAL

Peroxides [H_2O_2 (35% aqueous solution, 11.3 M), $(CH_3)_3COOH$ (70% aqueous solution, 7.2 M), 3-$ClC_6H_4C(O)OOH$ (57–86%; a mean value of 72% was considered for stoichiometric calculations)], and deuterated water (D_2O) were obtained from Aldrich or Fluka. White phosphorus was oxidized by peroxides in inert atmosphere inside Schlenk flasks. A mixture of D_2O, oxidizing agent (hydrogen peroxide, *tert*-butylhydroperoxide, and 3-chloroperoxybenzoic acid), and solvent (toluene, tetrahydrofuran, tetrachloromethane, and *n*-hexane) was purged with argon for 10 min, and a weighed amount of white phosphorus was added in an argon flow. The total volume of the solution was less than 5 mL. The solution was quickly heated in an oil bath up to the required temperature (60–90°C) with intense stirring on a magnetic stirrer. Stirring continued until the end of reaction (0.25–4 h). The aqueous phase of the reaction mixture was then analyzed via ^{31}P NMR spectroscopy with TPPMS oxide [TPPMS = $Na^+Ph_2P(3\text{-}SO_3C_6H_4)^-$] as an internal standard, while the organic phase was analyzed via gas chromatography/mass spectrometry (GC/MS) with naphthalene as an external standard. ^{31}P NMR spectra of the phosphorus-containing acids were recorded on a Bruker ACP200 spectrometer at 25°C using D_2O or C_6H_6 solvents. GC/MS analyses were performed on a Shimadzu QP 5000 instrument equipped with a capillary column (Supelco SPB-1; 30 m, ∅0.25 mm, 0.25 μm).

Table 1. Effect of temperature on the oxidation of P_4 by hydrogen peroxide in water

Experiment	T, °C	Conversion, %	t, h	C_1, %	C_2, %	C_3, %
1	25	8	2	3	3	2
2	60	57	1	20	24	13
3	90	70	1	12	35	23

Reaction conditions: argon atmosphere; solid P_4 29.7 mg, 0.24 mmol; 35% aqueous solution of H_2O_2 0.21 mL, 2.4 mmol; D_2O 1 mL; **1–3** were determined by $^{31}P\{^1H\}$ NMR: **1** is $P(O)H_2(OH)$, **2** is $P(O)H(OH)_2$, and **3** is $P(O)(OH)_3$.

RESULTS AND DISCUSSION

It was found that as the result of the reaction between white phosphorus and peroxides (ROOH) in water under argon at 25–90°C and ROOH-to-P_4 molar ratio corresponding to 10, a mixture of hypophosphorous $P(O)H_2(OH)$ (**1**), phosphorous $P(O)H(OH)_2$ (**2**), and phosphoric $P(O)(OH)_3$ (**3**) acids was formed. Products of the reaction were identified and their yields were determined via $^{31}P\{^1H\}$ NMR spectroscopy of the aqueous phase with D_2O instead of H_2O by recording the signals of three fully deuterated phosphorus-containing acids [18, 19]. Deuterated hypophosphorous acid **1-*d*$_3$** appeared as a quintet (δ 11, 47 ppm, $^1J_{P-D}$ = 85.6 Hz); phosphorous acid **2-*d*$_3$** yielded a 1 : 1 : 1 triplet centered at δ 5.0 ppm ($^1J_{P-D}$ = 102.5 Hz); while the signal of phosphoric acid **3-*d*$_3$** was a sharp singlet at δ 0.56 ppm, indicating there were no direct P–D bonds.

There was virtually no oxidation of P_4 by hydrogen peroxide in water at room temperature (Table 1, experiment 1).

A mixture of phosphorus-containing acids was formed in low yields within one hour at a temperature of 60°C (experiment 2). The partial conversion of P_4 is presumably caused by the insolubility of white phosphorus in water and the side thermal decomposition of H_2O_2 into O_2 and H_2O at elevated temperatures. When the temperature was raised to 90°C, the rate of the reaction grew only slightly, due to a simultaneous rise in the rate of the undesirable side reaction of thermal decomposition of hydrogen peroxide (Table 1, experiment 3). We found no proof that the disproportionation of P_4 proceeds in the presence of H_2O_2, as was claimed in [15]. The authors of that work presumably detected the disproportionation of product $P(O)H(OH)_2$ **2** into PH_3 and $P(O)(OH)_3$ **3** upon heating.

During the oxidation of P_4 by hydroperoxides, nonpolar organic solvent was added in order to improve the solubility of ROOH and white phosphorus. Two phases were in this case observed in the reactor: an organic phase with dissolved white phosphorus, and an aqueous phase in which inorganic acids **1–3** were concentrated. Peroxide was distributed in both phases. With the addition of toluene, the oxidation of P_4 by *tert*-butylhydroperoxide at 60°C was complete within 15 min (Table 2, experiment 1).

Table 2. Effect of temperature and solvents on the oxidation of P_4 by hydroperoxides in water

Experiment	T, °C	Solvent	Conversion, %[a]	t, h	C_1, %[a]	C_2, %[a]	C_3, %[a]
1	60	toluene	100	0.25	15	67	18
2	25	toluene	100	0.5	13	71	16
3[b]	25	toluene	63	0.5	12	37	14
4[c]	25	toluene	100	0.5	14	70	16
5	60	THF	100	1	22	66	12
6	60	CCl_4	100	1	13	69	18
7	60	*n*-hexane	100	4	11	76	13
8[d]	90	–	25	2	1	20	4
9	60	THF	90	2	16	69	5
10	60	toluene	100	2	20	72	8

Reaction conditions: argon atmosphere; solid P_4, 29.7 mg, 0.24 mmol; oxidizing agent: $(CH_3)_3COOH$ 70% aqueous solution, 0.33 mL, 2.4 mmol (experiments 1–8); $3\text{-}ClC_6H_4C(O)OOH$, 0.58 g, 2.4 mmol (experiments 9, 10); D_2O 1 mL; solvent 1 mL.

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

[b] $(CH_3)_3COOH$ 0.165 mL, 1.2 mmol.

[c] Solution of P_4 in toluene, 1 mL.

[d] D_2O 2 mL, without solvent.

Full conversion of white phosphorus was achieved even at room temperature (experiment 2). When the ROOH-to-P_4 molar ratio was reduced to 5, the conversion of P_4 fell consistently (experiment 3). Identical rates of the reaction were observed whether P_4 was added in solid form or dissolved in toluene (experiments 2, 4). The highest rate of the oxidation of P_4 by *tert*-butylhydroperoxide was observed in toluene (0.25–0.5 h), while the full conversion of white phosphorus was achieved after 1 h in THF and CCl_4, and after 4 h in *n*-hexane (experiments 5–7). When there was no organic solvent, the conversion of P_4 was only 25% after 2 h even at 90°C (experiment 8). When the oxidizing agent was replaced with 3-chloroperoxybenzoic acid, the reaction proceeded much more slowly; however, the distribution of products **1–3** and the effect of solvents did not change (Table 2, experiments 9, 10). Regardless of the conditions, the main product of the oxidation of white phosphorus by hydroperoxides in water was phosphorous acid **2** (up to 76%). Analysis of the organic phase by means of GC/MS revealed the presence of the products of reduction of hydroperoxides, i.e., *tert*-butanol and 3-chlorobenzoic acid.

According to our experimental results, the preparation of phosphorus-containing acids via the oxidation of P_4 by peroxides is described by stoichiometric equations

$$P_4 + 6H_2O + 2ROOH \rightarrow \underset{\mathbf{(1)}}{4P(O)H_2(OH)} + 2ROH, \quad (1)$$

$$P_4 + 6H_2O + 6ROOH \rightarrow \underset{\mathbf{(2)}}{4P(O)H(OH)_2} + 6ROH, \quad (2)$$

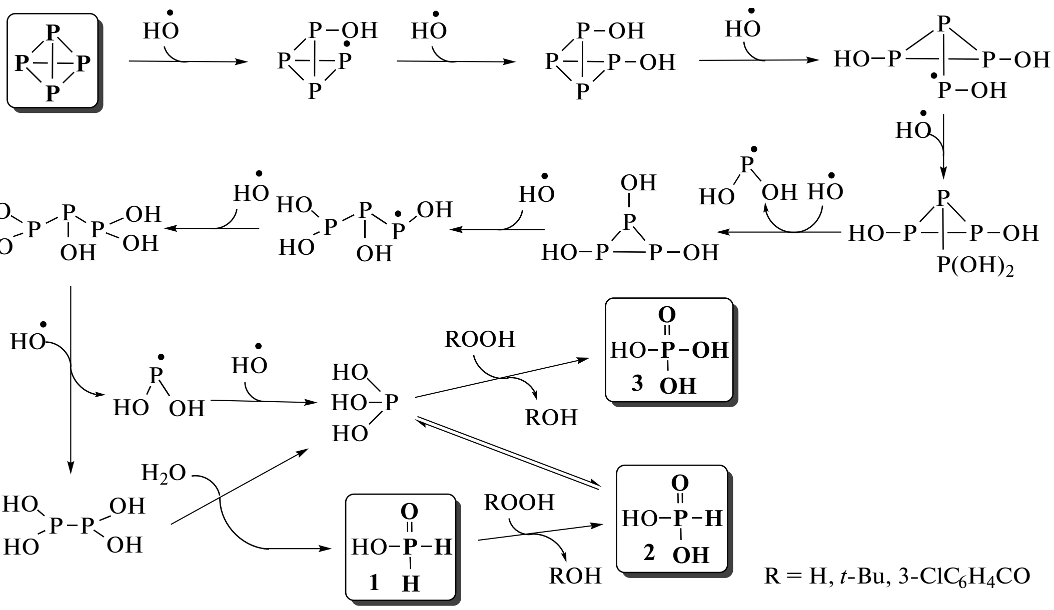
$$P_4 + 6H_2O + 10ROOH \rightarrow \underset{\mathbf{(3)}}{4P(O)(OH)_3} + 10ROH, \quad (3)$$

$$R = H,\ t\text{-Bu},\ 3\text{-ClC}_6H_4CO.$$

The rate of reactions (1)–(3) is limited to that of the homolytic cleavage of the unstable O–O bonds of ROOH, which depends not only on temperature and the structure of R, but also on the character of its association with solvent molecules and viscosity of medium [2]. Assuming an identical character of the products of the oxidation of P_4 by hydrogen peroxide and hydroperoxides in water, we propose a general radical mechanism of these reactions, which are initiated by the homolysis of ROOH with the formation of $RO^•$ and $HO^•$ radicals:

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}. \quad (4)$$

At temperatures of 25–90°C, only $HO^•$ radicals, which are strong oxidizing agents of organic and inorganic substrates [20], react with P_4 molecules. The reaction of $(CH_3)_3CO^•$ and $3\text{-ClC}_6H_4C(O)O^•$ radicals, which have lower chemical activity, bonding directly to white phosphorus in this range of temperatures is unlikely [2]. $HO^•$ radicals attacking the P_4 tetrahedron results in the homolytic cleavage of the first P–P bond and the formation of $(P_4OH)^•$ radicals (Scheme 1)



Scheme 1. Scheme of the proposed mechanism of P_4 oxidation by peroxides in water.

Bonding to the latter, $HO^•$ radical could yield intermediate bicyclic dihydroxytetraphosphine $P_4(OH)_2$. The sequential cleavage of the other five P–P bonds under the action of $HO^•$ radicals with the generation of $P(OH)_2^•$ radicals, intermediate cyclic $P_4(OH)_4$ and $P_3(OH)_3$, and linear $P_3(OH)_3$ and $P_2(OH)_4$ compounds is then possible. We suggest that the hydrolysis of tetrahydroxydiphosphine $P_2(OH)_4$ into hypophosphorous acid **1** and trihydroxyphosphine $P(OH)_3$, the precursor for P(III) and P(V) acids, is also possible.

Another possible way of forming intermediate $P(OH)_3$ is the recombination of $HO^•$ and $P(OH)_2^•$ radicals, which is also shown in the scheme of the mechanism. Trihydroxyphosphine is transformed into phosphorous acid **2** as the result of the rapid spontaneous interconversion of structural isomers. It is known that tautomeric equilibrium between $P(OH)_3$ and $P(O)H(OH)_2$ **2** in aqueous solution shifts almost completely toward phosphorous acid **2** [21]. According to the composition of the products, some part (15–30%) of trihydroxyphosphine is oxidized by peroxide and transformed into phosphoric acid **3**. Hypophosphorous acid **1** can also undergo peroxide oxidation into phosphorous acid **2** (scheme).

Compared to the cleavage of the first of the six P–P bonds of the tetrahedral P_4 molecule, subsequent steps of the cleavage of other P–P bonds of intermediate compounds $P_4(OH)_2$, $P_4(OH)_4$, $P_3(OH)_3$,

$P_3(OH)_5$, and $P_2(OH)_4$ proceed more quickly, in accordance with the substantial increase in the reactivity of P–P bond with upon moving from cyclic polyphosphines to linear counterparts, and with the increased number of substituents (hydroxyl groups) with one P atom [22]. It should be emphasized that the above intermediates are not detected by spectroscopy, due to their rapid conversion in the reaction solution. They are nevertheless considered the most likely intermediate compounds upon moving from P_4 molecules to phosphorus-containing acids. From a thermodynamic viewpoint, two driving forces make possible the direct oxidation of white phosphorus by peroxides in water: the large gain in energy during the formation of P–O, P–H, and P=O bonds of phosphorus-containing acids, and the cleavage of the P–P bonds of tetraphosphorus, the O–O bonds of peroxide (335, 322, 544 and 201, and 142 kJ/mol, respectively), and the high value of the standard redox potential of peroxides (1.77 V in the case of H_2O_2).

CONCLUSIONS

Under anaerobic conditions, white phosphorus is readily oxidized by hydrogen peroxide and hydroperoxides in water at 25–90°C into a mixture of hypophosphorous, phosphorous, and phosphoric acids. The rate of the reactions grows remarkably with the addition of nonpolar organic solvents. In direct correspondence to their ability to dissolve hydroperoxides and white phosphorus, the solvents are arranged in the following order, according to the acceleration of the reaction: toluene > THF $\cong$ CCl_4 > *n*-hexane $\gg$ D_2O. It was determined experimentally that *tert*-butylhydroperoxide is vastly superior to 3-chloroperoxybenzoic acid in terms of oxidizing ability. With hydrogen peroxide, the target reaction was accompanied by decomposition of H_2O_2 into O_2 and H_2O. Regardless of the composition of peroxides and solvents, the main product of the reaction was phosphorous acid (up to 76%). A general radical mechanism of the oxidation of white phosphorus by hydrogen peroxide and hydroperoxides in water, initiated by the homolysis of peroxide ROOH to yield $RO^{\bullet}$ and $HO^{\bullet}$ radicals, was proposed. During the reaction between $HO^{\bullet}$ radicals and molecules of white phosphorus, the homolytic opening of phosphorus thetrahedral molecules occurs with the final formation of tetrahydroxydiphosphine $P_2(OH)_4$, hydrolysis of which yields acid **1** and intermediate trihydroxyphosphine $P(OH)_3$. The latter produces acids **2** and **3** via the spontaneous interconversion of structural isomers and oxidation by peroxide, respectively.

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Translated by A. A. Muravev