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Controlled defect formation in elemental phosphorus as method for its chemical activation

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The reveiw surveys and systematizes data on the role of defect formation in activation of red phosphorus. The reactivities of different modifications of elemental phosphorus (*viz.*, white phosphorus, commercial red phosphorus, and red phosphorus containing high concentrations of biographical and induced defects) in inorganic and organic reactions were comparatively analyzed.

Key words: elemental phosphorus, activation, defect formation, biographical defects, induced defects.

Introduction

Conventional procedures for the preparation of organophosphorus compounds (OPC) are based on aggressive and highly toxic phosphorus halides and produce large amounts of acidic industrial wastes, which are difficult to dispose.[1—5] Because of this, the development of simple, technologically efficient, and environmentally safe methods for the synthesis of OPC is an urgent problem of the chemistry of these compounds. The use of elemental phosphorus as an alternative phosphorylating reagent shows promise for this purpose.[3—13] This approach is economically most attractive, because it excludes intermediate steps of the synthesis (for example, halogenation of elemental phosphorus) and employs the most efficient schemes of transformations into target products. Generally, conventional phosphorylation processes based on elemental phosphorus are performed with the use of white phosphorus at high temperatures, which substantially reduces the practical value of this method.

Among the most promising procedures for the direct formation of C—P bonds, which have been extensively developed in the last decade, of special note are methods based on the use of phosphorus-centered anions generated from elemental phosphorus (including its least reactive red modification) in heterogeneous highly basic media, such as systems consisting of alkali metal hydroxide and a polar hydroxyl-free solvent (DMSO or hexamethylphosphoramide (HMPA))[14—40] or an aqueous solution of alkali metal hydroxide, an organic solvent, and a phase transfer catalyst,[41—56] as well as in the alkali metal—*tert*-butyl alcohol—liquid NH_3 system.[57—77] As a result, a novel approach to the C—P bond formation has been developed, which made it possible to perform direct phosphorylation of organyl halides, electrophilic alkenes, acetylenes, and oxiranes by red phosphorus.

Recently, an original evidence has been reported that red phosphorus can be activated through the controlled defect formation in its structure.[34,78—92] In the solid-state physics and chemistry, the term "defect" (which is generally related to an anomaly of the phenomenon) assumes the meaning of a structural element, which is structurally different from the remaining regular portion of the substance and possesses specific local properties.[93] There are the following two main types of defects: biographical defects associated with a particular procedure for the preparation of solid compounds and induced defects that appear in solid samples due to an external effect.[93]

Red phosphorus, which is prepared by high-temperature,[81,94] photochemical,[95] or radiation-chemical[95] polymerization of white phosphorus as well as by plasma-thermal (electric arc) or photochemical (UV range) decomposition of phosphorus hydrides or halides,[95] contains biographical defects, whose nature and concentration are responsible for the chemical activity of this phosphorus polymer.[94] For example, red phosphorus containing high concentrations of biographical defects, which were produced upon extensive grinding or high-temperature heating of the phosphorus polymer synthesized by thermal polymerization of white phosphorus, was reported[81] to inevitably undergo self-ignition even at room temperature.

The induced defect formation under conditions of catalytic (metal impurities),[96—98] thermal,[81] mechanochemical,[81] photochemical,[78] or radiation-chemical[34,79,84,86,89,91,92] activation of red phosphorus also substantially increases the reactivity of the latter.

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The present review is devoted to a comprehensive analysis of the data on the origin and chemical essence of the defects in red phosphorus and the influence of defect formation on the chemical activity of this element, primarily, in direct phosphorylation of organic compounds. This problem has, as yet, received little study, although the data published in the literature primarily in the last 10—15 years provide evidence that the new approach to chemical activation of red phosphorus based on the controlled defect formation holds promise.

Biographical defect formation as method for activating red phosphorus

The method commonly used in industry for the preparation of red phosphorus involves prolonged thermal (>200 °C) polymerization of a melt of white phosphorus under an inert atmosphere.[81,99] It is believed[94] that the properties of the final product thus prepared are unreproducible because of the noncontrolled temperature conditions and reaction time, the presence of both technological impurities and those in the starting white phosphorus, and the step of grinding of the resulting polymer.

Red phosphorus prepared according to different procedures exhibits different physicochemical properties, and its color varies from bright-yellow to purple-red, brown, and even violet.[94] All these differences are associated with the structure of a specimen of red phosphorus prepared according to a particular procedure.[94]

Depending on the synthesis conditions, red phosphorus can occur as a complex mixture of both amorphous and crystalline fractions.[94,99,100] Crystalline phosphorus, in turn, can exist in several modifications.[101] In the context of the theory of phase transitions[94] and colloid chemistry of polymers,[102] particles of both amorphous and crystalline red phosphorus are assumed to fluctuate over many different parameters.[94] Substantial variations in the chemical properties of red phosphorus are attributed to microheterogeneity and sometimes to the multiphase state of this polymer.[94] The microheterogeneity of a polymer always leads to nonhomogeneous processes of its deformation, destruction, and, what is most important from the viewpoint of the present review, chemical transformations. The reason is that the polymers have regions, which differ in the strength of intermolecular and chemical bonds.[94] Because of this, red phosphorus interacts with reagents not homogeneously over the surface but locally at sites of particular biographical defects.[94] The latter can be divided into impurity defects and polymer structure defects of red phosphorus.

Impurity defects in red phosphorus. The following inorganic impurities should primarily be assigned to the biographical defects of red phosphorus: K, Ca, As, Fe (10^{-2} %); C, Na, Mg, Se (10^{-3} %); Mn, Cu, Cr, Pb, Ni, Si, Ba, Zn (10^{-4}—10^{-6} %).[96] These defects are necessarily present in red phosphorus because impurities pass from the starting monomer, *viz.*, white phosphorus, into the final phosphorus polymer.[97] Besides, some technologies involve high-temperature polymerization of white phosphorus, which is specially carried out in the presence of heat carriers (for example, in the presence of such metals as lead or bismuth).[103] Polymeric phosphorus thus prepared has a crystal structure, is violet in color, and contains noticeable amounts of the above-mentioned metals.[94] It was demonstrated that the above impurities are of importance as polymerization nucleation sites and that these impurities are directly involved in the further formation of the phosphorus polymer, which is manifested in the inheritance of the nucleus structure.[96,97]

The effect of such biographical defects on the reactivity of red phosphorus can be estimated on the basis of the physical concepts of contact phenomena in semiconductors and the electronic theory of catalysis.[98,104] Within the framework of this approach, redox processes involving red phosphorus are accounted for by the electrochemical nature of the impurity—red phosphorus galvanic pairs formed in a medium of an ionizing solvent (among them, in the presence of adsorbed atmospheric moisture). Using oxidation of red phosphorus as an example, it was demonstrated that there is a distinct correlation between the following three important characteristics of red phosphorus and impurities: the crystal lattice energy (E_{cryst}), the electron work function (φ), and the reduction potential (E^{o}).[98] Impurities characterized by higher E_{cryst} compared to that of red phosphorus catalyze oxidation; otherwise, impurities inhibit this process:

$$E_{\mathrm{cryst}}{}^{\mathrm{inh}} < E_{\mathrm{cryst}}{}^{\mathrm{P}} = 315\ \mu\mathrm{J\ mol^{-1}\ kg^{-1}} < E_{\mathrm{cryst}}{}^{\mathrm{cat}}$$

(hereinafter, the indices "inh," "P," and "cat" correspond to an inhibitor, red phosphorus, and a catalyst, respectively).

Analogous dependences are also true for two other characteristics:

$$E^{\mathrm{o,inh}} < E^{\mathrm{o,P}} = -0.51\ \mathrm{V} < E^{\mathrm{o,cat}},$$

$$\varphi^{\mathrm{inh}} < \varphi^{\mathrm{P}} = 4.28\ \mathrm{eV} < \varphi^{\mathrm{cat}}.$$

The characteristics used in the study[98] can serve as universal criteria for the prediction of the reactivity of red phosphorus in redox reactions proceeding in the presence of impurities. Taking into account that methods for the generation of phosphorus-centered anions from elemental phosphorus in the presence of strong bases[6—8,14—77] are typical redox processes, the results of the cited study[98] can be used for controlling the reactivity of this phosphorylating agent by both the controlled defect formation already in the step of preparation of red phosphorus and the introduction of impurities into commercial red phosphorus. In both cases, a new type of catalysis (or cocatalysis) is employed for the preparation of OPC based on elemental phosphorus.[13,34]

Solvent or impurity fragments chemically bound to the polymeric phosphorus structure can be considered[94] as another type of impurity biographical defects in red phosphorus prepared by the photochemical[95] or radiation polymerization of white phosphorus in organic solvents[95,105] or in the presence of an inorganic additive.[106] In this case, a local distortion of the regular alternation of the P—P—P bonds due to formation of the P—P—R bonds (R is a solvent or impurity fragment) is the main indicator of structure imperfection of red phosphorus. Apparently, the P—P bonds at such defects should be more polarized than the bonds in the regular structure of the phosphorus polymer and, consequently, should be more reactive under certain conditions. The polarization degree of the P—P bonds at the defects of red phosphorus under consideration and the directionality of these bonds (deficiency or excess of the electron density on the P atom bound to the fragment R) are determined by the nature of the radical. Since the generation of polyphosphorus anions from red phosphorus always begins with the attack of a nucleophile resulting in the P—P bond cleavage,[4,6—8,19,107] the P atoms of the polarized P—P—R bonds are most readily subjected to this attack because the activation energy of such processes is always lower than that of the nucleophilic attack on the nonpolarized P—P—P bonds of the main structure of the phosphorus polymer.[34] Hence, red phosphorus containing a certain initial concentration of the P—P—R defects can generate phosphorus-centered anions in the same concentration with some "kinetic advance" determined by the above-mentioned difference in the activation energies compared to defect-free red phosphorus.[34] This effect is of considerable importance when the generation of polyphosphorus anions is the rate-determining step of the synthesis of OPC based on red phosphorus. Interaction of these anions with an organic electrophile gives rise to new P—C bonds and, consequently, to new P—P—R defects. The latter, in turn, facilitate generation of new organylpolyphosphorus anions due to further destruction of the polymer structure of red phosphorus. In this case, the transformation of red phosphorus into OPC may become autocatalytic.[34] Phosphorylation can be accelerated only provided that the nature of the P—P—R fragment, the nucleophilic reagent that cleaves the P—P bond, and the organic electrophile are adequately chosen.[34]

Therefore, the biographical P—P—R defects in red phosphorus can be used for controlling the reactivity of this phosphorylating agent.

Intrinsic defects of phosphorus polymer. In addition to defects of red phosphorus associated with the presence of foreign chemical inclusions, there are also biographical defects associated with the structural features of the phosphorus polymer as such. Stabilization of highly reactive molecules of white phosphorus in the white—red—black phosphorus transformation sequence as well as transition from amorphous to crystalline red phosphorus occur due to partial relaxation of the strained P—P bonds at the expense of the larger bond angles.[108,109]

Electron microscopic study of commercial red phosphorus produced by high-temperature polymerization of white phosphorus demonstrated[96,110] that large violet particles 20—100 μm in size are surrounded by small bright-red particles 0.1—10 μm in size. It is assumed[81,94,96,97,99,100,110—112] that the large particles represent different modifications of crystalline red phosphorus, whereas the small particles are amorphous. The simultaneous presence of both amorphous and crystalline phases of red phosphorus was attributed to the involvement of microimpurities (nucleation sites) in polymerization of white phosphorus, the nucleation dominating over the nucleus growth[94,104,110] (apparently, the cited studies dealt with the rate-determining steps of white phosphorus polymerization). Investigation with layer-by-layer laser evaporation demonstrated[96] that the crystallized particles of red phosphorus always contain foreign chemical impurities as central nucleation sites, whereas the particles of amorphous red phosphorus consist exclusively of P atoms. From this it follows that the formation of amorphous red phosphorus started only after the particles of red phosphorus, which is polymerized at nuclei, have reached a particular size.[94,97,110]

The angle between the P atoms in amorphous red phosphorus is ~102°. However, this angle varies over a noticeably wider range than that in crystalline red phosphorus. It should be noted that the spread in the density of amorphous red phosphorus is 10—20% of the corresponding values observed for crystalline red phosphorus.[110,113] Such a large spread in the main parameters of the phosphorus polymer is associated with substantial distortions in its structure and the difference in the degree of sp hybridization of P atoms.[110] The differences in the ordered structures of amorphous and crystalline red phosphorus are responsible for the different character of defects of this polymer.[81] The defects in amorphous red phosphorus (which are sometimes called "broken bonds"[104]) are associated with the presence of unpaired valence electrons that are not involved in the P—P bond formation. These defects appear under the conditions of incomplete polymerization of white phosphorus.[97] In amorphous red phosphorus, structural distortions can appear also due to plastic deformations of the near-surface layer.[81] In contrast, crystalline red phosphorus contains microcracks, dislocations, and impurities of a residual amorphous phase or a microcrystalline structure as defects.[81]

Defects in amorphous and crystalline red phosphorus were studied by the ESR method,[81] which is widely used for revealing different structure imperfections.[114] The investigation by ESR spectroscopy demonstrated[81] that the formation of structure defects depends not only on the physicochemical features of polymerization or crystallization but also (often to a larger extent) on the conditions of thermal and mechanical treatment employed in the course of industrial production of red phosphorus. Thus, red phosphorus specially synthesized by polymerization of white phosphorus does not possess paramagnetic properties, and, consequently, contains no structure defects until it is crushed.[81] Mechanical destruction gives rise to paramagnetic centers on the surface of red phosphorus and a further increase in dispersity leads to an increase in the concentration of paramagnetic defects.[81]

The influence of thermal treatment on defect formation in red phosphorus is manifested only after heating above 450 °C when crystallization of red phosphorus starts, which is accompanied by the formation of defect paramagnetic crystalline structures.[81] A further increase in the temperature leads to an increase in the crystallinity index (Hinckley index Ch) with a simultaneous increase in the intensity of the ESR signal. Thus, the higher the temperature, the more intense the ESR signals and the higher the density of defects.[81] This indicates that further crystallization of red phosphorus induced by heating leads to changes in the character of its structure imperfection, including the appearance of mechanical stresses and formation of microcracks, dislocations, *etc.*[81] Specimens of red phosphorus prepared at the maximum experimental temperature (540 °C) are characterized by the maximum crystallinity index (Ch = 1.4) at the most intense signal of paramagnetic centers.[81]

Therefore, two main steps, *viz.*, thermal treatment and mechanical crushing, involved in the technology of the industrial production of red phosphorus are the most important sources of structure defects of the latter.[81]

Biographical defect formation as method for activating red phosphorus in its oxidation. The above-discussed study[98] showed the role of impurity defects (here, a particular chemical element serves as an impurity) in oxidation of red phosphorus with atmospheric oxygen. Simple and convenient criteria were proposed for the estimation of the effect of an impurity (crystal lattice energy E_{cryst}, electron work function φ, and reduction potential E^{o}) on the reactivity of red phosphorus, and a broad spectrum of inhibitors and catalysts for redox transformations of red phosphorus were considered.[98]

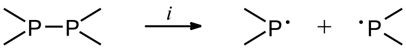
Apparently, the effect of the P—P—R biographical defects of red phosphorus (R is a solvent or impurity fragment chemically bound to the main structure of the phosphorus polymer) is manifested in high reactivity of organyldi- and organylpolyphosphines with linear ($R_2(P—P)_nR_2$) or cyclic structures ($(RP)_n$).[99,115,116] Within a certain approximation, these compounds can be considered as models of polymeric red phosphorus containing the above-mentioned defects.[99,115—122]

The influence of yet another type of the so-called intrinsic biographical defects of red phosphorus (associated with distortions in the structure of the phosphorus polymer, for example, in the course of grinding) on its reactivity toward atmospheric oxygen was considered in detail.[81] Mechanical destruction of red phosphorus gives rise to paramagnetic centers in the structure of a phosphorus polymer.[81] Such a defect formation exerts a radical effect on the chemical activity of the phosphorus polymer. Thus, when a certain concentration of defects is reached, initially nonpyrophoric red phosphorus ignites spontaneously on exposure to atmospheric oxygen, *i.e.*, behaves analogously to white phosphorus, which is chemically most active but nonparamagnetic.[81]

Defect paramagnetic crystalline structures are formed in red phosphorus also upon thermal treatment.[81] Specimens of red phosphorus prepared at the maximum temperature of polymerization of white phosphorus (540 °C) are characterized by both the maximum crystallinity index (Ch = 1.4) at the most intense ESR signal of paramagnetic centers and the maximum ignitability in air up to pyrophoricity (temperature of spontaneous ignition is 25—50 °C).[81] Therefore, the authors of the cited study[81] experimentally demonstrated the relation between the concentration of defects (paramagnetic centers) and chemical activity in oxidation of both amorphous and crystalline red phosphorus with atmospheric oxygen thus demolishing the myth of low inflammability and, all the more, of nonpyrophoricity of red phosphorus.

Unfortunately, the chemical nature of defects (paramagnetic centers) as a cause of a sharp increase in the reactivity of red phosphorus was not considered in the above-mentioned study.[81] Based on the data on the homolytic bond cleavage in polymers exposed to analogous physical actions,[114] it can only be hypothesized that the homolytic cleavage of the P—P bond takes place also in polymeric molecules of red phosphorus (Scheme 1).

Scheme 1



i. Mechanochemical treatment or heating.

The bicoordinate P atoms with unpaired electrons thus generated are paramagnetic phosphorus-centered radicals. In this case, the broken bonds serve, in actuality, as defects. Interactions of the radicals with dioxygen molecules, which are also biradicals, should give rise to the free-radical chain oxidation. A considerable exothermic effect of this reaction can cause spontaneous ignition and even thermal explosion.[123] This type of biographical paramagnetic defects of red phosphorus as the starting reagent is of obvious interest for chemists involved in the synthesis of OPC. First, this is a vehicle to control the reactivity of red phosphorus in radical processes of phosphorylation of organic compounds. Second, this allows generation of the phosphorus-centered cations (one-electron oxidation of radical defects) for the purpose of their use in reactions with organic nucleophiles. Third, this phenomenon can be used for generation of the phosphorus-centered anions (one-electron reduction of radical defects) with the aim of their use in reactions with organic electrophiles.

Biographical defect formation as method of activation of red phosphorus in organic synthesis for C—P bond formation. The data on the use of defect formation in red phosphorus as a new promising approach to the preparative synthesis of organophosphorus compounds are scarce. It was reported[124] that previously unknown trichloromethylphosphorus dibromide Cl_3CPBr_2 was synthesized by dissolution of red phosphorus containing the terminal CCl_3 groups (this reagent was prepared by the γ-radiation polymerization of white phosphorus in a solution in CCl_4) in bromine. The generation of alkyl- or arylphosphinic acids by oxidation of red phosphorus, which was synthesized by irradiation of white phosphorus in different organic solvents, with nitric acid was briefly described in the study.[125]

In recent years, activated red phosphorus, which was prepared by the radiation, thermal, or radiation-thermal polymerization of white phosphorus in the presence of graphite[106] or in solutions in benzene,[105] was successfully used in the synthesis of organophosphorus compounds.[34,82,85,87,88,90—92,126—128] Studies by ESR,[34,83,84,91,92] X-ray electron, and IR spectroscopy[129,130] demonstrated that activated red phosphorus contains the P—P—R biographical defects, where R is a fragment of graphite ($P_n{}^1$ sample) or benzene ($P_n{}^2$ sample). To compare the reactivity of the activated defect-containing red phosphorus ($P_n{}^1$ and $P_n{}^2$) with the reactivities of white and usual commercial red phosphorus, phosphorylation of different electrophiles (2-vinylnaphthalene, vinylpyridines, and phenylacetylene) with these reagents in superbasic media was studied.[34,82,85,87,88,90—92,126—128]

Activated defect-containing red phosphorus in reaction with 2-vinylnaphthalene. The activated red phosphorus $P_n{}^2$ (containing the P—P—R biographical defects, where R is the benzene fragment) reacted with 2-vinylnaphthalene on heating (90—96 °C, 7 h, argon) in the KOH—DMSO system in the presence of a small amount of water to give tris[2-(2-naphthyl)ethyl]phosphine oxide (**1**), 2-(2-naphthyl)ethylphosphinic acid (**2**), bis[2-(2-naphthyl)ethyl]phosphine (**3**), and bis[2-(2-naphthyl)ethyl]phosphine oxide (**4**) in a total yield of 76% (Scheme 2).[34,91,92]

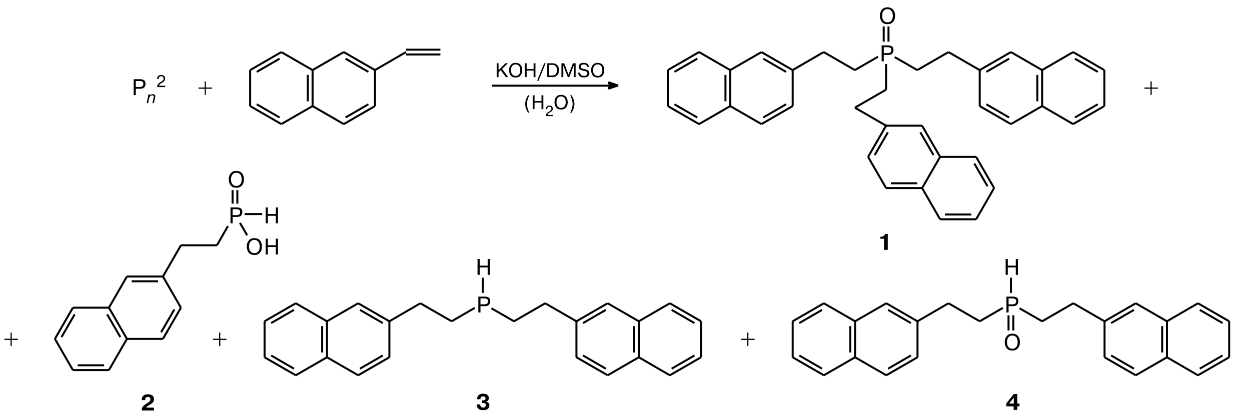
Under analogous conditions, the reaction of white phosphorus with 2-vinylnaphthalene proceeded more selectively to form tertiary phosphine oxide **1** in 58% yield.

Usual commercial red phosphorus reacted with 2-vinylnaphthalene under the same conditions to give the same tertiary phosphine oxide **1** in 44% yield. The latter reaction afforded acid **2** as a by-product in 11% yield.

The total yield of products **1** and **2** (55%) indicates that white and red phosphorus have comparable reactivities in phosphorylation of 2-vinylnaphthalene, whereas the reactivity of the activated red phosphorus is noticeably higher.

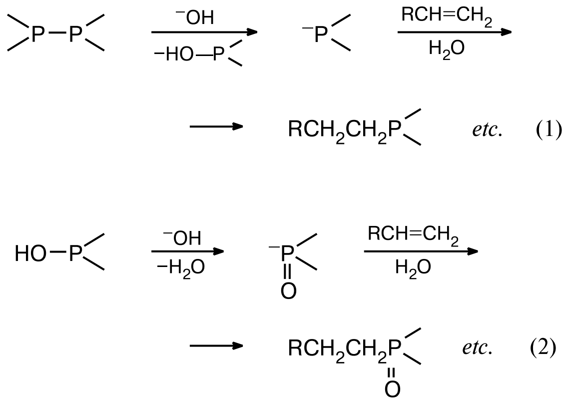
Phosphines are generated upon phosphorylation of 2-vinylnaphthalene due, apparently, to the addition of phosphide anions, which are generated from elemental phosphorus by a superstrong base, at the double bond of an electrophile (Scheme 3, reaction (1)). In contrast, oxygen-containing tetracoordinate phosphorus compounds **1**, **2**, and **4** can, evidently, be generated in two ways, *viz*., either by oxidation of the initially formed corresponding phosphines (in this process, DMSO or traces of atmospheric oxygen can serve as an oxidizing agent) or with the participation of phosphinite anions derived from

Scheme 2



(analogously to phosphide anions) elemental phosphorus and a base (see Scheme 3, reaction (2)).

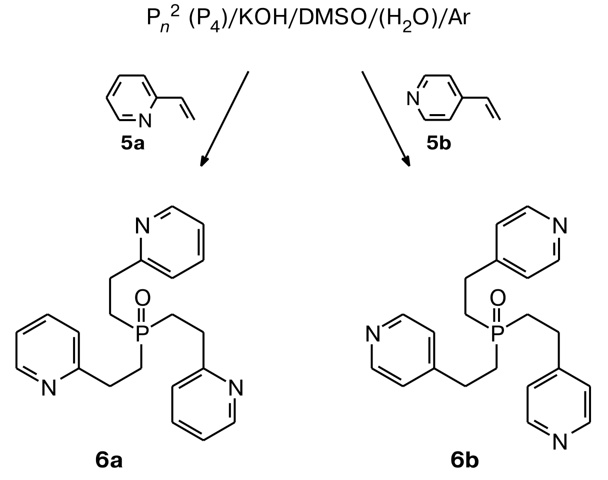
Scheme 3



Therefore, phosphorylation of 2-vinylnaphthalene by activated defect-containing red phosphorus (P_n^2) occurs more efficiently than that with the use of not only usual red phosphorus but of white phosphorus as well. This reaction allows one to synthesize previously unknown phosphines and phosphine oxides containing bulky radicals, which hold promise as ligands for the synthesis of metal complex catalysts and the design of new organophosphorus scintillators with desired properties.[34,131]

Phosphorylation of vinylpyridines by active modifications of elemental phosphorus. It was found[34,85,91,92,128] that the active modifications of elemental phosphorus, *viz.*, the defect-containing red phosphorus P_n^2 and white phosphorus, readily (even at room temperature) react with vinylpyridines **5a,b** in a KOH—DMSO suspension in the presence of a small amount of water to produce tris[2-(2-pyridyl)ethyl]phosphine oxide (**6a**) and tris[2-(4-pyridyl)ethyl]phosphine oxide (**6b**), respectively (Scheme 4).

Scheme 4

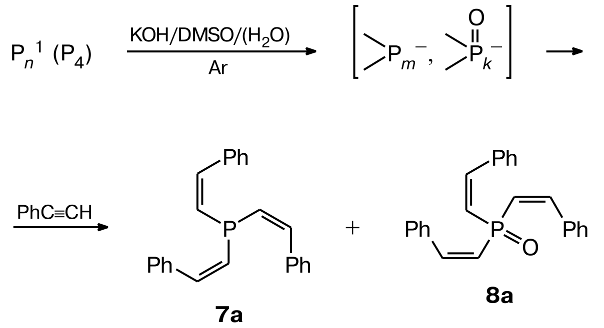


White phosphorus and activated red phosphorus showed comparable reactivities in the reactions with 4-vinylpyridine. Thus, phosphine oxide **6b** was obtained in 51—58% yield, and the conversion of phosphorus was 90—100%. At the same time, white phosphorus reacted with 2-vinylpyridine more efficiently than activated red phosphorus to form phosphine oxide **6a** in 72% yield, whereas the yield of the latter in the reactions with P_n^2 was 48%.[85,92]

In the reactions with vinylpyridines **5a,b** performed under comparable conditions, usual commercial red phosphorus was poorly efficient and gave phosphine oxides **6a,b** in yields of at most 10%,[34,85,92] the conversion of phosphorus being 28—55%.

Activated red phosphorus in reaction with phenylacetylene. Phosphorylation of phenylacetylene by the activated red phosphorus P_n^1 (containing the P—P—R biographical defects, where R is a graphite fragment) or white phosphorus P_4 occurs in the KOH—DMSO system at room temperature stereoselectively to form the *Z,Z,Z* isomers of tris(styryl)phosphine **7a** and tris(styryl)phosphine oxide **8a** in 49 and 15% yields (with the use of the activated red phosphorus P_n^1) or 48 and 10% yields (with the use of white phosphorus), respectively[34,82,87,88,90—92,126,127] (Scheme 5).

Scheme 5



The stereoselectivity of this reaction (see Scheme 5) is consistent with the rule of the *trans*-nucleophilic addition of the phosphide and phosphinite anions generated from elemental phosphorus at the triple bond.[6—8]

Under comparable conditions, usual red phosphorus was much less efficient in the reaction with phenylacetylene to give products **7a** and **8a** in a total yield of only 5%.[82,90]

Therefore, phosphorylation of 2-vinylnaphthalene,[34,91,92] 2- and 4-vinylpyridines,[85] and phenylacetylene[82,90] demonstrated for the first time that nonpyrophoric, low-toxic activated red phosphorus containing biographical defects is much more reactive than usual red phosphorus, its reactivity being similar to that of white phosphorus.[34,87,88,91,92,126—128]

Induced defect formation as method of activation of red phosphorus

Most of the above-considered biographical defects can be generated in commercial red phosphorus thus increasing its reactivity in chemical processes. Such defects, which are not directly associated with the production of red phosphorus, are commonly called induced.

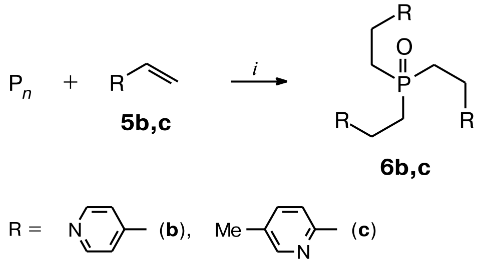
Inorganic processes. It is known that metal ions (in particular, copper ions) pre-adsorbed on red phosphorus not only sharply accelerate oxidation of red phosphorus but also substantially increase the selectivity of the process.[132] As mentioned above, impurities of other chemical elements also substantially facilitate oxidation of red phosphorus.[98] The fact that mechanochemical activation of red phosphorus has a considerable effect on the intensity of oxidation with atmospheric oxygen has been reported earlier.[81] Mechanochemical activation of red phosphorus was successfully used also for the highly selective preparation of calcium hypophosphite.[133] Ultraviolet radiation also enhances[78] the chemical activity of red phosphorus, for example, in the course of oxidation with atmospheric oxygen.

Yet another procedure for the generation of defects in solid substances is based on the radiation defect formation. In spite of abundant data accumulated by the modern radiation chemistry, there is, to our knowledge, the only study[79] devoted to the radiation defect formation in red phosphorus and the relation between the radiation-chemical defects in irradiated red phosphorus and its high chemical reactivity in oxidation with atmospheric oxygen and solid inorganic oxidizing agents. The data[81] on the presence of biographical electronic defects, *viz.*, paramagnetic centers, in red phosphorus were confirmed in the more recent study.[79] After exposure of a sample of red phosphorus under an inert atmosphere to hard ^{60}Co γ-radiation, the concentration of paramagnetic centers in phosphorus increased by a one-and-a-half order of magnitude. Upon subsequent exposure to atmospheric oxygen, the concentration of the paramagnetic centers sharply decreased. Taking into account this fact, it was concluded[79] that irradiation causes the predominant formation of the paramagnetic centers on the surface and that these radiation-chemical defects play the key role in oxidation of red phosphorus with atmospheric oxygen and alkali metal nitrates. For instance, mixtures of irradiated red phosphorus and the above-mentioned oxidizers ignited with explosion.

Direct synthesis of organophosphorus compounds. *Mechanochemical and ultrasonic activation of red phosphorus.* The possibility of the use of mechanochemical and ultrasonic activation of red phosphorus in the direct synthesis of organophosphorus compounds has been first exemplified by phosphorylation of vinylpyridines[36,37,40,134] and phenylacetylene.[36,134,135]

For example, ultrasonic treatment (Ultrasonic disintegrator UD-20 automatic instrument) of the reaction mixture resulted in 3—6-fold acceleration of the reactions of red phosphorus with 2-methyl-4-vinyl- and 2-methyl-5-vinylpyridines (**5b,c**) proceeding in the superbasic KOH—DMSO system with heating (90—95 °C) to give tris[2-(4-pyridyl)ethyl]- (**6b**) and tris[2-(methyl-5-pyridyl)ethyl]phosphine oxides (**6c**), respectively (Scheme 6).

Scheme 6

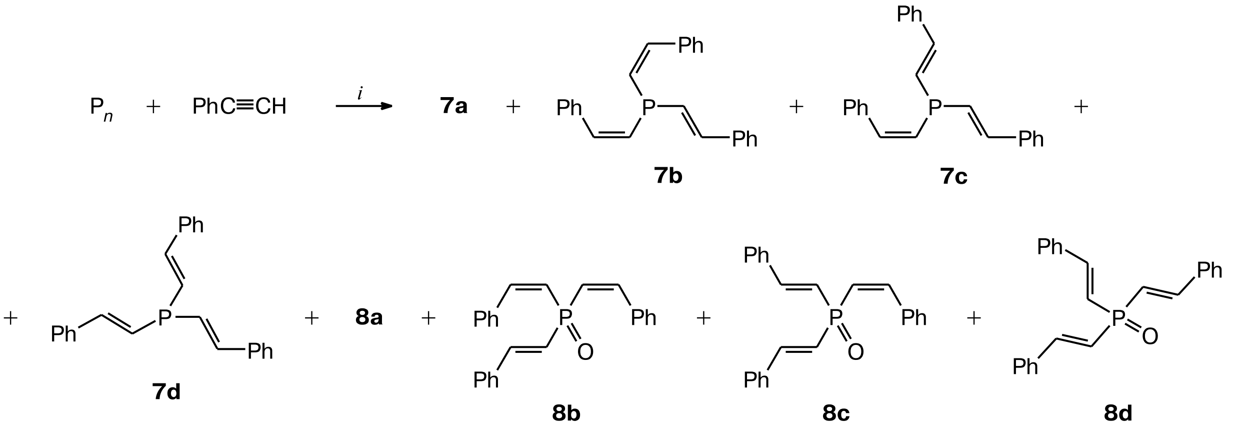


i. KOH/DMSO (H_2O), ultrasonics.

It was also demonstrated[36,134,135] that ultrasonic or mechanochemical (Pulverevette-6 ball centrifugal mill) treatment of the reaction mixture leads to a 2—7-fold increase in the rate of the reaction of red phosphorus with phenylacetylene, which occurs in the KOH—HMPA system on heating (75—80 °C). In addition, the process taking place after such treatment is no longer stereo- and chemoselective and affords stereoisomers of *E*,*Z*,*Z*-, *E*,*E*,*Z*-, *E*,*E*,*E*-tris(styryl)phosphine (**7b—d**) and *E*,*Z*,*Z*-, *E*,*E*,*Z*-, *E*,*E*,*E*-tris(styryl)phosphine oxide (**8b—d**) along with phosphine **7a** and phosphine oxide **8a** (Scheme 7). This was attributed[36,135] to the fact that the classical *anti*-nucleophilic addition of the phosphide anions to phenylacetylene competes (due to steric hindrances) with the *syn*-addition of the bulky polyphosphide anions or macroanionic centers generated in the crystal lattice of elemental phosphorus.

It should be noted that the data on the use of mechanochemical and ultrasonic activation of red phosphorus in the synthesis of organophosphorus compounds[36] were published for the first time virtually simultaneously with the above-considered study,[81] where analogous mechanochemical activation of red phosphorus was observed in the course of its oxidation with atmospheric oxygen. Three years later, the foreign authors[136] virtually repeated the pioneering information published in the studies[36,38] with no discussion of the mechanism of activation of red phosphorus.

Scheme 7

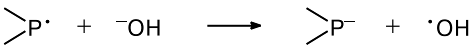


i. KOH/HMPA(H_2O), mechanochemical or ultrasonic treatment.

In the context of the nature of defect formation without considering the possibility of mechanochemical or ultrasonic activation of organic substrates used earlier,[36,37,40,134,135] the following mechanism of the influence of mechanochemical and ultrasonic activation of red phosphorus on phosphorylation of electrophiles can be proposed.

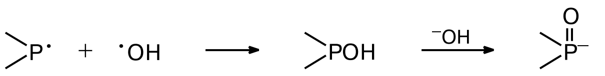
Like in the case of destruction of other polymers under analogous actions,[115] the homolytic P—P bond cleavage in polymeric red phosphorus generates simultaneously two phosphorus-centered radical defects (see Scheme 1). One of these defects captures an electron from the hydroxide anion thus being transformed into the phosphide anion, whereas the hydroxide anion is transformed into the $^{\bullet}$OH radical (Scheme 8).

Scheme 8



Then, recombination of the $^{\bullet}$OH radical with another phosphorus-centered radical takes place followed by the rearrangement giving rise to the phosphoryl bond (Scheme 9).

Scheme 9



The somewhat unfavorable first step involving oxidation of the hydroxide anion with the phosphide radical can be completely compensated by a substantial energy release upon the formation of the phosphoryl bond in the second step of the process, as in the case of the seemingly inexplicable addition of the OH^- anion to the nucleophilic P_4 molecule, which is, in essence, can also be considered as oxidation producing the phosphoryl bond.[4]

Therefore, the use of mechanochemical or ultrasonic activation allows one to easily generate the phosphide and phosphinite anions in equivalent amounts from red phosphorus and alkali metal hydroxide through the formation of radical defects. This should primarily increase the rate of phosphorylation of organic electrophiles involving these phosphorus-centered nucleophiles. However, it should be taken into account that the concentrations of the phosphide and phosphinite anions depend not only on the rate of defect generation but also on the rate of their consumption. This is of fundamental importance when the activation of red phosphorus and the phosphorylation of electrophiles proceeds as separate steps, *i.e.*, the effect of activation can vanish after a lapse of time.

It is of considerable interest to combine the mechanochemical (or ultrasonic) activation of red phosphorus with phosphorylation, when the reaction medium contains simultaneously an organic electrophile and red phosphorus activated by defect formation. In this case, the concentration of phosphorus-centered radical defects is limited only by the power of an apparatus used for mechanochemical or ultrasonic activation. The above-considered generation of phosphide and phosphinite anions (see Schemes 8 and 9) could depend heavily on the nucleophilicity of these species, *i.e.*, on their ability to abstract a proton from a proton donor (for example, H_2O) present in the reaction medium with a particular rate. If the nucleophilicity of the phosphide anions is higher than that of the phosphinite anions, the stationary concentration of the latter in the reaction medium can be substantially higher than the stationary concentration of the phosphide anions under the conditions of continuous activation. This difference in the concentration should be proportional (to a certain degree) to the intensity of generation of phosphorus-centered radical defects, *i.e.*, should virtually directly depend on the power of the apparatus used for ultrasonic or mechanochemical activation. Consequently, if the essentially nonequilibrium generation of phosphorus-centered anions from red phosphorus is performed in such a way, one can control the chemoselectivity of phosphorylation of organic electrophiles. Apparently, it is this effect that is manifested in a noticeable increase in the proportion of tris(styryl)phosphine oxide produced by phosphorylation of phenylacetylene with red phosphorus using ultrasonic or mechanochemical activation (see Scheme 7).[36,135] In addition, an advantage of such nonequilibrium processes is the fact that they do not require superbasic media, *i.e.*, expensive or toxic solvents (for example, DMSO, HMPA).

X-ray irradiation as method for activating red phosphorus. The radiation defect formation in usual commercial red phosphorus by ionizing electromagnetic radiation (X-ray range) was first investigated in detail in studies[34,83,84,86,89,91,92] in which the successful use of this activation of red phosphorus in the direct OPC synthesis was exemplified by phosphorylation of phenylacetylene.

Usual red phosphorus gives an ESR signal (ΔH = 150 G; g = 1.9500) belonging to unpaired electrons of the biographical defects.[34,83,84,91,92] This signal disappears in the ESR spectrum of the specimen obtained by X-ray irradiation of red phosphorus ($^{X}P_n$). This effect first discovered for red phosphorus is, apparently, associated with the redistribution of the unpaired electrons of the biographical defects induced by high-energy quanta to give the spatially separated nonparamagnetic anionic and cationic defects.[34,83,84,91,92]

With time (~10 h, 20 °C), the signal in the ESR spectrum of irradiated red phosphorus appears again and then increases up to the value, which is twice as high as that observed in the ESR spectrum of the starting red phosphorus. This fact can be related to the fact that an additional amount of nonparamagnetic anionic and cationic defects, which are produced by the radiation dissociation of chemical bonds in the polymeric red phosphorus, contributes to the relaxation process under consideration. The duration of the relaxation process rapidly decreases with increasing temperature (~15 min, 40 °C), which is indicative of its thermoactivation character and low activation energy[34,83,84,91,92] (Scheme 10).

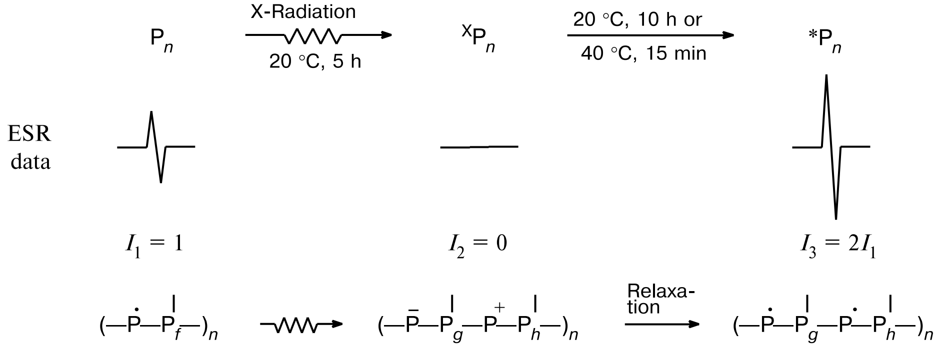
In the phase of nonparamagnetic ionic defects, the irradiated red phosphorus $^{X}P_n$ reacts with phenylacetylene in the KOH—DMSO system under argon both at room and high temperatures (54—56 °C) with 100% conversion. Under comparable conditions, the conversion of the starting (nonirradiated) red phosphorus was 18 and 48% at ~20 °C and 54—56 °C, respectively. Phosphorylation of phenylacetylene with both specimens of red phosphorus (P_n and $^{X}P_n$) afforded the *Z*,*Z*,*Z* and *E*,*Z*,*Z* isomers of **7a,b** and **8a,b** as the major reaction products, whose yields and ratios depended both on the nature of the starting red phosphorus and the reaction temperature (Scheme 11). The total yield of the products in the reaction with irradiated phosphorus was 2—2.2 times higher than that obtained with the use of the nonirradiated specimens.[34,84,86,89,91,92]

The reaction of the activated phosphorus $^{X}P_n$ with phenylacetylene proceeded stereoselectively to form predominantly the *Z*,*Z*,*Z* isomer of phosphine **7a** both at room and higher temperatures. The latter isomer was also obtained as the major product of phosphorylation of phenylacetylene with usual (nonirradiated) red phosphorus at 54—56 °C.

Under the above-described conditions (see Scheme 11), a phosphorus-containing polymer was generated in a noticeable amount. The chemical properties and elemental composition of this polymer $(C_8H_9O_3P)_k$ correspond to those of polystyrylphosphonic acid.[34,86,89]

Therefore, using 2-vinylnaphthalene, vinylpyridines, and phenylacetylene as examples, it was demonstrated for the first time that, being activated through the defect formation, red phosphorus can be successfully used in the synthesis of organophosphorus compounds. Apparently,

Scheme 10



Scheme 11

$$P_n\,(^{X}P_n) \xrightarrow[\text{KOH/DMSO/(H}_2\text{O)/Ar}]{\text{PhC}\equiv\text{CH}} \mathbf{7a} + \mathbf{7b} + \mathbf{8a} + \mathbf{8b}$$

the high reactivity of activated red phosphorus in these reactions is attributed to a higher (compared to usual red phosphorus) rate of formation of polyphosphide and polyphosphinite ions and also of phosphide and phosphinite ions under the action of the KOH—DMSO superbase. The addition of these ions at the double or triple bond of an electrophile affords the corresponding phosphines or phosphine oxides.

* * *

To summarize, the defect formation in red phosphorus produced by different modes of chemical or physical workup gives rise eventually to the appearance of phosphorus-centered intermediates, *viz.*, cations, anions, or radicals, in the structure of this allotropic modification of phosphorus. The nature and concentration of these species are largely responsible for the chemical reactivity of red phosphorus. The possibility of the selective generation of a particular type of defects is a prerequisite for the desired control over the reactivity of red phosphorus in reactions with organic nucleophilic, electrophilic, or radical reagents.

Further studies of the radiation defect formation in red phosphorus, which, along with the generation of ionic and radical defects, can give rise (in the presence of a solvent) to solvated electrons, holds considerable promise. These solvated electrons possess the superbasic and strong nucleophilic and reducing properties due to which they can additionally activate an organic substrate. This opens up new possibilities of performing phosphorylation reactions following different mechanisms.

The fact that red phosphorus exposed to ionizing radiation takes on the chemical properties different from those of nonirradiated phosphorus may also be of fundamental importance for the construction of ^{32}P-labeled compounds.[131] The radioactive red phosphorus $^{32}P_n$, which is prepared from usual red phosphorus $^{31}P_n$ by the nuclear (n, γ) transformation, serves as a universal starting material for the synthesis of different classes of phosphorus, including organophosphorus, radioindicators.[131] The red phosphorus $^{32}P_n$ subjected to the reactor and intrinsic γ-radiation necessarily contains the radiation-chemical defects and possesses chemical properties substantially different from those of usual red phosphorus.[131] In this case, the γ-irradiated usual nonradioactive red phosphorus $^{31}P_n$ can serve as a convenient model of chemical transformations of the radioactive phosphorus $^{32}P_n$ because large-scale experiments with this isotope are very expensive.[131] This model approach would be expected to sharply extend the assortment and fields of application of ^{32}P-labeled compounds.[131]

In addition, many chemical manifestations of the defect formation as a fundamental property of solid substances can successfully be used in the synthesis not only of organophosphorus but also of other heteroorganic compounds.

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