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Nanocomposites of Red Phosphorus as Novel Phosphorylating Reagents

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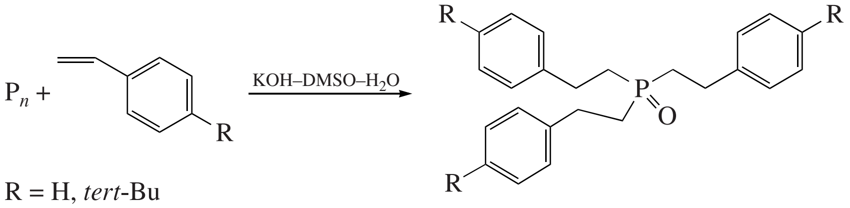
Red phosphorus in combination with superbasic systems like KOH–nonhydroxylic polar solvent (DMSO, HMPA)–water or in highly basic phase-transfer catalytic systems is increasingly used at present as a reagent for the synthesis of difficult-to-obtain organophosphorus compounds (phosphines, phosphine oxides) [1–3] by the one-pot phosphorylation of available electrophiles, such as aryl- and hetarylalkenes, acetylenes, organic halides, and alkene oxides (at present, these syntheses are more frequently cited in the literature under the general name of the Trofimov–Gusarova reaction [4–7]). For example, phosphorus-centered nucleophiles produced by these reagents make is possible to directly phosphorylate even weak electrophiles, such as styrenes, to form tertiary phosphine oxides [3, 8] (Scheme 1).



Scheme 1.

As is known, common amorphous red phosphorus consists of rather large particles with an average size of 40–60 μm [6, 9]. Nonetheless, the use of its nanosized modifications may substantially enhance its reactivity in phosphorylation reactions. We already noted the increased reactivity of nanocomposites of red phosphorus in the phosphorylation of 4-vinylbenzyl chloride in a concentrated aqueous solution of the KOH–dioxane–phase-transfer catalyst system [10]. However, this phenomenon has not been studied in detail before the present work.

In this paper, we report new data on the synthesis, structure, and higher reactivity of nanocomposites of red phosphorus in comparison with its common amorphous modifications.

A sample of nanocomposite of red phosphorus with organophosphorus compounds was obtained by radiation-induced (gamma radiation of ^{60}Co) polymerization of white phosphorus in benzene at ambient temperature (irradiation time 93 h, absorbed dose 117 kGy at a dose rate of 0.35 Gy/s) (Scheme 2).

$$P_4 \xrightarrow[C_6H_6]{^{60}Co} \text{nano-}P_n(\text{Ad});$$

Ad = C, graphite,
organophosphorus compounds

Scheme 2.

The obtained nanocomposite is a bright orange powder (self-ignition temperature is 485 K [11]). According to elemental analysis, this nanocomposite comprises mainly phosphorus (80.48%) and minor components:

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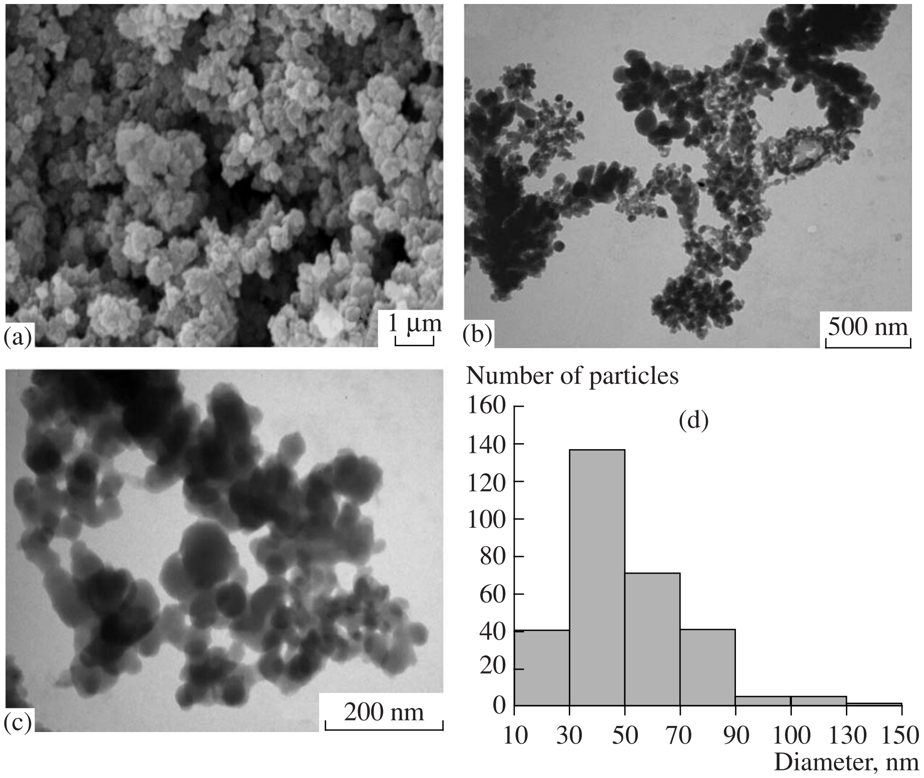


Fig. 1. Microscopic analysis of particle size of red phosphorus: (a) a general view of precipitate (SEM), (b, c) the size spread of particles (TEM), (d) the size distribution of particles.

carbon (8.13%), hydrogen (0.68%), and oxygen (about 10.71%). The presence of carbon and hydrogen in the sample indicates the chemical insertion of benzene molecules into the polymeric structure of phosphorus probably by the termination of chains with organic radicals or radical cations produced by benzene under the action of gamma radiation. Thus, the obtained sample can be considered as a composite comprising the polymers of red phosphorus with inclusions of organophosphorus polymers terminated with benzene molecules and/or the products of its radiation destruction.

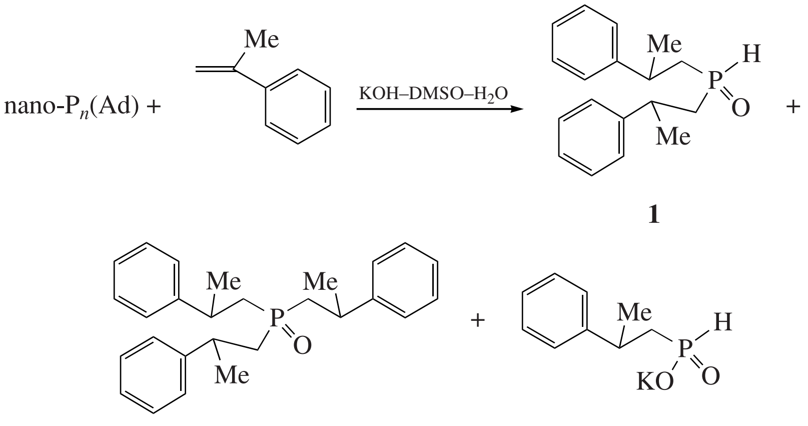
Indeed, the IR spectrum of the composite shows the absorption bands of benzene ring at 1580 and 1477 cm^{-1} (ν C=C), 737 and 690 cm^{-1} (δ CH), and the bands of stretching vibrations of P–C (740 cm^{-1}) and P–P bonds (485 and 519 cm^{-1}) [12]. All these data indicate the chemical binding of solvent fragments (benzene) to the resulting phosphorus polymer [6]. Oxygen is involved in the composite upon handling in air owing to the oxidation of the most chemically reactive cites (defects) [2, 9] and represented as functional groups with phosphorus–oxygen bonds: IR (cm^{-1}): 1143–1161 (ν P=O), 850–1050 (ν P–O, δ P–O–C, δ P–O–P, δ H–P–O) [12].

It should be noted that the IR spectrum of common red phosphorus of technical grade (State Standard GOST 4133 no. 00N1338, batch 101 of November 2001) along with the expected absorption bands at 523 cm^{-1} (ν P–P) also shows low-intensity absorption bands indicating the oxidation of red phosphorus in air (IR, cm^{-1}): 2311 (ν P–H), 1161 (ν P=O), 800–1050 (ν P–O, δ P–O–P, δ H–P–O), 744, 699 (δ P–P=O).

The Raman spectrum of the nanocomposite obtained shows the bands of bending and torsion vibrations of P–P bonds (δ P–P–P, τ P–P–P–P) in the range 100–290 cm^{-1}, intense bands at 356, 386, and 456 cm^{-1} (ν P–P) typical of cage species P_9, P_8, and P_7, respectively [13, 14], and the bands in the range 340–429 cm^{-1} that can be related to the disordered amorphous component of the nanocomposite. It should be noted that the Raman spectrum shows a specific set of narrow bands at 465, 504, and 600 cm^{-1} (ν P–P) characteristic of P_4 tetrahedron [15]. A weak band at 998 cm^{-1} is likely to refer to the vibrations of benzene ring (δ C–H), bands at 1350 and 1580 (ν C–C) seems to refer to graphite-like structures, while P–H stretching vibrations appear at 2247 cm^{-1}. At the same time, the Raman spectrum of technical amorphous red phosphorus shows no distinct maxima.

The data of scanning and transmission electron microscopy (SEM and TEM) indicate that the obtained sample is indeed a nanocomposite and consists of spherical or elliptical particles of 10–140 nm in size (Figs. 1a–1c). Figure 1d shows the size distribution of the particles, it is seen that the sample consists mainly (by 45%) of nanoparticles of 30–50 nm in size.

To estimate the phosphorylating ability of the obtained nanocomposite of red phosphorus, we studied its reaction with α-methylstyrene in comparison with common red phosphorus. The reaction of the red phosphorus nanocomposite proceeds on heating (120°C, 3 h) of the reagents in a KOH–DMSO system and leads to the formation of secondary (**1**) and tertiary (**2**) phosphine oxides and potassium phosphinite (**3**) in 95% total yield at the ratio 4.9 : 1.8 : 1. The conversion of the red phosphorus nanocomposite and α-methylstyrene was 100 and 17%, respectively (Scheme 3).



1

2

3

Scheme 3.

Under these conditions, the reaction leads also to minor amounts of phosphine and potassium hypophosphite, the products resulting from the reaction of elemental phosphorus with aqueous potassium hydroxide [8].

Technical amorphous red phosphorus reacts less efficiently with α-methylstyrene under similar conditions but more selectively to give tertiary phosphine oxide **2** in only 15% yield (the conversions of phosphorus and α-methylstyrene are 82 and 18%, respectively).

Thus, we have shown that elemental phosphorus nanocomposites obtained from white phosphorus with the use of high-energy radiation have enhanced reactivity as compared with common red phosphorus. In the presence of strong bases, these nanocomposites efficiently phosphorylate even weak electrophile as α-methylstyrene.

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