A new method for the preparation of solution of sodium pentaphosphacyclopentadienide

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Heating of a mixture of white phosphorus and sodium in diethylene glycol dimethyl ether in the presence of catalytic amounts of dibenzo-18-crown-6 affords a pure solution of sodium pentaphosphacyclopentadienide NaP_5. One of the intermediate products is trisodium heptaphosphide Na_3P_7. The influence of the nature of a metal (Li, Na, K) on the formation of the pentaphosphacyclopentadienide anion was studied.

Key words: homopolyatomic clusters, polyphosphides, pentaphosphacyclopentadienide anion, white phosphorus, alkaline metals, phase transfer catalysis.

Homopolyatomic clusters also named Zintl ions[1] and, in particular, metal polyphosphides,[2] attract keen attention of researchers. On the one hand, these compounds are intermediates in processes of elemental phosphorus transformation and, hence, studies of their structure and chemical properties allow deeper understanding of the mechanism of these reactions.[3] On the other hand, alkaline metal polyphosphides containing phosphorus atoms in different oxidation states represent unique systems for the design of related complex polydentate molecules and clusters of potential practical significance.[4] Thus, the development of new convenient methods for syntheses of alkaline metal polyphosphides is an important and urgent task.

The pentaphosphacyclopentadienide anion P_5^- (**1**) should be especially distinguished of the diversity of presently known alkaline metal polyphosphides. Anion **1** is the only polyphosphide with properties of an aromatic compound. According to the data of quantum chemical calculations,[5] this anion exists as a planar ring with six π-electrons, thus satisfying the aromaticity principle. In addition, anion **1** is an isolobal analog[6] of the cyclopentadienide anion (Cp^-), being one of the most popular ligands in organometallic chemistry. This forms a good foundation for comparison of chemical properties of both anions and makes it possible to contribute to the solution of the fundamental problem of the chemistry of organoelement compounds: the principle of diagonal relationship between carbon and phosphorus.[7]

Several approaches to the generation of anion **1** existing only in solution are presently known. Heating of a mixture of alkaline metal dihydrophosphide MPH_2 (M = Li, Na, K) and elemental phosphorus[8—10] produced a mixture of polyphosphides from which a pure solution of MP_5 was isolated by low-temperature recrystallization. However, a great amount of phosphine PH_3 is formed in this reaction, which requires special apparatus design of the synthesis. The reaction of white phosphorus with alkaline metals seems to be a more convenient method. However, reflux of a mixture of white phosphorus and sodium in diglyme[10] produces only a mixture of polyphosphides. The reaction of white phosphorus with sodium in tetrahydrofuran in the presence of equimolar amounts of crown ether also affords a mixture of polyphosphides from which sodium pentaphosphacyclopentadienide was isolated in the pure state by low-temperature recrystallization.[11] The formation of higher alkaline metal polyphosphides (Na_3P_{19}, Na_3P_{21}, *etc.*) with low solubility was mentioned in all studies on the topic.

We assumed that the presence of phase transfer catalysts in the reaction of white phosphorus with alkaline metals would increase the yield of anion **1** and decrease the fraction of by-products (higher polyphosphides). It also was of interest to reveal the role of other factors, such

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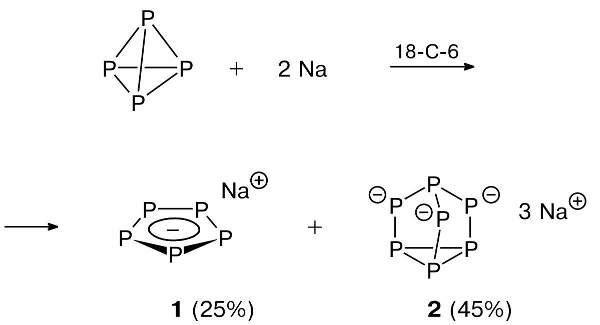
as the metal nature, reaction temperature, and solvent nature.

We found that the reaction of white phosphorus with sodium in a diglyme solution in the presence of catalytic amounts of the phase transfer catalyst (dibenzo-18-crown-6) substantially changes the distribution of the reaction products, which is confirmed by the ^{31}P NMR spectra of the reaction mixtures (Scheme 1, Fig. 1).

Scheme 1



The singlet at +469 ppm corresponds to sodium pentaphosphacyclopentadienide (**1**), and the other signals can be attributed to different higher sodium polyphosphides. Cooling followed by filtration of the reaction mixture makes it possible to obtain a solution of anion **1** containing no other polyphosphides. The calculation of the concentration by comparison of the signal intensities in the ^{31}P NMR spectrum of the obtained solution of P_5^- and a solution of phosphonium salt with a known concentration showed that the concentration of the solution was ~$5 \cdot 10^{-2}$ *M*, which corresponds to the ~22% yield of the pentaphosphacyclopentadienide anion based on the introduced phosphorus.

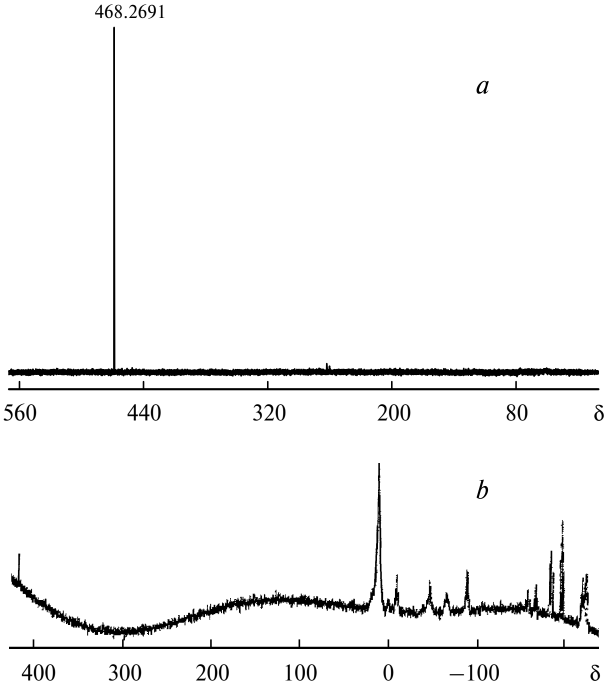
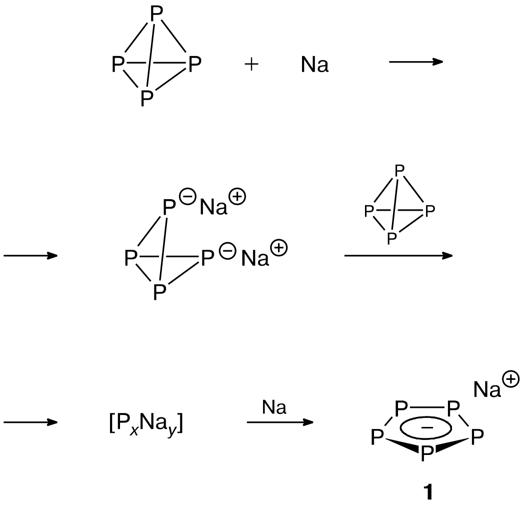


Fig. 1. ^{31}P NMR spectra of the reaction mixtures prepared by heating of a mixture of sodium and white phosphorus in diethylene glycol dimethyl ether for 5 h at 162 °C in the presence (*a*) and absence (*b*) of dibenzo-18-crown-6.

A more detailed analysis of the precipitate formed in this reaction showed that the main component of the precipitate is trisodium heptaphosphide (**2**), which was isolated from the reaction mixture in 45% yield by extraction with THF .

As a possible explanation for the influence of the phase transfer catalyst on the direction of the process, we can propose that the phosphide anion, which is formed in the reaction of white phosphorus with sodium, is a strong nucleophile[12] and reacts with the next P_4 molecule giving oligomeric sodium polyphosphides that are poorly soluble in diglyme and precipitate from the reaction mixture (Scheme 2).

Scheme 2



The presence of crown ether allows one to enhance the solubility of polyphosphides, which are rearranged in solution under the action of sodium, thus increasing substantially the yield of anion **1**.

Important factors affecting the yield of anion **1** are the metal nature and reaction temperature. It is known that elemental phosphorus interacts efficiently with alkaline metals in a solvent with the boiling point higher than the melting point of the metal.[13] Indeed, the use of lithium (m.p. 192 °C) instead of sodium also results in the formation of anion **1** but in much poorer yield and with lower purity. At the same time, when sodium was replaced by potassium (m.p. 39 °C) or a sodium—potassium alloy,

^{31}P NMR spectroscopy detected the formation of anion **1**. However, a large amount of polyphosphides is formed in this case. This can be related to a larger ion radius of the potassium atom, which probably predetermines a tendency for the formation of high polyphosphides.[2]

The choice of the solvent is also significant. Anion **1** was found to exist only in solution and cannot be isolated in the pure state. It can be assumed that the sodium atom in molecule **1** is solvated by solvent (diglyme) molecules, preventing interaction between the cation and anion and, correspondingly, stabilizing anion **1**. We found no cation-anionic interactions in the case of sodium 1,2-diphosphacyclopentadienide obtained in diglyme.[14]

Thus, we found that the reaction of white phosphorus with sodium in the presence of the phase transfer catalyst in diglyme changes the direction of the process and increases the yield of the pentaphosphacyclopentadienide anion.

Experimental

All procedures associated with arrangement of the synthesis, purification of starting reagents, and isolation of products were carried out in inert atmosphere (Ar) using the standard Schlenk technique. Diethylene glycol dimethyl ether was distilled above sodium in inert atmosphere. Prior to use white phosphorus was dried by successive washing with acetone, ethanol, and ether and then dried *in vacuo*. ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer with a working frequency of 121.7 MHz using 85% H_3PO_4 as external standard.

Synthesis of sodium pentaphosphacyclopentadienide solution. A mixture of white phosphorus (1.4 g, 0.011 mol), powdered sodium (0.6 g, 0.026 mol), and dibenzo-18-crown-6 (20 mg, catalytic amount) in anhydrous diglyme (40 mL) was stirred with reflux in argon atmosphere for 6 h. During stirring the mixture turned yellow. After cooling and filtration of the precipitate that formed, the resulting solution can be used for further syntheses without additional purification. The concentration of compound **1** in the solution was $\sim 5 \cdot 10^{-2}$ mol L^{-1}. ^{31}P NMR: +469.2 ppm (s).

The extraction of the precipitate with tetrahydrofuran followed by evaporation gave 3.17 g (45%) of trisodium heptaphosphide $(Na(diglyme)_2)_3P_7$ as an orange powder. Found (%): C, 38.52; H, 7.54; P, 20.45. $C_{36}H_{84}Na_3O_{18}P_7$. Calculated (%): C, 39.64; H, 7.76; P, 19.88. ^1H NMR (THF-d_8), δ: 3.22 (s, 18 H, MeO); 3.34, 3.42 (both t, 6 H each, OCH_2, $^3J_{H,H}$ = 5.4 Hz). ^{31}P NMR (THF-d_8), δ: −120 (br.s).

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