Inorganic Chemistry

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Nucleophilic Activation of Red Phosphorus for Controlled Synthesis of Polyphosphides

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Cite This: https://dx.doi.org/10.1021/acs.inorgchem.0c00108

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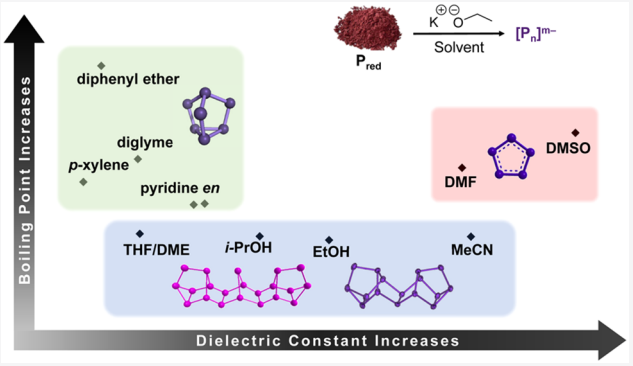
ABSTRACT: Reactions between red phosphorus (P_{red}) and potassium ethoxide in various organic solvents under reflux convert this rather inert form of the element to soluble polyphosphides. The activation is hypothesized to proceed via a nucleophilic attack by ethoxide on the polymeric structure of P_{red}, leading to disproportionation of the latter, as judged from observation of $P(OEt)_3$ in the reaction products. A range of solvents has been probed, revealing that different polyphosphide anions (P_7^{3-}, P_{16}^{2-}, P_{21}^{3-}, and P_5^-) can be stabilized depending on the combination of the boiling point and dielectric constant (polarity) of the solvent. The effectiveness of activation also depends on the nature of nucleophile, with the rate of reaction between P_{red} and KOR increasing in the order *t*-Bu < *n*-Hex < Et < Me, which is in agreement with the increasing order of nucleophilic strength. Thiolates and amides were also examined as potential activators, but the reaction with these nucleophiles were substantially slower; nonetheless, all reactions between P_{red} and NaSR yielded exclusively P_{16}^{2-} as a soluble polyphosphide product.



INTRODUCTION

Elemental phosphorus can exist as several allotropes, including white, red, black, and violet phosphorus. The most common of them, the white and red allotropes, have been favored as precursors for the synthesis of phosphorus-containing organic and inorganic chemicals and materials.[1−12] The ability of phosphorus atoms to form up to three homonuclear bonds leads to a rich variety of polyphosphide anionic structures, including extended networks, chains, and multinuclear clusters.[1,13−17]

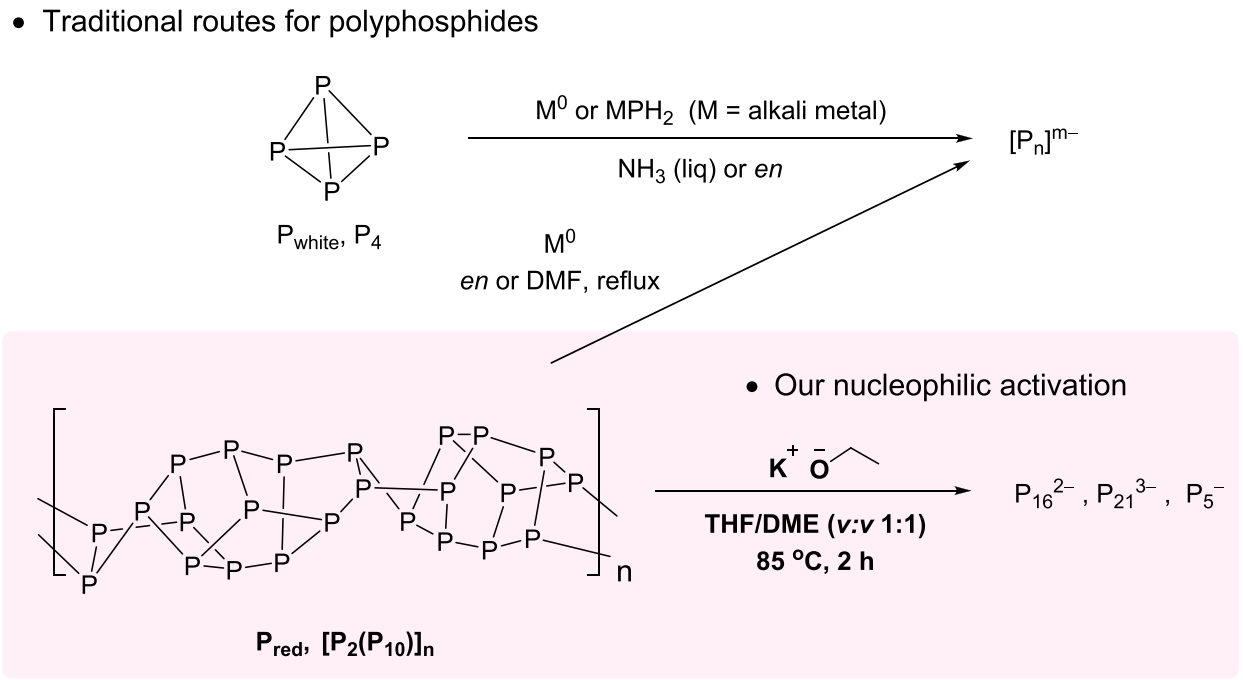
The synthetic routes to polyphosphide clusters can be divided in two broad categories. On one side are solid-state methods, such as annealing and chemical vapor transport, in which metals are typically reacted with red phosphorus (P_{red}) at elevated temperatures.[1,18−28] On the other side are solution methods, which typically utilize white phosphorus (P_{white}).[2,3,14,29−40] The pronounced reactivity of this low-melting (44 °C) and volatile allotrope originates from the strained bonds and easily accessible lone electron pairs in its tetrahedral P_4 molecules. The excellent reactivity and solubility of P_{white} notwithstanding, the use of this allotrope is problematic from safety and sustainability viewpoints, given its high volatility, flammability, and toxicity, which have led to restricted and regulated commercial offering.

The P_{red} allotrope offers an alternative, shelf-stable phosphorus source, but its solution-phase activation has received relatively little attention, due to its insoluble and inert nature caused by the amorphous polymeric structure.[41] Consequently, the initiation of reactions between metals and P_{red} usually requires higher temperatures, which are easily attained only with solid-state methods. Such methods, however, suffer from the high vapor pressure of phosphorus at elevated temperatures,[1] which creates the hazard of explosion and impedes the reaction scale-up. Furthermore, the majority of polyphosphides obtained by solid-state methods are insoluble in common solvents, which limits their utility as building blocks for further synthetic exploration. Thus, development of new approaches for the solution activation of P_{red} would enable comprehensive reactivity studies of the resulting polyphosphides in solution. So far, only a limited number of studies have pursued the activation of P_{red} in solution to generate soluble polyphosphide species.[42−45]

Another complication encountered in the solution chemistry of polyphosphides is the highly fluxional nature of these fragments, which can easily interconvert in the course of the reaction.[13,46] Thus, considering the activation of P_{red} or P_{white} in solution, it is important to control carefully the reaction conditions, such as temperature, solvent, and reaction time, in

Received: January 12, 2020

Scheme 1. Traditional Solution Synthetic Routes for the Transformation of Elemental Phosphorus Allotropes to Polyphosphides and Our Nucleophilic Activation That Employs Potassium Ethoxide[a]



[a]DMF = dimethylformamide, en = ethylenediamine.

order to achieve better understanding of the reaction pathways and direct the reaction toward the formation of a single polyphosphide species.

Recently, we developed a facile solution-based synthetic route to transform P_{red} to soluble polyphosphides under mild reaction conditions.[47] Potassium ethoxide (KOEt), which is a common organic nucleophile, was employed as an activator for P_{red}, and simple reflux in a tetrahydrofuran/dimethoxyethane mixture (THF/DME, 1:1 v/v) led to the complete dissolution of P_{red} within 2 h, affording a mixture of soluble polyphosphide species, P_5^-, P_{16}^{2-}, and P_{21}^{3-} (Scheme 1). Removing the solvent under a vacuum and redissolving the residual product in ethanol (EtOH) resulted in a solution containing a single polyphosphide species, P_{16}^{2-}. Additionally, the process has been adapted to a flow reactor, thus demonstrating that this method for activation of P_{red} is both scalable and practical.

Inspired by this discovery, we decided to expand the studies on the activation of P_{red} under varied reaction conditions to establish a more complete picture of the reactivity of this allotrope in solution. In particular, we have evaluated a variety of activation conditions that rely on the choice of solvent and reaction temperature, in an effort to develop reliable solution routes for the generation of polyphosphide clusters with various nuclearities. We have also explored other potential activators by screening several organic nucleophiles to identify efficient reagents that could selectively deliver a specific polyphosphides species. The results of these extensive studies on the solution-phase activation of P_{red} are described below.

MATERIALS AND METHODS

Synthesis. All reactions were performed in an Ar-filled glovebox. Red phosphorus (99.999%, Alfa Aesar) was used as received. Potassium alkoxides were prepared from K metal (99.5%, Alfa Aesar) and the corresponding alcohols by stirring for 12 h at room temperature (RT) and removing the excess of solvent under reduced pressure. Sodium thiolates were purchased from Sigma-Aldrich, except for sodium hexylthiolate, which was prepared by reacting 1-hexanethiol with sodium metal in THF, followed by drying under reduced pressure. Amides were purchased from Sigma-Aldrich and used without further purification. Acetonitrile (MeCN), hexane, toluene, THF, and EtOH were obtained as HPLC or ACS reagent grade solvents and further purified by passing through a system of double-drying columns packed with activated alumina and molecular sieves (Glass Contour Inc.). The other anhydrous solvents were purchased in SureSeal bottles from Sigma-Aldrich and used as received.

General Procedure for Solvent Screening Experiments. A 7 mL vial was charged with P_{red} (46.4 mg, 1.50 mmol) and freshly prepared KOEt (126 mg, 1.50 mmol). A desired solvent (3 mL) was added to the reaction vessel, which was then tightly closed with a screw-cap. The resulting suspension was stirred at reflux until all P_{red} had been consumed or until no visible changes were taking place anymore. The reaction mixture was allowed to cool to RT and sampled for analysis by NMR spectroscopy in an air-free NMR tube (Wilmad-LabGlass).

In the cases when an insoluble product was formed in the reaction, the precipitate was isolated and dissolved in DMF at RT to take advantage of the solubility of K_3P_7 and insolubility of P_{red} in this solvent. The mass of the precipitate that was not dissolved provided an estimate for the extent of the conversion of P_{red} to polyphosphides. The full dissolution of such precipitate in DMF indicated the complete conversion.

General Procedure for Activation with Thiolates. A 7 mL vial was charged with P_{red} (46.4 mg, 1.50 mmol) and a specific thiolate (1 equiv, 1.50 mmol), and the mixture was suspended in 3 mL of THF/DME (1:1 v/v). After heating at reflux for 24 h in the tightly closed vessel, the mixture was cooled to RT and sampled for analysis by NMR spectroscopy in an air-free NMR tube.

$^{31}P\{^1H\}$ NMR Spectroscopy. NMR spectra of the polyphosphide products were recorded with complete proton decoupling at frequencies of 600 MHz for ^1H and 243 MHz for ^{31}P. The chemical shifts were referenced to an 85% aqueous solution of H_3PO_4 at 0 ppm.

https://dx.doi.org/10.1021/acs.inorgchem.0c00108
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Each sample was prepared under an Ar atmosphere by sampling 0.5 mL of the reaction mixture, filtering, and dispensing into an air-free NMR tube, followed by insertion of a sealed coaxial insert (85% H_3PO_4 in D_2O) for locking and referencing. Products were identified by comparison to spectral data reported in the literature.

UV−vis Spectroscopy. Optical absorption spectra were recorded in the 200−800 nm range on a Varian Cary 300 Bio UV−vis spectrometer. All solutions were prepared in an Ar-filled glovebox by 50-fold dilution of sampled aliquots and transferred into quartz cuvettes for air-free measurements.

RESULTS AND DISCUSSION

Solvent Screening. We previously reported that the progress of the solution-phase activation of P_{red} by KOEt depended on the solvent used for reflux.[47] While low-boiling hydrocarbons, such as pentane and hexane, did not induce any transformation after 24 h, reflux in THF/DME or MeCN led to a similar mixture of soluble polyphosphides, with the reaction being complete within 2 h. We discovered that the same reaction in refluxing DMF resulted in complete dissolution of P_{red} within 30 min and exclusive formation of the aromatic P_5^- species, as shown by ^{31}P NMR (Figure 1).

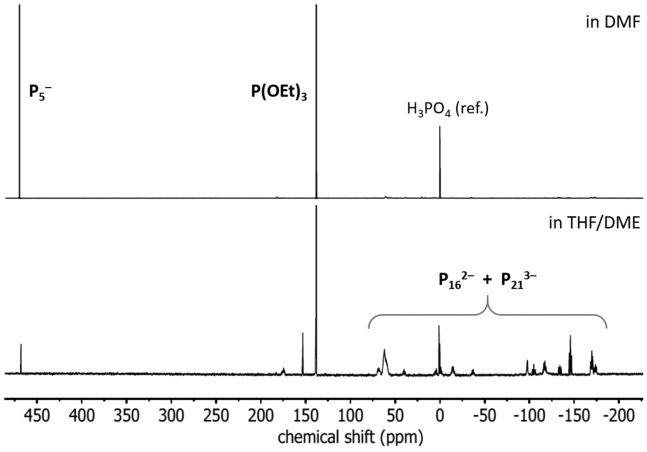

Figure 1. $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures obtained by the activation of P_{red} with KOEt in refluxing DMF (top) and in refluxing THF/DME (bottom).

Recognizing the significant impact of solvent on the activation of P_{red}, the reaction between the element and KOEt was explored in a range of organic solvents commonly available in a laboratory. The solvents were chosen to provide a range of boiling points (T_b) and dielectric constants (ε). Consequently, the reaction temperature was equal to the T_b of the particular solvent that, together with the solvent polarity, determined the nature and distribution of the resulting polyphosphide species, depending on their solubility and stability in the resulting reaction mixture.

All reactions were carried out under identical conditions, except for the reaction temperature, which was dictated by the T_b value. An equimolar mixture of P_{red} and KOEt in a solvent of interest was heated at reflux until P_{red} was completely consumed or no further visible changes were observed for a prolonged time (Table 1). The resulting polyphosphides were identified by solution ^{31}P NMR analysis, in accordance with chemical shifts reported in the literature,[29,48,49] except for P_7^{3-}, which was obtained as a precipitate in the majority of solvents due to the poor solubility of its potassium salt (see below). All reactions also generated $P(OEt)_3$ as a byproduct of the disproportionation. In Table 1, the molar ratio between different polyanions is shown for cases when two or more soluble polyanions were observed in the reaction mixture.

The formation of the heptaphosphide K_3P_7 was confirmed by solid-state ^{31}P NMR (Figure S1), which revealed a broad characteristic singlet at −117 ppm. It was also possible to redissolve this product in DMF and obtain a solution spectrum that confirmed the presence of P_7^{3-}.[50] The complete dissolution of K_3P_7 in DMF at room temperature provided confirmation for the complete conversion of P_{red} to polyphosphides in the reactions performed in *p*-xylene, diphenyl ether, diglyme, THF/DME, and pyridine (entries 3−7), in contrast to the lack of reactions in pentane or hexane (entries 1−2).

The reactions in solvents with T_b > 150 °C required shorter times (typically <1 h) to convert all P_{red} to polyphosphide fragments (entries 4, 5, 12, and 13). In spite of a high T_b (138 °C), *p*-xylene did not promote a fast reaction (entry 3), indicating that the ease of activation depends not only on the thermal energy but also on solvent's polarity. The majority of reactions in sufficiently polar solvents were complete within 3 h even at moderate T_b, although alcohols, such as EtOH and *i*-PrOH, performed poorly, as residual starting material was observed even after 24 h (entries 9, 10). The extent of P_{red} conversion to polyphosphides increased from 2% in *i*-PrOH and 9% in EtOH after 24 h to 11% and 20%, respectively, after 48 h. Besides the slow kinetics of this conversion, it is also worth pointing out the lack of P_5^- generation in these protic solvents, which also might explain the generation of only P_{16}^{2-} species under such conditions. In aprotic solvents, the simultaneous presence of P_5^- and P_{16}^{2-} was accompanied by the appearance of P_{21}^{3-} (entries 6, 11, and 13), most likely produced by condensation of the former two polyphosphide anions. Removing the THF/DME solvent from the mixture of P_5^-, P_{16}^{2-}, and P_{21}^{3-} (entry 6) and redissolving the residue in EtOH led to a solution containing exclusively P_{16}^{2-}. Thus, the aromatic P_5^- species appears to be incompatible with protic solvents.

Analysis of the reaction outcomes revealed a correlation between the type of polyphosphides formed and the T_b and ε values of the solvents, as shown in the correlation diagram (Scheme 2). High-boiling nonpolar solvents (with high T_b and low ε values), such as diphenyl ether, diglyme, and *p*-xylene, produced a large amount of a yellow precipitate, identified as K_3P_7, which contained the most reduced polyphosphide species, P_7^{3-} (Table 1, entries 3−5). The polyanions P_{16}^{2-} and P_{21}^{3-} mainly appeared in aprotic polar solvents with T_b < 100 °C. The major product obtained in alcohols, in spite of the slow reaction progress, was P_{16}^{2-}, which agrees with the observation by us[47] and others[46] that EtOH promotes the conversion of a polyphosphide mixture into the sole P_{16}^{2-} species. As argued above, the formation of pure P_{16}^{2-} in protic solvents might result from the instability of P_5^- under such conditions that also impede the formation of P_{21}^{3-}.

The formation of the planar aromatic P_5^- anion was especially noticeable in DMF and DMSO, which afforded the highest combination of T_b and ε values among the studied solvents (entries 12, 13). These reactions yielded very intense red-colored solutions. Thus, it appears that the activation in high-boiling and polar solvents leads to complete disassembly of the P_{red} structure into the elementary pentagonal phosphorus fragments, which have long been viewed as the fundamental building blocks of this amorphous poly-

https://dx.doi.org/10.1021/acs.inorgchem.0c00108
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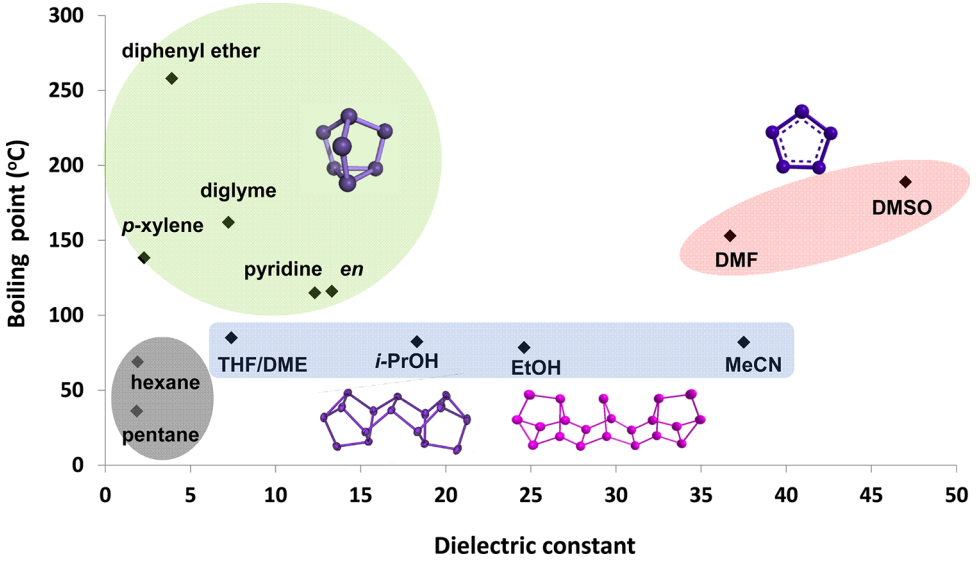
Table 1. Activation of P_{red} in Various Solvents

$$P_{red} + KOEt \xrightarrow[\text{reflux}]{\text{solvent}} K_mP_n + P(OEt)_3$$

entry	solvent	ε	T_b (°C)	reaction time (h)	soluble polyphosphide products[a]	solid product[a]
1	pentane	1.84	36.1	48	no conversion	
2	hexane	1.89	69	48	no conversion	
3	*p*-xylene	2.27	138	24		P_7^{3-}
4	diphenyl ether	3.9	258	0.5		P_7^{3-}
5	diglyme	7.23	162	0.5		P_7^{3-}
6	THF/DME (1:1)	7.2–7.6	85	2	P_{16}^{2-}, P_{21}^{3-}, P_5^- (7:17:1)	P_7^{3-}
7	pyridine	12.3	115	2	P_5^-	P_7^{3-}
8	ethylenediamine	13.3	116	3	P_7^{3-}, P_{11}^{3-} (7:1)	
9	*i*-PrOH	18.3	82.4	24	P_{16}^{2-} (2% conversion)	
10	EtOH	24.6	78.5	24	P_{16}^{2-} (9% conversion)	
11	MeCN	37.5	81.6	2	P_{16}^{2-}, P_{21}^{3-}, P_5^- (10:16:1)	
12	DMF	36.7	153	0.5	P_5^-	
13	DMSO	47	189	0.25	P_5^-, P_4CH^- (1:1.8), P_{16}^{2-}, P_{21}^{3-} (traces)	

[a]For brevity, only polyphosphide anions are indicated. The charge balance is provided by K^+ cations. Where two or more soluble polyanions were observed in solution, their molar ratio is indicated in parentheses. The ratio was quantified from the ^{31}P NMR spectra available in the Supporting Information file.

Scheme 2. Correlation between the Solvent's Characteristics and the Major Polyphosphide Products Observed in the Reactions between P_{red} and KOEt



morph.[41,51] In contrast to the reaction performed in DMF, which led to the clean generation of the P_5^--containing solution, the reflux of P_{red} and KOEt in DMSO led to the generation of P_5^- and its isoelectronic analogue, P_4CH^-, in the 1:1.8 molar ratio. The formation of P_4CH^- is likely promoted by partial thermal decomposition of DMSO, accelerated under basic conditions, with the formation of methylthiolate, formaldehyde, and other byproducts.[52] In a similar fashion, the formation of P_4CH^- was reported to accompany the activation of P_{white} to P_5^- by metallic sodium in refluxing diglyme.[49] In the present work, however, we did not observe such an effect during the activation of P_{red} with KOEt in diglyme.

Nucleophilic Scope. In our attempts to activate P_{red} with various potassium alkoxides, KOR, we observed that the reaction rate depended on the size of the alkyl substituent, R, with bulkier nucleophiles slowing down the activation process, probably due to steric hindrance effects. While activation of P_{red} with KOMe and KOEt proceeded to completion within 2 h, the reaction with KO(*n*-Hex) was slower and the one with KO(*t*-Bu) did not reach completion even after 24 h. Nevertheless, while the activation with KOMe, KOEt, and KO(*n*-Hex) yielded a mixture of polyphosphides, the reaction with KO(*t*-Bu) produced only P_{16}^{2-}. It is possible that the lack of formation of P_5^- (and P_{21}^{3-}) upon activation of P_{red} with KO(*t*-Bu) in THF/DME is caused by the slow kinetics of the reaction, similar to the observations in the activation with KOEt in EtOH or *i*-PrOH (Table 1). The P_{16}^{2-} anion is the least reduced polyphosphide species among those that we have observed thus far in our activation reactions, and therefore it appears that the disproportionation of P_{red} into $P(OEt)_3$ and polyphosphide anions is less efficient in such slow processes.

The consistent observation of the $P(OEt)_3$ byproduct clearly supports the hypothesis that the activation proceeds via nucleophilic attack of the alkoxide anion on the oligomeric structure of P_{red}, causing the gradual cleavage of P–P bonds

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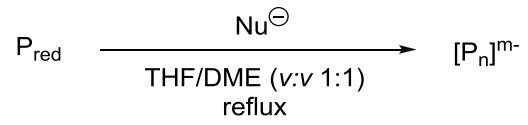
through a cascade of disproportionation and rearrangement events to generate stable and soluble polyphosphide clusters. Recognizing the feasibility of the nucleophilic initiation for the activation of P_{red} in solution, we have explored other nucleophilic reagents, presented in Table 2. In addition to alkoxides, thiolates and amides were selected because of their well-studied nucleophilic reactivity in organic synthesis.

Table 2. Activation of P_{red} with Various *O*-, *S*-, and *N*-Based Nucleophiles



reagent	reaction time (h)	soluble polyphosphide products
Alkoxides		
KOMe	2	P_{16}^{2-}, P_{21}^{3-}, P_5^-
KOEt	2	P_{16}^{2-}, P_{21}^{3-}, P_5^-
KO(*n*-Hex)	12	P_{16}^{2-}, P_{21}^{3-}, P_5^-
KO(*t*-Bu)	24 (incomplete)	P_{16}^{2-}
Thiolates		
NaSMe	24 (incomplete)	P_{16}^{2-} (traces)
NaSEt	24 (incomplete)	P_{16}^{2-}
NaS(*n*-Hex)	24 (incomplete)	P_{16}^{2-}
NaS(*i*-Pr)	24 (incomplete)	P_{16}^{2-}
NaS(*t*-Bu)	24 (incomplete)	P_{16}^{2-}
Amides[b]		
KHMDS	24 h	P_{16}^{2-}, P_{21}^{3-}, P_5^-
LDA	48 h (incomplete)	P_{16}^{2-}, P_{21}^{3-}, P_5^-
LiHMDS	36 h (incomplete)	P_{16}^{2-} (trace amount)

[a]For brevity, only the polyphosphide anions are indicated. The charge balance is provided by K^+ or Na^+ cations. [b]LDA = lithium diisopropylamide, LiHMDS = lithium bis(trimethylsilyl)amide, KHMDS = potassium bis(trimethylsilyl)amide.

Although amides generally serve as effective nucleophiles in organic reactions, we observed poor activity of these reagents toward activation of P_{red}. In the case of KHMDS, the full conversion was reached after 24 h, affording a mixture of soluble polyphosphide products. The use of lithium amides, such as LDA and LiHMDS, which are weaker nucleophiles than KHMDS, led to even longer activation times and lower product yields.

A few reports described the use of thiolates for activation of P_{red} or P_{white} in the presence of H_2O to produce thiophosphites or thiophosphates.[53−56] Likewise, we conducted reactions with various alkyl thiolates (Table 2) to evaluate their potential for activating P_{red} under reaction conditions similar to those used with alkoxides. A mixture of P_{red} and thiolate was heated in refluxing THF/DME (1:1 v/v). We observed that all reactions with thiolates were incomplete after 24 h, judging by the substantial amount of remaining starting materials. Longer reaction times led to degradation of the polyphosphide products, as established by comparing ^{31}P NMR spectra of soluble products obtained after 24, 48, and 72 h (Figure S2). Notably, despite incompleteness, these reactions produced solutions that contained only P_{16}^{2-}, similar to the observation made in the slow and incomplete activation of P_{red} by KOEt in EtOH or *i*-PrOH and by KO(*t*-Bu) in THF/DME. Thus, the exclusive formation of P_{16}^{2-} appears to be a general trend in the slower activation reactions. The optical absorbance of the resulting product solutions, indicative of the concentration of P_{16}^{2-}, increased in the order of R = Me < Et, *n*-Hex < *i*-Pr < *t*-Bu (Figure 2), with the highest conversion of 32% achieved in

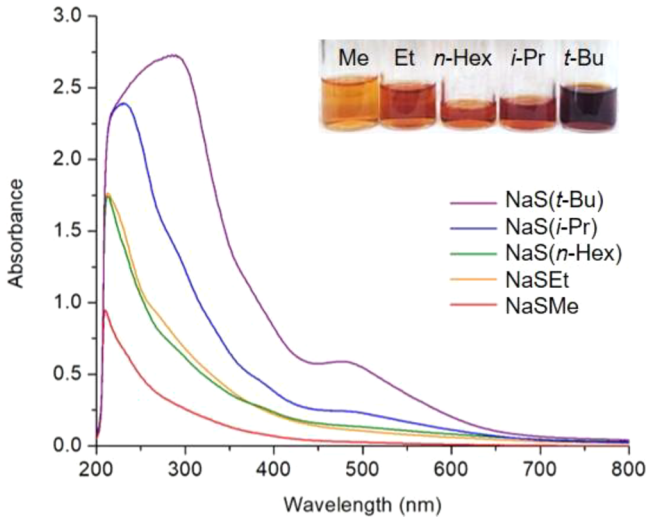


Figure 2. Optical absorption spectra of soluble polyphosphide products obtained in the 24 h reactions with thiolate activators in THF/DME (1:1 v/v). The inset shows the appearance of resulting solutions.

the case of NaS(*t*-Bu). The extent of activation of P_{red} by thiolates as a function of the alkyl substituent is in reverse order to that observed for alkoxides (Me, Et > *n*-Hex > *t*-Bu). Another interesting observation is that $P(SR)_3$ species was not detected at all in the reactions involving thiolates, in contrast to the consistent formation of $P(OR)_3$ in all reactions with the KOR activators.

We hypothesize that the slow reaction rates and the reverse reactivity trend observed for the thiolates is related to their lower solubility in the THF/DME solvent mixture. The higher solubility of NaS(*t*-Bu) in this solvent mixture might explain the higher concentration of soluble polyphosphides in the resulting solution. To increase the solubility of the thiolate reagents, we added a few drops of deaerated water to the reaction mixture, but such modification led to irreproducible results and degradation of the polyphosphide products even under air-free conditions.

The lack of the formation of $P(SEt)_3$ upon activation of P_{red} with thiolates suggests that these reactions proceed via a different mechanistic pathway as compared to the reactions with alkoxides, although we could not identify any specific sulfur-containing byproduct in the reaction mixture. Further insight into the mechanism of nucleophilic activation of P_{red} by alkoxides and thiolates could be provided by in-depth theoretical and mechanistic studies of these reactions.

CONCLUSION

We have demonstrated that the activation of red phosphorus can be achieved in various organic solvents, yielding soluble polyphosphide species. We observed that the distribution of polyphosphides obtained can be tuned as a function of solvent properties. The high-boiling and less polar solvents tend to generate more reduced heptaphosphide species, P_7^{3-}, while the high-boiling and polar solvents, such as DMF or DMSO, produce the aromatic P_5^- species in rather short reaction time (30 min). The reactions in protic solvents proceed much slower, producing only P_{16}^{2-}, without generating P_5^- or P_{21}^{3-}.

https://dx.doi.org/10.1021/acs.inorgchem.0c00108
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The use of thiolates for activation of red phosphorus does not facilitate the reaction as compared to alkoxides, but these reactions also led selectively to the P_{16}^{2-} species, although in substantially lower yields than observed for the activation with alkoxides. Thus, our strategy to activate P_{red} in solution has been expanded to a range of common organic solvents and nucleophiles, offering a convenient method for the dissolution of this seemingly "inert" form of the element. Notably, we have shown that certain reaction conditions allow selective synthesis of a specific polyphosphide anion, opening the way to using these species for further synthetic exploration. Reactivity studies of various soluble polyphosphides are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00108.

Figures of solid-state ^{31}P NMR spectra, $^{31}P\{^{1}H\}$ NMR spectra, and time-dependent ^{31}P NMR spectra (PDF)

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Funding

This project was supported by the Department of Defense (DOTC 13−01-INIT518) and in part by the National Science Foundation (CHE-1905499).

Notes

The authors declare no competing financial interest.

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https://dx.doi.org/10.1021/acs.inorgchem.0c00108
Inorg. Chem. XXXX, XXX, XXX−XXX