Propagation Mechanisms in Ring-Opening Polymerization of Small Phosphorus Heterocycles: Toward Free-Radical Polymerization of Phosphines?

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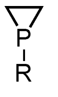
ABSTRACT: The mechanism and kinetics of the propagation step in the radical ring-opening polymerization of methylphosphirane, -phosphetane, and -phospholane, and also phenylphosphetane, were studied via high-level ab initio calculations. It was found that radical ring-opening polymerization should occur via attack of the carbon-centered propagating radical at the phosphorus center of the ring. This is a facile process (with reaction rates of the order of 10^4−10^6 L mol^{-1} s^{-1} at 298.15 K), driven by the creation of a transition structure that resembles a (relatively stable) stretched phosphoranyl radical. The reaction is fastest for the four-membered phosphetanes, reflecting the best compromise between the strain in the transition structure and the strain released by the partially broken ring bond. Though slightly slower, radical ring opening of the three-membered phosphirane should also occur, but the reaction of the five-membered phospholane is not thermodynamically favorable. On the basis of the calculations for the methyl- and phenyl-substituted heterocycles, we predict that radical ring-opening polymerization should be possible for phosphetane monomers and may also be feasible for phosphiranes, though in some situations it may be hindered by a β-scission reaction. Since the preferred propagation mechanism involves attack by a carbon-centered propagating species, we also predict that free radical copolymerization should provide a viable route to random copolymers of phosphines with normal olefins. This in turn offers the exciting prospect of incorporating phosphine units into normal polyolefins in order to alter their polarity, metal ion binding characteristics, and fire retardancy.

Introduction

Polymers containing an inorganic element in their backbone are well-known to show interesting and unique properties.[1] Most phosphorus polymers show excellent adhesion to metals, metal ion binding characteristics, and increased polarity; however, by far their most widespread commercial use is as flame-retardants, incorporated into textile fibers, thermoset resins, polyurethane, and cotton and paper finishes. The development of methods for the incorporation of phosphorus atoms directly into the backbone of ordinary polyolefins (such as polyethylene or polystyrene) is an exciting prospect, as they could potentially lead to a range of new materials, such as fire-retardant plastics or membranes with enhanced metal ion binding properties.

A synthetic method for the incorporation of phosphorus atoms into the backbone of ordinary polyolefins was recently reported by Tsang et al.[2] In this fascinating study, they demonstrated that the phosphaalkenes can undergo free-radical copolymerization with styrene and that the resulting copolymers are useful for polymer-supported catalysis. This followed their earlier work[3] in which they reported that phosphaalkenes could undergo homopolymerization in the presence of a radical or ionic initiator. Although no mechanistic studies of either process appear to have been reported, the propagating species formed by radical addition to a P=C double bond is likely to be either a carbon-centered radical with an α-phosphino substituent or a phosphorus-centered radical. Either way, the influence of the phosphorus atom might be expected to dominate the reactivity and selectivity preferences of the propagating species and limit the range of olefins for which random copolymers can be made. A polymerization process in which the phosphorus atom is further removed from the active chain end might thus expand the range of accessible materials and complement the addition polymerization process of Tsang et al.[2]

An alternative synthetic route to the incorporation of phosphorus atoms into the backbones of polyolefins would be through the free-radical copolymerization of olefinic monomers with small phosphorus heterocycles, such as phosphirane (**1**), phosphetane (**2**), or phospholane (**3**). Scheme 1 shows a possible reaction scheme for the production of a random copolymer of ethylene with the four-membered heterocycle, methylphosphetane (**2**, R = CH_3). Provided the radical ring-opening polymerization of phosphetane occurs via the C-centered radical as in (a), the propagating species is not unlike that in free radical homopolymerization of ethylene (b). Hence, the cross-propagation reactions (c) and (d) should occur and, in the very least, the formation of copolymers with ethylene should be possible, and copolymers with other olefins would be conceivable. Such a process could potentially lead to random copolymers containing the normal repeat unit of the parent polyolefin and a polyphosphine linkage. By varying the feed ratios of the comonomers, the concentration of the polyphosphine linkages in the chain could be tailored to any specific application. To date, neither the free-radical homopo-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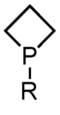
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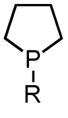
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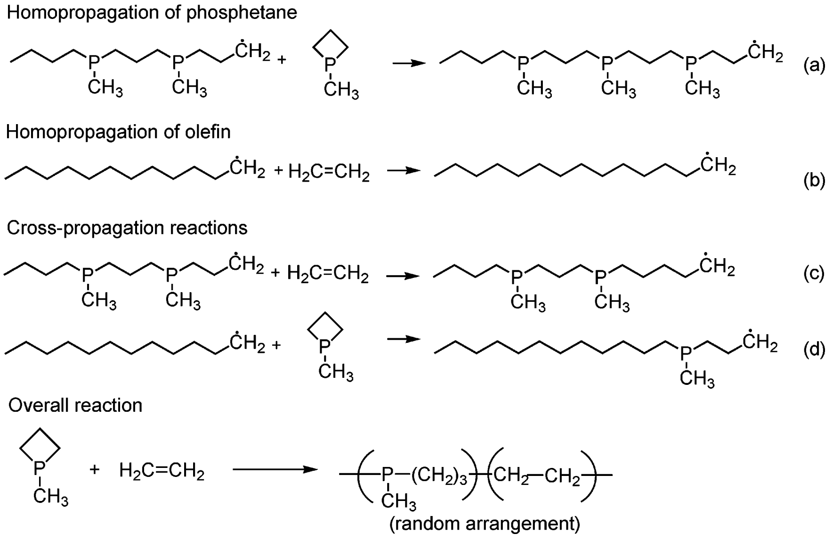
Scheme 1. Free-Radical Copolymerization of Methylphosphetane and Ethylene



lymerization nor copolymerization of phosphorus heterocycles appears to have been reported. The purpose of the present work is to use ab initio molecular orbital calculations to investigate this possibility with a view to guiding future experimental studies.[4]

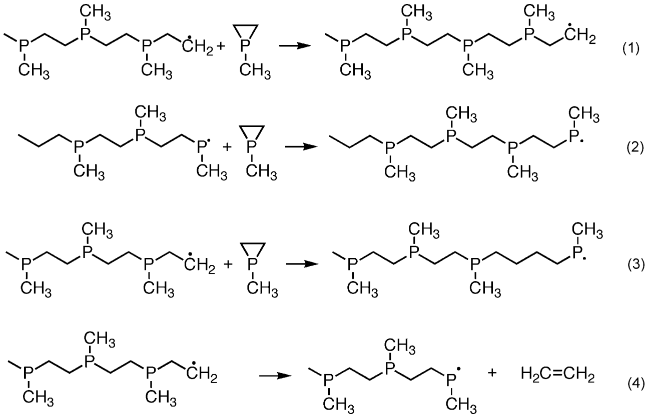
Although the radical ring-opening polymerization of small phosphorus heterocycles does not appear to have been reported, their polymerization using ionic initiators is well-known. Kobayashi and co-workers[5] have produced polyphosphines from the five- and six-membered species, 2-phenyl-1,2-oxaphospholane, 2-phenyl-1,2-thiaphospholane, and 2-phenyl-1,2-thiaphosphorinane, using a cationic initiator. Polyphosphines were then obtained via reduction of the resulting polymer. Other known ring-opening polymerizations include those of some 1,3,2-dioxaphospholanes and 1,3,2-dioxaphosphorinanes with benzyl halides.[6] Direct production of polyphosphines via the ring-opening polymerization of 1-(2,4,6-tri-*tert*-butylphenyl)phosphirane has also been achieved using ionic initiators.[6a,7] However, other phosphiranes and phosphetanes (such as *tert*-butylphosphirane, 1-(9-anthracene)phosphirane, and 3-*tert*-butyl-1-phenylphosphetane) have been found to be stable to polymerization in the presence of ionic initiators,[8] and indeed some phosphiranes (including 1-(9-anthracene)-phosphirane[8a] and 1-(2,4,6-tri-*tert*-butylphenyl)phosphirane)[6a] have also been shown to be stable to polymerization in the presence of radical initiators. Nonetheless, this does not necessarily preclude a radical ring-opening process for other appropriately substituted phosphiranes and for the phosphetanes. As noted above, alternative routes to polyphosphines have also been reported, including the addition polymerization of P=C bonds using both radical and ionic initiators[2,3] and a palladium-catalyzed cross-coupling process.[9] Moreover, other strained rings, such as phosphorus-bridged ferrocenophanes, have also been polymerized via living anionic ring-opening polymerization, and the resulting poly(ferrocenylphenylphosphines) have been used to coordinate to metals.[10]

The suggestion that a radical polymerization process may be possible for appropriately substituted phosphorus heterocycles comes from the observation that spontaneous (i.e., initiator-free) polymerization has been observed for a number of phosphiranes and phospholanes and is well documented for the case of the phosphetane. For example, in 1967 Wagner et al. reported the first synthesis of the parent phosphirane (**1**, R = H) and noted that it completely decomposed with hydrochloric acid below room temperature to an apparent polymeric phosphorus hydride within 24 h.[11a] Although it has been found that both 1-phenylphosphirane and 1-*tert*-butylphosphirane are stable liquids,[8b,11b] 1-phenylphosphetane (**2**, R = Ph) and 1-phenylphospholane (**3**, R = Ph) have been shown to exist in equilibrium with polymeric product in sufficiently concentrated solutions,[11b,c] while both 2,2,3-trimethyl-1-phenylphosphetane[11d] and 3-*tert*-butyl-1-phenylphosphetane[8c] have been observed to decompose or polymerize over a long period of time with standing and heating, respectively. Although the mechanism of these initiator-free ring-opening polymerization processes has not been established, a radical process seems plausible, and it appears that radical polymerization (for the phosphetanes at least) may be possible.

In the present work we use ab initio molecular orbital calculations to examine the possibility of a radical-ring opening route to polyphosphines and to determine the preferred propagation mechanism. Two possible models for chain propagation were considered: propagation via the C-centered radical and propagation via the P-centered radical. We also considered a possible cross-propagation mechanism in which the C-centered radical adds to a carbon atom rather than the phosphorus atom (thereby creating a P-centered radical) and the β-scission reaction in which the propagating radical loses a molecule of ethylene. These reactions are illustrated in Scheme 2 for the case of methylphosphirane. Our criterion for testing the feasibility of a radical polymerization process is on the basis of its ability to sustain a chain propagation reaction. That is, we determine whether the radical product of ring-opening is capable of opening the next phosphorus heterocycle and whether the propagation rate is high enough to compete with the known rates of radical termination reactions. We argue that if this is possible, and provided there are no side reactions that otherwise consume the propagating species, then polymerization should be feasible, and the design of a suitable free-radical initiator should be relatively straightforward.

In what follows we examine the feasibility of a radical polymerization process for methylphosphirane (**1**, R =

Scheme 2. Possible Radical Ring-Opening Propagation Steps for Methylphosphirane



CH_3), methylphosphetane (**2**, R = CH_3), and methylphospholane (**3**, R = CH_3), and also phenylphosphetane (**2**, R = Ph). We identify the preferred propagation mechanism and investigate the effects of chain length on the calculated reactivities, with a view to identifying suitable chemical models for the polymerization systems. We also study the effect of the ring size on the kinetics and thermodynamics of the various ring-opening reactions. Previous studies of the nucleophilic ring-opening reactions of some three- and four-membered heterocycles (including phosphirane and phosphetane) have noted that the three-membered ring is far more reactive than the four-membered ring despite their nearly identical stain energies and similar reaction exothermicities.[12] This has also been observed for the parent cyclopropane and cyclobutane molecules and has caused much debate.[13] Determining whether the same result is seen for the radical ring-opening reactions may help to shed light on this unusual phenomenon.

Computational Procedures

Standard ab initio and density functional theory calculations were carried out using the GAUSSIAN 03[14] and Molpro 2000.6[15] software. In the absence of specific assessment studies for the radical ring-opening polymerization reactions, calculations were performed at a high level of theory that has been demonstrated to yield reliable results for a wide range of other radical reactions, including radical addition to C=C and C=S double bonds, hydrogen atom abstraction, radical stabilization energies, and bond dissociation energies.[16] Geometries of all species were optimized at the B3-LYP/6-31G(d) level of theory, and care was taken to select the (global) minimum-energy conformation via extensive conformational searching at this level. The nature of each stationary point was established via B3-LYP/6-31G(d) frequency calculations, and transition structures were checked using intrinsic reaction coordinate (IRC) calculations performed at this level. Barriers and enthalpies were calculated using single-point energies obtained at the G3(MP2)-RAD level of theory. This high-level composite procedure aims to approximate URCCSD(T) calculations with a large triple-ζ basis set via additivity approximations and has been demonstrated to provide "chemical accuracy" (ca. 1 kcal mol^{-1}) when assessed against large test sets of thermochemical data.[17] Partition functions, and their associated enthalpies and entropies, were calculated using the B3-LYP/6-31G(d) geometries and (scaled[18]) B3-LYP/6-31G(d) frequencies via the standard textbook formulas, based on the statistical thermodynamics of an ideal gas under the rigid-rotor harmonic oscillator approximation.[19]

Reaction rates were evaluated using standard transition state theory, in conjunction with the calculated barriers and partition functions.[20]

$$k(T) = \kappa(T)\,\frac{k_{\mathrm{B}}T}{h}\,(c^\circ)^{1-m}\mathrm{e}^{(-\Delta G^\ddagger/RT)} = \kappa(T)\,\frac{k_{\mathrm{B}}T}{h}\,(c^\circ)^{1-m}\frac{Q_\ddagger}{\Pi_{\mathrm{reactants}}Q_i}\mathrm{e}^{(-\Delta E^\ddagger/RT)}$$

where $\kappa(T)$ is the tunneling correction factor (assumed to be unity for the present reactions), T is the temperature (298.15 K), k_{B} is Boltzmann's constant (1.380658 × 10^{-23} J $molecule^{-1}$ K^{-1}), h is Planck's constant (6.6260755 × 10^{-34} J s), $c°$ is the standard unit of concentration (mol L^{-1}), R is the universal gas constant (8.3142 J mol^{-1} K^{-1}), $Q^\ddagger$ and Q_i are the molecular partition functions of the transition structure and reactant i, respectively, $\Delta G^\ddagger$ is the Gibb's free energy of activation, and $\Delta E^\ddagger$ is the 0 K, zero-point energy corrected energy barrier for the reaction. The value of $c°$ depends on the standard-state concentration assumed in calculating the thermodynamic quantities (and translational partition function). In the present work, these quantities were calculated for 1 mol of an ideal gas at 298.15 K and 1 atm, and hence $c° = 0.040876$ mol L^{-1}.

To assist in the qualitative rationalization of the results, the deformation energies of the heterocycles were calculated at the G3(MP2)-RAD level of theory. These are defined as the energy difference between the isolated heterocycles in their optimized geometries and their geometry in the optimized transition structures. In addition, the vertical ionization energies (IEs) and electron affinities (EAs) of the isolated reactants were calculated at the G3(MP2)-RAD(+) level of theory. This procedure is similar to G3(MP2)-RAD; however, those energies normally calculated using a 6-31G(d) basis set are replaced with calculations using a 6-31+G(d) basis set in order to provide a better description of the anionic species. The energies for charge transfer between isolated reactants were calculated as the difference in the IE of the donor species and the EA of the acceptor species, in the usual manner. The charges and spin densities on the attacking radical and the site of attack in the transition structures were calculated using a NBO population analysis performed in GAUSSIAN at the B3-LYP/6-311+G(3df,2p) level of theory.

Finally, a Marcus analysis,[21] analogous to that adopted previously for the nucleophilic ring-opening reactions,[12] was also performed for the propagations via the P-centered radical. Under Marcus theory, the barrier is said to depend on the reaction enthalpy (ΔE_0) and the intrinsic barrier ($E_{\mathrm{a,int}}$) as follows.

$$E_{\mathrm{a,Marcus}} = E_{\mathrm{a,int}} + \frac{\Delta E_0}{2} + \frac{\Delta {E_0}^2}{16E_{\mathrm{a,int}}}$$

The intrinsic barrier is defined as the barrier of the corresponding reaction in the absence of a thermodynamic driving force, which in this case is modeled as

$$^\bullet\mathrm{P(CH_3)_2} + \mathrm{P(CH_3)_3} \rightarrow \mathrm{P(CH_3)_3} + {}^\bullet\mathrm{P(CH_3)_2}$$

For each reaction, the Marcus barrier ($E_{\mathrm{a,Marcus}}$) was calculated at the G3(MP2)-RAD level of theory and

Table 1. Kinetics and Thermodynamics (298 K)[a] of the Radical Ring-Opening of Phosphirane, Phosphetane, and Phospholane: Propagation via the C-Centered Radical, $CH_3{-}P(CH_2)_n + {}^{\bullet}CH_3 \rightarrow CH_3{-}P(CH_3)(CH_2)_{n-1}CH_2^{\bullet}$ (1)

	phosphirane $n = 2$	phosphetane $n = 3$	phospholane $n = 4$
	Propagation Reaction		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	14.9	8.9	13.5
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−124.0	−125.5	−135.2
$\Delta G^{\ddagger}$ (kJ mol^{-1})	51.8	46.3	53.8
k_{298} (L mol^{-1} s^{-1})	1.3×10^{5}	1.2×10^{6}	5.8×10^{4}
ΔH (kJ mol^{-1})	−102.9	−91.9	−20.3
ΔS (J mol^{-1} K^{-1})	−131.0	−114.1	−100.1
ΔG (kJ mol^{-1})	−63.9	−57.8	9.5
K (L mol^{-1})	3.8×10^{12}	3.3×10^{11}	5.2×10^{-1}
	Depropagation Reaction		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	117.8	100.8	33.8
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	7.0	−11.4	−35.1
$\Delta G^{\ddagger}$ (kJ mol^{-1})	115.7	104.2	44.2
k_{298} (L mol^{-1} s^{-1})	3.3×10^{-8}	3.5×10^{-6}	1.1×10^{5}

[a] Calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory in conjunction with the harmonic oscillator approximation (see text).

Table 2. Kinetics and Thermodynamics (298 K)[a] of the Radical Ring-Opening of Phosphirane, Phosphetane, and Phospholane: Propagation via the P-Centered Radical, $CH_3{-}P(CH_2)_n + {}^{\bullet}P(CH_3)_2 \rightarrow (CH_3)_2P(CH_2)_nP^{\bullet}(CH_3)$ (2)

	phosphirane $n = 2$	phosphetane $n = 3$	phospholane $n = 4$
	Propagation Reaction		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	51.6	80.4	119.3
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−139.2	−142.2	−135.4
$\Delta G^{\ddagger}$ (kJ mol^{-1})	93.1	122.8	159.7
k_{298} (L mol^{-1} s^{-1})	7.5×10^{-3}	4.7×10^{-8}	1.6×10^{-14}
ΔH (kJ mol^{-1})	−96.3	−90.0	−18.2
ΔS (J mol^{-1} K^{-1})	−148.1	−139.1	−129.2
ΔG (kJ mol^{-1})	−52.1	−48.6	20.3
K (L mol^{-1})	3.3×10^{10}	7.9×10^{9}	6.8×10^{-3}
	Depropagation Reaction		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	147.9	170.4	137.5
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	8.9	−3.1	−6.2
$\Delta G^{\ddagger}$ (kJ mol^{-1})	145.2	171.4	139.4
k_{298} (L mol^{-1} s^{-1})	2.2×10^{-13}	5.9×10^{-18}	2.4×10^{-12}

[a] Calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory in conjunction with the harmonic oscillator approximation (see text).

Table 3. Kinetics and Thermodynamics (298 K)[a] of the Cross-Propagation (3) and β-Scission (4) Side Reactions in the Radical Ring-Opening Polymerization of Phosphirane, Phosphetane, and Phospholane

	phosphirane	phosphetane	phospholane
	Cross-Propagation Reaction[b]		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	65.5	96.3	135.7
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−124.2	−133.3	−133.1
$\Delta G^{\ddagger}$ (kJ mol^{-1})	102.5	136.1	175.3
k_{298} (L mol^{-1} s^{-1})	1.7×10^{-4}	3.5×10^{-23}	4.6×10^{-30}
	β-Scission Reaction[c]		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	43.2	104.6	
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	9.4	5.1	
$\Delta G^{\ddagger}$ (kJ mol^{-1})	40.4	103.0	
k_{298} (L mol^{-1} s^{-1})	5.2×10^{5}	5.5×10^{-6}	

[a] Calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory in conjunction with the harmonic oscillator approximation (see text). [b] Reaction: $CH_3{-}P(CH_2)_n + {}^{\bullet}CH_3 \rightarrow CH_3(CH_2)_nP^{\bullet}(CH_3)$. [c] Reaction: $CH_3{-}P^{\bullet}(CH_3)CH_2CH_2 \rightarrow CH_3{-}P(CH_3)^{\bullet} + CH_2{=}CH_2$ for phosphirane and $CH_3{-}P(CH_3)CH_2CH_2CH_2^{\bullet} \rightarrow CH_3{-}P(CH_3)CH_2^{\bullet} + CH_2{=}CH_2$ for phosphetane.

compared with the corresponding observed (i.e., ab initio calculated) barrier at the same level. The "additional factor" is defined as the difference between the Marcus barrier and the observed barrier; the "strain contribution" is defined as the enthalpic component of the Marcus barrier (i.e., $\Delta E_0/2 + \Delta E_0^{\,2}/16E_{a,int}$).

Results and Discussion

Barriers, enthalpies, rates, and equilibrium constants at 298.15 K were calculated for the propagation step in the radical ring-opening polymerization of methylphosphirane (**1**, R = CH_3), methylphosphetane (**2**, R = CH_3), and methylphospholane (**3**, R = CH_3), and also for phenylphosphetane (**2**, R = Ph). As noted above, two possible models for chain propagation were considered: propagation via the C-centered radical (1) and propagation via the P-centered radical (2), as well as a possible cross-propagation mechanism (3) and the β-scission reaction (4).

$$R{-}P(CH_2)_n + {}^{\bullet}CH_3 \rightarrow CH_3{-}P(R)(CH_2)_{n-1}CH_2^{\bullet} \qquad (1)$$

$$R{-}P(CH_2)_n + {}^{\bullet}P(CH_3)_2 \rightarrow (CH_3)_2P(CH_2)_nP^{\bullet}(R) \qquad (2)$$

$$R{-}P(CH_2)_n + {}^{\bullet}CH_3 \rightarrow CH_3(CH_2)_nP^{\bullet}(R) \qquad (3)$$

$$\begin{aligned} CH_3{-}P(R)(CH_2)_{n-1}CH_2^{\bullet} \rightarrow & \\ & CH_3{-}P^{\bullet}(R) + H_2C{=}CH_2 \quad (n = 2) \\ & \rightarrow CH_3{-}P(R)CH_2^{\bullet} + H_2C{=}CH_2 \quad (n = 3) \qquad (4) \end{aligned}$$

We initially modeled the propagating radical using small models such as ${}^{\bullet}CH_3$ or ${}^{\bullet}P(CH_3)_2$ and considered only the methyl-substituted heterocycles. However, having identified the correct propagation mechanism, the propagation rate coefficient was calculated for successively longer chain lengths, with a view to identifying a suitable model size for the studying the polymerization reactions, and calculations were also performed on the more practical monomer, phenylphosphetane.

The main kinetic and thermodynamic parameters for the various ring-opening propagation reactions of methyl-substituted heterocycles are provided in Tables 1−3. The geometries of the reactants and transition states for reactions 1 and 2 are shown in Figure 1; complete geometries for all species are provided in the Supporting Information. All transition structures for attack at the ring carbon were found (via IRC calculations) to connect to a P-centered radical product; all transition structures for attack at phosphorus connected to C-centered radical products. In other words, it is the P−C ring bond (rather than the stronger C−C bond) that is broken during the ring-opening reaction.

From Tables 1−3, it is clear that propagation via a C-centered radical is far more favorable than the propagation via the P-centered radical. The rate coefficients for ring opening with a methyl radical (1.3×10^{5}, 1.2×10^{6}, and 5.8×10^{4} L mol^{-1} s^{-1}) are many orders of magnitude greater than those for the ring-opening reaction with dimethylphosphinyl radical (7.5×10^{-3}, 4.7×10^{-8}, and 1.6×10^{-14} L mol^{-1} s^{-1}). The cross-propagation reaction has even smaller rates (1.7×10^{-4}, 3.5×10^{-23}, and 4.6×10^{-30} L mol^{-1} s^{-1}). Interestingly, the propagation via the C-centered radical is most favorable for the four-membered ring; however, the P-centered radical and cross-propagation reactions are actually more favorable for the three-membered ring. Finally, we note that the β-scission reaction is not significant for the propagating species in phosphetane

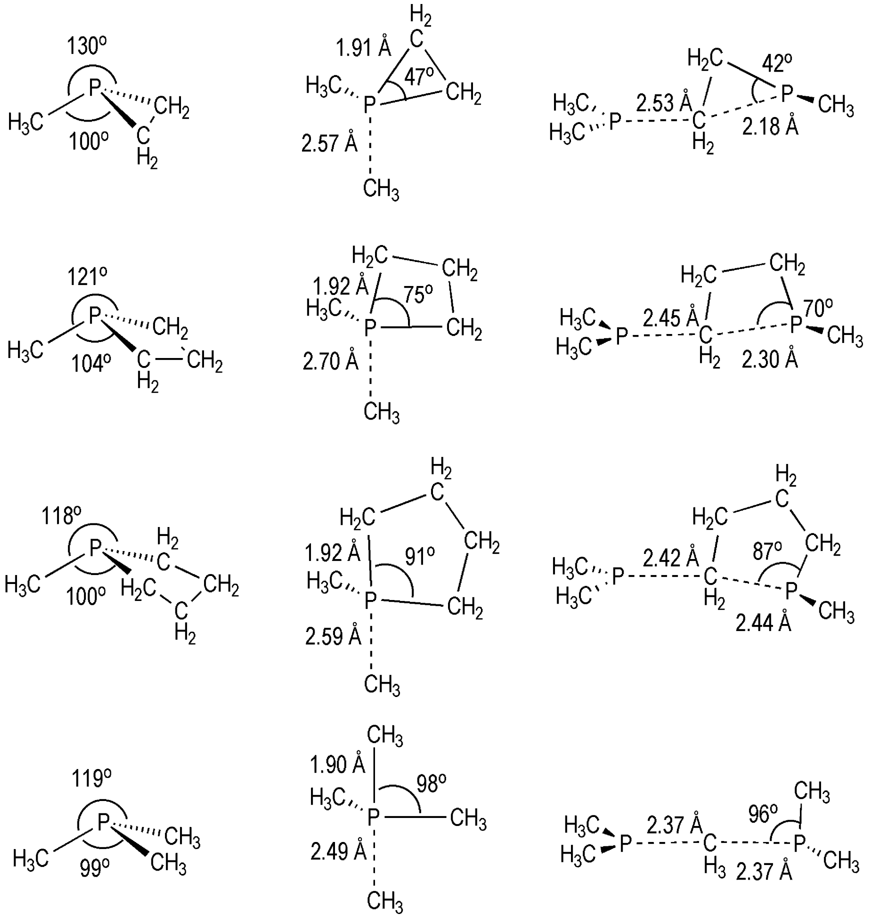


Figure 1. B3-LYP/6-31G(d) optimized geometries of the reactant phosphine and corresponding transition structures for radical ring opening via the C- and P-centered radicals (i.e., reactions 1 and 2, respectively) for methylphosphirane, -phosphetane, and -phospholane. The corresponding "strain-free" structures are included for purposes of comparison.

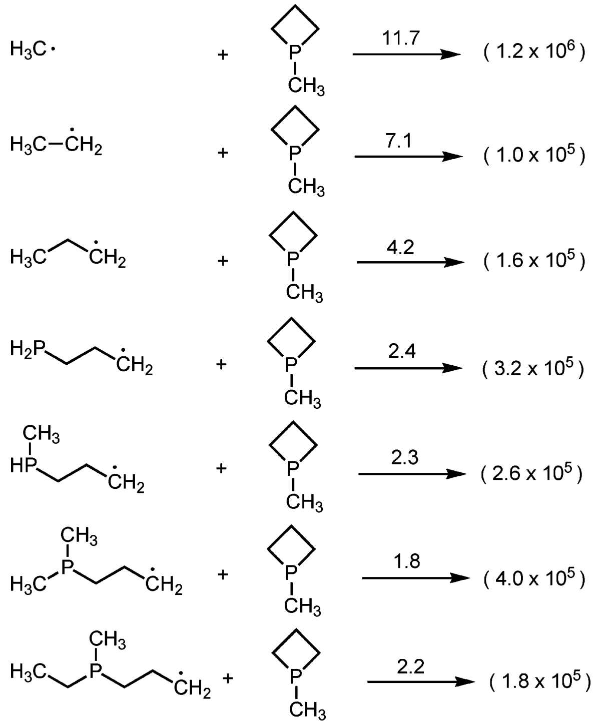
polymerization reaction but is significant for the phosphirane system. We first discuss the implications of these results for the radical ring-opening polymerization kinetics of small phosphorus heterocycles and then provide a qualitative theoretical rationalization of the main trends in the data.

Polymerization Propagation Mechanism. The rates for the model propagation via the C-centered radical (Table 1) are extremely fast (ca. 10^4-10^6 L mol^{-1} s^{-1} at 298.15 K); for comparison, the propagation rate in the free-radical polymerization of ethylene at the same temperature is only 96 L mol^{-1} s^{-1}.[22] On this basis, the propagation of the C-centered radical should out-compete the known rates of the bimolecular termination reactions of polymeric carbon-centered radicals, and a self-sustaining polymerization reaction should be possible. However, when we examine the reverse (depropagation) reaction, it is clear that, although negligible for the three- and four-membered rings, the depropagation dominates over propagation for the five-membered phospholane. For this reason the phospholanes are discarded as possible monomers in a polymerization process and excluded from further studies.

The rates for propagation via the P-centered radical (Table 2) are slower than for the C-centered radical propagation by more than a factor of 10^7, and it is thus clear that if the phosphorus-centered radical is formed, the polymerization process is unlikely to continue. It therefore becomes important to investigate the cross-propagation mechanism in which a C-centered radical adds to one of the carbon atoms adjacent to phosphorus on the ring, as this step would convert the C-centered radical into an unreactive P-centered radical. From Table 3, it is clear that the cross-propagation rates are extremely slow for the four- and five-membered rings and are thus insignificant. However, it is worth noting that the cross-propagation for the phosphirane is considerably faster than that of the phosphetane. It is therefore conceivable that, with different substituents, this side reaction may become a problem for the phosphirane but is highly unlikely to cause a problem for the phosphetane.

Another mechanism that may impair polymerization is the β-scission reaction in which the propagating radical loses molecule of ethylene (4). In the case of phosphirane polymerization, this reaction would involve the scission of a (relatively weak) P−C bond to produce ethylene and a relatively unreactive phosphorus-centered radical. From Table 3 it is clear that this reaction occurs with a fast rate in the case of phosphirane polymerization, comparable to its propagation rate at 298 K. Phosphirane monomers are thus likely to have low ceiling temperatures, and although this may be overcome through manipulation of the substituents and polymerization temperature, their utility may be compromised. In contrast, the phosphetane propagating radical does not readily undergo β-scission, since in this case a stronger C−C bond has to be broken. These monomers are thus more promising candidates for free radical polymerization, and we now limit the focus of our study to four-membered rings.

Scheme 3. Effect of Chain Size on the Barriers (kJ mol^{-1}) and Reaction Rates (L mol^{-1} s^{-1}) for the Ring-Opening Polymerization of Methylphosphetane



Since the methyl radical is expected to be far more reactive than the actual propagating radical in the C-centered propagation mechanism, we need to confirm that in a more realistic model the propagating radical is still sufficiently reactive. We also need to identify the smallest representative model that can be used in further studies. The barriers and rates for the reactions using propagating radicals of different sizes for the ring opening of methylphosphetane are shown in Scheme 3. These show that the barriers and rates of these reactions have largely converged when the methyl radical is substituted for a propyl radical, and hence the smallest propagating radical that adequately represents the propagating radical is $^{\bullet}CH_2CH_2CH_3$. The rate for the model polymerization reaction using this representative radical is 1.6×10^5 L mol^{-1} s^{-1}, still a very fast rate for a polymerization reaction.

Since the methyl-substituted heterocycles are well-known to be highly reactive, and not particularly stable, it is also important that we confirm that radical polymerization is possible for more practical monomers, such as phenylphosphetane. The propagation rate of this monomer, together with the rates of the two most likely side reactions (depropagation and β-scission), are provided in Table 4. From these data it is clear that the calculated propagation rate (8.2×10^5 L mol^{-1} s^{-1}) is still much faster than that of normal olefinic monomers such as ethylene, and the known side reactions remain insignificant, and thus we conclude that radical polymerization of phenylphosphetane should be possible.

In summary, it appears that a radical polymerization process should be feasible for the phosphetane monomers and may also be suitable (at low temperatures) for appropriately substituted phosphirane monomers. Although it is impossible to preclude all conceivable side reactions, we have demonstrated that the chain propagation step for the phosphetanes is fast and would certainly out-compete the obvious side reactions (cross-propagation, β-scission, and depropagation). Although we have not yet investigated the initiation process, it is clear that, in the very least, an ethyl radical would be suitable, and hence the copolymerization with ethylene could be initiated using standard free-radical initiators. Experiments to test this process, and further calculations to evaluate other initiators and investigate the feasibility of copolymerization with other monomers, are now underway.

Table 4. Kinetics and Thermodynamics (298 K) of the Propagation and Depropagation Reactions of Phenylphosphetane and also the β-Scission Side Reaction[a]

	propagation	depropagation	β-scission
$\Delta H^{\ddagger}$ (kJ mol^{-1})	7.8	100.9	104.6
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	−132.2	−18.5	2.5
$\Delta G^{\ddagger}$ (kJ mol^{-1})	47.2	106.4	103.9
k_{298} (L mol^{-1} s^{-1})	8.2×10^5	1.4×10^{-6}	3.9×10^{-6}

[a] Calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory in conjunction with the harmonic oscillator approximation (see text). Propagation and depropagation refer to the forward and reverse directions of reaction 1, in this case $Ph-P(CH_2)_3 + {}^{\bullet}CH_3 \rightarrow CH_3-P(Ph)(CH_2)_2CH_2^{\bullet}$, while β-scission refers to reaction 4, in this case $Ph-P(CH_3)CH_2CH_2CH_2^{\bullet} \rightarrow Ph-P(CH_3)CH_2^{\bullet} + CH_2{=}CH_2$.

Theoretical Aspects. In this work, a number of interesting and unusual trends in the radical chemistry of small phosphorus heterocycles have been revealed. For example, propagation via the C-centered radical is strongly favored over the P-centered radical mechanism, with the cross-propagation reaction the least favorable of all. This is despite the fact that their corresponding exothermicities are almost identical (and would be identical in the long chain limit). To understand this contrathermodynamic preference, we need to examine the transition structures for the alternative mechanisms (see Figure 1). The C-centered propagation reaction involves methyl radical attack at the phosphorus center of the heterocycle, to form what is effectively a stretched phosphoranyl radical (a phosphorus-centered radical with four carbon groups attached). Phosphoranyl radicals are relatively stable species,[23] and thus the phosphorus center is able to accept the unpaired electron density without first breaking the P−C bond of the ring. This is clear from the transition structures (Figure 1) and the spin densities on the phosphorus atom (see Table 5). Despite the early transition state (with the ring bonds largely intact), there is already considerable spin density on the phosphorus atom in the ring. Creation of the phosphoranyl radical is the driving force of the reaction and is responsible for the early transition structures, low barriers, and high reaction rates.

When a P-centered radical is added to one of the carbon centers in the ring, the analogous situation cannot occur (carbon-centered radicals with four attached groups are certainly not stable). Before the addition can occur one of the bonds in the ring must first break, and the transition state is thus much later. The energy cost of breaking the bond is not counterbalanced by the delocalization of electron density and bond formation in this case, and thus the barrier is much higher. This is clear from the stretched breaking bonds observed in the transition states (Figure 1) and also from the amount of deformation the ring undergoes to reach the transition state. Measurements of the level of deformation in the heterocycles at the transition state show that, for dimethylphosphinyl radical addition, the ring is significantly deformed, increasing as the ring size

Table 5. Charges, Spin Densities, and Deformation Energies of the Transition States and Vertical Charge Transfer Energies of the Reactants in Reactions 1−3[a]

reaction	$Q(R^\bullet)$[b]	$Q(A)$[b]	spin($R^\bullet$)	spin(A)	$\Delta E^\ddagger_{DEF}$	R^+ring^-	R^-ring^+
			C-Centered Radical Propagation (1)				
phosphirane	−0.086	0.760	0.762	0.062	1.9	10.90	9.53
phosphetane	−0.080	0.848	0.804	0.110	1.8	10.83	8.79
phospholane	−0.125	0.891	0.741	0.169	1.3	10.44	8.68
			P-Centered Radical Propagation (2)				
phosphirane	0.063	−0.144	0.689	−0.115	56.0	9.33	8.78
phosphetane	0.058	−0.125	0.710	−0.195	93.0	9.27	8.04
phospholane	0.096	−0.171	0.577	−0.115	283.4	8.88	7.92
			Cross-Propagation Reaction (3)				
phosphirane	−0.017	−0.080	0.724	−00.115	42.5	10.90	9.53
phosphetane	−0.012	−0.120	0.642	−0.115	73.3	10.83	8.79
phospholane	−0.017	−0.094	0.611	−0.103	106.4	10.44	8.68

[a] Charges (Q) and spin densities (spin) were obtained via an NBO analysis at the B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d) level of theory. The deformation energy ($\Delta E^\ddagger_{DEF}$) (0 K, kJ mol^{-1}) is defined as the energy difference of the ring in transition state geometry and isolated reactant, as calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory. Charge-transfer energies (eV) were calculated at the G3(MP2)-RAD(+)//B3-LYP/6-31G(d) level of theory, using vertical IEs and EAs of methyl radical (9.82 and −0.12), dimethylphosphinyl radical (8.25 and 0.64), methylphosphirane (9.42 and −1.08), methylphosphetane (8.67 and −1.01), and methylphospholane (8.56 and −0.62), respectively. [b] $R^\bullet$ is the attacking radical. In reactions 1 and 3 $R^\bullet$ is a methyl radical, and in reaction 2 $R^\bullet$ is a dimethylphosphinyl radical. A is the site of attack of the radical. In reaction 1 A is the phosphorus atom in the ring, while in reactions 2 and 3 A is one of the methylene groups adjacent to phosphorus in the ring.

increases (Table 5). This is in contrast to the C-centered propagation reaction, for which the deformation of the ring is small and slightly decreases with increasing ring size.

The cross-propagation mechanism, which involves methyl radical attack at carbon, also involves formation of a five-valent carbon-centered species. Hence, as in the case of the P-centered radical propagation, the P−C bond of the ring has to break before a significant bond formation reaction can compensate, and the reaction has a late transition state and a high barrier. Moreover, unlike the P-centered radical propagation, the transition state is not stabilized to any great extent via polar interactions, rendering it even less favorable. The charges on the radicals and centers for attack (Table 5) show that the phosphorus center in both the radical and the substrate has a positive charge while the carbon centers in the ring and methyl radical have a slight negative charge. Therefore, it is far more favorable for the negative ring carbon to attack the positive phosphorus than to attack the negative methyl radical.

The effects of ring size on the rates of the various reactions also show unusual trends. In the propagation via the C-centered radical the fastest rate is shown by four-membered phosphetane with the five-membered phospholane having the slowest. To explain this nonmonotonic trend, we need to examine the transition structures of the ring-opening reactions, together with the corresponding “unstrained” case, the reaction between methyl radical and the PMe_3 phosphine (Figure 1). The structure of the stretched phosphoranyl radical transition state in the unstrained case shows an axial−equatorial angle of 98°. The corresponding angle in the case of the three-membered methylphosphirane is only 47°, while that of the four-membered methylphosphetane ring is 75°—much closer to the unstrained case. It is clear that the four-membered methylphosphetane is better accommodated in a stretched phosphoranyl radical transition structure than the three-membered phosphirane. This is important, given that the transition structures are early and the rings are largely intact. Although opening the three- and four-membered rings releases approximately the same amount of energy, the more favorable formation of the transition state for the four-membered ring results in the much higher rate seen for this reaction. The five-membered methylphospholane is a much less strained system, and so opening its ring does not yield the very high exothermicity seen for the three- and four-membered cases. The energy released from the five-membered ring-opening reaction is far less than the entropy lost during the reaction. Although the rate of the reaction is still high, the rate of the reverse reaction dominates.

The effect of the ring size on the rates for propagation via the P-centered radical, and also for cross-propagation, is quite different to the case of carbon-centered radical attack at phosphorus. Now attack on the three-membered ring is more favorable than attack of the four-membered ring, with the five-membered ring again being the least reactive. This is not completely unexpected; the transition states for these reactions have geometries that are very different to those for attack at phosphorus. Not only does the attack occur at the carbon (rather than phosphorus), the transition structures are also much later. As a result, the release of strain in the ring is expected to be much more relevant than bond angles in the original rings. Although this explains the low reactivity of the five-membered ring, it does not explain the greater reactivity of the three-membered ring over the four-membered ring, since these systems have similar strain energies.

As noted in the Introduction, the unusually high reactivity of the three-membered rings has been reported previously in the nucleophilic analogues of these ring-opening reactions, both for the specific case of the phosphorus heterocycles and for a variety of other rings:[12,13]

$$RX^- + CH_3{-}X(CH_2)_n \rightarrow RX{-}(CH_2)_n{-}X^- \quad (X = CH_2, NH, PH, O, S)$$

Using a Marcus-type analysis,[21] Wolk et al.[12] quantified the “additional factor” in the lowering of the barrier for the three-membered rings for nucleophilic systems, suggesting that it amounted to 74 kJ mol^{-1} in the parent phosphirane system (**1**, R = H) and just 18 kJ mol^{-1} for the corresponding phosphetane. In the present systems, we calculate Marcus barriers for the phosphorus-centered radical attack on the three-, four-, and five-

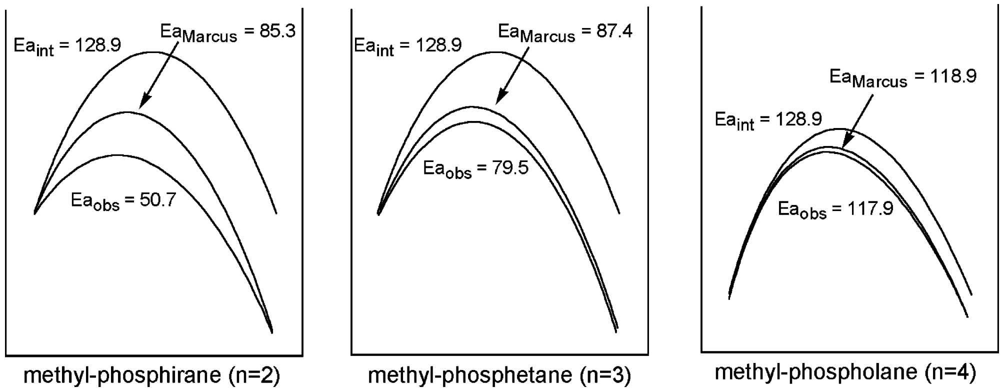


Figure 2. Reaction Profiles (0 K, kJ mol^{-1}) of the radical ring-opening reactions of phosphirane, phosphetane, and phospholane with a dimethylphosphinyl radical, $CH_3{-}P(CH_2)_n + {}^{\bullet}P(CH_3)_2 \rightarrow (CH_3)_2P(CH_2)_nP^{\bullet}(CH_3)$.

membered rings to be 85.3, 87.4, and 118.9 kJ mol^{-1}, respectively. When these are compared with the corresponding observed (ab initio calculated) barriers, one concludes that the barrier for the three-membered rings is lowered by an additional 35 kJ mol^{-1} and the barriers for the four- and five-membered rings are lowered by just 8 and 1 kJ mol^{-1}, respectively. The trends are illustrated schematically in Figure 2, from which it is also clear that the barriers for three- and four-membered rings contain a sizable contribution from strain release, compared with the less-strained five-membered ring.

The origin of the high reactivity of the three-membered rings (compared with four-membered rings) in nucleophilic reactions has been the cause of much debate.[12,13] Hoz and co-workers have speculated that the increase in reactivity is due to there being less orbital rehybridization needed to form the transition state in the case of the three-membered ring compared with the four-membered ring.[12,13d,e] This is because the orbitals on the ring carbons of the three-membered ring are distorted from sp^3 character. It is generally thought that the three-membered phosphiranes, unlike their four- and five-membered counterparts, have a bonding arrangement that it is part way between the cyclopropane analogue and an alkene–transition metal type π-complex.[24] Houk and co-workers have instead used molecular orbital arguments to show that odd-numbered rings may have higher reactivity than even-numbered rings because the breaking ring bond has additional antibonding character in former case.[13a–c] In our present radical reactions, we find that the usually high reactivity of the three-membered rings occurs only for the cross-propagation and P-centered radical propagation and is thus more associated with the site of attack than the breaking bond. Moreover, the "additional factor" is negligible for the five-membered ring, which is of course also an odd-numbered ring, but one in which the ring carbons are likely to be sp^3-hybridized. These observations tend to support the arguments of Hoz and co-workers,[12,13d,e] though the antibonding character of the breaking P–C bond may still play a role. Further studies of substituted rings and attacking radicals may help to shed further light on this interesting phenomenon.

Conclusion

High-level ab initio molecular orbital calculations indicate that radical ring opening of small phosphorus heterocycles by carbon-centered radicals is a highly facile process, driven by the creation of a transition structure that resembles a (relatively stable) stretched phosphoranyl radical. The reaction is fastest for the four-membered phosphetanes, reflecting the best compromise between the strain in the transition structure and the strain released by the partially broken ring bond. Though slightly slower, radical-ring-opening of the three-membered phosphirane should also occur, but the reaction of the five-membered phospholane is not thermodynamically favorable. In contrast, radical attack at the ring carbons (by either a carbon-centered or phosphorus-centered radical) would involve formation of a transition structure containing a stretched five-valent carbon species and is considerably less favorable. Interestingly, within these reactions, it is the three-membered rather than four-membered ring that it is considerably more reactive. This mirrors earlier studies of the nucleophilic analogues of these reactions and probably reflects the unusual hybridization of the carbon centers in the three-membered heterocycles.

On the basis of the calculations for the methyl- and phenyl-substituted heterocycles, we predict that radical ring-opening polymerization should be possible for phosphetane monomers and may also be feasible for phosphiranes, though in some situations it may be hindered by a β-scission reaction. Since the preferred propagation mechanism involves attack by a carbon-centered propagating species, we also predict that free radical copolymerization should provide a viable route to random copolymers of phosphines with normal olefins. This in turn offers the exciting prospect of incorporating phosphine units into normal polyolefins in order to alter their polarity, metal ion binding characteristics, and fire retardancy. Experiments to evaluate this process are now underway.

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Supporting Information Available: B3-LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries (Table S1) and pictures (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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