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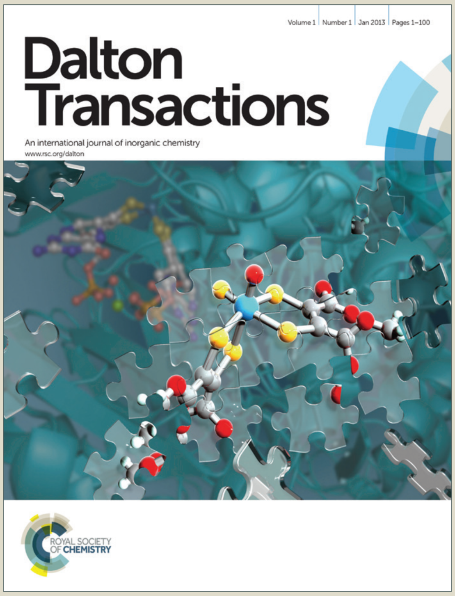

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Phosphane-ene chemistry: The reactivity of air-stable primary phosphines and their compatibility with the thiol-ene reaction

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Air-sensitive and air-stable primary phosphines (RPH_2) were compared for their ability to undergo photoinitiated phosphane-ene chemistry with 1-hexene. Despite their increased air-stability, the primary phosphines displayed equal to or greater reactivity when compared to air-sensitive alkyl or aryl analogues. The phosphane-ene reaction was also performed in the presence of 1-octanethiol to determine whether thiol-ene and phosphane-ene chemistries could proceed simultaneously. It was determined that the phosphane-ene process takes precedence over thiol-ene as P-H bond conversion was independent of thiol concentration. Tertiary phosphine (R_3P) and some secondary phosphine (R_2PH) products were found to react with thiols under the experimental conditions to create phosphine-sulfides (P-S), but this chemistry only proceeded at low P-H bond concentrations. These results suggests that hydrogen transfer reactions take precedence over P-S formation and demonstrate the unique relationship between phosphane-ene and thiol-ene chemistry.

Introduction

Synthetic chemistry is often the inspiration for new polymerization methodologies and techniques. While not every bond-forming reaction is suitable for polymer synthesis, the relatively few reactions that are used, such as free-radical polymerization of (meth)acrylates/styrenes, and a variety of condensation and cross-coupling reactions, represent the vast majority currently exploited.[1] This trend extends across the remainder of the periodic table, where only a very small number of reactions based on the inorganic elements are used for polymer synthesis. Notable examples of polymers fabricated using inorganic elements include silicones, polysilanes, thiol-ene networks, polyferrocenylsilanes, phosphaalkene polymers, and polyphosphazenes.[2–5] This sparse selection of successful systems relative to the abundance of inorganic elements originates from the difficulty in identifying low-cost and stable inorganic functional groups, capable of undergoing efficient polymerization reactions. Of the main group elements, phosphorus is highly attractive for polymer synthesis because of its high abundance, diverse chemistry, capability to form strong and stable bonds, and biocompatibility in various applications.[6,7] While a large variety of new phosphorus-containing monomers have been developed,[5,8–10] we are interested in utilizing the simplest organophosphorus functional group for this task, a primary phosphine (RPH_2). These functional groups are ideal candidates for polymer synthesis because they are currently produced industrially, easily synthesized in the lab, and possess diverse reactivity.[11–14]

We have synthesized polymer networks from primary phosphines and olefins using phosphane-ene chemistry, a process analogous to the widely exploited thiol-ene chemistry (Figure S13).[15] This approach allows for the fabrication of materials possessing phosphine functionalities that exhibit a variety of functional applications, including oxygen scavenging and solid-supported chemistry. Unlike the thiol-ene reaction,[3,4,16] the phosphane-ene reaction is less understood and few structure-activity relationships between different phosphines and olefins have been established.[17] This significantly impedes the development of this chemistry and its application in materials science. For example, several attempts to polymerize P-H bonds using radical chemistry have either been unsuccessful or inefficient, highlighting the need for a deeper understanding of P-H bond chemistry.[18–20] This issue is

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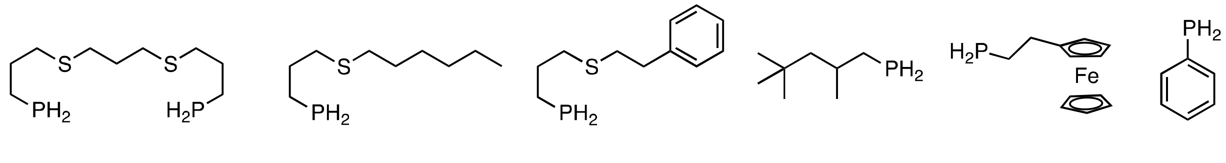

Figure 1: All air-stable (**1-3** and **5**) and air-sensitive (**4** and **6**) phosphines examined for their capability to undergo phosphane-ene chemistry.

further complicated by the use of air-stable primary phosphines, as the reactivity of these recently discovered functional groups relative to the air-sensitive varieties is still under development.[21] Currently there is strong evidence that reactivity is retained in the air-stable varieties, including but not limited to macrocycle and phosphoramidate formation,[22,23] however this has not been determined for radical additions of P-H bonds to olefins. Finally, there have been no studies on whether the phosphane-ene reaction can be performed in conjunction with the thiol-ene process despite their similar mechanisms. There is evidence that thiols behave catalytically and improve radical additions of other elements to double bonds,[24,25] but this has not been an examined for primary phosphines. Such an approach would allow for the fabrication of phosphorus-sulfur hybrid materials possessing characteristics of both systems, further developing the toolbox for inorganic-element containing polymers. In this context, we describe here an exploration of the chemistry for a variety of primary phosphines as it relates to phosphane-ene and thiol-ene chemistry. Both air-stable and air-sensitive alkyl and aryl phosphines were examined for their capabilities to undergo photoinitiated phosphane-ene chemistry with 1-hexene to establish a baseline for their relative reactivities (Figure 1). The goal is to provide a structure-activity relationship for these primary phosphines, allowing for further monomer design and utilization in polymerization reactions. The efficiency of the phosphane-ene reaction in the presence of a thiol was also elucidated to further understand the relationship between phosphane-ene and thiol-ene reactions. This was accomplished by altering the [C=C]/[P-H] and [S-H]/[P-H] ratios and observing the products formed. Our results provided key information enabling the development a model for this system as well as a comparison with the more well-known thiol-assisted hydrosilylation reactions.[24]

Experimental Section

Formulations were prepared in a nitrogen-filled MBraun Labmaster 130 glove box unless otherwise noted. Dried solvents were collected under vacuum in a flame dried Strauss flask and stored over 4Å molecular sieves in the drybox. Photoinitiator (Irgacure 819) was purchased from Ciba Chemicals and used as received. 1,3,5-Trially-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT), 1-octane thiol, 1-hexanethiol, and 2-phenylethanethiol were purchased from Sigma Aldrich and used as received. Lithium aluminum hydride (97%), 1,3-dithiopropane, and potassium *tert*-butoxide (97%) were purchased from Alfa Aesar and used as received. 1-hexene was purchased from Alfa Aesar and distilled prior to use. Cytop 183 was donated by Cytec Inc. as a 4.0 M solution in toluene. Solution phase Nuclear Magnetic Resonance (NMR) spectroscopy was conducted on a Varian INOVA 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C{^{1}H} 158 MHz ^{31}P{^{1}H} 162 MHz) unless otherwise noted. All ^{1}H NMR spectra were referenced relative to tetramethylsilane ($CDCl_3$; ^{1}H δ_H = 7.26 ppm). The chemical shifts for ^{31}P{H} NMR spectroscopy were referenced using an external standard (85% H_3PO_4; δ_P = 0). High resolution mass spectrometry was performed on a MASPEC II system, and ESI +/- mass spectrometry was performed on a Micromass LCT spectrometer.

Synthesis of $(EtO)_2(O)PC_3H_6SC_6H_{13}$ (2-P)

1-Hexanethiol (1.02 g, 7.38 mmol) and KO*t*Bu (0.85 g, 7.38 mmol) were dissolved in THF (250 mL) and heated to reflux. Diethyl (3-bromopropyl)phosphonate[14] was added dropwise and stirred for 2 hours. Volatiles were removed *in vacuo* at 40 °C and the residual material was dissolved in diethylether (100 mL). The mixture was filtered and volatiles were removed *in vacuo* leaving a colourless oil identified as **2-P** (1.78 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H $^3J_{HH}$ = 8 Hz, $S(C_5H_{10})CH_3$), 1.31 (t, 6H, $^3J_{HH}$ = 8 Hz, OCH_2CH_3), 1.35 (m, 6H, $S(CH_2)_2(CH_2)_3CH_3)$), 1.57 (quintet, 2H, $^3J_{HH}$ = 8 Hz, $SCH_2CH_2CH_2S$), 1.88 (m, 4H, PCH_2 and $SCH_2CH_2(C_4H_9)$), 2.50 (m, 2H $SCH_2(C_5H_{11})$), 2.59 (m, 2H, $PCH_2CH_2CH_2S$), 4.11 (m, 4H, OCH_2CH_3). ^{31}P{^{1}H} NMR (161.82 Hz, $CDCl_3$) δ 32.26 (s). ^{13}C{^{1}H} NMR (100.5 Hz, $CDCl_3$) δ 14.01 (s), 16.47 (d, $^3J_{CP}$ = 6 Hz), 22.53 (s), 22.59 (d, $^2J_{CP}$ = 4 Hz), 24.50 (d, $^1J_{CP}$ = 143 Hz), 28.55 (s), 29.60 (s), 31.42 (s), 31.87, (s), 32.57 (d, $^3J_{CP}$ = 17 Hz), 61.47 (d, $^2J_{CP}$ = 6 Hz). HR-MS Anal. Calcd for $C_{13}H_{29}O_3PS$: 296.1575. Found: [M+], *m/z* = 296.1581.

Synthesis of $H_2P(CH_2)_3S(C_6H_{13})$ (2)

Diethylether (100 mL) and $LiAlH_4$ (0.77 g 20.3 mmol) were combined and cooled to 0 °C under a nitrogen atmosphere. **2-P** (1.54 g, 6.75 mmol) was added dropwise to a stirring solution and left for 1 hour. Residual $LiAlH_4$ was carefully quenched with water and the ethereal layer was extracted with 6 M HCl (40 mL x 3), dried with $MgSO_4$, and decanted. Volatiles were removed *in vacuo* and residual oil was filtered through 200 nm syringe filters under a nitrogen atmosphere and identified as **2** (0.78 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, $^3J_{HH}$ = 8 Hz, CH_3), 1.30-1.38 (m, 6H, $SCH_2CH_2(C_3H_6)CH_3$), 1.60 (m, 4H, PCH_2 and SCH$_2$CH_2), 1.80 (m, 2H, PCH$_2$CH_2CH$_2$S), 2.49 (d of m, 2H, $^1J_{HP}$ = 184 Hz. Other signal at 2.95 ppm)), 2.51-2.57 (m, 4H CH_2SCH_2) ^{31}P{^{1}H} NMR (161.82 Hz, CDCl$_3$) δ -137.5 (s). ^{13}C{^{1}H} NMR (100.5 Hz, CDCl$_3$) δ 13.16 (d, $^1J_{CP}$ = 8 Hz), 14.18 (s), 22.70 (s), 28.74 (s), 29.81 (s), 31.60 (s), 32.28 (s), 32.61 (d, $^3J_{CP}$ = 6 Hz), 32.73 (d, $^2J_{CP}$ = 3 Hz). HR-MS Anal. Calcd for $C_9H_{21}PS$: 192.1102. Found: [M], *m/z* = 192.1097.

Synthesis of (EtO)$_2$(O)P(CH$_2$)$_3$S(CH$_2$)$_2$(C$_6$H$_5$) (3-P)

2-Phenylethanethiol (2.22 g, 9.15 mmol) and KOBu^t (1.06 g, 9.15 mmol) were dissolved in THF (250 mL) and heated to reflux. Diethyl (3-bromopropyl)phosphonate was added dropwise and stirred for 2 hours. Volatiles were removed *in vacuo* at 40 °C and the residual material was dissolved in diethylether (100 mL). The mixture was filtered and volatiles were removed *in vacuo* leaving a colourless oil identified as 3-P (1.74 g, 75%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.38 (t, 6H, $^3J_{HH}$ = 8 Hz, OCH$_2$CH_3), 1.93 (m, 4H, PCH$_2$CH$_2$ and CH$_2$Ph), 2.66 (m, 2H, SCH_2CH$_2$Ph), 2.82 (m, 2H, PCH_2), 2.94 (m, 2H, PCH$_2$CH$_2$CH_2S), 4.04 (m, 4H, OCH$_2$), 7.26 (m, 3H, C*H*), 7.36 (m, 2H, C*H*). ^{31}P{^{1}H} NMR (161.82 Hz, CDCl$_3$) δ 32.16 (s). ^{13}C{^{1}H} NMR (100.5 Hz, CDCl$_3$) δ 16.61 (d, $^3J_{PC}$ = 6 Hz), 22.67 (d, $^2J_{PC}$ = 5 Hz), 24.74 (d, $^1J_{PC}$ = 142 Hz), 32.81 (d, $^3J_{C\text{-}P}$ = 18 Hz), 61.54 (d, $^2J_{C\text{-}P}$ = 7 Hz), 126.47 (s), 128.57 (s), 140.55 (s). HR-MS Anal. Calcd for $C_{15}H_{25}O_3PS$: 316.1262. Found: [M+], *m/z* = 316.1250.

Synthesis of H$_2$P(CH$_2$)$_3$S(CH$_2$)$_2$(C$_6$H$_5$) (3)

Diethylether (50 mL) and LiAlH$_4$ (0.36 g 9.49 mmol) were combined and cooled to 0 °C under a nitrogen atmosphere. **3-P** (1.0 g, 3.16 mmol) was added dropwise to a stirring solution and left for 1 hour. Residual LiAlH$_4$ was then carefully quenched with water. The ether layer was extracted with 6 M HCl (20 mL x 3), dried with MgSO$_4$, and decanted. Volatiles were removed *in vacuo* and residual oil filtered through 200 nm syringe filters under a nitrogen atmosphere and identified as 3 (0.44 g, 65%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.65 (m, 2H CH$_2$CH_2CH$_2$), 1.86 (m, 2H, PCH$_2$), 2.51 (d of m, 2H, $^1J_{HP}$ = 192 Hz. Other signal appears at 2.99 ppm), 2.63 (t, 2H, $^3J_{HH}$ = 8 Hz, CH$_2$Ph), 2.82 (m, 2H, CH_2SCH$_2$CH$_2$Ph), 2.96 (m, 2H, SCH_2CH$_2$Ph), 7.2-7.4 (m, 5H, C*H*). ^{31}P{^{1}H} NMR (161.82 Hz, CDCl$_3$) δ -137.4 (s). ^{13}C{^{1}H} NMR (100.5 Hz, CDCl$_3$) δ 13.21 (d, $^1J_{CP}$ = 8 Hz), 32.94 (m), 33.82 (s), 36.58 (s), 126.55 (s), 128.67 (s), 140.75 (s). HR-MS Anal. Calcd for $C_{11}H_{17}PS$: 212.0789. Found: [M+] + 1.0078, *m/z* = 213.0872.

Irradiation Studies for various air-stable and air-sensitive phosphines

Primary phosphines (0.39 mmol, 0.195 mmol for 1) were dissolved in toluene to produce concentrated solutions (4.0 M, 2.0 M for 1)*, combined with 20 eq. 1-hexene (980 µL) and 2 mg of Irgacure 819 (30 µL of a solution in toluene). Solutions were mixed until complete dissolution and added to NMR tubes. Samples were then irradiated (UVA: 23 mW) at varying time intervals and analyzed using ^{31}P{^{1}H} NMR spectroscopy (5 second pulse delay) to monitor reaction progress.

*Cytop 183 (4) was provided as a 4.0 M solution in toluene from Cytec Inc. and used as received.

Irradiation Studies for primary phosphine 1 with varying [C=C]/[P-H] and [S-H]/[P-H] ratios

Primary phosphine **1** (0.0975 mmol) and measured amounts of 1-octanethiol, 1-hexene, and 1 mg of Irgacure 819 (30 µL of a solution in toluene) were mixed together thoroughly in NMR tubes. The solutions were irradiated (UVA: 23 mW) for 1 hour and diluted with 300 µL of toluene prior to analysis by ^{31}P{^{1}H} NMR spectroscopy. Peak integrations were used to determine conversion of P-H groups and quantify the product distribution.

Results and Discussion

Influence of primary phosphine structure on the phosphane-ene reaction

Air-stable primary phosphines **1** and **5** were synthesized according to literature procedures,[15,26] and **2**-**3** were synthesized to further examine the reactivity of phosphines possessing the H$_2$P(C$_3$H$_6$)SR functionality (See Experimental for details). The significance of sulfur and its proximity to the PH$_2$ functional group for air-stability is not yet fully understood and is a topic of debate;[21] however we chose this molecular architecture because of its simplicity, lack of steric bulk, and ease of synthesis. Upon examining these phosphines for their air-stability, we found that compounds **1**-**3** were stable as a 1 M toluene solution (reagent grade) in air, but oxidized slowly (~48 hours) in the absence in solvent, while **5** was stable in air in both cases. These results suggest that the term "air-stable" with respect to these phosphines should be viewed as a spectrum, ranging from completely resistant to only partially, and depends on experimental conditions. Alkyl and aryl primary phosphines **4** and **6** do not possess any stabilization towards oxidation and thus served as a comparison to the air-stable varieties.

Phosphines **1-6** were dissolved in toluene and excess 1-hexene containing the photoinitiator bis(2,4,6-trimethylbenzoyl)-phenylphosphinoxide (BAPO; Irgacure 819), and with UV-light for different time periods. Reaction progress was monitored using ^{31}P{^{1}H} NMR spectroscopy and P-H bond conversion was determined based on relative peak integrations (See SI for full procedure). This method conveniently allowed for quantitative measurements of primary (RPH$_2$), secondary (R$_2$PH) and tertiary (R$_3$P) phosphines (Figure 2a) as each successive alkylation results in a downfield chemical shift (Figure S14). Throughout the reaction progress, no other phosphorus signals were detected and the expected products formed were confirmed by mass spectrometry. In all cases, the reaction proceeded quickly during the initial phase but slowed down as photoinitiator was consumed (Figure 2b). The significant accumulation of secondary phosphine (up to ~40%) for all substrates suggests that its rate of formation is greater than for its consumption. This is likely because of the increased stability of secondary phosphinyl radicals as well as the increased steric hinderance around the phosphorus centre. The tertiary phosphine was still observed early in the reaction indicating that secondary phosphines do undergo conversion. A plot of total P-H bond conversion combines the first and second P-C bond forming reactions to evaluate the overall reaction progress (Figure S15). Phosphines exhibiting increased air stability (with the exception of **5**) underwent olefin addition at a rate equal to or greater than that of the pyrophoric phosphine **4**. Compound **5** exhibited different behaviour relative to the other phosphines, likely because its intense colour prevented photoinitiation from occurring at low initiator concentrations. The noticeably slow rate of reactivity of **6** is consistent with previous studies and resulted from the higher stability of the aryl phosphinyl radical relative to the alkyl varieties, promoting the reverse addition reaction as described by Pellon.[17] While **6** produced a modest amount of secondary phosphine, very little tertiary phosphine was observed. This incomplete conversion of primary to tertiary phosphine is highly undesirable for polymerizations, suggesting the inferiority of aryl phosphines for this task and the necessity for greater reactivity. In fact, our attempt at photopolymerizing **6** according to a literature procedure resulted in no gel fraction, with a P-H bond conversion of only 51% (Figure S16). These results are consistent with similar approaches where the polymerization of secondary aryl phosphines was not feasible under radical conditions.[19,27] On the other hand, the hydrophosphination reactivity of these air-stable varieties is comparable, if not better than the pyrophoric phosphines **4** and **6**, thus demonstrating that reactivity is not sacrificed for air-stability.

Tandem phosphane-thiol-ene systems

Phosphane-ene and thiol-ene polymerization reactions represent two methods sharing similar mechanisms. The prospect of combining these processes to proceed simultaneously is attractive, namely to create phosphorus-sulfur hybrid materials by copolymerizing thiols and phosphines with olefins.[3,15] A series of experiments were designed examining the effect of both the [C=C]/[P-H] and [S-H]/[P-H] ratios on phosphine product distribution and P-H conversion (Table 1, see Experimental for details and figure S17-S20 for spectra). Primary phosphine **1**, 1-hexene, and 1-octanethiol provided the necessary P-H, C=C, and S-H bonds for all experiments.

Irradiation of samples containing no thiol produced a product distribution similar to that described above, containing primary, secondary, and tertiary phosphines. Larger [C=C]/[P-H] ratios resulted in greater conversion, although the reaction was not quantitative and required an excess amount of olefin

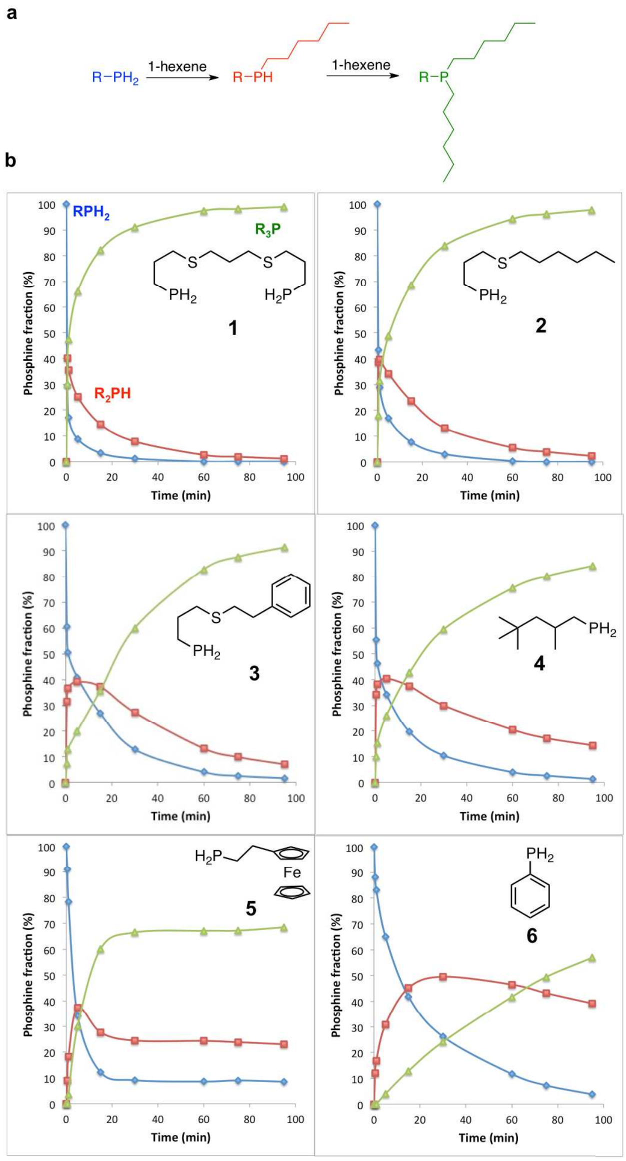

Figure 2: a) Sequential addition process of 1-hexene to a primary phosphine. b) Plots of the percent abundance of each primary (blue), secondary (red), and tertiary (green) phosphine as a function of irradiation time in 1-hexene. Values were obtained using ^{31}P{^{1}H} NMR spectroscopy and relative peak integrations.

Table 1: Phosphorus product distributions after irradiation determined by ^{31}P{^{1}H} NMR spectroscopy. 1-octanethiol and 1-hexene provided the respected C=C and S-H bonds for these experiments. Total P-H bond conversion was determined using the equation $100(f_{R3P} + f_{R3PS} + ((f_{R2PH} + f_{R2P(S)H})/2)$, where f is the fraction of the corresponding phosphine in the mixture obtained by peak integration.

[C=C]/[P-H]	[S-H]/[P-H]	RPH_2 (%)	R_2PH (%)	R_3P (%)	$R_2P(S)H$ (%)	R_3PS (%)	P-H conversion (%)
0.50	0.00	39.9	44.2	15.9	0.0	0.0	38.0
	0.25	45.4	40.9	10.6	2.6	0.6	32.9
	0.50	47.9	39.2	9.6	2.7	0.7	31.2
	1.00	46.5	39.3	10.2	3.0	1.0	32.3
1.00	0.00	10.7	31.5	57.9	0.0	0.0	73.6
	0.25	9.5	29.7	49.5	2.2	9.2	74.6
	0.50	11.8	36.1	40.0	2.2	9.9	69.1
	1.00	12.7	33.3	37.5	2.2	14.3	69.5
1.25	0.00	2.9	13.4	83.7	0.0	0.0	90.4
	0.25	2.4	10.1	63.8	1.8	21.9	91.7
	0.50	2.1	12.9	54.7	1.7	28.6	90.6
	1.00	2.6	10.5	39.2	1.2	46.4	91.5
1.50	0.00	0.0	3.2	96.8	0.0	0.0	98.4
	0.25	1.7	1.4	62.4	0.0	34.5	97.6
	0.50	0.0	1.0	20.3	0.0	78.4	99.3
	1.00	0.0	0.0	0.0	0.0	100.0	100.0

to reach ~100% conversion. When thiol was present, two new signals were observed (δ_{31P} = 29.0 and 47.4) and increased in intensity as more thiol was added. Analysis of these samples by mass GC/MS and ^{31}P NMR spectroscopy revealed the presence of the sulfurized version of hexylated **1** ($R_2P(S)H$ and R_3PS) along with octane, suggesting sulfur transfer from 1-octanethiol to the phosphine. Desulfurization of thiols and other sulfur reagents using phosphine is known and is believed to follow a radical mechanism (Scheme S1).[28] Given that P-H bonds were consumed at some point during the formation of these phosphine sulfides, they were included in the total P-H bond conversion. Curiously, their formation appears to dominate only at higher P-H conversions, even in experiments with high [S-H]/[P-H] ratios. Furthermore, the $R_2P(S)H$ concentration never reached higher than a few percent, while R_3PS eventually dominated the system. We found that **1** was unable to undergo sulfurization in a solution containing excess 1-octanethiol and photoinitiator, while the fully hexylated version of **1** (R_3P), was completely consumed to form the phosphine sulfide. Only when trityl mercaptan was used with primary phosphine **1** did we observe any primary phosphine sulfide formation (δ_{31P} = -16.3, $^{1}J_{P\text{-}H}$ = 273 Hz, Figure S21), likely because of the stable carbon radical produced through resonance stabilization. These results demonstrate that the sulfurization of phosphorus must occur *after* at least one hydrophosphination step when using 1-octanethiol, and that sulfurization is preferable with highly substituted phosphines that are present at high P-H conversions.

The dependence of P-H bond conversion on [C=C]/[P-H] ratios is clear, with 31-38% and 100% conversion at 0.5 and 1.5 respectively, and only a marginal dependence on [S-H]/[P-H] ratios. This is surprising, as we would expect thiols and phosphines to compete for 1-hexene, thus lowering the P-H bond conversion at high thiol concentrations. This was not observed. At high [C=C]/[P-H] and [S-H]/[P-H] ratios (1.5 and 1.0 respectively), complete conversion to R_3PS *exclusively* was observed, meaning that all P-H bonds were consumed and *half* of all thiols in solution participated in the oxidation of phosphine. At a [S-H]/[P-H] ratio of 0.5, significant R_3PS was observed, which corresponds to 78% desulfurization of all thiol added to the system. The thiol-ene product was observed by GC/MS, but its formation clearly does not compete with the phosphane-ene process, as P-H bond conversion relies primarily on [C=C]/[P-H] ratios. Thiols appear to perform as spectators with respect to olefin addition reactions yet react quickly with R_3P as its concentration increases. To help explain these results, a model was developed examining the possible reaction pathways (Figure 3).

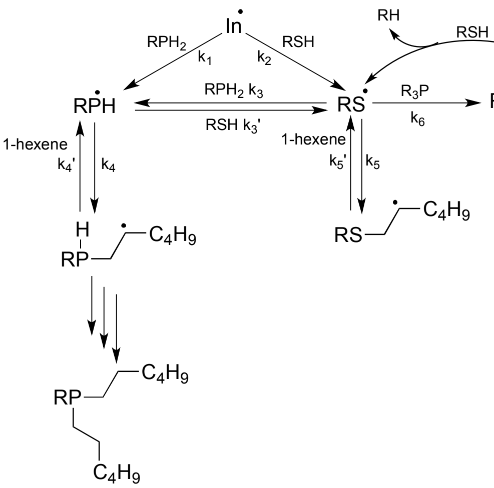

Figure 3: Possible reaction pathways for the photoinitiation of phosphane-thiol-ene systems.

Upon initiation, either phosphinyl or thiyl radicals may be formed (Figure 3, k_1 and k_2). Pellon determined that both phosphines and thiols are good hydrogen atom donors,[29] so it can be assumed that both likely form and equilibrate (k_3 and k_3'). Quantitative rate constants for this equilibrium are currently unknown, but studies using Et_3SiH, which possess a relatively strong Si-H bond, and adamantane-1-thiol have shown that the formation of the silyl radical is reasonably fast (3×10^4 M^{-1} s^{-1} vs 5×10^7 M^{-1} s^{-1} for the thiyl). Despite the endothermic nature for silyl radical formation ($\Delta H°_r$ = +4.88 kcal/mol), it effectively reduces alkyl halides.[30] The addition of Si-H bonds to olefins and ketones benefits from the catalytic behaviour of thiols by reducing the activation energies of otherwise more difficult hydrogen transfer reactions.[24] This phenomenon is referred to as polarity-reversal catalysis (PRC) and has been shown to explain other hydrogen transfers.[31] In the case of phosphines, the P-H bond dissociation energies (BDEs) are considerably lower than S-H by ~8 kcal/mol for $MePH_2$ (D_0 = 79.80 kcal/mol) vs MeSH (D_0 = 87.40 kcal/mol), and even greater for Me_2PH vs MeSH (~10 kcal/mol).[32–34] This significant difference would render the reaction corresponding to k_3' an endothermic and unfavourable process, forcing the equilibrium strongly towards the phosphinyl radical. This can explain why thiol-ene reactions do not compete with phosphane-ene reactions. Any thiyl radicals that are produced abstract a hydrogen atom from a nearby P-H bond to generate a phosphinyl species, which then undergoes olefin addition. While thiols increase the conversion for silanes, an increase in P-H bond conversion for phosphines was not observed because the rate-limiting step for hydrophosphination does not involve hydrogen transfer, but rather the reversible olefin addition reaction (k_4 and k_4').[17]

As both P-H bonds and olefin are consumed, the rate of reaction corresponding to k_3 and k_5 decrease significantly. Simultaneously, the concentration of R_3P increases and this product begins to compete for the thiyl radical to produce phosphine sulfide (k_6). The reported rate constant for the formation of *n*-Bu_3PS using *n*-C_4H_9S• and *n*-Bu_3P was found be fast, on the order of 10^9 mol^{-1} s^{-1} at 70°C, and exothermic ($\Delta H°_r$ = -25 kcal/mol).[35] In fact, this reaction is so fast that the sulfurization of $(EtO)_3P$ using *n*-C_4H_9S• (k = 2.5×10^8 mol^{-1} s^{-1} at 70°C, $\Delta H°_r$ = -26 kcal/mol) was only mildly affected by the presence of cyclohexene, and still proceeded quickly in the presence of styrene.[28,35] Even intermolecular thiol-ene reactions of unsaturated thiols were inhibited by $(EtO)_3P$, which instead formed fully saturated cyclized products.[28] While this reaction is indeed fast, we do not observe significant amounts of R_3PS until higher conversions when the P-H bond concentration has dropped (Table 1). The only experiments examining the competition between phosphorus oxidation and hydrogen abstraction were conducted by Walling and Pearson, who found that *t*BuO• would oxidize $(EtO)_3P$ faster than hydrogen abstraction of hydrocarbons like cyclohexane.[28] Given the exothermic and fast nature of phosphinyl radical formation from thiols, P-H bonds should be effective at preventing sulfurization. Indeed our results in table 1 support this. A control experiment was also designed where a distribution of primary, secondary, and tertiary phosphines was prepared (76% P-H bond conversion) and then subsequently excess thiol (1 mL, 1:1 thiol:toluene, v/v) and fresh initiator were added. After irradiation, very little sulfide product was formed with only 10% of all R_3P and R_2PH functional groups undergoing sulfurization, demonstrating the inhibitory effect P-H bonds possess and the speed at which hydrogen abstraction (k_3) takes place (Fig S22). Only when the $[R_3P]/[P\text{-}H]$ ratio becomes sufficiently high (i.e. at high P-H bond conversion) does sulfur transfer (k_6) dominate the system, which continues until either R_3P or thiol is depleted.

Conclusions

Air-stable and air-sensitive primary phosphines were examined for their ability to undergo phosphane-ene chemistry with 1-hexene. Despite the unusual stability of phosphines **1**-**3**, they underwent olefin addition equal to or better than **4**, a pyrophoric alkyl phosphine. Compound **6** was the least efficient because of the increased radical stability, resulting in slower olefin addition. These findings indicate that aryl phosphines are not good choices for radical-mediated polymerization reactions and instead can be replaced by air-stable alkyl varieties that do not sacrifice reactivity for stability. Combining both thiols and phosphines together leads to a more complicated process that favours phosphane-ene reactions over thiol-ene reactions. Thiols promote the formation of phosphinyl radicals, which then undergoes phosphane-ene chemistry. At low P-H bond concentrations, thiyl radicals will sulfurize the newly formed tertiary phosphine. While the prospect of creating phosphane-thiol-ene hybrid polymers is currently less than certain, our results demonstrate unique and unexpected behaviour of phosphines in the presence of thiols. Additional quantitative measurements will allow the relevant rate constants to be measured and compared, but this study provides insights into the relative values, which determine the ultimate products of this chemistry. Given the interest in the silane-thiol system, we believe phosphines offer a unique comparison to gain a fundamental understanding of these hydrogen transfer processes.

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