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Products and Mechanisms in the Oxidation of Phosphorus by Sulfur at Low Temperature

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The oxidation of phosphorus by sulfur at low temperatures (<100 °C) has been shown to produce complex mixtures that include 12 of the 17 known binary phosphorus sulfides. Two of these 17 sulfides have been observed in these mixtures for the first time. The rate-determining and first step in the reaction appears to be the formation of the S_8 diradical. This proposal is supported by the observed rate at which the sulfides are formed and the distribution of the sulfide product stoichiometries. Photoinitiation of this oxidation at 0 °C produces a similar array of sulfides. The differences in the product distributions between the thermal and photochemical processes facilitate the understanding of the mother−daughter relationships between the products. The effects of oxidation by sulfur and reduction by phosphorus have been determined for several of the known phosphorus sulfides. The characterizations of phosphorus compounds in molten mixtures of phosphorus and sulfur were performed by ^{31}P NMR and Raman spectroscopy directly on the reaction mixtures.

Introduction

The phosphorus sulfides are a class of compounds whose roots go back to the earliest experimentation with these two elements.[1,2] The richness and complexity of these compounds and their chemistry recently returned as an area of increased activity. The work of Bjorholm and Jakobsen[3] is noteworthy for both the identification of several new phosphorus sulfides and the use of chemical exchange NMR spectroscopy to establish the structural relationships between pairs of interconverting compounds. Their work has become invaluable for its assignments of both structures and NMR chemical shifts. Recently, Blachnik[4] has extended the family of known phosphorus sulfides by two members through the analysis of quenched samples from high-temperature equilibrations of phosphorus−sulfur mixtures.

A common analytical theme in these recent developments has been the use of ^{31}P NMR spectroscopy to analyze mixtures of phosphorus sulfides that contain from trace to high concentrations of the various structures. Prior to 1991 there were 10 sulfides known that had been characterized either by X-ray diffraction or by convincing application of NMR spectroscopy. Since that time, five new sulfides have been added to the collection by Bjorholm and Blachnik. Two more will be added with this report. All of the phosphorus sulfides that have been structurally characterized are shown in Figure 1.

The nomenclature of the phosphorus sulfides is muddled by a combination of Greek letter prefixes and Roman numeral suffixes. This communication uses the older practice of attaching a lower case Greek letter to those sulfides that display more than one isomer, advancing through the alphabet in the order in which they were reported. The names accompany the structures in Figure 1. The structures are uniquely named, and all of the old prefixed names are retained. Every attempt to design names that were structurally informative made them too long to be useful as nicknames.

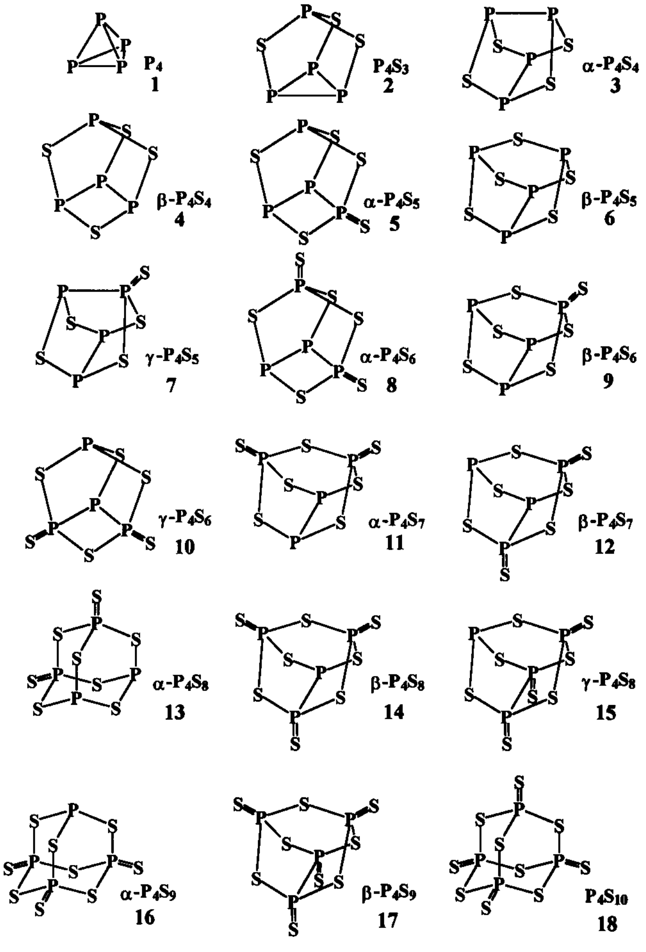

Figure 1. Known and proposed phosphorus sulfides.

Given the age of this class of compounds, it is remarkable how little of its reaction chemistry has been studied. Until recently the focus of most of the work with phosphorus sulfides has been the phase chemistry of phosphorus and sulfur and the structural and spectroscopic characterization of stable species. Mechanistic chemistry has been nonexistent. In the case of the

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(2) Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry;* Longmans, Green and Co.: London, 1931; Vol. VIII, pp 1047−1080.

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(4) Blachnik, R.; Peukert, U.; Czediwoda, A.; Engelen, B.; Boldt, K. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1637−1643.

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phosphorus sulfides, novel and intriguing paths must exist that interconvert the members of the class, and these paths have never been explored. Sulfur exists in these structures in two forms: as part of the cage (endocyclic) and as a thiono group (exocyclic). Phosphorus appears in the formal oxidation states from zero to five, inclusive.

This work is the beginning of a search for the transformations and mechanisms involved in the bimolecular reactions of phosphorus and sulfur. During the course of this effort, two new phosphorus sulfides have been identified. Several mechanistic explanations for the initially formed product distribution observed in the low-temperature (80 °C) reaction of P_4 and S_8 are also outlined. The most likely of these, on the basis of present observations, can be tied to the accepted mechanism for the polymerization chemistry of S_8.

Experimental Section

General Information. The raw materials for these studies included white phosphorus, sulfur, and commercial samples of P_4S_3 (**2**) and P_4S_{10} (**18**). The phosphorus was obtained from Monsanto Co. Some of the described reactions used phosphorus that had been passed over a column of activated carbon. No difference in chemistry was observed between the standard and the purified versions of white phosphorus. Sulfur was taken from three sources: Monsanto Co., Fisher Scientific, and 99.998% purity grade from Aldrich Chemical Co. There has been no evidence of a difference among any of these sulfur samples. P_4S_3 was obtained from Fluka Chemical Co. It was recrystallized from CS_2 prior to use. P_4S_{10} was purified by Soxhlet extraction; the process is described below. Carbon disulfide used for spectroscopy was used as received (Fisher); the carbon disulfide used as solvent for chemical reactions was dried by refluxing over P_4S_{10}. α-P_4S_5 (**5**),[6] β-P_4S_5 (**6**),[7] α-P_4S_7 (**11**),[8] and α-P_4S_9 (**16**)[9] were prepared according to literature procedures. All work was performed using either Schlenk or glovebox techniques. Because of the fact that P_4 is sensitive to light,[5] precautions were taken to make certain the long exposure reactions were protected from room light. Red phosphorus was not produced in the thermal experiments or by exposure of the samples to room light after they had undergone extensive reaction.

The NMR spectroscopy was performed on both 300 and 400 MHz (proton) spectrometers, all from Varian. Lock capability was obtained by using sealed melting point capillaries containing DMSO-d_6. The melting point capillaries were then used in standard 5 mm NMR tubes, without concern for centering the capillary. The spectra obtained under these conditions usually had adequate, and sometimes outstanding, resolution. If the spectrum of both P_4 and the phosphorus sulfides were to be observed in the same experiment, only the 300 MHz instruments could be used because the sweep width limitations on the 400 MHz instruments would not allow establishing the necessary 800 ppm window. Spectroscopy on samples in liquid P_4 or P_4/S_8 alloys performed on the 400 MHz instruments was commonly conducted with presaturation of the phosphorus peak. A delay between pulses of 2 s and standard homonuclear phosphorus decoupler power was employed. The decoupler was kept on during the delay and turned off during the pulse and acquisition. Referencing of the spectra was not performed. Instead, the instrumental offset for DMSO-d_6 was held constant. The chemical shifts were reproducible within 0.5 ppm, considered acceptable for this application.

Spin simulation and refinement calculations were performed using two different methods: the Serena Software program PMR and the PC version of LAOCN-5[10] were used in tandem for the early work. The program gNMR (Cherwell, Ltd., available from SoftShell) was used in the same manner as the other pair. All of the chemical shifts and coupling constants for the species reported in this study were obtained by fitting the spectroscopic data with either of these two programs. A table of this data can be found in the Supporting Information.

Reaction of 1:$^1/_8$ P_4/S_8 at 80 °C in an NMR Tube. A mixture of 3.54 g (0.114 mol P) of P_4 that had been filtered through charcoal and 0.916 g (0.0286 mol of S) of S_8 was prepared in a Schlenk tube under argon. The material was heated until it was molten. In a glovebag, 0.7 mL samples were removed with a syringe and filtered directly into NMR tubes containing a DMSO-d_6 capillary insert. The tubes were sealed at 12 Torr.

In one experiment, one of the NMR tubes containing P_4/S_8 was heated in a mechanically stirred oil bath 80 ± 0.2 °C. The tube was removed from the bath and cooled to room temperature to record a spectrum; the spectrometer was operated at 25 °C. Spectra were taken before the heating began and after 30, 120, 240, 360, 1320, 2400, and 3720 cumulative minutes at 80 °C. The tube was then placed in a 150 °C oil bath for 50 min and 3960 cumulative minutes. The composition of this mixture is described in the Results section.

Another tube was used to perform an 80 °C experiment directly in an NMR probe, so that the tube did not have to be removed during the experiment. Each spectrum was the result of 30 min of accumulation. After 7 h of data collection, the tube was removed from the spectrometer and placed in an 80 °C oil bath. The tube was monitored continuously to determine if equilibration to P_4S_3 had occurred. See the Results and Discussion sections for details. Representative NMR spectra from these studies can be found in the Supporting Information.

NMR Study of the Reactions of 1:*n* P_4/S_8 Mixtures Where *n* > $^5/_8$. Various amounts of crushed sulfur were added to each of eight NMR tubes. A mixture of 1:$^1/_8$ P_4/S_8 composition was prepared from 6.80 g of white phosphorus and 1.80 g of sulfur. The NMR tubes were filled as described above. One tube was also prepared with only the 1:$^1/_8$ P_4/S_8 material. The tubes were sealed under vacuum and heated in a water bath set at 80 and later 90 °C. Because of the slurry content and high viscosity, the NMR spectra of all samples except the 1:$^1/_8$ P_4/S_8 had to be obtained at 80 °C. Results of these experiments are presented in the Results and Discussion sections.

Reactions of Phosphorus Sulfides in Liquid Phosphorus (P_4). The following procedure was typical: In a glovebag, 5 mg of α-P_4S_5 was placed in an NMR tube followed by a piece of solid white phosphorus weighing approximately 1.0 g. Phosphorus was melted into the lower portion of the tube and the tube sealed under vacuum. The ^{31}P NMR spectrum of the mixture was recorded at 60 °C. The NMR tube was heated in an oil bath at 90 °C for 8 h and the NMR spectrum again recorded.

The system P_4S_3/P_4 was more extensively investigated. Dilute solutions of P_4S_3 in P_4 were prepared and tested as above. In addition, mixtures with the composition P_4S_2 (2:1 P_4S_3/P_4), which are liquid at room temperature, were prepared. The latter mixtures were heated at 94 °C for 70 h and at 250 °C for 5 h.

Reactions of Phosphorus Sulfides in Liquid 1:$^1/_8$ P_4/S_8. A liquid mixture of 13.55 g of phosphorus (0.438 mol of P) and 3.51 g of sulfur (0.109 mol of S) was prepared. NMR tubes adapted for sealing under vacuum were loaded with a DMSO-d_6 capillary insert and 3−5 mg of phosphorus sulfide (unweighed). The tubes were flushed with nitrogen. The phosphorus−sulfur mixture was filtered into the NMR tubes in a glovebag. The sealed tubes were heated at 80 °C for 30 min and quickly cooled; the ^{31}P NMR spectra were recorded at 25 °C. The tubes were heated for an additional 90 min and the spectra retaken. Analysis of the spectra is presented in the Results and in the Discussion sections.

Photochemical Initiation of the Oxidation of Phosphorus by Sulfur. NMR tubes containing a 1:$^1/_8$ P_4/S_8 mixture and capillary insert sealed under vacuum were prepared in the manner described above and also by distilling P_4 at 0.2 Torr onto sulfur and then filling NMR tubes that had been sealed to the receiver. The tubes were kept in the dark at 4 °C (i.e., in a refrigerator). Photolyses were performed by placing a tube in a circulating 0 °C bath. Although this temperature is below the liquidus curve for the phosphorus−sulfur system, the tube could be maintained unsolidified for several hours if undisturbed. The temperature during the photolyses was held in the range 0.5−3.0 °C.

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(7) Bues, W.; Somer, M.; Brockner, W. *Z. Anorg. Allg. Chem.* **1981**, *476*, 153−158.

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(10) Program QCMP-049, available from QCPE, University of Indiana, Bloomington, IN.

Irradiation came from a 150 W incandescent spotlight bulb positioned 5 cm from the tube. The ^{31}P NMR spectrum was recorded as a function of time. The length of time the sample spent at room temperature was held to a minimum; however, the NMR spectra had to be recorded at room temperature in order to prevent the precipitation of α-P_4S_7 and the solidification of the reaction mixture. These "high temperature excursions" were limited to 30 min and a temperature maximum of 25 °C.

In one such experiment, the tube was irradiated for 3 h at low temperature, and the ^{31}P NMR spectrum was recorded. The tube was then heated at 80 °C for 1 h, the sample cooled, and the spectrum retaken. This experiment was used to judge the thermal reactions of the sulfides produced by photolysis and is discussed below.

Raman Spectroscopic Investigation of the Reaction of Phosphorus and Sulfur. Sulfur and phosphorus, in the desired stoichiometry, were added as solids to a quartz vessel that consisted of a 49 mm tube having three ground joints sealed to the top. A 2.5 mL cup with a 1 cm quartz flat as a bottom was sealed to the bottom of the tube. A mechanical paddle stirrer was used to agitate the mixture. The cup was wrapped with nichrome wire; a J-Kem temperature controller was used to maintain temperature. The thermocouple, placed in the molten mixture, was stainless steel coated with tantalum. Sufficient material was used to fill the cup when the stirrer and thermocouple were in place. The fiber optic probe from the Raman spectrometer was placed beneath the tube, touching the quartz flat. Spectra were recorded at regular time intervals during a run that lasted 8−24 h.

Results

Identification of Phosphorus Sulfide Structures. All structural characterizations were performed by ^{31}P NMR spectroscopy. The chemical shifts and coupling constants of the known sulfides were used as a starting point. The differences between the chemical shifts measured in liquid phosphorus/sulfur melts and those measured in carbon disulfide fall in the range from +15.7 to −14.7 ppm, depending on the structure. The chemical shifts observed in liquid phosphorus more closely resemble those observed in CS_2 as opposed to those observed by Bjorholm and Jakobsen in molten "P_4S_4".[3] Though the chemical shifts were sensitive to the "solvent", there was very little variation in the measured coupling constants. The largest difference, approximately 10 Hz, was observed in α-P_4S_6 (**8**). It was the close correspondence of the coupling constants that allowed for straightforward identification of previously reported phosphorus sulfides. The assignment of the P_4S_{10} singlet was based on the spectrum of a dilute solution of α-P_4S_9 and P_4S_{10} dissolved in P_4. The NMR spectra of the two new sulfides were pieced together from unassigned coupling patterns and refined. A discussion of the spectra and a proof of structure based on reaction chemistry is presented in the accompanying paper. All of the measured chemical shifts and coupling constants (in CS_2, P_4, and, where reported, "P_4S_4") are found in the Supporting Information.

There are a few peaks in the ^{31}P NMR spectra of the materials produced by reaction at 80 °C that remain unassigned. A number of small and often broad singlets were observed in the region from 20 to −5 ppm, consistent with phosphate and phosphite species. A singlet often appeared at approximately 19.5 ppm for which an assignment has not been made. The chemical shift is reminiscent of a peak found in high sulfur P−S melts.[11]

Reactions at Stoichiometry $1{:}{}^1/_8$ P_4/S_8. Sulfur as a dilute solution in liquid phosphorus reacts with phosphorus in a slow and controlled fashion to give a complex mixture of phosphorus sulfides. The product distribution of such a reaction at 80 °C as a function of time is shown in Figures 2−4. In total, 12 of the 17 known or suspected sulfides appear as products in these reaction mixtures. These are as follows: P_4S_3 (**2**), α-P_4S_5 (**5**), α-P_4S_6 (**8**), β-P_4S_6 (**9**), γ-P_4S_6 (**10**), α-P_4S_7 (**11**), β-P_4S_7 (**12**), α-P_4S_8 (**13**), β-P_4S_8 (**14**), γ-P_4S_8 (**15**), α-P_4S_9 (**16**), and P_4S_{10} (**18**). α-P_4S_6 (**8**) is the most rapidly formed phosphorus sulfide during the first several hours of the reaction. Formed at nearly the same rate is α-P_4S_7. Finally, the third major product is α-P_4S_9. Although the concentration of most of the sulfides continue to grow during the reaction, that of α-P_4S_7 levels off at approximately 6 h, a result of the low solubility of α-P_4S_7 in any solvent including liquid phosphorus. The crystals of α-P_4S_7 that grew in the static $1{:}{}^1/_8$ P_4/S_8 reaction mixtures were large and very well formed. No other sulfide was observed to precipitate from solution during the 80 °C portion of the reaction.

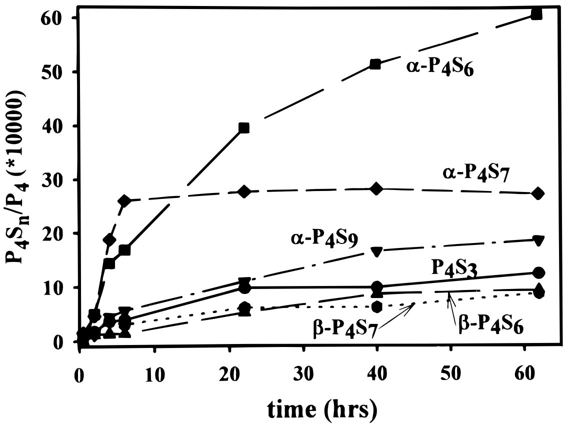

Figure 2. Product profile for the reaction of $P_4 + {}^1/_8\ S_8$ at 80 °C. Only the six most abundant products are shown.

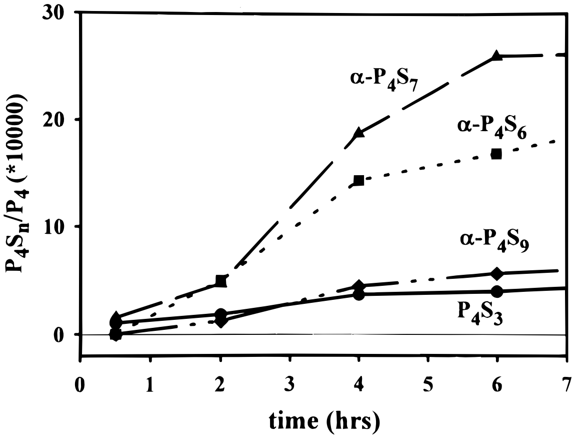

Figure 3. First 7 h of the reaction shown in Figure 2, showing the "primary" products. See Discussion for details.

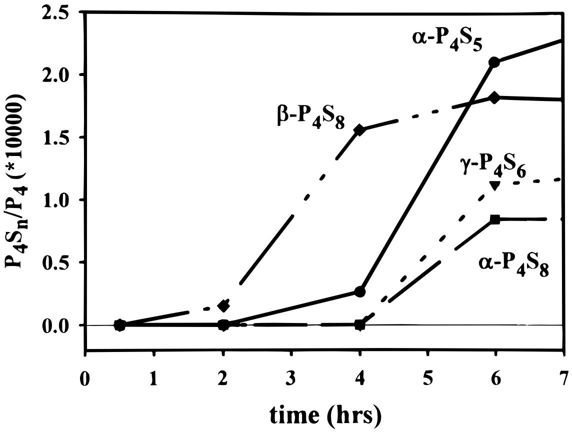

Figure 4. First 7 h of the reaction shown in Figure 2, showing the "secondary" products. See Discussion for details.

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(11) Demarcq, M. C. *Phosphorus Sulfur* **1987**, *33*, 127−134.

The composition of the mixtures produced during the first several hours was difficult to obtain with good precision. The T_1's of the sulfides in these mixtures are difficult to measure because of their low concentrations and the complexity of the spectra; delay time was also sacrificed in order to collect sufficient transients to obtain usable spectroscopy. The integrals often had to span coupling patterns that were more than 6 ppm wide (over 960 Hz at a proton frequency of 400 MHz). Thus, baseline drift and phasing problems presented a continual source of error. The last limitation was posed by the underdigitization of spectra taken at very wide sweep widths. However, the smoothness of many of the curves in Figure 2, and the flat concentration profile for α-P_4S_7, indicate these errors do not overwhelm the task of studying this reaction.

When an NMR tube containing a $1{:}^1/_8$ P_4/S_8 mixture was held at 80 °C for 55 days, the reaction mass remained a two-phase system comprised of precipitated solid, identified as α-P_4S_7, and a phosphorus-rich liquid. No change in the appearance of the tube occurred after the first several days of heating. The composition of the liquid portion, though measured from a low-resolution spectrum, showed a continued increase in the concentration of P_4S_3, the appearance of the two P_4S_4 isomers, and a gradual loss of the higher sulfides. This NMR tube was then heated in several steps in order to bracket the temperature at which equilibration of the sulfur in the α-P_4S_7 was redistributed into lower sulfides. No changes in the amount of precipitated solid occurred during heating at 100 °C for 7 days and 120 °C for 4 days. Upon heating of this mixture to 150 °C for 3 days, the mixture was transformed into a clear solution of P_4S_3 in P_4, containing minor amounts of other phosphorus sulfides. This collection included the following: α-P_4S_4 (**3**), β-P_4S_4 (**4**), α-P_4S_5 (**5**), γ-P_4S_5 (**7**), β-P_4S_6 (**9**), α-P_4S_7 (**11**), α-P_4S_8 (**13**), and several multiplets that could not be assigned to known compounds. (Spectra for these unassigned multiplets can be found in the Supporting Information.) Three of these sulfides, α-P_4S_4, β-P_4S_4, and γ-P_4S_5, were never found in any of the low temperature (80−90 °C) reaction mixtures during the first few days. The concentration of α-P_4S_7 was very low, and no trace of the other P_4S_8 isomers or higher sulfides could be found. The mixture was again heated to 150 °C for an additional 4 days; disappearing from the spectrum were α-P_4S_5, γ-P_4S_5, β-P_4S_6, α-P_4S_7, and α-P_4S_8, while the intensities of the unknown phosphorus resonances increased. These two changes are probably not coupled. Re-equilibration of this same material at 80 °C did not change the composition of the melt measurably.

Though integration of the ^{31}P NMR spectra of these mixtures is not very precise, one can obtain kinetic information from the early portion of these reactions. An initial slope analysis (based on loss of S_8) of the sum of sulfide concentrations for the first 6 h of the reaction yields an apparent first-order rate at 80 °C of 2.4×10^{-6} s^{-1}. The assumptions made in this analysis include the following: All of the products arise from a single, first-formed intermediate. There is no effective change in the S_8 concentration. None of the intermediates formed on the way to the stable products "activates" another 1 mol of S_8.

Reactions at Stoichiometries between $1{:}^1/_8$ P_4/S_8 and P_4S_{10}. Another set of experiments involved the use of sulfur-phosphorus mixtures, again prepared in NMR tubes, having much higher S:P_4 ratios: from 5 to 10. In all of these high-sulfur experiments the predominant species were the same (in order of decreasing relative concentration): α-P_4S_9, α-P_4S_7, α-P_4S_6, and β-P_4S_8. Upon continued heating of samples at 90 °C, several other phosphorus sulfides joined the first-formed four, including P_4S_3 and P_4S_{10}.

Reactions of Phosphorus Sulfides with Liquid Phosphorus. Dilute solutions of four of the synthetically available phosphorus sulfides in liquid phosphorus were prepared and heated for extended periods at 80−90 °C, and the mixtures were analyzed for the products of sulfur exchange. It is well-known that at high (200−400 °C) temperatures sulfur is rapidly exchanged between species forming an equilibrium distribution of sulfides.[3,4]

Only P_4S_{10} is rapidly and completely reduced by phosphorus at these temperatures. Approximately 75% of the P_4S_{10} was reduced to α-P_4S_9 during the time it took to tune the spectrometer and collect a spectrum at 60 °C, about 30 min. After 8 h at 90 °C no P_4S_{10} remained in the reaction mixture; the principal product was α-P_4S_9 (74%) along with five other minor components: α-P_4S_8 (5%), α-P_4S_7 (9%), β-P_4S_6 (9%), α-P_4S_4 (1%), and P_4S_3 (3%). Only small changes in composition were apparent on continued heating of the mixture at 90 °C.

Three lower sulfides, P_4S_3, α-P_4S_5, and α-P_4S_7, did not undergo significant reaction with P_4 at temperatures between 80 and 90 °C. Small (<1 mol %) quantities of various sulfides were observed in some spectra but were not quantified. Continued heating of dilute solutions gave rise to no changes in the spectra of the compounds, no precipitation, and no loss of integrated intensity relative to an external standard. P_4S_3 was studied extensively at both low and high concentration in P_4. A mixture having the composition 1:0.36 P_4S_3/P_4 was heated for 18 h at 90 °C. Less than 1% of the P_4S_3 was converted into other sulfides. These included α-P_4S_4, β-P_4S_4, α-P_4S_5, and β-P_4S_7. When a mixture having the composition 1:2.0 P_4S_3/P_4 (equivalent to the composition P_4S_2) was heated to 250 °C, the outcome was similar: More than 99% of the P_4S_3 was unchanged. However, among the extra resonances in the spectrum only α-P_4S_4 and β-P_4S_4 could be identified as members of the known sulfides.

Reactions of Phosphorus Sulfides with a Liquid Phosphorus−Sulfur Mixture. The rate at which several of the easily prepared sulfides react with sulfur in liquid phosphorus was probed at 80 °C. The intent was to determine if any of these sulfides react rapidly to form higher sulfides. A tube containing only the $1{:}^1/_8$ P_4/S_8 mixture was used as the control.

P_4S_3 is remarkably stable under these reaction conditions. After 30 min no reaction that could be ascribed to P_4S_3 was observed. At 2 h, the composition was similar to the control with a few exceptions: α-P_4S_5 is one of the major sulfides in the P_4S_3 reaction and missing from the control. The concentrations of some of the higher sulfides, γ-P_4S_8 and α-P_4S_9, were measurably smaller than the control.

α-P_4S_5 displays the most extensive chemistry of the studied sulfides. The three P_4S_6 isomers are all seen in approximately three times their respective concentration found in the control. α- and β-P_4S_7 are seen at twice their concentrations in the control.

α-P_4S_6 was shown to be oxidized to α-P_4S_7 though only at a pace that roughly doubled the α-P_4S_7 concentration.

α-P_4S_7 appears to be nearly inert to this form of oxidation by sulfur. As a result of exposing α-P_4S_7 to $1{:}^1/_8$ P_4/S_8, the only sulfide whose concentration is meaningfully different from the control was α-P_4S_9, which was observed at half the concentration of the control.

α-P_4S_9 showed only a small increase in the α-P_4S_7 concentration relative to the control. All other sulfides showed concentrations identical to the control.

The outcome of this series of experiments confirms that the sulfides seen by ^{31}P NMR spectroscopy in these molten reaction mixtures are not in rapid equilibrium with each other or with

Table 1. Comparison of the Product Distributions for the Photolysis and Thermolysis of a 1:$^1/_8$ P_4/S_8 Mixture[a]

compd	3 h of photolysis at 0 °C	3 h of photolysis and then 1 h of heating at 80 °C	4 h of heating at 80 °C
P_4S_3 **(2)**	7	4	8
α-P_4S_5 **(5)**	0	1	1
α-P_4S_6 **(8)**	16	12	30
β-P_4S_6 **(9)**	0	1	3
γ-P_4S_6 **(10)**	3	1	0
α-P_4S_7 **(11)**	31	63	39
β-P_4S_7 **(12)**	5	2	8
α-P_4S_8 **(13)**	0	1	0
β-P_4S_8 **(14)**	21	2	3
γ-P_4S_8 **(15)**	3	1	0
α-P_4S_9 **(16)**	13	13	9
P_4S_{10} **(18)**	0	0	0

[a] The data are relative mol percent figures. See the Experimental and Discussion sections for details.

the elements. Examples of these reactions in both the oxidizing and the reducing directions have been demonstrated while the rates of these reactions are observed to be slow (half-lives greater than 2−3 h for all studied sulfides).

Photochemical Initiation of the Oxidation of Phosphorus by Sulfur. Visible light irradiation of a 1:$^1/_8$ P_4/S_8 mixture at 0 °C led to the rapid appearance of several of the known sulfides. The composition of this mixture is given in Table 1 and is not corrected for a small amount of α-P_4S_7 that precipitated during the photolysis and remained undissolved while taking the NMR spectrum of the mixture.

Discussion

The two-component phase diagram of white phosphorus, P_4, and sulfur, S_8, is indistinct above 100 °C because the reaction between these two species becomes uncontrollably rapid at temperatures between 120 and 130 °C.[5] The temperature at which this reaction becomes uncontrollable depends on the size of the sample, the rate of heating, and any number of impurities. However, if the phase diagram below 100 °C is strictly interpreted, the composition of materials represented on the diagram should not depend on the age of the sample. In other words, the diagram should represent a mixture at equilibrium. One of the conclusions from this work must be that mixtures of P_4 and S_8 at 80 °C, and most certainly at even lower temperatures, are neither thermodynamically nor kinetically stable, being transformed, albeit slowly, to complex mixtures of phosphorus sulfides.

Recent work by Griffith and Ngo[12] has made use of the slow reactions taking place in mixtures of phosphorus and sulfur at temperatures in the range 100−120 °C. Using mixtures with P_4S_{10} stoichiometry, they succeeded in producing products nearly identical to those made from P_4S_{10} itself. Blachnik has also reported seeing evidence of the same chemistry.[4]

Twelve unique phosphorus sulfides have been observed as the products of the low-temperature oxidation of phosphorus by sulfur. These include the well-known and structurally characterized sulfides P_4S_3,[1] α-P_4S_5,[1,8] β-P_4S_6,[3,4] α-P_4S_7,[1,13] α-P_4S_9,[1,9] and P_4S_{10}.[1] Four other sulfides, which have been previously characterized only spectroscopically, were also observed: α-P_4S_6,[3,4] β-P_4S_7,[4] α-P_4S_8,[14] and β-P_4S_8.[4] Finally, two sulfides not previously described in the literature were observed in these mixtures. The first is an isomer of P_4S_6 that exhibits a plane of symmetry. In liquid phosphorus, this sulfide has the following phosphorus spectroscopic parameters: P_1, 160.71 ppm; $P_{2,3}$, 99.39 ppm; P_4, 61.77 ppm; $J(1,2)$, 43.2 Hz; $J(1,4)$, 43.9 Hz; $J(2,4)$, −303.8 Hz. Among the logical structures, only γ-P_4S_6 fit the ^{31}P NMR spectroscopy well. A strong case for the assignment of structure **10** to this compound is made in the accompanying paper.[15] The second compound is formed as a very minor component of these mixtures and has the following spectroscopic parameters: $P_{1,2}$, 90.2 ppm; P_3, 51.4 ppm; P_4, 42.3 ppm; $J(1,3)$, 19.4 Hz; $J(1,4)$, 33.1 Hz; $J(3,4)$, 157.9 Hz. The fact that there is no large (>200 Hz) coupling constant observable implies that the compound has no PP(=S) fragment.[3] The molecule must also have C_2 or C_s symmetry, more likely the latter. With these restrictions, the candidate that most intelligently fits this NMR data is γ-P_4S_8, structure **15**.

The kinetic profiles for many of the products observed can be divided into two categories: those found in Figure 3 that are visible in the earliest spectrum, recorded at 30 min, and those that delay their appearance from 2 to 6 h, found in Figure 4. As discussed below, no observed sulfide can be a primary product of the initial reaction. However, the group in Figure 3 (P_4S_3, α-P_4S_6, α-P_4S_7, α-P_4S_9) is considered “primary” because the concentration profiles appear not to be dependent on the concentrations of other *observed* products. The compounds in Figure 4 (α-P_4S_5, γ-P_4S_6, α-P_4S_8, β-P_4S_8), called “secondary”, delay their onset until the “primary” products are firmly established in the reaction mixture. The mechanisms by which two of the primary products are formed are considered below; the secondary products are assumed to require sulfur transfer to one of the primary products.

The identity of the products of this oxidation and the profile data found in Figures 2−4 provide sufficient information to propose (though not establish) a mechanism for the start of these reactions. The complexity of the products and the induction period in the kinetic profile both necessitate one or more steps linking the starting materials with the observed products. Because only stable, characterized products are observed by ^{31}P NMR spectroscopy, the first step in their formation must be slow, followed by a cascade of more rapid steps that terminate in the kinetic sink of one of the observed species. But what intermediate is formed in that first, slow step?

A number of candidates can be found in the literature. These include reactions centered on sulfur: the transfer of one sulfur atom[16] from S_8 to P_4; equilibration of S_8 to give smaller and more reactive sulfur rings such as S_6;[17] formation of S_2;[18−21] the formation of cycloheptasulfur thionsulfoxide;[22] the formation of S_8 diradical by S−S homolysis.[23] Two phosphorus candidates are possible: P−P homolysis to give the P_4 diradical; cleavage to form two P_2 molecules. Finally, several bimolecular reactions are plausible, including ring-opening addition of P_4 to S_8 or S_8 to P_4 and a complex formed by electron transfer to give a radical cation−radical anion pair.

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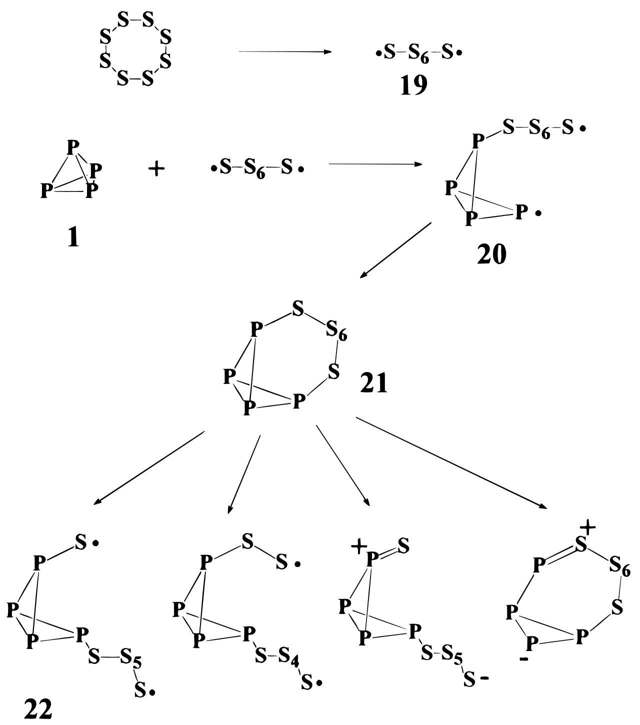

Figure 5. Proposal for the first four steps in the reaction of sulfur and phosphorus at temperatures below 100 °C.

Both the P_4 diradical[24] and P_2[25] are inaccessible at the temperatures of the reaction, making sulfur the far more likely source of the first-formed intermediate. The transfer of one or two sulfur atoms to a P_4 molecule would appear to lead to compounds having initially low S/P_4 ratios, inconsistent with the observed products. P_4S_3 is formed early in the reaction, but α-P_4S_5 is not. In fact, α-P_4S_5 is best explained by the slow oxidation of P_4S_3 (see below). Though the stability of the P_4S_4 isomers to the reaction conditions has not been studied, it is clear that P_4S_3 and α-P_4S_5 are sufficiently stable to be observed as the major products early in the reaction if the formation of the sulfides were to occur by the stepwise addition of one or two sulfur atoms at a time.

Bimolecular, 2-electron reactions between P_4 and S_8 are expected to be very slow because neither is a good nucleophile.[17,26] One-electron transfer from sulfur to phosphorus would generate, after radical pair collapse, the same intermediate discussed below and therefore is mechanistically impossible to distinguish. Initiation of this oxidation reaction by the formation of a high-energy S_n species (S_8 diradical, thionsulfoxide, or S_6) is therefore a logical starting point. The S_8 diradical (**19**) is the best known of the three and will be the focus of the following discussion. Either of the other two species would give rise to cage intermediates similar or identical to those produced by the S_8 diradical and can thus be considered alternate entries into the same manifold. The S_8 diradical is also consistent with many of the observations made in this study: the stoichiometry of the early products, the kinetics of the slow step in the reaction, and the similarity of the thermally and photochemically initiated reactions. If the S_8 diradical is the species formed in the initial, slow step, a proposal for the start of this reaction can be drawn as shown in Figure 5.

It is difficult to ignore the fact that a mixture of $1{:}^1/_8$ P_4/S_8 stoichiometry generates mostly products of P_4S_6 and higher stoichiometries. One molecule of each starting material appears to react to form a manifold of intermediates; these intermediates then rapidly incorporate sulfur into the phosphorus cage and only reluctantly lose sulfur back to the reaction mass. Though there are other explanations for the observed products, the nearly complete consumption of a molecule of S_8 by a molecule of P_4 is one of the most straightforward.

An initial-slope kinetic analysis provides an estimate of the rate of this first slow step, about 2.4×10^{-6} s^{-1}. The activation parameter data for the reaction $S_8 \Rightarrow {}^{\bullet}S-S_6-S^{\bullet}$ can be taken from the extensive rubber technology literature,[23,27] with the understanding that these rates are appropriate for the cross-linking of olefinic hydrocarbons. Since the capture of a sulfur radical by an olefin may be less efficient than capture by P_4, the preexponential term taken from the vulcanization studies may be smaller than appropriate for the oxidation of phosphorus. An activation energy of approximately 146 kJ/mol (35 kcal/mol) has been determined for the first-order formation of ${}^{\bullet}S-S_6-S^{\bullet}$ from S_8. The pre-exponential term has a large reported variation but typically falls in the range $10^{14}-10^{15}$. A rate at 80 °C of 2×10^{-7} s^{-1} is calculated from the activation energy and the largest pre-exponential term. The calculated rate is within a factor of 12 of the observed rate of oxidation.

Several oxidations were performed at low temperature (~0 °C) and initiated by visible light. It is well-known and well-documented that the polymerization of both phosphorus[5] and sulfur[28,29] can be initiated photochemically. The S_8 diradical intermediate involved in the photochemical polymerization of sulfur has been observed by ESR spectroscopy;[28] the suspected diradical involved in phosphorus polymerization has not been observed. The consequences of the production of either diradical are easily drawn and are found in Figure 6. Both radicals can either homo-oligomerize, an outcome not observed at least for phosphorus, or react with the other material in the melt. Cross addition beginning with either of the two diradicals will lead to the same intermediate, diradical **20**.

Among the unique alternatives discussed above, the initial formation of ${}^{\bullet}S-S_6-S^{\bullet}$ from S_8 is most consistent with both the properties of the reactants and the experiments performed. The fact that elemental sulfur easily forms diradicals and the known sensitivity of phosphorus toward formation of bonds with radicals[26,30,31] support the choice of building a model of this reaction based on an initial addition of **19** to P_4. The next question to be answered is whether the formation of **20** and **21** can lead to the observed products.

The chemistry of **21** is more difficult to specify. Several choices exist, including homolytic S−S bond cleavages and 2-electron processes, the products of which are also shown in Figure 5. Compound **21** must decompose more rapidly than the "initiation" reaction because, if the disappearance (in a first-order or pseudo-first-order fashion) of **21** were slow on this time scale, it would be visible in the ^{31}P NMR spectrum. It is not. Assuming that one part in ten thousand of a new

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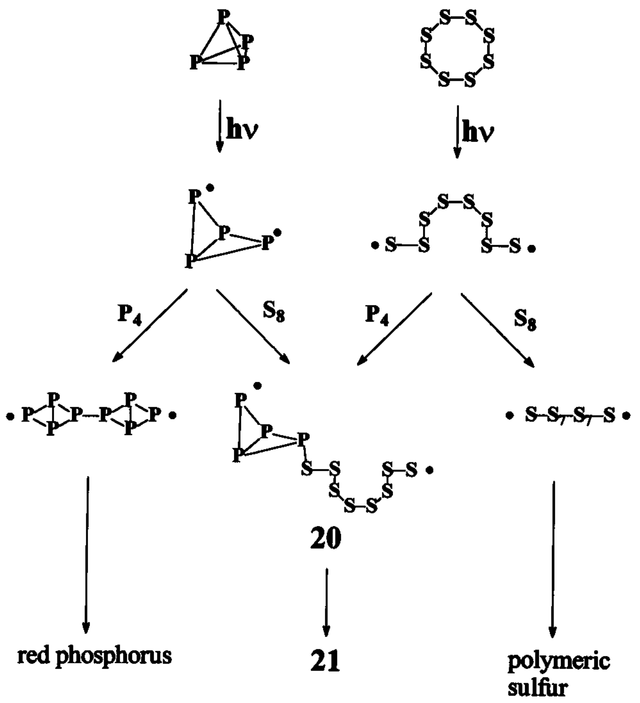

Figure 6. Production and fate of diradical species from P_4 and S_8 in mixtures of the two elements.

phosphorus species would be just visible, the first-order rate of disappearance of **21** or any other intermediate must be 3 orders of magnitude faster than its appearance in order for it to remain submerged from view. An estimate of the maximum half-life for such an intermediate would then be about 10 min. A good model for the formation of **22** from **21** is taken from the work of Danen and Newkirk[32] in which they find the S−S homolytic bond strength of compounds of general formula $R_2NS{-}SNR_2$ is about 25 kJ/mol lower than the equivalent bond in RSS−SSR. Were all of this difference applicable to the PS−SS bond cleavages in these cage polysulfides, intermediate **21** would react too rapidly to be visible.

Assuming the formation of **22**, there are many ways of rearranging sulfur and phosphorus atoms so as to give logical entries into the observed products. A collection of mechanistic steps that transforms **21** into α-P_4S_6 and α-P_4S_7 is shown in Figure 7. This scheme is meant only to be illustrative; yet most of the steps have a precedent in the chemistry of phosphorus (or carbon) radicals. The reactions envisioned include S−S bond cleavage, quaternization (a diradical recombination), rearrangement with ring expansion, and loss of sulfur. The intermediate **27** can continue on to give α-P_4S_7 by performing one more ring expansion. The series of steps shown for the transformation of **21** to **24** in Figure 7 constitutes a cleavage−addition−migration sequence to accomplish an oxidation and ring enlargement. Two of the reactions in this sequence have precedents in the rearrangements of a phosphite ester observed by Hudson.[33] Their work also demonstrated both the radical nature of the reaction of their phosphite ester and the fact that the rate was rapid at temperatures below 0 °C. The path drawn from **24** to **11** is but one of many. It relies on the same reactions used to transform **21** into **24**, adding only the loss of sulfur at the end. The path was drawn to retain the necessary P−P bond, to retain sulfur in the cage as long as possible, and to make every nonradical daughter structure appear to be more stable than its parent. Compound **27** cannot use this same collection of reactions and give rise to γ-P_4S_6, β-P_4S_7, any of the P_4S_8 or P_4S_9 isomers, or P_4S_{10}. At some point prior to the formation of **27**, phosphorus no. 1 (labeled in structure **26**) must be oxidized to a tetracoordinate phosphorus. This oxidation could involve an intra- or intermolecular transfer of sulfur.

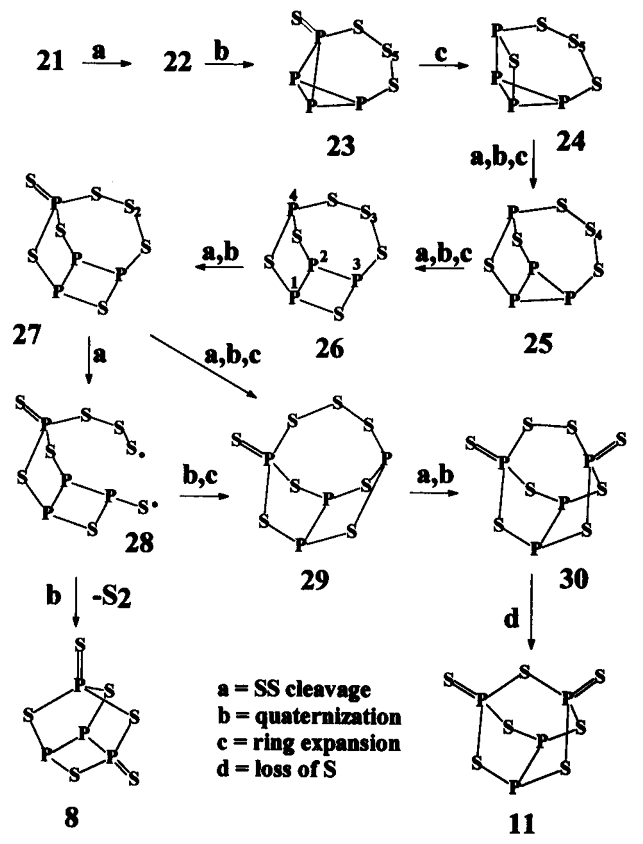

Figure 7. Proposal for the formation of α-P_4S_6 and α-P_4S_7 from the P_4S_8 intermediate **21**.

The mechanism illustrated in Figure 7 makes the assumption that sulfur is not lost from an intermediate until the final step in the formation of a stable (i.e., observed) sulfide. This choice was made in order to make use of the observation that compounds of low S:P_4 ratio are not made most rapidly. There is good precedent from the chemistry of elemental sulfur for the intramolecular cyclization to form small rings and small fragments from larger diradical chains.[26,34,35] Intermediates such as **22** could opt for S−S bond formation with a sulfur in the chain other than the S-radical terminus, forming instead a species like **21**, only with fewer sulfur atoms in the chain, and a S_n fragment. That this is not a major path is supported by the fact that P_4S_3 and α-P_4S_5 are not among the most rapidly formed products.

The low-temperature photochemical reactions have contributed far more than support for the S_8 diradical initiation of this reaction. The phosphorus sulfides in the photochemical experiments are taken from the same collection as those found in the thermal reactions but in remarkably different proportions (Table 1). α-P_4S_6 and α-P_4S_7 are two of the major products in both reactions. But P_4S_3 and α-P_4S_9 are the only other products observed in the early part of the thermal reaction, and they are

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absent from the photochemical reaction. Replacing them are a manifold of products built from γ-P_4S_6: γ-P_4S_6, β-P_4S_7, β-P_4S_8, and γ-P_4S_8. These four sulfides are not as thermally stable as other sulfides. Their sensitivity to higher temperature was confirmed by heating the irradiated mixture (total irradiation time of three hours) to 80 °C for 45 min and observing a significant decrease in the concentrations of these four sulfides. The decreases in relative concentration for the four were 80%, 60%, 90%, and 80%, respectively. Since the appearance profile for these sulfides in the thermal 80 °C reaction is relatively smooth, their observed concentrations are the result of both formation and either sulfur exchange or rearrangement to form other sulfides. Thus, sulfides observed only at low concentration appear to be formed and rapidly transformed, occupying part of the network of reactive intermediates. They may also be responsible for the attachment and removal of exocyclic sulfur atoms, as is necessary for the formation of α-P_4S_9. Until the syntheses of these unusual phosphorus sulfides have been accomplished, this analysis cannot be tested independently.

Conclusions

A number of unique results have been demonstrated by this exercise in phosphorus and sulfur chemistry. Foremost is the observation of slow but significant oxidation of phosphorus by sulfur at temperatures much lower than used to equilibrate these elements. The reaction appears to be initiated by the formation of a reactive sulfur species. At the moment the most likely candidate for this species is the S_8 diradical formed by the cleavage of an S−S bond. The choice of the diradical is supported by the kinetics of the reaction, the sulfur content of the major products, and the similarity between the thermally and photochemically initiated reactions. The initially formed products are found with high S:P_4 ratios, even from starting mixtures having low S:P_4 ratios, arguing that the products are generated in a series of rapid steps that are not dominated by the formation of one or more of the lower sulfides. These two observations were used to construct a mechanism for this oxidation, recognizing that the proposal is meant to stimulate interest in answering the questions that underlie these mechanistic steps. Finally, the family of phosphorus sulfides has been increased by the addition of two new members: γ-P_4S_6, **10**, whose structure is reasonably secure, and γ-P_4S_8, **15**, whose identity is less secure and should be trusted only after more supporting evidence is accumulated.

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Supporting Information Available: Listings of ^{31}P NMR data and representative NMR and Raman spectra (15 pages). Ordering information is given on any current masthead page.

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