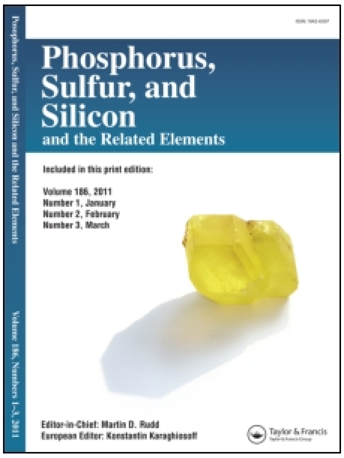

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Some Remarks on Obtaining of Very Pure P_4S_9

Zbigniew Brylewicz[a]; Remigusz Rudnicki[a]
[a] Department of Basic Chemistry, Warsaw University of Technology, Warsaw, Poland

To cite this Article Brylewicz, Zbigniew and Rudnicki, Remigusz(1994) 'Some Remarks on Obtaining of Very Pure P_4S_9', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 173 — 179

To link to this Article: DOI: 10.1080/10426509408020446

URL: http://dx.doi.org/10.1080/10426509408020446

Phosphorus, Sulfur, and Silicon, 1994, Vol. 89, pp. 173–179
Reprints available directly from the publisher
Photocopying permitted by license only

SOME REMARKS ON OBTAINING OF VERY PURE P_4S_9

ZBIGNIEW BRYLEWICZ and REMIGUSZ RUDNICKI
Department of Basic Chemistry, Warsaw University of Technology,
ul.Noakowskiego 3, 00-664 Warsaw, Poland

(Received December 20, 1993; in final form March 21, 1994)

Pure tetraphosphorus nonasulfide—form P_4S_9(I)—free of admixtures of other phosphorus sulfides was prepared in two steps. The first one was multistage extraction from the P—S melt containing only P_4S_9 and P_4S_7. The second was crystallization of the solid obtained in the first step.

Key words: Tetraphosphorus nonasulfide synthesis; extraction, crystallization; IR spectra; ^{31}P NMR spectra.

INTRODUCTION

There are many papers on various properties of tetraphosphorus nonasulfide but in fact there is none in which the method of obtaining very pure P_4S_9 would be described in details.

Tetraphosphorus nonasulfide was obtained by Meisel and Grunze in 1969.[1,2] They have proposed several methods of the synthesis. The obtained sulfides had various stoichiometry ($P_4S_{8.5}$—P_4S_9). Last stage of the synthesis is purification by crystallization. When CS_2 is used in the crystallization process the P_4S_9(I) modification is obtained. P_4S_9(II) modification is prepared when α-bromonapthalene is used in the process. The reproducibility of all the methods for obtaining P_4S_9(II) was very poor.[2]

The P_4S_9(III) modification[3] was obtained in 1990 by reaction of commercial P_4S_{10} with isopropanol mixed in a molar ratio 1/4. The solid product was purified by repeated fractional crystallization from CS_2. The reproducibility of the reaction was also very poor.

Tetraphosphorus nonasulfide—P_4S_9(I)—is usually obtained from phosphorus and sulphur melts containing 28–32% by wt. of P. The main components of the melts containing 28–30% by wt. of P are P_4S_{10} and P_4S_9. P_4S_9 and P_4S_7 are the main components of the melts containing 30–32% by wt. of P. Commercial preparations of P_4S_{10} contain[4] about 28.1–28.4% of P and about 30–40% by wt. of P_4S_9.

The aim of the present work was to find out a method of obtaining very pure [spectroscopically (IR, ^{31}P NMR) pure] tetraphosphorus nonasulfide—form P_4S_9(I)—free of any admixtures of other phosphorus sulfides.

RESULTS AND DISCUSSION

In a previous work on the obtaining spectroscopically pure (IR, ^{31}P NMR) tetraphosphorus decasulfide we have shown,[5] that it is practically impossible to obtain pure P_4S_9 phases from the preparations, which are mixtures of P_4S_9 and P_4S_{10}, by extraction with CS_2. This has confirmed the Meisel and Grunze's observation on crystallization of such preparations.[2] The reason lies in insufficient difference of solubilities of the two sulfides in CS_2.

M. C. Demarcq[6] described a method for obtaining pure P_4S_9 by stirring commercial P_4S_{10} with CS_2 for 10–15 min at room temperature. The solution obtained after filtering was supersaturated in P_4S_9. Upon standing overnight it gave crystals of P_4S_9(I). An impurity of 0.7% P_4S_{10} was found. We have repeated these experiments but products we obtained from various commercial decasulfides (Montedison products) contain greater amounts of P_4S_{10}. It is obvious that the purity of the sulfides obtained by such method will depend highly of the purity and some physico-chemical properties (e.g. specific surface) of the commercial P_4S_{10} used for the purification.

In this work multiple extraction with CS_2 was applied as a main method for purification of P—S melts. The purity of the products obtained was checked by the IR and ^{31}P NMR methods. The infrared spectra of P_4S_9 and P_4S_{10} recorded in CS_2 solution are presented in Figure 1. The absence of P_4S_{10} in the preparations was confirmed by the absence of 535 cm^{-1} band in the IR spectra. If that band was absent the absence of the other phosphorus sulfides was confirmed by ^{31}P NMR investigation.

In Table I we have shown the results of infrared absorption studies of both the products and the residues obtained in extraction of a melt of commercial P_4S_{10} with white P containing 30.0 ± 0.5% by wt. of P. The melt was a mixture of P_4S_{10} and P_4S_9. It results from the data shown in the Table, that the attempts of complete separation of P_4S_9 from P_4S_{10} failed despite of the fact, that the extracted preparation (GP-64) contained 66 ± 2% by wt. of nonasulfide (as detd. by IR

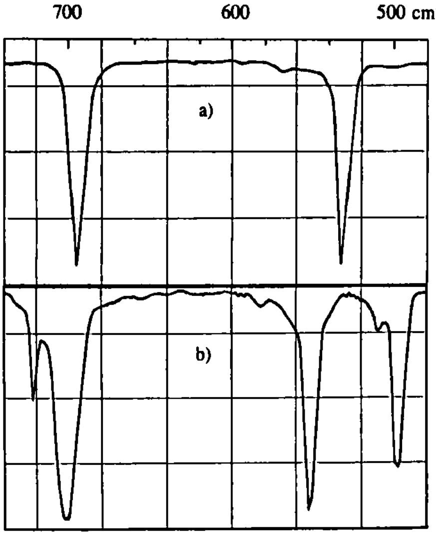

FIGURE 1 IR spectra of very pure P_4S_9 (a) and P_4S_{10} (b) (recorded in CS_2 solution).

TABLE I

Infrared absorption studies of precipitates and residues obtained in the extraction, with CS_2, of a melt of commercial P_4S_{10} and white phosphorus containing 30.0 ± 0.5% by weight of phosphorus

Sample	Band intensity in the IR spectrum		Remarks
	P_4S_{10} 533 cm^{-1}	P_4S_9 546 cm^{-1}	
GP-64	s	s	Melt of commercial P_4S_{10} and white phosphorus
GP-63	s	s	GP-64 sample after 9h extraction (precipitate)
GP-65	s	m	GP-64 sample after 13h (9+4) extraction (precipitate)
GP-66	s	s	GP-64 sample after 13h (9+4) extraction (residue)

In tables in the column remarks we give the overall duration of the extraction and, in parentheses, the durations of individual stages and kind of sample subjected to the IR analysis.

Denotation of IR band intensities: vs-very strong, s-strong, m-medium, w-weak, vw-very weak.

spectrophotometry[7,8]). The content of tetraphosphorus nonasulfide in the residue obtained after 13 h extraction increased to only 75%.

Meisel and Grunze[2] have mentioned that P_4S_9 can easily be obtained by crystallization of melts, which were the mixtures of P_4S_9 and P_4S_7, due to large difference in solubilities of the two sulfides in CS_2. In our attempts to obtain pure P_4S_9 we have prepared melts of commercial P_4S_{10} with white phosphorus (sample GP-67) and with red phosphorus (sample GP-73). The samples contained 31.5% by wt. of P and 73(GP-73) and 80(GP-67) % of P_4S_9.

The results of infrared studies of the melts and of the products and residues obtained in extraction with CS_2 have been shown in Table II. The samples GP-71, GP-82 and GP-83 were also studied by ^{31}P NMR.

Infrared studies of the mentioned preparation dissolved in CS_2 did not reveal any presence of P_4S_{10}. Analysis of ^{31}P NMR and IR showed that each sample contained about 7% by weight of P_4S_7. (The ^{31}P NMR spectra of P_4S_9, P_4S_{10} and P_4S_7 are discussed in References 2, 9–13). The NMR spectra of sample GP-82 contained also very small signal of P_4S_{10}, and the NMR spectra of GP-83 and GP-71 contained very small unidentified signals at chemical shift 100.3 ppm (GP-83) or 27.0 ppm (GP-71).

Commercial P_4S_{10} was melted with red phosphorus to give a product containing 30.5% by weight of P in order to reduce the contents of P_4S_7 in the melt. After careful grinding the melt was extracted with CS_2. Both the precipitates and the residues were studied by infrared absorption and ^{31}P NMR methods (Table III). The results have shown that all the samples contained considerable amounts of both P_4S_7 and P_4S_{10}.

TABLE II

Infrared absorption studies of precipitates and residues obtained in the extraction, with CS_2, of melts of commercial P_4S_{10} and white or red phosphorus, containing 31.5 ± 0.5% by weight of phosphorus

Sample	Band intensity in the IR spectrum		Remarks
	P_4S_{10} 533 cm^{-1}	P_4S_9 546 cm^{-1}	
GP-67	vw	s	Melt of commercial P_4S_{10} and white phosphorus
GP-68	w	s	GP-67 sample after 8h extraction (precipitate)
GP-69	-	s	GP-67 sample after 8h extraction (residue)
GP-70	w	s	GP-67 sample after 3h extraction (precipitate)
GP-71	-	s	GP-67 sample after 7h (3+4) extraction (precipitate)
GP-72	vw	s	GP-67 sample after 7h (3+4) extraction (residue)
GP-73	-	s	Melt of commercial P_4S_{10} and red phosphorus
GP-74	-	vs	GP-73 sample after 12h extraction (precipitate)
GP-75	-	m	GP-73 sample after 12h extraction (residue)
GP-83	-	vs	GP-74 sample after 3h extraction (precipitate)
GP-82	-	vs	GP-74 sample after 15h (3+12) extraction (precipitate)
GP-84	-	vs	GP-74 sample after 15h (3+12) extraction (residue)

Denotation see Table I.

In second part of our work we have tried to obtained pure P_4S_9 by crystallization of various preparations by means of CS_2. The difference between the solubilities of P_4S_9 and P_4S_7 (P_4S_9—0.53 g/100 g, P_4S_{10}—0.22 g/100 g and P_4S_7—0.029 g/100 g of CS_2)[14] has shown that products, containing about 10 percent or more P_4S_7, soluble in CS_2 can be saturated with P_4S_7 rather than with P_4S_9. For this reason we have tried to obtain pure P_4S_9 not from the melts but from the solids obtained during the extractions (preparations GP-63 and GP-82). The results of ^{31}P NMR and IR investigation of the solids obtained by the crystallization have shown that the product obtained from GP-63 preparation (mixture of P_4S_9 and P_4S_{10}) contained more P_4S_{10} than before crystallization. The same investigation for product obtained from GP-82 preparations (mixture of P_4S_9 and P_4S_7) have shown that it was free from any admixtures. The ^{31}P NMR (Figure 2) (3258 scans, 0.48 s repetition time, 36° pulse) and IR spectra have no signals from heptasulfide or other phosphorus sulfides.

TABLE III

Infrared absorption and ^{31}P NMR studies of precipitates and residues obtained in the extraction, with CS_2, of melt of commercial P_4S_{10} and red phosphorus, containing 30.5 ± 0.5% by weight of phosphorus

Sample	Band intensity in the IR spectrum		Existence of P_4S_7 band in the ^{31}P NMR	Remarks
	P_4S_{10} 533 cm^{-1}	P_4S_9 546 cm^{-1}		
GP-100	m	s	+	Melt of commercial P_4S_{10} and red phosphorus
GP-101	s	s	not determ.	GP-100 sample after 2h extraction (preciptate)
GP-102	s	s	not determ.	GP-100 sample after 4h (2+2) extract. (precip.)
GP-103	w	s	+	GP-100 sample after 4h (2+2) extract.(resid.)
GP-104	s	s	-	GP-103 sample after 2h extract.(precip.)
GP-105	s	s	+	GP-103 sample after 4h (2+2) extract.(precip.)
GP-106	w	s	+	GP-103 sample after 4h (2+2) extract.(resid.)

Denotation see Table 1.

The results of our studies have shown that obtaining very pure tetraphosphorus nonasulfide is more difficult than it was suggested in earlier work.[2] During the purification of melts containing, besides P_4S_9, also P_4S_{10} or P_4S_7, the products we have usually obtained were not pure in all cases where only extraction or crystallization was applied. The reason lies in insufficient difference in solubility of these compounds in CS_2. Basing on all the results of our work and on the solubilities of the sulfides we have came to conclusion, that the products obtained by Meisel and Grunze[2] were, most probably, mixtures of P_4S_9 and P_4S_7. These observations have been confirmed, as we think, in the work.[2] The purified preparations, obtained in that work, had compositions about $P_4S_{8.9}$, $P_4S_{8.92}$, $P_4S_{8.86}$. Basing on the solubilities of the nona- and heptasulfide we can make the conclusion that crystallization involving saturation with both P_4S_9 and P_4S_7 should contain about 5–10% by weight of P_4S_7, and their composition should correspond to $P_4S_{8.89}$. Our observations have shown that the easiest way to obtain very pure P_4S_9 was to obtain it from preparations containing about 5% of P_4S_7 or less. Unfortunately such melts contain usually beside P_4S_7 also P_4S_{10} which is difficult to remove. That is the reason why we have proposed two steps of the preparation of P_4S_9: 1—an extraction of melts containing P_4S_9 and 20–30% by weight of P_4S_7; 2—a crystallization of solid obtained in the first step.

EXPERIMENTAL

The IR absorption analyses were performed by means of a Specord 75 Carl Zeiss Jena. The spectra of the sulfides were recorded in CS_2 (Merck, spectrally pure) solution, by the compensation method, with

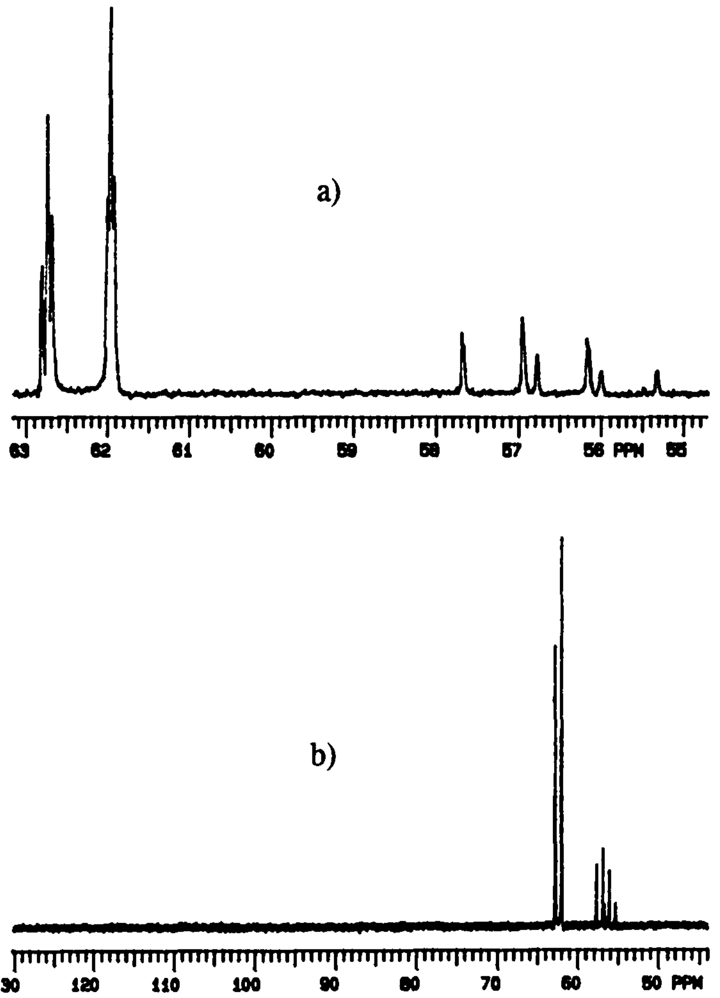

FIGURE 2 The 121 MHz ^{31}P NMR spectrum of very pure P_4S_9 recorded in CS_2 solution at the range: (a) 55–63 ppm; (b) 45–130 ppm.

KBr cell thickness 0.5 mm. The concentration of the solutions was about 2.5 g/dm^3, and the measuring range was 480–740 cm^{-1}.

The ^{31}P NMR spectra were recorded on Varian VXR 300 spectrometer at 121 MHz. Chemical shifts were recorded in ppm upfield from 85% orthophosphoric acid as external standard. The concentration of the solution was about 2.5 g sulfide per 1 dm^3 of CS_2 (Merck) and the measuring range was $-100 \div +200$ ppm.

Obtaining of very pure [spectroscopically (IR, ^{31}P NMR) pure] P_4S_9

a) Obtaining of the P—S melts. A mixture of 220 g of commercial P_4S_{10} (Montedison product, P content—28.1% by wt.) and 11.3 g of pure red phosphorus (POCh Gliwice) was placed in a Pyrex glass ampoule, which was then rinsed with dry oxygen-free nitrogen, and sealed in vacuum. The ampoule was heated for 12 h at 400°C in a sand bath. After very slow cooling the ampoule was opened and the melt, which contained only P_4S_9 and P_4S_7, was ground very carefully.

b) Step one—a multistage extraction with CS_2 (Merck, analytical grade). The extraction was carried out in a Soxhlet apparatus. The melt (about 40 g) was placed in a glass thimble and put into the extractor. Obtained after the first stage of the extraction (12 h) solid product (precipitate), crystallized in the flask was filtered, rinsed with a fresh portion of the solvent, and dried in vacuum. The obtained solid was next put into the new thimble and it was extracted with a fresh portion of the solvent. After 3 hours the extraction process was stopped. The precipitate obtained in the flask was removed and the residue in the thimble was extracted once more (12 h) with a fresh portion of the solvent. After that, the precipitate crystallized in the flask, was filtered, rinsed with a fresh portion of the solvent, and dried in vacuum (12 g of solid sulfide was obtained).

c) Step two—a crystallization with with CS_2 (Merck, analytical grade). The crystallization process was carried out in a flat-bottomed flash with a reflux condenser. The solid obtained in the first step (3 g) was placed into the flask and 100 cm^3 of CS_2 was added. The mixture was stirred and heated to boiling. If the sulfide was not dissolved 10 cm^3 of CS_2 was added (total about 170 cm^3 was used). The clear solution was stirred and cooled to room temperature. Upon standing overnight, the crystals obtained were filtered, rinsed with a fresh portion of the solvent, and dried in vacuum. A 1.2 g of very pure P_4S_9 was obtained.

The yield of the whole process of obtaining very pure P_4S_9 was 12%.

ACKNOWLEDGEMENT

This project was supported by the Committee of Scientific Research (Project No. 2 0648 9101).

REFERENCES

1. M. Meisel and H. Grunze, *Z. anorg. allg. Chem.*, **366,** 152 (1969).
2. M. Meisel and H. Grunze, *Z. anorg. allg. Chem.*, **373,** 265 (1970).
3. B. Wallis, G. U. Wolf and P. Leibnitz, *Z. anorg. allg. Chem.*, **588,** 139 (1990).
4. Z. Brylewicz, Ph.D. thesis, Warsaw University of Technology (1991).
5. Z. Brylewicz and R. Rudnicki, *Prace nauk. Akad. Ekonom. Wrocław, Chemia*, **610,** 263 (1992).
6. M. C. Demarcq, *J. Chem. Soc Dalton Trans.*, **1,** 35 (1990).
7. M. C. Demarcq, *Phosphorus Sulphur*, **11,** 65 (1981).
8. Z. Brylewicz and R. Rudnicki, Presented at National Conference of Polish Chemical Society in Toruń (Poland), September (1993).
9. C. Brevard and M. Demarcq, *Chem. Phys. Lett.*, **82,** 167 (1981).
10. R. Thamm, G. Heckmann and E. Fluck, *Phosphorus Sulphur*, **11,** 273 (1981).
11. T. Bjorholm, *Chem. Phys. Lett.*, **143,** 259 (1988).
12. E. R. Andrew, W. Vennart, G. Bonnard, R. M. Croiset, M. Demarcq and E. Mathieu, *Chem. Phys. Lett.*, **43,** 317 (1976).
13. R. Thamm, G. Heckmann and E. Fluck, *Phosphorus Sulphur*, **12,** 319 (1982).
14. H. Vincent and Ch. Vincent-Forat, *Bull. Soc. Chim. Fr.*, **2,** 499 (1973).