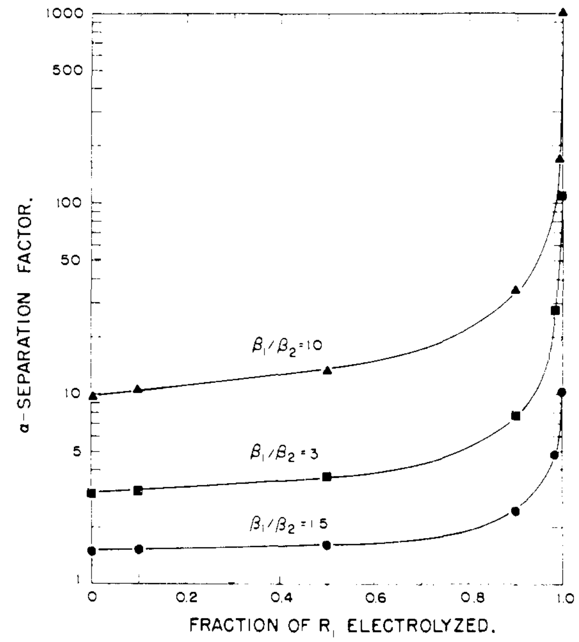

Fig. 4.—Plot of equation 6 for assumed values of β_1/β_2 in terms of completeness of removal of the most easily electrolyzed component.

The data which were obtained for the europium-samarium separation[2] were not compatible with an equilibrium interpretation, but they can be used here to test the forward reaction rate concept. For europium, 90% was removed after 55 minutes[2]; and for samarium, in an independent experiment, 20.4% was removed after 230 minutes.[3] Extrapolation of the latter value gives $\beta_1/\beta_2 \cong 42$. From equation 6, predicted values of α for 99 and 99.9% removal of europium are 856 and 5570, respectively. These values compare favorably with the measured values of 974 for 99.2% removal, and 2810 for 99.9% removal.[2,3]

More accurate data are available for the separation of europium and samarium, from experiments in which the cathode potential was high and the removal of europium was more nearly complete.[3] These data are listed in Table VI and show definitely the large increase in α as the europium removal is more nearly complete. Pure samarium in high yield was recovered from the electrolyte in these experiments.

TABLE VI

EUROPIUM-SAMARIUM SEPARATIONS[3]

Electrolyses of citrate complexes at a lithium amalgam cathode in alkaline solution. Cathode potential − 2.3 to − 3.0 volts *vs.* S.C.E. Temperature 30 to 39°.

% removal of Eu[a]	% removal of Sm	α
99.73	18.7	1600
99.83	17.6	2700
99.84	14.6	3700
99.95	26.2	5600
99.96	15.9	13200

[a] Accurate to within 0.02%.

Acknowledgments.—The spectrographic analyses were done by O. R. Simi. Some of the experiments on the terbium-dysprosium separation were done by C. J. D'Agostino, Jr. Approaches to the problem and interpretation of the results were helped considerably by discussions with R. D. Fowler, R. D. Baker, R. J. Bard, Henry Taube, H. A. Laitinen, J. C. Bailar, Jr., H. L. Friedman, R. N. R. Mulford, F. H. Ellinger, T. W. Newton, R. A. Penneman. The solution to the combined diffusion-rate equation was demonstrated by W. P. Ellis. The mineral was supplied by R. M. Kiehn. John F. Suttle and students at the University of New Mexico helped with cracking the monazite.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Concerning the Existence of Diphosphorus Trisulfide

BY A. R. PITOCHELLI[1,2] AND L. F. AUDRIETH

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Phosphorus trichloride undergoes quantitative thiosolvolysis in liquid hydrogen sulfide to give a product with the empirical composition P_2S_3. Extraction with CS_2 leads to isolation of P_4S_7; recrystallization from CS_2 at 170° yields both P_4S_5 and P_4S_7; chromatography using the same solvent suggests that this product is a mixture. The presence of P_4S_7, and possibly P_4S_5, in the alleged P_2S_3 is indicated by comparison of its X-ray diffraction pattern with those of the known sulfides. The infrared spectrum differs slightly from those of the well-characterized sulfides but demonstrates presence of a P=S linkage. Although diphosphorus trisulfide may be formed initially, it is undoubtedly quite unstable at ambient temperature and most certainly undergoes disproportionation in carbon disulfide.

Introduction

Only four sulfides of phosphorus with the formulas P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} thus far have definitely been shown to exist. Reports have nevertheless continued to persist in the literature,[3] and in modern text books and reference sources, to the effect that the reaction between the phosphorus trihalides and liquid hydrogen sulfide leads to the formation of diphosphorus trisulfide. Earlier claims that such a compound is formed when the stoichiometric amounts of red phosphorus and sulfur are heated together were shown to be incorrect by Helff[4] who demonstrated that a mixture of the tri- and hepta-sulfides actually is obtained. The nature of the product obtained by the thio-

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[1] Abstracted from the thesis submitted to the Graduate College of the University of Illinois in partial fulfillment of requirements for the doctorate degree, 1958.

[2] Universal Match Foundation Research Fellow in Chemistry 1955–1957. Fellowship Grants by the Universal Match Foundation of St. Louis, Missouri, are acknowledged with gratitude.

[3] A. W. Ralston and J. A. Wilkinson, THIS JOURNAL, **50**, 258 (1928).

[4] A. Helff, *Z. physik. Chem.*, **12**, 196 (1893).

solvolysis of phosphorus trichloride has not, however, been subjected to further study.

A number of more modern techniques were therefore used to gain an insight into the nature of this product. Reference samples of each of the known sulfides were prepared. Physical data useful for purposes of identification and comparison with the so-called P_2S_3 were accumulated. The stoichiometry of the reaction and the composition of the yellow product have been shown to conform to that expected for the formation of a diphosphorus trisulfide.

The infrared spectrum of the substance differs slightly from that of the known sulfides; this suggested that the product with the composition P_2S_3 is either a new compound or a mixture of known sulfides. Comparison of the *d*-spacings of the product with those of the known sulfides showed that it contained most of the more intense spacings characteristic of P_4S_7 and at least two characteristic of P_4S_5. A chromatographic study using carbon disulfide as the solvent revealed the presence of two components. Solvent extraction with carbon disulfide led to the isolation of pure P_4S_7; and, finally, high temperature recrystallization from carbon disulfide led to the isolation of both P_4S_5 and P_4S_7. The latter procedure was employed after an investigation of the claim of Dervin[5] to the effect that reaction between P_4S_3 and sulfur in carbon disulfide at elevated temperatures leads to the formation of "needles" of P_2S_4 and "spheres" of P_8S_{11} had been shown to be incorrect. Microanalytical and infrared data demonstrated that the actual products are P_4S_7 and P_4S_5, respectively. In all instances in which a CS_2 treatment has been employed, the experimental evidence points to the fact that the so-called P_2S_3 is a mixture! We are, however, of the opinion that a substance with the empirical composition P_2S_3 may be formed initially, but the preponderance of hepta-sulfide *d*-spacings in the diffraction pattern makes it appear that such a substance is unstable at ambient temperature. Our results further indicate that even if such a substance does exist, it must undergo disproportionation in solvents such as carbon disulfide to give P_4S_5 and P_4S_7.

Experimental

Since the various sulfides are susceptible to autoxidation, particularly in solution, special pieces of apparatus were designed and built to carry out extractions and chromatographic studies in a dry carbon dioxide atmosphere.[6] Infrared analyses were performed on a Perkin–Elmer Recording Infrared Spectrophotometer. The samples were dispersed in Nujol mulls. To obtain X-ray diffraction patterns, samples loaded into Lindemann glass tubes, under conditions avoiding contact with moisture and oxygen,[6] were placed in a 7cm. Hayes diffraction camera and exposed for 8-10 hr. to Cu Kα X-radiation. Details for preparation, purification and analysis of pure reference samples of P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} are given in the original thesis.[6]

Reaction of P_4S_3 and Sulfur in Carbon Disulfide at Higher Temperatures.—Dervin[5] had claimed that this reaction leads to the formation of both P_2S_4 and P_8S_{11}. Accordingly, a 27.5 g. sample of tetraphosphorus trisulfide and 4 g. of sulfur were dissolved in 100 cc. of carbon disulfide and heated under pressure to 170–200° for 3 hr. True to Dervin's claim a product mixture consisting of both spheres and needles was isolated. These were separated manually and each recrystallized in the modified Soxhlet apparatus. Their infrared spectra, melting points and analyses were consistent with those of the penta- and hepta-sulfides, respectively.

Anal. Calcd. for P_4S_5: P, 43.7; S, 56.3. Spheres, Found: P, 43.6; S, 57.9. Calcd. for P_4S_7; P, 35.6; S, 64.4. Needles, Found: P, 35.99; S, 64.4

The Thiosolvolysis of Phosphorus Trichloride.—Dry hydrogen sulfide gas was condensed over freshly distilled phosphorus trichloride. The solution was stored under pressure for 60-70 hr. at ambient temperature. The excess solvent then was allowed to escape and the reaction tube placed under vacuum to eliminate the last traces of hydrogen sulfide. A sample of the residual yellow solid was oxidized with a mixture of boiling nitric acid and bromine. Phosphorus was determined as magnesium ammonium phosphate and sulfur, as barium sulfate. Calculation of the empirical formula showed the composition of the product to be $P_2S_{3.08}$.

A sample of the freshly prepared reaction product was subjected to a fractional extraction with refluxing CS_2 in the modified Soxhlet apparatus. After 52 hr. of continuous extraction, the carbon disulfide solution had assumed a yellow color; a white needle-like crystalline product had separated from the solution. The latter was found to melt at 300–305° and was further identified as P_4S_7 through its infrared spectrum and by analysis.

Anal. Calcd. for P_4S_7: P, 35.6. Found: P, 35.9.

After evaporation of the solvent from the carbon disulfide-soluble fraction, a portion of the residual yellow solid (I) was subjected to infrared and microanalyses. Although its infrared spectrum resembled that of P_3S_5, microanalyses showed its phosphorus content to be much too low for the pentasulfide and slightly low for a compound corresponding to P_2S_3.

Anal. Calcd. for P_4S_5: P, 43.7; for P_2S_3: P, 39.2. Found: P, 38.1.

Another portion of the yellow solid (I) then was subjected to re-extraction. This treatment again led to the formation of white needles in the extract identified as P_4S_7 by a mixed melting point and infrared analysis. The carbon disulfide-soluble fraction (II) again showed an infrared spectrum resembling P_4S_5, but the phosphorus content was found to have decreased still further, approaching that of P_4S_7. (Found: P, 36.6.)

Because the infrared evidence so strongly suggested the presence of the pentasulfide, another attempt was made to isolate this substance. Extraction of the carbon disulfide soluble fraction (II) led to the isolation of still more P_4S_7 and recovery of a carbon disulfide-soluble fraction (III) with a still lower phosphorus content (Found: P, 33.6).

Since the heptasulfide is so insoluble in carbon disulfide (0.029 g./100 g. at 17°), there seems little chance that it is present in the carbon disulfide-soluble fraction in any quantity. Its continued reappearance on extraction seems reasonable only if it is assumed to be a product arising from either a reaction between carbon disulfide soluble components, or through disproportionation. The latter assumption is difficult to reconcile with the increasingly lower phosphorus content of the carbon disulfide-soluble residues.

Carbon disulfide was added to a sample of the freshly prepared reaction product and the suspension heated under pressure at 170° for 3 hr. Characteristic needles and spherules were isolated on cooling. These were separated manually, recrystallized by extraction with CS_2 and analyzed.

Anal. Calcd. for P_4S_5: P, 43.7; S, 56.3. Spheres, Found: P, 43.36; S, 57.2. Calcd. for P_4S_7: P, 35.6; S, 64.4. Needles, Found: P, 35.66; S, 63.8.

This finding demonstrates that the thiosolvolytic product whose empirical composition corresponds to P_2S_3 can be recrystallized from, or reacts in, carbon disulfide at high temperatures to give both the penta- and the hepta-sulfide.

The thermal behavior of the product gave no conclusive or readily interpretable results. Some sublimation is observed at 145–150°. The product begins to soften at 225° and then changes gradually into a viscous yellow-orange liquid up to 260°. On cooling it reverts to a yellow color. Reheating does not result in any further sublimation but softening and color changes occur as before. This behavior suggests decomposition of the product into thermally stable derivatives, an observation consistent with the suggestion that P_4S_5 is a

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(5) E. Dervin, *Bull. soc. chim.*, [2] **41**, 443 (1884).

(6) Experimental details may be found in the thesis entitled "The Phosphorus Sulfides," by A. R. Pitochelli, available on microfilm No. 58-1728, through University Microfilms, Ann Arbor, Michigan.

component of the product mixture, since tetraphosphorus pentasulfide disporportionates at 170° into the tri- and heptasulfides.

When carbon disulfide is used as the solvent, ascending paper chromatograms demonstrated that the tri- and pentasulfides both ascend with the solvent front, probably because of their high solubilities. Spraying with aqueous silver nitrate causes immediate development of a broad brown-black band. The hepta- and deca-sulfides, on the other hand, are found considerably below the solvent front. Development with silver nitrate causes formation of a narrow white band which turns brown within a minute's time. When this procedure was applied to the P_2S_3 product, two components were shown to be present, one of which appeared at the solvent front and developed in a manner characteristic for the tri- and penta-sulfides, whereas the other appeared below the solvent front and developed like the known samples of the hepta- and decasulfides. Here again the experimental evidence suggests that the so-called P_2S_3 is a mixture or that disproportionation occurs on solution in carbon disulfide.

X-Ray Diffraction Data for the Phosphorus Sulfides.—Comparison of the *d*-spacings for the P_2S_3 product which are listed in Table II with those of the known sulfides given in Table I suggests that most of these can be accounted for by assuming presence of the hepta-sulfide. Less certainty exists with respect to the presence of P_4S_5.

TABLE I

X-RAY DIFFRACTION DATA

R.I.	d	R.I.	d
(a) Tetraphosphorus trisulfide			
0.5	3.422	0.3	2.091
1.0	3.123	.3	2.051
0.7	2.972	.3	1.978
.5	2.781	.4	1.803
.5	2.739	.5	1.715
.5	2.680	.5	1.652
.2	2.531	.2	1.505
.3	2.465	.2	1.465
.1	2.386	.1	1.370
(b) Tetraphosphorus pentasulfide			
1.0	4.771	0.8	1.781
0.5	3.131	.4	1.737
.9	3.095	.3	1.675
.5	3.046	.3	1.639
(c) Tetraphosphorus heptasulfide			
1.0	6.214	0.1	2.576
0.5	5.254	.1	2.310
.5	4.388	.2	2.154
.1	3.904	.4	2.005
.7	3.358	.1	1.659
.8	3.104	.3	1.624
1.0	2.925	.1	1.586
0.2	2.662		
(d) Tetraphosphorus decasulfide			
0.5	4.498	0.3	2.475
.7	4.033	.3	2.465
.5	3.757	.2	2.301
.5	3.645	.5	2.190
.6	3.442	.7	1.730
1.0	2.925	.2	1.502
1.0	2.866		

TABLE II

X-RAY DIFFRACTION DATA FOR "P_2S_3"

R.I.	d	Assigned to
0.9	6.146	P_4S_7
.5	5.181	P_4S_7
.4	4.771	P_4S_5
.3	4.375	P_4S_7
.1	2.925	P_4S_7
.2	2.665	P_4S_7
.2	2.004	P_4S_7
.5	1.796	P_4S_5

Infrared Spectra of the Phosphorus Sulfides.—Absence of absorption in the rock salt range in the region characteristic of the $P=S$ bond is sufficient to distinguish the trisulfide from all other sulfides. The unique shapes and absorption frequencies for the $P=S$ bonds in the higher sulfides are sufficiently diagnostic to permit identification through infrared spectroscopy. Pure samples show absorptions at 674–668 cm.$^{-1}$ for P_4S_5, 689–672 cm.$^{-1}$ for P_4S_7 and 686 cm.$^{-1}$ for P_4S_{10}. The maximum absorption for "P_2S_3" occurs at 675 cm.$^{-1}$ which suggests only that the product contains one or more components with a $P=S$ linkage. Using a $P=S$ bond distance of 1.85 Å, Gore[7] arrived at a theoretical absorption frequency of 725 cm.$^{-1}$. By utilizing the average $P=S$ bond distance data, 1.94 Å., published in recent articles dealing with the structures of the known phosphorus sulfides,[8-11] a similar calculation led to a theoretical absorption frequency of 699 cm.$^{-1}$. Hooge and Christen[12] recently have assigned a value of 675 cm.$^{-1}$ for an isolated $P=S$ group. All values are in good agreement with the observed values recorded above.

URBANA, ILLINOIS

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