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Principles of Phosphorus Chemistry. XIII. Thiophosphate Salts and Esters

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By heating so as to dissolve various proportions of phosphorus pentasulfide in trialkyl or triaryl tetrathioorthophosphate, single-phase liquids undergoing continuous structural reorganization can be formed. Metastable equilibria between the usual structural building units—ortho, end, middle, branch—were shown by nuclear magnetic resonance (n.m.r.) to occur immediately upon dissolution of the P_2S_5 and upon further heating for a period as long as 50 hr. at temperatures in the range of 155 to 175°. End groups are present in equilibrium in much lesser amounts than would be expected for ideally random reorganization. Upon extended heating at 175° or short-term heating at considerably higher temperatures, autoredox reactions take place in the alkyl ester system so as to form S-S linkages which may be present in phosphorus-based structures. Under these conditions, triply connected phosphorus and phosphorus-free organic sulfur compounds have been shown to be present. These autoredox reactions appear to occur more rapidly in the phenyl than in the propyl and butyl ester systems. In the Na_2S - P_2S_5 system, chilling of melts gave glasses (amorphous to X-rays) in the range of Na_2S/P_2S_5 mole ratios from 0 to 3.5. N.m.r. data on these glasses freshly dissolved in ice-cold 10% aqueous sodium sulfide were interpreted to show that structural reorganization occurs in the melt, with end and, perhaps, middle structural building units being present to less than the random amount. Physical data are presented for the tributyl and tripropyl tetrathioorthophosphates, and new n.m.r. chemical shifts are reported.

In contradistinction to the well-known polyphosphates, there is little information^{2,3} on condensed thiophosphate esters or salts in which there are no oxygen atoms. This article deals with such esters and salts and is the first of several studies directed toward the elucidation of phosphorus-sulfur chemistry.

Experimental Details

Reagents.—The phosphorus pentasulfide used in most experiments was fresh, slowly-reactive-grade material made by Monsanto Chemical Company from elemental phosphorus and pure commercial-grade sulfur. It exhibited high crystallinity and the correct analysis for phosphorus and sulfur. In a few of the experiments, a highly purified recrystallized phosphorus pentasulfide was employed. This was made by dissolution of the commercial P_2S_5 in carbon disulfide, using a Soxhlet extractor. The rate of extraction was quite slow since only 100 g. of P_2S_5 dissolved in 40 hr. The extraction was repeated, at which time the phosphorus pentasulfide was collected as four fractions by changing the boiling flask of the extractor. Although all fractions except the last appeared to be pure, only the two middle fractions were used.

The tetrathioorthophosphate esters were prepared from Eastman high-purity *n*-propyl and *n*-butyl mercaptans. Butyl thiophosphate was made by refluxing 250 g. of C_4H_9SH with 85 g. of P_2S_5 for 2 hr. Fractional distillation (several mm.) of the resulting yellow liquid gave a 94.6% yield of $(C_4H_9S)_3PS$, b.p. 166° (2 mm.). Analysis showed 43.73% C and 8.11% H; theoretical: 43.6 and 8.23%, respectively. Likewise, refluxing 100 g. of C_3H_7SH with 44 g. of P_2S_5 for 12 hr. followed by low-pressure fractional distillation of the pale-yellow liquid product gave an 87% yield of $(C_3H_7)_3PS$. Analysis of this propyl ester (b.p. 142° at 2 mm.) gave 37.26% C and 7.44% H; theoretical: 37.47 and 7.34%, respectively.

The vapor-pressure equation given below for the butyl ester corresponds to a value of Trouton's constant of 20.9, a heat of vaporization of 14.3 kcal./mole and a calculated boiling point of 410° at 760 mm.

$$\log p_{mm} = -3125/T + 7.4521 \quad (1)$$

The vapor-pressure equation for the propyl ester (eq. 2) leads to a Trouton's constant of 24.0 and a 760 mm. b.p. of 347°. $\Delta H_{vap} = 14.9$ kcal./mole.

$$\log p_{mm} = -3229/T + 8.0865 \quad (2)$$

For the butyl ester, d^{25}_4 is 1.13 and n^{25}_D is 1.5667; for the propyl ester, d^{25}_4 is 1.16 and n^{25}_D is 1.5883.

The triphenyl tetrathioorthophosphate was prepared according to Rosnati.² It was found to have a melting

point of 87–88°, close to the value reported by Michaelis and Linke.⁴ The crude preparation obtained by refluxing 0.364 mole of thiophenol with 0.09 mole of phosphorus pentasulfide in 200 ml. of toluene gave a precipitate of the metathio-phosphate as described by Rosnati but in about five times the amount. Nuclear-magnetic-resonance (n.m.r.) investigation of the residual crude "ortho-thiophosphate" showed no peak for the metaphosphate but four constituents having chemical shifts of -93 ± 2 , -86 ± 2 , -79 and -63 p.p.m. After recrystallization of the crude product in alcohol, all peaks disappeared except the tetrathioorthophosphate resonance at -93 p.p.m. The phenyl trithio-metaphosphate exhibited a melting point of 167–170°, a value close to the reported² one of 165°.

The anhydrous sodium sulfide was made⁶ by dehydrating Fisher Cp. $Na_2S \cdot 9H_2O$ in a vacuum desiccator over concentrated sulfuric acid for more than three weeks. The sodium thioorthophosphates having from one to all of the four phosphate oxygen atoms substituted by sulfur were prepared according to the literature.⁶ The tetrathioorthophosphate salt was made several times in order to make sure that it had not hydrolyzed during preparation, since its n.m.r. chemical shift was very close to that of the trithioorthophosphate.

Reorganization of Thioorthophosphate Esters with P_2S_5 .—Preparation of thiopolyphosphate esters was achieved via the reorganization technique. The tetrathioorthophosphate ester $(C_4H_9S)_3PS$ in most cases was mixed with the appropriate amount of phosphorus pentasulfide under a nitrogen atmosphere in thick-walled Pyrex tubes, which were sealed off under vacuum. The following mole ratios of C_4H_9S/P were employed: 3.0 (no P_2S_5 used in this preparation), 2.6, 2.5, 2.0, 1.5, 1.4, 1.2, 1.0, 0.6 and 0.3. Various selections of these tubes were heated for fixed lengths of time at temperatures in the range from 100 to 300° in order to effect structural reorganization.

Preparation of Sodium Thiopolyphosphates.—A series of amorphous compositions exhibiting Na_2S/P_2S_5 mole ratios of 3.5, 2.5, 2.0, 1.5, 1.0, 0.7 and 0.0 were made by intimately mixing the proper proportions of dehydrated Na_2S with P_2S_5 under an atmosphere of dry nitrogen in a large dry box containing a balance, small electric furnace, copper chill-plates and other needed equipment. The intimate mixtures of the reagents were then briefly melted in a porcelain crucible in the dry-box furnace, with the melt being stirred with a platinum rod until it appeared homogeneous. The melt was then quickly poured onto a heavy copper quench-plate, and another heavy copper plate was immediately pressed on it to cause very rapid cooling. This technique, which is the same as that used to prepare⁷ vitreous sodium phosphates containing no sulfur, gave yellow transparent or

(4) A. Michaelis and G. L. Linke, *Ber.*, **40**, 3419 (1907).

(5) G. Brauer, "Handbuch der präparative Anorganischen Chemie," Ferdinand Enke, Stuttgart, 1954, p. 280.

(6) See pp. 439–444 of ref. 5.

(7) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishing Co., New York, N. Y., 1958, pp. 777–779.

(1) On leave of absence during 1960 from Monsanto Research S.A., Zurich.

(2) L. Rosnati, *Gazz. chim. ital.*, **76**, 272 (1946).

(3) E.g., M. Ferrana, *Compt. rend.*, **122**, 886 (1896).

translucent glasses which were completely amorphous to X-rays. These thiophosphate glasses were ground quickly in the dry-nitrogen atmosphere and stored in tightly sealed weighing bottles which were kept in a desiccator over P_2O_5 . Analysis showed that, under the experimental conditions employed, loss of P_2S_5 from the melt was slight and did not affect appreciably the elemental analysis.

N.m.r. Measurements.—High-resolution P^{31} n.m.r. techniques employed in previous papers of this series⁸ were used in this study. Many of the measurements on the sodium thiophosphates were carried out in a 10% aqueous sodium sulfide solution at room temperature. In these solutions and in solutions of the thiophosphate salts in plain water, n.m.r. data could only be obtained when the evolution of H_2S was slow, since the formation or motion of more than an occasional generated bubble upset the system so that the spectra were illegible. Because of low solubility in 10% sodium sulfide solutions as well as particularly rapid evolution of H_2S when the solutions approached saturation with the thiophosphate, the resonance peaks obtained on the majority of solutions of the $Na_2S-P_2S_5$ glasses were small and sometimes difficult to distinguish from the background noise. However, for the pure sodium thioorthophosphates in water or in 3% aqueous sodium sulfide, good resonances were found. Likewise, the resonances seen for the fluid thiophosphate esters were very good. Chemical shifts are presented in p.p.m. of the magnetic field, using 85% orthophosphoric acid as the reference standard, with negative shifts being downfield. Unless otherwise stated, all chemical shifts reported herein are believed to be correct to within ± 1 p.p.m.

Thiophosphate Esters. Results and Interpretation.—At room temperature, there is apparently no reaction between P_2S_5 and tributyl tetrathioorthophosphate. However, when mixtures of the two are heated to 110° , dissolution is completed in a matter of hours—4 hr. for $R \equiv (C_4H_9S)/P$ mole ratio = 2.6; and 6 hr. for $R = 2.0$. For $R \equiv 1.5$, dissolution of the P_2S_5 was not complete after many weeks at 110° . At 155° , the time for complete dissolution was also found to increase with increasing amounts of the P_2S_5 in the thioortho ester. For $R = 2.5$, dissolution was complete in 1 hr. and 10 min.; whereas, for $R = 1.4$, 3 hr. were needed. At higher temperatures, the rate of dissolution of the P_2S_5 was even more rapid. The obvious physical properties of the system after 2 to ca. 75 hr. at $155-165^\circ$ are shown in Fig. 1.

At temperatures in the range of $155-165^\circ$, the distribution of species in the cooled melt was found to be unchanged whether the n.m.r. measurements were made immediately upon dissolution of the P_2S_5 or as long as 50 hr. thereafter. These n.m.r. results are presented in Fig. 2 as a function of the R value.

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Upon heating at considerably higher temperatures or for much longer times, some of the n.m.r. peaks were found to disappear and new ones appear. This was most pronounced for samples heated at 300° for 2 hr., but the effect was quite appreciable upon heating for 300 hr. at 175° . However, at 175° for any length of time ranging from 2 to 50 hr., the n.m.r. results corresponded closely to the

(8) L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, *J. Am. Chem. Soc.*, **82**, 5305 (1960).

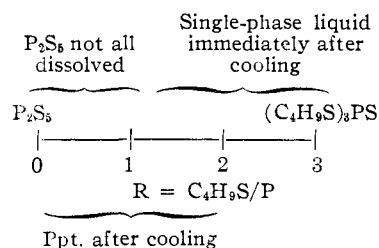


Fig. 1.—Physical behavior of the $(C_4H_9S)_3PS-P_2S_5$ system after heating for 5–50 hr. at $155-175^\circ$ and quenching to room temperature.

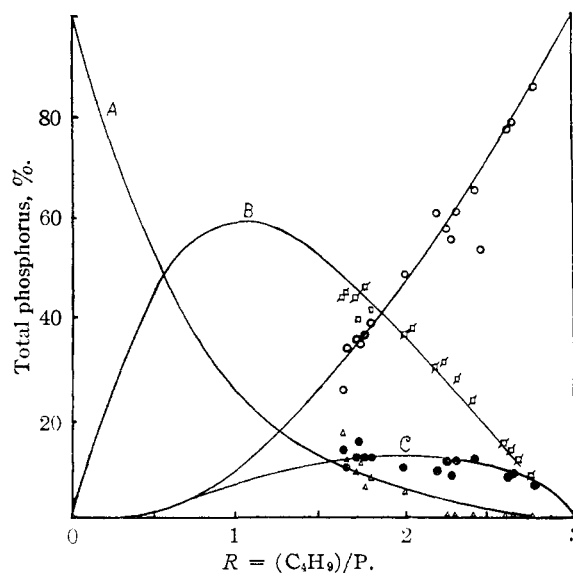


Fig. 2.—Ligand-interchange equilibria for the structure building units in the family of completely sulfur-substituted butyl thiophosphate esters. The curves are drawn for $K_1 = 0.05$ and $K_2 = 12$. The experimental points represent data from a number of different experiments in which mixtures of tributyl tetrathioorthophosphate with phosphorus pentasulfide were heated for various lengths of time from 5 to 50 hr. at temperatures ranging from $155-175^\circ$. \circ = ortho, \square = middle (Curve B), \bullet = ends (Curve C), and Δ = branches (Curve A).

data presented in Table I for "After heating moderately."

In Table I, all of the observed n.m.r. peaks for the $(C_4H_9S)_3PS-P_2S_5$ system are reported, along with remarks concerning their appearance and their assignments. The resonance peak at -93 p.p.m. corresponds to the ortho compound which could be obtained in pure form. The resonances at -86 and -22 p.p.m. are believed to correspond to the end group and middle group, respectively, since this assignment agrees with the stoichiometry of Fig. 2. Additional support for the middle-group assignment was obtained from the appearance of a single n.m.r. peak at -23 p.p.m., in addition to the ortho peak at -93 p.p.m., when phenyl trithiometa-phosphate (all middle groups) was dissolved in pure, warm tributyl tetrathioorthophosphate. As noted below, there is little or no difference in the P^{31} n.m.r. resonance when substituting an aryl-mercapto group for an alkylmercapto group in the thiophosphate esters.

TABLE I
N.M.R. CHEMICAL SHIFTS OBSERVED FOR THE THIOPHOSPHATE ESTER SYSTEM

Resonance in p.p.m. relative to 85% H ₃ PO ₄	After heating		
	Mildly	Moderately	Strongly
-116	Not observed	$R \leq 2$ ca. 5% at $R = 1.5$	Not observed
-111	Not observed	$R \leq 2$ ca. 3% at $R = 1.5$	Increases from zero at $R = 3$ to ca. 7% at $R = 1.5$
-103	Not observed	Begins to appear	Increases from zero at $R = 3$ to ca. 35% at $R \approx 2$, for 2 hr. at 300°
-93	Ortho. Present in all spectra, decreasing from 100% at $R = 3$ to 33% at $R = 1.5$		
-86	Increases from zero at $R = 3$ to ca. 10% at $R \leq 2$	No	No
-79	Not observed	No	From zero at $R = 3$ to ca. 30% at $R = 1.5$
-63	Not observed	For $R < 2$ in amounts of 10% or less	
-23	Middle group increases from zero at $R = 3$ to ca. 40% at $R = 1.5$	No	No

The n.m.r. resonance at -63 p.p.m. has been assigned to the thiophosphate branching group for two reasons: The first is that previous work⁸ in the thiophosphoryl halide systems indicated that this was the branching point. (The thiophosphoryl halides and the thiophosphate salts and esters have the same branching group.) The second reason is based on the precipitation of a phosphorus sulfide when the single-phase liquid systems corresponding to $R = 1.5$ were allowed to stand at room temperature for several minutes. Before the phase separation, the peak at -63 p.p.m. was present; but afterwards, it completely disappeared.

The resonance peak at -116 p.p.m. corresponds to tributyl thiophosphite, (C₄H₉S)₃P, which was obtained in pure form by an independent synthesis. This agrees well with the reported^{9,10} value of -117 ± 1 p.p.m. for thiophosphite esters. A thiophosphonate ester, RP(S)(SR₂), is said¹⁰ to have a chemical shift of -74 ± 3 p.p.m. when the alkyl group directly attached to the phosphorus is a methyl. Presumably, the resonance we observed at -79 p.p.m. corresponds to a butylthiophosphonate obtained from the Arbusov rearrangement of the thiophosphite exhibiting a chemical shift of -116 p.p.m. And, indeed, when tributyl thiophosphite was heated for 2 hr. at 170° with butyl bromide as a catalyst, two new peaks appeared, one of which had a chemical shift measured at -77 p.p.m. and was assigned to butylthiophosphonate.

From their high negative values, we would guess that the shifts at -111 p.p.m. and -103 p.p.m. correspond to compounds based on triply connected phosphorus. Molecular distillation of some of these strongly heated compositions gave a small fraction of phosphorus-free organic liquid containing sulfur. The boiling point of this fraction was in the range of that of dibutyl thioether.

The precipitates formed from the single-phase liquids for which $R = 1.4$ and 1.5 (see Fig. 1) were found to contain no organic constituents. Proxi-

mate analysis gave an S/P mole ratio of 1.2-1.3. X-Ray powder diffraction showed that the precipitates exhibited crystallinity, with 12 diffraction peaks corresponding to d spacings ranging from 9.6 to 2.80 Å. Comparison with standards¹¹ showed spacings corresponding to those of P₄S₁₀, P₄S₇ and, perhaps, S₈ and P₄S₅. However, some of the more important diffraction lines of each of these species were missing, so that their presence in the precipitates is open to question.

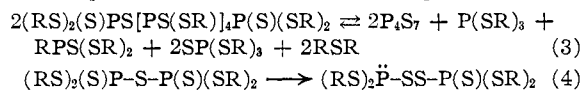
Only one composition was studied in the (C₆H₅S)₃PS-P₂S₃ system. In this case, phenyl trithiometaphosphate, shown to be pure by an n.m.r. spectrum of its solution in (C₄H₉S)₃PS, was melted at a temperature around 170°, and an n.m.r. spectrum was taken as soon as possible (within several minutes). Eight resonance peaks were observed. The four major peaks appearing at -93 (ortho), -86 (end), -63 (branch) and -23 p.p.m. (middle), corresponded to 10.4, 17.4, 31.5 and 22.9% of the total area under the peaks. The remaining peaks at -119 (predominates), -111, -103 and -67 p.p.m. accounted for the remaining 17.8% of the area. It appears from these data that substitution of phenyl for butyl in the system of thiophosphate esters causes an increase in the rate of reorganization so that the metastable equilibrium observed for the butyl thiophosphate esters is not detectable in the phenyl analogs. Again, reorganization equilibrium seems to be achieved immediately upon dissolution—this time, of the crystalline metaphosphate. Upon cooling the molten phenyl trithiometaphosphate, complete solidification occurred, and a solution of these crystals in gently warmed tributyl tetrathiophosphate showed all eight n.m.r. resonances, with the middle-group peak considerably enhanced (the major constituent). This means that, when the molten metaphosphate is chilled, crystallization from the multicomponent melt drives the reorganization equilibria in the direction of the pure metaphosphate.

(9) N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

(10) H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958).

(11) J. V. Smith, A. S. Beward, L. G. Berry, B. Post, S. Weissmann and G. E. Cohen, "Index to the X-ray Powder Data File," Am. Soc. Testing Mats., Philadelphia, Pa., 1960. Also see G. A. Rodley and C. J. Wilkins, *J. Inorg. & Nuclear Chem.*, **13**, 231 (1960).

Discussion.—The reactions occurring at high temperatures or upon long-term heating appear to be of the autoredox type, involving formation of S–S linkages with concomitant production of triply connected phosphorus or, perhaps, P–P bonds. Obviously a large number of possible autoredox reactions can be conceived. Two possible examples are given below. However, no claim is made that these specific reactions are occurring.



The apparent metastable equilibrium between ortho, end and middle groups shown in Fig. 2 can best be represented by the following values of the equilibrium constants for exchange of role between structure building units

$$K_1 = [\text{branch}][\text{end}]/[\text{middle}]^2 = 0.1 \quad (5)$$

$$K_2 = [\text{middle}][\text{ortho}]/[\text{end}]^2 = 14 \quad (6)$$

It should be noted that this is an extremely non-ideal system and that the end groups are present in much lesser amounts than would be expected for ideal randomness ($K_1 = K_2 = 0.333$).

Substitution of an aryloxy for an alkoxy group in phosphates causes the n.m.r. chemical shift to become more positive by 5–7 p.p.m. However, alkylmercapto and arylmercapto groups in thiophosphates appear to be indistinguishable within 1 p.p.m. by n.m.r. This behavior probably is due to the larger size and greater ability to change its hybridization (*i.e.*, “polarizability”) of the sulfur atom as compared to oxygen.

Sodium Thiophosphates. Results and Interpretation.—The gross properties of the Na_2S – P_2S_5 system obtained by quenching melts are given in Fig. 3. As shown by this figure, the glasses for which the $\text{Na}_2\text{S}/\text{P}_2\text{S}_5$ mole ratio lay between 0 and 3.5 (the highest value in this study) were all amorphous to X-rays, either in bulk or finely ground. Replicate preparations having $\text{Na}_2\text{S}/\text{P}_2\text{S}_5 \geq 3$ were clear, transparent, yellow glasses. However, the glasses for which $\text{Na}_2\text{S}/\text{P}_2\text{S}_5 \leq 2.5$ were cloudy yellow. This cloudiness probably means that there were either two liquid phases in the melt or that solid or liquid amorphous phase(s) separated on quenching. Inspection of the cloudy glass at a magnification of $30\times$ did not resolve the postulated phases.

When the finely divided thioorthophosphate glass ($\text{Na}_2\text{S}/\text{P}_2\text{S}_5 = 3$) was dissolved in ice-cold water, evolution of H_2S was not observed for the first few minutes. However, when the other glasses having higher or lower $\text{Na}_2\text{S}/\text{P}_2\text{S}_5$ ratios were treated in an identical manner, H_2S evolution was observed immediately. In an ice-cold 10% aqueous sodium sulfide, the rate of H_2S evolution was found to increase with decreasing $\text{Na}_2\text{S}/\text{P}_2\text{S}_5$, with gas evolution being immediately observed only for those glasses having $\text{Na}_2\text{S}/\text{P}_2\text{S}_5 < 2.5$.

In order to assign at least some of the n.m.r. chemical shifts obtained, the chemical shifts of the pure sodium orthophosphates ranging from Na_3PO_4 to Na_3PS_4 were measured immediately after dissolution in ice-cold 3% aqueous sodium sulfide. These shifts are reported in Table II, along with

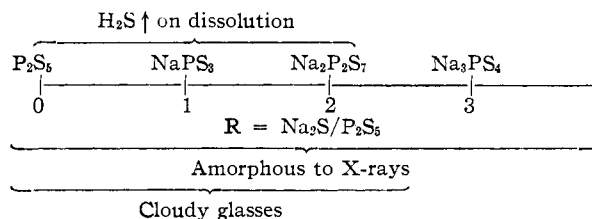


Fig. 3.—Physical behavior of the Na_2S – P_2S_5 system after quenching the melt.

the four other shifts obtained on solutions of the various Na_2S – P_2S_5 glasses.

The n.m.r. results obtained (1) immediately after dissolving the various Na_2S – P_2S_5 glasses in ice-cold 10% aqueous sodium sulfide, and (2) on the same solutions after standing for 3 hr. at room temperature are reported in Table III. The values for the amounts of the various species observed from the n.m.r. spectra are only rough approximations. Because of the small differences in chemical shift between the PS_4^{\equiv} and POS_3^{\equiv} ions, these cannot be distinguished readily from each other and are denoted in Table III by the letter A. From these data, it appears that species Y is a hydrolysis product of the completely sulfur-substituted middle group. The stoichiometry, which is only a rough approximation, indicates that this species should exhibit no more than three sulfur atoms per phosphorus. Species X is only found in solutions of *vitreous* P_2S_5 . It is presumably a hydrolysis product of the completely sulfur-substituted phosphate branch group. From the rough stoichiometry and the chemical shift, species X would appear to have two or, more probably, less than two sulfur atoms per phosphorus.

TABLE II

N.M.R. CHEMICAL SHIFTS RELATIVE TO 85% H_3PO_4 OBSERVED FOR SOLUTIONS OF SODIUM THIOPHOSPHATES

Orthophosphates	Shift ^a (p.p.m.)	Other species	Shift ^a (p.p.m.)
PS_4^{\equiv}	–87	B	+5
POS_3^{\equiv}	–86	C	+21
$\text{PO}_2\text{S}_2^{\equiv}$	–61	X	–46
$\text{PO}_3\text{S}^{\equiv}$	–32	Y	–71
PO_4^{\equiv}	0		

^a Positive shifts are measured upfield. All measurements to ± 1 p.p.m.

Characterization of species B and C as the sulfur-free end group and middle group, respectively, was based on the n.m.r. chemical shifts and other evidence. These species were found to be quite resistant to hydrolysis, as evidenced by allowing the solutions to stand for several days. Moreover, qualitative paper chromatograms were run on several of these aged solutions, and phosphate chain and ring molecule-ions were found.

Discussion.—The Na_2S – P_2S_5 glasses are amazingly unstable in water. Not only are the sulfur atoms rapidly substituted by oxygen from the water, but the P–S–P linkages appear to be cleaved very quickly. A qualitative study of the hydrolysis of the tetrathioorthophosphate ion indicated a half life for this species of *ca.* 20 min. in water at 25°.

TABLE III
N.M.R. ANALYSIS OF $\text{Na}_2\text{S}-\text{P}_2\text{S}_5$ GLASSES DISSOLVED IN 10%
SODIUM SULFIDE SOLUTION^a

$\text{Na}_2\text{S}/\text{P}_2\text{S}_5$	Immediately at 0°	Same solution after 3 hr. at 25°
0	0.4X + 0.6A	0.3 $\text{PO}_3\text{S}_2^{\text{m}}$ + 0.7 $\text{PO}_3\text{S}^{\text{m}}$
0.7	0.6Y + 0.4A	0.5Y + 0.5 $\text{PO}_3\text{S}^{\text{m}}$
1.0	Y	0.7Y + 0.3 $\text{PO}_3\text{S}^{\text{m}}$
1.5	Y	0.7Y + 0.3 $\text{PO}_3\text{S}^{\text{m}}$
2.0	Y	0.2C + 0.6 $\text{PO}_2\text{S}_2^{\text{m}}$ + 0.2 $\text{PO}_3\text{S}^{\text{m}}$
2.5	0.3Y + 0.7A	0.1B + 0.5C + 0.2A + 0.1 $\text{PO}_2\text{S}_2^{\text{m}}$ + 0.1 $\text{PO}_3\text{S}^{\text{m}}$
3.0	A	
3.5	0.3C + 0.4B + 0.3 PO_3S	0.4B + 0.3C + 0.3 $\text{PO}_3\text{S}^{\text{m}}$

^a The numbers in front of the letters or formulas designating chemical species represent the approximate fraction of the total phosphorus in that species (which may be a structure building unit). A is PS_4^{m} or POS_3^{m} ; B is probably a sulfur-free end group, $^-\text{O}_2\text{P}(\text{O}_{1/2}^-)_2$; C is probably a sulfur-free middle group, $^-\text{O}_2\text{P}(\text{O}_{1/2}^-)_2$; X is probably a hydrolysis product of the completely sulfur-substituted phosphate branch group; Y is probably a hydrolysis product of the completely sulfur-substituted middle group.

The fact that chain and ring phosphates are found by paper chromatography in the aged hydrolysis products corresponding to $\text{Na}_2\text{S}/\text{P}_2\text{S}_5 = 2.5, 3.0$ and 3.5 indicates that hydrolysis of the orthothiophosphate glass involves polymerization, through formation of P-O-P linkages. Polymerization concomitant with hydrolysis has been observed previously for the polyphosphoryl chlorides⁸ and, perhaps, for the polyphosphoramidates.¹² This means that it is difficult to visualize the original unhydrolyzed thiophosphate from knowl-

(12) *E.g.*, A. Narath, F. H. Lohman and O. T. Quimby, *J. Am. Chem. Soc.*, **78**, 4493 (1956).

edge of the hydrolysis fragments. Nevertheless, it would appear that the equilibrium⁸ for exchange of roles between structure building units are such that K_1 is near zero and K_2 is considerably larger, perhaps being considerably larger than unity. (See eqs. 5 and 6 for the definition of K_1 and K_2 .) The fact that only species A was observed for the glass exhibiting a $\text{Na}_2\text{S}/\text{P}_2\text{S}_5$ mole ratio of 3.0 immediately upon dissolution at 0° indicates that little or no free Na_2S is in equilibrium with the sodium phosphates so that K_3 is zero¹³ or close to this value.

The substitution of sulfur for oxygen in the orthophosphates causes a negative chemical shift as shown in Table II. Shift increments are $-32, -29, -25$ and -1 p.p.m. for each successive replacement of oxygen by sulfur. The small shift increment observed upon replacement of the final oxygen atom has been demonstrated to be real, since both the trithio- and tetrathioorthophosphate anions were present in several solutions investigated so that partially overlapping but separate resonances were seen simultaneously for the two species.

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(13) See pp. 724-731 of ref. 7. Also see J. R. Parks and J. R. Van Wazer, *ibid.*, **79**, 4890 (1957).

[CONTRIBUTION NO. 728 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

Alkyl- and Arylsulfur Trifluorides¹

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The first general synthesis of arylsulfur trifluorides has been found in the reaction of aryl disulfides with silver difluoride in 1,1,2-trichloro-1,2,2-trifluoroethane solvent. Fluorobutyl- and trifluoromethylsulfur trifluorides have been prepared by reaction of butyl disulfide and carbon disulfide or bis-trifluoromethyl trithiocarbonate with silver difluoride. The chemical and physical properties of the sulfur trifluoride compounds are described. In particular, the alkyl- and arylsulfur trifluorides have been shown to be useful reagents for selective conversion of carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups.

Until recently, organic derivatives of sulfur fluorides were a relatively unknown class of compounds.² Numerous unsuccessful attempts to prepare RSF , RSF_2 and RSF_3 compounds have been reported.³ In general the sulfur trifluoride

(1) This work was reported in a preliminary form by W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960), and at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) For a recent review of compounds containing sulfur-fluorine bonds see H. L. Roberts, *Quart. Rev.*, **15**, 30 (1961).

(3) (a) H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946). (b) R. N. Haszeldine in "Special Publication No. 12, Chemical Society Symposia," Bristol, 1958, The Chemical Society, Burlington House, W. I. London, 317 (see p. 331). (c) W. A. Sheppard and J. F. Harris, Jr., *J. Am. Chem. Soc.*, **82**, 5106 (1960).

compounds are known only with R as a perfluoro-alkyl group and are prepared, usually in low yields, from organic sulfur compounds by reaction with elemental fluorine or by electrolytic fluorination in anhydrous hydrogen fluoride. For example, the derivatives of sulfur tetrafluoride, CF_3SF_3 , $\text{SF}_5\text{CF}_2\text{SF}_3$, $\text{F}_3\text{SCF}_2\text{SF}_3$ and $\text{F}_3\text{SCF}_2\text{CO}_2\text{H}$, were prepared by fluorination of carbon disulfide and thioglycolic acid.⁴ Recently Chamberlain and

(4) (a) E. A. Tyczkowski and L. A. Bigelow, *ibid.*, **75**, 3523 (1953); (b) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).