−128° bath was distilled through another −128° bath to a −196° bath. Mass spectrum analysis[3] of the −128° fraction showed it to be 99% **difluoramine**; yield 587 cc. (74%).

The contents of the −196° traps were combined and the recovered N_2F_4 measured; yield 100 cc. (21%).

The material remaining in the reaction flask proved to be a mixture of unreacted thiophenol and diphenyl disulfide. The disulfide was isolated by dissolving the residue in ether, washing it with alkali to remove the thiophenol and removing the ether. The solid residue, m.p. 58–60° (lit.[7] m.p. 60–62°), had an infrared spectrum identical to that of an authentic sample of diphenyl disulfide.

n-Butylmercaptan and Tetrafluorohydrazine.—A mixture of 2.25 g. (0.025 mole) of *n*-butylmercaptan and 125 cc. (0.0056 mole) of tetrafluorohydrazine was heated in a stainless steel bomb for 2 hours at 50–60°. The bomb was cooled, the nitrogen which was produced was vented, and the difluoramine was collected in the same manner described; yield 98 cc. Several distillations were required to obtain 22 cc. (9%) of 98% pure difluoramine.

Arsine and Tetrafluorohydrazine.—The arsine was prepared by treatment of sodium arsenite with zinc and sulfuric acid.[8] A 300-cc. high pressure Hoke stainless steel cylinder was charged with 150 cc. (0.0007 mole) each of tetrafluorohydrazine and arsine and then immersed in a water-bath at 50° for 1 hour. The gaseous contents had the following composition: HNF_2, 53 mole %; N_2O, 34 mole %; AsH_3, 8.5 mole %; and N_2F_4, 4.3 mole %. Distillation of the product through a −130° bath (*n*-pentane slush) concentrated the difluoramine (88% pure), but last traces of arsine could not be removed; yield 156 cc. (52%). The nitrous oxide may have arisen from metal oxides present in the bomb, or from reaction of the products with the glass vacuum line.

CAUTION! During these experiments several traps, kept in liquid nitrogen protecting vacuum pumps, exploded when opened to the air and permitted to warm toward room temperature. It should always be remembered that several explosions have occurred[2,3] with difluoramine when condensed at −196°.

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[7] H. Lecher *Ber.*, **48**, 525 (1915).

[8] E. C. Markham and S. E. Smith, "General Chemistry," Houghton Mifflin Co., Boston, Mass., 1955, p. 362.

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS, MISSOURI]

Principles of Phosphorus Chemistry. VII. Reorganization of Polyphosphoryl Halides[1]

BY LEO C. D. GROENWEGHE, JOHN H. PAYNE AND JOHN R. VAN WAZER

RECEIVED DECEMBER 19, 1959

There are families of phosphoryl and thiophosphoryl halides, which were prepared as mixtures by reorganizing various proportions of POX_3, PSX_3, P_2O_5 and/or P_2S_5. The phosphoryl halides consist of un-ionized compounds in which there is one non-bridging oxygen atom for each phosphorus atom and the phosphorus atoms are connected to each other through oxygen bridges, with halogen atoms filling the rest of the four coördination sites per phosphorus. Thiophosphoryl halides result when some or all of the oxygen atoms are replaced by sulfur. In the reorganizing chloride system, sulfur preferentially replaces the non-bridging oxygens, as exemplified by the new compound, $Cl_2(S)POP(S)Cl_2$. In the phosphoryl chloride system, the equilibrium proportions of orthophosphoryl chloride and end, middle and branching groups were found to change with the empirical composition approximately in the manner previously predicted for the ideally random reorganization of uncharged molecules. Partial separation of randomly reorganized phosphoryl chloride mixtures was effected by thermal diffusion and vacuum distillation.

The first two members of the series of phosphoryl chlorides are known. These are the orthophosphoryl chloride, $OPCl_3$ and the pyrophosphoryl chloride, $Cl_2(O)POP(O)Cl_2$. Pyrophosphoryl chloride has been made by reacting phosphorus trichloride with nitrogen dioxide[2,3] and also by reacting orthophosphoryl chloride with phosphorus pentoxide in sealed tubes.[4,5] From this latter reaction, Gustavson[4] assumed that metaphosphoryl chloride was formed as the main product whereas Huntly[5] envisaged a complicated mixture of homologs from which he was able to separate and identify the ortho- and pyrophosphoryl chlorides. The "dissociation" and "reversible reaction" discussed by Huntly correspond to the more sophisticated concept of reorganization employed here.

It has been suggested[6] that polyphosphoryl chlorides form by reacting orthophosphoryl chloride with limited amounts of water so that hydrogen chloride is liberated. This may well be the case (see Paper VI of this series[7]) but, as will be shown later in this article, the methods employed[8] did not demonstrate the existence of polyphosphoryl halides. Very shortly after the manuscript of this paper was completed in late 1958, an article[9] covering similar subject matter appeared in the literature with an oversimplified interpretation. Some of the errors appearing in Grunze's work[9] are mentioned in the body of this paper.

Experimental Techniques

This study consisted of mixing various proportions of an orthophosphoryl halide and/or an orthothiophosphoryl halide with various proportions of phosphorus pentoxide and/or phosphorus pentasulfide. The orthophosphoryl halides and orthothiophosphoryl halides were the same preparations described in Paper V of this series.[10] The phosphorus pentoxide was a Baker C. P. product and the phosphorus pentasulfide was a Monsanto commercial-grade material. Both of them were well crystallized and of high purity. The reactants were heated in rocking thick-walled, sealed Pyrex tubes at 230° for about 65 hr. Since the compositions of the products thus obtained varied very little from the

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[1] The subject matter of this paper has been presented at several scientific meetings—the 133rd A. C. S. meeting in San Francisco, and the 134th A. C. S. meeting in Chicago, and at a number of the A. C. S. Local Sections in the Midwest during the month of March, 1957.

[2] A. Guether and A. Michaelis, *Ber.*, **4**, 766 (1871).

[3] R. Klement and K. Wolf, *Z. anorg. u. allgem. Chem.*, **282**, 149 (1955).

[4] G. Gustavson, *Ber.*, **4**, 853 (1871).

[5] G. N. Huntly, *J. Chem. Soc. (London)*, **59**, 202 (1891).

[6] H. Roux, Dissertation, Marseilles, 1946; H. Roux, Y. Teyseire and G. Duchesne, *Bull. soc. chim. biol.*, **30**, 592, 600 (1948); M. Viscontini and G. Bonetti, *Helv. Chim. Acta*, **34**, 2435 (1951).

[7] E. Fluck and J. R. Van Wazer, THIS JOURNAL, **81**, 6360 (1959).

[8] H. Roux, E. Thilo, H. Grunze and M. Viscontini, *Helv. Chim. Acta*, **38**, 15 (1955); H. Roux and A. Couzinie, *Experientia*, **10**, 168 (1954); H. Roux, M-L. Jacquet-Francillon and A. Couzinie, *Bull. soc. chim. biol.*, **36**, 386 (1954).

[9] H. Grunze, *Z. anorg. u. allgem. Chem.*, **296**, 63 (1958).

[10] L. C. D. Groenweghe and J. H. Payne, THIS JOURNAL, **81**, 6357 (1959).

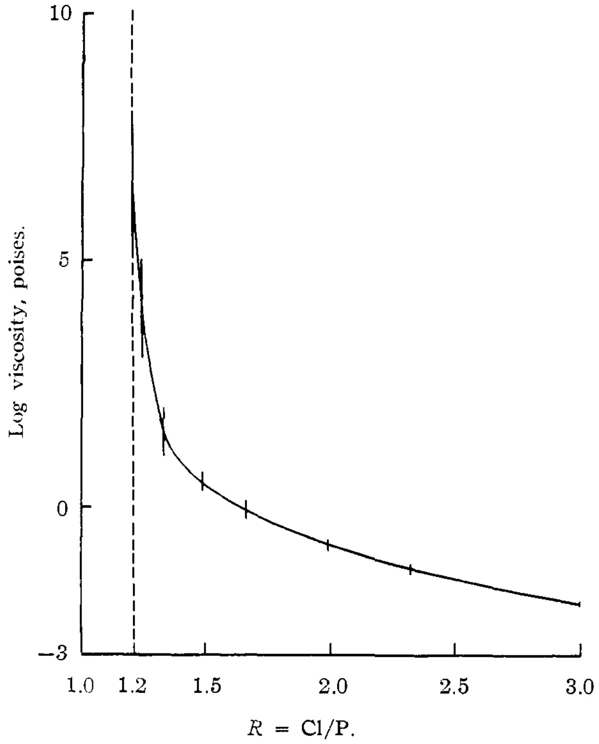

Fig. 1.—Viscosity of randomly reorganized phosphoryl chloride compositions at 25°.

compositions of duplicate experiments with 14 days heating period, it was concluded that equilibrium was attained in both cases. A few quick tests indicated that equilibrium must have been achieved in about a day. The glass tubes were enclosed in short lengths of iron pipe during heating. At the end of the heating period, the iron pipes were taken from the oven and allowed to cool in air before the glass tubes were removed. This was done on the assumption that the equilibrium obtainable at room temperature would be about the same as the one corresponding to 230°. Whether or not this is the case, we are sure that the measured equilibria correspond to room temperature since measurements after three years at 26° were identical, within experimental error, to those taken on the freshly-cooled samples. Since pure pyrophosphoryl chloride was found to revert partially to the corresponding equilibrium mixture upon being held at 26° for several months, the 3-yr. period was sufficiently lengthy to allow for complete reequilibration at room temperature.

The composition of the equilibrium mixtures was measured in the sealed tubes by the nuclear magnetic resonance (n.m.r.) technique, as previously described.[10] However, no correction was made for sweep non-linearity. Chemical shifts are reported in p.p.m. of the applied field using 85% H_3PO_4 as a standard (zero shift). Upfield shifts are denoted by a plus sign and downfield shifts by a minus sign. Since high-resolution n.m.r. spectroscopy primarily applies to liquids and since only an exceptional solid gives detectable resonance, emphasis in this study was on all-liquid compositions. When solids were present, it was found that essentially identical results were obtained with the sealed tubes and with the solid-free liquid decanted from the tubes. Equilibrium data were not obtained for any samples decanted from or containing solids.

Two stills were employed in this study. One was a regular vacuum unit with a short fractionating column. This still was used for distillations down to 1 mm. of Hg pressure. For higher vacuums, a pot-type still having a large cold-finger condenser was employed. This still was evacuated by an oil-diffusion pump through a 2 cm. i.d. tubing.

Thermal-diffusion separations were performed in a 30 ml. column made by the M. Fink Company, Cleveland, Ohio. This column was 76 inches long with a 0.012 inch gap between the inner, cold tube and the outer tube, which was heated. Thermal-diffusion runs lasted for 66 hr., using a hot-wall temperature of 55° and a cold-wall temperature of 15°. Ten equal fractions were taken by emptying the column at the ten equally-spaced levels from which it could be drained.

The paper-chromatographic analyses were carried out according to the technique generally used in this Laboratory.[11]

Polyphosphoryl Chlorides. Physical Properties.—Completely reacted mixtures of P_2O_5 and $POCl_3$ corresponding to values of the composition parameter[12,13] $R = Cl/P = 3[POCl_3]/([POCl_3] + 2[P_2O_5])$ lying between 1.24 and 3 were dark-colored, single-phase liquids. The composition corresponding to $R = 1.20$ was a clear amorphous solid exhibiting a small amount (*ca.* 0.01%) of a separate solid phase which appeared crystalline. It is believed that this solid was phosphorus pentoxide since for values of R less than 1.20, it was found that the P_2O_5 originally added did not completely react even after extended heating, with the amount of unreacted P_2O_5 increasing approximately linearly with the total P_2O_5 originally added.

The physical properties of the clear amorphous mass corresponding to $R = 1.20$ are somewhat similar to those of a 20% gelatin gel. This phosphoryl chloride composition is quite elastic and can be flexed considerably without breaking. When squeezed too hard between the fingers, it ruptures to give small particles such as are obtained from crushing an art-gum eraser. The elastic modulus of the mass was estimated to correspond to that of a moderately cross-linked elastomer, having a Young's modulus of *ca.* 10^4 dynes/cm.^{2}.

The room-temperature viscosity of the various equilibrium compositions was found to increase rapidly with decreasing R in the range of $R < 1.5$. Indeed the viscosity was seen to asymptotically approach infinity as the value of R decreased to *ca.* 1.2, as shown in Fig. 1.

Nuclear Magnetic Resonance Data.—In the phosphoryl chloride compositions obtained by heating together $POCl_3$ and P_2O_5, the "P^{31}" nuclear magnetic resonance spectrum always exhibited four and only four major peaks. the areas under which were found to vary with R according to a regular pattern. From the phosphorus and chlorine material balances, the broad resonance (*ca.* 6 p.p.m. or 100 c.p.s. wide) having a chemical shift of $+50 \pm 3$ p.p.m. was found to correspond to a chlorine-free structure or structural building unit[12,13] exhibiting an empirical composition equal to $PO_{5/2}$. Likewise the broad resonance found in the range of + 28 to + 32 p.p.m. (depending on the fine structure) corresponds to the empirical composition PO_2Cl, and the third resonance at + 7 to + 11 p.p.m. corresponds to $PO_{3/2}Cl_2$. Pure pyrophosphoryl chloride, $P_2O_3Cl_4$, has been found to have a chemical shift of + 9.9 p.p.m. The fourth chemical shift in the neighborhood of −2 p.p.m. is attributed to orthophosphoryl chloride, $POCl_3$. This is in agree-

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(11) E. Karl-Kroupa. *Anal. Chem.*, **28**, 1091 (1956).

(12) J. R. Parks and J. R. Van Wazer, THIS JOURNAL, **79**, 4890 (1957); J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

(13) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishing Co., New York, N. Y., 1958, Chapt. 12.

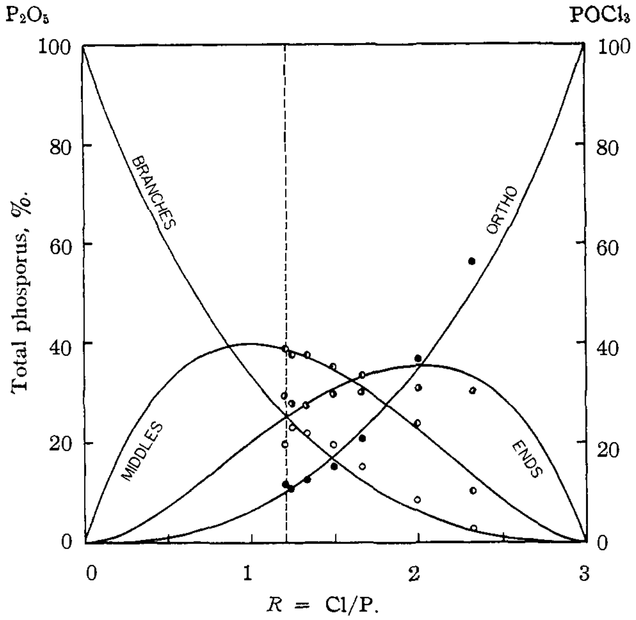
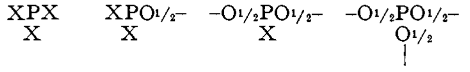


Fig. 2.—Graph showing distribution of structure units as a function of composition in the randomly reorganized system $POCl_3$–P_2O_5. The dotted line corresponds to the theoretical gel point.[12,13]

ment with the previously reported shifts of −1.9[14] and −2.2[10] for pure $POCl_3$.

The proportion of the total phosphorus in each of the four resonating structures or structural building units is shown as a function of R = Cl/P in Fig. 2. The curves labeled branches, middles, ends and ortho, respectively, correspond to the $PO_{5/2}$, PO_2Cl, $PO_{3/2}Cl_2$ and $POCl_3$ formulas.

Interpretation.—According to the classical picture, the four n.m.r. peaks discussed in the previous section would be assigned to four specific compounds: phosphoric anhydride, P_2O_5; metaphosphoryl chloride, PO_2Cl; pyrophosphoryl chloride, $P_2O_3Cl_4$; orthophosphoryl chloride, $POCl_3$. This assignment is, however, hard to reconcile with the change in physical properties observed as the over-all composition parameter R is varied. In accord with our findings on solutions of the vitreous phosphates,[15] it seems more logical to assign these four resonances to structural building units, as



$$\underset{X}{\overset{O}{XPX}} \quad \underset{X}{\overset{O}{XPO_{1/2}-}} \quad \underset{X}{\overset{O}{-O_{1/2}PO_{1/2}-}} \quad \underset{\substack{O_{1/2}\\ |}}{\overset{O}{-O_{1/2}PO_{1/2}-}} \qquad (1)$$

Isolated group or ortho structure — End group — Middle group — Branching group

where X = Cl and $O_{1/2}$ denotes an oxygen atom shared with an adjacent phosphorus.

The ends, middles and branches in this interpretation must be parts of more or less complicated polyphosphoryl chloride molecules, the parts achieving an equilibrium between themselves depending on the over-all composition as represented by R = Cl/P. There is another simultaneous equilibration process dealing with the shuffling of these structural building units between the various complete molecules. The theory of this kind of reorganization has been discussed in previous publications[12,13] from this Laboratory.

Two equations suffice to represent the equilibria between building units.[12] These are

$$K_1 = [\text{end groups}][\text{branching groups}]/[\text{middle groups}]^2 \qquad (2)$$

$$K_2 = [\text{isolated structures}][\text{middle groups}]/[\text{end groups}]^2 \qquad (3)$$

The curves shown in Fig. 2 represent $K_1 = 0.422 \pm 0.031$ and $K_2 = 0.639 \pm 0.052$. These values are weighted averages[10] of the respective equilibrium constants calculated for each set of points corresponding to the various compositions investigated. The absolute standard error in measurements on individual compositions was statistically calculated to be 2.06 mole % of the total phosphorus.

N.m.r. Fine Structure.—A typical nuclear magnetic resonance trace obtained from a randomly organized phosphoryl chloride composition exhibiting an over-all value of R = Cl/P = 2 is shown in Fig. 3. The resolvable splitting of the peak assigned to the end group is attributable to spin-spin coupling by middle or branch groups to which some of the end groups are attached. End groups attached to each other so as to give pyrophosphoryl chloride do not exhibit splitting and this accounts for most of the added height of peak A over peak B. A similar type of behavior has been observed[16] for the pyrophosphate ion and the regular phosphate end units.

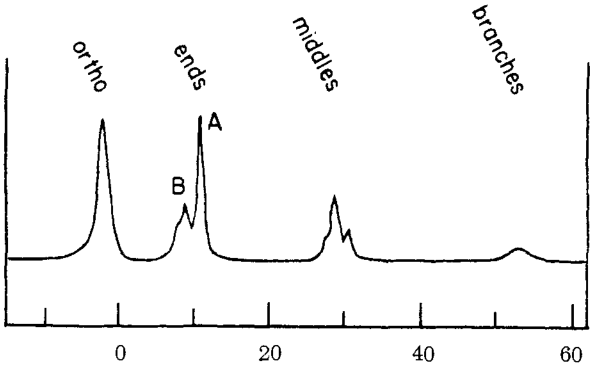


Fig. 3.—"P^{31}" nuclear magnetic resonance spectrum of a randomly reorganized polyphosphoryl chloride composition for which R = Cl/P = 2.00.

The middle-group resonance consists of a superposition of potentially resolvable triple, double, and single peaks. Triplets originate from structures such as a middle group between two ends (the tripolyphosphoryl chloride) or between two branches. The doublets come from a middle between an end and another middle (as in the tetrapolyphosphoryl chloride) or a middle between a middle and a branch. Singlets result from middle

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[14] N. Muller, P. C. Lauterbur and J. Goldenson, THIS JOURNAL, **78**, 3557 (1956).

[15] J. R. Van Wazer, C. F. Callis and J. N. Shoolery, *ibid.*, **77**, 4945 (1955).

[16] C. F. Callis, J. R. Van Wazer, J. N. Shoolery and W. A. Anderson, *ibid.*, **79**, 2719 (1957). J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *ibid.*, **78**, 5715 (1956).

groups between two other middle groups, as in the center of long chains or in unbranched rings. The branching-point resonance represents a more complicated case, being a superposition of several potentially resolvable quadruplets, triplets, doublets and singlets. Poor resolution of fine structure in the branching-point peak results from this superposition. Two other factors, acting in opposition, affect the broadness of the resonance peaks. Quadrupole broadening due to the chlorine atoms is a maximum for the resonance of the ortho structure and is zero for the branching groups; whereas "viscous" broadening is a maximum for the branching groups, many of which represent sites of localized high viscosity, since cross-linking causes the more complicated molecules to approximate a solid.

Data on Separation of Molecules.—Although only a few experiments were carried out, it appears that the ortho- and pyrophosphoryl chlorides can be nearly quantitatively distilled from a reorganized polyphosphoryl chloride composition without causing appreciable further reorganization. At room temperature or below, the orthophosphoryl chloride distills at a moderate vacuum (the last traces coming over at 1 mm. pressure at room temperature). The pyrophosphoryl chloride is removed at room temperature or below by distillation under high vacuum (the vacuum-line pressure being 10^{-4} mm. at the end of the distillation at room temperature).

By working at higher temperatures in a high vacuum, it is also possible to distill some tripolyphosphoryl chloride. Small amounts of this product can be found in the distillate when the pot temperature reaches 20°, with the bulk consisting of pyrophosphoryl chloride. When the pot temperature is gradually increased, fractions which are richer in tripolyphosphoryl chloride are obtained. The n.m.r. spectrum of the fifteenth fraction, which was distilled at a pot temperature of 56–57°, showed that about 25% of the phosphorus contained therein was present in molecules larger than pyrophosphoryl chloride.

This conclusion could be drawn because the n.m.r. spectrum showed only the presence of end groups and middle groups. The middle group resonance was found to resemble a 1.20:2.00:0.80 triplet as can be calculated for a spin–spin interaction on a middle group due to two attached end groups resonating at 20 p.p.m. downfield and J = 32 c.p.s.[17] The pyro contribution (see resonance peak A in Fig. 3) could be subtracted from the entire amount of end groups so as to leave a 3.60:4.40 doublet which corresponds mathematically to end groups attached to middle groups.[17] The end-group area thus obtained showed approximately two of these groups to be connected to each middle group. This reasonably reliable proof for the presence of the tripolyphosphoryl chloride is not in accord with Grunze's[9] conclusion that the tripoly molecule is absent from these compositions.

When the pot temperature in the high-vacuum distillation reached 65°, some splashing occurred because of the formation of more volatile compounds; but their quantity was not sufficiently great to be detectable in the distillate by n.m.r. The body of n.m.r. data was in agreement with this physical observation that the rate of reorganization during distillation was inappreciably slow at temperatures below 65–70°.

Although pyrophosphoryl chloride can be distilled from phosphoryl chloride compositions at only moderately low pressures, reorganization occurs during such distillation because of the increased pot temperature. In one distillation, it appeared that all of the end groups were removed as pyrophosphoryl chloride without disturbing the original proportions of middle groups and branch groups. If this is true, it seems that reorganization involving the making and breaking of P–Cl bonds is still slow. By increasing the pressure and/or taking a longer time at the higher temperatures, orthophosphoryl chloride can be distilled from phosphoryl chloride compositions in much greater amounts than were originally present in the reorganization mixture. This is also due to reorganization during distillation.

Separation by thermal diffusion was carried out on a randomly reorganized phosphoryl chloride composition having a value of R = Cl/P = 2 from which essentially all of the orthophosphoryl chloride had been removed by distillation at room temperature. After removal of the orthophosphoryl chloride, the n.m.r. spectrum looked exactly like the trace of Fig. 3 but without the resonance peak corresponding to the orthophosphoryl chloride. In the n.m.r. traces of the fractions taken from the thermal-diffusion column at the end of the experiment, the absence of the resonance peak for orthophosphoryl chloride showed that reorganization did not noticeably take place during the thermal-diffusion experiment. This was borne out quantitatively by the fact that the ratio of ends: middles: branches summed over the ten fractions from the thermal diffusion column was very close to this ratio for the starting material.

The n.m.r. traces of all of the thermal-diffusion fractions exhibited resonances corresponding to ends, middles and branches, with the branches being only barely detectable in the fraction of lowest molecular weight taken from the top of the column. The areas of the resonance peaks showed that this fraction consisted of 71.9% ends, 24.4% middles and 3.8% branches. The fine structure indicated that about 30% of the phosphorus was present as pyrophosphoryl chloride, the remainder probably consisting of a substantial amount of cyclic chlorides (trimeta, tetrameta, etc.) plus some tripoly, tetrapoly and higher molecular weight species. The small amount of branch groups in this fraction and appreciably larger amounts in the other low-molecular-weight fractions shows that these building units are present in the smaller molecules, such as isotetrapolyphosphoryl chloride.

In the n.m.r. trace corresponding to the fraction of highest molecular weight (bottom fraction), the proportion of end groups had decreased so as to represent 46.0% of the total phosphorus whereas the amount of middle and branched groups had increased to, respectively, 40.6 and 13.4%. As the molecular weight of the fractions increased, the fine structure of the end- and middle-group reso-

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[17] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

nance peaks diminished, with no fine structure whatsoever being observable in the fraction of highest molecular weight. Although the increased viscosity due to the larger molecules makes a contribution, it is thought this lack of fine structure indicates a highly random arrangement of the building units making up these molecules. As expected from a reorganization which is not far from ideal randomness, the viscosity of the material from the thermal-diffusion column increased gradually from fraction to fraction, going from a value of less than 0.5 poises for the top fraction to about three poises for the bottom fraction.

Discussion.—As previously stated, the distribution of molecular sizes for a given value of the composition parameter R can be treated[12,13] in terms of two separable operations: (1) setting up equilibria between structural building units and (2) sorting the building units into molecules or molecule ions. The fact that the observed values for the equilibrium constants ($K_1 = 0.42$ and $K_2 = 0.64$) for the change of functionality of the structure building units are reasonably close to the theoretical value of 1/3 shows that the chlorine atoms and bridging oxygen atoms exchange sites on a phosphorus atom in a rather random manner. Indeed, the free energies of formation at 25°[18] from glassy P_2O_5 and liquid $POCl_3$ of the end and middle groups are only 0.67 and 0.92 kcal. less than these values would be if complete randomness had prevailed.

The sorting of building units into molecules also appears to be a much closer approximation to the random-reorganization case than to the classical case of mixtures of ortho, pyro, meta and anhydride molecules. The latter corresponds to making each molecule out of only one kind of structural unit. However, the observed physical properties, molecular separation data, and n.m.r. fine structure agree in showing that a good proportion of the molecules over a wide range of R values are made up of more than one kind of structural unit.

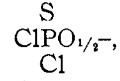
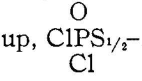
At $R = 2.00$, *ca.* 12% of the total phosphorus was found to be present as pyrophosphoryl chloride. This experimental value was derived from two independent sources: (1) analysis of the fine structure in the n.m.r. spectra of the lower-molecular-weight thermal-diffusion fractions and (2) high-vacuum distillation. According to the classical case, 31% of the total phosphorus would be present as pyro. However, random reorganization theory, according to the IBM-704 computation, predicts 15% as pyro—calculated on the basis of the observed distribution of structural units at $R = 2.00$.

The value of R below which an infinite network molecule(s) will form (the so-called "gel point")[12,13] is calculated to be 1.22 from a random-sorting study made with an IBM-704 digital computer. As shown by Figs. 1 and 2, this value corresponds to the measured asymptote for rapid increase of viscosity and to the point where a solid phase begins to appear. Again the experimental data correspond well to random reorganization.

Polyphosphoryl Halides.—Very little quantitative work was carried out on the $POBr_3$–P_2O_5 system since solid and liquid were found to coexist after equilibration. Thus the phosphoryl bromide composition exhibiting a value of $R = 2$, which was obtained after heating for 65 hr. at 230°, was a milky-colored, gelatinous-looking mass. The presence of a liquid phase was demonstrated by the fact that a high-resolution n.m.r. trace was obtained on this material. This trace was unusual in that only three major peaks were observed. From the position of a gap in the spectrum, the missing peak was tentatively assigned to the end-group function, which thus appears to be absent from the liquid phase.

Phosphoryl Chlorides Involving Combined Sulfur. Physical Data.—By use of various combinations of orthophosphoryl chloride, orthothionophosphoryl chloride, phosphorus pentoxide and phosphorus pentasulfide, reorganized compositions having various values of $R = Cl/P$ as well as various ratios of sulfur to oxygen can be prepared. A number of different sulfur : oxygen ratios were made for $R = 1.50$, and a homogeneous sulfur-containing liquid was found only for the S/P mole ratio of unity. For $R = 1.80$ and 2.00, homogeneous liquids also resulted for the same S/P ratio. Sulfur-containing compositions exhibiting more or less sulfur per phosphorus atom were solid–liquid mixtures.

N.m.r. spectra of the mixtures thus obtained showed that for the all-oxygen composition, the resonance peaks were all in the range of −2 to + 56 p.p.m. As sulfur was substituted for oxygen, a group of resonance peaks in the range of *ca.* −30 to + 2 p.p.m. was found to show up in increasing intensity until, when there was exactly one sulfur per phosphorus atom, essentially only this group of resonances could be seen. As the sulfur content was raised further, a new group of resonance peaks exhibiting chemical shifts in the range of *ca.* − 30 to − 65 p.p.m. showed up and finally completely replaced the other resonance peaks when sulfur was completely substituted for the oxygen.

Assignment in the N.m.r. Spectra.—Some of the observed resonance peaks have been assigned to individual structural units containing sulfur. The assignment of the peak at − 29 p.p.m. corresponding to $PSCl_3$ has been made in the literature.[10,14] The resonance corresponding to the end group in which a sulfur atom is in the isolated position and there is a bridging oxygen atom,  $\overset{S}{\underset{Cl}{ClPO_{1/2}}}$–, lies at − 28 p.p.m., a value which is so close to the shift for $PSCl_3$ that the two peaks cannot be resolved. As described below, dithionopyrophosphoryl chloride, $Cl_2(S)POP(S)Cl_2$, was separated in relatively pure form by high-vacuum distillation, and the assignment of this end-group resonance was made from this compound (− 28.2 p.p.m.). Another pure compound used for referencing was μ-monothiopyrophosphoryl chloride, $Cl_2(O)PSP(O)Cl_2$, which was prepared from $POCl_3$ and H_2S according to the method of Besson.[19] From it, we assigned the value of − 10 p.p.m. to the μ-S end group,  $\overset{O}{\underset{Cl}{ClPS_{1/2}}}$–.

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[18] E. Fluck, J. R. Van Wazer and L. C. D. Groenweghe, THIS JOURNAL, **81**, 6365 (1959).

[19] A. Besson, *Compt. rend.*, **124**, 151 (1897).

This grouping was found in small amounts in only a few of the mixtures investigated.

In the three cases (R = 1.50, 1.80 and 2.00) in which the S/P mole ratio equalled unity, it was possible to make tentative assignments on the basis of three material balances involving the Cl/P, O/P and S/P ratios. In all of these cases, there were three major resonance peaks, one of which was attributable to the sum of $PSCl_3$ and the thiono end group exhibiting a bridging oxygen, $\underset{\text{Cl}}{\overset{\text{S}}{\text{ClPO}_{1/2}}}-$. This leaves two unidentified peaks (probably attributable to the thiono middle group and thiono branching group) which can be identified from the three material-balance equations. In this manner, we have tentatively assigned the peak at − 20 p.p.m. to the thiono middle group, $\underset{\text{Cl}}{\overset{\text{S}}{-\text{O}_{1/2}\text{PO}_{1/2}}}-$, and the broad peak centered at − 3 p.p.m. to the thiono branching group, $\underset{\underset{|}{\text{O}_{1/2}}}{\overset{\text{S}}{-\text{O}_{1/2}\text{PO}_{1/2}}}-$. This latter peak overlaps with the peak corresponding to $POCl_3$ (−2 p.p.m.), but the two can readily be distinguished since the branching-group peak—like all branching-group resonances—is very broad and the $POCl_3$ peak is quite sharp. The n.m.r. showed further that less than 1 mole % of the phosphorus resonated in a sharp peak at −10 p.p.m. assigned to the group $\underset{\text{Cl}}{\overset{\text{O}}{\text{ClPS}_{1/2}}}-$.

Since the n.m.r. spectra corresponding to an S/P mole ratio of unity were always simple—*i.e.*, they exhibited only three major peaks, it seems very logical to assume that sulfur substituting for oxygen prefers to fill the isolated position. There is, however, a problem in the assignments made in the preceding paragraph. This is the fact that the single peak measured for the molecule $P_4O_6S_4$ in carbon disulfide solution was found[15] at −16 p.p.m. According to an electron-diffraction analysis[20] of the $P_4O_6S_4$ structure, this peak must also correspond to a thiono branching point. Either the assignment of the thiono branching point given in the preceding paragraph is incorrect, or there is a considerable difference in the electronic structure of this building unit in polythionophosphoryl chlorides and in a solution of the cage-like molecule, $P_4O_6S_4$. As previously noted,[15,21] it appears that the amount and distribution of π character and consequently the electron distribution around the phosphorus atom is extremely variable when there are P–S bonds, and this may be the explanation of the discrepancy.

One other assignment has been made in the n.m.r. spectra. This is the tentative assignment of the resonance at − 60 p.p.m. to the tetrathio branching group, $\underset{\underset{|}{\text{S}_{1/2}}}{\overset{\text{S}}{-\text{S}_{1/2}\text{PS}_{1/2}}}-$. This chemical shift was identified on the basis that it was the only resonance which was common to the liquid phases of the system based on reorganizing $PSCl_3$ with P_2S_5 and the system based on $PSBr_3$ with P_2S_5.

Separation by Distillation.—Some experiments on distillation were carried out on a composition for which the S/P mole ratio equals unity and R = 1.8. As was found for the sulfur-free phosphoryl chloride composition, both the ortho and pyro molecules could be separately removed. After distillation of the $PSCl_3$, the pyro structure was distilled in high vacuum (vacuum line pressure of 10^{-5} mm.) in the temperature range of 0 to 35°. The n.m.r. spectrum of the distillate showed that 99% of the total phosphorus was present in a structure resonating at *ca.* −28 p.p.m. Chemical analysis was carried out after hydrolysis in base for 2 hr. at 115° in a sealed tube.

Anal. Calcd. for $Cl_2(S)POP(S)Cl_2$: P, 21.8; S, 22.6; Cl, 50.0; O, 5.6. Found: P, 22.4; S, 21.3, Cl, 51.4; O, 5.0 (by difference).

Two cryoscopic determinations of molecular weight in benzene gave values of 241 and 242 as compared to the theoretical value of 284. The low values are attributable to a combination of hydrolysis, the presence of some $PSCl_3$ and possibly some dissociation in the benzene.

When distillations were carried out at higher temperatures (> 35°), reorganization occurred. It is interesting to note that a large number of structural building units (as many as ten for one particular fraction) were found as the reorganization products. Some of these n.m.r. peaks appeared in the region corresponding to chemical shifts more negative than −30 p.p.m. and thus are probably attributable to building units in which each phosphorus is connected to more than one sulfur atom. Formation of such building units is probably attributable to their appearance in the more volatile molecules. The volatility of these compounds does not necessarily decrease with increasing molecular weight as exemplified by the fact that the μ-thiopyrophosphoryl chloride (mol. wt. = 268), which is present in the randomly reorganized mixtures, does not distill until most of the thionopyrophosphoryl chloride (mol. wt. = 284) has been distilled.

Discussion.—It appears that the equilibrated reorganized compositions having various Cl/P ratios and an S/P ratio equal to unity consist mainly of thionophosphoryl chlorides. In other words, the sulfur preferentially locates in the non-bridging position in poly(phosphoryl-thiophosphoryl) chloride equilibrium mixtures. Only after essentially all nonbridging sites are filled does sulfur act as a bridging atom.

Partial Hydrolysis of $POCl_3$.—The product formed by slowly reacting equimolar amounts of orthophosphoryl chloride and water in the cold, "hydrated phosphorus oxychloride," has been suggested[6,8] to be a mixture of polyphosphoryl chlorides. The work carried out in our laboratory on the polyphosphoryl chloride system was begun by repeating the previously reported studies[8] and investigating the methods of analysis used in these studies. Unfortunately at the time this work was done, nuclear magnetic resonance equipment was

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(20) A. J. Stosick, THIS JOURNAL, **61**, 1130 (1939).

(21) J. R. Van Wazer, *ibid.*, **78**, 5709 (1956); H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

not available so that this discussion deals only with the veracity of the previously published analytical techniques and does not attempt to give a definite answer to the question of whether or not polyphosphoryl chlorides are produced from the reaction between $POCl_3$ and H_2O. In order to show that "hydrated phosphorus oxychloride" was a mixture of homologs, Roux, Thilo, Grunze and Viscontini[8] added pyridine, and then hydrolyzed the resulting mixture slowly with water in order to obtain a solution for paper chromatography. All of these operations were carried out in the cold. When this experiment was repeated in our Laboratory, we found condensed phosphates as did the original investigators. However, when pure $POCl_3$ was treated with pyridine and then water in exactly the same manner, condensed phosphates were again found. This means that condensation occurred during the analytical procedure which, hence, cannot be used to demonstrate the presence of condensed phosphoryl chlorides or other phosphate structures in "hydrated oxychloride."

Another analytical method, used by Roux and Couzinie as well as by Roux, Jacquet-Francillon and Couzinie,[8] was based on slow hydrolysis with ice water followed by neutralization and repeated fractional precipitation with acetone. Paper chromatography of the precipitates showed the presence of condensed phosphates when "hydrated phosphorus oxychloride" was used as starting material. By following this analytical procedure in detail, we found that the hydrolysis of pure pyrophosphoryl chloride gave only a small amount of material precipitated in the first acetone fractionation and none in the second. Paper chromatography of this precipitate as well as of the solution obtained directly from the hydrolysis showed that nearly all of the phosphorus was present as the orthophosphate ion, with only a trace of pyrophosphate. This study demonstrates that considerable amounts of the condensed phosphoric acids must have been present as such in the "hydrated phosphorus oxychloride."

Further hydrolysis studies in cold solutions of various basicity show that the dissolution procedure used by Grunze[9] prior to paper-chromatographic analysis must have caused considerable degradation of straight chains as well as scission of a P–O–P linkage for each branching group, which makes this procedure unuseable for even a qualitative determination of the composition of polyphosphoryl chloride mixtures.

A considerable amount of work was done[22] in our Laboratory in 1956 on the reaction of phosphorus oxychloride with water. In this study, the temperature during and subsequent to the addition of the water was varied, as was the rate of addition of the water and the pressure (between a good vacuum and 1 atm.). The use of hydrogen chloride absorbers such as secondary alkenes and tertiary amines was also explored. The analytical techniques employed were indirect chlorine analyses by quantitatively measuring the loss of HCl, paper chromatography and end-group titration,[23] the latter being interpreted in terms of the weight of the sample used, its proximate analysis and the ratio: H_2O_{added}/HCl_{lost}.

From this work it was concluded that mixtures consisting primarily of $POCl_3$ and/or dichlorophosphoric acid[7] with various condensed phosphoric acids could be readily produced. At elevated temperatures (> *ca.* 50°), phase separation occurred. The resulting fluid upper-layer consisted primarily of orthophosphoryl chloride and/or dichlorophosphoric acid plus some unidentified species; whereas the more dense, viscous phase was made up in great part of condensed acids exhibiting little or no chlorine in their structures. As shown[7] in Paper VI, an equimolar mixture of $POCl_3$ and water (which is the equilibrium version of hydrated phosphorus oxychloride" corresponding to ice temperatures or high HCl pressures) consist primarily of dichlorophosphoric acid. When $POCl_3$ was distilled from "hydrated phosphorus oxychloride" as reported in the literature,[8] there was undoubtedly concomitant loss of HCl to give condensed species similar to those discussed in Paper VI of this series.[7]

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[22] Much of this study was carried out by Prof. J. W. Gryder of Johns Hopkins University, who spent the summer of 1956 with Monsanto. This preliminary investigation was completed before we had a nuclear magnetic resonance spectrometer.

[23] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954); E. J. Griffith, *ibid.*, **28**, 525 (1956).