

existence of cycloborazanes higher than the pentamer was found, and it is unlikely that other reactions² produce open-chain polymers of higher molecular weight. The precipitation of cyclopentaborazane from the reaction solution is evidently not attendant with the cyclization step, since yields of the pentamer did not differ substantially whether the solvent was removed before or after precipitation was observed.

It is not known why the yields of cyclic aminoboranes were erratic when the reaction was run with sodium amide prepared by the use of diolefins. Even when no cyclic products were found, the amide had reacted completely to form sodium borohydride which indicates that at least the lowest ammonia (N-B)aminoborane had been formed. It seems that the cyclization with elimination of ammonia must be critically dependent upon the absence of certain polymeric or unsaturated organic materials.

Cyclic vs. Open Aminoboranes. In conjunction with other work from this laboratory there appear to be two distinct classes of unsubstituted aminoboranes, the cycloborazanes and the less well-defined, open-chain aminoboranes. The new cycloborazanes $(\text{BH}_2\text{NH}_2)_2$ and $(\text{BH}_2\text{NH}_2)_3$ have been characterized, and evidence was obtained that $(\text{BH}_2\text{NH}_2)_4$ is also formed. Cyclic

structures are accepted for the borazanes described here on the basis of the following criteria. The analytical data show ratios of constituents in accordance with the composition BH_2NH_2 , which precludes the possibility of end groups such as $-\text{BH}_3$. The relatively inert character of these compounds with respect to protolysis, indicating quaternary boron moieties, is also consistent with cyclic structures. In addition, $(\text{BH}_2\text{NH}_2)_3$ is identical with the product obtained by Dahl and Schaeffer from borazine.¹⁰

Unique X-ray powder diffraction patterns and infrared spectra have been obtained for each member of the cyclic $(\text{BH}_2\text{NH}_2)_n$ series. By contrast, the open aminoboranes are amorphous and give no characteristic X-ray pattern, and their infrared spectra do not differentiate samples prepared by several different techniques.² The lower cycloborazanes sublime *in vacuo* at characteristic temperatures, while the amorphous materials of equivalent molecular weight do not sublime but lose hydrogen at room temperature or on slight warming.

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The Alcoholysis of Polyphosphoric Acid

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Abstract: The reaction between polyphosphoric acid and several alcohols has been investigated. Product formation is clearly correlated to acid strength, with the fraction of phosphorus remaining as H_3PO_4 equal to $1/\bar{n}$ (\bar{n} = the average chain length). Titrations and P^{31} nmr data indicate that the chains are cleaved randomly with respect to unsubstituted phosphorus.

Condensed phosphoric acid has many uses in organic synthesis¹ and is especially interesting as a phosphorylating agent because of the moderate conditions of the reaction and the relatively mild effects of the reagent compared to phosphorus pentoxide or other phosphorus intermediates. Currently there are available several compositions above 100% H_3PO_4 , the properties of which vary as the strength of the acid increases.² The utility of these as phosphorylating agents may also be expected to vary. We therefore have explored the reaction between alcohols and condensed phosphoric acids to extend the rather limited information now available.^{3,4} We attempt to develop a theoretical explanation for the observed behavior *via* a statistical approach.

Experimental Section

Reaction Conditions. All reactions were carried out under anhydrous conditions and without solvent. When the alcohol was a liquid, the reactants were mixed at room temperature; otherwise the alcohol was warmed to just above its melting point, and then added rapidly to the acid.

A moderate (10–30°) temperature rise was noted on mixing. When no further heat was evolved, the mixture was heated to temperatures ranging from 50 to 100°, and held there until titration indicated no further change in the relative amounts of the various kinds of phosphorus present.

While a number of esters were prepared, only those having a chain length of eight or more carbon atoms were isolated in pure form. Isolation procedures involved work-up with ether in the usual way.⁴ Because of the relatively small influence of the hydrophilic phosphate group in the long-chain esters, some free alcohol was carried through the work-up to the final product. This is reflected in the elemental analyses of all but one of the purified materials (see Table I).

In addition to these purified materials, we have also studied, in greater detail, the reaction between polyphosphoric acid and *n*- and isobutyl alcohol. *t*-Butyl alcohol was dehydrated to isobutene on contact with polyphosphoric acid at room temperature.

- (1) F. D. Popp and W. E. McEwan, *Chem. Rev.*, **58**, 321 (1958).
- (2) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, Chapter 12.
- (3) E. Cherbuliez and H. Weniger, *Helv. Chim. Acta*, **29**, 2006 (1946).
- (4) A. K. Nelson and A. D. F. Toy, *Inorg. Chem.*, **2**, 775 (1953).

Table I. Purified Monoalkyl Phosphates, ROPO₃H₂

| Alcohol | Temp, °C | Reaction time, hr | Work-up solvent | Over-all yield, % | Calculated, % | | | Found, % | | |
|----------|----------|-------------------|-----------------------------------------------------|-------------------|---------------|------|------|----------|------|------|
| | | | | | C | H | P | C | H | P |
| Isodecyl | 50-80 | 18 | Et ₂ O | 80 | 50.4 | 9.7 | 13.0 | 50.5 | 9.7 | 13.2 |
| 2-Octyl | 70 | 24 | [(CH ₃) ₂ CH] ₂ O | 48 | 45.7 | 9.1 | 14.7 | 45.4 | 8.6 | 14.0 |
| Tridecyl | 50 | 12 | [(CH ₃) ₂ CH] ₂ O | 69 | 55.7 | 10.4 | 11.0 | 55.7 | 10.2 | 10.3 |
| Cetyl | 95 | 4 | (CH ₃) ₂ CO | 45 | 59.6 | 10.9 | 9.6 | 60.6 | 11.1 | 8.4 |
| 1-Octyl | 60 | 24 | Et ₂ O | 50 | 45.7 | 9.1 | 14.7 | 45.5 | 9.3 | 12.7 |

Analytical Procedures. (A) The principal method of analysis was potentiometric titration with standard 0.1 *N* NaOH, after the method of Gerber and Miles.^{5,6} This titration permits discrimination between monoprotic phosphate, such as dialkyl esters and unesterified middle groups of chain phosphates; diprotic phosphate, such as monoalkyl esters and unesterified end groups of chain phosphates; and free orthophosphoric acid. Only with the butyl phosphates, however, could a clear titratable aqueous solution be obtained at room temperature. Therefore the higher homologs were suspended in water, and acetone was added until the solution became clear.

A small amount of hydrolysis would be expected to occur during titration. Hence, determinations were made as rapidly as possible (3-5 min total time, using a Sargent Model D recording titrimer) and, for the compounds here reported, the uncertainty introduced by hydrolysis is overshadowed by the inherent precision of the method which, from our experience, is $\pm 0.5\%$ H₃PO₄.

(B) The other means of characterization of the reaction mixtures was P³¹ nuclear magnetic resonance. Spectra of aqueous, or aqueous acetone, solutions of the mixtures were obtained on a Varian 24.3-Mc spectrometer using 85% H₃PO₄ as an external standard. Preparation of the sample and recording of the spectrum was done as rapidly as possible to minimize hydrolysis of the various phosphate species.

A spectrum of neat 117% H₃PO₄ showed the H₃PO₄ peak at -1.7 ppm; the end and middle groups were broad bands, centered at +12.0 and +29.4 ppm, respectively. The exact position of these bands is somewhat dependent upon the P₂O₅ assay of the phosphate system under consideration, as shown in the early work of Van Wazer⁷ and, more recently, that of Crutchfield, *et al.*⁸ In fact, the middle groups of "anhydrous" 117% H₃PO₄ appear about 5 ppm further upfield than the middle groups of tetraphosphate at pH 0 as reported by Crutchfield.

Although P³¹ nmr data on alkyl phosphates are at best scanty, the available information indicated that an untreated mixture of monoalkyl, dialkyl, and orthophosphoric acids yields a spectrum of little use, owing to overlapping of the three peaks. However, Nielsen, Pustinger, and Strobel⁹ have reported a change in shift of -3.8 ppm in converting the free diethylphosphoric acid to its sodium salt. In hopes that the butyl phosphates could be resolved in this way, the spectrum of a 20% solution of "butyl acid phosphate" in 60% water-40% acetone, consisting of roughly equimolar quantities of mono- and di-*n*-butyl phosphate, was recorded. A single peak was observed at +0.38 ppm. On adjusting to pH 10 with NaOH, however, the dibutyl phosphate anion showed a multiplet at -3.5 ppm, while the monobutyl phosphate exhibited a poorly defined triplet at *ca.* 0 ppm. Hence, this method seemed adequate for the detection of dibutyl phosphate in the reaction mixture under study.

Materials. Polyphosphoric acid was from this laboratory. It contained 84.3% P₂O₅ (by titration) which corresponds to 117% H₃PO₄. Use of the flexible-chain theory of Van Wazer¹⁰ predicts an average chain length (\bar{n}) of 4.3 phosphorus atoms. Determination of \bar{n} by titration gave the same result within experimental error. Crystalline pyrophosphoric acid was obtained by crystalliza-

tion of 110% H₃PO₄ (2:1, H₂O:P₂O₅), and assayed 99% H₄P₂O₇ by titration.

The alcohols were reagent grade, obtained commercially, and used without further purification.

"Butyl acid phosphate" was the commercial product of the Inorganic Chemicals Division, Monsanto Co. This material is formed from P₄O₁₀ and *n*-butyl alcohol *via* scission of the P-O-P linkages to produce an equimolar mixture of mono- and dialkyl phosphate.

Elemental analyses were performed by the Analytical Laboratory, Physical Sciences Center, Monsanto Co., St. Louis, Mo.

Results

We have prepared *via* smooth reactions the following monoalkyl monophosphates from polyphosphoric acid: *n*-butyl, isobutyl, *n*-amyl, *n*-octyl, 2-octyl, isodecyl, tridecyl, hexadecyl (cetyl), and alkylphenylpolyethoxyethyl. We studied in detail reactions to make only a few of these.

Analyses of several purified esters are given in Table I. Results agree closely with calculated values for monoalkyl monophosphate considering the difficulty in removing all traces of free alcohol. Table II contains

Table II. P³¹ Nmr of Butyl Phosphates

| | % P ^a appearing at | | |
|------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|-----------|------------|
| | -3 ± 1 ppm | 0 ± 1 ppm | 11 ± 2 ppm |
| "Butyl acid phosphate" (made from BuOH + P ₄ O ₁₀) in 60% (CH ₃) ₂ CO-40% H ₂ O | 0 | 100 | 0 |
| "Butyl acid phosphate" in H ₂ O, pH 10 | 50 | 50 | 0 |
| <i>n</i> -BuOH + 117% PPA in 60% (CH ₃)CO-40% H ₂ O | 0 | 90 | 10 |
| <i>n</i> -BuOH + 117% PPA in H ₂ O, pH 10 | 0 | 90 | 10 |
| <i>i</i> -BuOH + 117% PPA in 60% (CH ₃) ₂ CO-40% H ₂ O | 0 | 90 | 10 |
| <i>i</i> -BuOH + 117% PPA in H ₂ O, pH 10 | 0 | 90 | 10 |

^a Estimated by peak-height measurements.

results of analyses of some butyl phosphates by nmr. These show that the esters made from polyphosphoric acid contain monoalkyl monophosphate, free acid, and end group phosphorus—no dialkyl monophosphate or middle group phosphorus.

Table III contains results of titration of various reaction mixtures. When the mole ratio of P-O-P linkages (from 117% H₃PO₄) to alcohol was 1:1, 10-15% of the phosphorus was found to remain as a monoprotic species even after several days. This did not occur when solid H₄P₂O₇ was used. Where 117% H₃PO₄ was used, 23-30% of the phosphorus was converted to H₃PO₄, some of which arose from decomposition of the ester into olefin and free acid. Use of solid H₄P₂O₇ resulted in leaving 50% of the phosphorus as H₃PO₄.

(5) A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **13**, 406 (1941).

(6) J. R. Van Wazer, E. J. Griffith, and J. F. McCulloch, *Anal. Chem.*, **26**, 1755 (1954).

(7) J. R. Van Wazer, C. F. Callis, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 4645 (1955).

(8) M. M. Crutchfield, C. F. Callis, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

(9) M. L. Nielsen, J. V. Pustinger, and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964).

(10) See ref 2, p 739 ff.

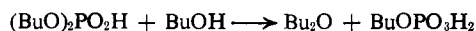
Table III. Percentages of Various Phosphate Species in Phosphorylation Reaction Mixtures after 24 to 72 hr

| Alcohol | Acid Species | \bar{n} | % phosphorus as | | | $1/\bar{n} \times 100$ |
|-----------------|----------------------------------------------------|-----------|----------------------------|---------------------|------------------|------------------------|
| | | | Diprotic (strong and weak) | Monoprotic (strong) | Ortho-phosphoric | |
| <i>n</i> -Butyl | | | | | | |
| Equimolar | 117% H ₃ PO ₄ | 4.4 | 65.2 | 11.0 | 23.8 | 23.2 |
| 80% excess | 117% H ₃ PO ₄ | 4.4 | 68.3 | 4.0 | 27.7 | 23.2 |
| Equimolar | Solid H ₄ P ₂ O ₇ | 2 | 50.0 | 0 | 50.0 | 50 |
| Isbutyl | | | | | | |
| Equimolar | 117% H ₃ PO ₄ | 4.4 | 65.2 | 11.5 | 23.3 | 23.2 |
| 30% excess | 117% H ₃ PO ₄ | 4.4 | 70.5 | 4.5 | 25.0 | 23.2 |
| <i>n</i> -Octyl | | | | | | |
| Equimolar | 117% H ₃ PO ₄ | 4.4 | 65.0 | 14.0 | 21.0 | 23.2 |
| 23% excess | 117% H ₃ PO ₄ | 4.4 | 75.0 | 2.0 | 23.0 | 23.2 |
| Equimolar | Solid H ₄ P ₂ O ₇ | 2 | 50 | 0 | 50 | 50 |

On reaching a fairly constant assay of species after about 72 hr, the orthophosphoric acid content was roughly one-quarter of the phosphorus in all cases.

Purification of the long-chain phosphates *via* solvent separation and subsequent retitration of the esters showed neither the presence of disubstituted phosphates nor of orthophosphoric acid. In all five cases where this was done, titration showed no appreciable diester. It is therefore most likely that none was formed since it should have been carried through to the purified product. Extensive hydrolysis of the diester on work-up is very unlikely since it was not in contact with strong acid or base for more than a few minutes and never heated above room temperature. Published¹¹ rate constants for the hydrolysis of dimethyl and dibenzyl phosphates predict half-lives of several hours, even at elevated temperatures, in both acid and base.

For all three cases in Table III in which 1 mole of alcohol was used for each P-O-P linkage in polyphosphoric acid there remained, after reaction, 11 to 14% monoprotic acid. In hopes of determining the nature of this material, excess alcohol was then added to the reaction mixtures. Titration after further reaction indicated that the monoprotic fraction had indeed been reduced. A check for dibutyl ether formation was made by dissolving a portion of the reaction mixture in 20% aqueous NaOH, continuously extracting with hexane for 24 hr, and analyzing the resulting extract *via* vapor phase chromatography. No appreciable ether formation was observed. Hence, a reaction of the sort



cannot account for the reduction in the monoprotic phosphorus present.

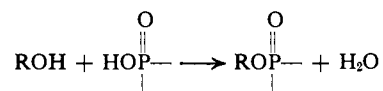
As shown in Table II, a check for dibutyl phosphate was made *via* nmr on the samples at pH 10. No peak was observed in the vicinity of -3.8 ppm. There was, however, a diffuse hump centered at +9.4 ppm in the *n*-butyl case and at +12.2 ppm for isobutyl alcohol. This resonance was present in both the acid form and in basic solution. Spectra of the longer chain phosphates were also obtained in acetone solution, but attempts to make aqueous solutions of their sodium salts yielded either gel-like suspensions or curdy precipitates. It was noted, however, that all of the reaction mixtures did show a peak at higher field; it varied with the alcohol used between +6 and +15 ppm. In no case

(11) J. R. Cox and O. B. Ramsay, *Chem. Rev.*, **64**, 329 (1964).

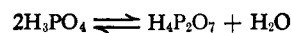
were there observed peaks indicative of unreacted middle groups (above 20 ppm).

Discussion

An acceptable theory of alcoholysis of polyphosphoric acid must explain the observed behavior, *i.e.*, the absence of dialkyl monophosphate, the formation of monoprotic species and species containing end-group phosphorus which are but slow to react further, and the formation of free H₃PO₄ in amounts clearly correlated to the average chain length of the starting polyphosphoric acid. We begin by considering the possibility of direct esterification by elimination of water



This evidently does not happen since addition of excess alcohol does not reduce the free H₃PO₄ level under our conditions (Table II).¹² Similarly, reorganization of the POP linkages does not influence the results under these reaction conditions. If the reaction



occurred at an appreciable rate, excess alcohol would be expected, through reaction with the H₄P₂O₇, ultimately to remove all the free H₃PO₄ leaving only ester and free water. The evidence in Table II shows that the rate of reorganization is slow compared with the total sojourn in the reactor.¹³ Again we emphasize that such reorganization should occur to an appreciable extent at higher temperatures or longer times. The evidence eliminates this possibility in our case, however.

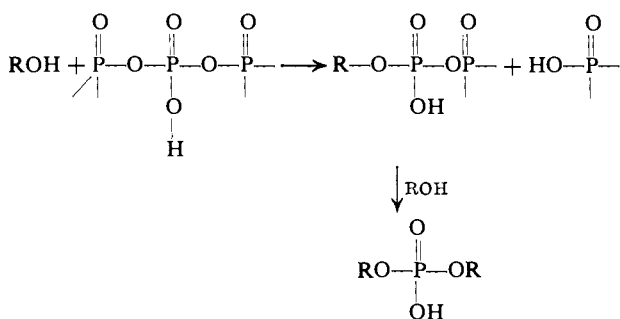
There are at least three possible ways that alcohols could attack polyphosphoric acid chains to produce esters with accompanying chain scission. These are, with variations, random attack, products controlled thermodynamically to favor dialkyl monophosphate formation, and control favoring monoalkyl monophosphate formation. We consider these possibilities, or combinations thereof, in order.

(12) There are equilibria involving ortho or condensed acids and the alkyl group in which direct esterification is the net result. In the case of orthophosphoric acid, one expects that equilibration over a sufficiently long time or at higher temperatures will yield all possible esters—mono-, di-, and trialkyl, and free water. Under the low temperatures and relatively short times used in this study, this does not occur in significant amounts.

(13) This reorganization has been indirectly detected by interpretation of kinetic data; the rate in alcohol is indeed found to be slow: E. Cherbuliez and J. P. Leber, *Helv. Chim. Acta*, **35**, 644 (1952).

For the sake of simplicity, we have chosen to illustrate random attack on a chain containing four phosphorus atoms, since the other cases give qualitatively identical results. Sequential steps, shown in Scheme I, yield 55.2% of the phosphorus appearing as monoalkyl monophosphate and 9.9% appearing as the dialkyl monophosphate. As the chain length increases, the percentage of dialkyl monophosphate formed will increase, and that of monoalkyl and orthophosphate will decrease until, in the limit of infinitely long chains, the distribution will be 25% dialkyl-, 50% monoalkyl-, and 25% orthophosphoric acid. Consequently, one would expect perhaps 15% of the phosphorus to be present as dialkyl ester upon complete alcoholysis of 117% H_3PO_4 . This is clearly not in agreement with the observed distribution of products in which no dialkyl monophosphate was observed.

Preferred dialkyl phosphate formation would necessarily involve sequential attack of two molecules of alcohol at the same middle phosphorus atom.



Since an acid molecule with a chain length of three or more phosphorus atoms is required in order to produce a molecule of diester, the *maximum number* of such molecules which could be formed in alcoholysis of an equilibrium distribution of polyphosphoric acid chains is

$$(j_3 + j_4) + 2(j_5 + j_6) + 3(j_7 + j_8) + \dots + [1 + (-1)^n] \frac{n-2}{4} (j_{n-1} + j_n) \quad (1)$$

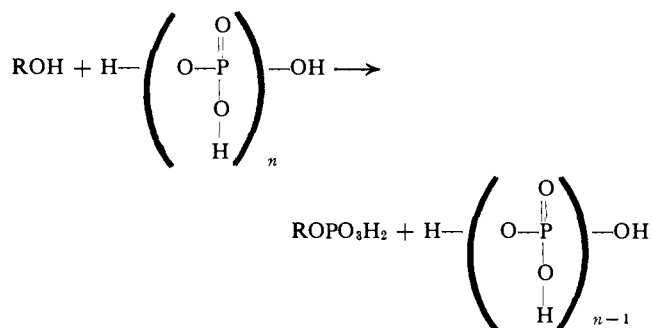
where j_n is the number of chains of length n . Dividing (1) by the total phosphorus content yields the fraction of phosphorus as dialkyl phosphate. The resulting expression may be rearranged to give

$$\% \text{ phosphorus as } (\text{RO})_2\text{PO}_2\text{H} = \sum_{n=3}^{\infty} \frac{[1 + (-1)^n]}{4} \times \frac{n-2}{n-1} \alpha_{n-1} + \frac{n-2}{n} \alpha_n \quad (2)$$

where α_n is the per cent phosphorus existing in chains of length n . Using the experimental values of α_n given by Van Wazer¹⁴ for polyphosphoric acid containing 84.3% P_2O_5 , and approximating the coefficients of α_n in eq 2 by $1/2$ for $n \geq 10$ (for which α_n has not actually been measured), this equation predicts a maximum of 35% of the phosphorus converted to $(\text{RO})_2\text{PO}_2\text{H}$. While Cherbuliez¹⁵ has reported a small amount (1.5%) of such product formed in the methanolysis of polyphosphoric acid, our failure to detect any diester, either by nmr or *via* direct work-up, leads to the conclusion that such a mechanism is certainly not in operation to any

appreciable extent. The small amount of diester formed in the methanolysis reaction may derive from direct esterification.

Preferred monoester formation would result if alcoholysis proceeded by nucleophilic stepwise attack of alcohol on the end phosphorus atom in the chain.



If cleavage were to occur exclusively in this manner from one end only, the fraction of phosphorus converted to monoalkyl phosphate is $(n-1)/n$; the fraction of phosphorus remaining as H_3PO_4 is $1/n$, where n is the average number of phosphorus atoms per chain.¹⁶

This reaction path partially explains the results of Table II in that the fraction of phosphorus as free H_3PO_4 is in fact $1/\bar{n}$ or very close to that number. However, if such a reaction course were strictly adhered to, there should be at any time during the reaction only monoalkyl monophosphate and inorganic acid fragments. The evidence is that there are alkylated end groups or chain phosphates (see Table II) and hence the reaction is not as straightforward as the above proposition implies.

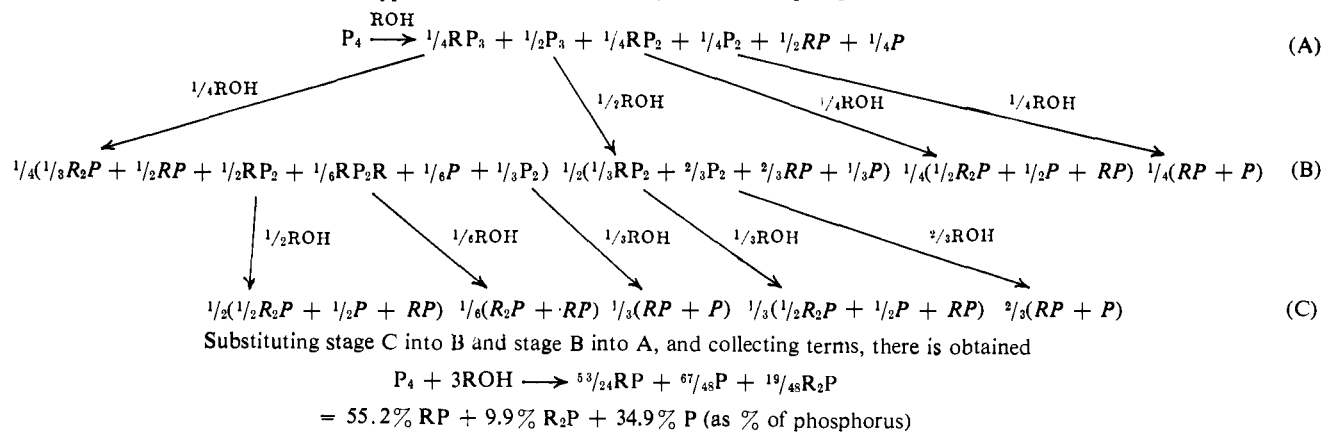
In all equimolar (ROH-POP) reaction mixtures, there appeared an appreciable amount of monoprotic phosphorus. There was no nmr evidence for either dialkylmonophosphoric acid or middle groups in long chains, only a diffuse band at *ca.* +10 ppm, typical of end group phosphorus. If this peak were free pyrophosphoric acid, not only would it fail to account for the monoprotic strong acid in the titration curve, but its position in the nmr spectrum would be expected to be almost independent of the alcohol in use. In fact, however, the position was observed to vary considerably, depending on the nature of the alkyl constituent of the reaction mixture. One must, therefore, postulate the existence of a mono- or symmetrically dialkylated pyrophosphoric acid. The esterified end group would behave as a monoprotic acid in titration and as an end group with but little shift from the resonance frequency of free acid groups in nmr; both types of behavior were, in fact, observed repeatedly.

While Nelson and Toy⁴ have reported the presence of "small" but unspecified amounts of these materials in the alcoholysis of pure $\text{H}_4\text{P}_2\text{O}_7$, our reaction of octanol with $\text{H}_4\text{P}_2\text{O}_7$ yielded no monoprotic phosphorus, as can be seen in Table III. The same reaction using

(16) It is interesting to note that this would be true whether or not the acid exists entirely as species of one chain length, *e.g.*, pyrophosphoric acid, which is the case when solid crystalline $\text{H}_4\text{P}_2\text{O}_7$ is used, or whether it is a mixture of species, *e.g.*, the melt produced from crystalline $\text{H}_4\text{P}_2\text{O}_7$ containing ortho, pyro, tripoly, and more highly condensed chains. The result is governed only by the $\text{H}_2\text{O}:\text{P}_2\text{O}_5$ ratio. Hence, reaction temperature in an anhydrous system would be important only in determining the rate of reaction and the formation of side products; it would not control the availability of reactive P-O-P linkages.

(14) Reference 2, p 748.

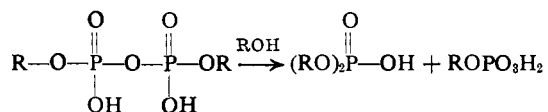
(15) E. Cherbuliez and H. Wenige, *Helv. Chim. Acta*, **29** 2006 (1946).

Scheme I. Reaction Scheme for the Hypothetical Random Alcoholysis of a Tetraphosphoric Acid Molecule^a

^a The coefficient of each species is the *amount predicted* by a completely random cleavage of P-O-P bonds. Italicized species have no P-O-P linkages remaining and hence are assumed to react no further. Stages B and C are expansions of A, required to reduce more highly condensed fragments to ortho species. Legend: P₄ = tetraphosphoric acid, P₂ = pyrophosphoric acid, etc., RP₂ = monoalkyl pyrophosphate, RP₂R = dialkyl pyrophosphate, RP = monoalkyl monophosphate, P = H₄PO₄.

117% H₃PO₄ gives about 14% monoprotic phosphorus. Hence, it is likely that these materials arise during the scission of the longer chains. The mode of reaction which best accounts for the observed products is a type of random cleavage, *i.e.*, random with respect to unalkylated phosphorus.

Reference to Scheme I will show that the initial precursor to diester is in general the species R-P_n. Owing to steric and inductive effects, it is not unreasonable to suppose that the alkylated phosphorus atom is rendered less susceptible to further attack at the same site. If this were the case, the only species which *must* give rise to dialkyl monophosphate is a symmetric dialkyl pyrophosphate, *via* the reaction



sym-Dialkyl pyrophosphate is the penultimate alcohol-

ysis product of a more highly condensed symmetrical polyphosphate, R-P_n-R, the probability of whose formation becomes appreciable only for long chains.

Again invoking the hypothesis of the deactivating alkyl group, one would expect the symmetrical dialkyl pyrophosphate to be fairly resistant to the final step of degradation to mono- and dialkyl orthophosphate.⁴ The major pyrophosphate fragment arising from the lower chain lengths is the unsymmetrical monoalkyl pyrophosphate (see Scheme I). Because one phosphorus is deactivated, this species would be expected to cleave in only one fashion, producing two molecules of monoester.

Thus, the monoprotic phosphorus detected in the reaction mixture can be accounted for by the above modification of random alcoholysis, attributing it to the mixture of these two alkylpyrophosphoric acids. Additional alcohol can react more readily with the unsymmetrical species, producing only additional monoester, and leaving the symmetrical species substantially untouched.