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The Molecular Constitution of Methyl and Ethyl Polyphosphate and the Langheld Esters[1]

John R. Van Wazer and Sarel Norval

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Abstract: Details concerning the molecular constitution of mixtures of alkyl polyphosphates (where alkyl = CH_3 or C_2H_5) prepared in various ways have been obtained from previously unreported fine structure of both hydrogen and phosphorus nuclear magnetic resonance spectra. These spectra demonstrate that the reaction of phosphorus pentoxide with an ether in chloroform solution occurs in a gelatinous surface layer in which there appears to be not only making but also breaking of P–O–P linkages and scrambling of these with the methoxyl and with catalytically active small amounts of hydroxyl groups. The first phosphorus-containing molecules to diffuse into the chloroform solution from this surface layer upon the phosphorus pentoxide are the trialkyl orthophosphate and then the tetraalkyl pyrophosphate. It is striking that in the reaction with an ether, the same products are obtained from the polymeric O and O′ forms of phosphorus pentoxide as from the P_4O_{10} bird-cage molecule. Equilibrium is achieved rather quickly so that the so-called "Langheld esters" consist of equilibrium or near-equilibrium mixtures of the normal esters of the linear polyphosphoric acids. The constitution of equilibrated mixtures of the methyl polyphosphates, ranging from the orthophosphate to the metaphosphate composition, have been carefully investigated and has been found not to deviate greatly from the molecular distribution predicted by (1) a pair of equilibrium constants for the scrambling of methoxyl groups with bridging oxygen atoms, plus (2) random sorting of the resulting molecular building units into chain molecules. Attempts to find ring molecules in the equilibrium mixtures indicate that the amounts of cyclics are undetectably small at all compositions on the finite side of the "gel point." It is shown that the silver salt made by treating sodium trimetaphosphate with silver nitrate is truly a silver trimetaphosphate but that this reacts with an alkyl iodide to give an equilibrium or near-equilibrium mixture of linear polyphosphates, with no evidence of trialkyl trimetaphosphate. The chemistry which has thus far been reported for the alkyl polyphosphates can be reasonably described by several equilibrium constants, kinetic half-lives, and activation energies—all of which are treated herein.

In several recent papers,[2–4] the molecular constitution of the products from the heterogeneous reaction of phosphorus pentoxide with diethyl ether has been described in terms of the first few molecular structures which would be obtained if there were a sequential stepwise etherolysis of isolated P_4O_{10} bird-cage molecules. From our knowledge of phosphorus chemistry and particularly of the ethyl polyphosphates,[5,6] this interpretation of the available data appeared erroneous and so the work described herein was undertaken to clarify further this highly complicated system. As part of this study, we attempted to make cyclic alkyl metaphosphates and have thus repeated the alleged preparation[7,8] of trimethyl trimetaphosphate. It was not surprising in view of our previous work[5] on making ethyl di- and triphosphates from silver salts to find that the reaction product contained no observable cyclic structure.

Experimental Section

Phosphorus Pentoxide. Fresh bottles of Mallinckrodt reagent grade product were the initial source of the phosphorus pentoxide. Several samples of this were sublimed under vacuum to give crystals of the H form which has been shown[9] to consist of P_4O_{10} bird-cage molecules. In addition, the O form was made by heating the hexagonal (H) modification in a sealed glass tube for 2 hr at 400°, and the O′ form was similarly prepared by heating for 24 hr at 450°. X-Ray diffraction[10] has demonstrated that the O form consists of an infinite sheet polymer made up of fused rings containing ten phosphorus atoms alternating with ten oxygen atoms. The O′ form of phosphorus pentoxide is also an infinite sheet polymer[11] which has smaller rings than the O form. The interlocking rings in this modification are made up of six phosphorus and six oxygen atoms.

Other Reagents. The methyl iodide, silver nitrate, sodium iodide, and anhydrous diethyl ether were all Mallinckrodt analytical grade reagents. The trimethyl orthophosphate from Aldrich Chemical Co. was purified by redistillation. The anhydrous dimethyl ether was from Matheson. The chloroform (Mallinckrodt analytical reagent) was purified by washing with water and drying over P_4O_{10}, followed by careful distillation from a small amount of fresh P_4O_{10}. It was found that the ethers stored over metallic sodium reacted at the same rate to give the same products as when they were taken from the freshly opened containers.

Reactions. In this study, 84 individual reactions were run. Since a chemical analysis by hydrogen nuclear magnetic resonance (nmr) was carried out several times and phosphorus nmr once or

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[1] This subject is discussed in a D.Sc. thesis submitted by S. Norval to the University of Pretoria, South Africa.

[2] G. Burkhardt, M. P. Klein, and M. Calvin, *J. Am. Chem. Soc.*, **87**, 591 (1965).

[3] G. Weill, M. Klein, and M. Calvin, *Nature*, **200**, 1005 (1963).

[4] W. Pollmann and G. Schramm, *Biochim. Biophys. Acta*, **80**, 1 (1964).

[5] E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **83**, 365 (1961).

[6] W. Wieker, H. P. Walter, and E. Thilo, *Chem. Ber.*, **97**, 2385 (1964).

[7] F. Cramer and H. Hettler, *ibid.*, **91**, 1181 (1958).

[8] V. J. Reilly, Ph.D. Thesis, Washington University, St. Louis, Mo., Jan 1949. Although the conclusions are mainly incorrect, this is an unusually perceptive work for its period.

[9] H. C. J. de Decker and C. H. MacGillavry, *Rec. Trav. Chim.*, **60**, 153 (1941).

[10] H. C. J. de Decker, *ibid.*, **60**, 413 (1941); W. L. Hill, G. T. Faust, and S. B. Hendricks, *J. Am. Chem. Soc.*, **65**, 794 (1943).

[11] C. H. MacGillavry, H. C. J. de Decker, and L. M. Nigland, *Nature*, **164**, 448 (1949).

twice during each run, there were produced over 650 nmr spectra, of which about 10% were subjected to a painstaking quantitative interpretation. These then served as a key for the ready interpretation of the other spectra. Attempts to repeat previous work as described in the literature[2,3,7,8] were carried out in standard laboratory equipment, employing all details that were specified. These studies were also run through a second time in order to make sure that the reported procedures were followed fairly and that nothing had been inadvertently distorted or overlooked. Except for these runs and some designed to show the effect of moisture on the products of the reactions involving phosphorus pentoxide, the experiments were generally made by combining the reagents in 5-mm precision-bore nmr tubes. These were either tightly stoppered with the usual plastic cap or, in the case of samples subjected to high temperatures or studied over a long period of time, were sealed shut with a needle-flame torch.

Great efforts were taken to avoid unwanted moisture pickup by the phosphorus pentoxide. In accord with previous work in our laboratory on dealing with hygroscopic and moisture-sensitive materials, it was found that rapid operations in a plastic drybag, which had been properly flushed with well-desiccated air, led to less water absorption than did handling in a carefully tended drybox.

Except for the data on equilibrated mixtures reported in Table II and some other scattered examples, the large number of experiments dealing with the interaction between phosphorus pentoxide and an ether have not been individually described in detail as was done in ref 2. Because of the widely varying reactivities of reagent grade samples of phosphorus pentoxide[12] and the avidity with which P_2O_5 absorbs water to give strongly catalytic acid functions, kinetically controlled experiments involving uncharacterized phosphorus pentoxide cannot be reproduced. This plus the fact that, when viewed in terms of their common factors, the experiments "made sense" and were clearly consistent with each other has led us to restrict our description of such data to general statements plus a few illustrative examples.

Nuclear Magnetic Resonance. The H^1 nmr studies without decoupling were generally carried out with a Varian A-60 spectrometer running at a frequency of 60.0 Mc and some H^1 spectra were also obtained with a field-sweep Varian HR-100 spectrometer running at 100.0 Mc. Hydrogen spectra decoupled from the phosphorus were run with the HR-100 unit using an NMR Specialties SD-60 decoupler. Since the phosphorus-saturating signal was not sufficiently strong over the full range of its band width to give decoupling at a single frequency setting, a different saturating frequency had to be employed for the various structure-building units. Thus optimum decoupling was achieved for trimethyl orthophosphate at 40.483100 Mc. For end groups in the various methyl polyphosphate molecules, the best decoupling was attained at 40.483575 Mc for the $\mathbf{e}{\dagger}e$ molecule,[13,14] 40.483615 Mc for $\mathbf{e}{\dagger}m$, and 40.483645 Mc for the $\mathbf{e}{\dagger}b$ arrangement. For middle groups in the methyl polyphosphate molecules, the following frequencies were used: 40.481385 Mc for $e\mathbf{m}{\dagger}e$, 40.481415 Mc for $e\mathbf{m}{\dagger}m$, and 40.481465 Mc for $m\mathbf{m}{\dagger}m$. The **HCOP** coupling constants for the methyl phosphates were as follows: 11.0 cps for the orthophosphate, in the range of 12.0–12.5 for the various end groups, and 12.0–13.0 for the various middle groups. For the methylene group of the ethyl polyphosphates, these coupling constants were reduced by about 2 cps; and the **HCCOP** coupling constants of the methyl hydrogens of the ethyl group were about 0.8 cps.

The P^{31} nmr spectra were obtained at 40.5 Mc with a field-sweep HR-100 Varian spectrometer. Although in a sealed-tube experiment the amount of branches can be calculated from the hydrogen spectra and the proportions of reagents used, the phosphorus nmr offers the only direct measure of the fraction of the total phosphorus present as branch groups in the over-all mixture. It was always used as a confirmatory analysis for branches. The P^{31} resonances at 40.5 Mc show sufficient fine structure so that the tetraethyl or tetramethyl pyrophosphate and the pentaethyl or pentamethyl triphosphate may be determined directly.

Other Analytical Techniques. Molecular distillations were performed at micron pressures in a centrifugal-disk molecular still, Type CMS-5, manufactured by the Consolidated Vacuum Corp., Rochester, N. Y. The condensing surface of this still was kept at $-10°$ and the temperature of the evaporating surface was varied as desired from room temperature up to 100°.

Solubility fractionation was carried out at room temperature by adding successively larger portions of ether to a 10% solution in chloroform of the chosen methyl polyphosphate equilibrium mixture. After the addition of each portion of ether, the faintly opalescent solution was stirred for about 10 min and then centrifuged to give a few drops of a clear gum or liquid, which was analyzed by nmr. The first portion of added ether was in the range of 5–10 ml per 200 ml of chloroform solution, and the final portion was several hundred milliliters. Intrinsic viscosity measurements were carried out in chloroform as the solvent, using a viscometer which had an efflux time of 106 sec for the pure solvent. Careful thermostating at room temperature was employed in the viscosity determinations, and it was found that the viscosity number (*i.e.*, the reduced viscosity) decreased linearly with concentration.

Thermal-diffusion separations were performed in a 30-ml column made by M. Fink Co., Cleveland, Ohio. This column was 76 in. long, with an 0.012-in. annular gap between the cooled inner tube and the heated outer tube (0.637 in. in diameter). Several thermal-diffusion runs lasting from 60 hr to 2 weeks were carried out using a hot-wall temperature of 50° and a cold-wall temperature of $-10°$. Ten equal fractions were taken by emptying the column at the ten equally spaced levels from which it could be drained.

No attempt was made to characterize the alkyl polyphosphates by elemental analysis since years of experience with these and similar organic phosphorus compounds have led to the conclusion that such measurements are more a test of the analyst's skill than a reliable measure of elemental composition. The best way to obtain this analytical information on the alkyl polyphosphates is to run a P^{31} nmr spectrum on a neat liquid or concentrated solution. The results have been reported in terms of the over-all ratio, R, of alkoxyl (plus hydroxyl) groups to phosphorus from the relationship $R = (3n + 2e + m)/(n + e + m + b)$, where the symbols n, e, m, and b represent the proportion of the total peak areas in the P^{31} spectrum corresponding to the *neso*, end, middle, and branch resonances, respectively. The hydroxyl content of the ester mixtures is obtained quantitatively from the proton spectra.

Interpretation of Nmr Spectra

The assignments of the *neso*, end, middle, and branch regions in the P^{31} spectra are the same as those first

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(12) Although there is essentially no information on the subject in the scientific literature, there are a number of confidential industrial research reports dealing with the variable reactivity of regular commercial phosphorus pentoxide. This work indicates that the reactivity is a complicated function of (1) the relative amounts of the various varieties of crystalline and amorphous P_2O_5, (2) the particle-size distribution of each variety of P_2O_5 and the degree of particle agglomeration, (3) the amounts and kinds of lower oxides and oxyacids, and particularly (4) the amounts, kinds, and spacial distribution of the condensed phosphoric acids formed by water pickup. [See J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p 269, for a brief description of the varieties of P_2O_5 to be found in the commercial product.]

The reactivity of CP phosphorus pentoxide has been found to vary as much as threefold (due to moisture pickup) from one part to another in an aged but previously unopened bottle. The reactivity measurements are generally carried out with alcohols instead of ethers.

(13) This notation has been employed in a number of recent papers[19,21,22] from our laboratory and is precisely described in ref 14. In brief, the symbols n, e, m, and b refer, respectively, to the *neso* compound (the smallest molecule in a family of compounds), in this case, the orthophosphoric ester; the end group; middle group; and branch group, respectively. In the case of the completely esterified alkyl polyphosphates, the *neso* or "ortho" compound is $(RO)_3PO$; and the end, middle, and branch building units have the following formulas, respectively: $(RO)_2(O)P(O_{1/2}-)$, $(RO)(O)P(O_{1/2}-)_2$, and $(O)P(O_{1/2}-)_3$, where $(O_{1/2}-)$ represents the oxygen atom bridging between a pair of neighboring phosphorus atoms, with only half an oxygen being shown in order to fulfill the requirements of stoichiometry.

Nmr chemical shifts as well as other properties (including the heats and free energies of reactions of a given building unit) are dependent on the neighboring building units if measured to sufficient precision. Therefore, when the P^{31} chemical shift of, say, an end group is affected by the kind of neighboring group to which it is bonded, the end group in question has been identified by boldface type, with the neighboring group which modifies its chemical shift being shown in italics; *e.g.*, $\mathbf{e}e$, $\mathbf{e}m$, and $\mathbf{e}b$ represent the three distinguishable end groups corresponding to the chemical shift being affected by only the nearest-neighbor building unit. The six distinguishable middle groups also corresponding to interaction only with the nearest-neighbor building units are $e\mathbf{m}e$, $e\mathbf{m}m$, $e\mathbf{m}b$, $m\mathbf{m}m$, $m\mathbf{m}b$, and $b\mathbf{m}b$. When the proton nmr spectra are analyzed in terms of the percentage of total alkoxyl groups observed for a given structure unit, the boldface letter is followed by a dagger (*e.g.*, $m\mathbf{m}{\dagger}m$) to indicate that an exchangeable substituent is being observed.

(14) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, 41, 3105 (1964).

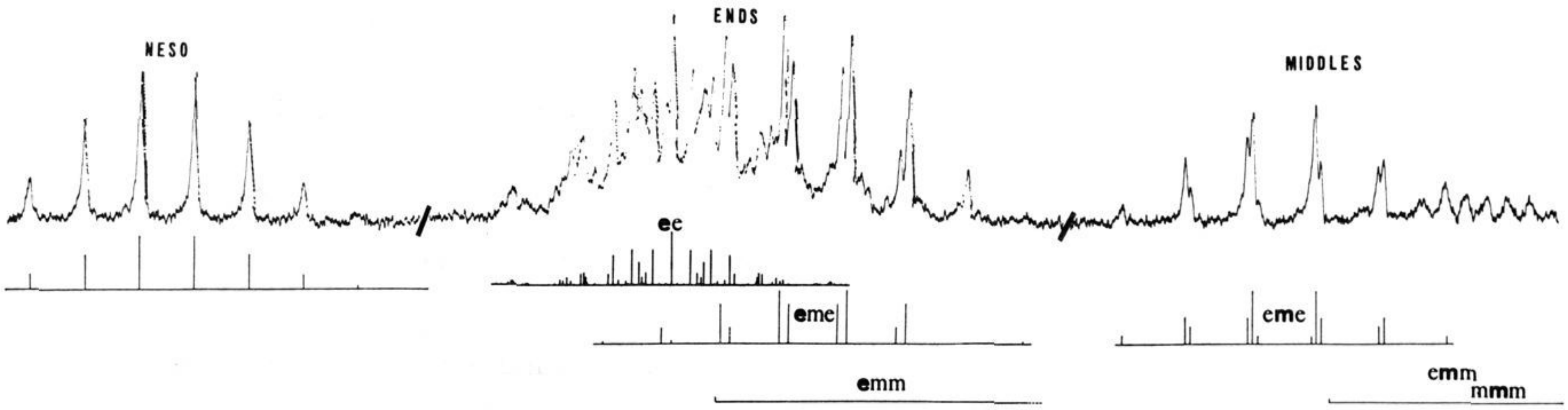

Figure 1. The well-resolved P^{31} nmr spectrum of an equilibrated methyl polyphosphate mixture exhibiting a value of $R \equiv (CH_3O + HO)/P = 1.939$. An analysis of the sets of lines due to the simpler molecules is given below the appropriate peaks.

made in our laboratory[15] and used later by Calvin, *et al.*[2,3] A typical highly resolved P^{31} spectrum obtained at 40.5 Mc is shown in Figure 1. Although overlapping of the complicated higher order spin–spin splitting in the P^{31} spectra taken at 40.5 Mc leads to undecipherable spectra for the higher alkyl polyphosphates, it does allow ready recognition of the orthophosphate esters and the molecules of either tetramethyl or tetraethyl pyrophosphate from the end-group portion of the spectrum and either pentamethyl or pentaethyl tripolyphosphate from the middle-group portion.

A set of typical proton spectra for equilibrated mixtures of methyl polyphosphates are presented in Figure 2, on the left side of which are shown the spin-split spectra obtained at 60 Mc and on the right side the P^{31}-decoupled spectra taken at 100 Mc. The *neso*, end, and middle regions of the decoupled spectra bear the correct area relationships to these same regions of the related P^{31} spectra, when it is taken into account that there are nine hydrogens per phosphorus for the *neso* molecule, six for an end group, and three for a middle group. This is also true for the individual **e***e* and *e***m***e* resonances. Furthermore, in an equilibrated series of samples, as exemplified by the spectra of Figure 2, the first peak to appear[16] as R = alkoxyl/phosphorus is reduced from 3 is **e**†*e* followed by **e**†*m* and *e***m**†*e*. The hydrogen and phosphorus spectra of tetramethyl pyrophosphate have also been obtained on nearly pure samples prepared by molecular distillation, as described in a following section, and these have been used as comparison standards.

Although at first glance the uncoupled nmr spectra obtained with a Varian A-60 spectrometer (exemplified by the left-hand spectra of Figure 2) may appear to be too complicated for interpretation, they are readily elucidated by comparison with the same spectra in which the phosphorus is decoupled. The regular progression downfield of the doublets corresponding to the *neso* molecule, the various end groups, and the various middle groups causes a great deal of confusion and overlapping in the central part of the undecoupled proton spectra. However, the *neso* and end groups may be determined from the upfield part of the spectra and the middle groups from the downfield part, as indicated by the labeling of the spectra on the left-hand side of Figure 2. Because of possible complications due to incomplete decoupling, the required switching of decoupling frequencies during a full sweep, and the possibility of an Overhauser effect,[17] the undecoupled spectra are in principle to be preferred for quantitative measurements over the decoupled ones.

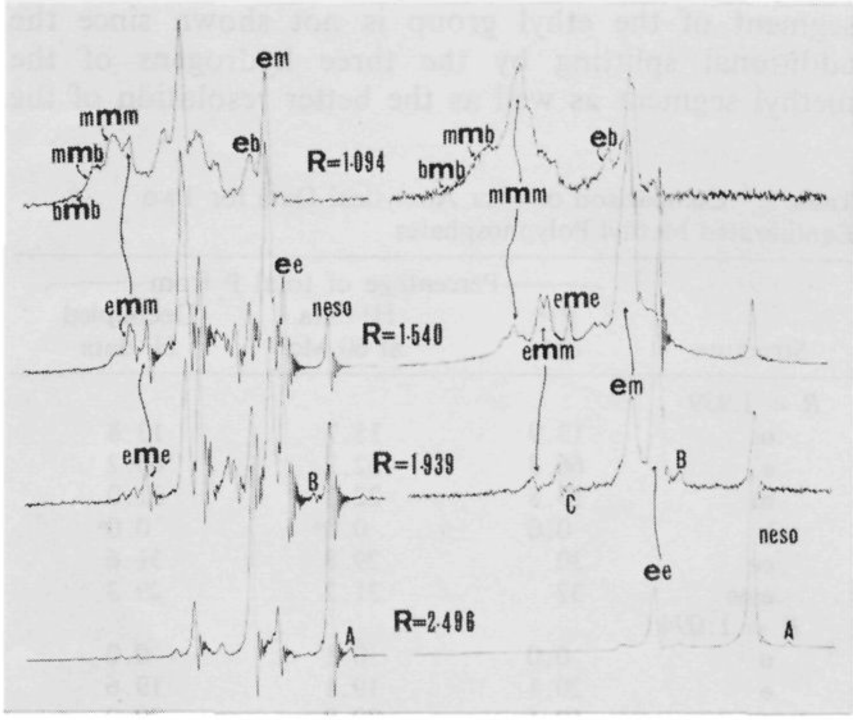

Figure 2. The methyl group region of the hydrogen spectra of equilibrated methyl polyphosphate mixtures exhibiting four different values of $R \equiv (CH_3O + HO)/P$. The right-hand spectra are decoupled ones taken at 100 Mc and the left-hand spectra are undecoupled taken at 60 Mc. The resonances due to the various methyl acid polyphosphates are labeled with letters as follows: A = $(CH_3O)_2HOPO$, B = $(CH_3O)(HO)(O)POP(O)(OCH_3)_2$, and C = $(CH_3O)_2(O)POP(O)(OCH_3)OP(O)(OH)(OCH_3)$.

In all of the work reported in this paper, careful checks were made to see that the interpretation of the P^{31} spectra as well as that for the undecoupled proton and phosphorus-decoupled proton spectra were consistent between each other and within themselves for a given sample. A typical set of checks for quantitative consistency are shown in Table I for two of the equilibrated compositions of methyl polyphosphates for which spectra are presented in Figure 2. These and similar data demonstrate that there is no detectable Overhauser effect.

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(15) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

(16) J. R. Van Wazer and L. C. D. Groenweghe, "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 33.

(17) A. Overhauser, *Phys. Rev.*, **92**, 411 (1953); also see J. D. Baldeschweiler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).

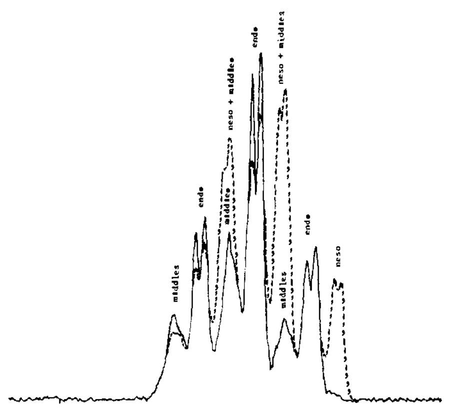

Figure 3. H^1 spectrum of the methyl region of an ethyl polyphosphate mixture ($R \equiv (C_2H_5O + HO)/P = 1.402$) before (solid line) and after (dotted line) adding triethyl orthophosphate to the contents of the nmr tube.

Typical undecoupled H^1 spectra at 60 Mc are presented in Figure 3 for two mixtures of ethyl polyphosphates, one containing no detectable orthophosphate and the other the same mixture with triethyl orthophosphate added to it. The spectrum for the methylene segment of the ethyl group is not shown since the additional splitting by the three hydrogens of the methyl segment as well as the better resolution of the nearest-neighbor building units causes confusion in the methylene region of the spectra, thus making it more difficult to interpret than the methyl region. As expected, the resonances for the methyl region are split into a 1:2:1 triplet by the two hydrogens of the neighboring methylene, with further splitting of these peaks into doublets due to interaction with the phosphorus. As illustrated by this figure, no specific information can be obtained about the amount of pyro- or tripolyphosphate from the hydrogen spectra, and hence the analysis for these species must be obtained from the phosphorus spectra taken at 40.5 Mc. Because of the poor resolution in the H^1 nmr spectra of the ethyl esters as compared to the methyl ones, the emphasis in the detailed study of the well-equilibrated polyphosphoric esters has been on the methyl polyphosphates.

Table I. Comparison of Nmr Analytical Data for Two Equilibrated Methyl Polyphosphates

	Percentage of total P from		
Structure	P^{31} data	H^1 data at 60 Mc	Decoupled H^1 data
R = 1.939			
o	13.9	15.7	13.8
e	66.3	62.2	65.2
m	19.8	22.1	21.0
b	0.0	0.0[a]	0.0[a]
ee	30	29.8	31.6
eme	32	31.2	29.3
R = 1.094			
o	0.0	0.1	0.0
e	20.1	19.1	19.6
m	69.1	70.8	70.2
b	10.8	10.0[a]	10.2[a]
ee	<3	0.4	<3
eme	4	3.6	. . .
eb	. . .	6.1	. . .

[a] Calculated by difference from **o**†, **e**†, **m**†, and the starting composition.

Reactions and Some Parameters Determining Reaction Velocities

Reaction between Ether and Phosphorus Pentoxide. Careful observation of more than a dozen experiments showed that, when a chloroform solution of dimethyl or diethyl ether is treated with phosphorus pentoxide using only normal precautions for protection from moisture, the surface of the submerged particles of the phosphorus pentoxide become coated with a viscid layer. Proton nmr shows about 10% of the total hydrogen is then present in the final reaction product as hydroxyl groups instead of alkoxyl groups. A number of experiments have convinced us that the OH groups are directly or indirectly[18] attributable to moisture picked up by the phosphorus pentoxide. When using phosphorus pentoxide which has been vacuum sublimed and successfully protected from moisture, the percentage of total hydrogen as hydroxyl groups can readily be lowered to 2–3% and has been reduced as low as 0.1%. The rate of dissolution in a given ether solution of vacuum-sublimed P_4O_{10} (H form) which has been carefully protected from moisture is about tenfold slower than the rate observed with commercial phosphorus pentoxide from previously opened bottles. We attribute this retardation to a combination of lessened acid catalysis[6] (*vide infra*) plus a diminution in surface area upon going to the larger and more compact particles of the sublimed P_4O_{10} even after grinding. Under the same conditions, ground samples of the O- and O′-polymeric forms of phosphorus pentoxide are found to react about as rapidly as the well-crystallized H form (P_4O_{10}) so that it appears the reaction rate is more sensitive to the available surface area and the water content (proton catalysis) than to the molecular form of the phosphorus pentoxide.

The initial products formed in the heterogeneous reaction between ether and phosphorus pentoxide were investigated by putting a chloroform solution of the ether on top of some phosphorus pentoxide in a tightly capped nmr tube. A series of 18 different runs were carried out on the reaction of either dimethyl or diethyl ether with either commercial phosphorus pentoxide (from a fresh bottle and several previously opened ones), vacuum-sublimed P_4O_{10}, or the O- or O′-polymeric forms of phosphorus pentoxide. In these runs the respective trialkyl orthophosphate was always found to be the first phosphorus compound to be seen in the proton or phosphorus nmr spectra. The next species to show up in the spectra is the appropriate tetraalkyl pyrophosphate, the *ee* molecule. Then in the proton nmr spectra, the **e**†*me* and the **em**†*e* resonances were the next to be observed. Even though the proton nmr (from the A-60 spectrometer) is 49 times more sensitive than the phosphorus nmr (from the HR-100 unit) for trimethyl orthophosphate and 33 times more sensitive for the tetramethyl pyrophosphate, the same sequence of peak appearances is generally observed in the P^{31} spectra. This result is due to the fact that, in the first part of the reaction, all of the

[18] Moisture pickup not only gives a quantitative yield of hydroxyl groups but may also lead to hydroxyl groups caused by the *acid-catalyzed* decomposition of the alkoxyl groups—especially formation of ethylene plus residual hydroxyls from ethoxyl groups.

observed species are increasing so that the orthophosphate peak is still predominant and hence is the first to show up when the chloroform becomes sufficiently concentrated in phosphorus compounds for a P^{31} signal to appear above the background noise. An important finding with the P^{31} nmr is that branch groups are not detected in the chloroform until the reaction has proceeded well along and the *neso*, end, and middle peaks are all large.

As the reaction between the chloroform solution of ether and the plug of phosphorus pentoxide proceeds, the surface of the phosphorus pentoxide becomes noticeably gummy and this gummy layer grows. Concomitantly, the remaining phosphorus pentoxide is seen to lose its particulate appearance and cake together into an even more viscid mass than the gummy layer. In one of the examples, when 0.2 g of sublimed P_4O_6 was thus allowed to react with 0.1 g of ether in 1 ml of chloroform, it was observed after 2 days at 70° that 6.5% of the total phosphorus had dissolved in the chloroform, with roughly half of the remaining nmr-detectable phosphorus being in the gummy layer and the other half in the very bottom of the tube where the P_2O_5 had by this time formed a viscid mass. In the chloroform solution, it was found that 20% of the total phosphorus was present as trimethyl orthophosphate, 55% as end groups (two-fifths of which was tetraethyl pyrophosphate), and 25% as middle groups with no branches. In the intermediate gummy layer and the bottom layer, the amount of *neso* compound represented only 7% of the total phosphorus. No branches were seen in the gummy layer and 4% of the total phosphorus was present as branches in the bottom layer. In both of these layers, which were about equal in volume, the remaining phosphorus was approximately evenly divided between ends and middles, with the viscosity being too high to give interpretable fine structure. In this particular case, where the over-all ratio, *R*, of methoxyl groups to phosphorus was 1.49, the branch groups would represent only 2.7% of the total phosphorus when equilibrium was finally reached.

Thilo, *et al.*,[6] have pointed out that, in the reaction of ether with phosphorus pentoxide, a gelatinous material (called "the insoluble side-product") which is not soluble in chloroform is formed approximately in proportion to the water content of the phosphorus pentoxide. Only when great pains have been taken to avoid water contamination of the phosphorus pentoxide can the formation of the insoluble side product be completely avoided. Several samples of this chloroform-insoluble material have been analyzed by hydrogen nmr and it was found that the ratio of the greatly broadened hydroxyl to methoxyl resonances was in the range of 0.1 to 0.3. In another series of more than a dozen experiments in which the heterogeneous reaction between ether and phosphorus pentoxide in chloroform was carried out in a flask under reflux conditions (with or without additional agitation), the presence of a gummy layer and the slow "gelatinization" of the phosphorus pentoxide was not always as clearly apparent as in the tall, slender nmr tubes. The use of coarse compact particles of the phosphorus pentoxide coupled with strict exclusion of moisture and through agitation of the chloroform appears to lead to a thinner (barely detectable) gummy layer than the other conditions tested.

Initial Part of Related P_2O_5 Reactions. The heterogeneous reactions in an nmr tube between a plug of phosphorus pentoxide and chloroform solutions of either (a) trimethyl or triethyl orthophosphate or (b) tetramethyl pyrophosphate have been investigated. When the reagent was an orthophosphate, the first nmr resonance observed in addition to the orthophosphate peak corresponded to the pyrophosphate. As in the case of the reaction of phosphorus pentoxide with ether, dissolution of the phosphorus pentoxide proceeded through a viscous phase. When tetramethyl pyrophosphate obtained from molecular distillation was used as the reagent, the first resonance to be seen in addition to that of the pyrophosphate was the orthophosphate. Again dissolution occurs through a gummy intermediate.

Reactions in the Gummy Layer. Since the gummy layer over a plug of phosphorus pentoxide exhibits a rather constant composition throughout much of the dissolution process and gives broadened nmr spectra, adequate kinetic measurements could not be made on it. However, the rate at which a somewhat similar concentrated system reaches equilibrium could be clearly studied by mixing trimethyl orthophosphate with the clear grease-like gum resulting from vacuum evaporation of the chloroform from an equilibrated methyl polyphosphate mixture having an *R* value of 1.094 and no more than a trace of hydroxyl groups in its hydrogen nmr spectrum. When the resulting viscous mixture was kept at 60°, the nmr spectrum was found to change with time so that the *neso* decreased and the various arrangements of end groups increased (in a manner quite similar to that shown in Figure 4).

The measured half-life for the *neso* compound to go from its starting value to the equilibrium value was 65 min at 60°. The addition of 8% of anhydrous $H_4P_2O_7$ to the viscous mixture reduced this half-life to 4 min. Since the time for dissolution of 90% of the phosphorus pentoxide in refluxing ether–chloroform solutions was found to range from 6 days for essentially water-free samples down to about 1 day for samples well contaminated with moisture, it is seen that the above-measured half-lives for the reaction of trimethyl orthophosphate with the long-chain phosphates are about 10^2 times shorter than the respective P_2O_5-dissolution times.

Discussion. The results presented in the three preceding sections are most logically explained on the basis of the initial formation of a crosslinked-network polymer (the gel phase) through which small molecules (the ether as well as the *neso* and shorter-chain phosphates) diffuse while simultaneously undergoing exchange reactions with the gel. It seems clear that the reaction scheme which the studies of Calvin, *et al.*,[2,3] were alleged to support has no physical meaning. Instead, the acid-catalyzed scission of P–O–P linkages at the surface of any form of phosphorus pentoxide (not only P_4O_{10}) involves phosphorylation as well as esterification so that an infinite-network molecular structure (held together by P–O–P linkages, with occasional hydroxyl groups sprinkled about) quickly forms immediately adjacent to the surface of the unreacted phosphorus pentoxide, which was undoubtedly covered with a more-or-less thin layer of polyphosphoric acids prior to the reaction with ether.

At each point within the gummy coating on the phosphorus pentoxide, it appears that an equilibrium molecular distribution is more or less reached, owing to the acid-catalyzed exchange processes for which the catalyst consists of the occasional OH groups. It is by this means that low molecular weight species corresponding to a "sol" fraction[19] are generated. These small molecules are expected to move rather freely throughout the gel, being subject to occasional scrambling reactions with the gel. The sol molecules reaching the interface between the gummy coating and the chloroform solution then diffuse into the chloroform. The smaller molecules should exhibit the greatest possibility of thus escaping from the confines of the gel and hence showing up first in the solution. Finally, when there is no more phosphorus pentoxide to supply branch groups, the gel gradually disrupts and dissolves in the entirety.

Reequilibration in Chloroform. By mixing chloroform solutions of trimethyl orthophosphate and a previously equilibrated mixture of methyl polyphosphate molecules, the kinetics of reequilibration[20] was investigated for four different ratios of reagents. Data from a typical equilibration study are shown in Figure 4, from which it can be seen that concentrations of the ortho and branch PO_4 groups decrease while the end and middle groups increase concomitantly. The middle groups then decrease slowly. These kinetic data are in accord with a scrambling process in which -OR and -OP groups exchange between pairs of phosphorus atoms. Thus the first major step of the reaction sequence of Figure 4 is the energetically favorable elimination of branch groups according to eq 1.

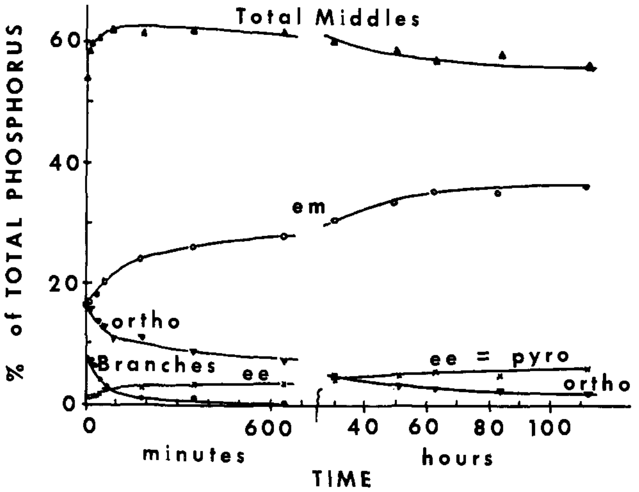

Figure 4. Kinetic data obtained at 70° by adding trimethyl orthophosphate to an equilibrated methyl polyphosphate mixture thereby changing $R \equiv (CH_3O + HO)/P$ mole ratio from 1.059 to 1.450.

$$\underset{\text{ortho}}{OP(OR)_3} + \underset{\text{branch}}{OP(O_{1/2}-)_3} \longrightarrow \underset{\text{end}}{OP(OR)_2(O_{1/2}-)} + \underset{\text{middle}}{OP(OR)(O_{1/2}-)_2} \quad (1)$$

This is followed by the slower reaction

$$\underset{\text{ortho}}{OP(OR)_3} + \underset{\text{middle}}{OP(OR)(O_{1/2}-)_2} \longrightarrow \underset{\text{end}}{2OP(OR)_2(O_{1/2}-)} \quad (2)$$

It should be noted that there are chemically meaningful exchange-pair reactions in addition to those of eq 1 and 2. All of these reactions involving exchange of -OR and -OP groups between the orthos, ends, middles, and branches come into play within a period of several hundred hours under the conditions of Figure 4. Although a complete mathematical analysis has not been made, rough calculations indicate that the observed changes with time of the amounts of ee, *em*, *eb*, and the various kinds of middle groups (as determined by nmr) are in accord with the reactions of eq 1 and 2 being virtually unaffected by the position of the building unit in the molecule.

Search for Unbranched Monocyclic Molecules

Attempted Preparation from Silver Salts. Several authors[6,7] have reported the preparation of the cyclic alkyl trimetaphosphate from the reaction between an alkyl iodide and the silver salt of the well-established sodium trimetaphosphate. We have reinvestigated these preparations using methyl iodide and have concluded that they are invalid. As shown in the previous section, the esters of the condensed phosphoric acids are quite labile materials and so the alkylation of the silver salt was done at room temperature.

Silver trimetaphosphate was first made according to Cramer and Hettler[8] and by Reilly's improved procedure.[8] In both cases, the resonance of the trimetaphosphate ion was the only P^{31} signal observed in an aqueous solution resulting from treating the anhydrous silver trimetaphosphate with sodium iodide.

Portions of each preparation of anhydrous silver trimetaphosphate were then placed in the bottom of nmr tubes to each of which a chloroform solution of methyl iodide was added. In about an hour at 25°, the first interpretably strong H^1 nmr spectrum was obtained. This corresponded to a complicated mixture of *neso*, end, and middle groups—similar to the kind of mixture observed for equilibrated samples. As time proceeded, the over-all spectrum was seen to become more intense with little change in the relative heights of the various nmr peaks. This indicated that there was a great deal of scrambling occurring concomitantly with the formation of the methyl polyphosphate esters.

These results led us to suppose that a silver salt or perhaps traces of elemental silver (formed because of inadequate shielding from light) might act as a powerful catalyst for scrambling reactions involving the alkyl phosphates, However, no acceleration was observed in the reaction rate when silver salts or reduced silver salts were added to a solvent-free mixture of trimethyl orthophosphate and a highly condensed methyl polyphosphate for which $R = 1.094$.

Occurrence in Equilibrium Mixtures. According to theory,[14] the proportion in an equilibrium mixture of any cyclic ester should be largest at the lower R values in the composition region in which the alkyl polyphosphates have been amenable to study. Increased dilution also favors ring formation in equilibrated systems,[14,21] but too great dilution will prohibitively

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[19] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 374–383, *et al.*

[20] For similar reactions in families of silicon compounds, see: K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 806 (1964), and J. R. Van Wazer and K. Moedritzer, *J. Chem. Phys.*, 41, 3125 (1964). In all-*neso* systems, the type of rate curves without maxima are exemplified by the article by H. K. Hofmeister and J. R. Van Wazer, *J. Phys. Chem.*, **69**, 794 (1965), whereas curves with maxima are described by K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964). For related mechanistic studies, see H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, in press.

[21] K. Moedritzer, J. R. Van Wazer, and C. H. Dungan, *J. Chem. Phys.*, 42, 2478 (1965); J. R. Van Wazer and K. Moedritzer, *ibid.*, **41**,

reduce the rate of exchange of parts between different molecules.

In the nmr study of other systems[21,22] where an appreciable amount of simple rings (the smaller unbranched cyclics) coexist with the chain molecules, the resonances corresponding to simple cyclic molecules are sharp peaks which often clearly stand out from the broad resonances of other middle groups which are subject to "local" viscosity broadening. The case of the related family of methoxyl-terminated poly(methylphosphonates)[22] is particularly pertinent in that several sharp peaks were seen to be superimposed upon the usual rather broad middle-group resonances when cyclic molecules were present. Throughout this work, we have been alert for middle-group resonances due to simple rings but we have not seen any at the four- to fivefold dilutions employed.

Since the trimeric and tetrameric methyl trimetaphosphates are expected to be limpid liquids exhibiting vapor pressures not many orders of magnitude lower than that of the tetramethyl pyrophosphate, molecular distillation from a spinning-disk still was carried out (immediately after removal of the chloroform) on several equilibrated samples exhibiting methoxyl:phosphorus mole ratios ranging from 0.95 to 1.1. Although the still pressure was below 25 μ, no sharp middle-group peaks were ever observed in the proton nmr spectra. With a spinning-disk temperature of 25°, the sole product from extended distillation was the tetramethyl pyrophosphate. As the temperature was raised, middle groups began to appear in the nmr spectra of the distillate but these were always accompanied by the appearance of the orthophosphate resonance and the amount of **e**†*m* resonance needed for all-chain molecules. Formation of the *neso* compound clearly showed that scrambling was taking place, becoming sufficiently rapid at a disk temperature of 50° to give 0.1 ml of $(CH_3O)_3PO$ in 1 hr when about 600 cc/hr of the sample was passed over the heated disk and then over a cooling coil.

It should be noted that, although we were unable to find any cyclic alkyl metaphosphates, no evidence is presented here to show that they cannot exist. However, except for very dilute solutions, fluid preparations of such cyclics are expected to equilibrate within a matter of days at room temperature to give the stoichiometrically equivalent mixture of chains.

Equilibrium Studies

Methyl Esters. Although pilot experiments showed that dissolution of the P_2O_5 and the resultant equilibration between the various molecular species was reached in about 3 hr at 120°,[23] the equilibrium data reported here were obtained on samples held at this temperature for 3 weeks. In addition, nmr spectra were run on some of these samples after they have been stored for several additional months at room temperature, and it was found that the spectra were unchanged, within experimental error. Phosphorus and undecoupled as well as decoupled hydrogen nmr were used to analyze the equilibrium mixtures. Typical hydrogen spectra in the methyl group region are shown in Figure 2. From these data, equilibrium constants for the exchange of functionality between the building units were calculated from the three kinds of spectra and were found not to vary systematically with R value. The weighted mean values[24] for the equilibrium constants K_1 = [*neso*] × [middles]/[ends]^2 and K_2 = [branches][ends]/[middles]^2 are, respectively, 0.044 and 0.048 from the P^{31} spectra, 0.055 and 0.051 from the undecoupled H^1 spectra, and 0.081 and 0.050 from the decoupled H^1 spectra.

By measuring the areas of the different peaks in the hydrogen nmr spectra, such as those shown in Figure 2, the relative proportions of the various observed arrangements of building units are obtained[1]—as normalized over the total methoxyl plus hydroxyl groups in the molecules. Theoretical values of these peak areas were also calculated from the equilibrium constants K_1 and K_2 on the assumption that the sorting of the various building units into molecules is a statistically random process. In Table II, the observed and calculated values of these same arrangements of building units are reported as renormalized over the total phosphorus. In addition, the table lists the percentage of the total phosphorus (calculated from the hydroxyl resonance in the H^1 nmr spectra) to which an OH group instead of a methyl group was found to be bonded. In both the kinetic and equilibrium studies of the methyl polyphosphates, no more than one hydroxyl group was ever observed on a single phosphorus atom, so that, for example, the only acidic orthophosphate seen was $(CH_3O)_2(HO)PO$. Although the amounts of acidic ortho-, pyro-, and tripolyphosphate species were directly determined from the H^1 spectra of methyl groups and the amount of middle groups bearing hydroxyls was calculated from these values and the hydroxyl resonance, the acidic species (which always represented a small fraction of the respective nonacidic species) are lumped together with the completely methoxyl-substituted equivalent species in Table II. To a first approximation, the small amounts of hydroxyl groups were distributed between the *neso*, end, and middle building units in proportion to the relative amounts of these units.

The data of Table II show that there are fewer molecules of tetramethyl pyrophosphate and more molecules of pentamethyl tripolyphosphate than would be expected from random sorting of the end, middle, and branch building units into molecules. The fact that there is less than the amount of tetramethyl pyrophosphate calculated on the assumption of a ring-free system[14,21] means that the amount of cyclic molecules cannot be estimated theoretically from the short-chain species and that the reorganization heat order, ρ, is greater than unity (*i.e.*, in this system there is a thermodynamic preference for ends to associate with middles rather than with other ends). Although the nmr spectra do not give sufficient resolution to carry out a precise evaluation of the higher order set of equilibrium con-

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3122 (1964); K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 2360 (1965).

(22) D. Grant, J. R. Van Wazer, and C. H. Dungan, *J. Polymer Sci.*, in press.

(23) In our prior study[5] of ethyl polyphosphates, it was stated that the acid-catalyzed formation of ethylene and hydroxyl groups from the ethoxyl groups limited the upper temperature for study to 115°. In the work reported herein, the use of phosphorus pentoxide well protected from moisture allows higher temperatures in equilibrating the ethyl polyphosphates. As expected, ever higher temperatures and longer heating times may be employed with the methyl polyphosphates at the same concentration of hydroxyl groups.

(24) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

Table II. Relative Concentrations of Various Building Units Observed in the Undecoupled Hydrogen Nmr Spectra of Equilibrated Mixtures of Methyl Polyphosphates

$R = \frac{\text{OCH}_3 + \text{HO}}{\text{P}}$	Percentage of total P: *neso*	ee	e*m*	e*b*	*eme*	e*mm*	e*mb*	*mmm*	*mmb*	*bmb*	Having OH groups	Branches
1.094	0.1	0.4	12.7	6.0	1.3	19.4	5.9	27.7	11.8	4.7	3.1	10.0
	(0.5)[a]	(2.1)	(14.2)	(3.7)	(0.8)	(10.2)	(2.6)	(33.5)	(17.7)	(2.3)		(11.6)
1.134	0.3	1.2	17.7	5.6	3.0	21.2		23.6	10.2	5.3	3.6	11.8
	(0.6)	(2.7)	(16.0)	(3.6)	(1.0)	(11.5)	(2.6)	(34.5)	(15.7)	(1.8)		(10.2)
1.168	0.3	1.5	19.1	5.3	5.6	20.2		25.7	8.5	4.1	2.4	9.7
	(0.7)	(3.2)	(17.5)	(3.6)	(1.2)	(12.6)	(2.6)	(34.2)	(14.0)	(1.0)		(9.0)
1.240	0.4	1.8	22.2	5.0	6.2	19.4		27.6	7.8	3.9	1.8	5.7
	(1.1)	(4.8)	(20.7)	(3.6)	(1.7)	(14.9)	(2.5)	(32.5)	(10.7)	(0.9)		(6.9)
1.287	0.7	2.4	27.5	4.0	7.0	21.0		21.2	5.9	3.4	1.5	6.9
	(1.3)	(5.9)	(22.5)	(3.4)	(2.0)	(16.0)	(2.3)	(30.9)	(9.0)	(0.7)		(5.9)
1.303	0.5	2.0	28.0	4.0	6.5	25.5		19.6	8.2	1.1	1.8	4.6
	(1.5)	(6.4)	(23.4)	(3.4)	(2.3)	(16.5)	(2.3)	(30.1)	(8.3)	(0.6)		(5.5)
1.470	1.9	5.6	39.5	2.6	8.6	20.6		13.5	2.4	0.5	1.5	4.8
	(3.0)	(12.4)	(28.6)	(2.5)	(4.1)	(18.9)	(1.7)	(21.9)	(3.8)	(0.2)		(3;0)
1.540	2.9	7.7	41.2	2.5	7.6	20.3		11.6	2.1	0.8	1.1	3.3
	(4.1)	(15.8)	(30.1)	(2.2)	(4.9)	(18.0)	(1.4)	(18.0)	(2.6)	(0.1)		(2.2)
1.823	13.1	23.3	34.2	0.0	14.4	6.6		7.0	0.0	0.0	2.6	1;4
	(11.0)	(31.6)	(28.4)	(1.0)	(7.4)	(13.2)	(0.5)	(6.0)	(0.4)	(0.0)		(0;6)
1.939	15.7	29.8	32.3	0.0	10.3	10.3		1.5	0.0	0.0	0.2	0:0
	(13.4)	(37.6)	(25.0)	(0.6)	(7.4)	(9.9)	(0.3)	(3.3)	(0.2)	(0.0)		(0;4)
2.247	37.1	33.5	17.2	0.0	7.3	4.8		0.0	0.0	0.0	0.1	0.0
	(33.4)	(45.4)	(12.8)	(0.1)	(5.0)	(2.8)	(0.0)	(0.4)	(0.0)	(0.0)		(0.1)
2.496	59.6	22.5	7.8	0.0	4.8	5.3		0.0	0.0	0.0	5.2[b]	0.0
	(52.6)	(39.0)	(5.3)	(0.0)	(2.3)	(0.6)	(0.0)	(0.0)	(0.0)	(0.0)		(0.0)

[a] Values calculated from $K_1 = 0.081$, $K_2 = 0.050$, assuming $\rho = 1$ and no finite cyclic molecules in the system. [b] This sample was made from commercial phosphorus pentoxide whereas the others were prepared from resublimed material.

stants necessary to describe a system for which $\rho \geq 2$, computer calculations[14] indicate that $\rho = 2$ and that the equilibrium constant involving second-order groups in unbranched chain molecules, $K = [\text{ee}][\text{mm}]/[\text{em}]^2$, is about twice as large as the constant K_1 defined earlier in this section. These values are consistent with the previously observed deviations from randomness and the resulting values[14] of $\rho = 3$–5 for the alkali metal salts of the polyphosphoric acids and $\rho = 1$ for the concentrated acids themselves and the acid salts. The triply charged *neso*, doubly charged end, singly charged middle, and uncharged branch groups in the salts should lead to a larger value of ρ than observed for the acids (which as the neat liquids are probably highly associated) and the esters examined herein.

Solubility fractionation of an equilibrated methyl polyphosphate mixture for which $R = 1.1$ gave the expected maximization of the *neso* and e†*e* resonance in the final fraction and em†*e* in the next to the last fraction, with the total amount of middle groups decreasing and the total amount of end groups increasing in the successive fractions as fractionation proceeded. The *m*m†*b* resonance maximized in the early fractions and the e†*be* and *m*b†*e*, em†*b* and *b*m†*b* in the middle fractions. In the thermal-diffusion studies, the *neso*, e†*e*, and *e*m†*e* were found at the top of the column and the *m*m†*m* at the bottom, but the separation of the large and small molecules was not as good as in the solubility fractionation. The fractions from the top of the column were noticeably more fluid than the starting mixture, whereas the fraction taken from the bottom of the column was extremely viscous. Similarly, the first fractions from the solubility fractionation were nearly rigid, difficultly soluble gels, whereas the last fraction to be precipitated was a free-flowing liquid. The intrinsic viscosity in chloroform for an over-all composition corresponding to $R = 1.2$ was found to be 2.1×10^{-2} ml of solvent/g of phosphate, a value which is twice as large as the one measured for the pure *neso* compound (1.1×10^{-2}).

The physical measurements described in the preceding paragraph are consistent with the underlying assumptions of the theoretical treatment of the data. These assumptions are that the sorting of methoxyl groups and bridging oxygen atoms on the phosphorus atoms to give the building units deviates greatly from randomness (as expressed by the difference of K_1 and K_2 from their random values of $^1/_3$) but that the arrangements of these building units into molecules are random when the perturbing effect of the nearest-neighbor unit ($\rho = 2$) is taken into account. According to this interpretation, there must be an increase in molecular weight as $R \equiv (\text{CH}_3\text{O} + \text{HO})/\text{P}$ is reduced from its maximum value of 3 to the value corresponding to the gel point, beyond which the average molecular weight is infinite.

From the appearance of the various equilibrated polyphosphate compositions from which the chloroform had been completely removed, as well as from the fact that the composition of the lowest R value which we were able to prepare had $R = 0.99$, we estimate that the gel point comes in the range of $1.0 \geq R \geq 0.9$. Using the mathematics for $\rho = 1$, the amount of cyclic molecules at the gel point is calculated[14] to be equivalent to *ca.* four ring closures per hundred P atoms. This calculation plus the abnormally low proportions of tetramethyl pyrophosphate and the absence of observed nmr peaks attributable to rings show that cyclic molecules are not important in this equilibrated system at R values greater than unity.

Ethyl Esters. The data given in Table I by Burkhardt, Klein, and Calvin[2] are consistent with a state of equilibrium between the building units. From these data, a weighted average value of K_1 = [ends][branches]/[middles]^2 = 0.022 was calculated, with a standard error[24] of 0.005. Within experimental error, this constant was found not to vary systematically with the over-all composition (R value) and is identical with the value of 0.02 previously reported[5] for this system.

Further demonstration that the data of these authors[2] refer to mixtures of molecules at or near equilibrium and do not support their postulated set of kinetically controlled reaction products was obtained on samples exhibiting the P^{31} nmr patterns shown for their materials B, E, and G, which we prepared by following their general procedures.[25] It was found that the nmr spectra obtained on these materials were essentially identical for each given over-all stoichiometry with (1) these same products after heating in sealed tubes for 3 days at 110°; (2) well-equilibrated mixtures[5] having the same over-all composition, made by treating triethyl phosphate with phosphorus pentoxide; and (3) similar equilibrated mixtures made by treating the equilibrium mixture exhibiting the tetraethyl pyrophosphate composition with phosphorus pentoxide. Furthermore, when triethyl phosphate was treated with "material B" so as to form an equilibrium mixture stoichiometrically equivalent to "material G," this gave the same nmr patterns as found for our fresh preparation of "material G." The intrinsic viscosity of the freshly prepared "material B" was the same as that found for a well-equilibrated ethyl phosphate or ethyl polyphosphate mixtures having the same over-all composition.

In the over-all process whereby ethyl ether and phosphorus pentoxide are converted to an equilibrium mixture of ethyl polyphosphates, the scrambling of ethoxyl groups with bridging oxygen atoms has a much higher driving force ($\Delta F^\circ \approx 1$ kcal) than the rearrangement of the resulting building units into the equilibrium distribution of molecules ($\Delta F^\circ <$ *ca.* 0.5 kcal), so that it is quite possible[26] that the preparations of Burkhardt, Klein, and Calvin were at equilibrium with respect to the building units (the relative amounts of which were the only information obtained from their nmr measurements) while not being completely in equilibrium with respect to the arrangement of these building units in the molecules. However, gross deviations from the equilibrium mixture of molecules are ruled out by the results obtained with our repeat preparations. Several attempts to obtain the low over-all ratio of (CH_3O + HO)/P, *i.e.*, R = 0.82, reported for "material A" failed in our laboratory where the lowest R value which could be made was 0.95. If the reported nmr data are correct, "material A" represents a molecular mixture which when completely at equilibrium should exhibit wall-to-wall macromolecules. Calculation[14] (equally applicable to both equilibrium and all nonequilibrium conditions) shows that there must be at least nine ring closures per hundred P atoms in this molecular mixture.

It is worthwhile noting "that the entire complex of measurements"[2] reported by Burkhardt, Klein, and Calvin are, within experimental error, in accord with the concept of an equilibrium or near-equilibrium mixture of molecules. Their inability to extract tetraethyl pyrophosphate from "material E" (see conclusion 4 on p 594 of ref 2) is to be expected, since it represents only 3% of the total phosphorus and the distribution coefficients for such an extraction would be expected to change only gradually when going from one member to another within a family of compounds such as the ethyl polyphosphates. The ebullioscopic molecular weights reported by these authors[2] are probably faulty, since the average molecular size in a mixture of related molecules is given by the relationship ([*neso*] + [ends] + [middles] + [branches])/([*neso*] + [ends]/2 − [branches]/2 + r), where r is the number of ring closures per building unit. This equation for the average molecular size is based solely on stoichiometric considerations and hence is independent of whether or not the molecular distribution represents equilibrium or a very different situation. It is also independent of the value of ρ. Assuming no ring closures, we see from this equation that the molecular weights of "materials B" through "G" are 1.3×10^4, 3.3×10^3, 1.7×10^3, 1.1×10^3, 805, and 635, respectively. The number of ring closures needed to account for the uniformly small molecular weights reported[2] for these materials ranges from 25 down to *ca.* 10 closures per hundred P atoms.

Although the agreement is not quantitative, the reported molecular weights represent the only data given in ref 2 which could be used to justify the assumption of highly cyclized structures such as the hypothetical set of reaction products described therein. However, in view of the evidence against a large amount of rings in the esters of polyphosphoric acids and the not-uncommon problems found in carrying out ebullioscopic measurements on reactive mixtures such as these, it seems reasonable to conclude that the reported low values for the molecular weights are due to experimental error.

"Langheld Esters" for Biochemical Studies. Rather than preparing alkyl polyphosphate mixtures for biological applications by the difficultly controllable reaction between ether and phosphorus pentoxide, it would be more desirable to make this reagent from the trialkyl orthophosphate and phosphorus pentoxide. For the sake of reproducibility, the resulting esters should be fully equilibrated or fractionated by a reproducible procedure for a well-equilibrated mixture. In either case, it is necessary to know the relative proportions of hydroxyl to alkoxyl groups and alkoxyl groups to phosphorus in order that the reagent be properly characterized. The nmr techniques employed in this paper seem to be the best available for such characterization.

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(25) Because of differences in crystallinity and water content of the phosphorus pentoxides, we were unable to make the compositions described in ref 2 without using at least a 50% longer refluxing time. A further problem in repeating the experiments is that the amount of "undissolved residue" removed by filtration was not given in ref 2.

(26) In the study of several other equilibrium-controlled systems of molecules, it has been noted that the ratios of the total amounts of *neso*, end, middle, and branch groups became constant considerably before changes in the relative proportions of the arrangements of various building units around each other (*e.g.*, e*e*, e*m*, and e*b*) leveled off. Both the entropy and enthalpy contribute to the driving force for the reactions involving change of functionality of the various building units; but further rearrangement of these building units within the various molecules is primarily driven by the entropy.