

The Preparation and Properties of Tetra-, Penta-, Hexa-, Hepta-, and Octaphosphates

E. J. Griffith and R. L. Buxton

Contribution from the Inorganic Chemicals Division, Monsanto Company, St. Louis, Missouri. Received October 21, 1966

Abstract: Gram quantities of pure polyphosphates containing from four to eight phosphorus atoms per molecule were prepared. The phosphates were hydrolyzed at pH values of 4, 7, and 11 at 30 and 60°. First-order specific rate constants were determined for the over-all degradation of each compound. The rate constants for the end-group clipping to the next lower phosphate and an orthophosphate and the rate constants for the split-out of trimetaphosphate from the chain phosphates were also determined.

The chemistry of pyro-, tri-, trimeta-, and tetrameta-phosphate has been the subject of hundreds of scientific articles during the past 100 years. The chemistry of the complex and complicated mixtures of poly- and metaphosphates contained in amorphous phosphate glasses and crystalline very long chain polymers has also been studied extensively. Despite the large volume of information gathered on the systems which have been studied, very little is known of the specific properties of the condensed phosphates containing more than four phosphorus atoms per molecule.¹⁻⁴ The knowledge of the properties of tetraphosphate is not extensive when compared with pyro- and triphosphates, but much valuable information has been gained on this anion during the past 20 years.⁵⁻¹³

Phosphates containing more than four phosphorus atoms and less than *ca.* 500 phosphorus atoms are not phase-diagram entities, and no simple method has been devised to prepare even gram quantities of the pure phosphates. The one exception is calcium hexaphosphate which can be prepared with relative ease.^{14,15} The compound is very insoluble and cannot yet be used to obtain useful quantities of soluble hexaphosphate salts, however.

The primary objective of this work is to establish a foundation for the comparison of the hydrolysis of polyphosphates as a function of their molecular size. The work is based on more than 20,000 qualitative and quantitative analyses. It is believed to be as reliable as the state of the science allows today without drastically limiting the number of compounds considered.

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Experimental Section

Preparation of the Pure Polyphosphates. Polyphosphoric acid was chosen as a source of polyphosphate anions. The acid was prepared by heating 85% orthophosphoric acid in a gold dish at 400° for 12 hr to yield a polyphosphoric acid with an average chain length near five. The average chain lengths were determined by end-group titrations.¹⁶

A 200-g sample of the phosphoric acid was dissolved in 2 l. of water, and the phosphate was extracted from the aqueous solution into 3400 ml of a 25% solution of *t*-caprylamine dissolved in xylene. The tertiary amine, Alamine 336S, was obtained from the General Mills Co. The two immiscible solvents were shaken together for 1 hr and then allowed to separate. The aqueous phase was discarded. The desired phosphates were stripped from the amine solution with 500-ml portions of 0.1 *N* aqueous ammonium hydroxide; 10 to 12 fractions removed the desired phosphates. The fractions were analyzed by paper chromatography. At this stage of the extraction each fraction contained three major components. About 50 g of polyphosphoric acid was recovered while 150 g was discarded as ortho- and longer chain phosphates, unwanted for this work.

The solutions of phosphates were stored in a refrigerator at 2° until ready to be reextracted. Before the phosphates could be reextracted, it was necessary to convert the ammonium salts back to the corresponding acids. Samples containing similar quantities of the same phosphates were combined and passed through a cation-exchange column containing 4 lb of Dowex 50W-X4 resin in the hydrogen form. The acidic solutions were then mixed with a fresh batch of 33% amine solution at the ratio of 160 g of amine solution to 500 ml of aqueous phosphate solution. The quantities of course depended on the number of phosphate solutions which were combined. The aqueous phase was again discarded after 1 hr of mixing. The phosphate was stripped from the amine solution with 100-ml portions of 0.1 *N* aqueous NH₃. In a typical extraction 20 fractions were obtained and the amine was completely stripped of phosphate. At this stage each fraction contained two major constituents. The extraction procedure was repeated with combined fractions containing similar phosphates. The third and usually final fractionation of the phosphate solutions was made in a similar way except the final extraction was made with 0.1 *N* NH₄NO₃ and the aqueous extract volume was reduced to 10 ml. The fractions contained one major fraction, a smaller quantity of a second phosphate, and traces of longer chain phosphates.

When only two major constituents must be separated, an anion-exchange chromatographic column may be heavily loaded and still give satisfactory separation of the two components. A column 1 cm in diameter with 27-cm bed depth was filled with Dowex 1-X8 resin in the chloride form.¹⁷ The column was treated with 400 ml of 0.30 *N* KCl solution adjusted to pH 5.0 with HCl. Then the column was loaded with 0.5 g of ammonium polyphosphates contained in 50 ml of the solvent extracted from the amine solution. The concentration of the eluting agent used depended upon the phosphates to be separated. If the solution contained tetra- and penta- or penta- and hexaphosphate, the column was eluted with

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0.30 N KCl adjusted to pH 5. If hexa- and heptaphosphates were to be separated, the concentration of KCl was adjusted to 0.35 N; if hepta- and octaphosphates were to be separated, the KCl concentration was increased to 0.40 N. When the longer chain phosphates (hexa-, hepta-, or octa-) were to be separated, the column was first treated with 400 ml of 0.3 N KCl to remove any shorter chain phosphates, and then the concentration was increased to the separation level.

The flow rate of the column was adjusted to 1 ml/min and 20-ml fractions were collected with an automatic fraction collector. When the first 90 fractions had been collected, the phosphate was located by spotting a drop of each fraction on a filter paper and then developing the filter paper as though it were a paper chromatogram which had not been subjected to solvent separation.

After the phosphates were located, the midfractions were chromatographed to ensure the purity of the fractions. Like fractions were then combined, and the water was removed from the solution with a thin-film vacuum evaporator connected to a water aspirator. The flask of the evaporator was maintained at approximately 40°. The evaporation was discontinued when the first crystals of KCl formed in the flask.

Dialysis was used to separate the KCl from the phosphate solutions. The saturated solution of KCl was put into a dialysis membrane 0.75×10 in., and then the membrane was suspended in 4 l. of distilled water. The removal of the KCl was rapid and complete. Within 3 hr, with three changes of the outside water, the chloride content inside the dialysis tube was barely detectable. This method was found to be superior to the various precipitation techniques based on benzidine,^{1,2} because the phosphate suffered no detectable degradation in this process and no foreign ions were added to the phosphate solution. Once the phosphates were concentrated and freed from the KCl, they were stored in a refrigerator at 2° until needed.

The samples of polyphosphates can be preserved much easier in solution than they can be as the amorphous solids which form when either a sodium or potassium salt is precipitated. In every case attempted the sodium or potassium salts reorganized within a week or two if the salts were stored as the solids. If the crystalline solids of either the guanidinium or acridinium phosphates were prepared by the methods Quimby⁶ employed to crystallize the tetraphosphate, they were stable if care was taken to make certain that the salts were dry.

Analysis of the Phosphates. It has been well established that the higher polyphosphates do truly exist and can be separated as pure substances by chromatographic techniques.¹⁶ It is not considered necessary to attempt to reestablish this fact. The analytical problems which were confronted were quantitative rather than qualitative.

Analytical methods¹⁹⁻³⁰ were needed which were reasonably rapid and at the same time reliable if the large number of analyses which were needed in a hydrolysis study were to be handled within the required time limits. After several hundred tests with columns, spinning papers, and thin-layer chromatograms, the decision was made to employ ascending paper chromatograms on a 10×11.5 in. sheet of Schleicher and Schuell 589 Orange Ribbon paper. The filter paper has the advantage of being easily referenced and graphic. Thin layer chromatograms are also graphic, but quantitative analyses of the phosphates were more difficult.

The acidic chromatographic solvent 92-D recommended by Kolhoff³¹ was used in this work but it was modified in one respect. Better separations were obtained with the longer phosphates if solid ammonium carbonate was substituted for the aqueous ammonia Kolhoff suggested. For solvents designed to separate hepta-, octa-

and nonaphosphates, 1.4 g of ammonium carbonate was used per 1 l. of solvent solution, while the solvents used to separate the shorter chain phosphates (tetra-, penta-, and hexa-) required 2.5 g of $(\text{NH}_4)_2\text{CO}_3$ /l. The basic solvent used in the two-dimensional chromatograms was that recommended by Karl-Kruppa.²⁶ The chromatographic chambers were standard 6×12 in. cylinders and contained 100 ml of solvent. The chromatographic chambers were thermostated at 17° in a modified commercial deep freezer equipped with a forced air fan. The temperature-sensing element in the refrigerator was replaced with a thermistor and an electronic relay to improve the temperature control of the freezer.

The phosphate solution to be tested (10–20 μ l) was placed 1.25 in. from the bottom of the filter paper as a band 0.75 in. long and $\frac{1}{8}$ in. wide. Each chromatogram held four spots or two duplicated samples. Attempts were made to store chromatograms at 2° while awaiting a vacant chromatographic chamber, but this technique caused errors if the chromatograms were stored for more than 24 hr because the phosphates degraded on the paper.

Chromatographic papers were allowed to remain in the chromatographic chamber for about 12 hr or until the solvents reached the top of the chromatograms. The chromatograms were then removed from the chambers, air-dried, and then dried for 5 min at 100° in a forced air oven.

The chromatographic sprays used to develop the chromatograms were those recommended by Hanes and Isherwood.³² At this point the treatment of the chromatogram depended upon its ultimate use. Parts of the chromatograms were quantitatively analyzed for the per cent of the phosphorus in the phosphate in question compared to the remainder of the phosphate on the chromatograms. These chromatograms were analyzed by the method recommended by Smith,^{26,33} using a Spectronic 20 spectrometer manufactured by the Bausch and Lomb Co. The spectrometer was fitted with a digital readout supplied by the same manufacturer.

Other chromatograms were analyzed for the distribution of phosphate species to give a total analysis of the phosphates. These chromatograms were analyzed by the method recommended by Bernhart and Chess,²⁷ and an Analytrol-RB spectrometer manufactured by the Beckman Instrument Co. was employed to perform the analyses. The latter method of analysis was not as accurate as the extraction technique, but a quantitative analysis was obtained for all species present. Hydrolyzing samples of octaphosphate contain as many as nine species, and the time required to obtain an analysis of each phosphate by the extraction technique was prohibitive. The two methods agreed within about 2% per species analyzed except for an occasional analysis when the errors, which we attributed to the authors, resulted in complete disagreement between the two methods. The data were discarded when the errors greater than about 2% per phase were committed.

The Rates of Hydrolysis of Polyphosphates. Nearly 100 papers have been published on the rates of hydrolysis of condensed phosphates yet only three works have been reported for the hydrolysis of individual polyphosphates longer than tetraphosphates.^{1,3,4} Even the hydrolysis of tetraphosphate has received but little attention,^{3,5,6} while only two works have been published on the hydrolysis of higher ring metaphosphates.^{34,35} Pyrophosphate has been studied in great detail.³⁶⁻⁷¹ The complex glasses, very long chain

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phosphate, and ultraphosphate have also received much attention.^{36-3640, 42, 49, 71-107} Work on triphosphate^{46, 47, 60, 53-55, 58, 59, 106-118} and smaller rings^{5-7, 45, 46, 114-123} is limited.

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In the work presented here the rates of hydrolysis were determined for tetra- through octaphosphates at pH values of 4.0, 7.0, and 11.0 at 30 and 60°. The concentrations of the polyphosphate solutions were adjusted to allow for a convenient analysis by paper chromatography since there was no obvious reason for adjusting the concentrations to any other values. The concentration of phosphate was adjusted as near to 50 µg of phosphorus per 10 µl of solution as was convenient; however, no differences in the data obtained could be attributed to changes in concentration of the phosphate even if the concentration was increased or decreased by as much as 200%.

Before the phosphates were hydrolyzed, they were converted from the potassium salts to either the sodium or tetramethylammonium salts. The conversion to the sodium salt was accomplished by passing the phosphate over a large excess of Dowex 50 resin which was converted to the sodium form with 0.2 N NaOH and then washed with distilled water until the wash water was no longer basic. The column used was simply a 100-ml buret which had been cut to 20 ml and contained 10 ml of dry resin. A similar technique was used for the tetramethylammonium conversion except the phosphate was first converted to the acid form with the cation-exchange resin, and then the phosphate was neutralized with 3% tetramethylammonium hydroxide. This was done to keep the excess tetramethylammonium ion concentration as low as possible.

Samples of 2 ml were found to be convenient for the hydrolysis studies. The samples were adjusted to the required pH with the aid of a Beckman Model G.S., battery-powered, pH meter. The usual precautions were observed and the pH was adjusted to within 0.01 unit of the required value. No sodium ion corrections were applied. After the pH was adjusted to the proper value the sample was transferred to a 2-dram glass vial, which was then placed in a thermostated water bath. The baths were obtained from the E. H. Sargent Co., but the thermoregulator was replaced by a more sensitive unit obtained from the H and B Instrument Co. The baths were capable of maintaining 30.00 ± 0.01 or 60.00 ± 0.01° for as long as 2 years without readjustment. The pH was maintained by periodic adjustments back to the original value when required.

The time the samples were maintained in the baths and the time at which samples were collected was monitored by two master interval timers. At the start of each hydrolysis experiment the local time was recorded, as well as the time on the master timers. The time was recorded to 0.1 hr in all cases except the very fast reactions where the time was measured in minutes.

A zero-time analysis was made on each sample before it was placed in a thermostat. If any trace of a higher polyphosphate than the one under consideration was found in a sample to be hydrolyzed, the sample was repurified. The shorter chain lengths caused no difficulties in the determination of rate constants. The presence of phosphates with chain lengths greater than the phosphate under consideration could not be accepted because there was no simple way to correct the errors caused by their degradation before their rate constants were known. At prechosen intervals, samples were withdrawn from the vials and analyzed. On the average eight data points were collected for each rate constant. Two types of chromatograms were prepared and each chromatogram was duplicated and placed in reserve in case an analytical result was questionable. The reserves were not maintained for more than 24 hr at 2° or they were considered to be useless. One-dimensional chromatograms were used to establish the per cent phosphorus present as the polyphosphate under study vs. the remainder of the phosphate contained in the sample being studied.

The duplicate half of the same chromatogram was analyzed by the Analytrol to give the percentage phosphorus present as the

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Table I. The Rate Constants for the Hydrolysis of Polyphosphates

Phosphate	pH	Specific rate constants, total reaction, k_t , min ⁻¹		ΔE_{\pm} , total reaction, kcal	Specific rate constants, trimeta split-out, k_m , min ⁻¹		ΔE_{\pm} , trimeta split-out, kcal	Specific rate constants, end-group clipping, k_e , min ⁻¹		ΔE_{\pm} , end-group clipping, kcal
		30°	60°		30°	60°		30°	60°	
Sodium salts										
Tetra-	4	7.5×10^{-6}	4.6×10^{-4}	27.5				7.5×10^{-6}	4.6×10^{-6}	27.5
	7	4.6×10^{-6}	2.0×10^{-4}	25.2				4.6×10^{-6}	2.0×10^{-6}	25.2
	11	2.0×10^{-6}	8.8×10^{-5}	25.3				2.0×10^{-6}	8.8×10^{-5}	25.3
Penta-	4	2.4×10^{-5}	6.3×10^{-4}	21.8	8.2×10^{-6}	9.8×10^{-5}	16.6	1.6×10^{-5}	5.3×10^{-4}	23.4
	7	1.5×10^{-5}	4.8×10^{-4}	23.2	4.4×10^{-6}	1.7×10^{-4}	24.6	1.4×10^{-5}	3.0×10^{-4}	20.5
	11	4.8×10^{-6}	2.5×10^{-4}	26.4	1.8×10^{-6}	8.4×10^{-5}	25.7	3.0×10^{-6}	1.7×10^{-4}	11.6
Hexa-	4	(3.4×10^{-5})	7.1×10^{-4}	20.3	9.7×10^{-6}	1.1×10^{-4}	16.4	2.4×10^{-5}	6.0×10^{-4}	21.5
	7	3.8×10^{-5}	7.6×10^{-4}	20.0	6.5×10^{-6}	2.5×10^{-4}	24.4	3.4×10^{-5}	4.9×10^{-4}	17.8
	11	8.0×10^{-6}	4.8×10^{-4}	27.4	(6.6×10^{-6})	2.9×10^{-4}	25.3	3.0×10^{-5}	2.0×10^{-4}	12.3
Hepta-	4	4.3×10^{-5}	7.9×10^{-4}	19.5	1.2×10^{-5}	1.3×10^{-4}	16.2	3.2×10^{-5}	6.5×10^{-4}	20.1
	7	7.5×10^{-5}	1.0×10^{-3}	17.3	9.2×10^{-6}	3.5×10^{-4}	24.3	6.6×10^{-5}	6.6×10^{-4}	15.4
	11	1.5×10^{-5}	7.7×10^{-4}	26.3	1.2×10^{-5}	5.8×10^{-4}	25.7	3.0×10^{-5}	1.9×10^{-4}	12.3
Octa-	4		8.5×10^{-4}						6.9×10^{-4}	
	7		1.4×10^{-3}							
	11		1.1×10^{-3}						1.2×10^{-4}	
Tetramethylammonium salts										
Penta-	4	1.4×10^{-5}	4.2×10^{-4}	22.7						
	7	6.9×10^{-6}	9.8×10^{-5}	18.0						
	11	8.6×10^{-7}	2.0×10^{-5}	21.0						
Hexa-	4	1.4×10^{-5}								
	7	9.5×10^{-6}	1.1×10^{-4}	16.3						
	11	4.2×10^{-6}								
Hepta-	7		7.5×10^{-4}							
	11		6.6×10^{-5}							

various degradation products if it was not needed as a duplicate for the single species analysis. A two-dimensional chromatogram was also set up to determine the percentage trimetaphosphate which formed from the longer chain phosphates. The two-dimensional chromatograms were divided into three parts: the phosphate under study, the trimetaphosphate, and the short-chain phosphates which were degradation products. This selection of samples gave an independent check in the values obtained from the one-dimensional chromatograms.

The analyses of samples are so involved and the possible sources of error are so numerous that no attempt will be made to discuss them. The reader is referred to the literature cited from which the analytical techniques were adopted. An estimate of the errors committed in determining the rate constants was made at the 95% confidence limits. These estimates reflect more the precision of the work than its accuracy. Rather than attempt to assign a more or less meaningless estimate of error to each rate constant, it can be safely stated that the error is less than $\pm 10\%$. Much more effort was expended by the authors to furnish a self-consistent group of data than to attempt to supply highly reliable data with tools that are inherently difficult to control. For this reason the rate constants developed in this work will be reported to only two significant figures. The reader can gain much greater feeling for the errors in the work by comparing the various plots of the rate constants *vs.* pH or chain length.

No major difficulties were encountered in the analyses of the sodium polyphosphates but the tetramethylammonium polyphosphates were particularly difficult to analyze when the longer phosphates were chromatographed. The major difficulty arises from the fact that the tetramethylammonium hexa-, hepta-, and octaphosphates streak badly in the chromatographic solvents which separate them within 12 to 16 hr. A second difficulty results from the tetramethylammonium ions which impart a blue color to a chromatogram when developed with the ammonium molybdate sprays used in this work. No method was devised to overcome these two sources of error, and the tetramethylammonium phosphate work was limited. The data obtained with the tetramethylammonium phosphates are reported but the errors are twice as large as those for the sodium polyphosphates.

The need for the tetramethylammonium data *vs.* sodium ion data has been discussed in a previous work.⁵⁹ It will be noted that there are several notable differences in the sodium phosphate data and the tetramethylammonium phosphate data.

Table I contains the first-order specific rate constants, for the over-all disappearance of a phosphate species, k_t ; the first-order rate

constant for the disappearance of a species by the clipping of an orthophosphate from the end of a chain, k_e ; and the first-order rate constant for the disappearance of a species by the splitting out of a trimetaphosphate from the linear polyphosphates, k_m . Both k_t and k_m were obtained from the analytical data. The end-group clipping rate constants were calculated from

$$k_t = k_e + k_m \quad (1)$$

$$-\frac{dC}{dt} = k_t C = (k_e + k_m)C \quad (2)$$

where C is the concentration of the species in question. In the calculations used in this work, C was expressed as the percentage of the phosphorus in the phosphate under consideration with respect to the total phosphorus in the sample solution.

Discussion of Results

To compare the various phosphates the authors plotted the data on two types of graphs. The first plot was $\log k$ *vs.* pH for each phosphate species at each temperature. The second plot was $\log k$ *vs.* the number of phosphorus atoms contained in the phosphate at a fixed temperature and pH. The conclusions drawn from these data are based upon these graphs, but unfortunately they are too numerous to reproduce. It is recommended that the reader seriously interested in the results plot the data himself.

The rates of degradation of sodium hexa-, hepta-, and octaphosphates by all routes simultaneously are greater at pH 7 than at pH 4 or 11. It was not unexpected that the over-all degradation at pH 11 was less than it was at pH 7, but it was unexpected that the rate at pH 7 was greater than it was at pH 4 as seen in Figure 1.

In every case tested the degradation of the phosphates followed the first-order rate law with respect to the reacting phosphate. No extensive effort was made to prove that the first-order law was observed, but the

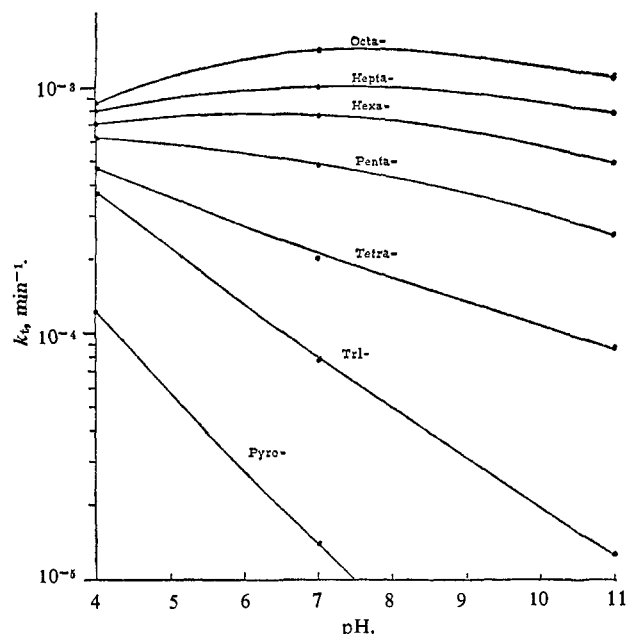


Figure 1. Specific rate constants for sodium polyphosphates as a function of pH at 60°: pyro- and tri- values from ref 59.

data contained no results which caused doubt that the first-order law was obeyed with the longer chain phosphates as it is with the shorter chain phosphates. The rate constants of Table I were derived from straight lines obtained when $\log C$ was graphed as a function of time. For test cases the straight-line relationship was maintained for three or more half-life periods. All of the rate constants, except the very small constants, are derived from data gathered during at least two half-life periods.

The stabilities of the polyphosphates decrease as the chain lengths increase, but the rate constants seem to be approaching some limiting value as chain length increases. The differences between the rate constants for tri- and tetraphosphates are much larger than the differences between hepta- and octaphosphates under the same experimental conditions as shown in Figure 2.

It is known that a chain phosphate may degrade by any one of at least three routes.⁹⁵ One mode of degradation results from the clipping of the end group of the chain to form orthophosphate and a phosphate chain one phosphorus atom shorter. A second mode is the degradation by the breaking of the chain somewhere in the middle of the chain to yield two chains. A third method of degradation results from the splitting out of a trimetaphosphate ring to leave a chain phosphate three phosphorus atoms shorter. Although the first and third methods of degradation were clearly evident, there were no clear indications when the total families were considered that the chain cleaved in the middle.

Rate constants were developed for the loss of the polyphosphates by splitting out trimetaphosphate. As shown in the midcolumns of Table I, the rates of loss of a phosphate by this route can be as great or greater than the loss by the hydrolysis of the ends of the chains.

The shortest chain phosphate which can degrade to trimetaphosphate is tetraphosphate. Only trimeta- and orthophosphate would remain. In the work with

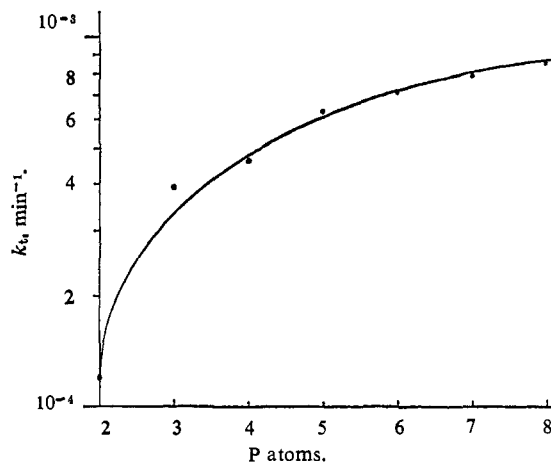
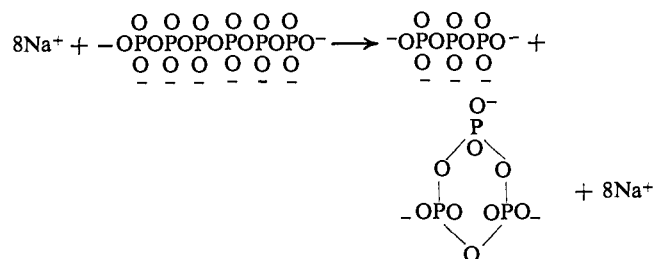


Figure 2. Specific rate constants for the total reaction of sodium polyphosphates as a function of molecular size at pH 4.0 and 60°: pyro- and tri- values from ref 59.

tetraphosphate, there was a small but detectable buildup of trimetaphosphate in the solutions. The concentrations of the trimetaphosphate was too small to yield reliable rate data. When the chain length of the phosphate was five phosphorus atoms or more, the buildup of trimetaphosphate was easily measured and rate constants were developed.

In the past there has been considerable speculation as to the mechanism of the "hydrolysis" of a chain phosphate to trimetaphosphate. It is the contention of the authors that this degradation is not hydrolysis at all but a reorganization of the phosphate as occurs in anhydrous systems when phosphates are heated. It can be seen that water need not be considered as a reactant. For example, the degradation of sodium hexaphosphate to trimetaphosphate and triphosphate may be represented as



and water is neither a reactant nor a product. In fact, a 1:1 mixture of trimetaphosphate and triphosphate is exactly the mixture one would expect from phase-diagram considerations¹²⁴ if an anhydrous sodium phosphate with a hexaphosphate composition were heated to speed the approach to equilibrium conditions.

The relationships among the rate constants for the tetramethylammonium phosphates were of a different form when compared to the corresponding sodium systems when a graph of $\log k_t$ vs. pH was constructed. This led to the conclusion that perhaps trimetaphosphate was not being formed in the tetramethylammonium systems as it was in the sodium systems. Heptaphosphate was converted to the tetramethylammonium salt and degraded at pH 11 and 60°. Small quantities of trimetaphosphate buildup could be

(124) E. P. Partridge, V. Hicks, and G. W. Smith, *J. Am. Chem. Soc.*, **63**, 454 (1941).

detected during the study, but the concentration of trimetaphosphate was never large enough to obtain a quantitative analysis of this species. It is doubtful that tetramethylammonium trimetaphosphate would result even if anhydrous tetramethylammonium heptaphosphate were heated to temperatures just high enough to cause it to reorganize. It can only be concluded that the sodium ions in the sodium polyphosphate system contributed to the formation of the trimetaphosphate that forms as a degradation product of the reaction.

The activation energies for the degradation of a polyphosphate to trimetaphosphate are independent of the chain length of the phosphates from which the trimetaphosphate forms. Conversely, the activation energies are very dependent upon the pH of the solution. The activation energies increase as the pH of the solutions increases (see Table I).

Once the rate constant k_t (for the total reaction by all routes) has been obtained and the rate constant for the split-out of trimetaphosphate, k_m , is known, the rate constant for end-group clipping, k_e , can be calculated. The rate constant for end-group clipping, k_e , is the difference between the rate constant for all reactions, k_t , and the rate constant k_m .

The rate data for the end-group clipping at pH values of 4 and 7 are in accordance with similar data developed in prior works with pyro-, tri-, and tetraphosphates.^{6,59} At pH 4 there are small differences between the values of the rate constants for the total reactions and the rate constants for end-group clippings since the phosphate degrades mostly by end-group clipping. Significantly different data were obtained for the end-group clipping at pH 11. At pH 11 the rates of degradation by end-group clipping are independent of the chain length above five phosphorus atoms. The values of k_e for hexa-, hepta-, and octaphosphate are all the same at pH 11 and 60°. The same is true for penta-, hexa-, hepta-, and probably octaphosphate at pH 11 and 30°.

The activation energies for end-group clipping decrease with increasing pH for each phosphate. This behavior was noted for sodium triphosphate⁵⁹ in a previous report. The activation energies for sodium triphosphate at pH values of 4, 7, and 10 are 27.6, 28.0, and 22.8 kcal, respectively.

The data for the tetramethylammonium phosphate systems are not sufficiently complete to draw many significant conclusions. The activation energies for the total reaction of pentaphosphate are similar in value to the sodium system at pH 4 and 7, but the large increase in activation energy at pH 11 was not found in the tetramethylammonium system. This is attributed to the observation that trimetaphosphate split-out does not occur to any appreciable extent in the tetramethylammonium system. In the sodium system as the pH increased, the temperature sensitivity of the trimetaphosphate split-out became greater while the temperature influence of the end-group clipping decreased sharply.

Numerous studies have shown pyrophosphate is more stable in aqueous solutions than triphosphate. It has also been demonstrated that triphosphate is more stable than tetraphosphate. The hydrolyses of shorter chain phosphates are catalyzed by hydrogen ions but not by hydroxyl ions, but the hydrolysis of the lower

membered ring phosphates, trimeta- and tetrametaphosphate, is catalyzed by both hydrogen and hydroxyl ions. No satisfactory explanations of these facts are known. This has probably resulted from the fact that the longer chain phosphates have been so difficult to prepare that no one has had the opportunity to compare the phosphates as a family at a variety of pH and temperature values.

The electron density about a POP linkage in a phosphate is very dependent upon the degree of polymerization of the phosphate in which it occurs. Kinetically, the most stable chain phosphate in aqueous solutions is pyrophosphate. The POP linkage in pyrophosphate is also the most electron-rich phosphate linkage possible. If one neglects the inner shells and considers the octet about the oxygens only, there are 56 electrons associated with the linkage. On the other hand, the most unstable of all phosphates in aqueous solution is phosphorus pentoxide, P_4O_{10} . This molecule has the minimum number of electrons per POP linkage it is possible for a phosphate to contain, namely 13.3 per POP linkage, neglecting the inner shells. These facts would surely lead one to believe there is a relationship between the electron density of a POP linkage and its stability in aqueous solutions. Table II shows the average number of electrons per POP linkage for the phosphate family.

Table II. The Electron Density of POP Linkages in Condensed Phosphates

Compound	Electrons in valence shells per POP linkage
Pyrophosphate	56
Triphosphate	40
Tetraphosphate	34.7
Pentaphosphate	32
Hexaphosphate	30.4
Heptaphosphate	29.3
Octaphosphate	28.6
Trimeta-, tetra-, penta-, metaphosphate, etc., or long- chain phos- phate	24.0
Phosphorus pentoxide	13.3

Data are available for the first time to test the concepts presented above; it is desirable to ask under what conditions the concept should be tested. Reflecting upon the behavior of the longer chain phosphates makes it obvious that only the pH 4 data are of use, because the longer chain phosphates degrade by two routes at pH values of 7 and 11. At pH 4 the predominant reaction is end-group clipping. Figure 3 is a graph of the $\log k_e$ at pH 4 and 60° vs. the average number of electrons per POP linkage. The values for pyro- and triphosphates were taken from the work of Van Wazer, Griffith, and McCullough.⁵⁹ The 30° data treated in the same manner also yield a straight line but of greater slope.

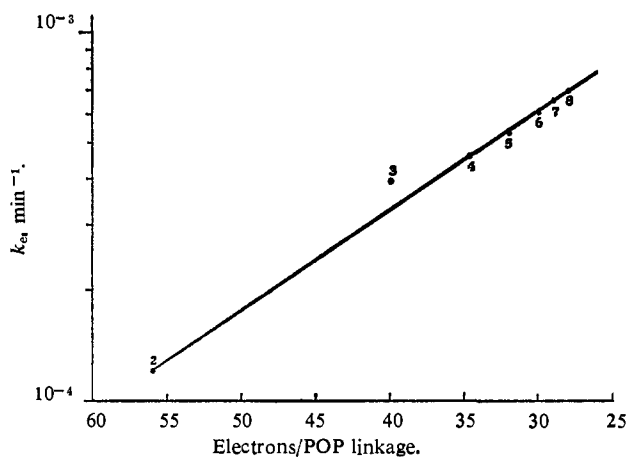


Figure 3. Specific rate constants for end-group clipping of sodium polyphosphates as a function of the average number of electrons per POP linkage: pyro- and tri- values from ref 59.

The number of electrons per POP linkage in a polyphosphate approaches the number of electrons per POP linkage in a ring metaphosphate as a limit, *i.e.*, 24.0 as the chain length of the polyphosphate approaches infinity. It is therefore possible to place an upper limit on the rate of hydrolysis of a long-chain phosphate as the phosphate degrades by end-group clipping in acidic media.

It is not surprising that pyrophosphate is the most stable of all phosphates in basic media. Moreover, since the ring metaphosphates have an intermediate number of electrons per POP linkage, these substances suffer both nucleophilic and electrophilic attacks.

The electron density per POP linkage is not the complete story on phosphate hydrolysis, however. The ring

metaphosphate's POP linkages are all isoelectronic, no matter how large or small the ring may happen to be. As previously shown by the authors,³⁴ the rate of degradation of a ring phosphate decreases as the size of the ring increases. The true ring hexametaphosphate is the most stable phosphate ever studied near neutral pH values. Unmistakably there are entropy considerations as well as electron-density considerations. The larger rings are resistant to hydrolysis because they are more flexible than the smaller rings and can distribute and dissipate the energy of collision as is evident from the very low activation energies for the hydrolysis of the large-ring phosphates.

Throughout the discussion of this work attention has been focused upon the rate of disappearance of a single species of phosphate without regard to the over-all degradation products. In a following article the phosphates will be treated as a family. Not only will the single species be considered, but also the relative concentration of the various degradation products which occur. Also a method was developed which allows one to predict the concentration of various species as a function of time based upon the simultaneous consideration of the rate constants presented in this work.

The data of this work were not treated as individual protonated species as has been done on several occasions with pyrophosphates.^{56,62,125} The treatment of protonated species is more mathematical than experimental and can easily be derived from these rate data and published *pK* values of the condensed phosphates¹²⁶ by modern computer techniques.

(125) J. Muus, *Z. Physik. Chem.*, **159A**, 268 (1932).

(126) R. R. Irani and C. F. Callis, *J. Phys. Chem.*, **65**, 934 (1961).