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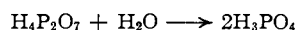
A Kinetic Study of the Hydrolysis of Pyrophosphates¹

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Most studies of the hydrolysis of $H_4P_2O_7$ (or of one of its salts) have been concerned with the rate of disappearance of pyrophosphate from a medium in which the hydrogen-ion concentration, and consequently also the reacting species, were changing. We have investigated the hydrolysis over a wide range of hydrogen-ion concentration and, by the use of P^{32} as an analytical tool, have kept the phosphate concentration so low that only minor changes of hydrogen-ion concentration occurred even in dilute solutions of strong acids. Adsorption of pyrophosphate on the walls of the vessel prevented the use of such low concentrations of pyrophosphate as to be altogether negligible in comparison to the concentration of acid catalyst. Velocity coefficients for the reactions of $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$ with water and with the hydrogen ion have been estimated at 50, 60 and 70° for an ionic strength of 0.15 (mostly sodium chloride), and in addition that for the reaction of $HP_2O_7^{3-}$ with water has been estimated at 70°. In carboxylate buffers the rate of hydrolysis of $H_2P_2O_7^{2-}$ decreases with increasing buffer concentration at a given buffer ratio and ionic strength; this phenomenon, which was not observed in *p*-bromoaniline buffers, may be due to complex formation between $H_2P_2O_7^{2-}$ and the carboxylic acid. In the separation of pyro- from orthophosphate, the precipitation of zinc pyrophosphate was found superior to that of cadmium pyrophosphate, because with the former, coprecipitation was smaller, and was more reproducible under the (constant) conditions employed.

Previous work on the hydrolysis of pyrophosphates² has been done chiefly for the purpose of determining the conditions for stability, rather than for studying the kinetics. Pyrophosphates are quite stable in alkaline solution. The hydrolysis is catalyzed by strong acids, and a kinetic study of the hydrolysis of $H_4P_2O_7$ alone (or one of its salts) is complicated by the change in hydrogen-ion concentration with the progress of the reaction



owing to the fact that $H_4P_2O_7$ is a stronger acid than H_3PO_4 .³ The more reliable of the earlier results were therefore obtained in solutions where the concentration of catalyzing acid was high relative to the initial concentration of pyrophosphate.

Of these, the most extensive are the results of Muus,^{3d} who carried out two series of experiments; in one, the solutions were $8.07 \times 10^{-4} M$ in $Na_4P_2O_7$, 0.034 to 0.124 *M* in HCl and 1 *M* in KCl, while in the other there was no KCl. Measurements were made at 20 and 40°, the solutions being analyzed colorimetrically for orthophosphate. The hydrogen-ion concentration was computed from values of the first three dissociation constants of $H_4P_2O_7$, which Muus determined electrometrically in 1 *M* KCl solution at 20°. Muus found the reaction to be of the first order in pyrophosphate

$$-d[P_2O_7]/dt = k[P_2O_7] \quad (1)$$

(where $[P_2O_7]$ represents the stoichiometric concentration) with k constant throughout an experiment. Muus found $k/[H^+]$ (where $[H^+]$ represents the concentration of the solvated proton) to be constant for the first series of experiments, and nearly constant for the second, and to be smaller for the first series (with KCl) than for the second. She pointed out that if a water reaction and a

hydrogen-ion-catalyzed reaction exist for each species, one would have

$$-d[P_2O_7]/dt = k_1'[H_4P_2O_7] + k_2'[H_3P_2O_7^-] + \dots + k_1''[H^+][H_4P_2O_7] + k_2''[H^+][H_3P_2O_7^-] + \dots \quad (2a)$$

or since in a constant medium

$$K_1 = [H^+][H_3P_2O_7^-]/[H_4P_2O_7], \text{ etc.,} \\ -d[P_2O_7]/dt = [H^+]\{k_1[H_4P_2O_7] + k_2[H_3P_2O_7^-] + k_3[H_2P_2O_7^{2-}] + \dots\} \quad (2b)$$

Since the hydrolysis is so slow in alkaline solution, she considered that the reactions of $HP_2O_7^{3-}$ and $P_2O_7^{4-}$ could be neglected. Since the ratio $k/[H^+]$ was found constant, and since the initial concentration of $H_3P_2O_7^-$ in her solutions was more nearly constant than that of $H_4P_2O_7$ or $H_2P_2O_7^{2-}$, Muus concluded, as Abbott had done previously, that the kinetic equation was probably

$$-d[P_2O_7]/dt = k'[H^+][H_3P_2O_7^-] \quad (3)$$

It appeared to us desirable to examine the hydrolysis over a wider range of hydrogen-ion concentration to learn, if possible, more about the relative reactivities of the various species. We planned to use radioactive phosphorus in the kinetic study in order to keep $[P_2O_7]$ very low and yet not sacrifice analytical accuracy. Although the theoretical limit of concentration using readily available P^{32} is *ca.* $10^{-8} M$, adsorption of the phosphates on the walls of the container forced us to employ initial values of $[P_2O_7]$ as high as $10^{-4} M$ in the experiments at low hydrogen-ion concentration. Even so, however, it proved possible to demonstrate the reactions of four individual species, $H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$ and $HP_2O_7^{3-}$, and to evaluate velocity coefficients for several of the reactions at 50, 60 and 70°.

Experimental Part

Counting Apparatus.—The radioactivity was measured with instruments manufactured by the Nuclear Instrument and Chemical Corporation; the scaling unit, with high-voltage supply, was their Model 61, and the counting tube their Model D-11 or D-12. The radioactive samples were counted, except in a few cases, to a 0.9 error of 1%, or more than 27,000 counts.

Thermostats.—The oil-filled thermostats regulated to $\pm 0.01^\circ$. The Beckmann thermometers were calibrated, at intervals, against a platinum resistance thermometer certified by the National Bureau of Standards. Since the kinetic measurements were carried out over a period of three years, during which time the settings of the regulators

(1) Abstracted from the dissertation submitted by David Owen Campbell to the Faculty of the Graduate School of Illinois Institute of Technology in January, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For a review see (a) R. Watzel, *Die Chemie*, **55**, 356 (1942); (b) R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947); (c) B. Topley, *Quart. Rev.*, **3**, 345 (1949).

(3) (a) G. A. Abbott, *THIS JOURNAL*, **31**, 763 (1909); (b) L. Pessel, *Monatsh.*, **43**, 601 (1922); (c) S. J. Kiehl and W. C. Hansen, *THIS JOURNAL*, **48**, 2808 (1926); (d) J. Muus, *Z. physik. Chem.*, **159A**, 268 (1932); (e) L. M. Postnikov, *Vestnik Moskov. Univ.*, **5**, No. 5, 63 (1950); (f) S. L. Friess, *THIS JOURNAL*, **74**, 4027 (1952).

changed slightly, the rate constant has been corrected, when necessary, to the selected temperature: 39.85, 49.83, 59.87 or 69.40°.

Materials.—All reagents, except the radioactive phosphorus, and the *p*-bromoaniline, were of C.P. or Analytical Reagent grade. Once-distilled water was used in preparing the solutions, since it gave the same results in the kinetic experiments as redistilled.

p-Bromoaniline from Eastman Kodak Co. was subjected to several recrystallizations in the form of the base and in the form of its hydrochloride.

The radioactive phosphorus (P^{32} , S-3) was procured as an acid solution of orthophosphate from the Oak Ridge National Laboratory. A level of radioactivity convenient for measurement was obtained by dilution of the radiophosphate to ca. 10 liters per millicurie.

Preparation of Radioactive Pyrophosphate.—The method first tried was the dehydration of NaH_2PO_4 ,⁴ radiophosphate plus NaH_2PO_4 carrier being heated at 255°. The yields of pyrophosphate were low, however, except when relatively large amounts of carrier were used. The method finally adopted was the dehydration of the disodium salt,⁵ our procedure for which follows.

Two or three mc. of the radiophosphate (usually less than 1 ml.) was transferred to a small platinum crucible, and neutralized to the phenolphthalein end-point with dilute sodium hydroxide. The carrier, 27 mg. of $Na_2HPO_4 \cdot 10H_2O$, was then added, and when it had dissolved, the solution was slowly evaporated to dryness, after which the crucible plus contents was heated to 700–750° for at least four hours. The product obtained was dissolved in water and transferred to a Pyrex flask; although the solution was alkaline, it was stored on ice. After dilution to yield a radioactivity convenient for analysis, the concentration was initially ca. $2 \times 10^{-6} M$.

By this method we obtained products in which ca. 90% of the total radioactivity was pyro-, the rest orthophosphate. The presence of the orthophosphate was due to the fact that in the preparation a little more caustic was added than needed for the conversion of the radiophosphate to Na_2HPO_4 ; this was done in order to prevent the formation of NaH_2PO_4 , which would yield more highly condensed phosphates than the pyro- at 700°.

The Procedure for the Kinetic Experiments.—The solution was made up in a volumetric flask of either 100- or 250-ml. capacity, and this usually served as the reaction vessel. The material of the vessel (Pyrex or Exax glass, or polyethylene) was without effect upon the rate. Five-milliliter aliquots were removed at selected times, the same pipet being used throughout an experiment. Each aliquot was discharged from the pipet into an excess of caustic in a 15-ml. centrifuge tube, and if the analysis was not to be made within a few hours, it was stored on ice, or frozen. The reaction was followed by precipitation of pyrophosphate as zinc pyrophosphate; the procedure for the analysis will be given later. In the case of the experiments carried out with hydrochloric or perchloric acid, aliquots of the completely hydrolyzed solution were titrated with standard sodium hydroxide with methyl red as indicator. The computation of the hydrogen-ion concentration from the titer will be described later.

The logarithm of the radioactivity of the $Zn_2P_2O_7$ precipitate was plotted vs. time, and if a linear relationship was found, the first-order velocity coefficient was computed by the method of least squares. Most reactions were followed for at least three half-times, during which ca. 15 aliquots were taken. It had been previously demonstrated by Hull⁴ that there is no exchange of phosphorus between ortho- and pyrophosphates.

The Analysis for Pyro- and for Orthophosphate.—To obtain quantitative precipitations, which require concentrations of a few thousandths molar, it was necessary to add inactive phosphate carrier to the reaction solution, in which $\{[PO_4] + [P_2O_7]\}$ was usually of the order of $10^{-4} M$. In consequence the analytical problem became the separation of pyro- and orthophosphates at concentrations which were determined by the amount of carrier and reagent added, and which could be kept practically constant.

Kiehl and Coates⁶ precipitated $Zn_2P_2O_7$ from solutions

containing other phosphates, and for a series of 27 mixtures had an average deviation of 0.9% between P_2O_7 taken and found. Less consistent results were obtained by Nylén,⁷ by Madorsky and Clark,⁸ and by Hull.⁴ Hull, in his study of exchange, found the precipitation of $Cd_2P_2O_7$ preferable to that of $Zn_2P_2O_7$, and a little later Kolthoff and Cohn⁹ investigated carefully the conditions for the separation of ortho- and pyrophosphates by precipitation of $Cd_2P_2O_7$. In our work, however, precipitation of $Zn_2P_2O_7$ was found preferable to that of $Cd_2P_2O_7$. And for the determination of orthophosphate, precipitation with ammonium molybdate reagent, as described by Jones,¹⁰ was found satisfactory.

It was necessary, in our work, to determine the extent of coprecipitation of ortho- with pyrophosphate, and to correct for it, since otherwise the hydrolysis, toward the end, would appear too slow. The determination was made by precipitating pyrophosphate from a solution containing radioactive orthophosphate and inactive pyrophosphate, and counting the precipitate. The total radioactivity was determined by counting the evaporate of an aliquot of the solution. The coprecipitation with $Zn_2P_2O_7$ was $(0.5 \pm 0.05)\%$ of the orthophosphate activity. That with $Cd_2P_2O_7$ was ca. 1%, and was much more dependent on experimental conditions. It may be mentioned that our gelatinous $Cd_2P_2O_7$ precipitates did not become crystalline on standing, which is contrary to the observation of Kolthoff and Cohn.

The details of the analysis for pyrophosphate are as follows. To the 5-ml. aliquot of reaction mixture there were added 2.6 ml. of 0.02 *M* $Na_4P_2O_7$ solution, 2.0 ml. of buffer solution of pH 3.6 also containing orthophosphate (1 *M* in ammonium acetate, 8 *M* in acetic acid, 0.2 *M* in H_3PO_4), and finally 4 ml. of zinc reagent (0.2 *M* in zinc acetate, 1.7 *M* in acetic acid). After standing for at least 20 minutes, the $Zn_2P_2O_7$ was centrifuged out. The precipitate was washed twice with 5 ml. of water, slurried, transferred quantitatively with a medicine dropper to an aluminum counting pan, dried under an infrared lamp, and counted. A few drops of alcohol added to the slurry caused it to spread evenly over the pan.

The analysis for orthophosphate was as follows. To the 5-ml. aliquot were added 0.5 ml. of 0.04 *M* H_3PO_4 solution, 1 ml. of 0.02 *M* $Na_4P_2O_7$, 1 ml. of phosphate-free detergent (to reduce the creeping of the precipitate), and 6 ml. of ammonium molybdate reagent prepared according to the directions of Jones.¹⁰ After 15 minutes the precipitate was centrifuged out. It was washed with 1 ml. of saturated NH_4NO_3 solution diluted with 4 ml. of water, then with 4 ml. of water, and transferred and counted as above. If some of the precipitate adhered to the side of the centrifuge tube it was dissolved in 3 *M* ammonia and transferred to the pan.

With the ammonium phosphomolybdate precipitate there was a demonstrable effect of the presence of the precipitate upon the count. Thus, when to 1-ml. aliquots of radioactive solution there was added the precipitate from 0.33 to 1.50 ml. of inactive orthophosphate carrier solution, for the pans with added precipitate the count was ca. 8% higher than that of the evaporate alone. Probably some of the radiation was reflected from the interface between precipitate and pan. With $Zn_2P_2O_7$, on the other hand, a similar test showed no difference, beyond the counting error, between pans with and without added precipitate. Since the assay of the batches of radioactive pyrophosphate (whose preparation was described in a preceding section) depends upon the molybdate precipitation, in determining the percentage of orthophosphate the total radioactivity was measured by precipitating ammonium phosphomolybdate from a completely hydrolyzed aliquot. In determining the percentage of pyrophosphate the total activity was taken as that of an evaporated aliquot.

All counts were corrected for background, for coincidence loss, and when necessary, for decay. All pyrophosphate counts were in addition corrected for coprecipitation of orthophosphate.

Adsorption.—The early kinetic runs were made in perchloric acid solution more concentrated than 0.1 *M*, with the initial pyrophosphate concentration $[P_2O_7]$ of the order

(7) P. Nylén, *Z. anorg. Chem.*, **229**, 36 (1936).

(8) S. Madorsky and K. Clark, *Ind. Eng. Chem.*, **32**, 244 (1940).

(9) I. M. Kolthoff and C. Cohn, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

(10) I. T. Jones, *Ind. Eng. Chem.*, **14**, 536 (1942).

(4) D. E. Hull, *This Journal*, **68**, 1269 (1941).

(5) E. P. Partridge, V. Hicks and G. W. Smith, *ibid.*, **63**, 454 (1941).

(6) S. J. Kiehl and H. Coates, *ibid.*, **49**, 2180 (1927).

of $10^{-5} M$, and straight lines were obtained when $\log (Zn_2P_2O_7 \text{ radioactivity})$ was plotted *vs.* time. Later, when the acid concentration was lowered below *ca.* $0.04 M$, curvature appeared; *cf.* curve A of Fig. 1.

To test for possible interaction with the surface of the container, an experiment was performed in which the volumetric flask that served as reaction vessel was partially filled with broken glass, making the surface/volume ratio *ca.* five times as large as originally. The plot showed the same sort of curvature as before, but the initial slope was steeper. A check of the total radioactivity was made from time to time during the run by evaporation of an aliquot withdrawn from the region just above the glass; after three days the count was lower than the initial count. At the end of the run the broken glass was washed with water, dried and counted; it was found to be radioactive. This experiment constituted proof of adsorption, and led us to make two series of tests: in one, we examined various materials for adsorption of phosphates, in the hope of finding one on which adsorption would be negligible; in the other, we studied the effect of container material, and of initial pyrophosphate concentration, upon the rate plots.

Adsorption tests were made in $0.005 M$ perchloric acid on Teflon, Tygon, polyethylene, Exax glass, Pyrex glass, quartz, platinum, silver, aluminum and copper. All adsorbed, glass the least, the metals most. Additional tests were made with glass and with polyethylene, as follows: Since there was always some orthophosphate in the radioactive pyrophosphate solution, a direct test of the adsorption of pyrophosphate alone could not be made; however, when sufficient inactive orthophosphate was added to the solution to make the specific activity due to orthophosphate too low for detection, the adsorption at first increased with time, then decreased, which indicates that pyro- is adsorbed in preference to orthophosphate. Soaking the adsorbent in a solution of inactive phosphate before placing it in the radioactive solution retarded the appearance of radioactivity on the sample, but after *ca.* 50 hours the result was the same. The adsorption on glass was dependent on the mode of cleaning, being considerably greater on glass cleaned with chromic acid than on glass cleaned with a detergent. Regarding the removal of radioactivity from the samples, it was found that washing with water caused no reduction in radioactivity after the first few rinses, but that washing with molar acid or base quickly reduced it to a small fraction of the original value. Adsorption was also tested in acetate buffers of *pH* 3.5–5, and found to be about the same as in $0.005 M HClO_4$. There was no measurable adsorption in three days' time from $0.2 M HClO_4$, but from $0.1 M$ there was adsorption. Thus adsorption occurred in the region of existence of the $H_2P_2O_7^{2-}$ and $H_2PO_4^-$ ions, and on all the materials examined. Similar results for the adsorption of orthophosphate at *pH* 2–3 were reported by Tompkins and Bizzell.¹¹

In the kinetic tests, the rate of disappearance of pyrophosphate was studied using glass flasks, and polyethylene bottles. The bottles were placed in copper cans for protection from the thermostat oil, additional heating being provided around the top of the can to maintain temperature in the solution. The glass and the polyethylene caused the same sort of curvature at low values of $[H^+]$ and $[P_2O_7]_i$. Since every material we had tried did adsorb phosphates, it seemed necessary to increase $[P_2O_7]_i$ to the point where adsorption would have a negligible effect. This was done, but with reluctance, since the increase in $[P_2O_7]_i$ made the evaluation of $[H^+]$ more difficult, and partially nullified the advantages of the radiochemical method. Curves B and C in Fig. 1 show the result of addition of inactive $Na_4P_2O_7$ to bring the pyrophosphate concentration to the stated value. Curve B is linear to *ca.* 94% of reaction, curve C to 97.5%, which is as far as the reaction was followed. The individual points are covered in the figure by the solid curves. The values of the second-order velocity coefficient $k/[H^+]$ computed from curve C and from the linear portion of curve B are 12.29 and 12.31 $l. \text{ mole}^{-1} \text{ hr.}^{-1}$, respectively. These experiments were carried out in glass flasks, but similar experiments in polyethylene bottles gave the same result, showing that there is no catalysis of the hydrolysis by the surface of the vessel. The conclusion indicated by these experiments, *viz.*, that curvature is eliminated from the rate

(11) P. C. Tompkins and O. M. Bizzell, *Ind. Eng. Chem.*, **42**, 1469 (1950).

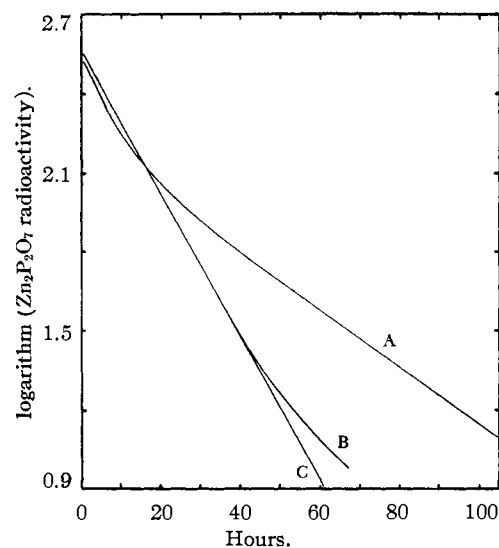


Fig. 1.—The effect of pyrophosphate concentration on the linearity of the rate plot: A, $P_2O_7 = 4 \times 10^{-6} M$, $HClO_4 = 0.00485 M$; B, $P_2O_7 = 8 \times 10^{-6} M$, $HClO_4 = 0.00495 M$; C, $P_2O_7 = 2 \times 10^{-4} M$, $HClO_4 = 0.00503 M$.

plots if the initial pyrophosphate concentration is as high as $2 \times 10^{-4} M$, was borne out by the subsequent work.

The Hydrogen-Ion Concentration.—After hydrolysis was essentially complete aliquots of the solution, containing perchloric or hydrochloric acid, and orthophosphate, were titrated with standard sodium hydroxide solution to the methyl red end-point or, alternatively, were titrated to the $H_2PO_4^-$ end-point using a *pH* meter. The titer gave $[H^+] + [H_3PO_4]_f$ at room temperature. Letting K'_j represent the *j*th dissociation constant of orthophosphoric acid, and the subscripts *i* and *f* initial and final values of the concentration, respectively, at the end of the reaction one has

$$[PO_4]_f = [H_3PO_4]_f + [H_2PO_4^-]_f = 2[P_2O_7]_i \\ [H_3PO_4]_f = 2[H^+]_i[P_2O_7]_i / \{K'_1 + [H^+]_i\} \quad (4)$$

The value of $[H_3PO_4]_f$ was obtained from the titer by successive approximation, $[H^+]$ being taken equal to the titer for the first approximation.

From inspection of the dissociation constants of ortho- and pyrophosphoric acids it will be seen that titration to the methyl red end-point corresponds to the end-point for $H_2P_2O_7^{2-}$ as well as for $H_2PO_4^-$, *i.e.*, titration of the solution at the start of the reaction would require the same volume of caustic, as at the end. This was also observed experimentally. The solution contained initially, besides the hydrogen ion, $H_4P_2O_7$, $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$. However, in sufficiently acid solution for $[H_4P_2O_7]$ to be significant, the correction to the titer owing to the presence of the phosphates becomes very small. Assuming that $[H_4P_2O_7]$ may be neglected

$$[P_2O_7]_i = [H_3P_2O_7^-]_i + [H_2P_2O_7^{2-}]_i, \text{ and} \\ [H_3P_2O_7^-]_i = [H^+]_i[P_2O_7]_i / \{K_2 + [H^+]_i\} \quad (5)$$

The value of $[H^+]$ obtaining when half the pyrophosphate has hydrolyzed may be taken, to a good approximation, as the average of $[H^+]_i$ and $[H^+]_f$, or as the titer minus $\{[H_3PO_4]_f + [H_3P_2O_7^-]_i\}/2$, at room temperature. The value wanted, however, is that at the temperature of the kinetic experiment. Since K_2 and K'_1 are not known for the conditions employed, and since in any case the corrections to the titer are small, it was assumed for the purposes of the calculation that

$$K_2 = K'_1 = K \quad (6)$$

and that at the half-time

$$[H^+] = \text{titer} - 3[H^+][P_2O_7]_i / 2\{K + [H^+]\} \quad (7)$$

$[H^+]$ was obtained by a series of approximations, with $[H^+]$ on the right-hand side of (7) taken equal to the titer for the first approximation. Finally $[H^+]$ was corrected to the temperature of the experiment by multiplying by the ratio

of the density of water at that temperature to the density of water at room temperature. The correction to the titer owing to the presence of the phosphates amounted to at most 6%, using reasonable values of K , and for acid concentrations above 0.02 M it was negligibly small. The change in hydrogen-ion concentration accompanying hydrolysis was too small to be detected on the rate plots.

When the reaction was carried out in a buffer solution, the hydrogen-ion concentration was computed from the composition of the buffer, and the dissociation constant of the buffer acid. Each case will be discussed as it arises. In preparing the solution for a kinetic experiment, the radioactive $\text{Na}_4\text{P}_2\text{O}_7$ solution was neutralized to the proper pH , the buffer was added, and the solution was warmed and made up to the mark at 70°.

The Kinetic Results

In Solutions of Strong Acids.—One experiment was carried out at 39.85° under conditions similar to those of Muus, *viz.*, in 0.1177 M hydrochloric acid solution, with $[\text{P}_2\text{O}_7]_i$ $8 \times 10^{-4} M$; $k/[\text{H}^+]$ was 0.133 l. mole⁻¹ hr.⁻¹. By plotting Muus's $k/[\text{H}^+]$ *vs.* $[\text{H}^+]^{1/2}$, a straight line was obtained, from which $k/[\text{H}^+]$ at $M_{\text{HCl}} = 0.1177$ was found by a short extrapolation to be 0.135. The results are identical when a correction is made for the difference in temperature of 0.15°.

Our results at 49.83, 59.87 and 69.40° are reported in Tables I, II and III. The second column of each table gives the acid normality at room temperature, obtained by titration of the completely reacted solution, as described. The third column gives $[\text{H}^+]$ at the temperature of the experiment, calculated from the titer assuming $K_2 = K_1' = K = 0.01$ (*cf.* equation 7).

TABLE I
KINETIC EXPERIMENTS AT 49.83°

No.	Titer	$[\text{H}^+]$	$[\text{P}_2\text{O}_7]_i$	k	$k/[\text{H}^+]$	μ
1	1.531	1.518	2×10^{-4}	0.931	0.613	1.519
2	1.496	1.484	6×10^{-5}	.907	.611	1.484
3	1.071	1.061	6×10^{-5}	.561	.528	1.061
4	1.033	1.025	2×10^{-4}	.534	.521	1.026
5	0.508	0.504	1×10^{-5}	.233	.462	0.504
6	.508	.504	1×10^{-5}	.229	.454	.504
7	.503	.503	8×10^{-4}	.234	.464	.507
8	.508	.503	8×10^{-4}	.229	.455	.507
9 ^a	.499	.495	1×10^{-4}	.216	.437	.495
10	.0800	.0793	2×10^{-5}	.0319	.403	.0794
11 ^a	.0806	.0797	2×10^{-4}	.0318	.399	.0808
12 ^a	.04027	.0397	2×10^{-4}	.0180	.453	.0406
13 ^a	.01993	.01956	2×10^{-4}	.01115	.569	.0206
14 ^a	.00998	.00973	2×10^{-4}	.00748	.767	.0106
15 ^a	.15006	.1485	2×10^{-4}	.0600	.403	.1494
16 ^{a,b}	.0989	.0978	2×10^{-4}	.0374	.382	.1486
17 ^{a,b}	.05003	.04937	2×10^{-4}	.01810	.366	.1503
18 ^{a,b}	.02001	.01964	2×10^{-4}	.00847	.431	.1506
19 ^{a,b}	.00995	.00972	2×10^{-4}	.00556	.572	.1507
20 ^{a,b}	.004975	.004834	2×10^{-4}	.00413	.853	.1508
21 ^{a,b}	.003031	.002945	2×10^{-4}	.00352	1.19	.1510
22 ^{a,b}	.001992	.001926	2×10^{-4}	.003235	1.68	.1510
23 ^{a,b}	.00106	.001026	2×10^{-4}	.00288	2.80	.1514
24 ^{a,b}	.000490	.000474	2×10^{-4}	.00272	5.75	.1514

^a Hydrochloric acid; others, perchloric acid. ^b Ionic strength 0.15, NaCl added.

The concentrations are in units of moles per liter. The fifth column gives the first-order constant k in reciprocal hours, calculated using natural logarithms; the sixth gives the second-order constant $k/[\text{H}^+]$ in l. mole⁻¹ hr.⁻¹. The last column gives the ionic strength.

The values of the first-order constant k decrease with decreasing $[\text{H}^+]$. The values of the second-

TABLE II
KINETIC EXPERIMENTS AT 59.87°^a

No.	Titer	$[\text{H}^+]$	$[\text{P}_2\text{O}_7]_i$	k	$k/[\text{H}^+]$	μ
1	0.00476	0.000458	2×10^{-4}	0.01030	22.5	0.1514
2	.001039	.001002	2×10^{-4}	.01106	11.0	.1514
3	.002019	.001943	2×10^{-4}	.01204	6.20	.1512
4	.003037	.002918	2×10^{-4}	.01341	4.59	.1511
5	.00500	.00484	2×10^{-4}	.01564	3.24	.1509
6	.01005	.00977	2×10^{-4}	.02025	2.07	.1508
7	.02012	.01966	2×10^{-4}	.02895	1.47	.1506
8	.05039	.04948	2×10^{-4}	.0560	1.13	.1504
9	.1000	.0984	2×10^{-4}	.1080	1.10	.1493
10 ^b	.15116	.1489	2×10^{-4}	.1643	1.10	.1497

^a Hydrochloric acid. Ionic strength 0.15, NaCl added. ^b No NaCl added.

order constant $k/[\text{H}^+]$ pass through a minimum at a hydrogen-ion concentration somewhat less than 0.1; this is seen most clearly in the experiments at 49.83° because here higher acid concentrations were investigated. The most striking trend, however, is the great increase in $k/[\text{H}^+]$ as $[\text{H}^+]$ becomes very small. And if k is plotted *vs.* $[\text{H}^+]$ over the range where $k/[\text{H}^+]$ is increasing with decreasing $[\text{H}^+]$, the curve obtained will be seen to have an intercept well above zero on the k axis. This is shown in Fig. 2 for the data at 69.40°.

TABLE III
KINETIC EXPERIMENTS AT 69.40°

No.	Titer	$[\text{H}^+]$	$[\text{P}_2\text{O}_7]_i$	k	$k/[\text{H}^+]$	μ
1	0.2385	0.2339	5×10^{-5}	0.639	2.73	0.2341
2	.232	.228	5×10^{-5}	.600	2.63	.228
3	.201	.197	1×10^{-5}	.503	2.56	.197
4	.197	.193	1×10^{-5}	.470	2.54	.193
5	.1823	.1790	1×10^{-5}	.435	2.43	.1790
6	.1690	.1655	4×10^{-6}	.437	2.64	.1655
7	.1650	.1605	1×10^{-5}	.432	2.69	.165
8	.1639	.1605	5×10^{-5}	.463	2.88	.1607
9	.1347	.1322	2×10^{-5}	.367	2.77	.1323
10	.1335	.1310	2×10^{-5}	.3603	2.75	.1311
11	.1335	.1310	2×10^{-5}	.3608	2.75	.1311
12	.133	.1305	2×10^{-5}	.344	2.64	.1306
13	.0972	.0954	5×10^{-5}	.296	3.10	.1956
14	.0928	.0911	5×10^{-5}	.0271	2.98	.0913
15	.0905	.0888	1×10^{-5}	.234	2.64	.0888
16	.0458	.0450	5×10^{-5}	.167	3.71	.0452
17	.02007	.01950	2×10^{-4}	.1041	5.34	.0205
18	.00818	.00790	2×10^{-4}	.0720	9.12	.0089
19	.00525	.00506	2×10^{-4}	.0627	12.4	.0061
20	.00508	.00495	8×10^{-5}	.0619	12.5	.0060
21	.00445	.00427	2×10^{-4}	.0573	13.4	.0053
22	.00429	.00407	3×10^{-4}	.0573	14.0	.0051
23	.00293	.00282	2×10^{-4}	.0527	18.7	.0039
24	.000918	.000877	2×10^{-4}	.0387	44.1	.0022
25 ^a	.1596	.1563	2×10^{-4}	.4258	2.72	.1571
26	.1595	.1562	2×10^{-4}	.4265	2.72	.1570
27 ^b	.0815	.0795	4×10^{-4}	.228	2.87	.1503
28 ^b	.0829	.08105	2×10^{-4}	.2297	2.84	.1518
29 ^b	.04182	.04080	2×10^{-4}	.1350	3.31	.1517
30 ^b	.04192	.04067	4×10^{-4}	.1350	3.32	.1516
31 ^b	.02100	.02020	4×10^{-4}	.0881	4.36	.1512
32 ^b	.02127	.02038	2×10^{-4}	.0910	4.40	.1517
33 ^b	.008765	.00846	2×10^{-4}	.05985	7.07	.1515
34 ^b	.00860	.00818	4×10^{-4}	.0598	7.31	.1512
35 ^{a,b}	.005225	.00503	2×10^{-4}	.0520	10.34	.1510
36 ^{a,b}	.00508	.00489	2×10^{-4}	.0517	10.38	.1510
37 ^{a,b}	.00307	.00297	2×10^{-4}	.0445	15.00	.1511
38 ^b	.00314	.00298	4×10^{-4}	.0446	14.97	.1511
39 ^{a,b}	.00118	.00113	2×10^{-4}	.0382	33.8	.1515
40 ^b	.000976	.000912	4×10^{-4}	.0374	41.0	.1513
41 ^b	.00052	.000490	4×10^{-4}	.0348	71.0	.1514

^a Hydrochloric acid; others, perchloric acid. ^b Ionic strength 0.15, NaCl added.

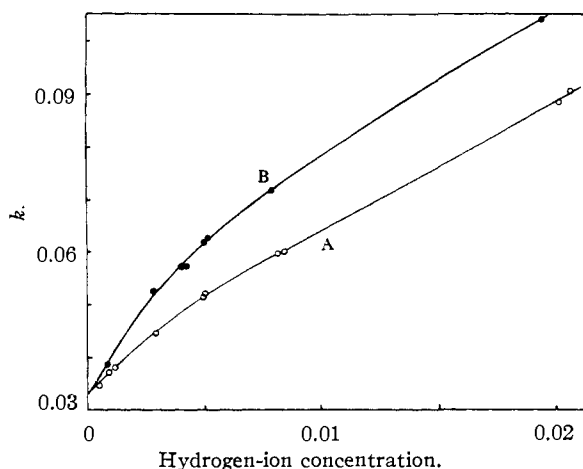


Fig. 2.—The rate constant at 69.40° for hydrogen-ion concentrations to 0.02 *M*: O, (A), 0.15 ionic strength, NaCl added; ●, (B), no NaCl added.

However, in 0.1 *M* sodium hydroxide solution no hydrolysis was observed in 41 days at this temperature. Figure 2 also shows that the reaction has a negative electrolyte effect. The variation of *k* with $[H^+]$ at larger values of $[H^+]$ is illustrated by Fig. 3.

In Buffer Solutions.—The results of the experiments carried out in buffer solutions are given in Table IV. The usual procedure of making successive dilutions of a stock solution was employed; in the table, experiments performed at the same time, and using the same stock buffer solution, are grouped together. Where the ionic strength is higher than that due to the charged constituent of the buffer, sodium chloride was added.

In the computation of $[H^+]$ in the acetate buffers, the values of the dissociation constant of acetic acid were estimated from equation (15-8-2) of Harned and Owen,¹² extrapolated to 70°. The values obtained are: 1.36, 1.73 and 2.44×10^{-5} at ionic strengths of 0, 0.02 and 0.15, respectively. In order to obtain a value of the classical dissociation constant of formic acid at 70° and $\mu = 0.15$, it was assumed that the ratio of this constant to the thermodynamic constant at 25° is the same for formic and acetic acids. The dissociation constant of the *p*-bromoanilinium ion is not known for the conditions of our experiments; however, it is of the same order as that of formic acid, and has been taken equal to that of formic acid in estimating $[H^+]$.

It will be seen that increasing the concentration of the carboxylic acid and its conjugate base, at constant ionic strength, resulted in a decrease in rate of hydrolysis. Moreover, at the higher concentrations of the carboxylate buffers, curvature appeared in the rate plots, the initial specific rate being *ca.* 5% greater than the final; the values reported for *k*, in the experiments with curvature, are the initial rates. It will be recalled that in the experiments with strong acids maintenance of $[P_2O_7]_i$ at 2×10^{-4} *M* sufficed to eliminate curva-

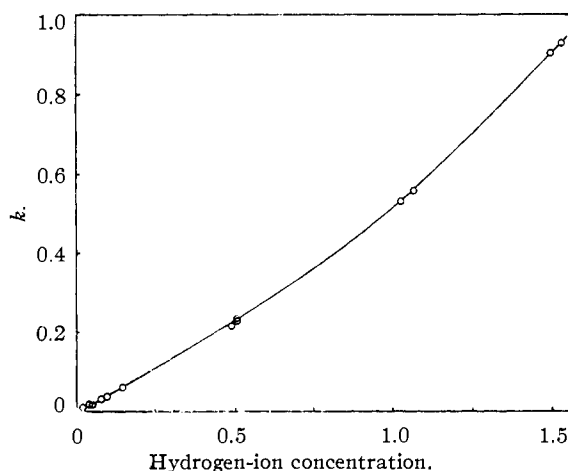


Fig. 3.—The rate constant at 49.83° for hydrogen-ion concentrations to 1.5 *M*.

ture. It will also be seen from Table IV that the decrease in *k* with increasing concentration of carboxylate buffer is accompanied by an increase in

TABLE IV
THE EXPERIMENTS IN BUFFER SOLUTIONS
Temp., 69.40°; $[P_2O_7]_i$, 2×10^{-4} *M*

No.	Acid	Base	$[H^+]$	<i>k</i>	μ^e
Acetic acid-sodium acetate					
1	0.00285	0.0045	9.5×10^{-6}	0.0280	0.0045
2	.0011	.0018	1.04×10^{-5}	.0256	.020
3 ^a	.0008	.0021	6×10^{-6}	.0238	.020
4	.0057	.0090	1.09×10^{-5}	.0282	.020
5	.0010	.0010	1.63×10^{-5}	.0289	.020
6	.0020	.0020	1.67×10^{-5}	.0284	.020
7	.0050	.0050	1.70×10^{-5}	.0278	.020
8	.0100	.0100	1.73×10^{-5}	.0279	.020
9	.0050	.0050	1.5×10^{-5}	.0277	.005
10 ^b	.150	.150	2.44×10^{-5}	.0285	.150
11 ^b	.100	.100	2.44×10^{-5}	.0275	.150
12	.050	.050	2.44×10^{-5}	.0284	.150
13	.020	.020	2.44×10^{-5}	.0293	.150
14	.005	.005	2.40×10^{-5}	.0300	.150
15 ^c	.150	.150	2.5×10^{-5}	.00724	.150
16 ^d	.150	.150	2.6×10^{-5}	.00224	.150
Formic acid-sodium formate					
17 ^b	0.150	0.150	2.44×10^{-4}	0.0301	0.150
18 ^b	.100	.100	2.44×10^{-4}	.0305	.150
19 ^b	.050	.050	2.43×10^{-4}	.0327	.150
20	.020	.020	2.40×10^{-4}	.0329	.150
21	.005	.005	2.23×10^{-4}	.0329	.150
22	.002	.002	2.0×10^{-4}	.0335	.150
<i>p</i> -Bromoaniline hydrochloride- <i>p</i> -bromoaniline					
23	0.00415	0.00415	2.2×10^{-4}	0.0329	0.150
24	.00852	.00852	2.3×10^{-4}	.0338	.150
25	.0181	.0181	2.4×10^{-4}	.0345	.150
Ammonium chloride-ammonium hydroxide					
26	0.001	0.010	10^{-10}	0.00082	0.001
27	.008	.002	$10^{-8.5}$.0043	.008

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 523.

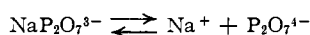
^a 0.01 *M* in tetrapropylammonium chloride; contained basic impurity. ^b Curved rate plots; true rates may be slower. ^c Experiment at 59.87°. ^d Experiment at 49.83°. * Solvent salt, NaCl.

[H⁺], especially for the formate buffers, so if the results were corrected for change in [H⁺], the trend in k would be still more pronounced. The experiments with *p*-bromoaniline buffers, on the other hand, show an increase in k with increase in buffer concentration; the results cover only a narrow range, however, because of the limited solubility of the base.

Discussion

Any explanation of the kinetic results must be based upon a consideration of the successive dissociations of pyrophosphoric acid. This was pointed out by Muus, but her data covered too narrow a range of hydrogen-ion concentration to demonstrate the reactivity of species other than H₃P₂O₇⁻. Although the dissociation constants are not known for the conditions of the kinetic experiments, it will be helpful to tabulate the existing values.

To this list there may be added the equilibrium constant for the reaction



given by Monk¹³ as 4.5×10^{-3} at 25°.

TABLE V

THE DISSOCIATION CONSTANTS OF H₄P₂O₇

Reference and conditions	K ₁	K ₂	10 ⁷ K ₃	10 ¹⁰ K ₄
18 ^{oa}	0.14	0.011	2.9	36
18 ^{ob}	2.1	4.06
20°, 1 M KCl ^c	2	.027	30	...
30 ^{od}	1.98	1.32

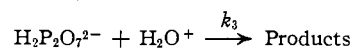
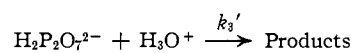
^a G. A. Abbott and W. C. Bray, *THIS JOURNAL*, **31**, 729 (1909). ^b I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **47**, 826 (1928). ^c J. Muus, *Z. physik. Chem.*, **159A**, 268 (1932). ^d C. Morton, *J. Chem. Soc.*, 1401 (1928).

The Results in Solutions of Strong Base.—Since in 0.1 M sodium hydroxide solution we detected no reaction in forty-one days at 70°, the hydrolyses of P₂O₇⁴⁻ and NaP₂O₇³⁻ are negligible.

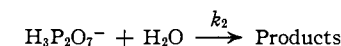
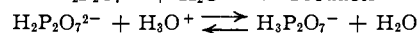
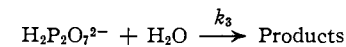
The Results in Buffer Solutions.—Runs 26 and 27 of Table IV show that the HP₂O₇³⁻ ion does hydrolyze. Since the concentration of the solvent is so much greater than those of the buffer constituents, and since [H⁺] for run 27 is close to the middle of the range of existence of HP₂O₇³⁻, it is logical to attribute the rate constant, $k = 0.0043$ hr.⁻¹, to the reaction between HP₂O₇³⁻ and H₂O. For run 26, at *p*H 10, k is only one-fifth as large as in run 27, and if it is assumed that the buffer constituents have no effect upon the rate, this means that the pyrophosphate exists as four parts P₂O₇⁴⁻ (or an unreactive association product) and one part HP₂O₇³⁻; K₄ calculated on this basis is 4×10^{-10} , in reasonable agreement with the tabulated values.

It will be seen from Tables I–IV that k does not change greatly with change in hydrogen ion concentration over the range from 10⁻³ to 10⁻⁵. In this region the H₂P₂O₇²⁻ ion predominates. At 70°, k decreases from 0.038 at [H⁺] = 10⁻³ to 0.033 at 2×10^{-4} and to 0.028 at 2×10^{-5} . In the experiments with carboxylate buffers H₂P₂O₇²⁻ can react with water or the hydrogen

ion; as pointed out above, the reaction is not accelerated by the buffer constituents, but instead is retarded by them to a slight extent. Since k changes by only 30% between [H⁺] = 10⁻³ and 2×10^{-5} , the reaction must be chiefly one with water. Below 2×10^{-5} , k drops off more rapidly, which can be attributed to the increase in [HP₂O₇³⁻]/[P₂O₇]. Since HP₂O₇³⁻ reacts with water more slowly than H₂P₂O₇²⁻, and since in these solutions [HP₂O₇³⁻] is considerably less than [H₂P₂O₇²⁻], the hydrolysis of HP₂O₇³⁻ may be neglected without causing serious error. To explain the increase in rate with increase in [H⁺] two courses are open: the acceleration may be attributed to hydrogen-ion catalysis of the hydrolysis of H₂P₂O₇²⁻, or it may be attributed to the reaction with water of H₃P₂O₇⁻, present at a concentration much less than the analytical concentration. Letting k_1 be the velocity coefficient for the water reaction of H₄P₂O₇, k_2 that for the water reaction of H₃P₂O₇⁻, etc., and letting k_1' be the velocity coefficient for the reaction of H₄P₂O₇ with H₃O⁺, k_2' that of H₃P₂O₇⁻ with H₃O⁺, etc., the reactions involved are either



or



In these solutions [P₂O₇] = [H₂P₂O₇²⁻] + [HP₂O₇³⁻], so the measured specific rate k is given by either

$$k = \{k_3[\text{H}^+] + k_3'[\text{H}^+]^2\}/\{K_3 + [\text{H}^+]\} \quad (8a)$$

or

$$k = \{k_3[\text{H}^+] + (k_2/K_2)[\text{H}^+]^2\}/\{K_3 + [\text{H}^+]\} \quad (8b)$$

if H₃P₂O₇⁻ is an intermediate in the hydrolysis of H₂P₂O₇²⁻. Equations 8a and 8b are mathematically indistinguishable.

The data for the acetate and formate buffers were treated by 8a, which was rearranged to give

$$k_3[\text{H}^+]/\{K_3 + [\text{H}^+]\} = k_c = k - k_3'[\text{H}^+]^2/\{K_3 + [\text{H}^+]\}$$

In order to have values of k independent of the buffer constituents, k was extrapolated to zero buffer concentration for the runs with a given buffer at constant μ and constant buffer ratio. The correction term on the right in the equation above was small, being less than 1% of k except in the formate buffers; it was computed from k_3' as determined from the experiments with strong acids, and from an approximate value of K₃. Thus there was obtained a set of k_c 's and corresponding [H⁺] from which k_3 and a new value of K₃ were computed by means of the equation

$$k_3[\text{H}^+] = k_c[\text{H}^+] + k_c K_3$$

The results are: $k_3 = 0.0323 \pm 0.0004$, $K_3 = 1.5$ to 2.5×10^{-6} , the lower value for $\mu = 0.15$. Because the computations involve small differences between numbers which are not known exactly, because [H₃P₂O₇⁻] may not be altogether negligible in the formate buffers, and because of the peculiar

(13) C. R. Monk, *J. Chem. Soc.*, 423 (1949).

effect of buffer concentration upon k , the results should be regarded as approximate.

The decrease in rate with increasing concentration of carboxylate buffer is the most striking conclusion to be drawn from these experiments. The decrease suggested to us that some specific factor might be operating, and that it would be desirable to try catalyst acids of other types. Although a number of the substituted anilinium ions are of the proper strength, they are as a rule not sufficiently stable under the conditions of the kinetic experiments; *p*-bromoanilinium, however, is relatively stable. Three experiments were carried out in *p*-bromoaniline hydrochloride-*p*-bromoaniline buffer solution, and in them k increased with increasing concentration of the buffer. Although the limited solubility of *p*-bromoaniline prevented a thorough test, the *p*-bromoaniline buffers did not retard the hydrolysis, but on the contrary accelerated it slightly.

In view of the ability of $\text{H}_2\text{P}_2\text{O}_7^{2-}$ to complex with many substances, and in view of its strong tendency to adsorb on all sorts of surfaces, it does not seem unreasonable to suggest that the inhibitory effect of carboxylic acids may perhaps be due to complex formation between the ion and the acid. If the complex was less reactive than $\text{H}_2\text{P}_2\text{O}_7^{2-}$ the kinetic results could be explained, and the existence of the complex could account for the curvature of the rate plots, at the higher acid concentrations, in the same fashion as adsorption on the walls of the container at low values of $[\text{P}_2\text{O}_7]_i$.

The Results in Solutions of Strong Acids.—The problem of analyzing the kinetic data is complicated by lack of knowledge of the dissociation constants of $\text{H}_4\text{P}_2\text{O}_7$ under the experimental conditions employed, and by the uncertainty about the value of K_1 even at lower temperatures. Only those kinetic experiments carried out at constant ionic strength and in swamping salt solution can be treated quantitatively, *viz.*, those experiments of Tables I, II and III for which $\mu = 0.15$ (mostly NaCl) and $0.03 \leq [\text{H}^+] > 0.0004$. If K_2 is taken as 0.01, at $[\text{H}^+] = 0.02$, $\text{H}_4\text{P}_2\text{O}_7$ constitutes 0.3% of the pyrophosphate if K_1 is as large as 2, and 12% if K_1 is as small as 0.1. We shall assume that K_1 is sufficiently large so that $[\text{P}_2\text{O}_7] = [\text{H}_3\text{P}_2\text{O}_7^-] + [\text{H}_2\text{P}_2\text{O}_7^{2-}]$ to a good approximation. Assuming that a water reaction and a reaction with the hydrogen ion exist for each species, and using the same symbolism as before, one has

$$-d[\text{P}_2\text{O}_7]/dt = k[\text{P}_2\text{O}_7] = \{k_2 + k_2'[\text{H}^+]\}[\text{H}_3\text{P}_2\text{O}_7^-] + \{k_3 + k_3'[\text{H}^+]\}[\text{H}_2\text{P}_2\text{O}_7^{2-}]$$

and upon putting in for $[\text{H}_3\text{P}_2\text{O}_7^-]$ and $[\text{H}_2\text{P}_2\text{O}_7^{2-}]$ their values in terms of $[\text{P}_2\text{O}_7]$, and rearranging, one obtains

$$k\{K_2 + [\text{H}^+]\} = k_2K_2 + \{k_3'K_2 + k_2\}[\text{H}^+] + k_2'[\text{H}^+]^2 \quad (9a)$$

On the other hand, if there are no hydrogen-ion reactions, and if part of the hydrolysis takes place via $\text{H}_4\text{P}_2\text{O}_7$, present at a concentration much less than the analytical concentration, one obtains

$$k\{K_2 + [\text{H}^+]\} = k_2K_2 + k_2[\text{H}^+] + (k_1/K_1)[\text{H}^+]^2 \quad (9b)$$

From the values of k and $[\text{H}^+]$ listed in Tables I, II and III it is in principle possible to determine the constants K_2 , k_3 , $\{k_3'K_2 + k_2\}$, and k_2' of equation 9a, or alternatively K_2 , k_3 , k_2 and (k_1/K_1) of 9b. To fit such equations to the data by the method of least squares requires that approximate values of the constants be known at the start; then corrections, treated as differentials, are calculated. However, unless the approximate values are close to the true values the method does not work. In the present case the only constant known, even roughly, was k_3 , so it was necessary to employ a different procedure.

A value was chosen for K_2 and equation 9a was treated in the form

$$y = a_1 + a_2x + a_3x^2 \quad (10)$$

where

$$y = k\{K_2 + [\text{H}^+]\}; \quad x = [\text{H}^+]; \\ a_1 = k_2K_2; \quad a_2 = \{k_3'K_2 + k_2\}; \quad a_3 = k_2'$$

The parameters a_1 , a_2 and a_3 in 10 were evaluated by the method of least squares, and the deviations of the calculated from the observed k tabulated. Another value of K_2 was then chosen, and the process repeated.

TABLE VI
THE PARAMETERS OF EQUATION 10 AND THE DEVIATIONS OF THE CALCULATED RATE CONSTANTS AT 69.40°

K_2	0.01	0.007	0.004	0.002	0.001	
k_3	.0337	.0336	.0333	.0325	.0311	
$k_3'K_2 + k_2$.0748	.0645	.0542	.0472	.0437	
k_2'	2.12	2.22	2.33	2.40	2.44	
$[\text{H}^+]$	k	100($k_{\text{calc.}} - k_{\text{obs.}}$)/ $k_{\text{obs.}}$				
0.00049 ₀	0.0348	2.7	2.5	2.0	0.9	-1.4
.00091 ₂	.0374	-0.1	-0.2	-0.3	-0.8	-1.6
.00113	.0382	-0.1	0.0	0.2	0.5	1.0
.00298	.0446	0.1	0.2	0.2	0.4	0.9
.00297	.0445	0.2	0.4	0.9	1.5	2.2
.00489	.0517	-2.1	-1.9	-1.7	-1.5	-1.2
.00503	.0520	-2.0	-1.7	-1.5	-1.3	-1.2
.00818	.0598	0.4	0.2	-0.2	-0.4	-0.7
.00846	.0599	1.5	1.4	1.3	1.2	1.0
.02068	.0910	-0.1	-0.1	0.0	0.0	0.0
.04067	.1350	0.6	1.5	2.4	3.2	3.6
.04080	.1350	0.8	1.7	2.7	3.6	3.9
.08105	.2297	-2.9	-0.9	1.3	3.0	3.9
.1562	.4265	-10	-7.2	-4.3	-2.2	-1.1
.1563	.4258	-10	-7.0	-4.1	-2.2	-0.9
av. dev.						
for 10 points	0.93	0.86	0.83	0.85	1.1	
for all points	2.2	1.8	1.5	1.5	1.6	

Table VI shows the application of equation 10 to the 70° data, using runs 32-41 of Table III. First, for the chosen K_2 , $[\text{H}^+]$ in a given experiment was calculated by equation 7, with K in 7 equal to K_2 . Second, having k and $[\text{H}^+]$, the parameters of 10 were evaluated by the method of least squares; *cf.* the figures at the top of the table. Third, k was computed from a_1 , a_2 , a_3 and $[\text{H}^+]$. The first column of Table VI gives $[\text{H}^+]$ calculated from 7 with $K = K_2 = 0.01$, as in the third column of Table III; the second column gives the observed first-order velocity constant. At the bottom of Table VI are given the average values of 100($k_{\text{calc.}} - k_{\text{obs.}}$)/ $k_{\text{obs.}}$ for the ten runs for which $[\text{H}^+] < 0.03$, and in addition, those obtained when 10 is extrapolated to include the runs for which $[\text{H}^+] > 0.03$.

TABLE VII
 THE PARAMETERS OF EQUATION 10 AND THE DEVIATIONS OF THE CALCULATED RATE CONSTANTS AT 59.87 AND 49.83°

Temp., °C.		59.87		49.83			
K_2	0.01	0.004		0.01	0.004		
k_3	0.00968	0.00943		0.00257 ₅	0.00256		
$k_3'K_2 + k_2$.0238	.0167		.00593	.00404		
k_2'	.761	.828		.283	.288		
[H ⁺]	k	% deviation		[H ⁺]	k	% deviation	
0.00045 ₃	0.0103 ₀	0.1	-1.2	0.00047 ₄	0.00272	0.5	0.3
.00100 ₂	.0110 ₆	-0.3	-0.5	.00102 ₆	.00288	1.2	1.1
.00194 ₃	.0120 ₄	1.4	1.8	.00192 ₆	.00323 ₅	-1.1	-1.0
.00291 ₃	.0134 ₁	-0.4	0.4	.00294 ₅	.00352	0.2	0.2
.00484	.0156 ₄	-1.1	-0.7	.00483 ₄	.00413	-0.4	-0.5
.00977	.0202 ₅	0.3	0.1	.00972	.00556	0.4	0.2
.01966	.0289 ₅	0.0	0.0	.01964	.00847	0.1	0.0
.0494 ₃	.0560	-6	-3.5	.04937	.01810	-6	-6
.0984	.108 ₀	-12	-12	.0978	.0374	-18	-17
.1489	.164 ₃	-1	-17	.1485	.0600	-25	-24
Av. dev. for 7 points	0.52	0.67				0.56	0.47
For all points	2.3	3.7				5.3	5.0

It will be seen that the reaction scheme fits the data to within 1%, when $[H^+] < 0.03$, for values of K_2 from 0.01 to 0.002. The fit is not sensitive to choice of K_2 within this range, so it is not possible to say with certainty which value of K_2 is best. Over the range from $K_2 = 0.01$ to 0.002 the estimated value of k_3 changes relatively little; its average is 0.0333 ± 0.0004 , as compared with 0.0323 ± 0.0004 from the experiments in buffer solution. The coefficient k_2' exhibits more change; its average value is 2.30 ± 0.11 . The parameter $a_2 = k_3'K_2 + k_2$ is quite sensitive to choice of K_2 . If the appropriate value of K_2 is put into a_2 , five linear equations in k_3' and k_2 are obtained; the five equations may be combined to give ten pairs, each of which may be solved for k_3' and k_2 . The averages of the values thus found are: $k_2 = 0.04027 \pm 0.00004$, $k_3' = 3.46 \pm 0.02$.

The data for 50 and 60° were treated in the same manner, except that the calculations were made for only two values of K_2 , 0.01 and 0.004; cf. Table VII. Again the data at low hydrogen-ion concentrations are fitted by equation 10 to better than 1%.

If the parameters a_1 , a_2 and a_3 of equation 10 are taken to represent k_3K_2 , k_2 and (k_1/K_1) of equation 9b, respectively, it is not possible, from the information at hand, to assign values to k_1 and k_2 . And if it is assumed that only the water reactions of the species $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$ contribute to the measured rate, the resulting equation

$$k\{K_2 + [H^+]\} = K_2k_3 + k_2[H^+]$$

does not fit the data. On the other hand, assuming K_2 to lie in the range 0.01 to 0.002, it is possible to assign values to the velocity coefficients of 9a which yield a calculated value of the specific rate agreeing with the observed value to better than 1% when $[H^+] < 0.03$ at $\mu = 0.15$.

Summary of Kinetic Data.—The individual velocity coefficients obtained as described are listed in Table VIII. The concentration of water is included in the velocity coefficients of the water reactions, *i.e.*, k_i is in hr.^{-1} and k_i' in $\text{l. mole}^{-1} \text{hr.}^{-1}$. It will be seen that k_2' and k_3' are about

the same, and so are k_2 and k_3 , *i.e.*, $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$ react at about the same rate.

 TABLE VIII
 THE VELOCITY COEFFICIENTS OF THE INDIVIDUAL REACTIONS
 AT $\mu = 0.15$ (MOSTLY NaCl)

Reactants	Velocity coefficient	Temp., °C.		
		50	60	70
$H_4P_2O_7 + H_3O^+$	k_1'	No quantitative information		
$H_4P_2O_7 + H_2O$	k_1	No quantitative information		
$H_2P_2O_7^- + H_3O^+$	k_2'	0.285	0.795	2.30
$H_3P_2O_7^- + H_2O$	k_2	.00278	.0120	0.0403
$H_2P_2O_7^{2-} + H_3O^+$	k_3'	.315	1.18	3.46
$H_2P_2O_7^{2-} + H_2O$	k_3	.00257	0.00956	0.0333
$HP_2O_7^{3-} + H_2O$	k_40043 ^a
$P_2O_7^{4-}$ or $NaP_2O_7^{3-} + H_2O$	k_5	No reaction was detected ^b		

^a $\mu = 0.008$. ^b In 0.1 M NaOH.

Although only qualitative conclusions can be drawn from the experiments at higher hydrogen-ion concentrations because electrolyte effects confuse the observations, $H_4P_2O_7$ probably reacts at about the same rate as $H_3P_2O_7^-$, or a little faster. Figure 3 shows the experiments at 50° in solutions of strong acids up to 1.5 M; it will be noticed that the curve is concave upward. Assuming that both water reactions and reactions with the hydrogen ion exist, at high hydrogen-ion concentrations

$$-d[P_2O_7]/dt = \{k_1 + k_1'[H^+]\}[H_4P_2O_7] + \{k_2 + k_2'[H^+]\}[H_3P_2O_7^-]$$

If $k_1 \approx k_2$, and $k_1' \approx k_2'$, and if the average values of the primed and unprimed coefficients are \bar{k}' and \bar{k} , respectively, the specific rate may be written as $k = k + \bar{k}'[H^+]$, approximately. Figure 3 shows that the departure from linearity is greater as $[H^+]$ increases, *i.e.*, with increasing $[H_4P_2O_7]/[P_2O_7]$, so $H_4P_2O_7$ probably reacts a little faster than $H_3P_2O_7^-$. It must be remembered, however, that the electrolyte effect on k_1' would probably be positive and linear, that on k_2' negative and exponential, and that a comparison of slopes at

different $[H^+]$'s means a comparison of velocity coefficients at different μ 's.

If one assumes that the species $H_4P_2O_7$ and $H_3P_2O_7^-$ have water reactions only, one obtains for the specific rate

$$k = \{K_1 k_2 + k_1 [H^+]\} / \{K_1 + [H^+]\}$$

The equilibrium constant K_1 would be expected to pass through a maximum between $\mu = 0.5$ and 1.5, the electrolyte effect on k_1 would be expected to be very small, and that on k_2 to be linear. Considering K_1 , k_1 and k_2 constant, the slope of the k vs. $[H^+]$ curve would be, as a first approximation

$$dk/d[H^+] = K_1(k_1 - k_2) / \{K_1 + [H^+]\}^2 = \frac{k_1 - k_2}{K_1 + [H^+]}$$

i.e., it would decrease with increase in $[H^+]$. This is opposite to the observed change, and it is concluded that $H_4P_2O_7$ does have a hydrogen-ion reaction as well as a water reaction. The increasing slope could be explained, to be sure, in terms of the water reaction of such a complex as $H_4P_2O_7 \cdot H^+$, but lacking evidence for its existence, the explanation in terms of the reaction of $H_4P_2O_7$ with H_3O^+ appears preferable.

In the literature there are reported values of the temperature coefficient of the hydrolysis, per ten-degree rise in temperature, varying from 2.6 to 3.5. This is readily explained by the varying contributions of the individual reactions with change in experimental conditions. Table IX shows the temperature coefficient and energy of activation of the net reaction for hydrogen-ion concentrations up to 0.15, at an ionic strength of 0.15. The velocity constant k was calculated by equation 10 for $[H^+] < 0.03$, using the values of a_1 ,

TABLE IX

THE VARIATION OF THE TEMPERATURE COEFFICIENT AND ACTIVATION ENERGY OF THE NET REACTION WITH HYDROGEN-ION CONCENTRATION AT $\mu = 0.15$

$[H^+]$	$\frac{k_{240}}{k_{220}}$	$\frac{k_{230}}{k_{220}}$	$\left(\frac{k_{240}}{k_{220}}\right)^{1/2}$	E_{238}	E_{228}	E_{233}
	kcal. per mole					
0.0001 ^a	3.75	3.65	3.70	30.1	27.7	28.9
.001 ^a	3.65	3.77	3.71	29.4	28.5	29.0
.005 ^a	3.46	3.75	3.60	28.3	28.4	28.3
.010 ^a	3.35	3.60	3.47	27.5	27.5	27.5
.020 ^a	3.23	3.39	3.31	26.7	26.2	26.4
.100 ^a	2.65	2.85	2.75	22.2	22.5	22.3
.150 ^b	2.59	2.72	2.65	21.7	21.5	21.5

^a Values of k calculated by means of equation 10 and the data of Tables VI and VII for $K_2 = 0.004$. ^b Values of k estimated from experimental data.

a_2 and a_3 given in Tables VI and VII for $K_2 = 0.004$. It was estimated for $[H^+] = 0.1$ by means of 10 and the tabulated deviations from the observed values; for $[H^+] = 0.15$ it was estimated from the observed values. The resulting k 's were corrected to 49.80, 59.80 and 69.80°, respectively, and the temperature coefficient and energy of activation were calculated from the k 's at each pair of temperatures; in the table, the subscript of E gives the median (in °K.) of the two temperatures employed.

Table X lists the values of the temperature coefficient, energy of activation and frequency factor of four individual reactions, as computed from the velocity coefficients of Table VIII, corrected to 49.80, 59.80 and 69.80°, respectively. For the calculations of $\log A$, E_{353} was used, and the k 's (water reactions) were divided by the concentration of water.

TABLE X

THE TEMPERATURE COEFFICIENT, ACTIVATION ENERGY AND FREQUENCY FACTOR FOR THE INDIVIDUAL REACTIONS

Velocity coefficient	$\frac{k_{240}}{k_{220}}$	$\frac{k_{230}}{k_{220}}$	$\left(\frac{k_{240}}{k_{220}}\right)^{1/2}$	E_{238}	E_{228}	E_{233}	$\log_{10} A^a$
	kcal./mole						
k_1^b	3.04	2.78	2.91	25.3	21.9	23.6	15.4
k_2^b	3.59	4.29	3.93	29.1	31.2	30.2	16.0
k_3^b	3.11	3.72	3.41	25.8	28.1	27.1	17.7
k_3^b	3.71	3.71	3.71	29.8	28.1	29.0	15.3

^a A is in units of liters per mole per hour. ^b Values calculated from the data of Table VIII.

It may be pointed out that the measured energy of activation at $[H^+] = 0.10$ and 0.15 in Table IX is less than the energy of activation of any of the reactions of $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$, given in Table X, which indicates that the hydrolysis of the $H_4P_2O_7$ molecule is coming in at these hydrogen-ion concentrations.

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