The Dissociation Constants and the Kinetics of Hydrolysis of Peroxymonophosphoric Acid[1a]

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Using a spectrophotometric technique, the successive acid ionization constants of H_3PO_5 have been found to be 8×10^{-2}, 3×10^{-6}, and $\sim 2 \times 10^{-13}$ at 25°. The hydrolysis of this peroxide to H_2O_2 and H_3PO_4 is first order in peroxy acid, and the rate increases with the concentration of added $HClO_4$. Rate constants, activation parameters, and other data suggest a mechanism involving nucleophilic attack by water on phosphorus in the species $H_4PO_5^+$ for the bulk of the hydrolysis process.

Introduction

The existence of two peroxyphosphoric acids was established in 1910 when Schmidlin and Massini prepared peroxydiphosphoric acid ($H_4P_2O_8$) and peroxymonophosphoric acid (H_3PO_5).[2] In contrast to the corresponding peroxysulfates, the chemistry of these peroxyphosphates has received relatively little attention. In this laboratory, the chemistry of the peroxyphosphates has been of interest. Studies of the aqueous chemistry of peroxydiphosphoric acid,[3] of the kinetics of the oxidation of bromide ion by H_3PO_5,[4] and of the decomposition of H_3PO_5[5] have been carried out. The present investigation involves a study of the kinetics of the acid hydrolysis

$$H_3PO_5 + H_2O \longrightarrow H_2O_2 + H_3PO_4$$
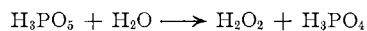
and a determination of the acid dissociation constants of H_3PO_5.

Experimental

Method of Preparation.—Several ways of preparing H_3PO_5 are described in the literature, and include: (1) the reaction of P_2O_5 with aqueous H_2O_2,[2] (2) the reaction of $H_4P_2O_7$ with H_2O_2,[2] and (3) electrolysis of solutions of phosphates containing fluoride and a trace of chromate between platinum electrodes.[6] More recently, there have been a group of patents dealing with the preparation of H_3PO_5 and its salts[7,8] and also some publications dealing with these materials.[9] We were, of course, not aware of the recent preparations,[7c–f,8] and the earlier preparations did not give the acid or salt in a reasonable state of either purity or stability. For this reason, a method of preparation was chosen whereby an aqueous solution of H_3PO_5 was obtained by the acid hydrolysis of a stable salt of $H_4P_2O_8$, *i.e.*

$$H_4P_2O_8 + H_2O \longrightarrow H_3PO_5 + H_3PO_4$$
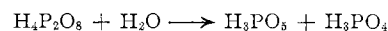
This approach is convenient, as a stable salt like $Li_4P_2O_8 \cdot 4H_2O$ can be prepared in high purity.[3,10]

Crude $K_4P_2O_8$ was prepared electrolytically using the procedure of Fichter and Gutzwiller[6] as modified by Crutchfield.[3] The gummy material obtained was converted to crystalline $Li_4P_2O_8 \cdot 4H_2O$ following the method of Chulski.[10] After several recrystallizations from water–methanol, a product was obtained which was 99.5% $Li_4P_2O_8 \cdot 4H_2O$ as determined by iodometric titration. A stock solution of approximately 0.2 M was prepared by dissolving 5.8 g. of $Li_4P_2O_8 \cdot 4H_2O$ in 100 ml. of water. This solution was filtered through a very fine sintered glass filter funnel and standardized by iodometric titration.[3] Solutions of approximately 0.1 N sodium thiosulfate and ceric sulfate were prepared and standardized using customary methods. Commercial chemicals used were reagent grade.

Equipment.—Absorption measurements were made at 25° on a Beckman Model DK-1 recording spectrophotometer using matched quartz cells. Measurements of pH were made using a Beckman Model G pH meter which was standardized before use with commercial certified buffer solutions.

Analytical Methods.—In the preparation of H_3PO_5, a small amount of H_2O_2 is also produced on further hydrolysis, *i.e.*

$$H_3PO_5 + H_2O \longrightarrow H_2O_2 + H_3PO_4$$
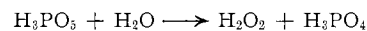
As a result of this further hydrolysis, a mixture of H_3PO_5, H_2O_2, and H_3PO_4 is always obtained.[11] The concentration of each of the two peroxides was determined using the following analytical procedures.

Peroxymonophosphoric Acid and Hydrogen Peroxide.—The sum of H_3PO_5 and H_2O_2 was determined iodometrically in a H_3PO_4–NaH_2PO_4 buffer at a pH of *ca.* 2. H_3PO_5 oxidizes I^- instantaneously at this pH. The oxidation of I^- by H_2O_2 is rather slow at this pH, but can be catalyzed by the addition of a trace amount of ammonium molybdate. An appropriately sized aliquot of the peroxide solution was added to an iodine flask containing 10 ml. of a freshly prepared 4% solution of KI, 5 drops of a 5% ammonium molybdate solution, and 50 ml. of the phosphate buffer. The flask was stoppered, the gutter was sealed with additional KI solution, and the contents were allowed to stand for 4 min. Under these conditions both peroxides oxidized the iodide ion quantitatively. When present, unhydrolyzed $H_4P_2O_8$ did not interfere in the analysis since its reaction with I^- is very slow at this pH. The liberated iodine was titrated with standard sodium thiosulfate to a starch end point.

(1) (a) Taken from the Ph.D. thesis of C. J. B., Brown University, 1962; (b) Eastman Kodak Fellow, 1961–1962.

(2) J. Schmidlin and P. Massini, *Ber.*, **43**, 1162 (1910).

(3) (a) M. M. Crutchfield, Ph.D. Thesis, Brown University, 1960; (b) M. M. Crutchfield and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 3533 (1960); (c) M. M. Crutchfield, chapter in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

(4) D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).

(5) E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *ibid.*, **85**, 2263 (1963).

(6) F. Fichter and E. Gutzwiller, *Helv. Chim. Acta*, **11**, 323 (1928).

(7) (a) E. W. Heiderich, U. S. Patent 2,765,216 (Oct. 9, 1953); (b) O. B. Mathre and D. M. Sowards, U. S. Patent 2,834,659 (March 25, 1957); (c) D. B. Lake and G. Mamantov, U. S. Patent 3,085,856 (March 11, 1958); (d) F. Beer and J. Müller, U. S. Patent 3,036,887 (July 23, 1959); (e) F. Beer and J. Müller, German Patent 1,143,491 (June 24, 1960); (f) J. Cremer and G. Müller-Schiedmayer, German Patent 1,148,215 (Aug. 9, 1961).

(8) The patent dates given are those for filing of the application. The dates of issue are later; *e.g.*, patent 7c was issued April 16, 1963.

(9) (a) G. Mamantov, J. H. Burns, J. R. Hall, and D. B. Lake, *Inorg. Chem.*, **3**, 1043 (1964); (b) P. W. Schenk, *Z. anorg. allgem. Chem.*, **326**, 139, 152 (1963).

(10) T. Chulski, Ph.D. Thesis, Michigan State University, 1953.

(11) Unless otherwise noted, the concentration of unhydrolyzed $H_4P_2O_8$ was always negligible.

Hydrogen Peroxide.—A cerimetric titration was used to determine the H_2O_2 concentration alone.[12] In the presence of added sulfuric acid, H_2O_2 reduces ceric ion quantitatively without interference from peroxymonophosphate. The end point was detected by the appearance of the yellow ceric ion color; a blank correction was necessary. It is important that this titration be carried out rapidly, for in the acid medium of the titration solution H_3PO_5 hydrolyzes to H_2O_2 and high titers may be obtained. No appreciable error was introduced if the flask was allowed to stand 3 min., however all titrations were completed within 2 min. after the aliquot was delivered.

Procedure. Spectrophotometric Runs.—Before each series of experiments, a fresh stock solution of H_3PO_5 was prepared by adding a 2.00-ml. aliquot of 6.00 M $HClO_4$ to a test tube containing 10.0 ml. of 0.189 M $Li_4P_2O_8$. The resulting solution was then placed in an oil bath at 55° and heated for 1 hr. Under these conditions, hydrolysis of the peroxydiphosphate was found to be more than 99% complete. Peroxymonophosphate constituted usually 95% of the active oxygen concentration, with the remaining active oxygen being due to H_2O_2. The test tube was then rapidly cooled to room temperature and to its contents were added 10.0 ml. of 2.5×10^{-6} M α,α'-dipyridyl and 33.0 ml. of either H_2O, dilute NaOH, or dilute $HClO_4$, the choice depending on the acidity desired. The stock solution thus prepared was analyzed using the procedures described above. Measurements of ultraviolet absorption as a function of pH were made on test solutions which were prepared as follows. Aliquots (10 ml.) of stock solutions were added to individual 25-ml. volumetric flasks. Additional $HClO_4$ or NaOH was added to the flask in order to adjust the pH to a desired value. Following dilution to the mark, the absorption and pH of the test solution were measured. Because of the instability of peroxymonophosphate, the measurements were made immediately following the preparation of each test solution. The presence of α,α'-dipyridyl was found to enhance the stability of these solutions during the course of the measurements.[5,13] The only species found to absorb significantly in the wave length region of interest were H_3PO_5 and H_2O_2. Knowing the H_2O_2 concentration and extinction coefficient, the total absorbance was corrected to give the absorbance due to peroxymonophosphate.

Hydrolysis Kinetic Runs.—Runs were carried out in glass-stoppered Pyrex volumetric flasks immersed in a constant-temperature water bath. The rates were measured over the range from 1.0 to 9.4 M $HClO_4$ and at temperatures of 25.0, 35.4, 48.5, and 61.0°. The temperature of the water bath was maintained to within ±0.05° at all temperatures except 61.0°, where it was ±0.2°. A solution of $Li_4P_2O_8$ of known concentration was thermally equilibrated in the reaction vessel while an appropriate volume of standard $HClO_4$ solution was equilibrated in a separate vessel. Time zero was usually noted when the acid solution was added with stirring to the reaction vessel. Aliquots (5-ml.) of reaction solution were withdrawn at intervals and analyzed for H_3PO_5 and H_2O_2. In several runs, the rapid hydrolysis of peroxydiphosphate to peroxymonophosphate was observed initially, however only those titers obtained after maximum conversion to peroxymonophosphate were used in rate constant calculations. The initial concentration of peroxydiphosphate was about 0.02 M in all runs. No attempt was made to control the ionic strength I in most kinetic runs. In one series of runs at different $HClO_4$ concentrations, however, the ionic strength was fixed at about 7.5 by the addition of $NaClO_4$.

For reasons discussed below, several kinetic runs were made on the acid hydrolysis of peroxydiphosphate to peroxymonophosphate. The procedure used in these runs was as follows: to 20.0 ml. of 8.0×10^{-2} M $Na_4P_2O_8$ obtained by conversion of $Li_4P_2O_8$ using an ion-exchange technique described by Crutchfield[3] were added 40.0 ml. of 0.14 M H_3PO_4 and 20.0 ml. of 0.40 M NaF solution. All reactants were thermally equilibrated at
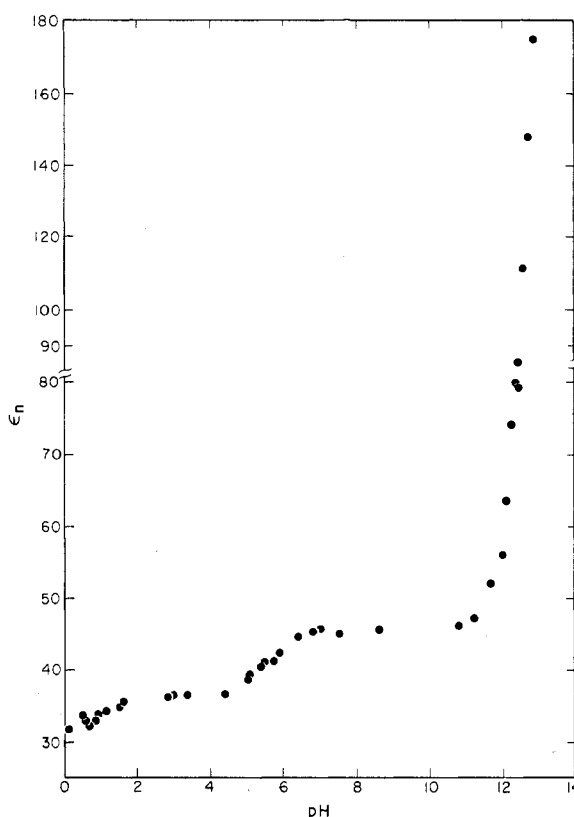
(12) *Cf.* F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

(13) C. J. Battaglia, Ph.D. Thesis, Brown University, 1962.

Figure 1.—Variation of ϵ_n with pH at 240 mμ and 25°.

62° before mixing. The resulting solution was added to a Pyrex glass-stoppered reaction vessel and placed in a constant-temperature bath also at 62°. The rate of formation of H_3PO_5 was followed using procedures similar to those described above. The pH of the reaction solution was measured at the beginning and end of each run.

Results and Discussion

Acid Dissociation Constants.[14]—The ultraviolet absorption spectrum of H_3PO_5 consists of a continuous steady rise in absorbance beginning at about 300 mμ with no maximum being reached down to 230 mμ.[15] Like other peroxy acids, the spectrum of aqueous H_3PO_5 was found to shift toward longer wave lengths when sodium hydroxide was added. The variation of the absorption with pH at λ 240 mμ is shown in Figure 1. The ordinate of Figure 1 is an apparent extinction coefficient, ϵ_n, which for each test solution is defined by Beer's law

$$\epsilon_n = \frac{A_P}{[P]_n b} \tag{1}$$

where A_P is the absorbance due to peroxymonophosphate, $[P]_n$ is the total peroxymonophosphate concentration of the nth test solution, and b is the cell length, 1 cm. in all experiments. It is apparent from Figure 1

(14) In view of the fact that our solutions contained H_3PO_4 as well as H_3PO_5 and that these two acid species have similar ionization constants, the normal method of pK_a determination by pH titration could not be employed.
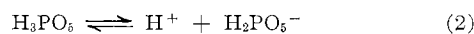
(15) The ultraviolet absorption spectra of a variety of peroxides, both inorganic and organic, were investigated, and the data are tabulated elsewhere.[13] It was found that all compounds of the type ROOR′, where R and R′ are substituents, have extinction coefficients of *ca.* 1 at 300 mμ, and that the coefficient increases monotonically to *ca.* 50 at 230 mμ. Peroxyanions of the type ROO⁻ show a similar structureless absorption pattern; however, the extinction coefficients are an order of magnitude larger.

that as the pH of the solution increases the absorbing peroxymonophosphate undergoes several distinct changes which result in increases in ϵ_n. These changes are reasonably interpreted in terms of proton dissociations.
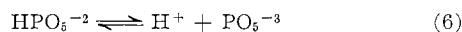
Peroxymonophosphoric acid, like phosphoric acid, is tribasic. One may write the equilibria and appropriate equilibrium constant expressions

$$H_3PO_5 \rightleftharpoons H^+ + H_2PO_5^- \quad (2)$$

$$K_{1a} = [H^+][H_2PO_5^-]/[H_3PO_5] \quad (3)$$

$$H_2PO_5^- \rightleftharpoons H^+ + HPO_5^{-2} \quad (4)$$

$$K_{2a} = [H^+][HPO_5^{-2}]/[H_2PO_5^-] \quad (5)$$

$$HPO_5^{-2} \rightleftharpoons H^+ + PO_5^{-3} \quad (6)$$

$$K_{3a} = [H^+][PO_5^{-3}]/[HPO_5^{-2}] \quad (7)$$

for the expected reactions in aqueous solution. We can relate the spectral changes to the equilibria given by eq. 2, 4, and 6. Thus, in the pH region from 0.2 to 4, the first dissociation is reflected by the increase in ϵ_n. At the first plateau, the peroxymonophosphate is predominantly $H_2PO_5^-$. Similarly, in the regions of pH from 4 to 7 and from 11 to 13, the corresponding changes in ϵ_n reflect the second and third dissociations, respectively. Thus, the second plateau corresponds to the region of pH where HPO_5^{-2} is the predominant peroxymonophosphate species; the plateaus corresponding to H_3PO_5 and PO_5^{-3} lie outside of the acidity range investigated. Over the entire pH range investigated, A_P of eq. 1 may be expressed as

$$A_P = [H_3PO_5]\epsilon_{H_3PO_5} + [H_2PO_5^-]\epsilon_{H_2PO_5^-} +$$
$$[HPO_5^{-2}]\epsilon_{HPO_5^{-2}} + [PO_5^{-3}]\epsilon_{PO_5^{-3}} \quad (8)$$

where the subscripted ϵ represents the extinction coefficient of the appropriate peroxymonophosphate species. In order to obtain K_a values from the spectrophotometric data, the following three assumptions were made regarding the concentrations of the various peroxymonophosphate species: (1) in the pH interval from 0 to 2, the absorbance, A_P, is due only to H_3PO_5 and $H_2PO_5^-$, *i.e.*, $[HPO_5^{-2}] \simeq [PO_5^{-3}] \simeq 0$; (2) in the pH interval from 4 to 7, $[H_3PO_5] \simeq [PO_5^{-3}] \simeq 0$; and (3) above pH 11, $[H_3PO_5] \simeq [H_2PO_5^-] \simeq 0$. The validity of these assumptions is discussed below. Using assumption 1 and eq. 8, for each test solution in the pH interval from 0 to 2 we have

$$[P]_n = [H_3PO_5]_n + [H_2PO_5^-]_n \quad (9)$$

and

$$A_{P,n} = [H_3PO_5]_n\epsilon_{H_3PO_5} + [H_2PO_5^-]_n\epsilon_{H_2PO_5^-} \quad (10)$$

Since $\epsilon_n[P] = A_{P,n}$, by appropriate substitution and rearranging we obtain the expression

$$\frac{[H_3PO_5]_n}{[H_2PO_5^-]_n} = \frac{\epsilon_{H_2PO_5^-} - \epsilon_n}{\epsilon_n - \epsilon_{H_3PO_5}} \quad (11)$$

Substitututing eq. 11 into eq. 3 and rearranging leads to the expression

$$\left(\frac{1}{K_{1a}}\right)\epsilon_n - \left(\frac{\epsilon_{H_3PO_5}}{K_{1a}}\right) = \frac{\epsilon_{H_2PO_5^-} - \epsilon_n}{[H^+]_n} \quad (12)$$
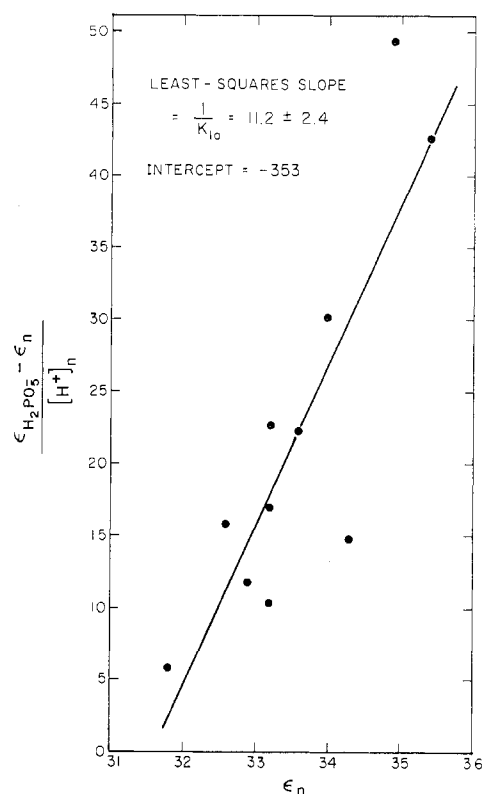

Figure 2.—Determination of K_{1a} using absorbance data at 240 mμ and eq. 12 in text.

Of the five quantities in eq. 12, ϵ_n and $[H^+]_n$ were measured experimentally while $\epsilon_{H_2PO_5^-}$ was obtained by averaging the values of ϵ_n in the first plateau of the ϵ_n vs. pH plot. Equation 12 predicts that a plot of $(\epsilon_{H_2PO_5^-} - \epsilon_n)/[H^+]_n$ vs. ϵ_n should be a straight line with a slope of $1/K_{1a}$ and an intercept $\epsilon_{HP_3O_5}/K_{1a}$. Figure 2 shows the fit of the absorption data at 240 mμ to this equation. The best straight line was obtained by least squares. To increase the reliability of this value, an identical treatment was carried out on data obtained at 230 mμ. Table I shows that the values of K_{1a} obtained at both wave lengths are in reasonable agreement.

Using assumptions 2 and 3 in the pH intervals from 5.0 to 6.40 and from 10.8 to 12.90, respectively, together with similar mathematical derivations, we obtain the expressions

$$K_{2a} = [H^+]_n\left(\frac{\epsilon_n - \epsilon_{H_2PO_5^-}}{\epsilon_{HPO_5^{-2}} - \epsilon_n}\right) \quad (13)$$

and

$$\epsilon_n = -\frac{1}{K_{3a}}\left\{[H^+]_n(\epsilon_n - \epsilon_{HPO_5^{-2}})\right\} + \epsilon_{PO_5^{-3}} \quad (14)$$

The value of $\epsilon_{HPO_5^{-2}}$ was obtained by averaging the values of ϵ_n in the second plateau of the ϵ_n vs. pH plot. Fitting the absorbance data in the pH interval from 5.0 to 6.4 to eq. 13 gave values of K_{2a} which are summarized in Table I. Included are values of K_{2a} obtained from data collected at 230, 240, and 250 mμ. The fit of the absorbance data in the pH interval

TABLE I

SUMMARY OF DISSOCIATION CONSTANTS OF
PEROXYMONOPHOSPHORIC ACID AT 25°

Acid	λ, mμ	Dissociation constant[a]	Remarks
H_3PO_5	230	$10^2 K_{1a} = 7.5 \pm 1.3$	$I \simeq 0.2$
H_3PO_5	240	$10^2 K_{1a} = 8.9 \pm 1.9$	$I \simeq 0.2$
$H_2PO_5^-$	230	$10^6 K_{2a} = 3.16 \pm 0.42$	$I = 0.14 \pm 0.01$
$H_2PO_5^-$	240	$10^6 K_{2a} = 3.01 \pm 0.65$	$I = 0.14 \pm 0.01$
$H_2PO_5^-$	250	$10^6 K_{2a} = 3.57 \pm 1.15$	$I = 0.14 \pm 0.01$
HPO_5^{-2}	240	$10^{13} K_{3a} = 1.6 \pm 0.5$	I varies[b]; see ref. 13
HPO_5^{-2}	250	$10^{13} K_{3a} = 1.6 \pm 0.5$	I varies[b]; see ref. 13

[a] Uncertainties given for K_{1a} and K_{2a} are standard deviations and for K_{3a} are estimated uncertainties. [b] Average $I \simeq 0.15$.

from 10.8 to 12.9 to eq. 14, where both K_{3a} and $\epsilon_{PO_5^{-3}}$ are unknown, was found to be poor. A lower limit for pK_{3a} was estimated by assuming a value of $\epsilon_{PO_5^{-3}}$ equal to the largest value of ϵ_n observed, *i.e.*, that value of ϵ_n at pH 12.90. Everett and Minkoff[16] found in the case of organic hydroperoxides at 240 mμ that $\epsilon_{ROOH} = 0.1\epsilon_{ROO^-}$. Similar results were obtained here,[15] thus this relationship appears valid for other peroxy acids. Applying it to peroxymonophosphate, an upper limit for pK_{3a} was estimated. The results are summarized in Table I. It is worth noting that the large change in ϵ on going from HPO_5^{-2} to PO_5^{-3} is strong evidence that this third ionization process is that due to the proton attached to peroxide oxygen.

It is to be noted that in this study activity effects have been neglected. However, as can be seen from Table I the data used to calculate K_{2a} were obtained at $I = 0.14 \pm 0.01$. Even under this condition pK_{2a} shows an uncertainty of ± 0.1, which is about the same uncertainty as obtained in the evaluation of K_{1a} where the ionic strength was not held constant. Because of this uncertainty, even under controlled conditions, this spectrophotometric method is not suitable for the evaluation of the dissociation constants of H_3PO_5 as a function of ionic strength in order to obtain thermodynamic constants.

The results tabulated in Table I indicate that the dissociation constants of H_3PO_5 are well separated; hence our assumptions concerning the spacings of the pK_a values which served as a basis in our division of the spectrophotometric titration curve are valid. Comparing the acid strength of peroxymonophosphoric acid ($pK_1 = 1.1$, $pK_2 = 5.5$, and $pK_3 = 12.8$) to phosphoric acid ($pK_1 = 2.1$, $pK_2 = 7.1$, and $pK_3 = 12.3$)[17] while keeping in mind the fact that our constants were determined at finite ionic strength, we find that K_1 and K_2 for H_3PO_5 are larger than the corresponding constants for H_3PO_4. Other cases where the peroxy acid is more acidic than the related oxy acid are telluric acid[18] and boric acid.[19] One can

(16) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

(17) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p. 481.

(18) J. E. Earley, D. Fortnum, A. Wojcicki, and J. O. Edwards, *J. Am. Chem. Soc.*, **81**, 1295 (1959).

(19) (a) H. Menzel, *Z. physik. Chem.*, **105**, 402 (1923); (b) J. O. Edwards, *J. Am. Chem. Soc.*, **75**, 6154 (1953).
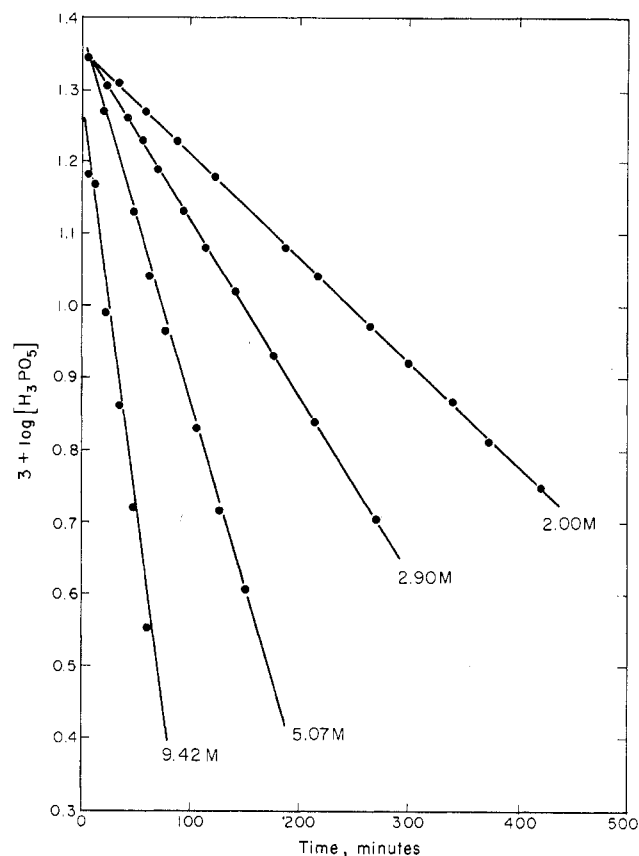

Figure 3.—Sample first-order hydrolysis rate plots at various perchloric acid concentrations at 48.5°.

explain this acid strengthening effect by the higher electronegativity of the OOH group as compared to an OH group. This is exemplified by the acid strength of H_2O_2 which is much greater than that of water.

The only previous estimates of the ionization constants for H_3PO_5 are based on kinetic data. At ionic strength 1.5, $K_1 \geq 5 \times 10^{-2}$ and $K_2 \simeq 1.4 \times 10^{-5}$ are reported[4]; as expected from the ionic strength difference, K_2 from the rate data is larger than that from the spectrophotometric data. The constant pK_3 was found to be 12.5 ± 0.2 in the rate of decomposition study[5,13]; this is in fair agreement with the value obtained in this study.

Hydrolysis Kinetics.—At all perchloric acid concentrations and temperatures investigated, the rate of the reaction

$$H_3PO_5 + H_2O \longrightarrow H_2O_2 + H_3PO_4$$
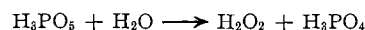
was found to obey the rate law

$$\frac{-d[H_3PO_5]}{dt} = k_1[H_3PO_5]$$

where k_1 is the pseudo-first-order rate constant dependent upon both the temperature and acidity of the reaction solution. Generally the reaction was followed over the course of at least two half-lives, and plots of log $[H_3PO_5]$ against time were linear. Figure 3 illustrates the data for several typical runs. Values of k_1 were calculated from the slopes of these linear plots. Significant deviation from linearity, however, was ob-

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF PEROXYMONOPHOSPHORIC ACID

Temp., °C.	$[H^+]^a$	$10^5 k_1$, sec.$^{-1}$
25.0	9.42	4.80
25.0	9.42	4.91
25.0	7.62	3.91
25.0	7.62	3.95
25.0	5.06	2.26
25.0	5.06	2.10
25.0	4.05	1.54
35.4	9.42	12.9
35.4	7.62	10.7
35.4	5.07	6.03
35.4	4.05	4.22
35.4	2.90	2.55
35.4	2.0	1.55
35.4	1.4	1.00
35.4	1.0	0.622
48.5	9.42	42.2
48.5	7.59	33.4
48.5	5.07	19.8
48.5	4.05	15.2
48.5	2.90	9.44
48.5	2.0	5.45
48.5	1.4	3.63
48.5	1.0	2.27
61.0	2.90	29.4
61.0	2.0	17.7
61.0	1.4	12.9
61.0	1.0	7.83

^{a} Perchloric acid concentration in moles liter^{-1}.

TABLE III

EFFECT OF $NaClO_4$ ON HYDROLYSIS RATE AT 48.5°

$[H^+]^a$	$[NaClO_4]^a$	I^b	$10^5 k_1$, sec.$^{-1}$	$10^5 k_1/[H^+]$, M^{-1} sec.$^{-1}$
7.59	None	7.6	33.4	4.40
5.89	1.46	7.4	29 ± 1^c	4.9 ± 0.2
5.1	2.44	7.5	12 ± 1^c	4.5 ± 0.2
5.07	2.44	7.5	24 ± 1^c	4.7 ± 0.2
2.82	4.50	7.3	14 ± 1^c	5.0 ± 0.3

^{a} Moles liter^{-1}. ^{b} Computed from the perchloric acid and sodium perchlorate concentrations. ^{c} Estimated uncertainty in initial slope of rate plot leads to the uncertainty in value of k_1.

TABLE IV

THE EFFECT OF ACIDITY ON ENERGY OF ACTIVATION^a

$[H^+]$, M	E_a, kcal. mole^{-1}
1.0	20.2
1.4	20.4
2.0	19.4
2.90	19.5
4.05	18.6
5.07	17.6
7.6	17.3
9.42	17.5

^{a} The values of E_a were obtained from rate data taken at three temperatures over a spread of at least 23° (see Table II). The estimated uncertainty is ± 1.0 kcal. mole^{-1}.

served in the series of runs where sodium perchlorate was added, and the cause of this deviation is discussed below.

The values of k_1 obtained were found to increase markedly with increasing $[H^+]$ as may be seen in Table II. However, this dependence fits neither of the two limiting forms of the Hammett–Zucker hypothesis,[20] *i.e.*, a linear dependence of rate on $[H^+]$ or on Hammett's acidity function, H_0. When log k_1 was plotted against log $[H^+]$ at each temperature, a reasonably straight line of slope 1.3 was obtained. The data may be treated in the manner suggested by Bunnett[21]; a plot of (log $k_1 + H_0$) against the activity of water is linear with a slope of 5.2 in the acid range from 1 to 5 M, but the plot shows significant curvature in the direction of decreasing slope at higher acidities. The value of the slope obtained here is similar to those found for other phosphate hydrolyses in this acidity range, suggesting a similar mechanism.

When sodium perchlorate was added, in order to test the effect of an inert salt on the rate, both a positive salt effect on the hydrolysis rate and an increased peroxide decomposition (loss of active oxygen) were observed. The decomposition caused curvature in the log $[H_3PO_5]$ against time plots and made it difficult to evaluate the exact rate enhancement due to the salt. Although fair estimates of k_1 were obtained from initial slopes of the rate plots in these cases, a thorough study of salt effects was not feasible. In all runs with added

$NaClO_4$, the ionic strength was maintained at about 7.5. Table III summarizes the results obtained.

The lack of a linear proportionality between k_1 and $[H^+]$ as seen in Table II is believed to be due to an electrolyte effect of the fully ionized $HClO_4$, since in the series of runs at constant ionic strength tabulated in Table III the rate is approximately linear with $[H^+]$. Thus, the slope of 1.3 obtained when log k_1 is plotted against log $[H^+]$ for data of Table II reflects not only the first-order dependence of the rate on $[H^+]$, but also a salt effect due to the increasing $HClO_4$ concentration. In some hydrolysis reactions carried out in concentrated salt solutions, which involve a neutral molecule and an ion reacting in the slow step, the rate constant has been found to be best represented[22] by an equation of the form

$$\ln k = \ln k_0 + \beta I$$

where k and k_0 are rate constants at ionic strengths I and zero, respectively, and β is an empirical constant. Applying this type of treatment to our data at 48.5°, k_1 may be expressed as

$$k_1 = k_2 [H^+] e^{\beta I}$$

where k_2 is a second-order rate constant. The values of k_2 and β, calculated from the rates of hydrolysis in 5.07 M $HClO_4$ and in that acid plus 2.44 M $NaClO_4$, are 2.62×10^{-5} M^{-1} sec.$^{-1}$ and 0.079, respectively. The line in Figure 4 shows the fit of the above equation to the rate data for $HClO_4$ media alone at 48.5° using the above values of k_2 and β. It is to be noted that the magnitude and sign of the salt effect of $HClO_4$ on the hydrolysis rate

(20) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).
(21) J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960); *ibid.*, **83**, 4956, 4968, 4973, 4978 (1961).
(22) *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 139, 140.
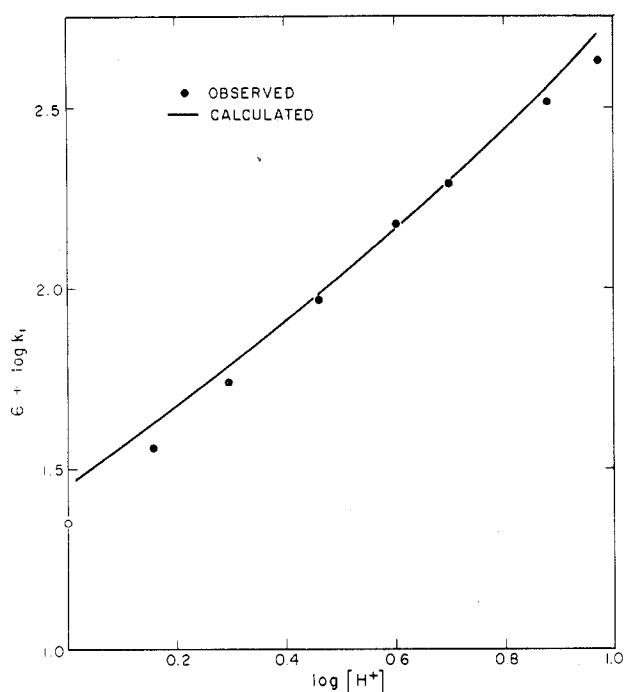
Figure 4.—Observed and calculated dependence of hydrolysis rate on perchloric acid concentration at 48.5°.

are assumed to be identical with those of $NaClO_4$. The use of this assumption gives reasonable albeit not perfect agreement.

Apparent activation energy values E_a, calculated at each $HClO_4$ concentration from Arrhenius plots, are summarized in Table IV. The E_a values decrease with increase in the acid concentration and are similar to values of E_a found for the acid-catalyzed hydrolysis of peroxydiphosphoric acid[3] and of simple P–O–P linkages in chain polyphosphates.[23] Thermodynamic activation parameters for the rate of hydrolysis in 1 M $HClO_4$ are $\Delta H^* = 19.6$ kcal. mole^{-1} and $\Delta S^* = -19$ cal. mole^{-1} deg.$^{-1}$ for a standard state of 1 M and 48.5°. The variation of E_a with acidity as seen in Table IV is real. Probably it represents the influence of the change in water activity on the relative solvation of ground state and transition state.

From a consideration of the pK_a values, one can show that in the range from 1.0 to 9.4 M $HClO_4$, peroxymonophosphate is present predominantly as the neutral species; there is a small contribution at lower acidity to the total peroxymonophosphate concentration from the monoanion $H_2PO_5^-$ ($\sim 10\%$ at 1 M $HClO_4$ at 25°). In the hydrolytic reactions of organic phosphate esters,[24] and also in the exchange reaction of O^{18} between water and orthophosphate in the dilute solution,[25] three reaction species are postulated in order to account for the observed rate–pH profile. These species are: the monoanion $ROPO_3H^-$, the neutral molecule $ROPO_3H_2$, and the conjugate acid of the neutral molecule $RO-PO_3H_3^+$.

(23) Reference 17, pp. 452–458.

(24) (a) C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3574, 3588 (1958); (b) C. A. Bunton, M. M. Mhala, K. G. Oldham, and C. A. Vernon, *ibid.*, 3293 (1960); (c) W. P. Jencks, *Brookhaven Symp. Biol.*, **No. 15**, 134 (1962).

(25) C. A. Bunton, D. R. Llewellyn, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.*, 1636 (1961).

The rates of phosphate monoanion hydrolyses are little dependent on the nature of the leaving anion[26] and are measurable at $\sim 100°$. Using these data it is estimated that the contribution of the monoanion hydrolysis to the observed hydrolysis rate in the acid range 1 to 9 M is negligibly small.

The rate of peroxymonophosphate decomposition increases as the acidity decreases, therefore hydrolysis is not experimentally observable at acidities much less than 1 M, for decomposition (albeit slow) is the dominant reaction. We cannot, for this reason, directly measure the rate of hydrolysis of the neutral molecule. The data in Tables II and III are for acidities where the bulk of the reaction is carried by the conjugate acid species. In fact, the data in both tables are quite compatible with the assumption that the conjugate acid is the only species that contributes significantly to the rate of hydrolysis in the range of acidities available. Thus the measured rate has been treated as being due only to the acid-catalyzed path.

After allowance is made for the salt effect, the rate is approximately proportional to [H$^+$], and the hydrolysis is formulated as a nucleophilic attack of a water molecule on the phosphorus atom in the conjugate acid species in the rate-determining step, i.e.

$$H_3PO_5 + H^+ \qquad H_4PO_5^+$$
$$H_4PO_5^+ + H_2O \longrightarrow H_3PO_4 + H_2O_2 + H^+$$
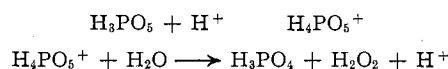
It is well known that fluoride ion is an exceptionally good nucleophile in displacement reactions on tetrahedral phosphorus.[24c,27] On this basis, we felt that addition of fluoride ion to acid solutions of peroxydiphosphate would accelerate the production of peroxymonophosphate if the hydrolysis occurs by a direct bimolecular nucleophilic displacement rather than a unimolecular decomposition of the peroxydiphosphate followed by a rapid attack of the nucleophile on the phosphorus atom of the intermediate. Indeed, such was found to be the case. The pseudo-first-order rate constant for the hydrolysis of peroxydiphosphate to peroxymonophosphate at 62°, pH 4.6, and in the presence of 0.1 M NaF was found to be 5.5×10^{-5} sec.$^{-1}$. Extrapolation of Crutchfield's data[3] at 63° to pH 4.7 yields a pseudo-first-order rate constant of 0.42×10^{-5} sec.$^{-1}$.[28] Thus the rate enhancement by more than a factor of ten, which is observed when the reaction solution contains fluoride ion, suggests a bimolecular nucleophilic displacement reaction. Peroxydiphosphate was used in this experiment because the analogous experiment with peroxymonophosphate is not possible on account of the decomposition of peroxymonophosphate. However, since both peroxyphosphates show similar kinetic behavior, our conclusion is presumably applicable to peroxymonophosphate. Since Crutchfield[3] found no evidence for general acid catalysis, it appears that a

(26) C. A. Vernon, Special Publication No. 8, The Chemical Society, London, 1957, p. 17.

(27) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(28) A control experiment without added fluoride was made at pH 2.2 and the pseudo-first-order rate constant obtained was 9.7×10^{-6} sec.$^{-1}$. This value compares favorably with the value 12×10^{-6} sec.$^{-1}$ interpolated from Crutchfield's data.

second reaction, not involving hydrolysis, is introduced by the presence of fluoride ion. In view of this, together with the observation that the pH of the reaction solutions containing fluoride ion increased from 4.6 to 4.9 over the course of about 40% reaction, it is felt that the observed acceleration is due to the reaction

$$F^- + O\text{-}P\text{-}OO\text{-}P\text{-}O^{-2} \xrightarrow{H_2O} F\text{-}P\text{-}O^- + HOO\text{-}P\text{-}O^- + OH^-$$
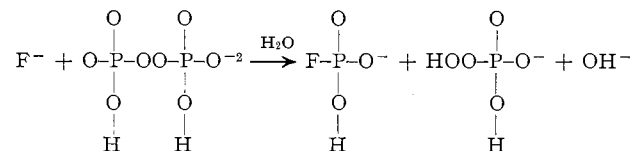
for which we have some evidence.[29]

Table V lists values of rate constants for a number of acid-catalyzed hydrolyses of substituted phosphates carried out under similar reaction conditions. It is particularly noteworthy that the rate obtained in this research, with RO = HOO, is three to four orders of magnitude larger than that for any of the other substituents. Thus the perhydroxyl ion is an excellent leaving anion, being better than the less basic phenolate ion; this observation deserves particular comment.

It is well established that the anions of monosubstituted peroxides are remarkably reactive nucleophiles,[27] and the available data suggest that this is a transition-state effect rather than abnormal binding

(29) The actual presence of the monofluorophosphate ion in such experiments has been shown by Miss Reet Paju and Mr. Bruce Fitch of this laboratory. Identification was made by preferential precipitation and identification of the silver salt Ag$_2$FPO$_3$ and by n.m.r. spectra of the solutions after reaction was complete.

TABLE V

RATE CONSTANTS FOR THE ACID-CATALYZED HYDROLYSES OF PHOSPHATES OF THE TYPE ROPO$_3$H$_2$[a]

RO[b]	Rate constant	Ref.
OH	$0.55 \times 10^{-6}\ M^{-1}\ sec.^{-1}$	25
OCH$_3$	$1 \times 10^{-6}\ M^{-1}\ sec.^{-1\,c}$	24a
OC$_6$H$_5$	$<4 \times 10^{-6}\ M^{-1}\ sec.^{-1}$	26
OOH	$1900 \times 10^{-6}\ sec.^{-1\,d}$	This work

[a] At 100° in aqueous solution. [b] Leaving anion is RO$^-$. [c] For P–O bond fission. [d] At 1.0 M HClO$_4$; estimated using $k_1 = 7.83 \times 10^{-5}$ sec.$^{-1}$ at 61° and $E_a = 20.2$ kcal. mole^{-1}.

strength in the product. This being the case, it is a consequence of the law of microscopic reversibility that peroxy anions should be good leaving groups in displacement reactions. This is exactly what is observed, for both H$_3$PO$_5$ and H$_4$P$_2$O$_8$ hydrolyze rapidly in comparison with other substituted phosphates. It seems reasonable to conclude that the "alpha effect"[27] will also be observed with leaving groups in nucleophilic displacements.

All of the data obtained here (rates, acid dependence, activation parameters, fluoride ion catalysis, etc.) can be readily explained by a mechanism involving attack of water as a nucleophile on the phosphorus atom in the peroxyphosphates.

Linear Deammonation Products of Sulfamide and Their Derivatives[1]

BY PIERO NANNELLI, AMEDEO FAILLI, AND THERALD MOELLER[2]

Although both imidodisulfuric diamide (imidodisulfamide) and diimidotrisulfuric diamide are cleaved by phosphorus(V) chloride, the analogous 3-methylimidodisulfuric diamide and 3,5-dimethyldiimidotrisulfuric diamide react smoothly with this reagent to yield the highly reactive and synthetically useful bis(trichlorophosphazo) derivatives. The chlorine atoms in these compounds are readily replaced by phenyl and phenoxy groups *via* nucleophilic substitution, with the formation of more hydrolytically stable products. An analysis of the infrared spectra of a number of these derivatives has permitted assignments of observed frequencies to the significant structural units. Data on other physical properties are given also.

The synthesis of phosphazo chlorides by the reaction of sulfamide or its N,N-dialkyl derivatives with phosphorus(V) chloride was first reported by Kirsanov.[3,4] This type of reaction and the properties of its products have been investigated more recently and in considerable detail by Moeller and Vandi.[5] It has been of

(1) Presented to the Inorganic Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1964.
(2) To whom correspondence should be directed.
(3) A. V. Kirsanov, *Zh. Obshch. Khim.*, **22**, 1346 (1952).
(4) A. V. Kirsanov and Z. D. Nekrasova, *ibid.*, **27**, 1253 (1957).
(5) T. Moeller and A. Vandi, *J. Org. Chem.*, **27**, 3511 (1962).

interest to extend the latter study to the synthesis of phosphazochlorides from the linear imidopolysulfamides that form as deammonation condensation products of sulfamide and to an evaluation of the physical and chemical characteristics of these compounds.

Although the —NH$_2$ groups of both imidodisulfuric diamide (IV) and diimidotrisulfuric diamide (VII) undergo the Kirsanov reaction with phosphorus(V) chloride, reaction of the NH groups results in cleavage of the sulfur–nitrogen bonds. This difficulty is obvi-