The Ce(IV)–H_3PO_3[14] reaction has been found to have common characteristics with this reaction, *e.g.*, complex formation and first-order hydrogen ion catalysis, but to proceed at much slower rates.

(14) R. L. Carroll, unpublished results.

Acknowledgments. We wish to thank Professor Robert E. Harris of this laboratory for helpful discussion on this problem, and Professor David E. Troutner for use of the counting facilities in the Radiochemical Laboratory of the Chemistry Department.

The Kinetics and Mechanism of the Hydrolysis of Pyrophosphite

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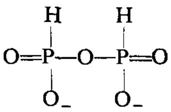
Abstract: The kinetics of the hydrolysis of pyrophosphite has been investigated over an extensive pH range. The rate law for the reaction can be expressed as

$$-\text{rate}/[\mathrm{H_2P_2O_5^{-2}}] = k_0 + \sum_{\mathrm{a}} k_{\mathrm{a}}(\mathrm{HA})_{\mathrm{a}} + \sum_{\mathrm{b}} k_{\mathrm{b}}(\mathrm{B})_{\mathrm{b}}$$

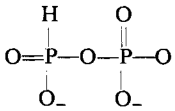
where k_a and k_b are the catalytic coefficients and $(\mathrm{HA})_a$ and $(\mathrm{B})_b$ are the concentrations of all Brønsted acids and Lewis bases, respectively. The catalytic coefficients for several carboxylic acids and a variety of bases are reported along with the temperature coefficients for the specific rate constants for the hydrogen ion and hydroxide ion. Evidence for the formation of intermediate species by the base catalysis reaction was obtained by high resolution P^{31} nmr spectra of partially hydrolyzed pyrophosphite solutions. On the basis of the kinetics and nmr studies and previously reported observations, the mechanism of the hydrolysis reaction is discussed.

Although the sodium salt of pyrophosphorous acid, $Na_2H_2P_2O_5$, has been known[1] since 1888, the kinetics of its hydrolysis has never been satisfactorily defined. The disodium salt is very soluble in water and the pH of its aqueous solution is about neutral. This is the only evidence at present regarding the acid strength of pyrophosphorous acid.[2] The symmetrical pyrophosphite anion undergoes hydrolysis[3–6] to 2 moles of orthophosphite, and the structure has been shown to be[7]



$$\mathrm{O{=}\overset{\displaystyle H}{\underset{\displaystyle O_-}{P}}{-}O{-}\overset{\displaystyle H}{\underset{\displaystyle O_-}{P}}{=}O}$$

The complexity of the hydrolysis reaction is indicated by the study of Blaser and Worms,[6] where they reported large effects due to certain salts, and by the studies of other investigators[1,3–5] who did not arrive at a rate law defining the reaction. Several of these salts react with the pyrophosphite ion to give products other than the orthophosphite ion; *e.g.*, the fluoride ion reacts to give the monofluorophosphite ion, and the orthophosphate ion reacts in neutral solution to give the isohypophosphate ion



$$\mathrm{O{=}\overset{\displaystyle H}{\underset{\displaystyle O_-}{P}}{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O_-}{P}}{-}O^-}$$

a process called transanhydrization by Blaser.[6,8] We have found other examples of this type which will be reported in this paper.

The pyrophosphite ion, unlike the condensed phosphates, has been reported to show very weak complexing ability with cations in aqueous solution,[9] indicating an absence of chelation stabilization. This difference has been interpreted in terms of less π bonding in the P–O–P linkage of the pyrophosphite ion which should relate to the hydrolytic instability.

The pyrophosphite species is of special interest to the field of phosphorus chemistry because its behavior typifies much of the chemistry of condensed species of the lower oxidation states of phosphorus. Because of the importance of the hydrolysis reaction itself in understanding the nature of the P–O–P linkage, and the sparsity of thorough kinetics studies in this realm of phosphorus chemistry, contributions in this area are sorely needed.

Experimental Section

Materials. Sodium pyrophosphite was prepared by the method described by Amat.[1] The material was assayed by iodine titration, the results of which were confirmed by P^{31} nmr spectra of concentrated water solutions. Of the phosphorus present, 95.5% was in the form of pyrophosphite and 4.5% was present as phosphite. All other chemicals were of reagent grade quality.

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(1) L. Amat, *Compt. Rend.*, **106**, 1351, 1400 (1888).

(2) S. Ohashi in "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 132–134.

(3) L. Amat, *Compt. Rend.*, **108**, 1056 (1889).

(4) L. Amat, *ibid.*, **112**, 527, 614 (1891).

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(6) B. Blaser and K. H. Worms, *Z. Anorg. Allgem. Chem.*, **312**, 146 (1961).

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Analytical Method. The analysis of pyrophosphite in the presence of phosphite was carried out by a procedure which was a modification of the method employed by Jones and Swift for the determination of phosphite in the presence of hypophosphite.[10]

The reaction of iodine with phosphite in approximately neutral solution occurs very rapidly while the reaction with pyrophosphite is very slow under these conditions. The analysis of phosphite was conducted in a solution buffered with a maleic acid buffer between pH 6 and 7. Our experiments have shown that the phosphate buffer used by Jones and Swift could not be employed because of the rapidity of the reorganization reaction between phosphate and pyrophosphite. The present study indicates that pyrophosphite hydrolyzes very slowly in buffered solutions of maleic acid. Hence the phosphite ion concentration can be determined in the presence of the pyrophosphite ion in this buffer system.

The usual analysis of a 0.05-g sample of sodium phosphite is described below. Oxygen was removed from a flask containing 25 ml of a 1 *M* maleic acid buffer at a pH between 6 and 7 by passing N_2 through the solution for several minutes. Standardized iodine solution (20 ml) and a 25-ml aliquot of the reaction mixture were then added to the flask. The flask was then stoppered and stored in the dark for 15 min before acidifying with 5 ml of 6 *N* acetic acid and titrating with a standardized thiosulfate solution to the starch end point. This method gives phosphite concentrations to about ±0.5%.

The pyrophosphite concentration was determined as the difference between the total phosphorus in the +3 oxidation state and the phosphorus present as phosphite. The former was determined after hydrolyzing all the pyrophosphite to phosphite in concentrated HCl.

Rate Measurements. The kinetics experiments were conducted at temperatures between 0 and 30° in a thermostated bath controlled in this range to ± 0.1°.

The acidity between pH 2 and 10 was measured by a Beckman Expanded Scale pH meter. The pH of the reaction mixture was measured after approximately one half-life.

In strong acid or base solutions the concentration of hydrogen ion or hydroxide ion was adjusted with standardized stock solutions.

For reactions having a half-life of 0.5 hr or more, the transfer of aliquots was made by pipets. For faster reactions the transfer was made by employing a syringe provided with a large delivery tip for rapid withdrawal and ejection of aliquots. For rapid reactions a thermostated reaction vessel equipped with a magnetic stirrer for rapid mixing was employed. At uniform intervals during the course of the reaction, five to seven aliquots were withdrawn for analysis. Zero time was taken at the time of adding a known amount of pyrophosphite solution (5–10 ml) to the temperature-equilibrated reaction mixture.

Sodium chloride was used to maintain unit ionic strength throughout this study. No interaction due to sodium ions is expected based upon the very weak complexing ability displayed by the pyrophosphite with the transition metal ions.[9]

Previously determined values for the p*K* of the following buffer systems were employed in calculations: glycolic acid–glycolate,[11] acetic acid–acetate,[12] hydrogen maleate–maleate,[13] ammonia–ammonium,[14] and hydrogen carbonate–carbonate.[15] The two p*K* values for the glycine system, 2.38 and 9.48, were determined at 30° as part of this study.

Nmr Measurements. P^{31} nuclear magnetic resonance spectra were recorded on a Varian Associates high resolution spectrometer system described previously.[16] Proton nmr spectra were recorded on the Varian Associates Model A-60 spectrometer. Measurement of resonance peak positions were made relative to 85% H_3PO_4 and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.

Results and Discussion

A series of 42 kinetic experiments designed to define the over-all rate law and to produce a consistent set of rate constants for the hydrolysis of the pyrophosphite ion were conducted in media varying from strongly acidic to strongly basic. The pH was held constant throughout each run by means of either a high buffer concentration or by high concentrations of acid or base compared with the total pyrophosphite concentration. The results of all the kinetic experiments are summarized in Tables I through IV.

Table I. Summary of Rate Data in Strong Acid Solutions[a]

Run	Temp, °C	$[Na_2H_2\text{-}[P_2O_5]_0 \times 10^3$	$[H^+]$	$k \times 10^1$, min^{-1}	k_{H^+}, l. mole^{-1} min^{-1}
XII-2	30.0	10.20	0.0975	3.119	3.20
XIII-2	30.0	3.00	0.0975	3.057	3.13
XIII-3	30.0	3.00	0.0975	3.060	3.14
XIII-1	30.0	6.00	0.293	15.66	5.35
XII-1	30.0	9.40	0.975	12.6	13.0
XV-2	15.6	6.00	0.292	3.742	1.281
XIV-1	0.3	6.00	0.294	0.491	0.167
XIV-2	0.1	6.00	0.0980	0.0980	0.098

[a] Ionic strength = 1.0; concentrations in moles/l.

Table II. Summary of Rate Data in Strong Base Solutions

Run	Temp, °C	$[Na_2H_2\text{-}P_2O_5]_0 \times 10^3$, *M*	$[OH^-]$, *M*	*k*, min^{-1}	k_{OH^-}, l. mole^{-1} min^{-1}
XI-1	30.0	9.68	0.0975	1.892	19.40
XI-2	30.0	10.32	0.0390	0.730	18.72
XI-3	30.0	9.68	0.0975	1.848	18.95
XIII-5	30.0	3.00	0.0975	1.780	18.26
XV-1	16.5	6.00	0.0975	0.552	5.67
XIV-4	0.2	6.00	0.0980	0.156	1.59

Table III. Summary of Rate Data in Acidic Buffer Solutions[a]

Run[b]	pH	$[Na_2H_2\text{-}P_2O_5]_0 \times 10^3$, *M*	Σ[HA][c]	[HA],[d] *M*	*k*, min^{-1}
I-1	2.53	9.25	0.200	0.0833	3.96×10^{-3}
I-2	2.49	9.25	0.400	0.175	6.34×10^{-3}
I-3	2.46	9.25	0.800	0.296	1.10×10^{-2}
II-1	2.09	9.25	0.800	0.270	2.00×10^{-2}
II-2	2.08	9.25	0.400	0.133	1.36×10^{-2}
III-1	3.90	9.50	0.200	0.107	2.24×10^{-4}
III-2	3.81	9.50	0.400	0.214	3.67×10^{-4}
III-3	3.76	9.50	0.800	0.363	6.94×10^{-4}
IV-1	4.76	9.65	0.200	0.100	9.37×10^{-5}
IV-2	4.70	9.50	0.400	0.213	1.60×10^{-4}
IV-3	4.66	9.60	0.800	0.448	3.08×10^{-4}
VIII-1	4.67	9.35	0.400	0.222	1.99×10^{-4}
VIII-2	4.66	9.35	0.400	0.222	1.88×10^{-4}
V-1	6.29	9.60	0.100	0.0490	6.14×10^{-5}
V-2	6.27	9.55	0.200	0.0983	9.55×10^{-5}
V-3	6.19	9.30	0.400	0.216	1.53×10^{-4}
XVII-1	6.58	9.45	0.400	0.129	1.49×10^{-4}
XVII-2	5.92	9.45	0.400	0.275	1.90×10^{-4}

[a] Ionic strength = 1.00, 30°. [b] Series I and II, glycine buffer; series III, glycolic acid buffer; series IV, acetic acid buffer; series V and XVII, maleic acid buffer; series VIII, acetic acid buffer with 0.200 *M* glycine in (1) and 0.100 *M* glycine in (2). [c] Σ[HA] = total buffer concentration. [d] [HA] = concentration of acidic species of buffer.

For most of the experiments, the reaction was followed for at least one half-life. In all cases a plot of the logarithm of the pyrophosphite concentration as a

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(10) R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953).

(11) P. B. Davis and C. B. Monk, *Trans. Faraday Soc.*, **50**, 129 (1954).

(12) R. G. Bates and R. Gary, *J. Res. Natl. Bur. Std., Ser. A*, **65**, 495 (1961).

(13) N. E. Topp and C. W. Davies, *J. Chem. Soc.*, **87**, (1940).

(14) R. G. Bates and G. D. Pinching, *J. Am. Chem. Soc.*, **72**, 1393 (1950).

(15) Y. Kanko and A. K. Airola, *Z. Physik. Chem.*, **A179**, 307 (1937).

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

Table IV. Summary of Rate Data in Basic Buffer Solutions

Run[a]	pH	$[Na_2H_2P_2O_5]_0 \times 10^3$, M	Σ [HA][b]	[B],[c] M	k, min^{-1}
VI-1	9.56	9.40	0.400	0.0705	5.77×10^{-3}
VI-2	9.49	9.30	0.200	0.0305	3.75×10^{-3}
VI-3	9.40	9.35	0.080	0.0103	2.28×10^{-3}
VI-4	9.55	9.35	0.400	0.0687	5.64×10^{-3}
XVI-1	8.93	9.40	0.400	0.0879	1.07×10^{-2}
XVI-2	9.39	12.00	0.800	0.357	4.81×10^{-2}
XVI-3	9.43	12.00	0.400	0.189	2.78×10^{-2}
XVI-4	9.41	9.50	0.200	0.0913	1.36×10^{-2}
IX-1	*9.02*	*9.35*	*0.400*	*0.183*	9.25×10^{-3}
IX-2	9.02	9.35	0.200	0.0911	5.11×10^{-3}
IX-3	9.01	9.35	0.100	0.0453	2.72×10^{-3}

[a] Series VI, carbonic acid buffer; series XVI, glycine buffer; series IX, ammonia buffer. [b] Σ[HA] = total buffer concentration. [c] [B] = concentration of basic species of buffer.

function of time was linear at a constant pH, indicating a first-order dependence with respect to the latter. Five typical plots of this kind are shown in Figure 1 for experiments in the presence of glycine. The standard deviation for most of the observed first-order rate constants, k, was less than 3% of the values reported in Tables I through IV. The individual catalytic coefficients and an estimate of their standard deviations were determined by a linear regression least-squares method.

Catalysis by H_3O^+ and OH^-. The data of Tables I and II point out the catalysis by both the hydrogen ion and the hydroxide ion. The catalysis by hydrogen ion follows no simple order dependence in strong acid solutions. This can be seen in Table I where the hydrogen ion concentration was varied from 0.0975 to 0.975 M at 30°. The observed first-order rate constant, k, varied from 3.1 to 13 l. mole^{-1} min^{-1}. The observed first-order rate constant is defined as being equal to $(d[H_2P_2O_5^{-2}]_T/dt)/[H_2P_2O_5^{-2}]_T$, where $[H_2P_2O_5^{-2}]_T$ represents the total pyrophosphite concentration. The variation of k can be interpreted in terms of the degree of protonation of the pyrophosphite species as a function of acid concentration. The acid, $H_4P_2O_5$, is known to be strongly acidic, although its rapid hydrolysis prevents any accurate measurements of the dissociation constants for the two strongly acidic hydrogens. The rate data suggest that $H_3P_2O_5^{-1}$ and $H_4P_2O_5$ are more unstable toward hydrolysis than $H_2P_2O_5^{-2}$. The catalytic coefficients for the more acidic pyrophosphite species cannot be derived without the knowledge of the dissociation constants for these acids.

The catalytic coefficient, k_{H^+}, for the hydrolysis of the $H_2P_2O_5^{-2}$ ion, however, was estimated in buffer solutions of glycine, glycolic acid, and acetic acid, where the pyrophosphite is essentially all in the unprotonated form. The value derived from these data over about four pH units is 1.0 ± 0.3 l. mole^{-1} min^{-1}, indicating a first-order dependence of the rate on the hydrogen ion concentration. The large uncertainty is due to the fact that k_{H^+} was determined from the intercept of a plot of eq 1 below.

In Table II are the results of experiments carried out at high pH (>12), where the only reaction is the catalysis of $H_2P_2O_5^{-2}$ ion by hydroxide ion. The results of several experiments indicate a first-order dependence with respect to the OH^- concentration.

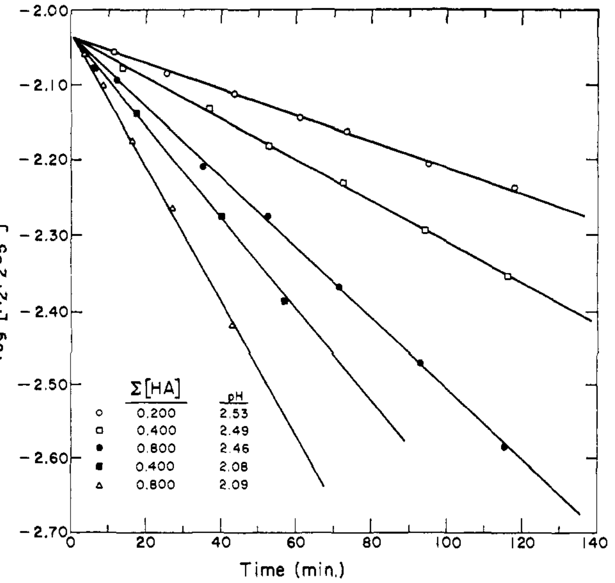

Figure 1. The first-order disappearance of the pyrophosphite as a function of pH in glycine solutions at 30°.

The average value obtained for the catalytic coefficient, k_{OH^-}, at 30.0°, when considering all the runs at that temperature in Table II, is 18.8 ± 0.7 l. mole^{-1} min^{-1}.

Catalysis by Other Acids and Bases. Several different buffer systems were chosen for study between pH 2 and 10. The results obtained using buffers in the acid region are listed in Table III. In this table Σ[HA] and [HA] represent the total buffer concentration and the concentration of the acidic species of the buffer, respectively.

Series I through IV represent runs for glycine, glycolic acid, and acetic acid. The rate law followed by these buffer solutions has the form

$$k = k_{H^+}(H^+) + k_{HA}[HA] \qquad (1)$$

where k_{HA} represents the catalytic coefficient for the acidic species of the buffer. In this treatment employing pH data, (H^+) is the reciprocal of the antilog of the pH. The individual coefficients were determined by plotting $k/(H^+)$ *vs.* $[HA]/(H^+)$, giving an intercept of k_{H^+} and a slope equal to k_{HA}.

Series I and II in Table III are experiments using glycine in which the pH was varied from 2.08 to 2.53, and the total buffer concentration was varied between 0.200 and 0.800 M. Glycine exists as a zwitterion in aqueous solution. In this region the acidic species is $CH_2N^+H_3CO_2H$ and the basic species is $CH_2N^+H_3CO_2^-$. By experiment it was established that only the acidic species contributed to the catalysis in this region. This is shown by runs IV-2, VIII-1, and VIII-2 in Table III. An upper limit of 10^{-4} l. mole^{-1} min^{-1} was estimated for the catalytic coefficient for the species $CH_2N^+H_3CO_2^-$ under conditions where all the glycine is present as this form. The contribution of this species to the over-all catalysis in series I and II is negligible. A value of $2.16 \pm 0.48 \times 10^{-2}$ l. mole^{-1} min^{-1} was determined for the catalytic coefficient, $k_{CH_2N^+H_3COOH}$.

Series III are experiments carried out at a pH of approximately 3.8 in solutions buffered with glycolic

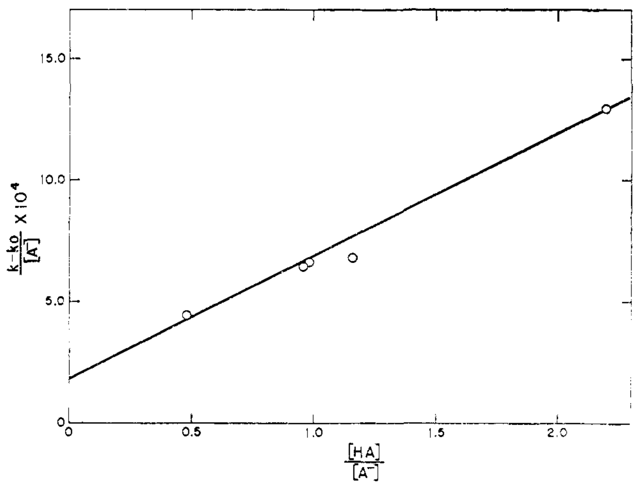

Figure 2. Kinetic data for solutions of acid maleate and maleate at 30° plotted according to eq 2.

acid. The catalytic coefficient, $k_{CH_2OHCOOH}$, calculated from these data is $1.81 \pm 0.33 \times 10^{-3}$ l. mole^{-1} min^{-1}.

Series IV and VIII are experiments carried out in acetic acid at a pH of approximately 4.7. In this series of experiments the reaction due to the buffer catalysis accounts for approximately 85% of the total reaction at the highest buffer concentration (0.800 M). The value obtained for k_{CH_3COOH} is $5.92 \pm 0.19 \times 10^{-4}$ l. mole^{-1} min^{-1}. In the calculation of the latter a correction was made for the contribution made by catalysis of the solvent which is discussed later.

Series V and XVII are experiments carried out in maleic acid buffer solutions at a pH between 5.92 and 6.58 in which the total buffer concentration was varied from 0.100 to 0.400 M. It was found that the observed rate constant could be defined by

$$k = k_0 + k_{^-O_2CCHCHCO_2H}[^-O_2CCHCHCO_2H] + k_{^-O_2CCHCHCO_2^-}[^-O_2CCHCHCO_2^-] \quad (2)$$

where k_0 is the catalytic coefficient for the solvent.

The constant k_0 is evaluated from the data of series V in which the pH is essentially constant. At a constant ratio of the acid to base species of the buffer, the above expression simplifies to the relationship

$$k = k_0 + k_1\Sigma[HA] \quad (3)$$

where Σ[HA] is the total concentration of the buffer. The plot of k *vs.* Σ[HA] gives a straight line with an intercept equal to k_0, $3.27 \pm 0.35 \times 10^{-5}$ min^{-1}.

The respective catalytic coefficients for maleic acid in eq 2 were evaluated by plotting $k'/[A^-]$ *vs.* $[HA]/[A^-]$ (Figure 2) where k' is defined as $k - k_0$. The catalytic coefficient for the base species, $k_{^-O_2CCHCHCO_2^-}$, is $1.30 \pm 0.60 \times 10^{-4}$ l. mole^{-1} min^{--1}, and the catalytic coefficient for the corresponding acid, $k_{HO_2CCHCHCO_2^-}$, is $4.97 \pm 0.47 \times 10^{-4}$ l. mole^{-1} min^{-1}.

Table IV represents the results of reactions carried out in buffer solutions at higher pH. The kinetics in buffered solutions of glycine, ammonia, and carbonate indicate that the hydrolysis of pyrophosphite ion is more strongly catalyzed by bases than by acids. This was also evident from the results of hydrogen ion and hydroxide ion catalysis.

For the three basic buffer systems, the observed rate constant can be represented by

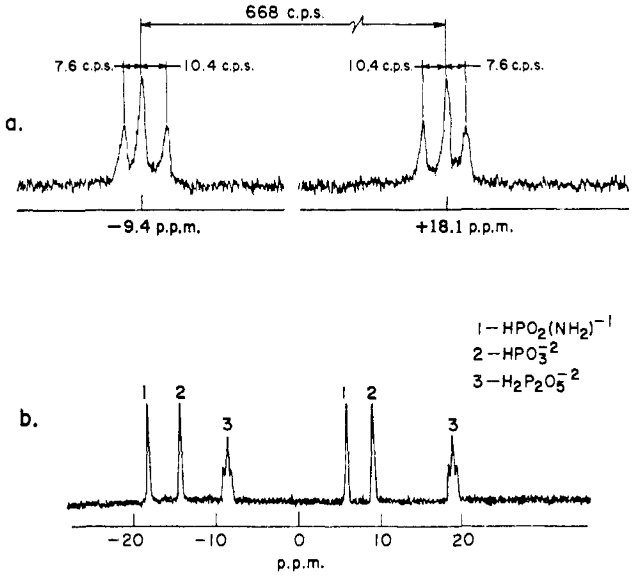

Figure 3. P^{31} spectra of aqueous solutions of (a) pyrophosphite ion and (b) a mixture of phosphite, amidophosphite, and pyrophosphite, occurring during the hydrolysis of pyrophosphite in ammonia–ammonium sulfate buffer at pH 9.2.

$$k = k_{OH^-}(OH^-) + k_B[B] \quad (4)$$

where k_B and [B] represent the catalytic coefficient and concentration of the basic form of the buffer, respectively. Except for the carbonate buffer, the first term in eq 4 makes only a small contribution to the over-all rate of the reaction. In the treatment of these data, the respective catalytic coefficients were obtained from a plot of $k/(OH^-)$ *vs.* $[B]/(OH^-)$. The (OH^-) was calculated from the pH and a value 1.47×10^{-14} for K_w at 30°.

Group VI represents the data for runs made in carbonate–hydrogen carbonate buffers. The catalytic coefficient for the carbonate ion, $k_{CO_3^{-2}}$, was found to be $4.37 \pm 0.25 \times 10^{-1}$ l. mole^{-1} min^{-1}. Although it has not been established unequivocally that the HCO_3^{-1} ion does not catalyze the hydrolysis of the pyrophosphite at this pH, it would seem unlikely under these conditions.

The results for solutions buffered with glycine are given in series XVI of Table IV. The catalytic coefficient for the $CH_2NH_2CO_2^-$ ion, $k_{CH_2NH_2CO_2^-}$, was found to be $1.19 \pm 0.09 \times 10^{-1}$ l. mole^{-1} min^{-1}. The catalysis by the $CH_2N^+H_3CO_2^-$ ion is also negligible at this pH.

Series IX gives the results for solutions buffered with ammonia. The results indicate that ammonia, like glycine, greatly accelerates the hydrolysis of the $H_2P_2O_5^{-2}$ ion. The value for the catalytic coefficients determined from these data for k_{NH_3} is $4.70 \pm 0.18 \times 10^{-2}$ l. mole^{-1} min^{-1}.

Employing an activity coefficient of 0.63 for the hydroxide ion in sodium chloride at unit ionic strength,[17] one can compare the average value obtained for k_{OH^-} from the basic buffer systems (43 ± 15 l. mole^{-1} min^{-1}) with the value obtained from Table II (18.8 ± 0.7 l. mole^{-1} min^{-1}). The values are in agreement

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(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p 452.

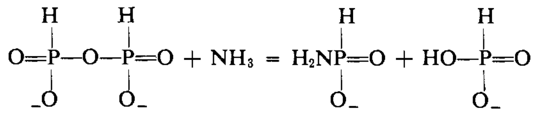
within the limits of uncertainty. The large uncertainty for the value obtained from the buffer solutions is due to the small contribution made by the hydroxide-catalyzed reaction to the total rate in this pH range.

Nmr Studies on Pyrophosphite Solutions. Blaser and Worms[6] have shown that some anions interact with $H_2P_2O_5^{-2}$ to yield products other than orthophosphite in aqueous solution. Therefore, P^{31} nmr was employed in the characterization of the reaction products in basic buffer solutions.

Before proceeding with the presentations of the nmr results on these systems, the P^{31} nmr spectrum of the pyrophosphite ion itself should be discussed. Figure 3a represents the P^{31} spectrum of the pyrophosphite ion in a saturated aqueous solution at a pH of 4.2. The spectrum, which was run at a higher resolution than that previously described,[7] shows not simply the doublet as was reported earlier but fine structure in the form of a widely split pair of asymmetrical triplets. This is analogous to the spectrum reported[18] for $P_2O_3Cl_2F_2$ except that the triplet asymmetry is in the opposite direction. The same spectrum is obtained by H^1 nmr which is consistent with an A_2X_2 analysis[19] in terms of the following set of spin-coupling constants (in cps): $|J_{P_1H_1}| = |J_{P_2H_2}| = 668$, $|J_{P_1P_2}| = 18.2$, and $|J_{P_1H_2}| = |J_{P_2H_1}| = 1.4$. The asymmetry of the peaks requires that the constants $|J_{P_1H_1}| = |J_{P_2H_2}|$ be of the same sign as $|J_{P_2H_1}|$. The nmr results are conclusive evidence for the symmetry of the pyrophosphite ion.

The P^{31} chemical shifts for the pyrophosphite ion and orthophosphite ion relative to 85% phosphoric acid are +4.38 and −3.13 ppm respectively, in the same medium. The H^1 nmr chemical shifts for the pyrophosphite ion and orthophosphite ion relative to 3-(trimethylsilyl)-1-propanesulfonic acid are −6.92 and −6.84 ppm, respectively. The very small difference for the latter indicates similar environments for the hydrogen atom bonded to phosphorus in the pyrophosphite and orthophosphite ions.

In ammonia solutions the hydrolysis of the pyrophosphite yields equal quantities of phosphite and amidophosphite. The reaction can be represented by the equation



$$O{=}\overset{H}{\underset{-O}{P}}{-}O{-}\overset{H}{\underset{O_-}{P}}{=}O + NH_3 = H_2N\overset{H}{\underset{O_-}{P}}{=}O + HO{-}\overset{H}{\underset{O_-}{P}}{=}O \quad (5)$$

Figure 3b represents the relative composition of the phosphite and amidophosphite after part of the pyrophosphite had been hydrolyzed. The amidophosphite is characterized by a chemical shift of −6.39 ppm and a coupling constant of 578 cps. This mixture was produced by hydrolyzing pyrophosphite at a pH of 9.20 containing initially 3.5% NH_3, 25% $(NH_4)_2SO_4$, and 12.5% $Na_2H_2P_2O_5$.

The preparation of the amidophosphite ion has never before been reported in the literature. It is evident that it is more hydrolytically stable than pyrophosphite in basic solutions. Also it has been shown to undergo oxidation by iodine readily in neutral solutions.

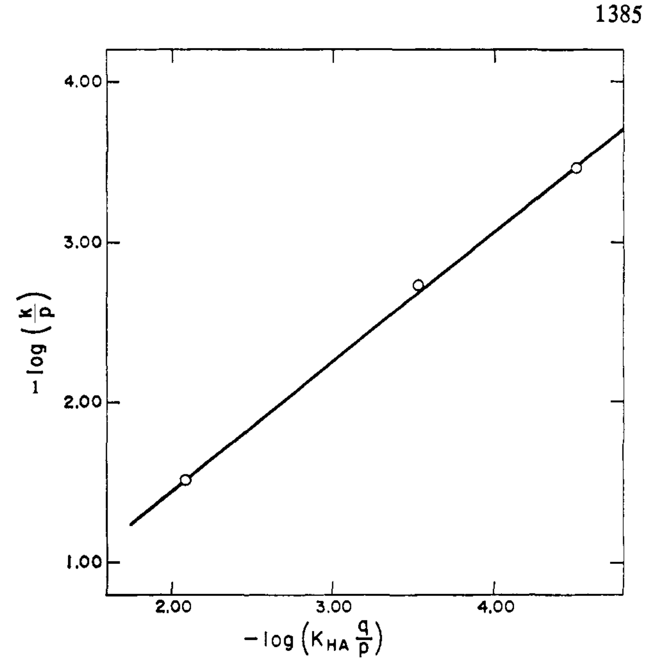
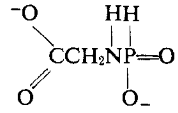


Figure 4. Brønsted plot for glycine, glycolic acid, and acetic acid at 30°.

Similarly, for the hydrolysis of pyrophosphite in the presence of glycine at pH 9.0, an intermediate is produced with a P^{31} chemical shift of −7.1 ppm and a coupling constant of −560 cps. However, in this case only about 10% of the hydrolyzed product after one half-life is present as the new species. The species has not been isolated but probably has the form



It is evident that this ion undergoes hydrolysis more readily than does the amidophosphite. It would be expected that other P-N bonded species could be produced by the reaction of the appropriate amines with pyrophosphite.

For the carbonate–bicarbonate system no intermediates were observed. This is to be expected because of the ease of hydrolysis of P-O-C bonds.

Discussion of Mechanism. The hydrolysis of pyrophosphite in acid and base systems can be represented by a rate law of the form

$$(-d[H_2P_2O_5^{-2}]/dt)/[H_2P_2O_5^{-2}] = k_0 + \sum_a k_a[HA]_a + \sum_b k_b[B]_b \quad (6)$$

where k_a and k_b are specific catalytic coefficients for the acids and bases, respectively, and k_0 is the catalytic coefficient for water. The $[HA]_a$ and $[B]_b$ represent the concentrations of any Brønsted acid and Lewis base, respectively.

It is commonly assumed that the catalytic behavior of acids and bases involve proton transfer. This is most certainly the case in acid media where the Brønsted slope, α, from Figure 4, is 0.8, which indicates a very high sensitivity of the hydrolysis rate to the acid strength.

Two conceivable mechanisms for the hydrolysis in acid media entail the following two rate-determining processes: (1) a proton-transfer step resulting in the cleavage of a P-H bond in a manner similar to the

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(18) M. M. Crutchfield, C. F. Callis, and J. R. Van Wazer, *Inorg. Chem.*, 3, 280 (1964).

(19) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 309.

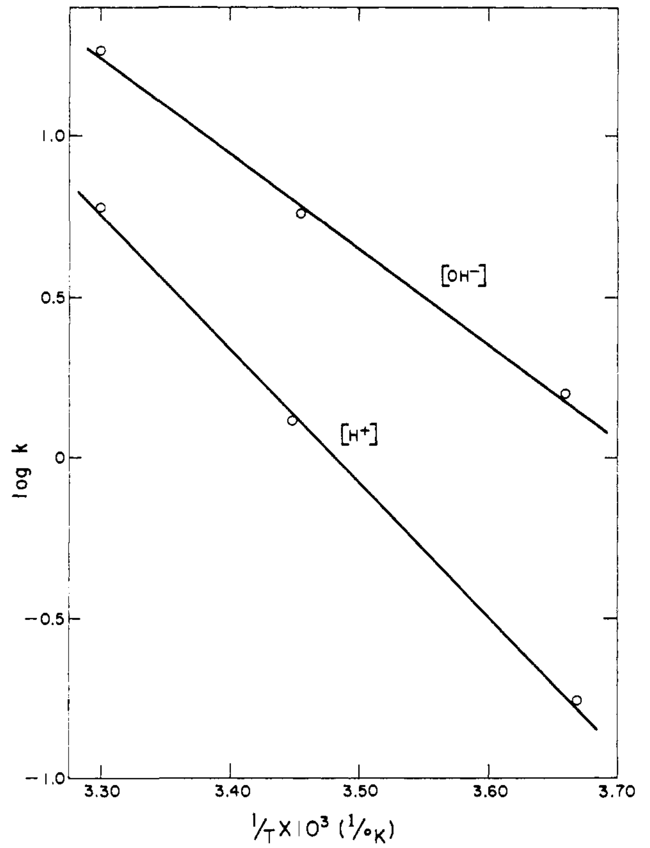


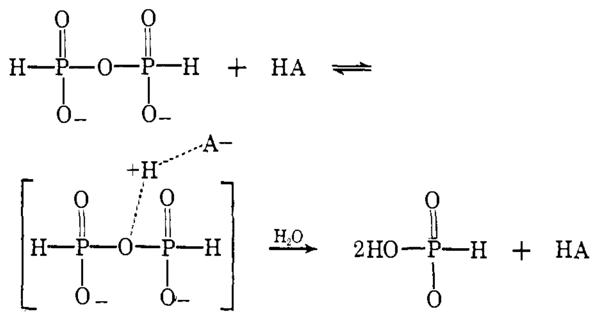
Figure 5. Arrhenius plots for the hydrolysis in 0.0975 *M* hydroxide and in 0.294 *M* acid.

mechanism involving the tautomeric equilibria proposed by Mitchell[20] for reactions of phosphorous and hypophosphorous acids, and (2) a proton addition at the site of the bridging oxygen atom.

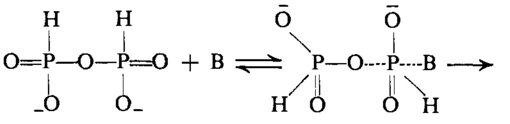
The first mechanism does not seem likely in view of the results of Griffith and McKeown,[21] on the kinetics of the oxidation of phosphorous acid by iodine under the conditions where the rate law has the form $k_{H^+}[H_3PO_3][H^+]$. They reported a value of 9.87×10^{-3} l. mole^{-1} min^{-1} at 45° for k_{H^+} compared with our value of 1.0 l. mole^{-1} min^{-1} at 30° for the hydrogen ion catalysis of the hydrolysis of pyrophosphite. In strong acid solutions where the protonated forms of pyrophosphite exist k_{H^+} has even larger values. Great differences in the P–H bond reactivity would not be expected for the pyrophosphite compared with orthophosphite. The H^1 nmr data show these two species to have hydrogens with very similar environments.

The more likely mechanism (2) involves the addition of a proton from any Brønsted acid to the bridging oxygen atom, which can be represented as shown in (7) where the rate-controlling step is presumed to be the proton transfer from the acid, HA, to the oxygen of the P–O–P linkage.

The hydrolysis of the pyrophosphite ion in basic solutions probably takes place by the nucleophilic attack at the phosphorus atom, forming a new bond with the phosphorus as a P–O bond of the P–O–P bridge is broken. The results from our nmr study showing the formation of P–N bonds with ammonia and glycine, the results of others[6,8] showing the formation of P–F bonds and the transanhydrization reactions, and the absence of a simple Brønsted relationship for the base catalysis all lend support for this mechanism.


(7)

A plausible mechanism for the basic catalysis is


$HPO_2B + HPO_3^{-2}$ (8)

$$HPO_2B + H_2O \longrightarrow H_2PO_3^- + B + H^+ \qquad (9)$$

When an intermediate product of the basic hydrolysis has hydrolytic stability, as in the cases listed above, the intermediate has been observed. However, when a base such as carbonate or carboxylate ion attacks the phosphorus, no stable intermediate is produced because of the ease of hydrolysis of P–O–C linkages.

Activation energies were determined for both the hydrogen and hydroxide ion catalyzed hydrolysis of pyrophosphite from the data of Table I and Table II. The Arrhenius plots in Figure 5 give the activation energies for the hydrogen and hydroxide ion catalyzed hydrolysis. Values of 18.7 and 12.7 kcal mole^{-1}, respectively, are determined from these data. The entropies of activation are +10.9 and −8.1 eu, respectively.

The entropies are compatible with simple electrostatic models which predict +20 and −20 eu for ionic reactions of these types.[22] Likewise, on the basis of ionic charge considerations, the acid catalysis would be expected to show a higher activation energy as the result of loss of hydration stemming from neutralization of charge in forming the activated complex.

The data of Van Wazer, *et al.*,[23] on the hydrolysis of pyrophosphate and tripolyphosphate indicate that these condensed phosphates are considerably more stable toward hydrolysis than is pyrophosphite in acid solution. No evidence of base catalysis has been found for the hydrolysis of linear condensed phosphates.

The following argument is advanced as an explanation for the difference in hydrolytic stability of condensed phosphates and pyrophosphite in acid solutions. Acid hydrolysis by the mechanism shown above, in which the attack of the H^+ ion on the P–O–P linkage occurs at the oxygen atom, is promoted by the avail-

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[20] A. D. Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920); **119**, 1266 (1921); **121**, 1624 (1922); **123**, 629, 2241 (1923).

[21] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **35**, 767 (1940).

[22] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 54.

[23] J. R. Van Wazer, E. J. Griffith, and J. F. McCullough, *J. Am. Chem. Soc.*, 77, 287 (1955).

ability of a localized pair of electrons on the oxygen atom. The kinetic data suggest that delocalization by π bonding occurs to a lesser extent in the pyrophosphite than in the pyrophosphate linkage, making it more receptive to attack by the hydrogen ion. This explanation is consistent with the conclusion reached by Grant and Payne[9] in explanation of the absence of chelation stabilization in pyrophosphite complexing.

The hydrolysis of pyrophosphite resembles closely that of trimetaphosphate which is both acid and base catalyzed.

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Equilibria Involving the Formation, Hydrolysis, and Olation of Oxovanadium(IV) Chelates in Aqueous Solution[1,2]

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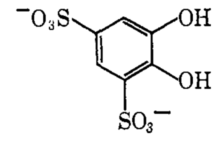
Abstract: The interaction of the oxovanadium ion with 3,5-disulfopyrocatechol, salicylic acid, 5-sulfosalicylic acid, 5-sulfo-8-hydroxyquinoline, and salicyl phosphate was studied by potentiometric measurement of hydrogen ion concentration. Data taken over a range of metal ion and ligand concentrations were used to determine formation constants of the metal chelates having a 1:1 molar ratio of ligand-to-metal ion, their hydrolysis constants, and the equilibrium constants for the formation of binuclear diolated chelates. Suggestions are made for the bonding and structures of these coordination compounds in aqueous solution.

The purpose of the investigation was to determine the complex species present in systems containing vanadyl salts, organic ligands, and salicyl phosphate by potentiometric measurements. Such information is required for a study of the kinetics of the vanadyl ion and vanadyl chelate catalyzed solvolysis of salicyl phosphate in aqueous solution, to be reported in a subsequent paper. As a result of this study, the species present in solution will be described in terms of the stability constants of the metal chelate compounds formed, the equilibrium constants for the formation of polynuclear complexes, and the acid dissociation constants of all other solution constituents.

A search of the literature revealed that only a few equilibrium formation constants of vanadyl chelates have been reported. Constants for the formation of the ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) and cyclohexanediamine-N,N,N′,N′-tetraacetic acid (CDTA) chelates have been reported by Schwarzenbach, *et al.*[4] The formation constant for the interaction of the vanadyl ion and oxalic acid has been described.[4] Several constants also have been reported by Trujillo and co-workers with acetylacetone, pyrocatechol, 1,10-phenanthroline, and 8-hydroxyquinoline.[5-8]

The ligands employed in the investigation were 3,5-disulfopyrocatechol (I), salicylic acid (II), 5-sulfosalicylic acid (III), 5-sulfo-8-hydroxyquinoline (IV), and salicyl phosphate (V). The selection of I–IV was predicated on the fact that these were the only readily available ligands which formed partially co-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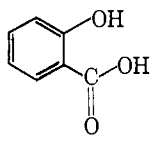
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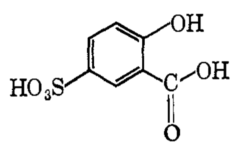
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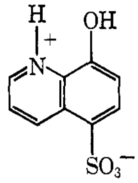
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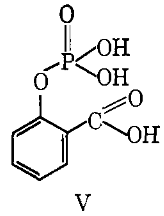
V

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(2) This work was supported by the National Science Foundation under Research Grants G-9998 and G-21055 to Clark University and Illinois Institute of Technology, respectively.

(3) Department of Chemistry, Illinois Institute of Technology, Chicago, Ill.

(4) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

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(6) R. Trujillo and I. Brito, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B52**, 407 (1956); *Chem Abstr.*, 50, 15320 (1956).

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(8) R. Trujillo and I. Brito, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B53**, 313 (1957); *Chem. Abstr.*, **54**, 2076 (1960).