was decanted from the oil, to which petroleum ether was added. Persistent scratching caused formation of a white powder of $[(C_3H_7(C_6H_5)_2P)_3PtCl]B(C_6H_5)_4$, which was isolated by filtration, washed with petroleum ether, and dried at 30° (3 torr) for 10 hr.

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Isohypophosphate: Kinetics of the Hydrolysis and Potentiometric and Nuclear Magnetic Resonance Studies on the Acidity and Complexing

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The kinetics of the hydrolysis of isohypophosphate was studied in strong acid, strong base, and several buffered mixtures at 25.0, 40.0, and 60.0° in 0.5 *M* sodium chloride. The reaction is catalyzed by all Brønsted acids and by nucleophiles. The detailed rate law is written in terms of the protonated forms of isohypophosphate undergoing hydrolysis. For acid catalysis each protonated form hydrolyzes faster than any of the less protonated forms. An enhancing effect of added metal ion on the rate of base-catalyzed hydrolysis was also observed. The heats of activation for the catalysis of the $H_2P_2O_6^{2-}$ anion by H_3O^+, acetic acid, glycolic acid, and water are 26.1, 18.3, 19.0, and 24.9 kcal/mole, respectively. The pK^0 values and formation constants for 1:1 complexes of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} were determined at 25.0° in tetramethylammonium chloride and compared with the complexing properties of pyrophosphite and pyrophosphate. Nuclear magnetic resonance studies indicate that the least acidic hydrogen atom is most strongly associated with the PO_4 group. Also, evidence for the order of deprotonation of the two strongly acidic protons is given. Analysis of the ^{31}P nmr chemical shifts for the P(III) and P(V) atoms at various metal ion concentrations suggests that the anion probably acts as a bidentate ligand.

Introduction

The kinetics of hydrolysis and metal ion complexing of condensed phosphates[1-4] and pyrophosphite[5,6] have been shown to be greatly different. Condensed phosphates undergo specific acid catalysis and are not subject to attack by nucleophiles, whereas pyrophosphite is both general acid and base catalyzed. Moreover, condensed phosphates[1,4] have been shown to undergo hydrolysis more rapidly in the presence of alkali metal ions, where no effect has been observed for pyrophosphite.[5] Grant and Payne[6] have shown that the pyrophosphite ion forms weaker metal ion complexes than condensed phosphates. Isohypophosphate,[7,8] which has the formula $H_nHP_2O_6^{(3-n)-}$, contains a P–O–P linkage involving P(III) and P(V) atoms. Hence, it is of particular interest in understanding the properties of condensed phosphorus compounds since it combines the properties of the condensed phosphates and the properties of lower oxidation states.

Also, since isohypophosphate contains phosphorus atoms in the +3 and +5 oxidation states, a ^{31}P nmr study on this compound could be of great value in defining the deprotonation steps and yielding information on the structure of its complexes with metal ions.

Experimental Section

Chemicals.—Trisodium isohypophosphate was prepared and purified by the method of Blaser and Worms[9] using phosphorus trichloride and sodium hydrogen phosphate as starting materials. Also, trisodium isohypophosphate was prepared by allowing sodium pyrophosphite to react in an aqueous solution with a large excess of sodium hydrogen phosphate and purifying as before.[9] Assay of the purified material by iodine titration and ^{31}P nmr indicated over 96% of the phosphorus was in the form of isohypophosphate. Tetramethylammonium isohypophosphate was prepared by ion exchange of the sodium salt through a Dowex 50 W-X2 resin in the tetramethylammonium form. This material, after removal of most of the water by evaporation, was stored at −10° until used. All other materials were of reagent grade quality.

Kinetics Measurements.—The analytical procedure and the techniques for rate measurements for reactions run in NaCl are essentially identical with those described previously,[5] with the exception that a phosphate buffer was employed rather than the maleate buffer for quenching the reaction mixture. The same procedure was used for reactions run in tetramethylammonium chloride except that the tetramethylammonium ion was removed by ion exchange before analysis. This was necessary since tetramethylammonium ions precipitate in the presence of triiodide.

The kinetics experiments were conducted at 25, 40, and 60° in a thermostated bath controlled at these temperatures to ±0.1°.

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

(2) R. P. Mitra, H. C. Malhotra, and D. V. S. Jain, *Trans. Faraday Soc.*, **62**, 173 (1966).

(3) S. M. Lambert and J. I. Watters, *J. Am. Chem. Soc.*, **79**, 4262 (1957); **79**, 5606 (1957); **81**, 3201 (1959).

(4) E. J. Griffith and R. L. Buxton, *ibid.*, in press.

(5) R. E. Mesmer and R. L. Carroll, *ibid.*, **88**, 1381 (1966).

(6) D. Grant and D. S. Payne, *J. Inorg. Nucl. Chem.*, **26**, 1985 (1964).

(7) B. Blaser, *Ber.*, **68**, 1670 (1935); **86**, 563 (1953); B. Blaser and K. Worms, *Angew. Chem.*, **67**, 409 (1955); *Chem. Techn.*, **7**, 631 (1955); also, paper given at the Phosphorus Symposium held at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 1956.

(8) E. Thilo and D. Heinz, *Z. Anorg. Allgem. Chem.*, **281**, 303 (1955).

(9) B. Blaser and K. Worms, *ibid.*, **301**, 18 (1959).

Constant ionic strength was maintained with sodium chloride or recrystallized tetramethylammonium chloride.

The p*K* values for glycolic acid and acetic acid used in the calculation of the specific rate constants were determined in 0.5 *M* NaCl at 25, 40, and 60° as a part of this study.

Acidity and Complexing.—The acidity and stability constants were determined from potentiometric titration data employing a Beckman Expandomatic pH meter equipped with a Sargent S-30050-15 glass electrode. The pH meter was calibrated with Fisher buffers at pH values of 2, 4, 7, and 9. The buffers checked within ±0.03 pH unit with each other. All experiments were conducted in boiled distilled water and in a nitrogen atmosphere.

The acidity constants were determined at 25° in tetramethylammonium chloride solutions at ionic strengths of 0.1, 0.2, 0.5, and 1.0. The experimental procedure and computations were the same as previously described.[10]

The stability constants for Ca^{2+}, Mg^{2+}, Li^+, Na^+, and K^+ were determined at 25° in 0.5 *M* tetramethylammonium chloride. The stability constants for these metal ions

$$\beta_{MH_iL} = \frac{[MH_iL]}{[M][H_iL]} \qquad (1)$$

were calculated[10] from the usual mass balance equations using an IBM 7044 computer. The normal procedure was to add the solution containing the metal ion in about 15 increments to a solution containing isohypophosphate, the pH of which had been adjusted to a value where the $H_2P_2O_6^{2-}$ and $HP_2O_6^{3-}$ concentrations were nearly equal. After each addition the pH was recorded. The usual care was taken to minimize changes in ionic strength.

^{31}P Nmr and Infrared Measurements.—^{31}P nmr spectra were recorded on a Varian Associates spectrometer system described previously.[11] The phosphorus chemical shifts and spin coupling constants were obtained as a function of protonation and complexing as described previously.[11,12]

The infrared measurements were recorded on a Beckman IR-4.

Results

The potentiometric titration data for the acidity and complexing studies are deposited with the American Documentation Institute.[13]

In Table I are listed the p*K* values at 25° at different ionic strengths. The acidity constant *K* is defined as $(H^+)[H_{i-1}L]/[H_iL]$ where (H^+) is equal to antilog −pH.

Table I

Acid Dissociation Constants for Isohypophosphoric Acid in Tetramethylammonium Chloride at 25°

Ionic strength μ	pK_1[b]	pK_2	pK_3
0	(0.6)[a]	1.67 ± 0.06[c]	6.26 ± 0.06
0.1	...	1.67 ± 0.06	6.25 ± 0.06
0.2	...	1.67 ± 0.04	6.24 ± 0.04
0.5	...	1.50 ± 0.04	6.26 ± 0.04
1.0	...	1.71 ± 0.06	6.33 ± 0.04

[a] Values for the p*K* given in parentheses are estimated. [b] Value estimated from kinetic data in 0.5 *M* NaCl is 0.5 ± 0.2. [c] Errors shown are 95% statistical limits.

The potentiometric measurements were made over the pH range *ca.* 1.7 to 8.5. Rapid hydrolysis of the ligand prevented obtaining reliable data at lower pH. All measurements were made on fresh solutions of the tetramethylammonium salt.

The logarithms of the stability constants, log β_{ML}, for calcium, magnesium, lithium, sodium, and potassium in 0.5 *M* tetramethylammonium chloride are 2.27 ± 0.02, 2.65 ± 0.03, 0.82 ± 0.04, 0.50 ± 0.04, and 0.36 ± 0.05, respectively. The errors are reported in terms of statistical 95% confidence limits and are average values of at least five determinations at various metal:isohypophosphate ratios.

The ^{31}P nmr spectrum of a 1.75 *M* solution of tetramethylammonium isohypophosphate is shown in Figure 1. A spectrum of isohypophosphate was reported earlier[14] at a resolution that did not allow calculation of the coupling constants. The spectrum in Figure 1 consists of three doublets for which the following assignments are made: coupling constants of $|J_{HP_1}| = 627$ cps, $|J_{P_1P_2}| = 17.7$ cps and chemical shifts of $\delta_{P_1} = 5.68$ ppm and $\delta_{P_2} = 5.88$ ppm. The nmr spectrum of isohypophosphate is consistent with its structure

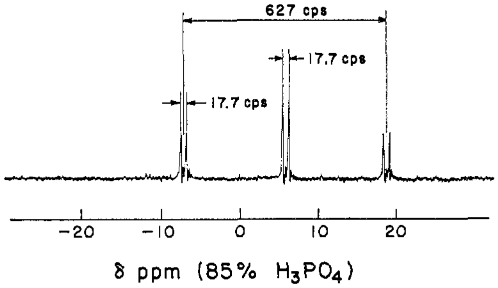
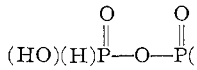


Figure 1.—The ^{31}P nmr spectrum of 1.75 *M* tetramethylammonium isohypophosphate.



$$(HO)(H)\overset{\overset{\displaystyle O}{\|}}{P}—O—\overset{\overset{\displaystyle O}{\|}}{P}(OH)_2$$

Results showing the effect of the number of bound protons on the coupling constants are reported in Table II. Figure 2 shows the effect of pH on the chemical shifts of the P(III) and P(V) atoms.

Table II

The Effect of Proton Association on Coupling Constants

pH	$J_{P_1P_2}$[a]	$J_{P_2P_1}$[a]	J_{HP_1}[b]
2.30	19.6	19.2	695.8
3.45	17.9	18.2	671.1
5.13	18.2	18.9	665.0
7.35	17.0	17.0	653.0
9.70	17.3	17.3	648.0
10.62	16.8	16.8	643.9
11.90	16.8	16.6	625.8

[a] *J* values are in cps and are accurate to within ±0.5 cps. [b] *J* values are in cps and are accurate to within ±5 cps.

The ^{31}P nmr chemical shift for the P(III) and P(V) atoms of isohypophosphate as a function of Li^+:$HP_2O_6^{3-}$ ratios at pH 10 are reported in Figure 3. The

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(10) R. P. Carter, R. L. Carroll, and R. R. Irani, *Inorg. Chem.*, **6**, 939 (1967).

(11) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *ibid.*, **1**, 813 (1962).

(12) M. M. Crutchfield and R. R. Irani, *J. Am. Chem. Soc.*, **87**, 2815 (1965).

(13) These data have been deposited as Document No. 9361 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(14) C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957).

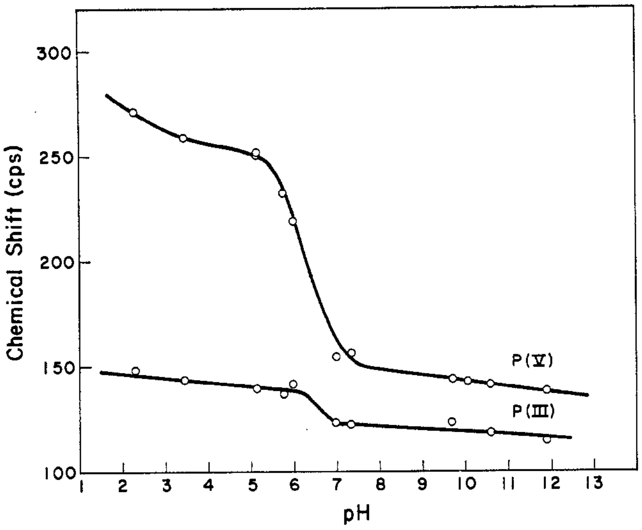

Figure 2.—The ^{31}P chemical shifts for the two phosphorus atoms of isohypophosphate (0.50 *M*) as a function of pH at 24.29 Mc.

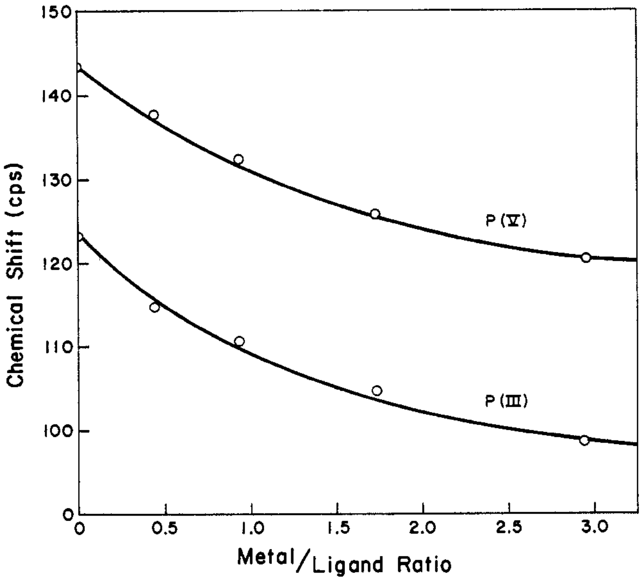

Figure 3.—The ^{31}P chemical shifts of the two phosphorus atoms of isohypophosphate (0.50 *M*) as a function of the $[Li^+]/[HP_2O_6^{3-}]$ ratios at pH 10 and 24.29 Mc.

fact that the peaks shift in position and no additional peaks are observed is proof that the complexed metal ion exchanges rapidly with the isohypophosphate ion.

For the kinetics study, the rate data were analyzed by a least-squares method using a 7044 computer. The initial concentrations and observed first-order rate constants, *k*, defined as being equal to $(d[H_4P_2O_6]_T/dt)/[H_4P_2O_6]_T$, are summarized for all runs in Tables III and IV. $[H_4P_2O_6]_T$ represents the total isohypophosphate concentration. The reactions were followed with few exceptions for at least one half-life. A plot of the logarithm of the total isohypophosphate concentration *vs.* time at constant pH is linear for runs followed through several half-lives indicating that the reaction is first order with respect to the total isohypophosphate concentration.

TABLE III

SUMMARY OF RATE DATA IN ACIDIC MEDIA IN 0.5 *M* SODIUM CHLORIDE

Temp, °C	$[H_4P_2O_6]_T$, $M \times 10^3$	pH	[HA], *M*	*k*, sec^{-1}
		H_3O^+		
25.0	9.83	1.136[a]	...	9.15×10^{-4}
25.0	9.87	0.816[a]	...	2.62×10^{-3}
25.0	12.13	0.631[a]	...	6.68×10^{-3}
25.0	9.88	0.423[a]	...	1.29×10^{-2}
40.0	8.87	1.086[a]	...	2.67×10^{-3}
40.0	9.71	0.710[a]	...	1.31×10^{-2}
40.0	9.53	0.622[a]	...	2.68×10^{-2}
40.0	11.60	0.375[a]	...	6.07×10^{-2}
		$CH_2(NH_2)CO_2H$		
25.0	9.79	2.090	0.064	5.00×10^{-5}
25.0	9.97	2.459	0.053	1.56×10^{-5}
25.0	10.02	2.456	0.105	1.93×10^{-5}
25.0	9.84	2.470	0.213	2.57×10^{-5}
25.0	10.04	2.260	0.118	3.47×10^{-5}
25.0	9.13	2.210	0.246	4.28×10^{-5}
25.0	9.29	2.260	0.471	4.87×10^{-5}
		$CH_2(OH)CO_2H$		
25.0	9.81	3.896	0.062	8.03×10^{-7}
25.0	9.77	3.886	0.126	1.27×10^{-6}
25.0	9.77	3.916	0.241	1.98×10^{-6}
40.0	10.54	4.056	0.049	3.55×10^{-6}
40.0	10.46	4.063	0.096	5.20×10^{-6}
40.0	10.42	4.029	0.204	9.23×10^{-6}
60.0	10.01	3.985	0.055	3.00×10^{-5}
60.0	9.95	3.900	0.126	4.57×10^{-5}
60.0	9.98	3.904	0.251	7.73×10^{-5}
		CH_3CO_2H		
25.0	8.81	4.498	0.103	3.00×10^{-7}
25.0	8.58	4.527	0.198	4.35×10^{-7}
25.0	8.93	4.528	0.396	8.62×10^{-7}
40.0	10.47	4.923	0.059	1.04×10^{-6}
40.0	10.40	4.848	0.133	1.85×10^{-6}
40.0	10.42	4.740	0.312	3.72×10^{-6}
60.0	10.06	4.934	0.058	8.22×10^{-6}
60.0	9.66	4.870	0.058	1.28×10^{-5}
60.0	10.03	4.812	0.281	2.27×10^{-5}

[a] Values calculated from concentrations and activity coefficients.

Discussion

Acidity, Complexing, and ^{31}P Nmr.—Isohypophosphoric acid contains two strongly acidic hydrogen atoms and one weakly acidic hydrogen atom. The values in p*K* units extrapolated to zero ionic strength are 0.6, 1.67, and 6.26, respectively (Table I). It is of interest to compare these values with acidity data reported recently[2] for pyrophosphoric acid. The first, second, and third pK^0 values are 0.91, 2.10, and 6.70, respectively. These constants are slightly larger than the corresponding p*K* values for isohypophosphoric acid. Unfortunately, acidity constant data for pyrophosphorous acid have not been reported, although preliminary studies in this laboratory indicate that the acid hydrogens are more strongly acidic than the analogous hydrogen of isohypophosphoric acid.

The strength of the metal ion complexes of isohypophosphate is in accordance with what would be expected if the degree of interaction is related to the chelation stabilization effect. The log β_{ML} values are approxi-

TABLE IV

SUMMARY OF RATE DATA IN BASIC SOLUTION AT 60°

$[H_4P_2O_6]_T$, M $\times 10^3$	$[OH^-]$, M	Ionic strength[d]	$[Na^+]$, M	k, sec^{-1}	$k/[OH^-]$, l. mole^{-1} sec^{-1}
8.18	0.484	0.5	0.500	1.78×10^{-4}	3.68×10^{-4}
8.43	0.194	0.5	0.500	6.75×10^{-5}	3.48×10^{-4}
8.48	0.387	0.5	0.500	1.34×10^{-4}	3.48×10^{-4}
6.96	0.208	0.5	0	7.80×10^{-6}	3.75×10^{-5}
6.88	0.500	0.5	0	1.88×10^{-5}	3.77×10^{-5}
7.74	0.197	0.5	0.197	1.57×10^{-5}	7.95×10^{-5}
12.12	0.192	1.0	0.497	6.65×10^{-5}	3.47×10^{-4}
11.94	0.192	1.0	0.192	3.03×10^{-5}	1.58×10^{-4}
12.20	0.192	1.0	1.000	1.38×10^{-4}	7.17×10^{-4}
11.46[a]	0.208	0.5	0	2.75×10^{-7}	1.32×10^{-6}
10.17[b]	...	1.0	1.000	4.37×10^{-7}	...
10.17[c]	...	1.0	1.000	3.22×10^{-7}	...

[a] Temperature 25°. [b] Reaction run in a solution which was 0.200 M in carbonate at pH 9.24. [c] Reaction run in a solution which was 0.050 M in carbonate at pH 9.20. [d] Ionic strength adjusted when necessary with tetramethylammonium chloride.

mately a factor of two smaller than those reported[3] for complexing of the unprotonated pyrophosphate ion. The complexing of metal ions by pyrophosphite has been shown[6] to be very weak, *i.e.*, the stability constant for Cu^{2+} is of the same order as that obtained for the alkali metal ions with the unprotonated pyrophosphate ion. No complexing of the monoprotonated species, $H_2P_2O_6^{2-}$, by calcium or magnesium could be detected from the potentiometric data.

Since the stability toward hydrolysis and the complexing properties for pyrophosphate, isohypophosphate, and pyrophosphite suggest trends in π bonding in the P=O bond and P—O—P linkage, the infrared spectra of the sodium salts of these anions were examined. The values obtained for P—O—P stretching frequencies are 910, 905, and 893 cm^{-1}, respectively. The values obtained for the P=O stretching frequencies are 1146, 1210, and 1380 cm^{-1}, respectively. The infrared data reported for pyrophosphate are in satisfactory agreement with those reported earlier.[15]

The increase in π bonding in the P—O—P linkage is reflected in the slight increase in stretching frequencies in going from pyrophosphite to pyrophosphate and also the increase in localization of electrons in the P=O bond is clearly indicated by the increase in the stretching frequency of the aforementioned bond in going from pyrophosphate to pyrophosphite. Since for these compounds the complexing ability can be correlated with the amount of π bonding in the P—O—P linkage, it is likely that this property leads to chelation stabilization for the metal ion complexes as was suggested earlier by Grant and Payne.[6]

Changes in the ^{31}P nmr chemical shifts and phosphorus spin coupling constants with pH have given information about the structure and the successive deprotonation steps for condensed phosphates.[11] Also, changes in the chemical shift with added metal ion have been interpreted in terms of the nature and structure of the complex ions formed.[12] Isohypophosphate, with only two phosphorus atoms each in a different magnetic environment, is an excellent candidate for such an investigation.

The addition of the first hydrogen (Figure 2) to $HP_2O_6^{3-}$ at about pH 6–7 produces a very large shift upfield for the P(V) atom (*ca.* 100 cps) and a smaller shift in the same direction for the P(III) atom (*ca.* 15 cps). This indicates that the weakly dissociated proton is much more strongly associated with the PO_4 group as would be expected from charge considerations and the fact that a terminal PO_4 group always has associated with it one strongly acidic and one weakly acidic hydrogen atom. The small shift in the P(III) peaks suggests that the proton may be located somewhere between the two phosphorus atoms, but somewhat closer to the P(V) atom. An alternate and more likely explanation is simply that a small change occurs in the bonding at the P(III) atom with the addition of a proton to the PO_4 group. Also, it would appear from the changing slope of only the P(V) curve below pH 3 that the second most acidic hydrogen is also associated more strongly with the terminal PO_4 group. However, one question arising in interpretation of nmr data of this kind is that the chemical shifts of phosphorous acid and phosphoric acid themselves do not respond in the same manner to the perturbation of proton addition.[16]

The coupling constants, J_{PP} and J_{HP_1}, of isohypophosphate increase with increasing acidity (Table II). It is not known to what extent this is due to changes in hydration of the anions present as the charge is neutralized or to other factors. However, in some condensed phosphates, an opposite effect was observed[11] which suggests a fundamental difference in the interactions of these species.

The complexing of lithium ion was also studied by ^{31}P nmr at pH 10, where all the isohypophosphate is in the $HP_2O_6^{3-}$ form. Since the stability constants for complexes with alkali metals are considerably smaller than those for complexes with polyphosphates, one would not expect to find the abrupt change in chemical shift when the 1:1 metal-to-ligand ratio is reached. Figure 3 shows the effect of added lithium ion on the chemical shifts of the P(III) and P(V) atoms. Both nuclei respond in the same manner to complexing with the added lithium ion up to $[Li^+]/[HP_2O_6^{3-}]$ ratios of about 3, where >90% of the $HP_2O_6^{3-}$ is in the $LiHP_2O_6^{2-}$ complex. Such behavior would be expected if the lithium ion were located between the phosphorus atoms as would be the case when the anion acts as a bidentate ligand.

The effects of changes in bulk magnetic susceptibility in this system are expected to be small. The magnitude of the chemical shifts for lithium complexing with isohypophosphate is about two-thirds of that observed for lithium complexing by pyrophosphate.[12] For the latter, the shifts are known to be largely the measure of the interaction of the metal ion with the polyphosphate. Also, the chemical shifts for isohypophosphate approach

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(15) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 493 (1954).

(16) K. Moedritzer, *Inorg. Chem.*, **6**, 936 (1967).

a limiting value in the manner expected from the magnitude of the stability constant.

Attempts to perform similar experiments with magnesium ion complexing were unsuccessful because of the insolubility of magnesium salts.

Kinetics of Hydrolysis in Acidic Media.—The kinetics in acid media must be defined in terms of the species $H_4P_2O_6$, $H_3P_2O_6^-$, $H_2P_2O_6^{2-}$, and $HP_2O_6^{3-}$, since each of these species would be expected to exhibit different stability toward hydrolysis.

In solutions containing no weak acids other than the substrate the rate data can be described by the generalized rate expression

$$-\frac{d[H_4P_2O_6]_T}{dt} = k[H_4P_2O_6]_T = (H^+) \sum_{n=4}^{n=1} k_n[H_nP_2O_6^{(4-n)-}] \tag{2}$$

where k_n are the catalytic coefficients for the hydrolysis of the respective species of isohypophosphate. Values for k_4 and k_3 can be obtained at pH greater than about 1, while k_2 and k_1 must be obtained at higher pH in solutions which are buffered to maintain constant pH during the ensuing reaction.

Values for k_4 and k_3 were estimated from the following expression by a least-squares procedure, using values of K_2 and k_2 determined elsewhere in this paper

$$k = \frac{k_4(H^+)^3 + k_3K_1(H^+)^2 + k_2K_1K_2(H^+)}{K_1K_2 + K_1(H^+) + (H^+)^2} \tag{3}$$

The results are reported in Table V. Values for k_2 at 25 and 40° calculated from eq 4 are 3.22 × 10^{-3} and 2.03 × 10^{-2} l. mole^{-1} sec^{-1}, respectively. These results clearly show that the greater the protonation of isohypophosphate, the greater the instability toward acid catalyzed hydrolysis.

TABLE V

ESTIMATES OF CONSTANTS FROM EQUATION 3[b]

	25.0°	40.0°
k_4[a]	6.7 ± 1.7 × 10^{-2}	3.3 ± 0.8 × 10^{-1}
k_3[a]	<9.2 × 10^{-3}	<2.8 × 10^{-2}
K_1	0.35 ± 0.2	0.5 ± 0.2

[a] Units = l. mole^{-1} sec^{-1}. [b] Indicated errors are 95% statistical limits.

Several experiments were conducted between pH 2 and 5 using glycine, glycolic acid, and acetic acid to maintain constant hydrogen ion concentration. In this pH range only the species $H_2P_2O_6^{2-}$ need be considered. The kinetics in this pH range can be represented by the rate law

$$-\frac{d[H_2P_2O_6^{2-}]}{dt} \Big/ [H_2P_2O_6^{2-}] = k = k_{0(2)} + k_{a(2)} \sum^{a} (HA)_a \tag{4}$$

This expression is typical for a general acid catalyzed reaction where $k_{0(2)}$ is the rate coefficient for the solvent and k_a represents the specific rate constant for any Brønsted acid. In glycine and glycolic acid solutions, $k_{0(2)}$ was negligible but represented a significant portion of the rate in acetic acid solutions.

Table VI summarizes the kinetics results and activation parameters for the catalysis by these acids. A plot of the Brønsted relationship at 25° for these acids yields a straight line with a slope of 0.66, compared to 0.80 reported for the hydrolysis of pyrophosphite.[5] Since the slope is a measure of the sensitivity of the substrate to the catalyzing acid, it follows that isohypophosphate is less sensitive to catalysis by Brønsted acids than pyrophosphite. This is also consistent with the absence of general acid catalysis in the hydrolysis of pyrophosphate.[17]

TABLE VI

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS INVOLVING $H_2P_2O_6^{2-}$

Reactant	Temp, °C	Rate constants,[a] l. mole^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
H_3O^+	25.0	3.22 ± 0.27 × 10^{-3}	26.1	+31.8
	40.0	2.03 ± 0.03 × 10^{-2}		
	60.0	1.55 ± 0.01 × 10^{-1}		
H_2O	40.0	2.87 ± 0.60 × 10^{-6}[b]	24.9	+12.2
	60.0	3.47 ± 0.98 × 10^{-6}[b]		
$CH_2(NH_2)CO_2H$	25.0	5.03 ± 0.20 × 10^{-5}	...	...
$CH_2(OH)CO_2H$	25.0	6.63 ± 0.03 × 10^{-6}	19.0	−2.2
	40.0	3.60 ± 0.03 × 10^{-6}		
	60.0	2.28 ± 0.07 × 10^{-4}		
CH_3CO_2H	25.0	1.93 ± 0.03 × 10^{-6}	18.3	+1.6
	40.0	9.58 ± 0.13 × 10^{-6}		
	60.0	5.78 ± 0.27 × 10^{-5}		

[a] Errors represented are statistical 95% limits. [b] Units = sec^{-1}.

Kinetics of Hydrolysis in Basic Media.—Unlike the condensed phosphates, the isohypophosphate ion, $HP_2O_6^{3-}$, is catalyzed by bases, but to a lesser extent than was observed for the pyrophosphite ion.[5] The results of the rate data given in Table IV show the first-order dependence on the hydroxide ion for the hydrolysis of $HP_2O_6^{3-}$. The rate constant, k_{OH^-}, obtained from data at the same sodium ion concentration (0.5 *M*) and at hydroxide ion concentrations of 0.484, 0.387, and 0.194 *M* is 3.55 × 10^{-4} l. mole^{-1} sec^{-1}. However, the value obtained for k_{OH^-} in 0.5 *M* tetramethylammonium chloride is approximately an order of magnitude smaller than the value obtained in 0.5 *M* sodium chloride. In runs at 0.208 and 0.500 *M* hydroxide ion the values are 3.75 × 10^{-5} and 3.77 × 10^{-5} l. mole^{-1} sec^{-1}, respectively (Table IV).

Reactions were run in solutions buffered with carbonate to test whether the hydrolysis of the isohypophosphate ion is subject to catalysis by bases other than by hydroxide ion. Experiments run at constant pH and at total carbonate concentrations of 0.200 and 0.050 *M* (Table IV) show slight sensitivity toward catalysis by the carbonate ion. The observed first-order rate constants are 4.37 × 10^{-7} and 3.22 × 10^{-7} sec^{-1}, respectively.

Unlike the hydrolysis of the pyrophosphite ion,[5] no identifiable intermediates were detected by ^{31}P nmr. Conditions which are necessary to promote base cataly-

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[17] D. O. Campbell and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **76**, 893 (1954).

sis also greatly accelerate the hydrolysis of the intermediates.

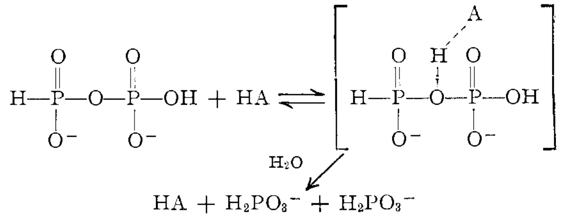
The effect of added sodium ion on the rate of hydrolysis is readily seen in Table IV. A plot of $k/[OH^-]$ *vs.* total sodium ion concentration at constant ionic strength gives a curve of slightly upward curvature, indicating that the dependence is not solely a function of the bound metal but a bulk metal ion concentration effect as well. If the rates were only a function of the $NaHP_2O_6^{2-}$ concentration $k/[OH^-]$ would approach a constant value at high metal ion concentration.

The nature of the catalysis by alkali metal ions is not understood. Van Wazer, *et al.*,[1] investigating the hydrolysis of pyrophosphate and triphosphate using sodium and tetramethylammonium salts as the swamping electrolyte, have observed catalysis by sodium ion at pH ≥ 4. Since the hydrolysis of condensed phosphates is not catalyzed by bases, the effect of metal ion on the rate of hydrolysis for isohypophosphate could be completely different, since it probably would involve a bimolecular reaction between two like charged anions, whereas condensed phosphates would involve a reaction of a water molecule or alkali metal ion with the polyphosphate anion.

From reaction rate theory,[18] one would predict a 100-fold (or 10 eu) difference in the frequency factors for the catalysis of the hydrolysis of $HP_2O_6^{3-}$ and $NaHP_2O_6^{2-}$ by hydroxide ion. Another factor that should be considered is the effect of the added alkali metal ion on the hydration sphere of the anion. This factor would appear in the activation enthalpy as well as the activation entropy term.

The enthalpy and entropy of activation were determined for the reaction of $HP_2O_6^{3-}$ with hydroxide ion in tetramethylammonium chloride at an ionic strength at 0.5. The values are 18.3 kcal/mole and -7.8 eu, respectively.

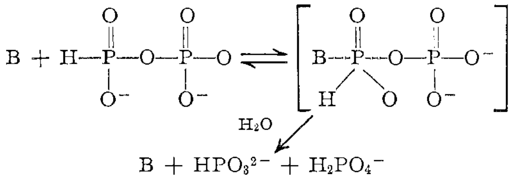
Mechanisms for Acid and Base Catalyzed Hydrolysis.—A mechanism consistent with our hydrolysis results in acidic media is



(5)

where HA represents any Brønsted acid. According to our mechanism the attack by any Brønsted acid occurs at the oxygen atom in the P–O–P linkage. As would be expected from this mechanism, the availability of an electron pair at the oxygen site will determine the reactivity of the substrate with the Brønsted acid. This is consistent with the kinetics as reflected by the Brønsted α values for the condensed phosphates, isohypophosphate, and pyrophosphite and the degree of π bonding in these systems. All the evidence[1-6] indicates that the condensed phosphates have a higher degree of π bonding than pyrophosphite, and it would follow that isohypophosphate would be intermediate between these two extremes. Likewise, the amount of π bonding adequately explains the greater instability of the more protonated forms of isohypophosphate. As more protons are added, the electrons are withdrawn from the π bonds in the P–O–P linkage. The resulting effect on the enthalpy of activation more than compensates for the entropy effect working in the opposite direction as charge is neutralized.

The base catalysis of isohypophosphate probably occurs by nucleophilic attack at the P(III) atom since (1) condensed phosphates do not exhibit base catalysis and (2) the P(III) site would be expected to be more positive. The proposed mechanism consistent with the kinetic data is similar to the mechanism proposed for the pyrophosphite system, where the intermediates were identified by ^{31}P nmr, and is



The tendency for compounds containing a P–O–P linkage to undergo base catalysis appears also to be related to the amount of π bonding in the linkage. The order of increasing susceptibility is pyrophosphate $<<$ isohypophosphate $<$ pyrophosphite.

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(18) K. J. Laidler, "Chemical Kinetics," International Chemical Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 132–134.