The 12-layer rhombohedral anion stacking sequence has been described in detail for In_2ZnS_4.[11] The anion arrangement may be divided into overlapping regions of cubic and hexagonal close packing as shown on the left-hand side of Figure 3. On the basis of the distribution of the cations among the octahedral sites of the close-packed anion structure, the unit cell may be divided into alternate layers, in the z direction, of cation-deficient B1 (NaCl) and B8 (NiAs) structure types as shown on the right-hand side of Figure 3. The cation layers at the boundaries of the B1 and B8 regions are only one-third occupied. Since the configuration of the scandium atoms around each tellurium atom in the B8-type regions is that of a trigonal prism, the Sc centered octahedra in these regions are linked along c by sharing faces. In other directions in these regions, and in all directions of the B1 type regions, the octahedra share edges only. A rather similar situation has been found in the system $Ti_{2+x}S_4$,[12] where the structure is based on the simpler anion stacking sequence ABAC.. The Ti atoms are all in octahedral sites while half the S atoms are in octahedral coordination and half have the trigonal prism configuration.

ScTe has been prepared by Men'kov, *et al.*,[13] and is reported to have a B8-type structure with $a = 4.122$ Å. and $c = 6.753$ Å. It would appear that in the nonstoichiometric material $Sc_{2.3}Te_3$ some filling of the partially occupied metal sites has occurred, but this cannot be established by direct comparison of the X-ray powder photographs since the intensity differences would be quite small. On further increasing the scandium proportion it is to be expected that at some point a phase transition will occur to a scandium-deficient B8-type structure.

The interatomic distances in Sc_2Te_3 are given in Table IV. The Sc–Te distances are all close to the value 2.88 Å. calculated from the ionic radii 0.731 Å. for Sc^{3+} and 2.151 Å. for Te^{2-} used in comparing the rare earth sesquichalcogenides.[4] However, the occurrence of NiAs-like regions in the structure suggests that a high proportion of covalent bonding is actually present. From the cell dimensions quoted for ScTe the distances may be calculated as 2.92 Å. for Sc–Te and 3.37 Å. for Sc–Sc in this compound. If the Sc_2Te_3 structure were undistorted the Sc–Sc distance would be almost identical with that in ScTe. However, the fractional Sc atoms at $\pm 0, 0, {}^5/_{12}$ are distorted away from the atom at $0, 0, {}^1/_2$ so that the Sc–Sc distance is increased to 3.45 Å. The average first neighbor distance in scandium metal is 3.28 Å.

TABLE IV
INTERATOMIC DISTANCES IN Sc_2Te_3

Atoms	d, Å.
Sc_I–Te_{II}	2.91
Sc_{II}–Te_I	2.92
Sc_{III}–Te_I	2.94
Sc_{III}–Te_{II}	2.88
Sc_{II}–Sc_{III}	3.45

The rather complex structure found in Sc_2Te_3 is clearly an intermediate one between a B1 (or a disordered Sc_2S_3) structure and a B8 structure. In such cases the arrangement adopted is probably a consequence of a small energy minimization with respect to alternative arrangements and is not easily predictable. However, the fact that the $Sc_{2+x}Te_3$ structure occurs over the range $2 \leq x \leq 2.3$ suggests that it is a particularly stable one.

Acknowledgments.—We thank K. L. Cheng for chemical analysis and R. J. Paff for X-ray powder diffraction photographs.

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The Acid-Catalyzed Hydrolysis of Pyrophosphoric Acid[1]

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The hydrolysis of undissociated pyrophosphoric acid in water is catalyzed by strong acids. Plots of the first-order rate constant against acid concentration curve upward slightly, but are very similar for hydrochloric, perchloric, and sulfuric acids. Added salts slightly increase the reaction rate. The kinetic form of the hydrolysis, and the values of the Arrhenius parameters, suggest that the mechanism falls into the A2 category. Experiments in aqueous methanol, in acid and at pH 4, show that no methyl phosphate is formed, suggesting that metaphosphate ion is not a reaction intermediate, or more probably is not partitioned indiscriminately between methanol and water.

The hydrolysis of inorganic pyrophosphate has been studied very extensively in the pH region 1–10[3–5] and the over-all rate constants have been dissected into the individual rate constants relating to the undissociated

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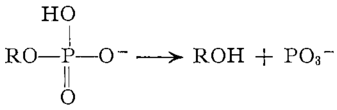
pyrophosphoric acid and to the various anions formed from it.[4,5]

It is generally believed that hydrolyses of monoanions of monoalkyl and -aryl phosphates, and of acetyl phosphate, proceed by elimination of metaphosphate ion, and that the driving force for reaction comes from release of electrons from a formally negative oxygen atom, concerted with proton transfer to the displaced RO group, either directly or through water molecules.[6]



$$RO{-}\overset{\displaystyle HO}{\underset{\displaystyle \| \atop O}{P}}{-}O^- \longrightarrow ROH + PO_3^-$$

Such a mechanism is clearly applicable to the hydrolyses of some of the inorganic pyrophosphate ions and explains the similarity between the Arrhenius parameters for these reactions and those of the monoanions of alkyl and aryl phosphates, *e.g.*, for hydrolysis of $H_3P_2O_7^-$ E = 31.2 kcal. mole^{-1} and $\Delta S^* = +4$ e.u., and for $H_2P_2O_7^{2-}$ E = 28.1 kcal. mole^{-1} and $\Delta S^* = +1$ e.u.[4] Values in these ranges are frequently observed in hydrolyses of the monoanions of monoalkyl and -aryl phosphates.[6]

Table I[a]

Time, min.	0	10	20	30	40	55	70	90	110	140	175	∞	
O.D.	0.042	0.114	0.160	0.197	0.247	0.300	0.345	0.400	0.437	0.470	0.505	0.560	0.560
log (O.D.$_\infty$ − O.D.$_t$)	1.014	0.951	0.903	0.861	0.797	0.717	0.630	0.505	0.391	0.255	0.042		

[a] The O.D. values are corrected to a 0.5-ml. sample.

It has been suggested that metaphosphate ion may be an intermediate in some of the hydrolyses of organic pyrophosphates,[7] and the kinetic form of the alcoholysis of tetrabenzyl pyrophosphate could be explained in terms of elimination of a substituted metaphosphate, although this mechanism was considered to be improbable on other grounds.[8]

However, acid hydrolysis of phosphate esters can occur by mechanisms which fall into the A2 category.[9,10] Campbell and Kilpatrick found that addition of 1.5 M hydrochloric acid speeded hydrolysis of pyrophosphoric acid,[4] but this acid-catalyzed hydrolysis has not been studied in detail. Pyrophosphoric acid is the anhydride of orthophosphoric acid, and therefore we might expect its acid hydrolysis to be similar to those of the simple phosphate esters, or that of acetyl phosphate.[6] We have used two kinetic tests of mechanism. The first is the Zucker–Hammett hypothesis,[10,11] and the second is the generalization that for substrates of similar type the entropy of activation, ΔS^*, for A1 hydrolyses will be close to zero, but will be considerably more negative for A2 hydrolyses.[12] The Zucker–Hammett hypothesis has considerable limitations,[11,13,14] but appears to be reasonably satisfactory as applied to hydrolyses of simple alkyl phosphates,[15] and to the oxygen exchange of orthophosphoric acid,[16] and should therefore also be applicable to the present system.

We also examined the products of solvolysis in methanol–water mixtures, because if free metaphosphate ion were an intermediate it could be captured by both water and alcohol, to give a mixture of orthophosphoric acid and methyl phosphate.[6,17–19]

Experimental

Tetrasodium pyrophosphate (Baker Analyzed Reagent) was found to be free from orthophosphate ion and was used without purification. For kinetic experiments the pH was adjusted by addition of HCl or NaOH. The reaction at pH 4 was followed kinetically only up to 10% so that the pH did not change. There is a negative salt effect upon the hydrolysis of pyrophosphate,[4] whose effect can be eliminated by working with low electrolyte concentrations.

The hydrolysis was followed by determining orthophosphate ion spectrophotometrically by the method of Fiske and Subba-Row,[20] using a Spectronic 20 colorimeter.

For runs at 35° or below stoppered flasks were used and aliquot portions were withdrawn, cooled, and made alkaline to stop the hydrolysis. Sealed tubes were used at temperatures above 35°. The pyrophosphate concentration was 5–10 × 10^{-4} M.

All solutions were made up using twice distilled and then deionized water. Details of a kinetic run at 35.0° follow: $[Na_4P_2O_7] = 10^{-3}$ M, $[H_2SO_4] = 3.0$ M; portions of 0.5 ml. were withdrawn at intervals (1.0-ml. portions were withdrawn for the first few points of the run). The concentration of orthophosphate was determined colorimetrically (Table I).

The absence of methyl phosphate in the products of solvolysis in aqueous methanol was demonstrated by determining the amount of free inorganic phosphate formed during reaction of the pyrophosphate and comparing it with the total phosphate formed when the solution was heated for a time sufficient to allow hydrolysis of any methyl phosphate which might have been formed. The hydrolysis of methyl phosphate is so much slower than that of pyrophosphate that no organic phosphate would be lost during the hydrolysis of pyrophosphate. The results given in Table II show that no methyl phosphate was formed during any of the reactions of pyrophosphate in aqueous methanol.

Results

Kinetics. In Water.—The first-order rate constants, k_ψ, for the acid hydrolyses are given in Table III.

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TABLE II

SOLVOLYSIS PRODUCTS IN AQUEOUS METHANOL[a]

Temp., °C.	CH_3OH, vol. %	Free phosphate, mM	Total phosphate, mM
0	70	1.00	1.00
35	30	0.96	0.97
35	50	0.95	0.95
35	70	0.89	0.89
100	50	0.97	0.97
100	50	1.03	1.03
60	60[b]	0.89	0.89

[a] In 2.6 M H_2SO_4 unless specified. [b] At pH 4.

TABLE III

RATE CONSTANTS OF HYDROLYSIS

Acid Hydrolysis at 35.0°; $10^5\ k_\psi$ (sec.$^{-1}$)

[Acid], M	H_2SO_4	HCl	$HClO_4$
1.0	4.47, 4.47	. . .	. . .
2.0	13.3	. . .	. . .
3.0	21.0	19.1	19.1
3.50	. . .	. . .	25.2
4.0	37.5	32.8	. . .
5.0	59.9	51.5	. . .

Values of $10^5 k_\psi / C_{H^+}$ at 35.0°

[Acid], M	H_2SO_4	HCl	$HClO_4$
1.0	4.47	. . .	. . .
2.0	6.7	. . .	. . .
3.0	7.0	6.4	6.4
3.50	. . .	. . .	7.2
4.0	9.4	8.2	. . .
5.0	12.0	10.3	. . .

Added Salts; 4.0 M HCl at 35.0°

Salt	LiCl		$CaCl_2$		$ZnCl_2$
[Salt], M	1.00	1.50	0.10	1.00	0.10
$10^5 k_\psi$, sec.$^{-1}$	38.3	44.7	35.2	38.3	35.2

Added Salts; pH 4.0 at 100.0°

Salt		$LiClO_4$	$BaCl_2$
[Salt], M	. . .	1.00	5×10^{-5}
$10^6 k_\psi$, sec.$^{-1}$	20.3	10.7	20.8

Added Methanol at 35.0°[a]

CH_3OH, vol. %	30	50	70
[H_2SO_4], M	2.72	2.64	2.72
$10^5 k_\psi$, sec.$^{-1}$	20.4	20.4	22.3

Effect of Temperature

[H_2SO_4], M	1.0	1.0	1.0	1.0	3.05	3.05
Temp., °C.	25.0	35.0	45.0	60.0	25.0	53.6
$10^5 k_\psi$, sec.$^{-1}$	2.02	4.47	11.1	34.2	11.7	105

[a] In methanol–water 60:40 v./v., at pH 4.0; $10^6 k_\psi = 2.4$ sec.$^{-1}$, at 60°.

The first dissociation constant of pyrophosphoric acid is approximately 10^{-1}, and therefore in 1 M sulfuric acid >90% of the pyrophosphate will be present as undissociated acid, and the amount of monoanion, $H_3P_2O_7^-$, will be negligible in more concentrated mineral acid.[4,5]

Therefore in the acid region we can write the rate of reaction as $v = k_\psi$[pyrophosphate] and analyze the variation of k_ψ with changing acid concentration C_{H^+}.

Our rates of acid hydrolysis are much faster than those at higher pH,[3–5] and the contributions due to the hydrolysis of undissociated pyrophosphoric acid and its anions can be neglected.

As shown in Table III the values of k_ψ/C_{H^+} increase only slowly with increasing acid concentration, but depend little upon the nature of the acid. A plot of log k_ψ against log C_{H^+} is linear with slope 1.5. We have also applied Bunnett's treatment to our results,[11] either by plotting log $k_\psi + H_0$ against log a_{H_2O}, giving values of the slope, w, of 4.5 for sulfuric and perchloric acids, and 3.5 for hydrochloric acid, or by plotting log k_ψ − log C_{H^+} against log a_{H_2O}, giving a slope, w^*, of 0.4 for all three acids.

These values of w and w^* are on the borderline between those which Bunnett considers to be diagnostic of A2 reactions in which water acts as a nucleophile, and those in which it acts also as a base.[11] They are very different from those for A1 reactions. However, they are similar to the values found for hydrolyses of organic phosphates and the oxygen exchange of phosphoric acid where independent evidence supports an A2 mechanistic classification.[15,16]

Added salts slightly increase the reaction rate in 4 M hydrochloric acid (Table III).

The temperature coefficient of hydrolysis was measured at 1 and 3.05 M sulfuric acid. In 1 M sulfuric acid, where over 90% of the pyrophosphate is present as undissociated acid, the Arrhenius parameters are: log $A = 7.1$, $E = 16$ kcal. mole^{-1}, and in 3.05 M sulfuric acid where only the undissociated acid is present log $A = 7.0$ and $E = 15$ kcal. mole^{-1}. The value of the entropy of activation, calculated for 1 M sulfuric acid at 25°, is −29 e.u. for hydrolysis in 1 M acid and −31 e.u. for hydrolysis in 3.05 M acid.

In Aqueous Methanol.—A few rate measurements were done using methanol–water mixtures (Table III). The values of k_ψ are very close to the (extrapolated) values of k_ψ for hydrolysis in aqueous sulfuric acid. Similarly at 60° using methanol–water 60:40 v./v. at pH 4.0 our value of $10^6 k_\psi = 2.4$ sec.$^{-1}$ is very close to the interpolated rate constants for hydrolysis in water,[4,5] where $10^6 k_\psi = 2$–4 sec.$^{-1}$.

Discussion

The variation of rate constant with acid concentration is that expected for an A2 hydrolysis, based on analogies with reactions on the alkyl phosphates.[15,16] Similarly the values of the entropy of activation are in the range associated with A2 hydrolyses, in which water, acting as a nucleophile, attacks an electrophilic center.[12]

Addition of methanol has almost no effect upon reaction rate for a given acid concentration. For a number of other A2 hydrolyses the addition of organic solvents to water has little effect on reaction rate, unless the water content of the solvent becomes very low.[21,22] However, addition of alcohol or dioxane also has little effect upon the rate of hydrolysis of monoanions of monoalkyl phosphates,[17,18] where reaction probably involves elimination of metaphosphate ion. Similarly at pH 4 our measured rate constant for hydrolysis of

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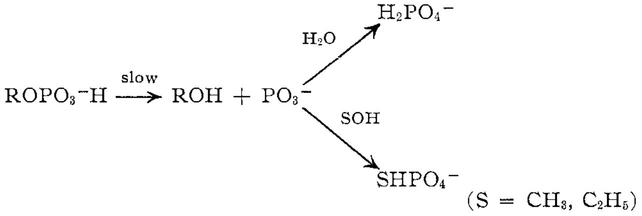
dianionic pyrophosphate in aqueous methanol is very similar to that in water alone.[4,5]

The small effect of added salts in the acid hydrolysis would be unexpected if reaction followed an A1 mechanism, because those added salts which increase the protonating power of acids also generally increase the rates of these reactions.[10,23] Although polyvalent cations catalyzed the hydrolysis of organic phosphates,[6,7,24] they are almost without effect in our acid hydrolyses where the proton is the only important catalyst. Attempts to study their effect upon the hydrolysis at higher pH were frustrated by the insolubility of pyrophosphates of the bivalent metals. Campbell and Kilpatrick observed negative salt effects upon the hydrolysis of pyrophosphate at pH 1–10,[4] and we find that at pH 4 the rate is almost halved by addition of 1 *M* lithium perchlorate (Table III). Possible contamination by heavy metals was apparently not responsible for this result, because addition of 5 × 10^{-5} *M* barium chloride did not change the rate constant significantly.

Metaphosphate as a Reaction Intermediate.—Several workers have obtained evidence for metaphosphate ion as a reaction intermediate by carrying out solvolyses of monophosphate anions in mixtures of alcohol and water and trapping the metaphosphate ion as alkyl phosphate.[17–19]



From experiments with aryl phosphates and glycerol-2-phosphate, it seems that water, methanol, and ethanol have similar reactivities toward the postulated metaphosphate ion. Generally speaking reactive intermediates, such as carbonium ions, discriminate little between hydroxylic solvents,[25] and therefore formation of methyl or ethyl phosphate is good evidence for metaphosphate ion as a reaction intermediate. All the evidence suggests that metaphosphate ion is a reactive intermediate whenever the phosphate ester contains the group $-OP_3OH^-$, and therefore it could well be formed from the mono-, di-, and trianions of pyrophosphoric acid (*cf.* ref. 7). However, we found no methyl phosphate when pyrophosphoric acid was hydrolyzed in acid solution or at pH 4. The absence of methyl phosphate in the acid hydrolysis is not unexpected, because water could well be a better nucleophile than methanol toward the conjugate acid of pyrophosphoric acid, $H_5P_2O_7^+$. Its absence in hydrolysis at pH 4 is surprising, because the predominant ionic species are $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$, and from analogy with the behavior of phosphate monoesters we expected then to be able to eliminate metaphosphate. There appear to be two possible explanations for these results: (i) The solvent attack on $H_3P_2O_7^-$ and $H_2P_2O_7^{2-}$ is the rate-limiting step of reaction, but if this explanation is correct it is hard to see why bimolecular solvent attack does not occur during hydrolysis of phosphate esters, or during oxygen exchange of the orthophosphate ion.[6,15,26] (ii) The metaphosphate ion is an intermediate, but discriminates between water and methanol. This second explanation seems the more likely, because the pyrophosphate ion itself is probably solvated by water, rather than methanol, and a metaphosphate ion when eliminated would therefore be surrounded by water molecules with which it would react. To this extent one could consider that "free" metaphosphate ion is never formed in these reactions. Jencks and Gilchrist have studied solvolyses of phosphoramidate catalyzed by either hypochlorite ion or nitrous acid, where the metaphosphate ion is a probable intermediate.[19] However, in aqueous alcohol the ratios of phosphate to alkyl phosphate differ from those found for solvolyses of phosphate esters. As was noted this situation arises also in carbonium chemistry, where the fate of the carbonium ion may depend upon its source, *e.g.*, similar product compositions are generally obtained if the carbonium ion comes from ionizations of uncharged substrates, *e.g.*, alkyl halides in mixed solvents, or in salt solutions, but not if it is formed from some energetic ionic intermediate, as in deamination or deoxidation.[27]

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