series of compounds. It is unlikely that steric factors are responsible for the trend, since alcohols have low steric requirements for interaction.[9,29] The results indicate that to a CH_2 group, the CH_3 group is more electron releasing than the SiH_3 or GeH_3 groups. These results are not in agreement with the order of electron release suggested by Srivastava and Onyszchuk[36] for the GeH_3 and CH_3 groups, from their infrared studies of the acetate derivatives of CH_4 and GeH_4. The results are not strictly comparable, however, since the compounds involved are structurally different. The order is also not consistent with the experimental inductive effects of the related $(CH_3)_3C$, $(CH_3)_3Si$, and $(CH_3)_3Ge$ groups, although again different systems were studied.[37] The possibility of an interaction between the lone pairs of electrons on oxygen and the d orbitals of silicon or germanium through a CH_2 group should be given some further consideration in light of the present results.[38]

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On the Acidity of Substituted Methylenediphosphonates and Their Interaction with Alkali Metal Ions

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The acidity of and Li^+, Na^+, K^+, and Cs^+ complexing with a series of substituted methylenediphosphonates have been determined at 25° in 0.5 M tetramethylammonium chloride. The acid properties of the alkyl-substituted methylenediphosphonates have been shown to be correlated with the electron-donor ability of the substituents attached to the bridging carbon atom. Also, $\log \beta_{MH_iL}$ ($i = 0, 1$) is predicted by an equation involving the reciprocal of the radius of the bare cation and the sum of the Taft σ^* values. For 1-hydroxyethylidene-1,1-diphosphonic acid evidence is presented for intramolecular binding of the protons and the metal ions by the hydroxyl group.

Introduction

Previous studies[1-3] on methylene- and polymethylenediphosphonic acids, $H_2O_3P(CH_2)_nPO_3H_2$, showed that the pK values for the least acidic hydrogen atom and the values of the formation constants of alkaline earth metal ion complexes both decreased with increase in the value of n. The largest decrease in the interaction of diphosphonates with cations was noted in going from methylenediphosphonic acid, MDP, to dimethylenediphosphonic acid.

This paper includes a study of the effect on proton dissociation and alkali metal complexing upon substituting alkyl and hydroxy groups for the methylene hydrogens in MDP. In particular, an objective is to determine if the interaction of alkali metal ions with these diphosphonates is primarily ionic and specific site binding in character as opposed to a random nonspecific interaction. In the case of condensed phosphates[4] and isohypophosphate,[5] evidence obtained from ^{31}P nmr studies suggested specific site binding. Unfortunately, the changes in the ^{31}P nmr chemical shifts and spin–spin coupling constants for the phosphonate polyanions upon metal complexing are too small to be used for such a study.

Experimental Section

Chemicals.—Methylenediphosphonic acid (MDP) was prepared as previously described[6] but was further purified by crystallization of a tetrasodium salt. *Anal.* Calcd for $H_2C(PO_3)_2Na_4 \cdot 9H_2O$: C, 2.8; H, 4.7; P, 14.5. Found: C, 2.9; H, 4.6; P, 14.5. Aqueous solutions of the MDP salt were converted to the free acid by cation exchange with the hydrogen form of a Dowex 50 resin.

Ethylidene-1,1-diphosphonic acid, $CH_3CH(PO_3H_2)_2$ (EDP), and isopropylidenediphosphonic acid, $(CH_3)_2C(PO_3H_2)_2$ (PDP), were prepared by hydrolysis of their tetraethyl esters. The esters were prepared by stepwise methylation of the carbanion

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of MDP ester.[7,8] *Anal.* Calcd for $H_2O_3PCH(CH_3PO_3H_2)$: C, 12.6; H, 4.2; P, 32.6. Found: C, 12.7; H, 4.1; P, 32.5. *Anal.* Calcd for $H_2O_3PC(CH_3)_2PO_3H_2$: C, 17.7; H, 4.9; P, 30.4. Found: C, 17.6; H, 5.0; P, 30.4. Octylidene-1,1-diphosphonic acid, $C_7H_{15}CH(PO_3H_2)_2$ (ODP), was prepared in a similar manner, as reported recently.[9]

Crystalline 1-hydroxyethylidene-1,1-diphosphonic acid, $CH_3C(OH)(PO_3H_2)_2$ (HEDP), was prepared by the reaction of PCl_3 with water and acetic acid.[10] *Anal.* Calcd for $H_2O_3PC(OH)(CH_3)PO_3H_2 \cdot H_2O$: C, 10.7; H, 4.5; P, 27.7. Found: C, 10.8; H, 4.6; P, 27.6. Constant ionic strength was maintained with recrystallized tetramethylammonium chloride,[11] free of residual amine and CO_2. The recrystallized tetramethylammonium chloride was converted to tetramethylammonium hydroxide by anion exchange.

The aqueous solutions of the diphosphonic acids and tetramethylammonium hydroxide were carefully standardized prior to potentiometric measurements.

Potentiometric Measurements and Calculations.—The potentiometric procedures for determination of acidity and formation constants were described previously.[12] All measurements were made at 25° in 0.5 M $(CH_3)_4NCl$. The concentrations of $[H^+]$ and $[OH^-]$ were calculated from pH measurements using the expressions

$$\gamma_{H^+} = \frac{(H^+)}{[H^+]} \qquad (1)$$

and

$$K^{w}_{\text{apparent}} = (H^+)[OH^-] \qquad (2)$$

where (H^+) is antilog (−pH) and brackets indicate concentrations. Several independent determinations of γ_{H^+} and K^{w}_{apparent} in 0.5 M $(CH_3)_4NCl$ gave values of 0.865 ± 0.005 and $1.244 \pm 0.002 \times 10^{-14}$, respectively. These values were used in calculating the free hydrogen and hydroxide ion concentrations.

The acidity constants, K_i, and formation constants, β_{MH_jL}, for the substituted methylenediphosphonic acids, are represented by the equations

$$K_i = \frac{(H^+)[H_{a-i}L]}{[H_{a-i+1}L]} \qquad (3)$$

$$\beta_{MH_jL} = \frac{[MH_jL]}{[M][H_jL]} \qquad (4)$$

Results

The five diphosphonic acids described in this paper titrate as tetrabasic acids having two strongly dissociated hydrogen atoms (p$K < 3$) that show no independent inflection points. Only MDP exhibits a stepwise titration curve for the remaining two weakly dissociated hydrogen atoms with two definite breaks. No break in the pH titration curve for the least acidic hydrogen atom is observed for EDP, PDP, ODP, and HEDP when titrated with tetramethylammonium hydroxide. Independent titrations of concentrated solutions of ODP, EDP, PDP, and HEDP in 1 M NaCl with NaOH show an inflection point for the most weakly dissociated hydrogen atom because of the lowering of the apparent pK values by complexing with sodium ion.

The values of pK_2, pK_3, and pK_4 for MDP, EDP, ODP, PDP, and HEDP are tabulated in Table I, along with estimated errors at the statistical 95% confidence limits. Each pK value is the average of at least 20 computed values obtained from several independent titrations.

TABLE I

ACID DISSOCIATION CONSTANTS FOR THE DIPHOSPHONATES AT 25° IN 0.5 M $(CH_3)_4NCl$

Ligand[a]	pK_2	pK_3	pK_4
PDP	2.94 ± 0.02	7.75 ± 0.05	12.4 ± 0.2
HEDP	2.54 ± 0.05	6.97 ± 0.05	11.41 ± 0.05
EDP	2.66 ± 0.03	7.18 ± 0.03	11.54 ± 0.04
MDP	2.49 ± 0.04	6.87 ± 0.02	10.54 ± 0.02
ODP	...	7.45 ± 0.05	11.9 ± 0.15

[a] Abbreviations: PDP, isopropylidenediphosphonic acid; HEDP, 1-hydroxyethylidene-1,1-diphosphonic acid; EDP, ethylidene-1,1-diphosphonic acid; MDP, methylenediphosphonic acid; ODP, octylidene-1,1-diphosphonic acid.

The values of pK_1 for the diphosphonates are below 1 and cannot be measured adequately by our procedure. Arbitrary choices of pK_1 values below 1 had no effect on the computer fit of the titration curves with the calculated values for pK_2. The pK_2 values in Table I were calculated assuming pK_1 = 1.

The stability constants for the 1:1 cesium, potassium, and sodium ion complexes with the monoprotonated (β_{MHL}) and the unprotonated (β_{ML}) forms of the four anions are reported in Table II, along with estimated errors at the statistical 95% confidence limits.

TABLE II

β_{MH_jL} VALUES FOR SUBSTITUTED METHYLENEDIPHOSPHONATE WITH ALKALI METAL IONS IN 0.5 M $(CH_3)_4NCl$ AT 25°

Metal	Ligand	Log β_{MHL}	Log β_{ML}
Li^+	PDP	1.38 ± 0.04	3.83 ± 0.10
	EDP	0.99 ± 0.04	3.12 ± 0.12
	MDP	0.82 ± 0.03	2.48 ± 0.05
	HEDP	1.08 ± 0.03	3.35 ± 0.06
Na^+	PDP	0.57 ± 0.05	2.08 ± 0.04
	EDP	0.50 ± 0.03	1.51 ± 0.09
	MDP	0.39 ± 0.03	1.13 ± 0.08
	HEDP	0.54 ± 0.03	2.07 ± 0.05
K^+	PDP	0.35 ± 0.03	1.60 ± 0.07
	EDP	0.28 ± 0.03	1.20 ± 0.10
	MDP	0.20 ± 0.02	1.02 ± 0.04
	HEDP	0.36 ± 0.03	1.79 ± 0.04
Cs^+	PDP	0.35 ± 0.03	1.40 ± 0.05
	EDP	0.09 ± 0.02	1.02 ± 0.09
	MDP	0.04 ± 0.02	0.84 ± 0.05
	HEDP	0.24 ± 0.04	1.60 ± 0.10

Each log β value represents an average of at least 10 independent determinations with total M to total L ratios varying between 0.5 and 35.[13] Also, the log β_{MHL} and log β_{ML} values for the 1:1 lithium ion complexes with these ligands are reported in Table II. However, the reported log β values represent calcula-

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tions using only runs where total metal to total ligand ratios did not exceed 2. This was necessary because of the apparent existence of higher order complexing, which will be discussed later. The number of runs that were used for calculating β_{ML} and β_{MHL} values for lithium was at least four.

In all computations for $\beta_{\mathrm{MH}_i\mathrm{L}}$, only two forms of the ligand were assumed to coexist at a specific pH, *i.e.*, $\mathrm{H}_i\mathrm{L}$ and $\mathrm{H}_{i-1}\mathrm{L}$. Overlap by a third protonated species was negligible because of the large differences between the successive acidity constants. (The minimum separation between pK_i and pK_{i-1} for the diphosphonates was about 4 pK units.)

Discussion

Acidity.—Comparing the pK values in Table I, it is apparent that the values for pK_2, pK_3, and pK_4 increase with increase in alkyl substitution. The most significant effect occurs with the most weakly dissociated hydrogen atom, where the substitution of each methylene hydrogen atom by a methyl group results in an increase in the value of pK_4 by about 1 pK unit. Similar effects have been reported for alkylphosphonic[14,15] acids and polymethylenediphosphonic acids.[3] The Taft treatment has been satisfactorily applied to the proton dissociation of several alkylphosphonic acids[15] ($\mathrm{RPO_3H_2}$). Also, the effect on proton dissociation of the electron-withdrawing power of substituents attached to a bridging carbon atom has been treated quantitatively.[16]

The trend in the pK_i values, excluding HEDP, for this family of compounds is what would be expected from the electron-withdrawing abilities of the substituents. Employing the Taft polar substituent constants,[17] σ^*, for the alkyl substituents attached to the methylene carbon, a plot of pK_i *vs.* $\Sigma\sigma^*$ yielded a straight line with a correlation coefficient for pK_3 and pK_4 of 0.986 and 0.993, respectively. The statistically poor correlation coefficients 0.850 and 0.645, respectively, were obtained when HEDP was included in the correlation. The fact that ODP fits the alkyl-substituted correlation indicates that steric effects are negligible for substitution of large groups for the methylene hydrogens. Moreover, for the strict dependence of pK_i on $\Sigma\sigma^*$ to hold for a given series of compounds would require all effects, other than electron withdrawing, to remain essentially constant.

Employing the Taft equation derived from the pure alkyl-substituted methylenediphosphonates, the calculated values for pK_3 and pK_4 for HEDP are 6.56 and 9.48 as compared with the observed values of 6.97 and 11.41, respectively. These large deviations clearly show that effects other than polar must be considered in explaining the acidity of HEDP.

For the polymethylenediphosphonates,[3] it has been shown that extensive interaction between the two phosphonate moieties does occur, but, with the increase in the distance between the two functional groups, pK_4 − pK_3 approaches the predicted statistical limiting values of log 4. Also, it is of interest to note that the magnitude of (pK_3 + pK_4)/2 is very close to that of pK_2 for the corresponding alkyl phosphonate. Apparently, the P–C–P bond angle in diphosphonates is controlled mostly by the repulsion between the two large phosphonate groups, with alkyl substitution on the methylene group being a second-order effect.

It is reasonable to assume that the hydroxyl group in HEDP acts as an additional bonding site to the two phosphonate moieties. Such a participation probably occurs *via* a five-membered ring. In the case where more than two hydrogens are associated with the HEDP anion the interaction of the hydroxyl group with the acidic protons is probably more diffuse.

The intramolecular participation of the hydroxyl group in the bonding of protons is probably more important than changes in the hydration properties upon adding the hydroxyl group to the diphosphonate structure.

Alkali Metal Ion Complexing.—During the course of our study, no evidence was observed for complexing of alkali metal ions by the diprotonated diphosphonates. The pH titration curves for $\bar{a}$ values below 2 were identical in the presence or absence of alkali metal ions. The only exception was some detection of very weak complexing of Li^+ by diprotonated HEDP. As discussed later on, the OH group in HEDP appears to contribute to metal ion complexing.

Li^+ was found to form 2:1 complexes with the unprotonated diphosphonates

$$\mathrm{LiL}^{3-} + \mathrm{Li}^+ \rightleftharpoons \mathrm{Li_2L}^{2-} \qquad (5)$$

The equilibrium constant for eq 5 was 15 ± 5 for PDP and HEDP, and about 3 for MDP and EDP. No significant 2:1 complexing was observed for Na^+, K^+, or Cs^+. Except for very weak complexing of HEDP, the monoprotonated diphosphonates do not form 2:1 complexes with any of the alkali metal ions.

It has been suggested[18] that if the formation of a complex between a cation and an anion is purely electrostatic and if the interaction is large enough to displace the solvation shell of the cation, then there should exist a linear relationship between the change in free energy accompanying the formation of the complex and the ionic potential of the cation. This appears to be the case for the interaction of alkali metal ions with diphosphonates since plots of log β_{ML} *vs.* $1/r$[19] with each diphosphonate gave fairly parallel straight lines with correlation coefficients in the range 0.965–0.983. Similar plots of log β_{MHL} *vs.* $1/r$ also gave fairly straight and parallel lines, but with a different slope than was ob-

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[17] Values for σ^* were taken from ref 16: $\mathrm{CH_3}$, 0.00; $\mathrm{C_2H_5}$, −0.10; H, 0.49; $\mathrm{C_7H_{15}}$, −0.17; OH, 1.55. The value for $\mathrm{C_7H_{15}}$ was obtained assuming a polar substitution effect for $\mathrm{C_5H_{10}}$ of 0.070 unit.

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tained for the log β_{ML} *vs.* $1/r$ plots. The correlation coefficients ranged from 0.975 to 0.999.

The interaction of metal ions by polyphosphates[20,21] has been interpreted previously in terms of electrostatic binding. Moreover, from a simple electrostatic model[4] it has been shown that specific site binding would be energetically favored if the ions lost sufficient waters of hydration to reduce the distance of interaction and thus reduce the effective dielectric constant of the solvent.

Plots of log β_{MH_iL} for Li^+, Na^+, K^+, and Cs^+ against the $\Sigma\sigma^*$ values for MDP, EDP, and PDP can be represented by a linear relationship. The statistical fits are shown in Table III. The average deviation between experimental and calculated log β_{MH_iL} values is less than 0.04 unit. The plot for log β_{CsHL} against $\Sigma\sigma^*$ gave a poorer fit because of the experimental uncertainties in the formation constants.

TABLE III

PARAMETERS FOR THE CORRELATION OF LOG β_{MH_iL} FOR MDP, EDP, AND PDP FOR A SPECIFIC ALKALI METAL ION AS A FUNCTION OF $\Sigma\sigma^*$: LOG $\beta_{MH_iL} = A - \rho^*\Sigma\sigma^*$

Metal complex	A	ρ^*	Av log β(calcd) − log β(measd)	Correlation coefficient
LiL	3.82	1.378	0.02	0.999
NaL	2.05	0.969	0.04	0.994
KL	1.56	0.592	0.05	0.978
CsL	1.37	0.571	0.09	0.980
LiHL	1.34	0.571	0.05	0.975
NaHL	0.58	0.184	0.01	0.992
KHL	0.35	0.153	0.00	0.999
CsHL	0.32	0.316	0.05	0.932

When HEDP was included in the σ^* correlations, the fit was significantly poorer and well beyond the uncertainties of log β_{MH_iL} and σ^* values. The calculated values for HEDP were larger than would be predicted using the parameters in Table III. The measured values for log β_{MHEDP} for Li^+, Na^+, K^+, and Cs^+ are larger than the calculated values by 1.78, 1.52, 1.15, and 0.92 units, respectively. Similarly, the following positive deviations were calculated from Table III for log β_{LiHL}, log β_{NaHL}, and log β_{KHL} with HEDP: 0.63, 0.25, and 0.24.

These large positive deviations are believed to be due to the participation of the hydroxyl group of HEDP in metal ion binding, as was previously discussed with the acidity data.

For the interaction of the alkali metal ions with either the tri- or tetravalent anions, the proportionality constant, ρ^*, decreased with increase in the radius of the cation. Also the largest change in ρ^* occurred in the series with the tetraanion (Table III). Since ρ^* is a measure of the susceptibility of a given series of reactions to the inductive effect of the substituents,[22] one would expect from simple electrostatic consideration that the monovalent cation with the smaller radius would be affected to a greater extent by the substituents than one of larger radius. That is, if all other effects are constant, a cation such as Li^+ would require more work to separate it from the polyanion than the larger Cs^+.

Figure 1 illustrates the type of fit obtained when (log β_{MH_iL}) + $\rho^*\Sigma\sigma^*$ is expressed as a function of $1/r$. The vertical line drawn through each point represents the maximum deviation of the results with the three ligands PDP, EDP, and MDP, while each point represents the mean value. Certainly, the normalization of the ligands other than HEDP achieved through the use of the Taft σ^* values is excellent since the values calculated for a given metal ion as a function of (log β_{MH_iL}) + $\rho^*\Sigma\sigma^*$ differ by at most 0.11 unit, and in most cases the variance is much less.

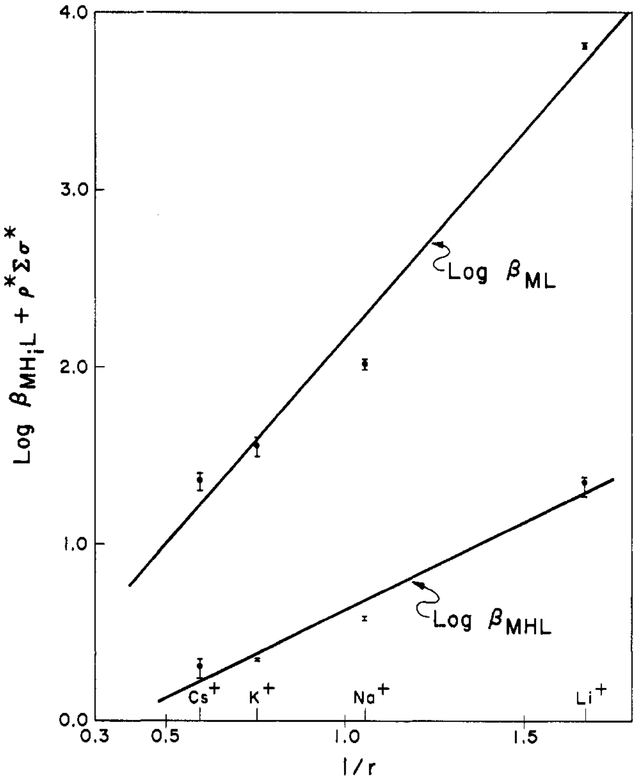

Figure 1.—Plot of (log β_{MH_iL}) + $\rho^*\Sigma\sigma^*$ as a function of $1/r$ for the alkyl-substituted methylenediphosphonates PDP, EDP, and MDP.

A least-square fit of the data shown in Figure 1, indicated by the solid line, gave the equations

$$(\log \beta_{ML}) + \rho^*\Sigma\sigma^* = -0.16 + (2.33/r) \quad (6)$$

$$(\log \beta_{MHL}) + \rho^*\Sigma\sigma^* = -0.36 + (0.99/r) \quad (7)$$

Equations 6 and 7 fit the data with standard deviations of 0.15 and 0.12, respectively. The reasonable fit for the over-all data with the $1/r$ function indicates that electrostatic attraction is a major factor in determining the magnitude of the stability constants of alkali metal ions with diphosphonates. However, since the standard deviations of the fit are larger than the experimental error for the log β_{MH_iL} values, interpretation of the results by a purely electrostatic interaction is probably an oversimplification.

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In a recent study on the Raman spectra of metal complexes, Brintzinger and Plane[23] have concluded that metal binding by pyrophosphate is essentially electrostatic with *at least* one PCO_3 group coordinated through two O atoms to the metal ion. Because of steric effects, they have proposed that the pyrophosphate ion acts as a tridentate anion. It is reasonable to assume similar interactions by the isoelectronic methylenediphosphonates, with HEDP having an additional bonding site.

It is of interest to note that large deviations from linearity were obtained for plots of log $\beta_{\mathrm{MH}_i\mathrm{L}}$ against ionization potential. This is contrary to that reported[17] for the metal hydroxides where plots of log β against z^2/r or the ionization potential were linear. The similarity between the two plots could be fortuitous since for the alkali metal ions only Na^+ and Li^+ were included in the correlation.

The entropies of hydration of metal ions are proportional to the reciprocal of the crystal radii.[24] The excellent fit of log $\beta_{\mathrm{MH}_i\mathrm{L}}$ *vs.* $1/r$ suggests that the enthalpy changes accompanying alkali metal ion complexing by diphosphonates are either negligible or independent of alkali metal ion. Work is underway to measure the enthalpy change for metal ion complexing to determine the relative significance of the ΔH and ΔS terms to the stability of these ionic complexes.

Acknowledgment.—The authors gratefully acknowledge the assistance of Mr. R. A. Russell for the computer calculations made in this study.

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The Crystal and Molecular Structure of Dipotassium Phenyl Phosphate Sesquihydrate ($K_2C_6H_5PO_4 \cdot 1.5H_2O$)

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The structure of $K_2C_6H_5PO_4 \cdot 1.5H_2O$ has been determined by X-ray diffraction study. The crystals are orthorhombic (a = 5.91, b = 12.01, c = 30.80 A, space group Pbcn) with eight molecules per unit cell. The intensities of 728 independent reflections were recorded photographically and estimated with a densitometer. The structure was solved by a symbolic sign method and has been refined to a conventional R factor of 11%. The phosphate group is in the form of a distorted tetrahedron, with one long ester P–O distance of 1.64 A and three essentially equal P–O distances of 1.51, 1.53, and 1.53 A. The bond angles at the phosphorus atom vary from 101 to 114°. There are three different potassium ions in the cell, one in a general position and two in special positions. If the limit of potassium coordination is taken as 3 A, K(1) in a general position is coordinated to four oxygen atoms, K(2) in a special position is coordinated to six oxygen atoms, and K(3) also in a special position is coordinated to four oxygen atoms. Of the phosphate oxygen atoms two are coordinated or hydrogen bonded to three other atoms and one is coordinated or hydrogen bonded to four other atoms in addition to the covalent bond to the phosphorus atom. This has the effect of producing a tightly bonded crystal with small thermal vibrations, particularly evident in the phosphate group. This also appears to cause the three nonester oxygen atoms to be equidistant from the phosphorus atom.

Introduction

The hydrolysis of organic phosphates has been studied for a number of alkyl and aryl phosphates.[1-3] The structures of organic phosphates, in particular a comparison of the P–O–C linkages, should help in interpretation and understanding of the kinetic results, even though extrapolation from crystal structures to structures in solution is difficult. It is particularly interesting and informative to consider the effects of metal coordination and hydrogen bonding on the structures, inasmuch as in several instances the presence of a metal ion has appreciably effected the hydrolysis rates.[4] Such results suggest the possibility of a metal ion complex in solution in these cases. A complex between the monoanion, PO_4R^-, and a water molecule has been proposed to explain the structural requirements for hydrolysis of monoesters as well as cyclic phosphate esters.[5,6] Structural results[7,8] indicate a rather significant effect of hydrogen bonding and complex formation on P–O and PO–C distances which may be significant when considering various factors affecting the kinetics. The structure of dipotassium phenyl phosphate with 1.5 molecules of water of hydration is, to

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