pH Dependence of Phosphorus-31 Chemical Shifts and Coupling Constants of Some Oxyacids of Phosphorus

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The ^{31}P chemical shifts of a series of oxyacids of phosphorus were found to vary linearly with the degree of neutralization. This effect has been interpreted on a quantum mechanical basis in terms of additive contributions to the chemical shift due to variations in the effective electronegativity of the oxygen atoms bonded to phosphorus upon association with hydrogen, OPO bond angles, and occupation of phosphorus d_π orbitals.

Prior investigators have shown that the ^{31}P chemical shifts of orthophosphate solutions[1] as well as of solutions of the condensed phosphates[2] become more negative with decreasing acidity. However, it was noticed in connection with some other studies[3] that, as the acidity of solutions of diphosphonic acids was decreased, the chemical shift became more positive. This suggested a detailed study of the influence of varying degrees of neutralization on the ^{31}P nmr spectra of the acids of phosphorus in general.

Experimental Section

The studies reported here were carried out with a Varian HR-60 spectrometer operating at 24.288 Mc. The samples were investigated as aqueous solutions by mixing the desired proportions of 10 M NaOH (or a concentrated strong acid) with saturated aqueous solutions of the chosen acids of phosphorus and then diluting to a fixed phosphorus concentration for each series of acids. Each sample was measured in triplicate and the peak positions determined in this way were reproducible to within 2–3 cps. The phosphorus concentrations in molarities were 0.6 for the dimethylphosphinate system, 2 for the phosphite, hypophosphite, and phenylphosphinate systems, and 3 for the methylphosphonate system. However, as shown in Table I, it was found that varying the solution concentrations in this general range had a relatively small effect on the chemical shifts and coupling constants as compared to that due to changing the degree of neutralization. Also replacing the sodium by tetramethylammonium ion had an inappreciable effect on the chemical shifts of the completely neutralized acids thus indicating that sodium complexing plays a minor role.

Chemical Shifts

In all cases, the chemical shift was found to vary linearly with degree of neutralization, when going from the acid to the completely neutralized salt. However, when neutralization was complete, addition of further base had no appreciable effect on the chemical shift. Alternatively, addition of a very strong acid (such as perchloric or hydrochloric) to the salt-free phosphorus acid caused the chemical shift to continue to change in the same direction it had varied as the degree of neutralization was brought to zero. The experimental results are shown in Figure 1, in which it should be noted that addition of hydrogens to the PO_4^{3-} ion

TABLE I

CONCENTRATION DEPENDENCE OF ^{31}P NMR CHEMICAL SHIFTS, δ, AND COUPLING CONSTANTS, J_{P-H}, OF HYPOPHOSPHOROUS AND PHOSPHOROUS ACIDS IN WATER

| Concn, | $H_2P(O)(OH)$ | | $HP(O)(OH)_2$ | |
M	δ,^{a} ppm	J_{P-H}, cps	δ,^{a} ppm	J_{P-H}, cps
10	−12.2	566	−5.8	690
8	−12.3	565	−5.5	686
6	−12.1	564	−5.2	682
4	−11.9	560	−5.0	676
2	−11.7	556	−4.7	672
1	−11.3	554	−4.5	670
0.75	...	...	−4.4	669
0.5	−10.9	550	−4.4	666
0^b	−10.5	547	−3.9	664

^{a} External reference: 85% H_3PO_4. ^{b} Data for zero concentration are extrapolated.

causes a positive change in the chemical shift, $\Delta\delta = +6$ ppm; whereas, for all of the other acids, there is a negative change—with $\Delta\delta$ ranging from −1 for HPO_3^{2-} to −14 for $(CH_3)_2PO_2^-$. As measured from the region between the acid and monosodium salt, the negative change in $\Delta\delta$ with increasing acidity for the anions other than the orthophosphate is about three times greater when a methyl group is bonded to the phosphorus as when this methyl is substituted by a hydrogen. Likewise, it is 2.5 times greater when there are two hydrogens or two methyl groups bonded to the phosphorus as compared to one hydrogen or one methyl, respectively.

From the shape of the curves in Figure 1, it is obvious that the observed changes in chemical shift must be attributed to the association of protons with the anions. It is known that such associated hydrogens undergo rapid exchange from one acid molecule to another and from the acid to the aqueous solvent. This probably means that the observed chemical shift represents an average of the permissible spatial placements of the associated hydrogen(s) with respect to the phosphorus and its framework of four neighboring atoms. Thus, for purposes of theoretical interpretation of the data of Figure 1, these hydrogens may be considered as perturbing the electronic characteristics of the oxygen atoms bonded to the phosphorus. In a recent, thorough quantum mechanical treatment of ^{31}P chemical shifts,[4,5] it has been pointed out that for molecules in which the

(1) R. A. Y. Jones and A. R. Katritzky, *J. Inorg. Nucl. Chem.*, **15**, 193 (1960).
(2) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 831 (1962).
(3) K. Moedritzer and R. R. Irani, *J. Inorg. Nucl. Chem.*, **22**, 297 (1961).
(4) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
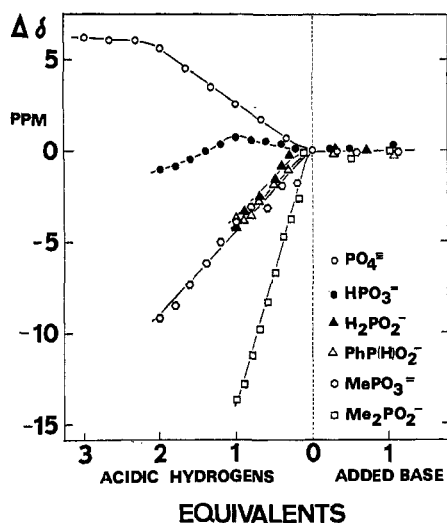(5) J. H. Letcher and J. R. Van Wazer, *ibid.*, **44**, 2916 (1966).

Figure 1.—Variation of the ^{31}P chemical shift of some oxyacids of phosphorus with the degree of neutralization as measured from the neutral salt. The chemical shifts (in ppm) of the neutral salts are -6.0 for PO_4^{3-}, -3.3 for HPO_3^{2-}, -7.3 for $H_2PO_2^{-}$, -17.4 for $C_6H_5P(O)(H)O^{-}$, -20.6 for $CH_3PO_3^{2-}$, and -42.1 for $(CH_3)_2PO_2^{-}$.

phosphorus has a coordination number of 4, the ^{31}P chemical shift is comprised of a σ-bond contribution determined solely by the p-orbital occupation and a π-bond contribution determined by the total occupation of the phosphorus d orbitals. Thus

$$\delta = \delta_0 + \delta_\sigma + \delta_\pi \tag{1}$$

where δ is the chemical shift referenced to 85% phosphoric acid, δ_0 is the absolute shift of the reference standard, and δ_σ and δ_π are the σ and π contributions, respectively.

The theory showed that δ_π is negative and is proportional to the increase in total occupation of the d_π orbitals of the phosphorus, being independent of the distribution of this total π character among the various bonds. Numerical evaluation leads to the conclusion that for phosphorus having four neighboring atoms, $\delta_\pi = 147n_\pi$, where n_π is the total nunber of electrons in the d_π orbitals of the phosphorus atom being viewed by ^{31}P nmr. Since the nmr chemical shift is primarily sensitive to the angular rather than the radial part of the wave function, the p-orbital occupation was treated in this study in terms of the following adjustable parameters: the angular geometry, consisting of the molecular symmetry and the bond angles, and the polarity of the σ bonds. This polarity was approximated by adding an ionic contribution to the unit electronic charge which would have resulted from equal sharing of the pair of electrons in a bond, with the ionic contribution coming from an empirical relationship[6] involving Pauling electronegativities. The term δ_σ is also inherently negative and may be calculated for a given molecular symmetry from the bond angles and from the electronegativity differences between the phosphorus atom and its substituents. The "true" or ab-

(6) C. A. Coulson, "Valence," corrected 2nd ed, Oxford University Press, London, 1963, p 141.

solute zero for an nmr chemical shift must, of course, correspond to an unshielded nucleus, and isolated ions exhibiting noble gas electronic structures should show essentially no paramagnetic shielding. On this basis, it is not surprising to find that the detailed quantum mechanical analysis of ^{31}P chemical shifts[4-7] has shown that the σ-bond contribution to the shift ranges from zero for a hypothetically complete transfer of the bonding electrons from the phosphorus to the substituents, through a maximum negative value, and then back to zero for the other limiting case of complete transfer of the bonding electrons from the substituents to the phosphorus. The maximum negative value of δ_σ occurs when the electronegativities of the substituents are equal to or close to that of phosphorus. For polarities in the range corresponding to P–O bonds, this means that an increase in the effective electronegativity of the oxygen will cause an increase in the chemical shift—a behavior which is opposite to the naïve idea that such withdrawing of electrons should lead to deshielding.

In order to interpret the data presented in this paper, the change in the ^{31}P chemical shift due to small variations in (a) the effective electronegativity of the neighboring oxygens due to association of hydrogen, (b) the bond angles, and (c) the total occupation of the phosphorus d_π orbitals was calculated by means of a computer program[8] based on the theory[4,5] outlined in the previous two paragraphs. As is generally the case for small perturbations of any mathematical function, the changes brought about by varying the individual parameters (a, b, or c above) could be treated as additive contributions. Equation 2 has been derived on this basis from the general theory

$$\Delta\delta = C\Delta\chi_0 - 147\Delta n_\pi - A\Delta\theta \tag{2}$$

where $\Delta\chi_0$ is the change in the effective electronegativity of the oxygens caused by their association with the hydrogen(s), Δn_π is the change in the total number of electrons in the d_π orbitals of the phosphorus induced by variations in the π character of the P–O bond brought about by hydrogen association, $\Delta\theta$ is the increase in OPO bond angle caused by association of the hydrogen, and C and A are numbers which vary from one oxyacid to another. For the PO_4 group, C is 180 and A is zero for the T_d symmetry of PO_4^{3-} and 0.3 for the C_{3v} symmetry of $OP(OH)_3$; for the HPO_3 group,[9] $C = 115$ and $A = 4.9$; for the H_2PO_2 group,[10] $C = ca.$ 20 and $A = 0.4$; for the CH_3PO_3 group,[11] $C = 130$ and $A = 2.7$; and for the $(CH_3)_2PO_2$ group,[9] $C = ca.$ 70 and $A < 0.1$, with $\Delta\theta$ being measured in degrees. From these values of A, it is apparent that bond-angle

(7) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 2926 (1966).

(8) J. R. Van Wazer and J. H. Letcher, Chapter 3 in "Topics in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., Vol. 5, in press.

(9) The geometry of the HP(O)(OH)$_2$ structure is reported in an X-ray study by S. Furberg and P. Landmark, *Acta Chem. Scand.*, **11**, 1505 (1957); also see D. E. C. Corbridge, *Acta Cryst.*, **9**, 991 (1956).

(10) An X-ray study of the ammonium hypophosphite is given by W. H. Zachariasen and R. C. L. Mooney, *J. Chem. Phys.*, **2**, 34 (1934).

(11) The geometry of this molecule has been estimated from the NH$_4$PO$_3$ zwitterion structure done by E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Cryst.*, **6**, 621 (1953).

variations will have little or no effect on the change of chemical shift with pH for the orthophosphate ion but may well be a major factor for the phosphite ion.

From electron-pushing arguments, one can conclude that association of a hydrogen with an oxygen should increase the effective electronegativity of this oxygen so that, upon formation of the acid from the salt, there ought to be a positive contribution to $\Delta\delta$ from the first term of eq 2. On the basis that π bonding acts as a feedback mechanism to minimize charge differences within molecules,[12] one might expect that Δn_π should also be positive so that there would be a negative contribution to $\Delta\delta$ from the second term of eq 2. Thus the σ and π effects are reasonably expected to act in opposite directions. In the case of the dimethylphosphinate, $\Delta\delta$ is negative and the change in the ^{31}P chemical shift due to bond-angle variation is small so that for this $(CH_3)_2PO_2$ group there appears to be an increase in the occupation of the d_π orbitals of the phosphorus upon acidification. The negative value of $\Delta\delta$ upon acidification indicates that for the phosphinates an increase in π bonding far outweighs the effect on the ^{31}P chemical shift of any changes in the σ-bond structure. A similar argument applies to the hypophosphite, $H_2PO_2^-$, and may reasonably be extended to the methylphosphonate, $CH_3PO_3^{2-}$, and the phosphite, HPO_3^{2-}, ions. However, in the latter two cases, moderately small bond-angle changes should also make contributions to the observed change in ^{31}P chemical shift upon acidification since the values of the coefficient A for these structures are significantly large. Following the same line of argument, it seems that for the orthophosphate, the expected increase upon acidification in electronegativity (with respect to the phosphorus) of the oxygen owing to its association with a proton has a greater effect on the ^{31}P chemical shift than the presumed increase in phosphorus d_π-orbital occupation. Of course, the data do not rule out a decrease in d_π occupation when going from the neutralized to acidic orthophosphate.

The data rationalization in the above paragraph is in accord with the usual intuitive picture of bonding. Thus, the variation in phosphorus d_π occupancy by a given total perturbation of the electronic structure of the oxygen atoms would be expected to increase within the following series of atomic groupings: $PO_4 < HPO_3$ or $CPO_3 < H_2PO_2$, $H(C)PO_2$, or C_2PO_2. Upon progressing along this series of atomic arrangements around phosphorus, there is a diminishing number of oxygen atoms which can feed electrons into the available phosphorus d orbitals so that the effect of association of, say, one hydrogen per phosphorus is accentuated. In all cases, only a few hundredths of a π electron can account for the observations; and a bond-angle increase of

Figure 2.—Variation of coupling constants J_{P-H} in oxyacids of phosphorus with the degree of neutralization as measured from the neutral salt at constant phosphorus concentration.

$1°$ or so will have an appreciable effect on the chemical shifts of the $(CH_3)_2PO_2$, HPO_3, and CH_3PO_3 structures.

Coupling Constants

As shown in Figure 2, neutralization of the acids leads to a drop in the spin–spin coupling constant for the hydrogen atom(s) directly bonded to the phosphorus. Similarly to the chemical shifts, these coupling constants were found to remain at an approximately constant value upon addition of more base than corresponds to complete neutralization.

According to the general theory[13] of coupling constants, the most important contributor to spin–spin interactions is the Hamiltonian involving the Fermi contact term. Thus, the changes in an H–P coupling constant, ΔJ, resulting from association of protons with oxygen atoms bonded to the phosphorus are thought to be due to a change in the occupation of the 3s orbitals of the phosphorus participating in the P–H bond(s). This change in bonding 3s occupation is a sensitive function of variations in the phosphorus bond angles and will, of course, also be affected indirectly by the occupation of the σ orbitals of the oxygen. The value ΔJ = $+100$ cps found when going from HPO_3^{2-} to H_2-(HPO_3) roughly corresponds to a $100/570 = 18\%$ change in the phosphorus s-orbital participation in the P–H bond. If the entire effect were attributed to rehybridization, about a $10°$ change in bond angle would be needed to account for the observed ΔJ. Therefore, the effect is probably due to a combination of a change in total σ-bond orbital occupation plus some rehybridization.

The coupling between phosphorus and the protons attached to carbon atoms in the phosphonic and phosphinic acids was not noticeably affected by the acidity of the solution. However, it was found that the spin–spin multiplets expected in the ^{31}P spectra of the organically substituted phosphorus acids were coalesced when measured in solutions of the pure acids. De-

(12) This naive approach appears to be in agreement with another simple argument based on overlap of the orbitals containing the unshared pairs of electrons of an oxygen with the appropriate phosphorus d orbitals since the POH bond angle probably averages out to be considerably larger than the tetrahedral angle (say, 120°). For bond-angle data, see D. E. C. Corbridge, "Topics in Phosphorus Chemistry," Vol. 3, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., p 57.
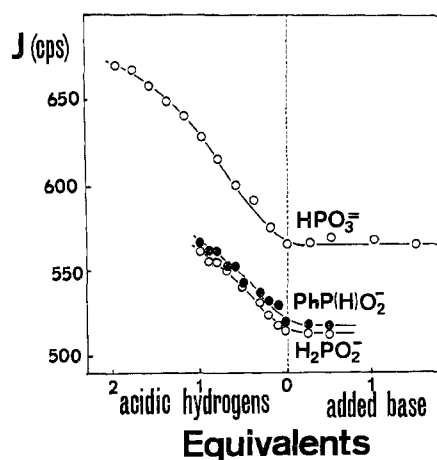
(13) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953); also see N. F. Ramsey and E. M. Purcell, *ibid.*, **85**, 143 (1952).

creasing acidity of the solutions—with the instrument settings remaining constant—greatly improved multiplet resolution, and, in the alkaline systems, perfectly resolved multiplets were seen. This effect was first observed[3] for the triplet in the ^{31}P spectrum of methylenediphosphonate. Even the salt of phenylphosphinic acid, $C_6H_5P(O)(H)OH$ (which in acid solution exhibits the P–H doublet with no fine structure), showed a triplet fine structure in both of the doublet peaks. These triplets are attributable to coupling of the phosphorus atoms with the *ortho* hydrogens of the phenyl group and the over-all phenomenon probably is due to exchange processes involving the protons in the solution. A similar effect was observed for the salt of phenylphosphonic acid, $C_6H_5P(O)(OH)_2$.

Nitrilotri(methylenephosphonic acid), Ethyliminodi(methylenephosphonic acid), and Diethylaminomethylphosphonic Acid: Acidity and Calcium(II) and Magnesium(II) Complexing

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The acidity constants for nitrilotri(methylenephosphonic acid), ethyliminodi(methylenephosphonic acid), and diethylaminomethylphosphonic acid are reported. The available information, including measurements of pK and ^1H and ^{31}P nmr chemical shifts as a function of the number of bound protons per ligand, indicates that these ligands exist as dipolar ions in solution. Complexing of alkaline earth metal ions by nitrilotri(methylenephosphonic acid) is shown to be principally due to interaction with the phosphonate part, with little interaction by the nitrogen. The contrast with ligands containing the acetate moiety is discussed. Complexing data show that successive replacement of methylenephosphonic groups by ethyl groups results in weaker Ca^{2+} and Mg^{2+} complexes.

Introduction

Considerable interest has developed during recent years in the complexing properties of molecules containing N-acetate moieties. In particular, the literature dealing with nitrilotriacetic acid (NTA) is quite extensive. The effect of the substitution of acetate by methylenephosphonate on the nitrogen has been of interest also. It has been shown[1] that the replacement of one acetate by a methylenephosphonate group resulted in a significant increase in the Ca^{2+} and Mg^{2+} stability constants, while replacement by two methylenephosphonate groups resulted in a slight decrease in the Ca^{2+} stability constant.[2]

With the development of a new synthetic route for preparing α-aminomethylphosphonic acids,[3] it was of interest to measure the acidity and Ca^{2+} and Mg^{2+} stability constants for molecules containing one, two, and three methylenephosphonates attached to nitrogen.

In order to define more clearly the individual deprotonation steps of the α-aminomethylphosphonic acids, ^1H and ^{31}P nmr chemical shifts were obtained as a function of the number of bound protons per molecule. This approach has been beneficial in confirming the existence of NTA and related N-acetates as dipolar ions in solution.[4]

Experimental Section

Chemicals.—Nitrilotri(methylenephosphonic acid) (NTMTP), ethyliminodi(methylenephosphonic acid) (EIDMP), and diethylaminomethylphosphonic acid (DEAMP), isolated as the monopotassium sesquihydrate salt, were prepared according to known methods.[3] *Anal.* Calcd for $N(CH_2PO_3H_2)_3$: C, 12.05; N, 4.68; P, 31.08. Found: C, 12.14; N, 4.61; P, 31.35. Calcd for $CH_3CH_2N(CH_2PO_3H_2)_2$: C, 20.60; N, 6.01; P, 26.61. Found: C, 20.54; N, 5.90; P, 26.80. Calcd for $(CH_3CH_2)_2N$-$(CH_2PO_3HK)\cdot1.5 H_2O$: C, 25.85; N, 6.03; P, 13.33. Found: C, 26.07; N, 5.90; P, 13.40.

Potentiometric Measurements.—The potentiometric titrations for determination of acidity and metal complexing constants employed a Beckman Expandomatic pH meter with a Sargent S-30050-15 glass electrode. The pH meter was calibrated with Fisher buffers at pH values of 2, 4, 6, 7, 9, 10, and 11. The pH meter was calibrated several times during a titration using the buffer in the pH region of the titration. Also the buffers checked with each other within ±0.03 pH unit. The distilled water used to make up the solutions was boiled to remove any residual CO_2 that may interfere in the titration. All experiments were conducted in a nitrogen atmosphere.

Acidity Constants.—Acidity constants were determined at $25.0°$ in 1 M KNO_3. Primary standard grade KNO_3 was used in all experiments.

In a typical experiment, y ml of a solution that is C_1 molar in H_aL (where H_aL represents the completely protonated ligand)

(1) G. Schwarzenbach, H. Ackermann, and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).
(2) S. Westerback, K. S. Rajan, and A. E. Martell, *J. Am. Chem. Soc.*, **87**, 2567 (1965).
(3) K. Moedritzer and R. R. Irani, *J. Org. Chem.*, **31**, 1603 (1966).

(4) D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, 3645 (1963).