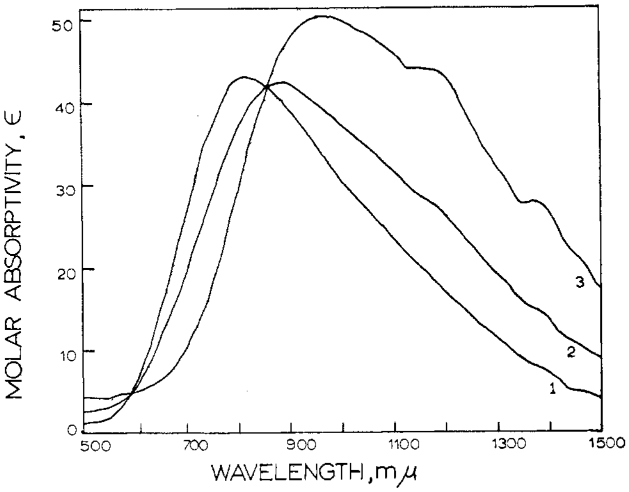

Figure 1.—Spectrum of $Cu(NIPA)_2(ClO_4)_2$ in nitromethane with varying amounts of excess ligand: (1) $Cu(NIPA)_2(ClO_4)_2$; (2) $Cu(NIPA)_2(ClO_4)_2$ + slight excess of NIPA; (3) $Cu(NIPA)_2(ClO_4)_2$ + large excess of NIPA.

POP stretching frequency.[14] Both the PNP and PNC stretching frequencies for complexes of NIPA are shifted to higher frequencies (Table II). The effect of coordination on the P=O stretching frequency is not easily interpreted. The peak assigned to the P=O stretch for the ligand is rather broad. In the complex this peak seems to be split into a sharp strong peak at ~1200 cm^{-1} and a sharp medium-intensity peak at ~1170 cm^{-1}. Walmsley and Tyree[11] reported splitting of the P=O stretching vibrations in some bidentate P=O ligands when more than one type of ligand was present in the inner coordination sphere. Cotton, Barnes, and Bannister[15] attributed P=O splitting or broadening to coupling between two P=O vibrations *via* the metal atom to which both are coordinated or to the existence of nonequivalent ligands in the crystal. Splitting was not usually present in perchlorate complexes. However, in $((C_6H_5)_3PO)_4Co(ClO_4)_2$ a sharp medium-intensity peak was observed at 1203 cm^{-1} and a strong peak at 1160 cm^{-1}. The peak at 1160 cm^{-1} was assigned to the P=O stretching vibration. No assignment was given for the peak at 1208 cm^{-1}.

The shifts in the PNP and PNC stretching frequencies may be explained similarly to those for the POP and PN stretching frequencies in OMPA.[14] The bond between the oxygen and the metal ion tends to withdraw electron density from the P=O bond and thus decrease the double-bond character. This results in a decrease in the P=O stretching frequency. Since electron density is drained from the P=O bond, there is a tendency for the lone pair on each of the nitrogen atoms to be delocalized into the available dπ orbitals of the phosphorus. The bond order between phosphorus and nitrogen would be expected to increase and this would cause an increase in the PNP and PNC stretching frequencies.

Chelation seems to be the important factor in stabilizing the complexes since stable complexes are formed in spite of the low positions of NIPA in the spectrochemical and nephelauxetic series. The substitution of the more electropositive N-methyl group for the bridge oxygen of OMPA has little influence on the stability of the complexes.

Acknowledgment.—Portions of this work were supported by USPHS Grant No. GM-15451-01.

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Effects of pH and Zinc Complex Formation on Phosphorus–Hydrogen Coupling Constants and Proton Chemical Shifts in Hypophosphorous and Phosphorous Acids

BY T. E. HAAS AND H. D. GILLMAN[1]

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The variation of J_{PH} with hydrogen ion concentration for solutions containing phosphite and hypophosphite species is shown to arise from rapid proton exchange among the various species present. Complex formation with zinc is shown to lead to similar increases in J_{PH}. The data are analyzed to give formation constants for mono- and bis(hypophosphito)zinc complexes.

Introduction

Two recent papers deal with variation with pH of phosphorus–hydrogen coupling constants and ^{31}P chemical shifts in phosphorous and hypophosphorous acid (among others). Moedritzer[2] studied the variation of the ^{31}P chemical shift and J_{PH} with degree of neutralization of the acids in aqueous solution. Sheldrick[3] studied the variation of J_{PH} in strongly acidic media—sulfuric acid from 12 to 98%.

The present paper is concerned with the origins of the variations in J_{PH} in terms of the chemical species in-

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[1] NDEA Title IV Fellow.

[2] K. Moedritzer, *Inorg. Chem.*, **6**, 936 (1967).

[3] G. M. Sheldrick, *Trans. Faraday Soc.*, **63**, 1077 (1967).

volved and with an extension of such observations to more general acid–base interactions of phosphite and hypophosphite, specifically to complex formation with zinc(II) ions.

Results and Discussion

pH Variation.—The variation of J_{PH} with the degree of neutralization of the acid forms H_3PO_2 and H_3PO_3 would seem to be attributable to rapid proton exchange among the predominant species present, *i.e.*, H_3PO_2–$H_2PO_2^-$, H_3PO_3–$H_2PO_3^-$, or $H_2PO_3^-$–HPO_3^{2-}. This hypothesis is easily tested by measuring J_{PH} as a function of the pH of the solutions. The results are shown in Figure 1. Measurements were carried out at constant phosphorus concentration and constant ionic strength (μ = 1.0). The solid lines in the figure represent a least-squares fit to the observed data,[4] the several coupling constants and the acid dissociation constants being treated as parameters. The results are summarized in Table I. The experimental data show that the observed variation of J_{PH} is indeed due to rapid proton exchange among the several protonated species, each of which has a well-defined J_{PH}. There is one point of disagreement between our calculations and those of Sheldrick:[3] he gave 554 cps for J_{PH} of H_3PO_2, and we find 573 cps. As our result is calculated on the basis of the equilibrium between acid and anion, where one can have some confidence that the species are well defined, we feel that our number is the more reliable.

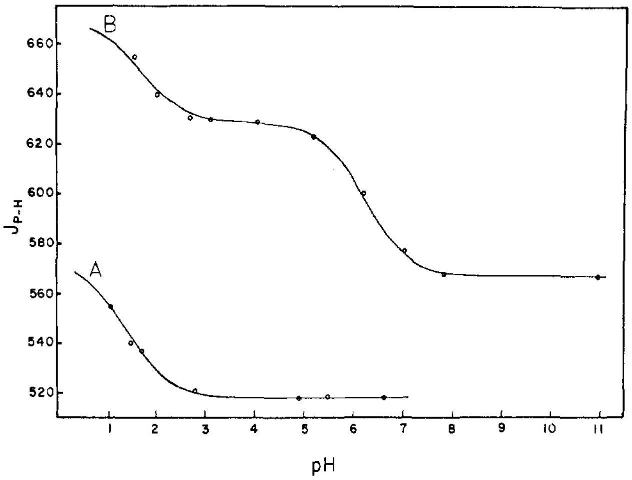

Figure 1.—J_{PH} *vs.* pH for hypophosphorous acid (A) and phosphorous acid (B). The points are experimental results and the solid curves are the theoretical least-squares fits to the observed points.

Also given in Table I are coupling constants for the fully protonated species $H_2P(OH)_2^+$ and $HP(OH)_3^+$, as proposed by Sheldrick.[3] These are observed coupling constants in 98% H_2SO_4. We *assume* that protonation is complete (or very nearly complete) in this medium, on the basis of a leveling off of the increase in coupling constant with H_2SO_4 concentration above ~90% H_2SO_4. The values of J_{PH} for the protonated species are in reasonably good agreement with those Sheldrick derived. On the basis of these results we have calculated (approximate) equilibrium constants for the protonations

Table I

Coupling Constants and p*K* Values for Hypophosphorous and Phosphorous Acids

Hypophosphorous acid		Phosphorous acid	
Species	J_{PH}, cps	Species	J_{PH}, cps
$H_2PO_2^-$	518	HPO_3^{2-}	567
$H_2P(O)(OH)$	573	$HP(O)_2(OH)^-$	629
$H_2P(OH)_2^+$	671	$HP(O)(OH)_2$	669
		$HP(OH)_3^+$	804
$pK = 1.40$		$pK_1 = 1.70$	
$R^a = 0.9$ cps		$pK_2 = 6.22$	
		$R^a = 1.5$ cps	

[a] $R = \Sigma_i[(J^i_{\mathrm{obsd}} - J^i_{\mathrm{calcd}})^2/N]^{1/2}$; *N* is the number of observed points.

$$H_2P(O)(OH) + H^+ \rightleftharpoons H_2P(OH)_2^+ \qquad K \simeq 0.02$$

and

$$HP(O)(OH)_2 + H^+ \rightleftharpoons HP(OH)_3 \qquad K \simeq 0.06$$

These values were derived from observed coupling constants in relatively dilute (compared to Sheldrick's experiments) perchloric acid (2–5 *M*). These numbers are probably upper limits for at least two reasons. First, they are calculated on the basis of concentrations, and the activity coefficient of H^+ is well known to be greater than unity (and increasing) in this range of acid concentration. Second, if the protonation in 98% sulfuric acid is not complete, the apparent concentrations of the protonated forms calculated from the observed J_{PH} will be too high. We prefer not to interpret our results in terms of the two-step protonations proposed by Sheldrick,[3] involving an intermediate H_3O^+–H_3PO_2 hydrogen-bonded species; although we cannot rule it out, it is not necessary to the interpretation of our data.

The observation of the fairly ready protonation of these phosphorus acids, giving species presumably of the forms $H_2P(OH)_2^+$ and $HP(OH)_3^+$, is probably of significance for the mechanisms of exchange reactions and reductions by these acids. Such reactions have been found in several instances to be acid catalyzed. Rate laws which contain terms of the form $k[H^+][H_3PO_2]$ can be written as $k'[H_4PO_2^+]$ with $k' = k/K$, where *K* is the equilibrium constant given above. Thus the acid-catalyzed exchange of the phosphorus-bonded hydrogens in H_3PO_2[5] may be formulated as a dissociation of H^+ by P–H bond breaking to give "active H_3PO_2"

$$H_2P(OH)_2^+ \rightleftharpoons HP(OH)_2 + H^+$$

in competition with the simple reversal of the oxygen protonation.

There is a small effect on observed coupling constants

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[4] These calculations were carried out using a program written here for operation on an IBM 360/65. Calculations were performed at the MIT Information Processing Services Center.

[5] A. Fratiello and E. W. Anderson, *J. Am. Chem. Soc.*, **85**, 519 (1963); W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 277 (1959)

arising from the presence of additional cations or anions in the solutions. For example, the observed J_{PH} of sodium hypophosphite in 1 *M* NaOH is 518 cps, whereas tetramethylammonium hypophosphite in 1 *M* $[(CH_3)_4N]OH$ gives a coupling constant of 514 cps. The observed coupling constant of a sodium hypophosphite solution was also found to increase, in a slow, linear fashion, with increasing sodium nitrate or sodium perchlorate concentration, but with greater slope for perchlorate than for nitrate solutions.

In contrast to the behavior of J_{PH} and the ^{31}P chemical shift, we find only a very small variation of the phosphorus-bonded proton chemical shift with degree of protonation. The chemical shift for $H_2PO_2^-$ has the value τ 2.98; for H_3PO_2, τ is 2.91, a change of less than 5 cps. Similarly, for HPO_3^{2-}, τ is 3.29, and, for H_3PO_3, τ is 3.10.

Complex Formation.—Complex formation with zinc leads to a sizable increase of J_{PH} over the free-anion value, although not as large as that observed for protonation. The analysis of the experimental data to determine the formation constants of the zinc complexes is not quite as straightforward as in the case of the protonations. Several hypophosphito complexes may be present, controlled by the equilibria $M + nL \rightleftharpoons ML_n$, where M represents Zn^{2+}, L represents $H_2PO_2^-$, and each complex has an associated coupling constant J_n and over-all formation constant β_n. The observed coupling constant is a weighted average of hypophosphite in all species

$$J_{obsd} = J_0\frac{[L]}{C_L} + \sum_{n=1}^{N} J_n \frac{n[ML_n]}{C_L}$$

where J_0 is the coupling constant for the free ion and C_L is the total ligand concentration in all forms. The above expression can be rewritten in terms of [L] and the β_n

$$J_{obsd} = \frac{J_0[L] + \sum_n J_n n\beta_n[M][L]^n}{C_L} \tag{1}$$

In the present work the above equation was simplified using the assumption that all J_n $(n \neq 0)$ were equal to a single J_c. We do not expect that the coordination of a hypophosphite oxygen atom in place of a water oxygen atom should have a large effect on the ability of the zinc ion to perturb a second hypophosphite attached to it.

We also have some direct experimental evidence to verify this in the case of aluminum complexes,[6] where we have been able to observe separate proton resonances for complexed and uncomplexed hypophosphite. Of particular importance here is the observation that only a single resonance (doublet) is observed for mononuclear hypophosphitoaluminum complexes, over a concentration range where more than one $Al(H_2PO_2)_n$ complex is expected to be present. From the form of eq 1 it is clear that any error in the assumption of equal J_n will be reflected in errors in the calculated β_i such that the products $\beta_i J_c$ have the true value $\beta_i^0 J_i$, β_i^0 being the correct value of the formation constant.

Using this assumption, eq 1 can be rewritten

$$J_{obsd} = \frac{J_0[L] + J_c\sum_n n\beta_n[M][L]^n}{C_L} = \frac{[L]}{C_L}J_0 + \frac{C_L - [L]}{C_L}J_c \tag{2}$$

A more useful equation is the expression

$$\Delta J = J_{obsd} - J_0 = \frac{C_L - [L]}{C_L}(J_c - J_0)$$

which allows calculations of the free ligand concentration [L] from the total known ligand concentration and J_{obsd} (if J_c is also known). The values of [L] and $\bar{n}$ are given by

$$[L] = C_L\left(1 - \frac{\Delta J}{J_c - J_0}\right) \tag{3a}$$

$$\bar{n} = \frac{\Delta J}{J_c - J_0}\frac{C_L}{C_M} \tag{3b}$$

In the absence of knowledge of J_c, a parametric family of curves $\Delta J C_L/C_M$ *vs.* C_L can be plotted with C_M as the parameter. Points of constant $\Delta J C_L/C_M$ provide data for a graph of C_L *vs.* C_M for constant $\bar{n}$, which are lines of slope $\bar{n}$ and intercept [L]. This treatment is similar to that used for determining stability constants from spectrophotometric data when extinction coefficients are unknown, and the further calculations are standard.[7]

Stability constants for hypophosphitozinc complexes were determined at 25° and constant ionic strength $\mu = 4.0$. In one series of experiments ionic strength was maintained with sodium nitrate; in a second, with sodium perchlorate. A correction for the presence of the perchlorate or nitrate, as described in the previous section, was applied to the observed J_{PH}. As the values of $\bar{n}$ never exceeded 1, it was sufficient to restrict attention to β_1 and β_2. The value of J_c was found to be 540 cps, 22 cps higher than that for NaH_2PO_2. The formation constants for the reactions in the different media at 25° are: perchlorate, $\beta_1 = 3.5 \pm 0.5$, $\beta_2 = 1.5 \pm 1$; nitrate, $\beta_1 = 2 \pm 0.5$, $\beta_2 = 1 \pm 0.5$. The formation constants are small and precision is not great, but the results are adequate to indicate that hypophosphite is a rather weakly coordinating ligand.

Experimental Section

Fisher 50% hypophosphorous acid was concentrated and purified by the method of Jenkins and Jones.[8] The phosphorous acid was Fisher reagent grade and was used as received. Standard solutions of tetramethylammonium hydroxide were prepared from Eastman 10% solutions. Zinc nitrate and zinc perchlorate were reagent grade chemicals, used as received. Stock solutions of these salts were prepared and analyzed for zinc as zinc ammonium phosphate.[9]

Proton magnetic resonance spectra were obtained on a Varian A-60A spectrometer. Coupling constants were measured by the audio-side-band technique, using a Hewlett-Packard audio oscillator and frequency counter. Quadruplicate measurements gave results consistent to within ±0.2 cps. Chemical shifts

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(8) W. A. Jenkins and R. T. Jones, *J. Am. Chem. Soc.*, **74**, 1353 (1952).

(9) N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N.Y., 1939, p 1059.

were measured relative to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as internal standard for all solutions except the strongly basic ones, in which it was insoluble. For these solutions, DSS was used as an external standard.

Buffer solutions were prepared to approximate pH values and known, high ionic strengths. Appropriate amounts were taken to ensure total ionic strengths of 1.0 in the solutions studied. Both J_{PH} and pH were measured values for the same solution.

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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Nucleophilic Displacement of Bromide from Phosphorus with Some 2-Substituted Perfluoroisopropoxide Anions. Formation of μ-Oxo-difluorophosphine, μ-Oxo-difluorophosphoryl, and μ-Oxo-difluorothiophosphoryl Compounds

BY MAX LUSTIG[1]

Received May 3, 1968

A series of new μ-oxo-fluorophosphorus compounds—2-cyano-2-(μ-oxo-difluorophosphine)hexafluoropropane, 2-cyano-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-cyano-2-(μ-oxo-difluorothiophosphoryl)hexafluoropropane, 2-azido-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-isothiocyanto-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-thiocyanato-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, and 2,4-bis(trifluoromethyl)-4-(μ-oxo-difluorophosphine)-3-azapentene-2—has been synthesized. These compounds were prepared by the reaction of the corresponding 2-halogenoidoperfluoroisopropoxide anion with the appropriate phosphorus(III) bromide difluoride or phosphorus(V) oxide bromide difluoride. The synthetic methods and some physical properties of these compounds are recorded and discussed.

Several μ-oxo-fluorophosphate(III) esters of the type $(CF_3)_2C(X)OPF_2$, where X = Br, I, or H, have been prepared by the addition of phosphorus bromide difluoride, PF_2Br, or phosphorus iodide difluoride, PF_2I, to hexafluoroacetone, HFA, and by the reaction of the PF_2I–HFA addition compound with hydrogen iodide in the presence of mercury.[2] However, these methods for the synthesis of μ-oxo-difluorophosphorus compounds have limited application.[2] A more general approach has been found which involves reactions employing halogenoidohydrin salts.

Halogenated ketones are known to form stable addition compounds with sodium cyanide[3] and the resulting cyanohydrin salts have been shown[3b] to undergo esterification in the presence of an acyl, sulfur, or phosphorus chloride or an anhydride. We have used this approach to include the reactions of phosphoryl and thiophosphoryl bromide difluoride and phosphorus bromide difluoride with sodium 2-cyanoperfluoroisopropoxide, $Na^+(CF_3)_2C(CN)O^-$, to prepare the corresponding μ-oxo esters. This general method has been extended to include other halogenoidohydrin salts, derived from the ligands N_3^- and SCN^-. The latter were prepared *in situ* as the precursors to the fluorophosphate esters. When the OCN^- ion was allowed to react with HFA, carbon dioxide was evolved, and the resulting solid reacted with PF_2Br to yield the interesting new azapentene, $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$, containing the μ-oxo-difluorophosphine group.

Experimental Section

Reagents.—The PF_2Br,[2] POF_2Br,[2,4,5] PSF_2Br,[4,5] and $Na^+(CF_3)_2C(CN)O^-$ [3a] were synthesized and purified by known methods. The NaCN, NaN_3 NaOCN, NaSCN, and the HFA were obtained from the General Chemical Division of the Allied Chemical Corp. The salts were dried by pumping *in vacuo* at 100° and were used without further purification. The nitrobenzene, which was stored over 5A molecular sieves, was procured from the Eastman Kodak Co. Spectroquality acetonitrile was obtained from Matheson Coleman and Bell, Division of the Matheson Co.

Apparatus and General Procedure.—A standard Pyrex vacuum apparatus was used for transfer and purification of volatile materials. Mercury manometers were covered with Kel-F No. 10 oil. The μ-oxo phosphorus derivatives were prepared in 50-ml Pyrex bulbs each fitted with a Fischer-Porter Teflon valve. Gaseous mixtures were characterized by pressure–volume–temperature (*PVT*) measurements and analyzed mass spectrometrically. Solids and liquids of low volatility were handled within a nitrogen drybox.

$(CF_3)_2C(CN)OPF_2$.—In a typical experiment 4.06 mmol each of $Na^+(CF_3)_2C(CN)O^-$ and PF_2Br were added together to the reactor at $-196°$. The bulb was allowed to warm to room temperature over a 15-min period and was allowed to stand an additional 15 min. The volatile products were then passed through a set of traps at -95, -126, and $-196°$. The $-95°$ trap caught pure $(CF_3)_2C(CN)OPF_2$ (3.05 mol, 75.1% yield), the $-126°$ trap caught a small amount of an unidentified material as well as a trace of the μ-oxo derivative, and the last trap held PF_3 (0.25 mmol), PF_2OPF_2 (0.27 mmol), and traces of CO_2 and POF_3. *Anal.* Calcd for C_4F_8NOP: C, 18.40; F, 58.23; N, 5.37; P, 11.86. Found: C, 18.37; F, 58.0; N, 5.48; P, 11.4.

$(CF_3)_2C(CN)OP({=}O)F_2$.—A mixture of the sodium cyanohydrin salt and POF_2Br (5.60 mmol each) was treated as above. The $(CF_3)_2C(CN)OP({=}O)F_2$ (4.88 mmol, 87.1% yield) was caught in the $-95°$ trap. *Anal.* Calcd for $C_4F_8NO_2P$: C,

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(1) Department of Chemistry, Memphis State University, Memphis, Tenn. 38111.

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