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A Kinetic Study of the Monohypophosphite Complex of Iron(III) in Perchloric Acid Solutions[1a]

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The acid dissociation quotient of hypophosphorous acid is 0.135 ± 0.006 *M* at 25.0° and ionic strength 1.00 *M* (nitric acid–lithium nitrate medium), evaluated by pH measurements at a glass electrode. Under the same conditions the first acid dissociation quotient of phosphorous acid is 0.107 ± 0.005 *M*. The rate of formation and aquation of the monohypophosphitoiron(III) ion follow the expression $d[FeH_2PO_2^{2+}]/dt = \{a + (b/[H^+])\}[Fe^{3+}][H_3PO_2] - \{c + d[H^+]\}[FeH_2PO_2^{2+}]$ with the values (*M* and sec units) $a = 35 \pm 3$, $b = 13 \pm 3$, $c = 0.23 \pm 0.02$, and $d = 0.083 \pm 0.010$ at 25.0° in a perchloric acid–lithium perchlorate medium of ionic strength 1.00 *M*. The stability constant derived from the kinetic data for the reaction $Fe^{3+} + H_3PO_2 = FeH_2PO_2^{2+} + H^+$ is $152 \pm 10\ M^{-1}$ and that for the reaction $Fe^{3+} + H_2PO_2^- = FeH_2PO_2^{2+}$ is $(1.1 \pm 0.1) \times 10^3\ M^{-1}$.

Introduction

Complexes of hypophosphite ion with metal ions have not been studied extensively, although the substitution-inert complex $CrH_2PO_2^{2+}$ has been isolated and the kinetics and equilibrium of its formation have been studied.[2] The labile iron(III)–hypophosphite complex has been studied by spectrophotometric[3] and potentiometric[4] techniques, but no rate studies have been published.

A study of the forward and reverse rates of reaction I

$$Fe(H_2O)_6^{3+} + H_3PO_2 = (H_2O)_5Fe(H_2PO_2)^{2+} + H_3O^+ \qquad (I)$$

has been carried out. This work was also concerned with the evaluation of the equilibrium quotient for reaction I, Q_I, and necessarily involved consideration of the equilibrium quotient Q_a for acid dissociation of monobasic hypophosphorous acid.

Aside from the intrinsic interest of extending the general knowledge on complex-forming properties of a ligand that has been little studied, these results are of interest in adding to the body of information on iron(III) complexation rates and mechanisms.[5–9]

Experimental Section

Materials.—Iron(III) perchlorate, hypophosphorous acid, and lithium perchlorate were prepared and analyzed as before.[2,6] Lithium nitrate was recrystallized twice from conductivity water. Reagent grade 72% perchloric acid was used without further purification; nitric acid was boiled before use. Reagent grade phosphorous acid was recrystallized from water.

Measurements.—A Beckman Research pH meter and a Cary Model 14 spectrophotometer were used. The kinetic data were obtained using a stopped-flow apparatus[6] based on the design of Dulz and Sutin.[10] Values of transmittance (photomultiplier voltage) were read from the ordinate of the oscillograms at appropriate time intervals.

Since erratic pH readings were obtained in the presence of perchlorate ion, presumably caused by precipitation of $KClO_4$ at the reference electrode containing saturated KCl solution, the solutions on which pH measurements were made contained nitric acid and lithium nitrate to maintain 1.00 *M* ionic strength. The pH meter was calibrated by the use of HNO_3–$LiNO_3$ solutions similar in composition to the solutions of interest and covering the entire range of pH in which the sample values lay.

Kinetic Data.—In all experiments the concentration of hydrogen ion remained constant, as did the fraction of the uncomplexed H_3PO_2 existing as $H_2PO_2^-$. The kinetic data can be considered as a case of opposing first- and second-order reactions. Using the abbreviation $HX = H_3PO_2$, the equation to be considered is

$$Fe^{3+} + HX \rightleftarrows FeX^{2+} \quad (k_f', k_a') \qquad (1)$$

where k_f' and k_a', both of which depend on hydrogen ion concentration, are defined by the rate expression given in eq 2.

$$d[FeX^{2+}]/dt = k_f'[Fe^{3+}][HX] - k_a'[FeX^{2+}] \qquad (2)$$

In all of the experiments, the formal concentration of iron(III) considerably exceeded that of H_3PO_2, to avoid formation of the higher complexes that are known to exist.[3,4] Such being the case, only a small per cent of the iron(III) was converted to the FeX^{2+} complex in most runs even when a considerable fraction of H_3PO_2 was complexed. When eq 2 is expanded in terms of a reaction variable and the equilibrium condition is applied, the small extent of complexation of iron(III) allows terms in $[FeX^{2+}]^2$ to be neglected and gives the approximate expression in eq 3, in

$$d[FeX^{2+}]/dt = \{k_a' + k_f'(C_{Fe} + C_{HX})\}\{[FeX^{2+}]_\infty - [FeX^{2+}]_t\} \qquad (3)$$

which formal concentrations are designated as *C*. The expectation is that the approach to equilibrium will follow pseudo-first-order kinetics; according to eq 3 the rate constant evaluated from the slope of a plot of ln $\{[FeX^{2+}]_\infty - [FeX^{2+}]_t\}$ *vs.* *t* will be $k_a' + k_f'(C_{Fe} + C_{HX})$. In practice, under the circumstances where the reaction conditions were adjusted such that the total change did not exceed 0.1 absorbance unit, the oscillogram readings *V* could be used directly. Plots of log $(V_{t+\tau} - V_t)$ *vs.*

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[2] J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 1365 (1966).

[3] K. M. Masalovich, P. K. Agasyan, and E. R. Nikolaeva, *Russ. J. Inorg. Chem.*, 1074 (1967).

[4] R. I. Novoselov, Z. A. Muzykantova, and B. V. Ptitsyn, *ibid.*, 442 (1964).

[5] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[6] D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

[7] F. P. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).

[8] N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

[9] C. H. Langford and E. M. Chung, *J. Am. Chem. Soc.*, **90**, 4485 (1968).

[10] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

t (Guggenheim method[11]) were made, from whose slopes pseudo-first-order constants were calculated. Typical plots are shown in Figure 1, illustrating that the data were consistent with a first-order rate expression governing the approach to equilibrium. The rate studies were carried out at a constant ionic strength of 1.00 M, maintained with lithium perchlorate. Kinetic studies were carried out at wavelengths of 250–350 nm and in all cases the rate constants were independent of the wavelength used.

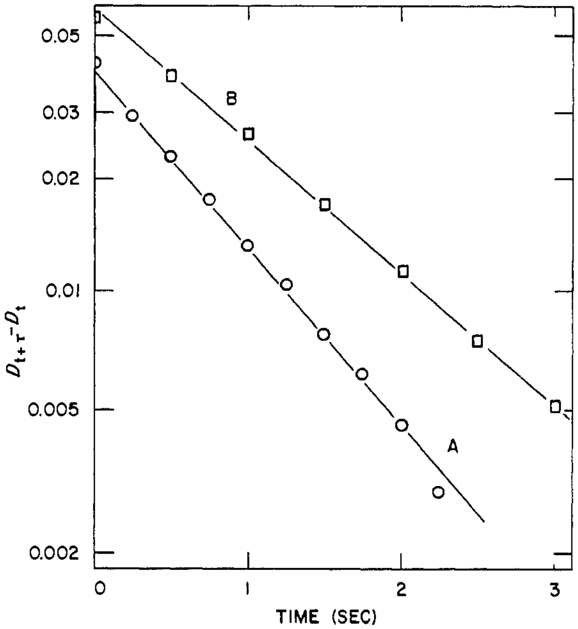

Figure 1.—Rate plots indicating the pseudo-first-order rate of approach to equilibrium: (A) $[Fe^{3+}]_0 = 6.40 \times 10^{-3}$ F, $C_{H_3PO_2} = 4.0 \times 10^{-4}$ F, 0.150 M H^+, λ 300 nm, $\tau = 2.25$ sec; $k_{app} = 1.08$ sec^{-1} (obsd), 1.09 sec^{-1} (calcd, eq 6); (B) $[Fe^{3+}]_0 = 1.00 \times 10^{-2}$ F, $C_{H_3PO_2} = 5.0 \times 10^{-4}$ F, 0.940 M H^+, λ 310 nm; $\tau = 3.5$ sec, $k_{app} = 0.80$ sec^{-1} (obsd), 0.808 sec^{-1} (calcd, eq 6).

Results

Acid Dissociation of H_3PO_2.—Hypophosphorous acid is partly dissociated in the hydrogen ion range of interest, $0.1 \leq [H^+] \leq 1.0$ M. The acid dissociation quotient, Q_a, does not appear to have been previously evaluated at 1.00 M ionic strength at 25.0°. Measurements of pH were made on solutions of H_3PO_2 and HNO_3 mixed in quantities to give a range of conditions and pH's. The compositions of the solutions studied are summarized in Table I; the pH values are reported with limits indicating the precision of the calibration function at the pH of that solution.

The computation of Q_a depends on the difference of two numbers which, in some experiments, were quite close. For example, in the first experiment of Table I the computed Q_a is proportional to the difference of two numbers which differ by only 11%; more typically, the differences were 25%. Except for the first entry, however, the precision appears acceptable and gives the value $Q_a = 0.135$ M, which will be used in the subsequent rate computations under the assumption that it remains unchanged in perchlorate solutions at the same ionic strength and temperature.

Table I

Evaluation of the Acid Dissociation Constant of Hypophosphorous Acid at 1.00 M Ionic Strength and 25.0°

Formal concn				
H_3PO_2	HNO_3	$LiNO_3$	Obsd pH	Q_a,[a] M
0.0250	. . .	0.979	1.651 ± 0.01	(0.185 ± 0.002)
0.0500	. . .	0.963	1.406 ± 0.004	0.142 ± 0.007
0.0500	0.0100	0.955	1.324 ± 0.004	0.141 ± 0.008
0.100	. . .	0.938	1.177 ± 0.004	0.132 ± 0.005
0.0500	0.0400	0.930	1.140 ± 0.003	0.130 ± 0.010
0.0500	0.0800	0.895	0.969 ± 0.001	0.130 ± 0.003
0.0500	0.100	0.878	0.897 ± 0.002	0.149 ± 0.014
0.0500	0.120	0.859	0.842 ± 0.004	0.134 ± 0.013

[a] $Q_a = [H^+][H_2PO_2^-]/[H_3PO_2]$. The uncertainty is the average deviation of the two values computed from the limits of the observed pH values.

Rate Studies.—According to eq 3, k_{app} should be a linear function of $C_{Fe} + C_{HX}$. The results at two hydrogen ion concentrations are illustrated in Figure 2, which depicts the data at 0.150 and 0.600 M H^+. Table II summarizes the slopes and intercepts of such plots at each hydrogen ion concentration studied. A function more useful than the apparent second-order rate constant, k_f', is $k_f'\{1 + (Q_a/[H^+])\}$, which expresses the rate in terms of the concentration of free H_3PO_2 rather than the total hypophosphite concentration.

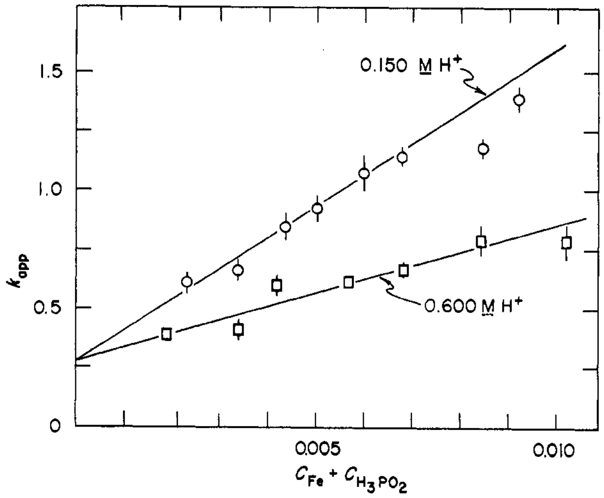

Figure 2.—Plots of k_{app} (sec^{-1}) vs. $C_{Fe} + C_{H_3PO_2}$ for 0.150 and 0.600 M H^+.

The last column in Table II represents the equilibrium quotient for reaction I as written which is calculated directly from the rate parameters k_f'' and k_a' at each hydrogen ion concentration, irrespective of the dependences of those rate constants upon $[H^+]$.

There is a small but apparently real increase in k_a' and $k_f''/[H^+]$ with increasing $[H^+]$. This dependence suggests a rate expression[12] with two parallel reaction pathways as shown in eq 4. Upon substitution for two

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(11) E. A. Guggenheim, *Phil. Mag.*, **2** [7], 538 (1926). First-order rate constants were also evaluated from plots of log $(V_\infty - V_t)$ *vs.* t, which were linear to 85% completion. The rate constants proved to be moderately sensitive to the value chosen for V_∞ within the range of its accuracy. The scatter of rate constants in replicate experiments was consequently somewhat larger than when the Guggenheim method was used, for the difference $V_{t+\tau} - V_t$ randomizes the effects of the precision of reading the values of V from the Polaroid photographs of the oscilloscope traces. The agreement of the rate constants was usually within 3% average deviation from the mean for four successive determinations using the same set of solutions.

(12) J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968), and references therein.

Table II

Rate Parameters[a] for Aquation and Formation of $FeH_2PO_2^{2+}$ at 25.0° and $\mu = 1.00\ M$

	k_a', sec^{-1}		k_f', $M^{-1}\ sec^{-1}$		k_f'',[c] $M^{-1}\ sec^{-1}$		
$[H^+]$, M	Obsd	Calcd[b]	Obsd	Calcd[b]	Obsd	Calcd[b]	$10^{-2}Q_I$[d]
0.100	0.25 ± 0.02	0.24	167 ± 7	154	393 ± 16	362	1.57
0.150	0.28 ± 0.03	0.24	131 ± 6	129	249 ± 11	245	1.33
0.320	0.25 ± 0.03	0.26	87 ± 5	86	123 ± 7	122	1.58
0.600	0.28 ± 0.02	0.28	58 ± 3	58	67 ± 4	67	1.43
0.940	0.31 ± 0.01	0.31	45.9 ± 1.5	43.6	52.5 ± 1.7	49.8	1.59

[a] The uncertainties tabulated for k_a' and k_f' represent the standard deviation in fitting the data to eq 3. [b] Calculated values are from final parameters. [c] $k_f'' = k_f'\{1 + (Q_a/[H^+])\}$. [d] $Q_I = k_f'\{[H^+] + Q_a\}/k_a' = k_f''[H^+]/k_a'$.

$$d[FeX^{2+}]/dt = \{k_1 + k_3[H^+]\}\{[Fe^{3+}][HX]/[H^+]\} - \{k_2 + k_4[H^+]\}[FeX^{2+}] \qquad (4)$$

of the rate parameters and by using the usual relation of forward and reverse rate constants (eq 5), the rate

$$Q_I = [FeX^{2+}][H^+]/[Fe^{3+}][HX] = k_1/k_2 = k_3/k_4 \qquad (5)$$

expression becomes a function of but two variables. The resulting expression for k_{app} is given by eq 6.

$$k_{app} = \{k_2 + k_4[H^+]\}\left\{1 + \frac{Q_I(C_{Fe} + C_{HX})}{Q_a + [H^+]}\right\} \qquad (6)$$

Using $Q_a = 0.135\ M$ and $Q_I = 152$, the calculated rate parameters are $k_2 = 0.23 \pm 0.02\ sec^{-1}$ and $k_4 = 0.083 \pm 0.010\ M^{-1}\ sec^{-1}$. From these results the values $k_1 = 35 \pm 3\ sec^{-1}$ and $k_3 = 13 \pm 3\ M^{-1}\ sec^{-1}$ were then computed according to eq 5. The relatively large standard deviations associated with the rate parameters k_3 and k_4 indicate that the reaction pathway represented by these rate constants remains a relatively minor one even at high $[H^+]$.

For some purposes the equilibrium shown in reaction II is useful. The value of Q_{II} is given by Q_I/Q_a and is $1.1 \times 10^3\ M^{-1}$.

$$Fe(H_2O)_6^{3+} + H_2PO_2^- = (H_2O)_5Fe(H_2PO_2)^{2+} + H_2O \qquad (II)$$

Table III

Evaluation of the First Acid Dissociation Constant of Phosphorous Acid at 1.00 M Ionic Strength and 25.0°

Formal concn				
H_3PO_3	HNO_3	$LiNO_3$	Obsd pH	Q_a',[a] M
0.0250	0.0100	0.966	1.524 ± 0.001	0.116 ± 0.004
0.0400	0.0400	0.933	1.190 ± 0.002	0.101 ± 0.003
0.0400	0.0600	0.915	1.085 ± 0.001	0.103 ± 0.002
0.0400	0.100	0.878	0.924	0.108
0.0400	0.140	0.840	0.805 ± 0.001	0.110 ± 0.006
0.0450	0.160	0.820	0.749 ± 0.001	0.113 ± 0.006

[a] $Q_a' = [H^+][H_2PO_3]/H_3PO_3]$. The uncertainty is the average deviation of the two values computed from the limits of the observed pH values.

Studies on Phosphorous Acid.—Similar pH studies were done (Table III) on phosphorous acid, H_3PO_3, giving the value $Q_a' = 0.107\ M$ (25.0°, $\mu = 1.00\ M$, nitrate solution). A limited number of measurements of the rates and equilibria of iron(III) complexation were also carried out. The magnitude of rates was similar to that noted in the studies with hypophosphorous acid, but the work was not sufficiently extensive to define the system quantitatively.

Interpretation and Discussion

The value of $Q_a = 0.135\ M$ for H_3PO_2 appears to have been the result of the first study with a considerable variation of the per cent dissociation at constant ionic strength. Kolthoff[13] studied the dissociation in a medium in which the ionic strength was contributed largely by the dissociated ions and found Q_a changed with concentration. Griffith, *et al.*,[14] reported at $\mu = 1.13\ M$ (potassium chloride medium), $Q_a = 0.094$, and $0.074\ M$ at 16 and 30°, respectively. Other authors[3] cited a value $Q_a = 0.12\ M$ at $\mu = 0.2\ M$ and 20°, although its source is not referenced. The results of the present study are not necessarily in disagreement with the earlier studies if the different conditions of temperature and ionic strength are considered. One source of a possible systematic difference should, however, be noted. In the present studies, values read from the pH meter were not used to compute directly a_{H^+}; rather, the pH scale was calibrated in terms of similar nitric acid–lithium nitrate solutions under the assumption nitric acid is a completely dissociated electrolyte with $[H^+]$ equal to the formal concentration of HNO_3. This in effect defines Q_a as a concentration quotient, whereas the earlier potentiometric studies probably measured a_{H^+}.

The value determined here by similar methods for H_3PO_3 was $Q_a' = 0.107\ M$ (25°, $\mu = 1.00\ M$) which can be compared with the values determined[15] by a potentiometric method in a potassium chloride medium of $\mu = 0.6\ M$, giving $Q_a' = 0.098$ and $0.068\ M$ at 18 and 45°, respectively.

Four different workers have reported values for the stability constant of $FeH_2PO_2^{2+}$ with widely discrepant results. Banerjee[16] gave the value $Q_{II} = 6 \times 10^2\ M^{-1}$ under unspecified conditions. A potentiometric study[4] of the effect of H_3PO_2 on the Fe^{2+}–Fe^{3+} potential resulted in the value $Q_{II} = 4.2 \times 10^3\ M^{-1}$ (25°, $\mu = 0.13\ M$). This study has been criticized,[3] however, since reduction of Fe^{3+} by H_3PO_2 was noted in the presence of the Pt electrode at rates far higher than found on their absence. We confirmed the lack of appreciable reduction of Fe^{3+}. It also appears that these workers[4] apparently ignored the acid dissociation of H_3PO_2 at $[H^+] = 0.1\ M$; the apparent assumption that it was a strong acid would lead to a value of Q_{II} that is too small by a factor of $1 + ([H^+]/Q_a)$. After applying this correction, using $Q_a = 0.12\ M$ ($\mu = 0.2\ M$, 20°),[3] the value is $Q_{II} = 8 \times 10^3\ M^{-1}$, compared to the value[3]

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(13) I. M. Kolthoff, *Rec. Trav. Chim.*, **46**, 350 (1927).

(14) R. O. Griffith, A. McKeown, and R. P. Taylor, *Trans. Faraday Soc.*, **36**, 752 (1940).

(15) R. O. Griffith and A. McKeown, *ibid.*, **36**, 766 (1940).

(16) S. Banerjee, *Sci. Cult.* (Calcutta), **16**, 115 (1950).

$1.0 \times 10^4\ M^{-1}$ ($\mu = 0.13\ M$, 20°) obtained spectrophotometrically.

The value computed from these kinetic results, $Q_{II} = 1.1 \times 10^3\ M^{-1}$ ($\mu = 1.00\ M$, 25.0°), again, is not necessarily in disagreement considering the different conditions. The direction of the difference is consistent with the expected effect of ionic strength upon Q_{II}.

The value $k_3 = 13 \pm 3\ M^{-1}\ \text{sec}^{-1}$ is consistent with the other rates[5,6,17-19] noted for substitution on $Fe(H_2O)_6^{3+}$ and indicates that, as in those cases, the probable predominant feature controlling the rate is dissociation of a coordinated water molecule.

As with other cases involving weak acids the "proton ambiguity" prevents a direct answer from kinetic studies to whether the rate term $k_1[Fe^{3+}][HX]/[H^+]$ corresponds to the reaction of $Fe(H_2O)_6^{3+}$ and X^- or $(H_2O)_5FeOH^{2+}$ and HX. Using the appropriate acid dissociation quotients, the second-order rate constants for these two alternatives were computed to be 2.7×10^2 and $2.1 \times 10^4\ M^{-1}\ \text{sec}^{-1}$, respectively.

Following the arguments advanced earlier[5,6,17-19] we shall attempt to decide between the alternatives, not on the basis of the form of the reaction kinetics, but on the apparent "reasonableness" of the magnitudes of the rate constants under the alternative formulations. The rate constants for reactions of nonbasic anions, in which the proton ambiguity is absent, correspond to a range of 2–127 $M^{-1}\ \text{sec}^{-1}$ for substitution on $Fe(H_2O)_6^{3+}$ and to a range of (0.4–3) $\times 10^4\ M^{-1}\ \text{sec}^{-1}$ for the reactions of $(H_2O)_5FeOH^{2+}$ with monoanions.

When the present reaction is interpreted as involving the $Fe(H_2O)_6^{3+}$ and $H_2PO_2^-$, the rate constant of 270 $M^{-1}\ \text{sec}^{-1}$ calculated above exceeds the range of values established for similar processes. The discrepancy is, however, not large, and the value, although it is close to the rate of the $Fe(H_2O)_6^{3+}$–H_2O exchange,[20] does not appear to be impossibly large. For the reaction to be attributed to Fe^{3+} and $H_2PO_2^-$ would, however, require $H_2PO_2^-$ either to be an exceptionally good nucleophile or to form an unusually stable ion pair with $Fe(H_2O)_6^{3+}$. There is at present no supporting evidence for this. On the other hand, the value for the second formulation, $FeOH^{2+} + H_3PO_2$, fits comfortably into the pattern expected for such a reaction. The interpretation we offer of the present rate studies is consequently that the mechanism probably involves the reaction of $FeOH^{2+}$ and H_3PO_2. This assignment must, however, be regarded as tentative.

The analogous reaction of Cr^{3+} and H_3PO_2 proceeded by one pathway corresponding to the transition state $[CrH_3PO_2^{3+}]^{\ddagger}$. On the basis of the kinetic data[21] and from rate correlations[22] it appeared that the process involved substitution at phosphorus and not at chromium. This proposal accounts not only for the kinetic results which were unexpected for Cr(III) substitution but also for the unexpected differences found here between iron(III) and chromium(III). The rates of the present study are too high to be interpreted in terms of substitution at phosphorus, however, and they are in accord with the expected pattern of substitution at iron.

Acknowledgment.—We are grateful to Professor J. E. Powell for the use of the pH meter employed in these studies.

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[20] (a) R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961); (b) M. R. Judkins, Ph.D. Thesis, University of California at Berkeley, issued as Report UCRL 17561 from Lawrence Radiation Laboratory.

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