

Kinetics and Mechanism of Complex Formation Reactions in the Iron(III)–Phosphate Ion System at Large Iron(III) Excess. Formation of a Tetranuclear Complex

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The kinetics and mechanism of the iron(III)–phosphate ion reaction were studied at large iron(III) excess using the stopped–flow method at 10.0 °C in 1.0 M NaClO₄. In the first few hundred milliseconds of the reaction, the formation of a novel tetranuclear complex was confirmed. The following composition is proposed for the new species: Fe₄(PO₄)(OH)₂(H₂O)₁₆⁷⁺. According to detailed kinetic studies, the formation of this species is first order with respect to Fe₂(OH)₂(H₂O)₈⁴⁺ and H₂PO₄[−] and presumably proceeds via a dinuclear intermediate species. At longer reaction times slow dissociation of the tetranuclear complex controls the formation of the thermodynamically favored Fe(PO₄)(H₂O)₅ complex. The overall reaction was interpreted in terms of the following reactions: Fe₂(OH)₂(H₂O)₈⁴⁺ ⇌ 2Fe³⁺_{mn}; Fe₂(OH)₂(H₂O)₈⁴⁺ + P(V) ⇌ Fe₂P^V; Fe₂P^V + Fe₂(OH)₂(H₂O)₈⁴⁺ ⇌ Fe₄P^V; Fe³⁺_{mn} + P(V) ⇌ Fe(PO₄)(H₂O)₅. (Fe³⁺_{mn} = Fe(H₂O)₆³⁺ + Fe(OH)(H₂O)₅²⁺; P(V) = H₃PO₄ + H₂PO₄[−]; Fe₂P^V = Fe₂(HPO₄)(OH)(H₂O)₈³⁺; Fe₄P^V = Fe₄(PO₄)(OH)₂(H₂O)₁₆⁷⁺.) The pH dependence and relevant rate and equilibrium constants are reported for the individual reaction steps.

Introduction

In a recent study, we have shown that spectral changes observed in the iron(III)–sulfite ion system at metal ion excess are due to complex formation between the dimeric dihydroxo-iron(III) species (Fe₂(OH)₂⁴⁺) and sulfur(IV).^{1,2} Our main objective was to find an appropriate model system in which the complex formation reactions of Fe₂(OH)₂⁴⁺ can be studied without the interference of subsequent redox steps. So far, Fe₂L type complexes were reported in a few redox reactions of iron(III) with organic reactants.^{3–5} According to our preliminary studies, a direct reaction also occurs between Fe₂(OH)₂⁴⁺ and the phosphate ion.

While the equilibria in the iron(III)–phosphate ion system have been studied in detail,^{6–10} kinetic data were determined only for the formation of FeH₂PO₄²⁺ and Fe(H₂PO₄)₂⁺.¹¹ That work was done at large phosphate ion excess and low iron(III) concentration. Now we report a kinetic study at large iron(III) excess that was designed to explore the ligand substitution reactions of the Fe₂(OH)₂⁴⁺ complex.

Experimental Section

Reagents. Reagent grade Na₂HPO₄·2H₂O (Reanal, Hungary) and low chloride iron(III) perchlorate (Aldrich) were used without further

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Table 1. Stability Constants for the Protolytic Reactions of Iron(III) and Phosphate Ion

reaction	parameter	value	ref
Fe ³⁺ = FeOH ²⁺ + H ⁺	log β _{h1}	−3.03 ^a	2
2Fe ³⁺ = Fe ₂ (OH) ₂ ⁴⁺ + 2H ⁺	log β _{hd}	−2.98 ^a	2
Fe ³⁺ = Fe(OH) ₂ ⁺ + 2H ⁺	log β _{h2}	−6.7 ^b	23
H ₃ PO ₄ = H ₂ PO ₄ [−] + H ⁺	log K _{a1}	−1.39 ± 0.02 ^a	d
H ₂ PO ₄ [−] = HPO ₄ ^{2−} + H ⁺	log K _{a2}	−6.31 ± 0.01 ^a	d
Fe ³⁺ + H ₃ PO ₄ = FeHPO ₄ ⁺ + 2H ⁺	log β _{m1}	1.28 ^c	11
Fe ³⁺ + H ₃ PO ₄ = FePO ₄ + 3H ⁺	log β _{m2}	0.78 ^c	11

^a 10.0 °C, μ = 1.0 M (NaClO₄). ^b Estimated by extrapolation to 10 °C. ^c 25.0 °C, μ = 3.0 M (NaNO₃). ^d This work.

purification. The iron(III) and free acid concentrations of the stock solutions were determined as described earlier.^{12,13} Experiments were carried out at 10.0 ± 0.1 °C in 1.0 M NaClO₄.

Instrumentation. UV–vis spectra were recorded on a HP-8543 diode array spectrophotometer. A GK2401C combination glass electrode was used for pH measurements with a PHM85 pH meter (Radiometer), and the pH meter readings were converted into [H⁺] as described earlier.¹⁴ In the kinetic runs, the pH (= −log[H⁺] ≤ 2.50) was calculated from the composition of the samples. Kinetic measurements were performed with an Applied Photophysics DX-17 MV sequential stopped–flow apparatus at 2 and 10 mm optical paths as reported earlier.^{2,15} Nonlinear least-squares fitting procedures were carried out with the software package SCIENTIST.¹⁶

Results and Discussion

Protolytic Equilibria and Kinetics. The stability constants used for the protolytic reactions are listed in Table 1. The acid dissociation constants of phosphoric acid were determined in the present study using standard pH potentiometry. The

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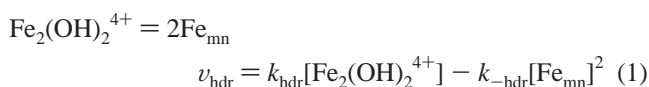
Table 2. Kinetic Parameters for the Complex Formation Reactions in the Iron(III)–Phosphate Ion System ($T = 10.0\text{ }^{\circ}\text{C}$, $\mu = 1.0\text{ M}$ (NaClO_4))

parameter	value
k_{h1}	$(5.9 \pm 0.4) \times 10^{-2}\text{ s}^{-1}$
k_{h2}	$1.08 \pm 0.02\text{ M}^{-1}\text{ s}^{-1}$
k_{h3}	$(5.8 \pm 0.7) \times 10^{-4}\text{ M s}^{-1}$
k_{-h1}	$71\text{ M}^{-1}\text{ s}^{-1 a}$
k_{-h2}	$1.2\text{ M}^{-1}\text{ s}^{-1 a}$
$k_{-h3}\beta_{h2}$	$6.5 \times 10^{-4}\text{ M s}^{-1 a}$
k_2	$(1.44 \pm 0.02) \times 10^5\text{ M}^{-1}\text{ s}^{-1}$
k_3	$2.4 \pm 1.0\text{ M}^{-1}\text{ s}^{-1}$
$k_{4a}\beta_{h1} + k_{4b}K_{a1}$	$0.80 \pm 0.16\text{ s}^{-1}$
k_5	$(4.7 \pm 0.1) \times 10^3\text{ M}^{-1}\text{ s}^{-1}$
k_{-2}	$0.18 \pm 0.03\text{ s}^{-1}$
K_{42}	$(7 \pm 2) \times 10^4\text{ M}^{-1}$
K_{20}	$8 \times 10^5\text{ M}^{-1 b}$
$\epsilon\{\text{Fe}_2(\text{OH})_2^{4+}\}$, 340 nm	$2760 \pm 180\text{ M}^{-1}\text{ cm}^{-1}$
$\epsilon\{\text{Fe}_2(\text{OH})_2^{4+}\}$, 370 nm	$630 \pm 40\text{ M}^{-1}\text{ cm}^{-1}$
$\epsilon\{\text{FeOH}^{2+}\}$, 340 nm	$700 \pm 50\text{ M}^{-1}\text{ cm}^{-1}$
$\epsilon\{\text{FeOH}^{2+}\}$, 370 nm	$160 \pm 10\text{ M}^{-1}\text{ cm}^{-1}$
$\epsilon\{\text{FePO}_4\}$, 340 nm	$160 \pm 30\text{ M}^{-1}\text{ cm}^{-1}$
$\epsilon\{\text{FePO}_4\}$, 370 nm	~ 0

^a Calculated from the appropriate combination of forward rate constants and equilibrium constants. ^b Calculated from the kinetic parameters as $K_{20} = k_2/k_{-2}$.

experimental data were evaluated with the software package PSEQUAD.¹⁷

The protolytic equilibria involving various phosphate species and the monomer forms of iron(III) were treated as fast preequilibria. In contrast, the formation and dissociation of $\text{Fe}_2(\text{OH})_2^{4+}$ are relatively slow and interfere with some of the reactions studied here. Recently, we have proposed an improved mechanism for the dissociation of $\text{Fe}_2(\text{OH})_2^{4+}$ and confirmed the following rate law:¹⁵



where $[\text{Fe}_{\text{mn}}] = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}]$ and

$$k_{\text{hdr}} = k_{h1} + k_{h2}[\text{H}^+] + \frac{k_{h3}}{[\text{H}^+]}$$

$$k_{-\text{hdr}} = \frac{\beta_{h1}}{(\beta_{h1} + [\text{H}^+] + \beta_{h2}/[\text{H}^+])^2} \left(k_{-h1}\beta_{h1} + k_{-h2}[\text{H}^+] + \frac{k_{-h3}\beta_{h2}}{[\text{H}^+]} \right)$$

The values of k_{h1} , k_{h2} , k_{h3} , k_{-h1} , k_{-h2} , and k_{-h3} were determined for the conditions applied here as described earlier (Table 2).¹⁵

Spectral Observations in the Iron(III)–Phosphate Ion System. Composite spectral changes were observed when solutions of the phosphate ion were mixed with excess iron(III) (Figure 1). After a fast initial decay, the absorbance steadily increased and reached its final value within a few minutes in the 300–430 nm region. We refer to the two distinct time regimes of the reaction as first and second phase, respectively. Below 300 nm the first phase was less apparent and completely disappeared at shorter wavelengths.

To avoid complications arising from slow formation of the dinuclear hydroxo complex (eq 1), reagents of equal pH were mixed in the kinetic experiments.² The initial concentration of

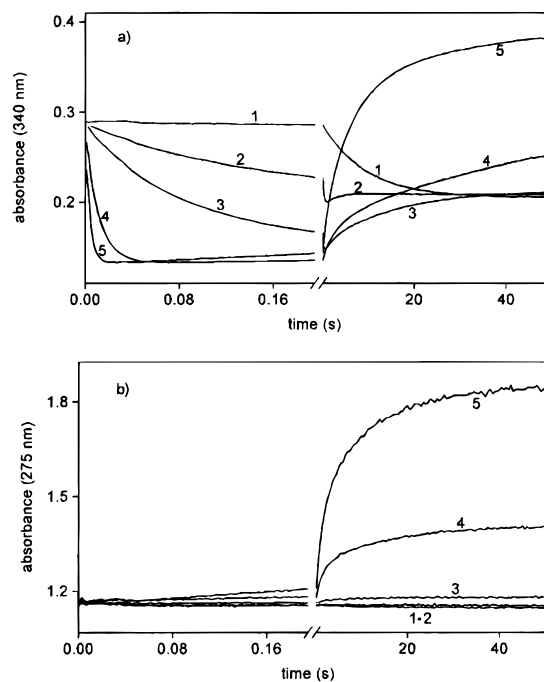


Figure 1. Comparison of kinetic curves obtained at two wavelengths under the following conditions: $[\text{Fe(III)}] = 4.86\text{ mM}$, $[\text{Fe}_2(\text{OH})_2^{4+}]_0 = 0.073\text{ mM}$, $\text{pH} = 1.60$, $\text{P(V)} = 0$ (curve 1), $2.0 \times 10^{-5}\text{ M}$ (curve 2), $6.0 \times 10^{-5}\text{ M}$ (curve 3), $5.0 \times 10^{-4}\text{ M}$ (curve 4), $1.5 \times 10^{-3}\text{ M}$ (curve 5), $T = 10.0\text{ }^{\circ}\text{C}$, $\mu = 1.0\text{ M}$ (NaClO_4), optical path length 10 mm (340 nm) and 2 mm (275 nm).

$\text{Fe}_2(\text{OH})_2^{4+}$ was controlled by selecting appropriate total iron(III) concentration and pH. The main absorbing species are $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$ at 340 nm. While the concentration of $\text{Fe}(\text{OH})^{2+}$ is practically constant, the dimer dissociates into the monomer forms in a slow process (eq 1). Thus, at $[\text{P(V)}] = 0$ the absorbance is nearly constant in the first phase and the absorbance change reflects the change in $[\text{Fe}_2(\text{OH})_2^{4+}]$ at longer reaction times. The initial absorbance at $t = 0$ is independent of the phosphate ion concentration, indicating that fast reaction steps do not occur within the dead time of the stopped–flow (SF) instrument.

In the first phase, the amplitude and the rate of the absorbance decay are increased by increasing $[\text{P(V)}]$. Because $[\text{Fe}^{3+}_{\text{mn}}] \gg [\text{P(V)}]$, the small contribution of the monomeric iron species to the absorbance is constant and the spectral effects cannot be assigned to the reactions of $\text{Fe}^{3+}_{\text{mn}}$. Thus, the observations confirm the formation of a weakly absorbing product in a fast reaction between P(V) and $\text{Fe}_2(\text{OH})_2^{4+}$.

In the second phase, the final absorbance increases with increasing $[\text{P(V)}]$ (i.e., phosphate ion is also involved in the slower process). A comparison of the kinetic curves in Figure 1a reveals that the reaction(s) of P(V) in the second phase and the dissociation of $\text{Fe}_2(\text{OH})_2^{4+}$ are kinetically coupled and the experimental traces correspond to a complex kinetic process.

Kinetic traces at the 275 nm absorbance maximum of the $\text{FeH}_2\text{PO}_4^{2+}$ complex¹¹ showed marginal absorbance change in the initial phase even at the highest $[\text{P(V)}]$ applied (Figure 1b). This confirms again that the fast absorbance change in the 340–430 nm range is due to the formation of a novel phosphato complex with $\text{Fe}_2(\text{OH})_2^{4+}$. The amplitude of the corresponding spectral effect, ΔA , is defined as the difference between the absorbances measured at $t = 0$ and at the end of the first phase. The normalized value of ΔA is shown as a function of the initial $[\text{P(V)}]/[\text{Fe}_2(\text{OH})_2^{4+}]$ ratio at 340 and 370 nm in Figure 2. The

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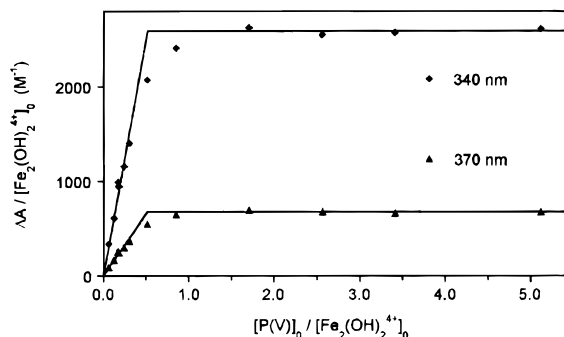
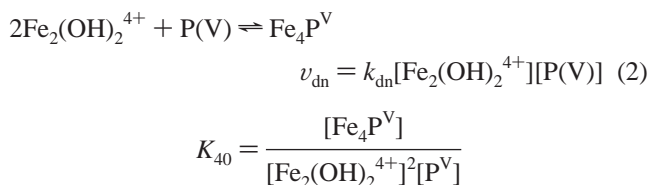


Figure 2. Determination of the stoichiometry for the $\text{Fe}_2(\text{OH})_2^{4+} + \text{P}(\text{V})$ reaction: pH = 1.60, $T = 10.0^\circ\text{C}$, $\mu = 1.0\text{ M}$ (NaClO_4), optical path length 10 mm.

well-defined break points in these curves are consistent with a 1:2 stoichiometric ratio for the reactants. The same stoichiometry was verified by using the Job method.¹⁸ It was also confirmed that the product has negligible absorbance in the near UV–visible spectral region.

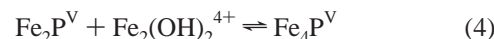
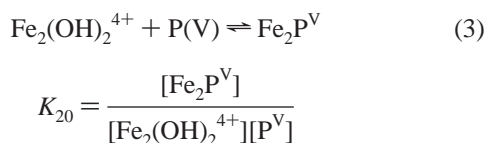
To account for the spectral changes, it needs to be assumed that a relatively stable complex is formed in the first phase in which the phosphate ion simultaneously coordinates to two hydroxo dimer complexes. We refer to the novel tetranuclear species as $\text{Fe}_4\text{P}^{\text{V}}$. On the basis of plausible considerations, the tetranuclear complex should form via an $\text{Fe}_2\text{P}^{\text{V}}$ -type species. However, direct evidence does not support the formation of such a species. In Figure 2, the straight lines correspond to the limiting case of extreme stable complex formation. The slight deviation of the experimental data from these lines is consistent with the relatively high stability of $\text{Fe}_4\text{P}^{\text{V}}$.

First, the formation kinetics of the $\text{Fe}_4\text{P}^{\text{V}}$ complex was studied by the initial rate method. The slopes of the plots of $\log v_0$ as a function of $\log[\text{Fe}_2(\text{OH})_2^{4+}]$ or $\log[\text{P}(\text{V})]$ were reasonably close to 1.0, indicating that the reaction is first order in both $\text{Fe}_2(\text{OH})_2^{4+}$ and $\text{P}(\text{V})$. The complex formation in the first phase is summarized as follows:



Under the conditions applied, reaction 2 almost always goes to completion. Thus, the experimental data do not allow us to determine K_{40} with acceptable precision, and it is only safe to state that $\log K_{40} > 8.0$.

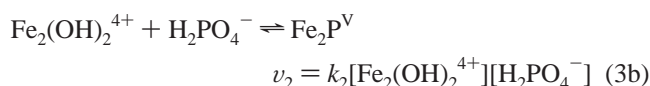
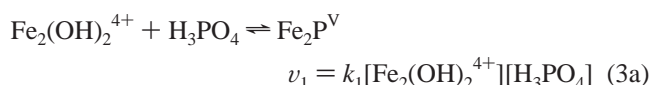
The formation of the $\text{Fe}_4\text{P}^{\text{V}}$ complex in a single step would require the two hydroxo dimers and the phosphate ion to react in a concerted fashion. Such a mechanism would be consistent with an overall third-order rate law and can be excluded. We propose that an $\text{Fe}_2\text{P}^{\text{V}}$ -type complex is formed in steady state and that the following path is operative:



$$K_{42} = \frac{[\text{Fe}_4\text{P}^{\text{V}}]}{[\text{Fe}_2(\text{OH})_2^{4+}][\text{Fe}_2\text{P}^{\text{V}}]}$$

This scheme is consistent with the experimental rate law provided that the first step is rate-determining and that subsequent coordination of the second $\text{Fe}_2(\text{OH})_2^{4+}$ unit is fast. Because the equilibria are shifted toward the formation of $\text{Fe}_4\text{P}^{\text{V}}$, the reverse reactions can be neglected. The kinetic traces were fitted on the basis of eq 2 using a nonlinear least-squares algorithm and estimating the values of k_{dn} , $\epsilon(\text{Fe}_2(\text{OH})_2^{4+})$, and $\epsilon(\text{Fe}_4\text{P}^{\text{V}})$.¹⁶ The respective molar absorptivities at 340 nm (2760 ± 180 and $700 \pm 50\text{ M}^{-1}\text{ cm}^{-1}$) are in excellent agreement with the results obtained from independent equilibrium studies (2890 and $620\text{ M}^{-1}\text{ cm}^{-1}$).²

The pH dependence of k_{dn} could be interpreted by considering the protolytic equilibria between the dominant forms of the ligand, H_3PO_4 and H_2PO_4^- . Reaction 3 is basically the combination of the following two steps



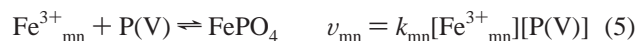
and

$$k_{\text{dn}} = \frac{k_1[\text{H}^+] + k_2K_{a1}}{K_{a1} + [\text{H}^+]}$$

The reactivities of the conjugate acid and base forms of a ligand typically differ by several orders of magnitude. Because H_2PO_4^- and H_3PO_4 are always present in comparable concentrations, reaction 3a is inferior compared to reaction 3b and $k_1[\text{H}^+] \ll k_2K_{a1}$. On the basis of this approximation, the fitted values for k_2 and $\log K_{a1}$ are $(1.44 \pm 0.02) \times 10^5\text{ M}^{-1}\text{ s}^{-1}$ and -1.41 ± 0.02 , respectively. The value for $\log K_{a1}$ is in excellent agreement with the result obtained from the equilibrium measurements, -1.39 ± 0.02 .

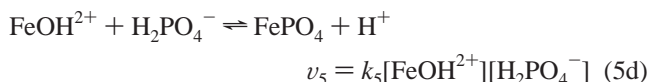
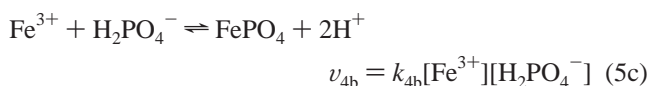
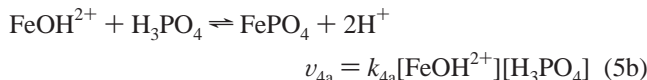
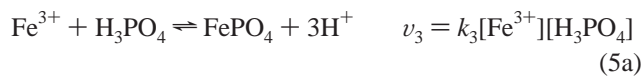
At this point it is important to note that either reaction 3 or reaction 4 may involve proton release. Because the values and pH dependencies of K_{20} and K_{42} could not be determined, experimental data are not available for the proton budget in these steps. Some information could be obtained for the stoichiometry of $\text{Fe}_2\text{P}^{\text{V}}$ and $\text{Fe}_4\text{P}^{\text{V}}$ from the rate equation of the backward reaction, which is significant in the second phase of the reaction.

Reaction between Monomer Iron(III) Species and Phosphate Ion. As demonstrated in Figure 1, spectral effects in the slower second phase are consistent with the formation of a monophosphato complex. Our experimental data are consistent with the results reported for the formation of $\text{FeH}_2\text{PO}_4^{2+}$ by Wilhelmy and co-workers.¹¹ However, we formulate this complex as FePO_4 because earlier studies⁹ confirmed that this is the dominant species in the pH range studied:



The rate constants for this reaction were determined at phosphate ion excess on the basis of the following model:

(18) Job, P. *Ann. Chim.* **1928**, 9, 113.

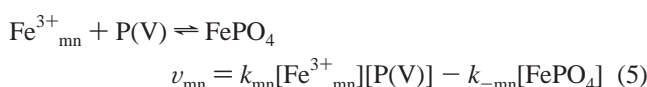
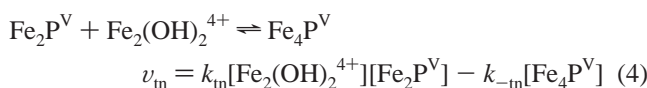
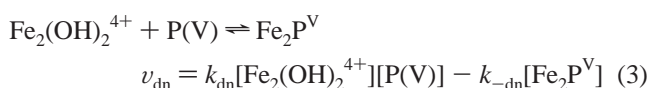
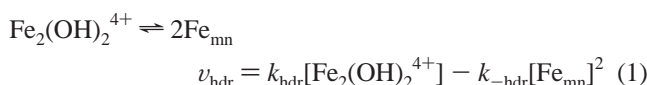


Under pseudo-first-order conditions reaction 5 is shifted to the right and the following expression can be derived for k_{mn} :

$$k_{mn} = \frac{k_3[\text{H}^+]^2 + (k_{4a}\beta_{h1} + k_{4b}K_{a1})[\text{H}^+] + k_5\beta_{h1}K_{a1}}{(\beta_{h1} + [\text{H}^+])(K_{a1} + [\text{H}^])}$$

In the fitting procedure β_{h1} and K_{a1} were included with fixed values obtained from equilibrium measurements. The results are listed in Table 2.

Kinetic Model at Iron(III) Excess. The reaction was followed until the absorbance reached its final value (~40–50 s). Matrix rank analysis¹⁹ of the time-resolved spectra confirmed the existence of three absorbing species: $\text{Fe}_2(\text{OH})_2^{4+}$, FeOH^{2+} , and FePO_4 . As discussed before, spectral effects also confirmed the transient tetranuclear complex. Thus, the kinetics of the overall reaction can be interpreted in terms of repositioning the hydrolytic reactions and the formation of $\text{Fe}_4\text{P}^{\text{V}}$ and subsequently FePO_4 :



In the final calculations 23 kinetic curves (each with 1000 data points) obtained at 340 and 370 nm were fitted simultaneously to the model with the software package ZiTa.²⁰ The kinetic parameters were estimated by using a combined numeric differential equation solver–nonlinear least-squares algorithm. The pH dependence of k_{hdr} , $k_{-\text{hdr}}$, k_{dn} , and k_{mn} was determined independently as reported earlier. The corresponding rate and equilibrium constants as well as the molar absorbancies of the absorbing species were fixed at their known values. Spectrophotometric observations and calculations based on equilibrium data⁹ confirmed that practically the total amount of phosphate

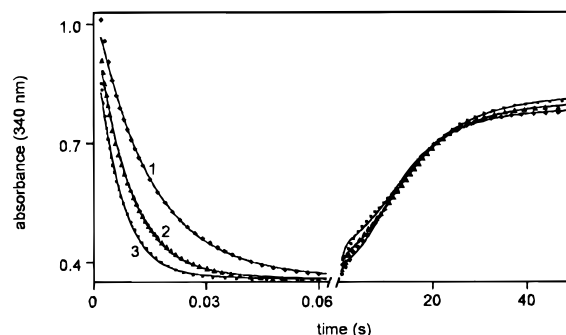


Figure 3. Experimental and fitted kinetic traces at two wavelengths on two time scales under the following conditions: $[\text{Fe(III)}] = 0.0103$ M, $[\text{Fe}_2(\text{OH})_2^{4+}]_0 = 0.293$ mM, pH = 1.60 (for all curves), $[\text{P(V)}]_0 = 0.50$ mM (curve 1), $[\text{P(V)}]_0 = 0.75$ mM (curve 2), $[\text{P(V)}]_0 = 1.00$ mM (curve 3), $T = 10.0$ °C, $\mu = 1.0$ M (NaClO₄).

ion is present as FePO_4 at the end of the reactions and $k_{-\text{mn}}$ was set to zero.

The formation of $\text{Fe}_4\text{P}^{\text{V}}$ from the dinuclear complex was considered to be fast, and k_{tn} was set to 10^9 M⁻¹ s⁻¹. The rate constants $k_{-\text{tn}}$ and $k_{-\text{dn}}$ and the molar absorbancies of FePO_4 were allowed to float. The molar absorbance of FePO_4 at 370 nm was fixed at zero in the final evaluation. Variation of k_{tn} from 10^7 to 10^{10} M⁻¹ s⁻¹ had no effect on the goodness of fit. When smaller values were used, the error of the fit became larger. As a result of this variation, the fitted value for $k_{-\text{tn}}$ changed significantly but the $k_{\text{tn}}/k_{-\text{tn}}$ ratio remained constant. This proves again that reaction 4 is a fast equilibrium step and that $K_{42} = k_{\text{tn}}/k_{-\text{tn}}$. Calculations with subsets of the kinetic traces at constant pH confirmed that both K_{42} and $k_{-\text{dn}}$ are independent of pH. It follows that $k_{-2} = k_{-\text{dn}}$ and the equilibrium constant for reaction 3b can be calculated from the kinetic parameters as $K_{20} = k_2/k_{-2}$. The rate and equilibrium constants obtained in the present study are collected in Table 2. The agreement between measured and fitted kinetic traces is shown in Figure 3.

The lack of any pH dependence of K_{42} and $k_{-\text{dn}}$ indicates that the formation of $\text{Fe}_2\text{P}^{\text{V}}$ and $\text{Fe}_4\text{P}^{\text{V}}$ is not associated with proton release. However, it is very unlikely that subsequent coordination of two hydroxo dimers to H_2PO_4^- does not induce the deprotonation of the ligand and leaves the OH bridges intact in the $\text{Fe}_2(\text{OH})_2^{4+}$ units. Most likely, these complexes are formed in a fashion analogous to the dinuclear sulfite complex $\text{Fe}_2(\text{SO}_3)(\text{OH})(\text{H}_2\text{O})_8^{3+}$.² It seems to be very feasible that the detailed mechanism for reactions 3 and 4 includes simultaneous loss of an OH bridge from the $\text{Fe}_2(\text{OH})_2^{4+}$ dimer and deprotonation of the ligand. Thus, the stoichiometries for $\text{Fe}_2\text{P}^{\text{V}}$ and $\text{Fe}_4\text{P}^{\text{V}}$ would be $\text{Fe}_2(\text{HPO}_4)(\text{OH})(\text{H}_2\text{O})_8^{3+}$ and $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$, respectively.

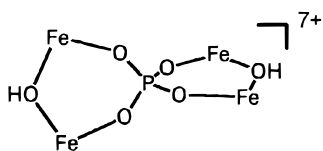
Various coordination modes of the ligand can be envisioned in the tetranuclear complex. Because of the outstanding stability of this species, the coordination of the phosphate ion to only one iron(III) in the dimer units is very unlikely. It can be inferred that the phosphate ion acts as a bridging ligand by replacing one OH group in both dimers. We propose that each oxygen atom of the phosphate ion is coordinated to a different iron(III) center as demonstrated by Chart 1.

The odd feature of $\text{Fe}_4\text{P}^{\text{V}}$ is the relatively high stability despite the large overall positive charge of the complex. It seems to be very plausible that the +7 charge is localized mainly on the four iron atoms. Repulsive forces between the positively charged metal centers should destabilize the tetranuclear complex. The very existence of this species may indicate that the coordinated

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Chart 1



water molecules somehow offset the effects of the repulsion. It should be added that the average charge of an iron atom is somewhat smaller in the tetranuclear complex than in $\text{Fe}_2(\text{OH})_2^{4+}$. This difference can be an additional stabilizing factor in the $\text{Fe}_4\text{P}^{\text{V}}$ complex. These considerations are supported by solid-phase structures of heteropolymetalates and organically templated iron(III)–phosphates where all four oxygens of a phosphate ion are coordinated to metal ions.^{21,22}

To our knowledge, evidence for the existence of a $\text{Fe}_4\text{P}^{\text{V}}$ -type complex in aqueous solution has not been reported before.

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Therefore, it is open to question whether the formation of such a tetranuclear complex occurs specifically with the phosphate ion or also with other ligands. This problem will be addressed in our ongoing studies.

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Supporting Information Available: Extended kinetics graphs and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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