

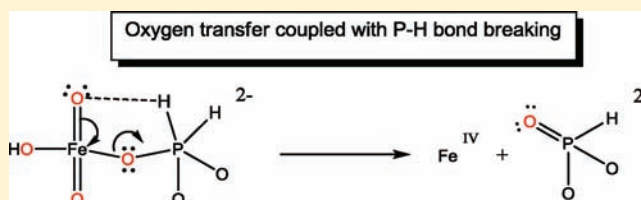
Oxidation of Phosphorus Centers by Ferrate(VI): Spectral Observation of an Intermediate

Shaun M. Hightower, Bret B. Lorenz, Jonathan G. Bernard, and Michael D. Johnson*

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003, United States

S Supporting Information

ABSTRACT: The kinetics and mechanism for the oxidation of phosphite, hypophosphite, phenylphosphite, and trimethylphosphite by ferrate(VI) are reported. Hypophosphite is rapidly oxidized to phosphite which is slowly oxidized to phosphate, trimethylphosphite is oxidized to trimethylphosphate, and phenylphosphite is oxidized to phenylphosphate. ^{18}O induced shifts of the ^{31}P NMR signals support oxygen transfer from ferrate(VI) to the phosphorus center during the oxidation process. Deuteration of the hydridic hydrogens in hypophosphite and phosphite resulted in significant kinetic isotope effects on the reaction rates. It is proposed that ferrate(VI) acts as a two-electron oxidant in conjunction with oxide transfer coupled with phosphorus hydrogen bond breaking for phosphite and hypophosphite and simple oxygen transfer for trimethylphosphite and phenylphosphite.



INTRODUCTION

Over the past several years it has been established that iron undergoes catalytic reactions that involve oxidation states above +3.¹ Unfortunately, within these oxidation states the aqueous ions are generally unstable, and relatively little information about the structures or reactions of these oxidation states is known. Because of this, we have carried out a series of studies of the reactions of iron(VI), also known as the ferrate ion, FeO_4^{2-} , with a variety of substrates. The present study presents the kinetics and proposed mechanisms for the oxidations of a series of phosphorus centers by iron(VI).

The oxidations of phosphorus compounds have been studied with a variety of oxidants such as Bi(V) ,² chloramine T,³ OH radicals,⁴ Ce(V) ,⁵ Ag(I) ,⁶ Ag(II) ,⁷ V(V) ,⁸ and AuCl_4^- .⁹ Formation of M–O–P intermediates as well as outer-sphere redox processes has been proposed.

Haight et al. concluded that H_2PO_2^- is not oxidized nor does it form an anhydride with the chromate ion.¹⁰ It is interesting, however, that hypophosphorous acid does form a spectrally observable anhydride intermediate with chromate that subsequently undergoes oxidation to form phosphorous acid. This evidence led Haight to conclude that an OH group on the phosphorus center must be present for anhydride formation. Haight et al. also studied the chromate(VI) oxidation of phosphorous acid at high P(III) concentrations, $0.1 \text{ M} < [\text{H}_3\text{PO}_3] < 1.0 \text{ M}$.¹¹ A kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 4.0$ was observed, and they reported a rate law for the Cr(VI) and phosphorous acid reaction as follows:

$$\text{rate} = \frac{[\text{Cr(VI)}][\text{H}_3\text{PO}_3](k_1[\text{H}^+] + k_2[\text{H}_3\text{PO}_3])}{(1 + K_f[\text{H}_3\text{PO}_3])}$$

They proposed that an oxygen bridged intermediate is formed and that the large deuterium isotope effect points to the cleaving of a P–H bond in the rate-determining step. On the basis of this evidence, Haight concluded that the removal of H^+ from the P–H bond by H_2O or H_2PO_3^- precedes an internal redox step involving the oxygen bridged intermediate.

A kinetic study of Cr(V) and hypophosphorous acid was carried out by Ghosh and Gould between pH 2 and 4.¹² The oxidation of the formally P(I) center was shown to be a $2e^-$ process to form phosphite. They proposed that an oxygen-bridged intermediate, in which the bridge is formed from the hypophosphite oxygen, is the primary reaction pathway.

The oxidation of both P(I) and P(III) centers by permanganate was studied by Zahonyi-Budo.¹³ They found that H_3PO_3 is oxidized by MnO_4^- approximately 250 times more slowly than H_3PO_2 . For hypophosphorous acid a kinetic isotope effect of $k_{\text{H}}/k_{\text{D}}$ of 4.6 was observed. As for chromate(VI), this suggests that cleavage of the P–H bond occurs in the rate determining step. Zahonyi-Budo proposed a mechanism involving hydride abstraction via a bridged intermediate with simultaneous loss of a proton.

Mehrotra also reported the permanganate oxidation of phosphorous acid and found the reaction was first order with respect to both reactants.¹⁴ The hydrogen ion dependence was shown to be independent of ionic strength. He interpreted this to indicate that the reaction proceeds via an intramolecular pathway as opposed to a reaction between ions.

Oxidations involving iron(VI) continue to be an important area of investigation.¹⁵ In our earlier work on the iron(VI) oxidation of several different nitrogen containing substrates, we

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were forced to invoke the formation of iron–substrate intermediates based on kinetic arguments which often, but not always, involved oxygen transfer.¹⁶ Related intermediates have also been proposed by Lee in the oxidation of alcohols and by Johnson and Reed in the oxidation of sulfur containing ions.¹⁷ Thus far, however, no direct observations have been made of any iron(VI) intermediate during its oxidation of a substrate.

As part of our ongoing investigations into the chemistry of FeO_4^{2-} , we have studied the reactions of ferrate(VI) with hypophosphite, phosphite, and organic phosphorus compounds. While the original intent of this work was simply to study the heretofore unexplored reactions, the unexpected formation of observable intermediates makes this an important piece of iron(VI) chemistry. The present study of the ferrate oxidation of phosphorus centers has led to the proposal of a mechanism that involves oxygen transfer coupled with the breaking of a P–H bond in the transition state. The product analysis, kinetics, and mechanism of these reactions are described along with the first spectral observations of bridged iron(VI)–substrate intermediates.

EXPERIMENTAL SECTION

Materials. Sodium hypophosphite and phosphorous acid (normal and deuterated) and phenylphosphorous acid were purchased from Aldrich Chemicals and used without purification. Trimethylphosphite was purchased from Fischer Scientific. All other chemicals were reagent grade and used without further purification.

The potassium ferrate was prepared by the method of Thompson, Schreyer, and Ockerman.¹⁸ Purity of the ferrate was determined spectrophotometrically as previously described.¹⁶ Typical purities of >90% were obtained, and the reaction rates were independent of sample.

Stock solutions of reductants were prepared using water from a Barnstead Nanopure system. The ionic strength was maintained at 1.0 M with sodium perchlorate, and sodium phosphate buffers and sodium hydroxide were used to control pH. The efficacious selection of phosphate buffers also prevented precipitation of the iron(III) hydroxides produced upon reduction of ferrate(VI).

Kinetic Measurements. The reaction rates were measured spectrophotometrically using a D110 Dionex stopped-flow spectrophotometer interfaced with an OLIS data collection and processing system. The reactions were monitored at 505 nm under pseudo-first-order conditions, >10-fold excess reductant, throughout. The substrate concentrations were in the millimolar range, and the pH range studied was between 8 and 11. Oxidations were also carried out at 1.0 M NaOH for phosphite, which used an HP8452A diode array spectrometer. The exponential absorbance changes were fitted using the OLIS fitting routines. Each rate constant is an average of 3–5 trials. Temperature was controlled to within 0.1 °C using a constant temperature bath.

Rapid scanning experiments were carried out using an OLIS RSM-1000 spectrophotometer equipped with an OLIS stopped-flow. Conventional spectrophotometric experiments used an HP8452 system equipped with a thermostatted cell holder. Absorbance versus time changes were fitted using OLIS fitting routines to obtain rate constants.

Product Analysis and Tracer Studies. The final iron product was determined using colorimetric tests described previously.¹⁶ The final phosphorus oxidation products were identified by ^{31}P NMR using an external standard (conc H_3PO_4). Spent reaction mixtures (with no phosphate buffer) were drawn through a 0.22 μm nylon filter to remove precipitated ferric hydroxides. The filtrate was passed through a 1 cm \times 5 cm CM25-Sephadex column to remove any remaining dissolved iron(III). This was followed by elution with one column volume of distilled water. The eluted samples were rotary evaporated to dryness, redissolved in a minimum amount of water, and placed in an NMR tube. The chemical shifts were determined and compared

with chemical shifts of known samples under identical conditions. A 400 MHz Varian NMR was used to collect data. These experiments were carried out at different pHs (9 and 10), and no difference in products was observed.

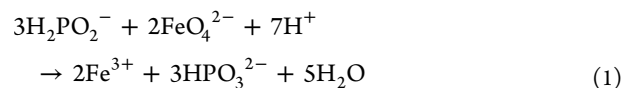
Gas chromatography was used to identify the product for the oxidation of trimethylphosphite to trimethylphosphate. A spent aqueous reaction mixture was extracted with methylenechloride, and the extraction mixture was injected on a Superox GC column to separate starting materials from reaction products. Assignment of retention times was carried out using known standards. Again, these were carried out at different pHs, and no differences were observed.

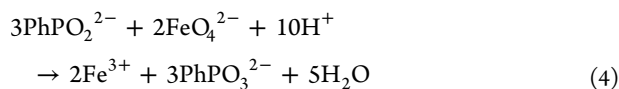
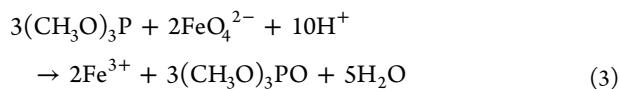
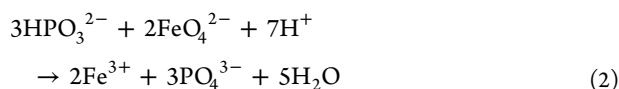
In order to determine whether oxygens from ferrate(VI) were transferred to the phosphorus center during oxidation, ^{18}O labeling studies were carried out. A sample of potassium ferrate(VI) was dissolved into 90% ^{18}O labeled water, the oxygens were allowed to equilibrate (~15 min), and solvent water was removed via vacuum drying.^{19a} This solid sample was rapidly dissolved in an aqueous solution of the phosphorus reducing agent, which resulted in bleaching of the violet color within 30 s, much faster than the solvent exchange rate of the ferrate oxygens.^{19a} The pH of the spent mixture was approximately 9. The spent reaction mixture was treated as described above for the NMR product analysis procedure, and the transfer of oxygen was determined using the ^{18}O induced shift in the ^{31}P signal.^{19b} To check for induced oxygen exchange, normal sodium phosphate, sodium phosphite, and sodium hypophosphite were treated by the product isolation procedure described above in the presence of enriched solvent, and no O-18 enrichment was observed in any of these compounds. This confirms that any incorporation of O-18 into the final products arises from transfer from the iron center.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis. The ionic phosphorus reaction products were identified using NMR whereas GC analysis was used to observe trimethylphosphate. For hypophosphite, phosphite, and phenylphosphite, the oxidations were carried out with a slight excess of these reductants over ferrate, the ^{31}P NMR spectrum contained peaks of the parent compound, and its oxidation product as confirmed with known samples of these compounds. Trimethylphosphite was oxidized with ferrate, and the solution was extracted with methylene chloride. Only one product peak was observed with a retention time identical to that of an authentic trimethylphosphate sample. The final iron product was identified by standard qualitative analytical techniques described elsewhere, and in each case, iron(III) was observed.²⁰

With hypophosphite and trimethylphosphite the reaction stoichiometries were determined by direct titration with ferrate, and for these a $(1.6 \pm 0.2)/1$, $(1.5 \pm 0.3)/1$ ratio of reductant/ferrate was observed, respectively. The pH varied between 8 and 9 for the stoichiometry determinations. Redox for these two reactions was rapid, so a clear end point (the purple ferrate(VI) ion remained) was observed. Unfortunately, a precise direct titration with phosphite or phenylphosphite was not practical as the reactions were too slow and the ferrate decomposed significantly during the titration. However, rough estimates of the stoichiometry support a 1.5:1 ratio. On the basis of these results, a 3:2 reductant to ferrate ratio is proposed for all the reactions studied, which is congruent with the reaction products observed. The following reactions can be written:





Reaction Kinetics. Absorbance versus time plots for the disappearance of ferrate (505 nm) fit nicely to a single exponential decrease to provide the observed pseudo-first-order rate constants. Plots of these rate constants versus reductant concentration, P (P denotes phosphite, hypophosphite, phenylphosphite, or trimethylphosphite where appropriate), were linear, thereby establishing first order terms with respect to P and ferrate, see Figure 1 inset. The slopes of these lines (the

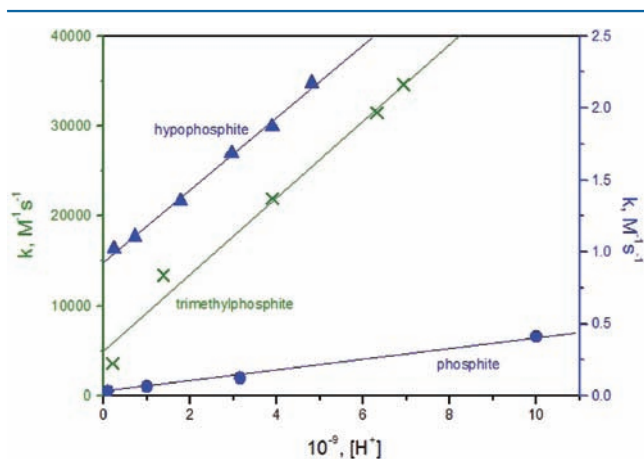


Figure 1. Hydrogen ion dependence of reaction rates. Inset: Representative substrate dependence on reductant concentrations. For both plots: trimethylphosphate, left y-axis; other reductants, right y-axis. Conditions: $I = 1.0 \text{ M}$ (NaClO_4), sodium phosphate buffer = 0.05 M , $T = 25.0 \text{ }^\circ\text{C}$.

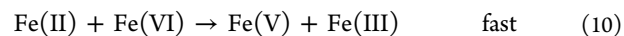
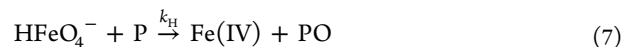
second order rate constant) were determined between pH 8 and 11 and are shown in Figure 1 as plots versus the hydrogen ion concentration. The observed linear plot with a positive y-intercept is best described by the following rate law, eq 5, where k_0 is the intercept and k_1 is the slope of the line.

$$-d([\text{Fe(VI)}])/dt = (k_0 + k_1[\text{H}^+])[\text{FeO}_4^{2-}][\text{P}] \quad (5)$$

The pK_a s for hypophosphorous acid, phosphorous acid, and phenylphosphorous acid are low (1.2, 1.43, 2.1, respectively).²¹ Since the experiments were conducted above pH 8, protonation is assumed to involve the ferrate ion, pK_a 7.3²² at $25 \text{ }^\circ\text{C}$. Since trimethylphosphite possesses no acidic hydrogens, protonation must occur at ferrate(VI).

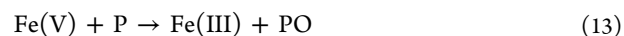
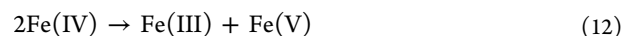
In order to check for the production of radicals, these reactions were carried out in the presence of acrylonitrile which is well-known to polymerize when radicals are produced. For each of these systems, no polymerization was observed which suggests that radicals are not formed. We have used this test for systems described in ref 16. The lack of observation of radicals suggests that a 2-electron redox reaction occurs for these reactions and is supported by our oxygen transfer experiments and our spectral observation of an intermediate in these oxidations.

A general mechanism consistent with this rate law can be written as follows. In this mechanism we have assumed that the process occurs via a 2-electron oxidation process, and on the basis of our work with sulfite, this occurs via oxygen transfer.



On the basis of this mechanism, k_1 from eq 5 equals $k_H K_a^{-1}$ where K_a is the acid dissociation constant for the ferrate ion. Using Sharma's value for the HFeO_4^- acid dissociation constant, 5.01×10^{-8} at $25.0 \text{ }^\circ\text{C}$,²² a value for k_H was calculated for each substrate, see Table 1. Details of this are given in Supporting Information.

Another scheme can be written to account for the production of Fe(III) in the fast steps, eqs 9–11, that involves the rapid disproportionation of Fe(IV) followed by a rapid Fe(V) oxidation.



This alternative gives the same stoichiometry for the overall reaction, but the reaction rates for the Fe(IV) and Fe(V) oxidations of these substrates are unknown. Previous work by Bielski et al. on other substrates has shown that the +4 and +5 oxidation states react at least 2–3 orders of magnitude faster than does Fe(VI), so there is no kinetic basis to eliminate this pathway.²³

To differentiate between these two possibilities requires the estimation and comparison of rate constants for reactions 10 and 12. The following gives a brief analysis of these two scenarios. Although the reaction rate constant for eq 10, the Fe(II)–Fe(VI) reaction, has not been measured using hexaquairon(II) or a corresponding “aqua–hydroxo” complex, the aquapentacyanoferrate(II)/ferrate(VI) rate constant has

Table 1. Proton Independent and Proton Dependent Rate Constants for Ferrate(VI)–Substrate Reactions^a

	H_2PO_2^-	HPO_3^{2-}	$(\text{CH}_3\text{O})_3\text{P}$	PhPO_2^-
$k_0 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	0.93 ± 0.11	0.021 ± 0.005	4900 ± 300	0.036 ± 0.003
$k_H \text{ (M}^{-1} \text{ s}^{-1}\text{)}^b$	13 ± 1	1.9 ± 0.1	$(2.2 \pm 0.2) \times 10^5$	1.2 ± 0.6

^aConditions: $T = 25 \text{ }^\circ\text{C}$, 0.05 M sodium phosphate buffer, 1.0 M (NaClO_4) ionic strength. ^bCalculated from $K_a k_a$ using K_a values in text and Supporting Information.

Table 2. Thermodynamic Parameters for the Ferrate(VI) Oxidation^a

	H ₂ PO ₂ ⁻		HPO ₃ ²⁻		(CH ₃ O) ₃ P		PhPO ₂ ⁻	
	k _H	k _O	k _H	k _O	k _H	k _O	k _H	k _O
ΔH [‡] (kJ/mol)	45 ± 1	32 ± 2	61 ± 5	100 ± 10	18 ± 1	22 ± 3	50 ± 1	91 ± 2
ΔS [‡] (J/mol K)	-73 ± 10	-140 ± 30	-35 ± 11	-77 ± 9	-170 ± 20	-99 ± 15	-130 ± 30	-98 ± 5

^aConditions: I = 1.0 M NaClO₄, 0.05 M sodium phosphate.

been reported equal to 10⁸ M⁻¹ s⁻¹.²⁴ This would suggest that reaction 10 would be very fast and not rate determining.

To probe eq 12, if we assume 10³ fold higher rate constant for Fe(IV) compared to Fe(VI) for the oxidation of H₂PO₂⁻, then in the reductant concentration range in this study, k_{calc} in 1 M OH⁻ could vary between 0.1 and 100 s⁻¹. Bielski has reported the disproportionation rate constant for Fe(IV) to equal 2 s⁻¹ in 1 M OH⁻,²⁵ which is competitive with the hypophosphite/Fe(IV) reaction under these conditions. Of course, whether these calculated rates present a true picture over the pH range used in this study is uncertain, and further kinetic experiments are required to directly measure these rates. We have initiated studies of iron(V) reactions with phosphite and hypophosphite using pulsed radiolysis to generate this oxidation state. Preliminary results indicate that both of these reactions are slower than the disproportionation of iron(V) with estimates of the bimolecular rate constants to be less than 10² M⁻¹ s⁻¹ at pH 9.²⁶

Values for both k_O and k_H were determined at three temperatures (10, 25, and 35 °C), and standard Eyring plots were linear. Using these data, the activation parameters were calculated, Table 2. The temperature dependence of the monohydrogenferrate(VI) pK_a was used in these calculations using Sharma's data.²² As can be seen, a significant activation enthalpy is observed, and more importantly, a very negative activation entropy was calculated for the reaction of both protonated and deprotonated ferrate with each substrate. These large negative entropy values imply that significant organization occurs during each reaction, which supports the formation of an intermediate between ferrate and the phosphorus centers during the redox process. Although an oxygen bridge between the iron and phosphorus center is most likely, oxygen labeling studies were carried out to confirm this.

Rapid Scanning and O-18 Labeling Experiments. In conjunction with other studies in this laboratory, it was noted that reaction mixtures of ferrate(VI) and oxyions in 1.0 M NaOH produced spectra where the absorption maxima were shifted from ferrate(VI) in 1.0 M NaOH. When solutions of ferrate(VI) (λ_{max} = 505 nm, see Supporting Information for spectrum) and phosphite were mixed in 1.0 M NaOH, a new peak at 560 nm formed rapidly, see Figure 2, and then slowly disappeared over a few minutes. The rate of appearance of this new peak was first order with respect to ferrate and excess phosphite, see Figure 2 inset, and plots of k_{obs} versus [phosphite] had a significant y-intercept. This was interpreted as an equilibrium where the slope/intercept (0.86 M⁻¹ s⁻¹/0.29 s⁻¹) gives K_{eq} = 3.0 M⁻¹. The disappearance of this peak fits a first order absorbance decrease (at 560 nm) where k_{diss} was 0.001 s⁻¹ and was independent of the phosphite concentration.

If we assume K_{eq}*k determined at 1.0 M NaOH for the phosphite–ferrate(VI) reaction should equal k_o determined between pHs 8 and 10, then this product equals 0.003 M⁻¹ s⁻¹. The observed value for k_o equals 0.021 M⁻¹ s⁻¹. Considering the vastly different conditions by which these two numbers were obtained, a factor of 7 difference seems acceptable

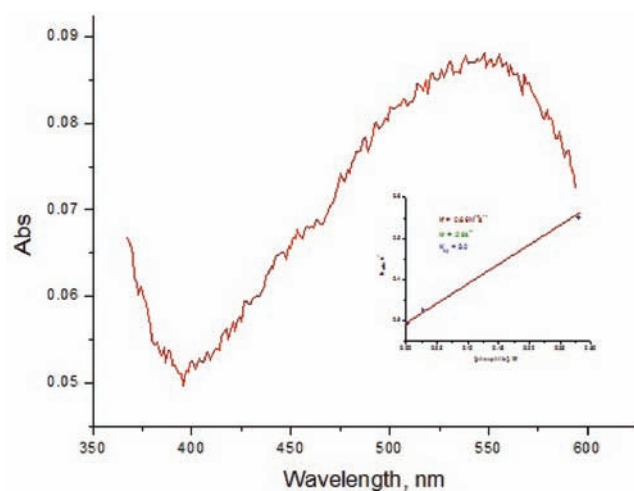


Figure 2. Spectrum of ferrate(VI)–phosphite complex. Conditions: 1.0 M NaOH, 25 mM phosphite, 0.5 mM ferrate(VI), T = 25 °C.

agreement and supports our proposed mechanism. A reasonable explanation for why we observe this in 1.0 M NaOH and not around pH 9 is that iron(VI) exists completely in its deprotonated form, FeO₄²⁻, and in this form it is much slower (about 100×) to oxidize the bound substrate.

It is well-known that chromate(VI) reacts with similar oxyanion substrates to form chromium esters and the equilibrium constant for the ferrate/phosphite system is comparable with similar chromate systems.²⁷ Since oxygen transfer has been shown to occur during the oxidation of sulfite to sulfate by ferrate and a similar spectral shift is observed when solutions of ferrate(VI) and sulfite are mixed in 1.0 M NaOH, it is reasonable to assume that these spectra are of a ferrate(VI)–substrate ester, i.e., [O₃Fe–O–PO₃H₂]⁴⁻. The two reactions observed for phosphite then are ester formation followed by an intramolecular 2-electron transfer that involves an oxygen transfer.

Bielski has reported the spectrum of the iron(IV)–pyrophosphate complex in alkaline media.²⁸ His work shows a peak at 420 nm, which differs little from the “aqueous” alkaline iron(IV) spectrum. Iron(V) has two absorptions (approximately 490 and 390 nm) which are the same for the aqueous and carbonate species. Both of these systems have spectral characteristics that are very different from our observation of a peak at 560 nm for the iron(VI)–phosphite reaction intermediate which is a 55 nm shift from aqueous iron(VI). The significant differences from our absorption maximum for the iron(VI)–phosphite system and those of alkaline “aqueous” iron(IV) and iron(V) along with the spectral data for the iron(IV)–pyrophosphate species support, but admittedly do not eliminate, our assumption that we are observing an iron(VI)–phosphite intermediate. Unfortunately, we cannot obtain a pure solid for this intermediate to better probe its nature. Its subsequent decay in solution also hinders

formation of a frozen sample where the only species present is the intermediate. In addition, work by Sharma on the question of one versus two electron transfer reactions for ferrate(VI) shows that for sulfite, selenite, and arsenite a two electron pathway is favored.²⁹ Since we have seen similar shifts in the UV-vis spectrum of ferrate(VI) with these reductants in 1 M NaOH, we favor the formation of bridged iron(VI)–phosphorus intermediate.

Assuming that an iron(VI)–phosphite dimer is formed and subsequently undergoes intramolecular electron transfer, it should show transfer of an oxygen from the ferrate(VI) ion to the final phosphate product. Oxygen labeling experiments were carried out using ¹⁸O labeled potassium ferrate(VI). It is clear from the ¹⁸O induced shift of the ³¹P NMR signal shown in Figure 3 that oxygen is transferred from ferrate to the

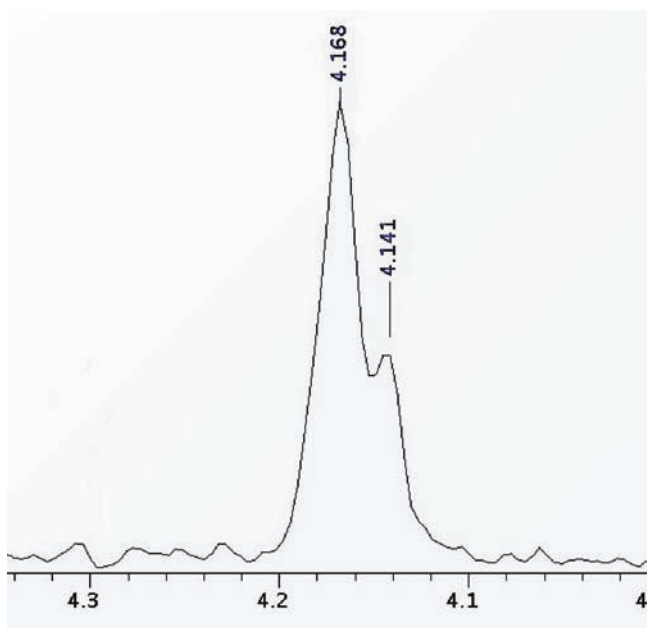


Figure 3. ³¹P NMR of the phosphite formed from the oxidation of hypophosphite with ¹⁸O labeled ferrate(VI). The resonance at 4.141 ppm is due to ¹⁸O shift of the ³¹P signal at 4.168 for phosphite without ¹⁸O labeling.

phosphorus center during oxidation of phosphite. Since phosphate and phosphite are slow to exchange their oxygens with solvent water and the redox reaction occurs more rapidly than the exchange rate of the ferrate oxygens with solvent, the formation of an iron–oxygen–phosphorus bridge is invoked to account for this transfer. The same oxygen transfer was observed for all of the phosphorus complexes in this study using ³¹P NMR.

Kinetic Isotope Effects. Since many investigations into phosphite and hypophosphite oxidation reactions have involved hydride abstraction from the phosphorus center, the effects of deuteration of the substrate on the reaction rates were examined. As a control, the reactions were run in D₂O using normal phosphite, hypophosphite, and trimethylphosphite, which either do not have hydridic hydrogens or exchange their hydrogens very slowly with D₂O. In each case there was no effect of using D₂O over H₂O as the solvent; i.e., no solvent based isotope effect was observed. When the hydridic hydrogens on the phosphorus centers were deuterated, however, substantial kinetic isotope effects were observed; see

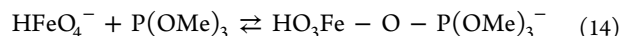
Table 3. It is clear that a P–H bond breaks to reach the transition state.

Table 3. Kinetic Isotope Effects^a

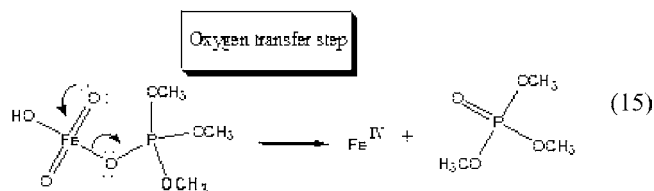
	$k_{\text{H}}/k_{\text{D}}$ in D ₂ O with P–H	$k_{\text{H}}/k_{\text{D}}$ in H ₂ O with P–D	$k_{\text{H}}/k_{\text{D}}$ in D ₂ O with P–D
H ₂ PO ₂ [−]	1.0	9.6	10
HPO ₃ ^{2−}	1.1	8.3	8.5
P(OCH ₃) ₃	1.0 ^b		

^aConditions: $T = 25\text{ }^{\circ}\text{C}$, 0.05 M sodium phosphate buffer (pH or pD = 9), 1.0 M (NaClO₄) ionic strength. ^bWhile the substrate contains no P–H bond, the reaction was run to give a baseline for D₂O effects on reaction rates.

Proposed Ferrate(VI) Reaction Intermediates. On the basis of the above observations, a picture of the intermediate in the four reactions may be formulated. For each system an oxygen bridged species arises via ester formation with the ferrate(VI) center. While direct coordination to the iron(VI) center by a phosphorus oxygen is possible, it is not favored in these systems since the oxygen from the iron(VI) was observed to be transferred to the phosphorus center. This suggests formation of an intermediate with an Fe–O–P bridge using an iron based oxygen. Such bridging should be quite facile for trimethylphosphite or phenylphosphite to form a 4-coordinate phosphorus center, and both of these substrates are observed to “rapidly” reduce ferrate(VI). The two steps are shown below.



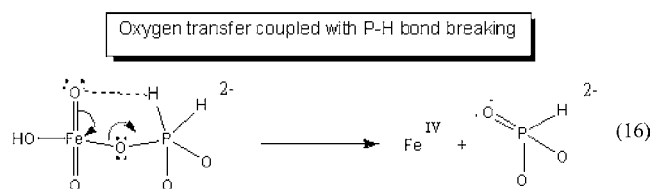
As a control for later studies, these reactions were also carried out in 99 atom % D₂O and showed no *solvent isotope effect*, i.e., $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.0 \pm 0.1$.



In contrast to the trimethylphosphite reduction, the ferrate oxidations of phosphite, hypophosphite, and phenylphosphite are much slower. This could be due to two factors: valence shell expansion of the phosphorus center (to form a 5-coordinate species) and/or abstraction of a hydridic hydrogen from the phosphorus. For these centers, bridging via a ferrate(VI) oxygen accounts for the transfer of oxygen to the final phosphorus product, so in this sense, they are the same as to the first two systems described. However, when these reactions are carried out with deuterated substrates, i.e., D₂PO₂[−] and DPO₃^{2−}, the reactions are substantially slower and showed kinetic isotope effects, $k_{\text{H}}/k_{\text{D}}$, of 10 and 8.5, respectively. This indicates that the breaking of a P–H bond occurs in the transition state. This can be accounted for as illustrated with hypophosphite and presumably also occurs with phosphite.

The pathway in eq 16 is similar to that proposed by Gould et al. for electron transfer via an intramolecular hydride abstraction in a cobalt(III)–hypophosphite complex.¹²

The reaction mechanism proposed is also similar to that suggested by Haight et al. for the chromate(VI) oxidation of hypophosphite.¹⁰ He proposed that coordination of the



hypophosphite followed by deprotonation of the P center resulted in an internal redox step. This was believed to be general base catalyzed. In order to check for a general base mechanism for ferrate–hypophosphite, the reaction was carried out using a sodium borate buffer instead of sodium phosphate at pH 9. No difference in rate was observed between these two buffers. Therefore, in the above mechanism the ferrate oxygen is involved in the hydrogen abstraction since there is no observed general base catalysis, as might be expected if simple deprotonation of the phosphorus center were involved.

To further probe this mechanism, labilization of a P–H bond with respect to exchange to solvent water was attempted by coordination with a non-redox-active center such as molybdate.³⁰ Solutions of phosphite and molybdate were mixed in D₂O and adjusted to pD ~ 9 and ¹H NMR spectra collected over time. Even after exposure times of several hours there were no decreases of the P–H signals in the NMR spectra. This indicates, though not unambiguously, that coordination of a phosphorus hydride moiety to high oxidation state metals does not labilize the P–H bond. This could mean that the chromate(VI) oxidation mechanisms reported by Haight et al. require modification to reflect an intramolecular abstraction/breaking of the P–H bond.

CONCLUSIONS

For the first time in iron(VI) oxidation chemistry, a quasistable intermediate that involves an oxygen bridge ester has been observed. The subsequent electron transfer process involves transfer of an oxygen from the iron(VI) center to the final phosphorus product. In addition, for those phosphorus substrates containing hydridic hydrogens, the breaking of the P–H bond occurs in the transition state and is presumably via abstraction with an iron(VI) oxygen.

ASSOCIATED CONTENT

Supporting Information

Additional figure, table, and details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: johnson@nmsu.edu. Phone: (575) 646-3627. Fax: (575) 646-2394.

Notes

The authors declare no competing financial interest.

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