

been invoked to account for the nonexistence of AsCl_5 .³⁴ This apparent relative instability of the highest oxidation states of the nonmetallic elements of the first long period has been discussed at length, but the explanations offered have been less than convincing.³⁴ The effect appears real, but its causes are probably complex.

It is important to realize that perbromate ion is only a little more strongly oxidizing than periodate, and the difference is not, in itself, sufficient to explain

(34) W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, Inc., New York, N. Y., 1965, p 117 ff.

why perbromates have been so hard to prepare. However, the perbromate ion is only slowly reduced,⁸ indicating the presence of a high activation barrier between Br(V) and Br(VII) . This barrier plus the fairly high electrode potential could account for the difficulties encountered in the synthesis of perbromates.

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Mechanism of the Reduction of Vanadium(V) by Hexacyanoferrate(II) in Acidic Aqueous Solution

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The rapid reaction between vanadium(V) and hexacyanoferrate(II) proceeds at least partially *via* an inner-sphere mechanism involving an intermediate postulated to be a vanadium(IV)–iron(III) binuclear complex. The oxidation–reduction step follows a rate equation $-d[\text{V(V)}]/dt = k_{\text{ox}}[\text{VO}_2^+][\text{Fe(II)}]$ with $k_{\text{ox}} = (1.2 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 8° and 0.50 M ionic strength. The intermediate decays in a first-order process independent of all concentrations when VO_2^+ is present in excess. The activation parameters for this process are $\Delta H_0^\ddagger = 14.1 \pm 0.3 \text{ kcal/mol}$ and $\Delta S_0^\ddagger = -4.4 \pm 1.1 \text{ eu}$, with $k_0 = 34.1 \text{ sec}^{-1}$ at 25° and 0.50 M ionic strength. With excess iron(II) the rate equation contains an additional term, first-order in the excess iron(II) concentration, which is subject to several interpretations. The associated activation parameters are $\Delta H_1^\ddagger = 6.53 \pm 0.55 \text{ kcal/mol}$ and $\Delta S_1^\ddagger = -15.8 \pm 1.9 \text{ eu}$, with $k_1 = 3.51 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° .

Introduction

The reduction of chromium(VI) by hexacyanoferrate(II) and several other substitution-inert iron(II) complexes has recently been shown to follow a different kinetic pattern than that observed with aquoiron(II) and a number of other reducing agents.¹ In particular, the reductions by the cyanoiron(II) complexes were found to proceed, at least partially, by inner-sphere processes in which the bridging ligand originates on the reducing agent, in contrast to the normal situation where the oxidizing agent supplies the bridging ligand. Since vanadium(V) is isoelectronic and probably also isostructural (VO_2^+ or more probably V(OH)_4^{+2} or possibly $\text{V(OH)}_4\text{OH}_2^{+3,4}$) with chromium(VI), the reduction of VO_2^+ by Fe(CN)_6^{4-} has been investigated in an attempt to determine whether the rather novel mechanism in which the reducing agent supplies the bridging ligand in fact has a more general existence.

Experimental Section

Solutions of vanadium(V) perchlorate were prepared by dissolution of Fisher purified vanadium pentoxide or Fisher sodium orthovanadate in an excess of perchloric acid. Solutions were analyzed by titration with iron(II) in approximately 6 M sul-

furic acid to a ferroin end point. These analyses agreed to within 1% with the concentrations determined from the visible spectra and from the weight of material dissolved. Vanadium(IV) perchlorate solutions were prepared by electrolytic reduction of a V_2O_5 suspension in perchloric acid⁵ or by reaction of equivalent amounts of barium perchlorate and vanadyl sulfate (Alfa Inorganics). Barium sulfate was removed by centrifugation. Solutions were analyzed by titration with cerium(IV) sulfate to a ferroin end point in acetic acid solution.⁶ The hydrogen ion concentration was determined by titration of the acid released from a column of ion-exchange resin in the H^+ form and correction for the acid displaced by VO_2^+ . Solutions of potassium ferrocyanide, potassium ferricyanide, lithium perchlorate, and perchloric acid were prepared and analyzed as previously described.¹

The kinetics of the reduction of VO_2^+ by Fe(CN)_6^{4-} were determined with a Durrum stopped-flow spectrophotometer, using previously described techniques.¹ Spectra were measured with a Cary 14 recording spectrophotometer. Spectra of the intermediate were calculated from the difference in transmittance between the intermediate (at the time of initial observation) and the products, using stopped-flow oscillograms measured at various wavelengths with an oscilloscope calibrated to determine transmittance changes exactly. Two limiting interpretations were made of the absorbances calculated in this manner. (1) It was assumed that the entire reaction involves the formation of the intermediate so that the calculated absorbance equals the absorbance of the intermediate. This assumption was used to determine the spectrum shown in Figure 2. (2) Assuming that

(1) J. P. Birk, *J. Am. Chem. Soc.*, **91**, 3189 (1969).

(2) M. T. Pope and B. W. Dale, *Quart. Rev. (London)*, **22**, 527 (1968).

(3) G. Schwarzenbach and G. Geier, *Helv. Chim. Acta*, **46**, 906 (1963).

(4) H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4411 (1962).

(5) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

(6) K. Sriramam and G. G. Rao, *Talanta*, **13**, 1468 (1966).

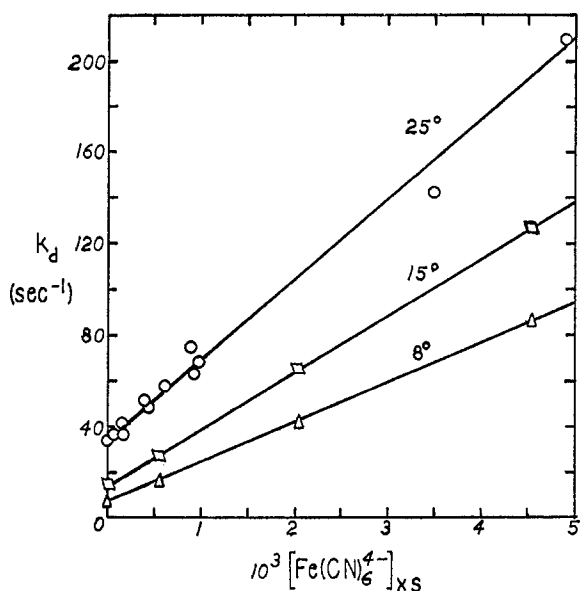


Figure 1.—Plots of k_d vs. the excess $\text{Fe}(\text{CN})_6^{4-}$ concentration, showing conformity to eq 2.

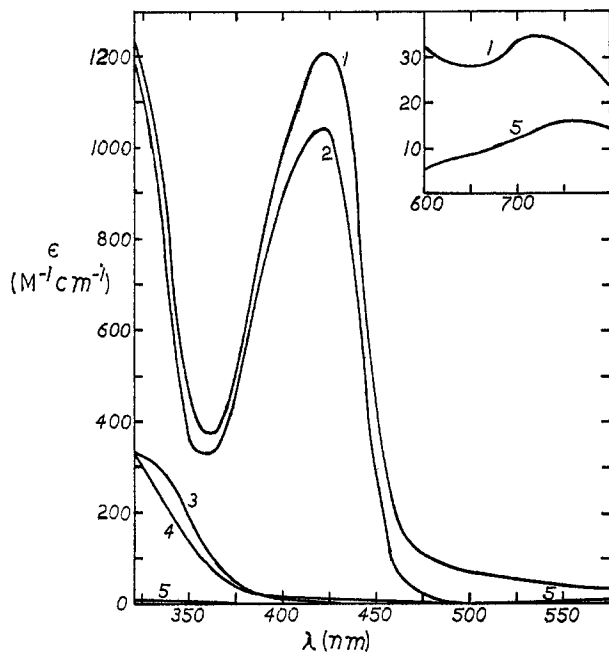


Figure 2.—Visible absorption spectra in aqueous perchlorate solutions: (1) intermediate, (2) $\text{Fe}(\text{CN})_6^{3-}$, (3) $\text{Fe}(\text{CN})_6^{4-}$, (4) VO_2^+ , (5) VO^{2+} .

only a small fraction of the reaction involves the formation of the intermediate, the absorbance of the intermediate is given by the difference between the initial and final absorbances.⁷ Under this assumption, it is not possible to calculate absolute molar extinction coefficients of the intermediate.

Results

Formation of the Intermediate.—When less than stoichiometric amounts of $\text{Fe}(\text{CN})_6^{4-}$ are added to a solution of VO_2^+ , spectral changes are complete within the few seconds necessary to mix the solutions. The absorbance of the products throughout the range 300–800 nm corresponds to within $\pm 2\%$ of that expected for

(7) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965).

formation of VO^{2+} and $\text{Fe}(\text{CN})_6^{3-}$. When $\text{Fe}(\text{CN})_6^{4-}$ is present in excess, subsequent slower absorbance changes occur, due to interactions between VO^{2+} and $\text{Fe}(\text{CN})_6^{4-}$, ultimately resulting in the formation of a precipitate if concentrations are greater than *ca.* $4 \times 10^{-4} M$.

Although the absorbance at 300–800 nm undergoes an over-all increase during reaction, absorbance decreases are observed on a millisecond time scale at room temperature or below, indicating the probable formation of an intermediate. It was possible to observe the formation of the intermediate only at temperatures below 10° and concentrations lower than $10^{-4} M$. The kinetics of formation of the intermediate were studied at 8° in solutions of $0.500 M$ ionic strength maintained with lithium perchlorate, at wavelengths in the range 400–450 nm. Results are presented in Table I. Owing to a rather large noise to signal ratio in most of these experiments, the individual rate constants are estimated to have an uncertainty of about $\pm 30\%$. Within this uncertainty, the data conform most simply to the rate equation

$$-d[\text{Fe}(\text{II})]/dt = -d[\text{VO}_2^+]/dt = k_{\text{ox}}[\text{VO}_2^+][\text{Fe}(\text{II})] \quad (1)$$

When the initial concentration ratio was greater than *ca.* 5:1, the data were treated according to a pseudo-first-order rate equation. Since the reactions were very fast, only data near the end of the reaction could be obtained, so a first-order treatment is justified. Under other conditions, the data were treated according to a second-order rate law. Although it might be tempting to interpret an apparent trend in the data with a more complex rate equation, the data are not sufficiently precise to merit such a treatment and the trend may well be due to a consistent error made in the extrapolation of data to the time of mixing which is necessary for these very rapid reactions. There is apparently no dependence on $[\text{H}^+]$ in the range 0.01 – $0.10 M$ even though the relative amounts of the various protonated forms of ferrocyanide would be expected to change within this range.^{8,9} Since the predominant forms of ferrocyanide at these acidities are $\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$, presumably one or more protons are involved at this step in the reaction mechanism. Unfortunately these rate data provide little indication as to whether the products of the first step are predominantly intermediate or VO^{2+} and $\text{Fe}(\text{CN})_6^{3-}$.

Decomposition of the Intermediate.—The kinetics of the absorbance decreases, attributed to decomposition of the intermediate, have been studied at $0.500 M$ ionic strength, over the range of $[\text{H}^+]$ from 5×10^{-4} to $0.50 M$, under two sets of conditions: (a) with excess VO_2^+ over the concentration ranges 1×10^{-5} – $5 \times 10^{-4} M$ intermediate (assuming all reaction proceeds *via* the intermediate), 2×10^{-7} – $5 \times 10^{-3} M$ excess VO_2^+ , 0 – $2 \times 10^{-3} M$ VO^{2+} , and 0 – $2 \times 10^{-3} M$ $\text{Fe}(\text{CN})_6^{3-}$; (b) with excess $\text{Fe}(\text{CN})_6^{4-}$ over the concen-

(8) J. Jordan and C. J. Ewing, *ibid.*, **1**, 587 (1962).

(9) G. I. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2022 (1967).

TABLE I
RATE CONSTANTS FOR THE REACTION OF VO_2^+ WITH $\text{Fe}(\text{CN})_6^{4-}$ AT 0.100 M H^+ , 0.500 M IONIC STRENGTH, AND 8°

$10^5[\text{VO}_2^+]_0, M$	$10^5[\text{Fe}(\text{CN})_6^{4-}]_0, M$	$10^{-5}k_{\text{ox}}, M^{-1} \text{sec}^{-1}$	$10^5[\text{VO}_2^+]_0, M$	$10^5[\text{Fe}(\text{CN})_6^{4-}]_0, M$	$10^{-5}k_{\text{ox}}, M^{-1} \text{sec}^{-1}$
8.10	1.01	0.7	2.03	2.01	1.3 ^a
8.10	2.03	1.0	1.01	1.01	1.6
4.05	1.01	0.9	1.01	0.98	1.5
4.05	4.02	1.1	1.01	4.05	1.7
2.03	1.01	1.5	1.01	8.10	0.8
2.03	2.01	1.2			Av 1.2 ± 0.3

^a $[\text{H}^+] = 0.010 M$.

tration ranges 2×10^{-5} – $1 \times 10^{-3} M$ intermediate, 5×10^{-7} – $5 \times 10^{-3} M$ excess $\text{Fe}(\text{CN})_6^{4-}$, 0 – $2 \times 10^{-3} M$ $\text{Fe}(\text{CN})_6^{3-}$, and 0 – $2 \times 10^{-3} M$ VO_2^+ .

With VO_2^+ in excess, the reaction followed first-order kinetics, with rate constant k_d , which was independent of all concentrations. Although most measurements were made at 500 nm, the value of k_d was independent of wavelength in the range 350–600 nm.

With $\text{Fe}(\text{CN})_6^{4-}$ in excess, the system was not so well behaved. In all such experiments, the absorbance decreases attributed to intermediate decomposition were followed by slower small absorbance increases. As shown in Figure 1, the value of k_d obtained from the absorbance decreases by the Guggenheim method¹⁰ undergoes an apparent increase with increasing $[\text{Fe}(\text{CN})_6^{4-}]$, according to the rate equation

$$k_d = k_0 + k_1[\text{Fe}(\text{II})]_{\text{excess}} \quad (2)$$

The question arises whether this increase in k_d is due to the existence of another path for the decomposition of the intermediate, as implied by eq 2, or whether it is due to interference from the subsequent absorbance increase, whose rate also apparently increases with increasing $[\text{Fe}(\text{CN})_6^{4-}]$. To consider this question fully, two further experiments must be considered. The rate constant was independent of added $\text{Fe}(\text{CN})_6^{3-}$ but increased slightly with added VO_2^+ . With $5.06 \times 10^{-5} M$ intermediate and $4.49 \times 10^{-4} M$ excess $\text{Fe}(\text{CN})_6^{4-}$, k_d assumed values of 48.0, 56.6, and 64.1 sec^{-1} with VO_2^+ concentrations of 0, 5×10^{-4} , and $2 \times 10^{-3} M$, respectively. In addition, although most experiments were carried out at 500 nm, where the subsequent absorbance increases were relatively small, the rate constant is not independent of wavelength. In an experiment with $5.06 \times 10^{-4} M$ intermediate and $3.49 \times 10^{-3} M$ excess $\text{Fe}(\text{CN})_6^{4-}$, k_d had the values 131 sec^{-1} at 600 nm, 142 sec^{-1} at 500 nm, 530 sec^{-1} at 450 nm, and $>500 \text{ sec}^{-1}$ at $\leq 400 \text{ nm}$ (*i.e.*, only an absorbance increase was observed). Good pseudo-first-order kinetics were observed at 600 and 500 nm but not at 450 and 400 nm. Since VO_2^+ has an effect only when $\text{Fe}(\text{CN})_6^{4-}$ is in excess, the dependence of k_d on $[\text{VO}_2^+]$ can reasonably be attributed to a concurrent reaction of VO_2^+ with $\text{Fe}(\text{CN})_6^{4-}$. Independent studies of this reaction indicate that it occurs at a rate slow compared to the reactions of interest here and that it follows a complex kinetic scheme. The reaction of VO_2^+ and $\text{Fe}(\text{CN})_6^{4-}$ is too slow by about an order of magnitude to account entirely for the subsequent absorbance in-

creases observed in the absence of added VO_2^+ . However, since one must consider both the rate of reaction and the magnitude of the absorbance change, the increase in k_d on addition of VO_2^+ can be accounted for at least semiquantitatively by this concurrent reaction. However, in the absence of added VO_2^+ , the absorbance changes due to this reaction would not be sufficiently large to give rise to the rate behavior described by eq 2.

Considering the above arguments and the fact that the absorbance increase occurs only in the presence of excess $\text{Fe}(\text{CN})_6^{4-}$, this increase must be the result either of a reaction between $\text{Fe}(\text{CN})_6^{4-}$ and the intermediate, giving a new intermediate which decays more slowly, or of a unimolecular conversion of the intermediate to a new intermediate which reacts more slowly with $\text{Fe}(\text{CN})_6^{4-}$. In the former case, eq 2 would be a valid description of the disappearance of the intermediate, while in the latter case the apparent increase in k_d would be due to interference from the absorbance increase.

Several arguments can be advanced for the validity of eq 2. At 500 nm, where most experiments were carried out, the absorbance increase was fairly small and much smaller than the increase at 450 nm where a definite interference was noted. The absorbance increases observed in most experiments were probably too small to cause apparent increases in k_d of the magnitude observed. If these increases had been large enough to cause interference, the system would have followed a consecutive first-order reaction scheme, giving rise to significant deviations from first-order kinetics. However, Guggenheim plots showed excellent linearity. Lastly, it is difficult to envisage chemical species which could correspond to the second case described above, while there is ample precedent (discussed below) for reactions between $\text{Fe}(\text{CN})_6^{4-}$ and binuclear complexes, with rate constants very similar to the value of k_1 observed here. Hence it is concluded that the k_1 term likely does represent an additional path for decomposition of the intermediate and that the slower absorbance increases are due to interactions involving products of this reaction path. The absorbance increase has not been investigated in detail since it does not follow simple kinetics, possibly due to interference from the reaction between VO_2^+ and $\text{Fe}(\text{CN})_6^{4-}$.

Values of the rate constants k_0 and k_1 and of the associated activation parameters are presented in Table II. The activation parameters were determined by fitting all data simultaneously to the Eyring equation, using a nonlinear least-squares computer program in which

(10) E. A. Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

TABLE II
VALUES OF THE RATE CONSTANTS AND ACTIVATION PARAMETERS
FOR DECOMPOSITION OF THE INTERMEDIATE

Temp, °C	k_0 , sec ⁻¹	k_1 , M ⁻¹ sec ⁻¹
25	34.1	3.51×10^4
15	14.5	2.31×10^4
8	7.67	1.70×10^4
Associated parameter	Value	
ΔH^\ddagger , kcal/mol	14.1 ± 0.3	6.53 ± 0.55
ΔS^\ddagger , eu	-4.4 ± 1.1	-15.8 ± 1.0

each datum point was weighted as $1/k_d^2$.¹¹ The activation parameters for the k_0 path were also determined using only the data with excess VO_2^+ and had essentially the same values as given in Table II. The activation parameters reproduce the values of k_d with an average deviation of 4.6%.

The spectra of the intermediate, determined as described in the Experimental Section, and those of reactants and products are shown in Figure 2. The spectrum shown was calculated assuming that the entire reaction proceeds by way of the intermediate. The only evidence that this is a valid assumption comes from a series of experiments in which the initial VO_2^+ concentration was varied in the range 1×10^{-4} – 1×10^{-3} M, while the $\text{Fe}(\text{CN})_6^{4-}$ concentration in each case was maintained at 1×10^{-3} M in excess of the VO_2^+ concentration. If a significant portion of the reaction proceeds directly to VO^{2+} and $\text{Fe}(\text{CN})_6^{3-}$, the value of k_d would be expected to increase slightly with increasing initial VO_2^+ concentration, as noted in the series of experiments with added VO^{2+} . However, the rate constant had the same value in each experiment, so it appears likely that the reaction does proceed primarily by way of the intermediate.

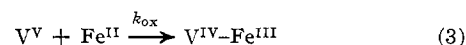
The spectrum of the intermediate was also calculated assuming that only a small portion of the reaction proceeds by way of the intermediate. The resulting spectrum has maxima at 330, 435, and 710 nm with relative peak heights of 0.33, 1.00, and 0.097 (it is not possible to determine absolute extinction coefficients in this case).

Discussion

Two feasible postulates can be made for the identity of the intermediate—a binuclear complex containing either V(IV) and Fe(III) or V(V) and Fe(II). It is possible that the absorbance enhancement could be due to ion-pair formation with the oppositely charged reactants, but it is improbable that the rate of ion-pair formation would be as low as that observed for the formation of the intermediate. The spectrum of the intermediate, which is very similar to that of a mixture of $\text{Fe}(\text{CN})_6^{3-}$ and VO^{2+} (see Figure 2), is particularly informative. Spectra of binuclear complexes generally closely resemble those of the component ions, although absorbance maxima are usually somewhat displaced and

have increased intensity. An example of such a phenomenon is the spectrum of $(\text{EDTA})\text{Co-NC-Fe}(\text{CN})_5^{5-}$ (EDTA = ethylenediamine tetraacetate), an intermediate formed in the reaction between $\text{Co}(\text{EDTA})^{2-}$ and $\text{Fe}(\text{CN})_6^{3-}$.¹² Regardless of which assumption is made in the calculation of the spectrum of the intermediate, the resulting spectrum is quite reasonable for a binuclear $\text{V}^{\text{IV}}\text{-Fe}^{\text{III}}$ complex, probably with one or more bridging cyanides, but is not consistent with a $\text{V}^{\text{V}}\text{-Fe}^{\text{II}}$ complex.

The absence of variation of the rate constant for dissociation of the intermediate with variation in the initial concentrations at constant excess Fe(II) concentration indicates that reaction proceeds predominantly by formation of the intermediate since the presence of significant concentrations of VO^{2+} would cause noticeable variation in the rate constant. It appears likely then that the reaction proceeds primarily by an inner-sphere mechanism (eq 3) although some contribution by an outer-sphere path in which products are formed directly cannot be ruled out. No data are available



on the rate of substitution of V(V), but since the coordination number of vanadium is increased from 4 or 5 in $\text{V}(\text{V})^{2-4}$ to 6 in $\text{V}(\text{IV})$,¹³ the rate of formation of the intermediate is not unreasonably high for an inner-sphere process. The reduction of VO_2^+ by $\text{Fe}(\text{CN})_6^{4-}$ thus provides a further example of an inner-sphere reaction in which the bridging ligand is supplied by the reducing agent rather than the oxidizing agent. This phenomenon was previously noted in the reduction of HCrO_4^- by $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$ (bipy = 2,2'-bipyridine), and $\text{Fe}(\text{bipy})_2(\text{CN})_2$ where isolation of $\text{Cr}^{\text{III}}\text{-Fe}^{\text{III}}$ binuclear complexes indicated that the $\text{Cr}^{\text{IV}}\text{-Fe}^{\text{II}}$ reactions were inner sphere and consideration of the Marcus relation for outer-sphere reactions indicated that the $\text{Cr}^{\text{VI}}\text{-Fe}^{\text{II}}$ reactions were probably also inner sphere.¹ Likely requirements for such a "reverse ligand transfer" process are an oxidizing agent which undergoes rapid substitution in its first coordination sphere or which expands its first coordination sphere on reduction and a reducing agent which is fairly inert toward substitution and which has reasonably good bridging ligands.

Since there was no observed dependence of the rate on $[\text{H}^+]$ in the range 0.01–0.10 M, where $\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ are the predominant forms of ferrocyanide,^{8,9} it is highly probable that one or more protons are being introduced into the transition state at this point in the mechanism. Since the relative amounts of the protonated Fe(II) species change in this range of $[\text{H}^+]$, it would appear that these species react with VO_2^+ at very similar rates. Similar conclusions were reached in the ferrocyanide reduction of MnO_4^- .¹⁴ The predominant path for the aquoiron(II) reduction of VO_2^+ showed a first-order dependence on

(11) The programs used are based on the reports from Los Alamos Scientific Laboratory, LASL-2367 + addenda, and were modified to operate on the IBM 360/75 computer.

(12) A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).

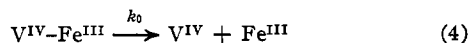
(13) C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

(14) M. A. Rawoof and J. R. Sutter, *J. Phys. Chem.*, **71**, 2767 (1967).

$[H^+]$,¹⁵ but other paths with zero-order¹⁵ and second-order¹⁶ dependences were also found.

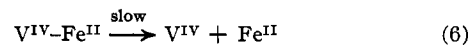
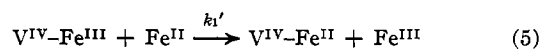
It is interesting to speculate whether the $Fe(CN)_6^{4-}$ reduction of MnO_4^- , which is isoelectronic with VO_2^+ and $HCrO_4^-$, also proceeds by an inner-sphere process. The reaction follows a rate equation first order in each reactant,¹⁴ so the first step in the reduction is rate determining. If the reactions all proceed by similar mechanisms, it would be reasonable to expect that the pseudo-second-order rate constants under given conditions would be related to the oxidation potentials of the oxidizing agents. Although Cr(VI) and Mn(VII) are generally considered to be stronger oxidizing agents than V(V), the V^V-Fe^{II} reaction is the most rapid. However, since it is presumably the first electron-transfer step in each case which is rate determining, the appropriate oxidation potentials to be compared are those for reduction to the nearest oxidation state: V^V-V^{IV} , 1.0 V;¹⁷ $Cr^{VI}-Cr^V$, ≤ 0.6 V;¹⁸ $Mn^{VII}-Mn^{VI}$, 0.56 V.¹⁷ Rate constants for the oxidation of ferrocyanide in solutions containing 0.10 M H^+ are: VO_2^+ , $1.2 \times 10^6 M^{-1} sec^{-1}$ (8°, 0.50 M ionic strength); $HCrO_4^-$, $4.1 \times 10^4 M^{-1} sec^{-1}$ (25°, 0.50 M ionic strength);¹ MnO_4^- , $\sim 2 \times 10^5 M^{-1} sec^{-1}$ (25°, 0.093 M ionic strength).¹⁴ The rate constants do correlate fairly well with the oxidation potentials, indicating that the reduction of MnO_4^- may also proceed by an inner-sphere reaction. However, the successful application of the Marcus theory to this system tends to favor an outer-sphere mechanism.¹⁴

The second observable step in the mechanism for reduction of VO_2^+ by $Fe(CN)_6^{4-}$ is postulated to be the dissociation of the binuclear complex

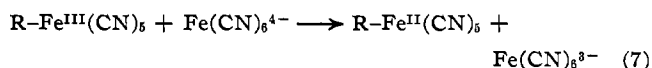


This path corresponds to the term in the rate equation (eq 2) which is independent of the concentrations of reactants and products. The other path for dissociation of the intermediate, which shows a first-order dependence on the excess $Fe(II)$ concentration (assuming this effect is real), must involve a reaction with $Fe-$

(II) and is amenable to two interpretations consistent with the available data. The first interpretation involves a redox reaction producing a second binuclear complex which dissociates more slowly, thus accounting for the observed slow absorbance increases

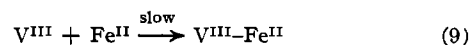
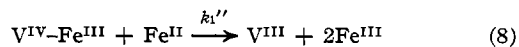


This interpretation suffers from the fact that the $V^{IV}-Fe^{II}$ complex would not be expected to absorb less than its component ions. However, support for this mechanism is obtained from other studies of $Fe(CN)_6^{4-}-Fe^{III}$ reactions



Such reactions have been found to occur in other systems involving binuclear intermediates when $R = (EDTA)Co^{III}-NC^{2-}$ or $(NC)_5Co^{III}-NC^{3-}$.¹⁹ The rate constants for these reactions at 25° are 3×10^4 and $1.6 \times 10^4 M^{-1} sec^{-1}$, respectively, which compare favorably with the value of k_1' at 25°, $3.5 \times 10^4 M^{-1} sec^{-1}$. Furthermore, these rate constants resemble those found for the $Fe(CN)_6^{4-}$ reduction of monosubstituted pentacyanoferrate(III) complexes:²⁰ $R = NH_3$, $0.7 \times 10^4 M^{-1} sec^{-1}$; H_2O , $0.1 \times 10^4 M^{-1} sec^{-1}$; $P(C_6H_5)_3$, $8 \times 10^4 M^{-1} sec^{-1}$.

A second possible interpretation for this path involves a redox reaction producing $V(III)$



Independent experiments have shown that $V(III)$ and $Fe(CN)_6^{4-}$ do form a purple complex at roughly the appropriate rate. Unfortunately this reaction does not follow a simple kinetic pattern, so it has not yet been possible to make quantitative comparisons of rates.

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