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Mechanisms of the Reactions of Vanadium(V) with Cyanobipyridyliron(II) Complexes and of Vanadium(IV) with Tris(2,2'-bipyridyl)iron(III)^{1a}

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The reactions of vanadium(V) with tetracyano(2,2'-bipyridyl)iron(II) and dicyanobis(2,2'-bipyridyl)iron(II) apparently proceed by inner-sphere mechanisms, producing binuclear Fe(III)-V(IV) complexes as immediate products. The reactions proceed with rate constants of $(2.4 \pm 0.3) \times 10^6 M^{-1} \text{sec}^{-1}$ and $(8.3 \pm 0.2) \times 10^6 M^{-1} \text{sec}^{-1}$, respectively, at 10° and 0.50 *M* ionic strength. At 25°, 0.25 *M* H⁺, and 0.50 *M* ionic strength, the reaction of vanadium(V) with tris(2,2'-bipyridyl)iron(II) proceeds more slowly than aquation of Fe(II). The reaction of vanadium(IV) with tris(2,2'-bipyridyl)iron(III) follows the rate equation $-d \ln [\text{Fe}(\text{bipy})_3^{3+}] / dt = (a + b[\text{H}^+]^{-1})[\text{VO}_2^{2+}]$ with $a = (7.15 \pm 0.86) \times 10^{-2} M^{-1} \text{sec}^{-1}$ and $b = (5.37 \pm 0.15) \times 10^{-2} \text{sec}^{-1}$ at 25° and 0.50 *M* ionic strength. A test was made of the application of the Marcus theory to the prediction of mechanism in the reduction of chromium(VI) by cyanoiron(II) complexes.

Introduction

The reductions of chromium(VI) by Fe(CN)₆⁴⁻, Fe(bipy)(CN)₄²⁻ (bipy = 2,2'-bipyridine), and Fe(bipy)₂(CN)₂ produce iron(III)-chromium(III) binuclear complexes.² These results indicated that in the three-step reduction of Cr(VI), at least the last step, the reduction of Cr(IV), proceeded by an inner-sphere mechanism. The failure of the Marcus theory,³ when applied to these reactions and to the reduction by Fe(bipy)₃²⁺, was interpreted as an indication that the reductions by the cyanoiron(II) complexes were also inner sphere in the first reaction step (reduction of Cr(VI)).² These reactions furnish strong evidence for the existence of an inner-sphere reaction in which the bridging ligand was donated by the reducing agent rather than the oxidizing agent. A further example of this "reverse ligand transfer" mechanism was found in the reaction between VO₂⁺ and Fe(CN)₆⁴⁻, which was unambiguously demonstrated to be inner-sphere by the identification of an unstable Fe(III)-V(IV) binuclear complex as the initial reaction product.⁴ We have examined the reactions of VO₂⁺ with Fe(bipy)(CN)₄²⁻, Fe(bipy)₂(CN)₂, and Fe(bipy)₃²⁺ to determine whether the cyanoiron(II) complexes also proceed by inner-sphere mechanisms. These reactions could then also be used to test the validity of the mechanistic conclusions reached for the Cr(VI)-Fe(II) reactions on the basis of failure of the Marcus relation.

Experimental Section

The preparation and analysis of solutions of vanadium(V),⁴ vanadium(IV),⁴ perchloric acid,⁴ and lithium perchlorate² were carried out as previously described. The iron(II) complexes, K₂Fe(bipy)(CN)₄ and Fe(bipy)₂(CN)₂, were prepared by the method of Schilt.⁵ Tris(2,2'-bipyridyl)iron(II) and -iron(III) perchlorates and their *o*-phenanthroline analogs were prepared by the method of Burstall and Nyholm.⁶

The kinetics of the reduction of VO₂⁺ by Fe(bipy)(CN)₄²⁻ and by Fe(bipy)₂(CN)₂ were determined at 10° and 0.50 *M* ionic strength with a Durrum stopped-flow spectrophotometer at 500 nm. Kinetic studies of the reactions of VO₂⁺ with Fe(bipy)₃²⁺ and of VO₂⁺ with Fe(bipy)₃²⁺ were carried out at 25° and 0.50 *M* ionic strength using a Cary 14 recording spectrophotometer at 522 nm with previously described techniques.² At least a ten-

fold excess of one reagent was maintained to ensure pseudo-first-order conditions. Data were treated by the Guggenheim method.⁷ Constant ionic strength was maintained by addition of LiClO₄.

Preliminary studies on the Fe(bipy)₃²⁺ + VO₂⁺ reaction were carried out using a stock solution of Fe(III) in 0.50 *M* HClO₄. Even though the solution was stored in an ice bath, there was apparently sufficient decomposition to cause complications. The observed pseudo-first-order rate constant consisted of a sum of terms—one first order in [VO₂⁺], one first order in [VO₂⁺], and one independent of both species. This behavior could not be reproduced quantitatively in series of experiments carried out on different days or with different Fe(III) stock solutions, so Fe(III) was added as a solid to thermostated solutions containing all species but VO₂⁺. Reaction was initiated by addition of VO₂⁺ when dissolution of Fe(III) was complete. The initial concentration of Fe(III) was estimated from the absorbance increase during the reaction.

Results

The reaction of VO₂⁺ with Fe(bipy)(CN)₄²⁻ and Fe(bipy)₂(CN)₂ proceeds by a two-step mechanism involving the production and decomposition⁸ of a binuclear intermediate. On the basis of the results of a study of the reaction of VO₂⁺ with Fe(CN)₆⁴⁻⁴ and spectral and kinetic studies of the above reactions,⁸ the intermediates are thought to be V(IV)-Fe(III) complexes which decompose to produce VO₂⁺ and Fe(bipy)(CN)₄²⁻ or Fe(bipy)₂(CN)₂⁺. The first step in this sequence, which is to be described here, is thus considered to be an oxidation-reduction reaction. Only a limited study of these reactions could be carried out because of the relatively small range of concentrations and temperatures in which a good separation of the two reaction steps could be obtained. Since these reactions were very fast, an upper limit was set on the concentration range by the rates which could be observed with the stopped-flow apparatus.

Reaction of VO₂⁺ with Fe(bipy)(CN)₄²⁻.—The kinetics of the reduction of VO₂⁺ by Fe(bipy)(CN)₄²⁻ were determined at 10° and 0.50 *M* ionic strength over the concentration ranges indicated in Table I. Although there may be some systematic variation in the data, results were independent of which reactant was in excess, of [H⁺], and of added [VO₂⁺]. It is possible that the rate law could be more complex, but we feel that the precision of the data does not warrant more than a simple mixed-second-order rate law

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

(1) (a) Taken in part from the M.S. thesis of S. V. W. (b) National Science Foundation Trainee, 1969-1970.

(2) J. P. Birk, *J. Amer. Chem. Soc.*, **91**, 3189 (1969).

(3) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

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(5) A. A. Schilt, *J. Amer. Chem. Soc.*, **82**, 3000 (1960).

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TABLE I
RATE CONSTANTS FOR THE REDUCTION OF VO_2^+ BY
 $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$ AND BY $\text{Fe}(\text{bipy})_2(\text{CN})_2$ AT
 10° AND $0.50 M$ IONIC STRENGTH

$10^5[\text{Fe}(\text{II})]_0$	$10^5[\text{VO}_2^+]_0$	$10^4[\text{VO}_2^+]_0$	$10^2[\text{H}^+]_0$	$10^{-6}k_{\text{ox}}, M^{-1}$ sec^{-1}^a
$\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$				
0.484	4.96	...	1.50	2.9 ± 0.1
0.484	4.96	5.13	1.50	2.9 ± 0.1
4.98	0.496	...	1.51	2.9 ± 0.1
0.968	9.93	...	1.49	2.9 ± 0.2
10.0	0.993	...	1.51	2.6 ± 0.1
2.00	19.9	...	1.48	2.1 ± 0.1
2.00	19.9	...	3.74	2.1 ± 0.1
2.00	19.9	...	7.50	2.0 ± 0.2
2.00	19.9	...	10.0	2.0 ± 0.1
20.0	1.99	...	1.52	2.0 ± 0.1
4.98	49.6	...	1.50	2.3 ± 0.6
49.8	4.96	...	1.50	2.3 ± 0.4
$\text{Av} = 2.4 \pm 0.3$				
$\text{Fe}(\text{bipy})_2(\text{CN})_2$				
0.99	9.93	...	1.50	0.85 ± 0.03
2.00	19.9	...	1.48	0.85 ± 0.10
2.00	19.9	...	7.50	0.81 ± 0.04
2.00	19.9	5.13	1.48	0.83 ± 0.04
4.99	49.6	...	1.50	0.82 ± 0.05
$\text{Av} = 0.83 \pm 0.02$				

^a Uncertainties are average deviations for three to six determinations at the same concentrations.

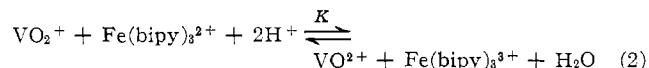
We attribute the variation in k_{ox} to experimental scatter since the maximum deviation from the average is barely outside one average deviation and since with half-lives in the range 0.6–5 msec, we are reluctant to place much reliance on the validity of a more complex rate law. The only reasonable alternate rate law would contain an additional term zero order in the excess reactant, which might in fact arise from some degradation of the absorbance trace by the electronic filtering circuit in the instrument at these high rates. A treatment of this sort would lower the value of k_{ox} slightly from $(2.4 \pm 0.3) \times 10^6$ to $2.2 \times 10^6 M^{-1} \text{sec}^{-1}$.

Reaction of VO_2^+ with $\text{Fe}(\text{bipy})_2(\text{CN})_2$.—The redox reaction of VO_2^+ with $\text{Fe}(\text{bipy})_2(\text{CN})_2$ was studied at 10° and $0.50 M$ ionic strength over the concentration ranges given in Table I. This reaction was somewhat slower than that of $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$, with half-lives in the range 2–8 msec. The data are nicely consistent with a simple second-order rate law (eq 1) with $k_{\text{ox}} = (8.3 \pm 0.2) \times 10^5 M^{-1} \text{sec}^{-1}$.

Reaction of VO_2^+ with $\text{Fe}(\text{bipy})_3^{3+}$.—Attempts to study the reaction of VO_2^+ with $\text{Fe}(\text{bipy})_3^{3+}$ were not successful due to aquation of $\text{Fe}(\text{II})$. The reaction was followed at 522 nm with $0\text{--}0.016 M \text{VO}_2^+$, $1.0 \times 10^{-4} M \text{Fe}(\text{II})$, $0.25 M \text{H}^+$, $0.50 M$ ionic strength, and, in one experiment, $0.0143 M \text{VO}_2^+$. The rate of the reaction was independent of added VO_2^+ or VO^{2+} . The measured first-order rate constant at 25° , $(3.75 \pm 0.06) \times 10^{-4} \text{sec}^{-1}$, is in reasonable agreement with previous determinations of the rate constant for aquation of $\text{Fe}(\text{bipy})_3^{3+}$ under similar conditions ($4.65 \times 10^{-4} \text{sec}^{-1}$ ⁹ or $3.84 \times 10^{-4} \text{sec}^{-1}$ ¹⁰). Thus it would appear that, throughout the concentration range, aquation of $\text{Fe}(\text{bipy})_3^{3+}$ proceeds more rapidly than oxidation by VO_2^+ . An upper limit on the rate constant can be set as $k_{\text{ox}} \leq 2.3 \times 10^{-2} M^{-1} \text{sec}^{-1}$.

An alternate approach to this reaction is suggested by its reversibility; using published oxidation poten-

tials,^{11–13} the equilibrium constant for reaction 2 is esti-



mated to be $K \lesssim 0.14 M^{-2}$. The value of K is subject to considerable uncertainty since the oxidation potentials for the two couples are nearly equal and any uncertainty in these potentials is greatly magnified in their difference. It is suspected that this number would be an upper limit on K because of the medium dependence of the V(IV)–V(V) couple.¹³ If K does indeed approach this upper limit, a study of the reaction between VO_2^+ and $\text{Fe}(\text{bipy})_3^{3+}$ under pseudo-first-order conditions should yield the rate constants for both the forward and the reverse reactions.

Reaction of VO_2^+ with $\text{Fe}(\text{bipy})_3^{3+}$.—The reaction between VO_2^+ and $\text{Fe}(\text{bipy})_3^{3+}$ was studied at 25.0° , $0.500 M$ ionic strength, and 522 nm over the initial concentration ranges 2.3×10^{-5} – $1.2 \times 10^{-4} M \text{Fe}(\text{bipy})_3^{3+}$, 3.8×10^{-3} – $5.8 \times 10^{-2} M \text{VO}_2^+$, 1.0×10^{-3} – $3.2 \times 10^{-2} M \text{VO}_2^+$, and 0.0147 – $0.474 M \text{H}^+$. The Guggenheim method⁷ was used to treat the data since aquation of $\text{Fe}(\text{bipy})_3^{3+}$ caused interference in the later portions of the reaction, especially in the slower reactions. Plots were generally linear for at least three half-lives. The observed pseudo-first-order rate constants, k_{obsd} , were independent of $[\text{VO}_2^+]$ throughout the range of $[\text{VO}_2^+]$. A typical set of experiments with $(2\text{--}7) \times 10^{-5} M \text{Fe}(\text{bipy})_3^{3+}$, $1.43 \times 10^{-2} M \text{VO}_2^+$, $0.258 M \text{H}^+$, and $10^2[\text{VO}_2^+]_0 = 0.10, 0.20, 0.40, 0.80, 1.60,$ and $3.20 M$ had values of $10^3 k_{\text{obsd}} = 3.55, 3.61, 3.48, 3.59, 3.63,$ and 3.33sec^{-1} , respectively. The values of k_{obsd} as a function of $[\text{VO}_2^+]$ at $0.258 M \text{H}^+$ are given in Table II. As demonstrated

TABLE II
DEPENDENCE OF OBSERVED RATE CONSTANTS ON
 $[\text{VO}_2^+]$ FOR THE REACTION OF VO_2^+ WITH
 $\text{Fe}(\text{bipy})_3^{3+}$ AT 25° AND $0.258 M \text{H}^+$

$10^2[\text{VO}_2^+]_0^a$	$10^3 k_{\text{obsd}}, \text{sec}^{-1}^b$	$k_{\text{obsd}}[\text{VO}_2^+]^{-1},$ $M^{-1} \text{sec}^{-1}$
0.380	1.30 ± 0.04 (7)	0.342
0.388	1.20 ± 0.09 (8)	0.310
0.760	2.29 ± 0.07 (7)	0.301
0.775	2.07 ± 0.11 (6)	0.267
1.43	3.53 ± 0.08 (6)	0.247
1.43	4.20 ± 0.06 (4)	0.294
1.45	3.78 ± 0.09 (5)	0.261
2.86	9.44 ± 0.69 (7)	0.330
2.91	7.74 ± 0.36 (7)	0.266
4.28	12.9 ± 0.4 (7)	0.303
5.70	18.0 ± 1.5 (7)	0.315
5.81	17.7 ± 1.1 (8)	0.304

$\text{Av} = 0.295 \pm 0.023$

^a $[\text{VO}_2^+]_0 \gg [\text{Fe}(\text{bipy})_3^{3+}]_0$. ^b Values are averages of a number (given in parentheses) of determinations at various $[\text{VO}_2^+]$.

by Figure 1, k_{obsd} has a simple first-order dependence on $[\text{VO}_2^+]$. Similar behavior was observed at other $[\text{H}^+]$. Average values of $k_{\text{obsd}}[\text{VO}_2^+]^{-1}$ determined over a range of $[\text{VO}_2^+]$ at various $[\text{H}^+]$ are given in Table III. A plot of $k_{\text{obsd}}[\text{VO}_2^+]^{-1}$ vs. $[\text{H}^+]^{-1}$, given in Figure 2, indicates the rate equation

$$k_{\text{obsd}}[\text{VO}_2^+]^{-1} = a + b[\text{H}^+]^{-1} \quad (3)$$

(11) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall Inc., New York, N. Y., 1952.

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TABLE III

VARIATION OF SECOND-ORDER RATE CONSTANTS WITH $[H^+]$ FOR THE REACTION OF VO_2^+ WITH $Fe(bipy)_3^{3+}$ AT 25°

$[H^+]$	$k_{\text{obsd}}[VO_2^+]^{-1}$, $M^{-1} \text{sec}^{-1}$	
	Obsd ^a	Calcd ^b
0.0147	3.70 ± 0.13 (5)	3.73
0.0286	2.11 ± 0.09 (5)	1.95
0.0294	2.04 ± 0.08 (4)	1.90
0.0495	1.09 ± 0.07 (5)	1.16
0.0588	0.93 ± 0.15 (3)	0.985
0.0982	0.66 ± 0.10 (6)	0.618
0.258	0.295 ± 0.023 (12)	0.280
0.328	0.219	0.235
0.336	0.236 ± 0.031 (3)	0.231
0.370	0.221	0.217
0.411	0.186	0.202
0.453	0.190	0.190
0.474	0.186	0.185

^a Values are averages for a number (given in parentheses) of determinations at different $[VO_2^+]$. ^b Calculated from eq 3 and the parameters given in the text.

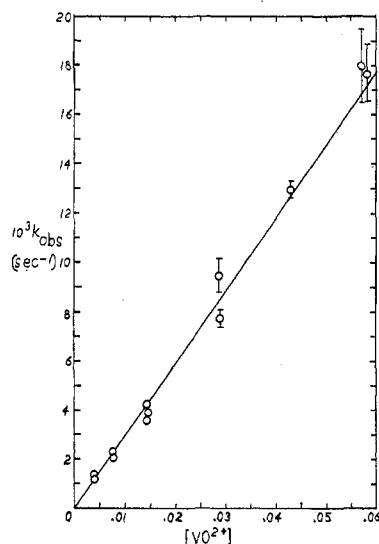


Figure 1.—Plot of k_{obsd} vs. $[VO_2^+]$ for the reaction of VO_2^+ with $Fe(bipy)_3^{3+}$ at $0.258 M H^+$.

Data were fit to this equation using a nonlinear least-squares computer program¹⁴ in which each data point was weighted as $(k_{\text{obsd}}[VO_2^+]^{-1})^{-2}$, giving the values $a = (7.15 \pm 0.86) \times 10^{-2} M^{-1} \text{sec}^{-1}$ and $b = (5.37 \pm 0.15) \times 10^{-2} \text{sec}^{-1}$, which reproduce the values of $k_{\text{obsd}}[VO_2^+]$ as shown in Table III.

Although the data are capable of several interpretations, since the stoichiometric equation (eq 2) is not unique, considering the principle of microscopic reversibility, the form of the rate equation for the reaction of VO_2^+ with $Fe(bipy)_3^{3+}$ can be used to predict a likely rate equation for the reaction between VO_2^+ and $Fe(bipy)_3^{2+}$

$$-d \ln [Fe(bipy)_3^{2+}] / dt = (c[H^+]^2 + d[H^+])[VO_2^+] \quad (4)$$

where $c = aK$ and $d = bK$. This is the most reasonable form of the rate law consistent with the principle of microscopic reversibility since all other forms would have greater than first-order dependences on both metal ions. Since K is not known with great certainty, values of c and d cannot be accurately predicted, but the use of the estimated value $K \leq 0.14 M^{-2}$ gives c

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

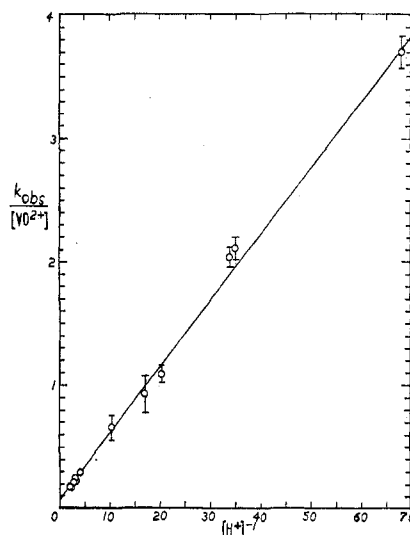


Figure 2.—Plot of $k_{\text{obsd}}[VO_2^+]^{-1}$ vs. $[H^+]^{-1}$ for the reaction of VO_2^+ with $Fe(bipy)_3^{3+}$, demonstrating the validity of eq 3.

$\approx 1.00 \times 10^{-2} M^{-3} \text{sec}^{-1}$ and $d \approx 7.5 \times 10^{-3} M^{-2} \text{sec}^{-1}$. This gives a lower limit on the rate constant for reduction of VO_2^+ by $Fe(bipy)_3^{3+}$ in $0.25 M H^+$ as $\geq 8.2 \times 10^{-3} M^{-1} \text{sec}^{-1}$ (and $\leq 2.3 \times 10^{-2} M^{-1} \text{sec}^{-1}$ from arguments above) and in $0.50 M H^+$ as $\geq 2.9 \times 10^{-2} M^{-1} \text{sec}^{-1}$.

Discussion

The reduction of vanadium(V) by $Fe(bipy)(CN)_4^{2-}$ and $Fe(bipy)_2(CN)_2^2$ follows a mechanism similar to that observed for the reaction with $Fe(CN)_6^{4-}$.⁴ The observation of a two-step reaction is interpreted in terms of an inner-sphere mechanism. These reactions are somewhat novel in that the bridging ligand must necessarily be donated by the reducing agent, since substitution on $Fe(II)$ would involve an unlikely seven-coordinate species. Although no data are available for the rate of substitution on $V(V)$, the rate of the redox reaction does not seem unreasonably high for a reaction involving such a substitution. Since the coordination number of vanadium in acidic aqueous solution is increased from four or five¹⁵⁻¹⁷ in $V(V)$ to six¹⁸ in $V(IV)$, expansion of the coordination sphere of $V(V)$ prior to the redox step does not seem energetically prohibitive.

Proven examples of inner-sphere reactions involving donation of the bridging ligand by the reducing agent are the reactions of chromium(VI) with $Fe(CN)_6^{4-}$, $Fe(bipy)(CN)_4^{2-}$, and $Fe(bipy)_2(CN)_2^2$.² Since the $Cr(III)$ products consisted entirely of $Cr(III)$ - $Fe(III)$ binuclear complexes and the reaction apparently occurred by three one-electron steps, at least the reduction of $Cr(IV)$ by these iron complexes must have been inner-sphere.

It was postulated² on the basis of rate comparisons suggested by the Marcus theory^{3,19} that the first step in these reactions, the reduction of $Cr(VI)$, also occurred by an inner-sphere process. The Marcus relation was applied to the $Ce(IV)$ oxidation of the above series of

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TABLE IV
RATE COMPARISONS FOR THE OXIDATION OF IRON(II) COMPLEXES

Complex	$M^{-1} \text{ sec}^{-1}$			$k_{\text{Ce}}/k_{\text{Cr}}$	$k_{\text{Ce}}/k_{\text{V}}$
	$10^{-6}k_{\text{Ce}}^a$	$10^{-4}k_{\text{Cr}}^b$	$10^{-6}k_{\text{V}}$		
$\text{Fe}(\text{CN})_6^{4-}$	1.90	2.20	1.2 ^c	86	1.6
$\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$	12.5	9.40	2.4 ^d	133	5.2
$\text{Fe}(\text{bipy})_2(\text{CN})_2$	8.4	6.21	0.83 ^d	135	10
$\text{Fe}(\text{bipy})_3^{2+}$	0.196	0.00151	$\geq 0.029 \times 10^{-6}$ ^e	1.43×10^4	$\leq 6.8 \times 10^6$

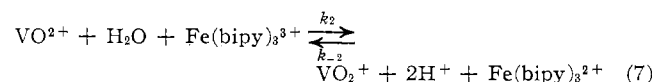
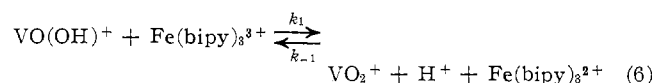
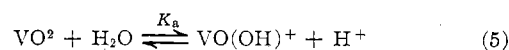
^a In 0.50 *M* H_2SO_4 at 25°; ref 20. ^b In 0.50 *M* HClO_4 at 25°; ref 2. ^c At 8°, 0.01–0.10 *M* HClO_4 , 0.50 *M* ionic strength; ref 4. ^d At 10°, 0.015–0.10 *M* HClO_4 , 0.50 *M* ionic strength; this work. ^e Value estimated for 25°, 0.50 *M* HClO_4 , 0.50 *M* ionic strength; this work.

$\text{Fe}(\text{II})$ complexes as well as $\text{Fe}(\text{bipy})_3^{2+}$ ²⁰ and was consistent with an outer-sphere path for these reactions. One of the predictions of the Marcus relation is that the relative rates of oxidation of a series of reducing agents by two oxidants should be independent of the identity of the reducing agent if the reactions are outer sphere. The failure of such a comparison for the reactions of the iron(II) complexes with Ce(IV) and Cr(VI) was interpreted as an indication that the Cr(VI) oxidation of the cyanoiron(II) complexes was inner sphere.²

Since the reduction of V(V) by the cyanoiron(II) complexes is known to be inner sphere, a similar comparison of relative reaction rates provides a test of the above conclusions. Table IV lists the rate constants and relative rate constants for the oxidation of Fe(II) by Ce(IV), Cr(VI), and V(V). Comparison of rate constants for Ce(IV) with Cr(VI) and for Ce(IV) with V(V) gives a rate constant ratio which is relatively constant in each case for the cyanoiron(II) complexes but which is significantly larger for $\text{Fe}(\text{bipy})_3^{2+}$. Since the Ce(IV) oxidations appear to proceed by outer-sphere mechanisms and since the reduction of V(V) is known to be inner sphere for the cyanoiron(II) complexes but is probably outer sphere for $\text{Fe}(\text{bipy})_3^{2+}$, the discrepancy in the rate constant ratio appears to arise from a change in mechanism. These results support the conclusions reached for the chromium(VI) oxidation of the Fe(II) complexes.² The direction of the discrepancy further supports these mechanistic conclusions. The small rate constant ratios for the cyanoiron(II) complexes indicate that the reactions of these complexes with Cr(VI) and V(V) are fast compared to the predicted outer-sphere rates. It is feasible for the reactions to proceed by inner-sphere mechanisms only if such mechanisms are energetically

more favorable. Hence the reactions must proceed at rates greater than those predicted by the Marcus theory.

The $[\text{H}^+]$ dependence of the reaction between VO^{2+} and $\text{Fe}(\text{bipy})_3^{3+}$ is consistent with a mechanism



where there could possibly be intermediates (*e.g.*, protonated forms of V(V)) formed as immediate products in reactions 6 and 7 and where K_a is small (1.0×10^{-6} – 4.4×10^{-8})²¹ and $a = k_2$, $b = k_1K_a$, $c = k_{-2}$, and $d = k_{-1}$. The results of this study are in qualitative agreement with the reactions with the analogous *o*-phenanthroline-iron complexes.^{13,22} At 25° in 0.33 *M* H_2SO_4 the rate constant for $\text{VO}^{2+} + \text{Fe}(\text{phen})_3^{3+}$ was 10.4 $M^{-1} \text{ sec}^{-1}$ (decreasing with increasing $[\text{H}_2\text{SO}_4]$) and for $\text{VO}_2^+ + \text{Fe}(\text{phen})_3^{2+}$ was 0.12 $M^{-1} \text{ sec}^{-1}$ (increasing with increasing $[\text{H}_2\text{SO}_4]$).¹³ A preliminary study²² of these reactions at 25° and 0.25 *M* H^+ in nitrate media of 0.50 *M* ionic strength yielded the rate constants $\sim 1.0 M^{-1} \text{ sec}^{-1}$ and $\sim 1.6 M^{-1} \text{ sec}^{-1}$ for the V(IV)–Fe(III) and V(V)–Fe(II) reactions, respectively.

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