

temperature probe. The solvents employed were of the best commercial grade available and were used without further purification.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum- π -allyl. To a suspension of 26.4 g (0.1 mole) of molybdenum hexacarbonyl in 200 ml of acetonitrile was added 15 ml (excess) of allyl bromide. The reaction mixture was stirred and heated until 10 l. of gas, as measured by a wet-test meter, was evolved. About 50 ml of liquid was then distilled out under nitrogen, and after the mixture was cooled, a suspension of 35 g (0.11 mole) of $\text{KHB}(3,5\text{-Me}_2\text{pz})_3$ was added. The reaction mixture was stirred at 45° for 20 min and was then drowned in 1.5 l. of cold water containing 10 ml of concentrated hydrochloric acid. The product was filtered off and obtained in 31.6 g (64.6%) yield after chromatography on alumina. It was purified further by recrystallization from toluene; the yellow crystals turn red on heating and gradually decompose from about 250°. This compound is reversibly thermochromic (yellow \rightleftharpoons red).

When previously isolated $(\text{MeCN})_2\text{Mo}(\text{CO})_2\text{-}\pi\text{-C}_3\text{H}_5$ was used in the above reaction, the yield rose to 70.4%.

Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{BMoN}_6\text{O}_2$: C, 49.0; H, 5.52; N, 17.1. Found: C, 49.0; H, 5.71; N, 17.1. Ir (cyclohexane): CO at 1944 and 1850 cm^{-1} . Uv (cyclohexane): 380 $\text{m}\mu$ (ϵ 1320); sh 260 (13,900); 218 (36,600). Nmr (CDCl_3): τ s 4.23, m \sim 5.9, d ($J = 7$ cps) 6.34; s, 7.15, s, 7.57, s 7.67, s 7.82, d ($J = 10$ cps) 8.07 in 3:1:2:3:6:6:3:2 ratio. These peaks were assigned,¹⁸ respectively, to the 4-H, π -allyl central H, *syn*-H's, 3-methyls (1 + 2), 5-methyls (2 + 1), and *anti*-H's.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum- π -2-phenylallyl. This compound was obtained as yellow crystals in 18% yield by the above procedure. After recrystallization from toluene-heptane mixture, it decomposed gradually from \sim 240°.

(18) The assignment of the 3-Me and 5-Me rests on (a) greater difference in chemical shifts expected for the nonidentical 3-methyls than for 5-methyls and (b) faster collapse of the 5-methyls than for the 3-methyls as observed in the limiting high-temperature spectrum for $\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{Mo}(\text{CO})_2\text{-}\pi\text{-CH}_2\text{CMeCH}_2$ and partially collapsed high-temperature spectra of the π -allyl and $\pi\text{-CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2$ analogs.

Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{BMoN}_6\text{O}_2$: C, 55.1; H, 5.48; N, 14.8. Found: C, 55.1; H, 5.97; N, 14.8. Ir (cyclohexane) CO at 1947, 1861 cm^{-1} . Nmr (CDCl_3): τ m 3.1–3.5, s 4.31, s 4.38, s 5.95, s, 7.15, s 7.43, s 7.90, s 8.03, s 8.46 in 5:2:1:2:3:6:6:3:2 ratio assigned, respectively, to phenyl, 4-H's (2 + 1), 3-Me (1 + 2), 5-Me (2 + 1), and *anti*-H's.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratedicarbonylmolybdenum- π -2-methylallyl. This compound was obtained as yellow crystals in 23% yield by the above procedure. After recrystallization from toluene it melts at 264–266° dec when placed in the apparatus at 250°. When heated gradually from room temperature, it slowly decomposes from 255°.

Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{BMoN}_6\text{O}_2$: C, 50.0; H, 5.75; N, 16.7. Found: C, 50.5; H, 5.68; N, 16.7. Ir (cyclohexane): 1945, 1853 cm^{-1} . Nmr (CDCl_3): singlets at τ 4.17, 4.28, 6.51, 7.13, 7.44, 7.65, 7.89, 8.50, and 8.75 in 2:1:2:3:6:6:3:2:3 ratio assigned, respectively, to 4-H (2 + 1), *syn*-H's, 3-Me (1 + 2), 5-Me (2 + 1), *anti*-H's, and 2-Me.

Hydrotris(4-bromo-1-pyrazolyl)boratedicarbonylmolybdenum- π -allyl. This compound was obtained as yellow crystals in 36% overall yield by the three-step sequence published earlier.⁶ It was recrystallized from toluene; decomposes gradually from 260°.

Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{BBr}_3\text{MoN}_6\text{O}_2$: C, 26.1; H, 1.87; Br, 37.3; N, 13.15. Found: C, 26.7; H, 2.00; Br, 37.3; N, 13.1. Ir (cyclohexane): 1964, 1883 cm^{-1} . Nmr (CDCl_3): broad (\sim 30 cps) hump $\tau \sim$ 1.8, s 2.24, m with sharp peak at 6.22, d ($J = 9.0$ cps) 8.30 in 3:3:3:2 ratio, assigned to 3-H's, 5-H's, central π -allyl H, *syn*-H's, and *anti*-H's.

Hydrotris(4-bromo-1-pyrazolyl)boratedicarbonylmolybdenum- π -2-methylallyl. This compound was prepared by the above procedure and was obtained as yellow crystals in 36% yield. It was recrystallized from toluene, mp 242–244°.

Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{BBr}_3\text{MoN}_6\text{O}_2$: C, 27.4; H, 2.13; N, 12.8. Found: C, 27.8; H, 2.19; N, 12.7. Ir (cyclohexane): 1965, 1884 cm^{-1} . Nmr (CDCl_3): singlets at τ 1.68, 2.21, 6.34, 8.22, and 8.34 in 3:3:2:3:2 assigned to 3-H's, 5-H's, *syn*-H's, methyl, and *anti*-H's.

Kinetics and Mechanisms of the Reduction of Chromium(VI) by Substitution-Inert Iron(II) Complexes in Acidic Aqueous Solution

James P. Birk

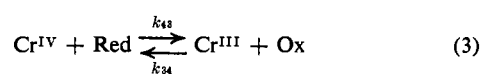
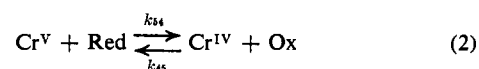
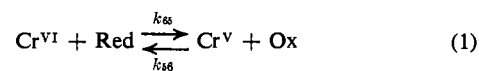
Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received November 25, 1968

Abstract: The kinetics of the reaction of chromium(VI) with $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ (bip = 2,2'-bipyridine), $\text{Fe}(\text{bip})_2(\text{CN})_2$, and $\text{Fe}(\text{bip})_3^{2+}$ have been examined over wide ranges of initial concentrations at 25.0° in perchlorate solutions of 0.50 *M* ionic strength. Each reaction follows the rate equation, $-\text{d}[\text{HCrO}_4^-]/\text{dt} = k_2[\text{HCrO}_4^-][\text{Fe}(\text{II})]$, where k_2 is a complex function of $[\text{H}^+]$. A major product of the reactions of the cyanoiron(II) complexes is in each case apparently a Cr(III)–Fe(III) binuclear complex. A comparison of these results with those of previous studies on related systems indicates that the form of the rate equation can be correlated quite well with the relative substitution-inertness of one-equivalent reducing agents.

The reduction of chromium(VI) by one-equivalent reducing agents and oxidation of chromium(III) by one-equivalent oxidizing agents has been interpreted in terms of three successive one-electron transfer steps.^{1–5}

For most such reactions studied (oxidation of Cr(III)

(1) J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).



by Ce(IV)¹ and reduction of Cr(VI) by Cr(III),² Fe²⁺,³ VO²⁺,⁴ and NpO₂⁺,⁵), the conversion of Cr(V) to Cr(IV) or the reverse has been rate determining. This is generally attributed to a rate-determining change in coordination number from four in Cr(V) to six in Cr(IV).¹ Assuming a steady-state concentration for Cr(V) in the reduction of Cr(VI), the rate equation is given by

$$-d[\text{HCrO}_4^-]/dt = k_{65}k_{54}[\text{Cr(VI)}][\text{Red}]^2 / (k_{54}[\text{Red}] + k_{56}[\text{Ox}]) \quad (4)$$

Although the complete form of this rate equation was observed for Red = NpO₂⁺, for the other systems studied (Red = Fe²⁺, VO²⁺), the limiting form with $k_{56}[\text{Ox}] \gg k_{54}[\text{Red}]$ (or the analogous form for the oxidation of Cr(III) by Ce(IV)) was observed. The other limiting form with $k_{54}[\text{Red}] \gg k_{56}[\text{Ox}]$ has been observed only as one of two terms in the rate equation for the reduction by Fe(phen)₃²⁺ (phen = 1,10-phenanthroline).³ The most obvious difference between Fe(phen)₃²⁺ and the other ions studied is the rate of substitution in the first coordination sphere. The possibility arises that the form of the rate equation may provide an indirect criterion to distinguish between inner-sphere and outer-sphere reductions of chromium(VI). This paper, which describes the results of a kinetic study of the reduction of Cr(VI) by Fe(CN)₆⁴⁻, Fe(bip)(CN)₄²⁻ (bip = 2,2'-bipyridine), Fe(bip)₂(CN)₂, and Fe(bip)₃²⁺, initiates an attempt to elucidate more fully the factors which give rise to a change in the form of the rate equation, *i.e.*, in the identity of the rate-determining step.

Experimental Section

Materials. AR grade potassium dichromate, sodium dichromate, potassium ferrocyanide, and potassium ferricyanide were recrystallized three times from distilled water. Chromium(VI) solutions were analyzed by measurement of the chromate absorbance at 372 mμ.⁶ Solutions of ferrocyanide and ferricyanide were prepared by weight and were used within 1 hr after preparation. Ferrocyanide solutions were freed of potassium ion for many of the experiments by passage through a column of Amberlite IR-120 cation-exchange resin in the H⁺ form, followed by quantitative washing and appropriate dilution.

Potassium tetracyano(2,2'-bipyridine)iron(II), hydrogen tetracyano(2,2'-bipyridine)iron(III), dicyanobis(2,2'-bipyridine)iron(II), and dicyanobis(2,2'-bipyridine)iron(III) perchlorate were prepared and purified according to the method of Schilt.⁷ Solutions of these complexes were prepared by weight, and the concentrations were checked by spectral measurements, which were in agreement with those of Schilt⁷ and of George, Hanania, and Irvine.⁸

Tris(2,2'-bipyridine)iron(II) and -iron(III) perchlorates were prepared by the method of Burstall and Nyholm.⁹ Concentrations of solutions of the iron(II) complex were determined from the absorbance at 522 mμ, where the extinction coefficient is 8650 M⁻¹ cm⁻¹.¹⁰

Lithium and sodium perchlorates were prepared by reaction of the corresponding carbonates with perchloric acid. The products were recrystallized two or three times from distilled water. Solutions were analyzed by titration of the acid released when an aliquot was

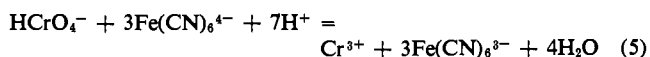
passed through a column of cation-exchange resin in the H⁺ form. Perchloric acid solutions were dilutions of Baker Analyzed 70% HClO₄, which was not further purified. All other materials were of the best available grade. All solutions were prepared with distilled water.

Kinetics Experiments. The kinetics of the reduction reactions were determined with a Durrum stopped-flow spectrophotometer (5 msec ≤ *t*_{1/2} ≤ 30 sec) or a Cary 14 recording spectrophotometer (*t*_{1/2} ≥ 5 sec) at 25.0° and 0.50 *M* ionic strength. Iron(II) solutions were prepared just prior to use with thermally equilibrated components and were shielded from light at all times. Constant temperature was maintained during slow reactions followed with the Cary 14 by circulating constant-temperature water through coils surrounding the spectrophotometer cell holder (Applied Physics Part No. 1444100). The cell holder, which was rendered water tight and had a quartz plate fastened over each end window, was filled with water so that the reaction vessel was immersed in a small constant-temperature water bath. Conventional syringe techniques were used to initiate the slow reactions.

Product Analysis. Slow passage of a dilute solution of the products of the HCrO₄⁻-Fe(CN)₆⁴⁻ reaction through long columns of Dowex 50W-X8 and 1-X8 cation and anion resins yielded a pale yellow solution of a presumably uncharged complex which contained chromium, iron, and cyanide. Chromium was oxidized to chromium(VI) by potassium persulfate using silver nitrate as a catalyst. After boiling to destroy excess persulfate, chromium(VI) was determined spectrophotometrically by the diphenylcarbazide method.¹¹ Iron was converted to aquoiron(III) by evaporating to fumes with perchloric acid. Dilution and evaporation to fumes was repeated several times to remove the chloride ion eluted from the anion-exchange resin. Methanol was added to reduce any chromium(VI) formed, and the absorbance was measured at 240 mμ (ε 4220 M⁻¹ cm⁻¹).¹² Cyanide was determined by a slight modification of the method of Colman^{13,14} developed to determine the cyanide content of ferrocyanide solutions. This procedure consists of destroying the complex, distilling HCN into a sodium hydroxide solution, and titrating cyanide with silver nitrate to a potassium iodide end point.

Results

Stoichiometry and Products. Rube,¹⁵ using aquoiron(III) solution as an external indicator, and Burriel and Sierra,^{16,17} using benzidine acetate indicator, have used ferrocyanide to titrate acidic solutions of chromium(VI). Excellent analytical results indicated the stoichiometry



Ion-exchange separation of the products, yielding an uncharged complex, casts doubt on the identification of the Cr(III) product as Cr(H₂O)₆³⁺, but is consistent with a complex containing ferricyanide, Cr(H₂O)₅(NC)Fe(CN)₅. Solutions of the complex showed negative tests for ferrocyanide (addition of Fe³⁺), ferricyanide (addition of Fe²⁺), and chromium(VI) (addition of *s*-diphenylcarbazide). The visible spectrum has an intense absorption maximum at 340 mμ (ε ≈ 3.5–4.0 × 10³ M⁻¹ cm⁻¹) and a relatively weak maximum at *ca.* 550 mμ (ε ~50). This is different from the spectra of Fe(CN)₆³⁻ (303 mμ (ε 1770), 322 (1470), 420 (1050)), Fe(CN)₆⁴⁻ (320 mμ (ε 340), 420 (sh, ε ~5); spectrum is acid dependent), and Cr³⁺ (408 mμ (ε 16), 575 (13)).

Analyses of several samples of the complex yielded the results: Cr/Fe = 1.0 ± 0.2 and CN⁻/Fe = 5.4 ±

(2) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

(3) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963).

(4) J. H. Espenson, *ibid.*, **86**, 5101 (1964).

(5) J. C. Sullivan, *ibid.*, **87**, 1495 (1965).

(6) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(7) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(8) P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

(9) F. H. Burstall and R. S. Nyholm, *J. Am. Chem. Soc.*, 3570 (1952).

(10) M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942).

(11) G. P. Rowland, Jr., *ibid.*, **11**, 442 (1939).

(12) R. Bastion, R. Weberling, and F. Pallila, *Anal. Chem.*, **28**, 459 (1956).

(13) H. G. Colman, *Analyst*, **33**, 267 (1908).

(14) H. G. Colman, *ibid.*, **35**, 295 (1910).

(15) C. Rube, *J. Prakt. Chem.*, **95**, 53 (1865).

(16) F. Burriel and F. Sierra, *Anales Soc. Espan. Fis. Quim.*, **32**, 87 (1934).

(17) F. Sierra and F. Burriel, *ibid.*, **30**, 441 (1932).

0.2. Because of the rather small volumes of AgNO_3 used in the CN^- analysis, the accuracy of this analysis is probably less than the indicated precision. The identity of the uncharged complex is further confirmed by an experiment in which excess ferrocyanide was allowed to react with an acidic $2.01 \times 10^{-3} M \text{HCrO}_4^-$ solution. Excess iodine was added, producing iodine by reaction with ferricyanide.¹⁸ Iodine was titrated with potassium thiosulfate solution. The analysis indicated that the reaction products contained $3.87 \times 10^{-3} M \text{Fe}(\text{CN})_6^{3-}$ (i.e., 1.93 $\text{Fe}(\text{CN})_6^{3-}$ per $\text{Cr}(\text{VI})$ reduced), so that one $\text{Fe}(\text{CN})_6^{3-}$ must have been converted to a form which is incapable of oxidizing iodide ion. This is consistent with the formation of a 1:1 $\text{Cr}(\text{III})\text{-Fe}(\text{III})$ complex.

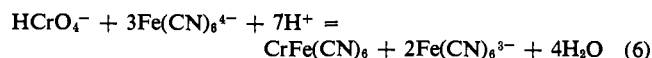
The stoichiometry was further checked by potentiometric and spectrophotometric titrations. Results of several potentiometric titrations established the mole ratio of $\text{Fe}(\text{CN})_6^{4-}$ reacting per HCrO_4^- as 3.1 ± 0.2 . Results of spectrophotometric titrations, which are more precise, are given in Table I. These titrations consisted of the addition of various amounts of one reagent ($\text{Fe}(\text{II})$ or $\text{Cr}(\text{VI})$) to a constant amount of the other reagent and acid, dilution to constant volume, and measurement of the absorbance at the indicated wavelength. Plots of absorbance *vs.* concentration of the added reagent showed sharp breaks at all wavelengths at concentrations corresponding to a stoichiometric ratio of 3.0 $\text{Fe}(\text{II})$ per $\text{Cr}(\text{VI})$. At wavelengths shorter than 400 $m\mu$, a second, less distinct break occurred at a ratio of about 3.7. These results were independent of purging with N_2 or O_2 , of the length of time (in the range 5–30 min) between mixing and spectral measurement, and of the identity and small variations in concentration of the reagent present in constant initial concentration.

Table I. Spectrophotometric Titrations of HCrO_4^- and $\text{Fe}(\text{CN})_6^{4-}$

$[\text{H}^+], M$	$\lambda, m\mu$	$[\text{Fe}(\text{II})]/[\text{Cr}(\text{VI})]^a$
4.69×10^{-3}	350	2.97, 3.6
1.54×10^{-2}	350	$2.93 \pm 0.04, 3.7 \pm 0.1$
9.89×10^{-2}	450–310 ^b	2.97 ± 0.04
9.89×10^{-2}	400–300 ^b	3.7 ± 0.1

^a Determined from the concentrations at which a break occurs in a plot of absorbance *vs.* concentration of added reagent. ^b Determinations were made at 10- $m\mu$ intervals within this range, using the same solutions.

Although the stoichiometry with respect to H^+ was not checked, all the above results are consistent with the equation

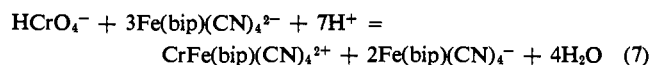


The source of the break in the spectrophotometric titration plots at the nonstoichiometric ratio of 3.7 Fe/Cr is not known. Data were generally taken to a ratio of 10–15, so it is possible that this end point actually occurs at a ratio of 4.0, but appears to occur at a lower ratio since extrapolation of a straight line from data at higher ratios may be inaccurate. This would indicate an interaction such as ion-pair formation between ferrocyanide and a

product of the oxidation–reduction reaction. This interaction would not be complete at a 1:1 ratio of $\text{Fe}(\text{CN})_6^{4-}$ to reaction product, causing curvature rather than a sharp break in the titration plot.

The stoichiometry of the reduction of HCrO_4^- by $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ was determined by a spectrophotometric titration. Over the wavelength range 340–560 $m\mu$, plots of absorbance at a given wavelength *vs.* the ratio $[\text{Fe}(\text{II})]/[\text{Cr}(\text{VI})]$ showed sharp breaks at a ratio of 3.08 ± 0.05 . A second, much less distinct break occurred at a ratio of 3.7 ± 0.2 in the wavelength range 440–580 $m\mu$.

Ion-exchange separation of the products of this reaction indicated the formation of a positively charged complex, not $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. A yellow band remained on a column of Dowex 50W-X8 and could be eluted fairly readily with 1.0 $M \text{NaClO}_4$, indicating a probable charge of +2, consistent with the formulation $\text{Cr}(\text{H}_2\text{O})_5\text{Fe}(\text{bip})(\text{CN})_4^{2+}$. The spectrum of this complex had absorption maxima at $\sim 420 m\mu$ ($\epsilon \sim 1500 M^{-1} \text{cm}^{-1}$), 340 (sh, $\epsilon \sim 3000$), and 307 ($\epsilon \sim 4000$). An elemental analysis of the complex was not attempted. Assuming the above formulation for the positively charged product, the spectrum of the products could be adequately accounted for by the stoichiometry



A spectrophotometric titration of HCrO_4^- with $\text{Fe}(\text{bip})_2(\text{CN})_2$ yielded plots of absorbance at constant wavelength *vs.* $[\text{Fe}(\text{II})]/[\text{Cr}(\text{VI})]$ which showed sharp breaks at a ratio of 3.05 ± 0.05 throughout the wavelength range 340–560 $m\mu$. At higher ratios the plots were curved slightly, but the position of a second end point could not be distinguished.

When $\text{Fe}(\text{bip})_2(\text{CN})_2$ was allowed to react with excess acidic 0.02 $M \text{Cr}(\text{VI})$, a brown precipitate, whose aqueous solution spectrum was identical with that of $\text{Fe}(\text{bip})_2(\text{CN})_2^+$, was formed. On passage of the solution through a column of Dowex 50W-X8 cation-exchange resin, a tight reddish brown band remained. Extensive elution with 1.0 $M \text{HClO}_4$ caused no change in the position or length of the band. Although 2.0 $M \text{HClO}_4$ did not move the band, it did very slowly elute a yellow complex which was spectrally similar to $\text{Fe}(\text{bip})_2(\text{CN})_2^+$. Since it is unlikely that this univalent ion would be so difficult to displace from the resin, the reddish brown band probably consists of $\text{Cr}(\text{H}_2\text{O})_5\text{Fe}(\text{bip})_2(\text{CN})_2^{4+}$ which is slowly hydrolyzed. The stoichiometry thus appears analogous to those given above (eq 6 and 7).

The stoichiometry and products of the reaction with $\text{Fe}(\text{bip})_3^{2+}$ were not checked, but are presumably analogous to those determined for $\text{Fe}(\text{phen})_3^{2+}$.³ The complication arises here, however, particularly at high $[\text{H}^+]$, that aquation of $\text{Fe}(\text{bip})_3^{2+}$ proceeds at a rate comparable to the oxidation by HCrO_4^- . Also, at low $[\text{H}^+]$, the product $\text{Fe}(\text{bip})_3^{3+}$ slowly oxidizes water, giving back reactant $\text{Fe}(\text{bip})_3^{2+}$.

Kinetics of the HCrO_4^- – $\text{Fe}(\text{CN})_6^{4-}$ Reaction. The kinetics of the reaction between HCrO_4^- and $\text{Fe}(\text{CN})_6^{4-}$ were studied at 25.0° and 0.50 M ionic strength maintained with LiClO_4 , with $\text{Fe}(\text{II})$ in excess, over the following concentration ranges: 1×10^{-6} – $4 \times 10^{-5} M \text{Cr}(\text{VI})$, 2×10^{-5} – $2 \times 10^{-3} M \text{Fe}(\text{CN})_6^{4-}$, 0–2 \times

(18) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957, p 344.

Table II. Rate Constants for the Reaction of HCrO_4^- with $\text{Fe}(\text{CN})_6^{4-}$ at $9.95 \times 10^{-3} M \text{H}^+$

$[\text{HCrO}_4^-]_0, M$	$[\text{Fe}(\text{CN})_6^{4-}]_0, M$	$[\text{Fe}(\text{CN})_6^{3-}]_0, M$	$k_{\text{obsd}},^b \text{sec}^{-1}$	$10^{-3}k_2,^c M^{-1} \text{sec}^{-1}$
9.58×10^{-7}	2.07×10^{-5}	...	0.123 ± 0.012	5.94
1.92×10^{-6}	5.25×10^{-5}	...	0.273 ± 0.004	5.20
3.83×10^{-6}	1.04×10^{-4}	...	0.603 ± 0.003	5.83
7.66×10^{-6}	2.07×10^{-4}	...	1.19 ± 0.01	5.75
1.92×10^{-5}	5.25×10^{-4}	...	2.86 ± 0.05	5.45
1.92×10^{-5}	5.25×10^{-4}	5.14×10^{-4}	2.90 ± 0.07	5.52
1.92×10^{-5}	5.25×10^{-4}	1.03×10^{-3}	2.93 ± 0.04	5.58
1.92×10^{-5}	5.25×10^{-4}	2.05×10^{-3}	2.85 ± 0.03	5.43
2.87×10^{-5}	1.05×10^{-3}	...	6.29 ± 0.04	5.97
3.83×10^{-5}	2.07×10^{-3}	...	11.1 ± 0.1	5.38
				5.61 \pm 0.22
$8.44 \times 10^{-4} d$	1.05×10^{-4}	...	33.4 ± 1.6	13.2
$8.44 \times 10^{-4} d$	1.06×10^{-4}	...	71 ± 11	28
$4.47 \times 10^{-4} d$	5.24×10^{-5}	...	14.9 ± 1.0	11.1
$1.86 \times 10^{-4} d$	2.10×10^{-5}	...	5.26 ± 0.22	9.5
$9.44 \times 10^{-5} d$	1.05×10^{-5}	...	1.82	6.5
$4.75 \times 10^{-5} d$	5.24×10^{-6}	...	0.98 ± 0.14	6.85

^a Total initial $\text{Fe}(\text{CN})_6^{4-}$ concentration ($[\text{Fe}(\text{CN})_6^{4-}] + [\text{HFe}(\text{CN})_6^{3-}] + \dots$). ^b Average of four or five experiments on the same solution. Uncertainties given are average deviations. ^c $k_2 = k_{\text{obsd}}/[\text{Fe}(\text{CN})_6^{4-}]_0$ when $[\text{Fe}(\text{II})] > [\text{Cr}(\text{VI})]$; $k_2 = k_{\text{obsd}}/3[\text{HCrO}_4^-]$ when $[\text{Cr}(\text{VI})] > [\text{Fe}(\text{II})]$. ^d Concentration of $\text{Cr}(\text{VI})$ was corrected for formation of $\text{Cr}_2\text{O}_7^{2-}$, using eq 10.

$10^{-3} M \text{Fe}(\text{CN})_6^{3-}$, and 5×10^{-4} – $0.5 M \text{H}^+$. Low concentrations of K^+ (from $\text{K}_4\text{Fe}(\text{CN})_6$) were found to have no effect, but most of the experiments were carried out in the complete absence of K^+ . For most of the experiments the concentration conditions $[\text{H}^+]_0 \geq 10[\text{Fe}(\text{II})]_0$ and $[\text{Fe}(\text{II})]_0 \geq 25[\text{Cr}(\text{VI})]_0$ were observed. This was sufficient to ensure excellent linearity ($\geq 95\%$ of reaction in most cases) of plots of $\ln(D_t - D_\infty)$ vs. time where D is absorbance at the indicated time.

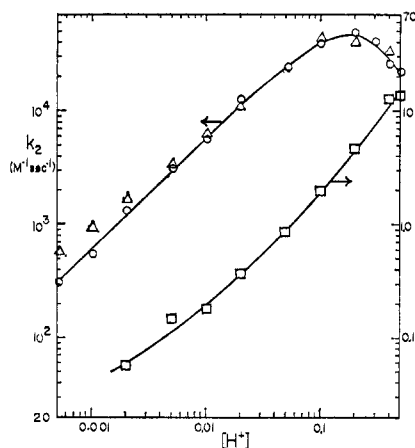


Figure 1. Plots of k_2 vs. $[\text{H}^+]$ on a log-log scale: \circ , $\text{Fe}(\text{CN})_6^{4-}$ in Li^+ media (line calculated from eq 9); Δ , $\text{Fe}(\text{CN})_6^{4-}$ in Na^+ media; \square , $\text{Fe}(\text{bip})_3^{2+}$ (line calculated from eq 15).

Four or five repetitive measurements were always made on each reaction mixture, giving pseudo-first-order rate constants ($k_{\text{obsd}} = -d \ln [\text{HCrO}_4^-]/dt$) reproducible to $\pm 2\%$. Although most experiments were carried out at $380 m\mu$, the results were independent of wavelength throughout the range 350 – $450 m\mu$. Data at $9.95 \times 10^{-3} M \text{H}^+$, which incorporate the greatest variations in $[\text{HCrO}_4^-]_0$, $[\text{Fe}(\text{CN})_6^{4-}]_0$, and $[\text{Fe}(\text{CN})_6^{3-}]_0$, are presented in Table II. These data indicate a first-order dependence on $[\text{Fe}(\text{CN})_6^{4-}]$ and zero-order dependence on $[\text{Fe}(\text{CN})_6^{3-}]$

$$-d[\text{HCrO}_4^-]/dt = k_2[\text{HCrO}_4^-][\text{Fe}(\text{II})] \quad (8)$$

where $[\text{Fe}(\text{II})] = [\text{Fe}(\text{CN})_6^{4-}] + [\text{HFe}(\text{CN})_6^{3-}] + \dots$

A previous study of the kinetics of this reaction, using the so-called "jet method" with conductometric detection, was carried out in H_2SO_4 solutions by Stefanovskii.¹⁹ The results of this study were not sufficiently precise to unambiguously distinguish between a first- or second-order dependence on $[\text{Fe}(\text{CN})_6^{4-}]$, although Stefanovskii concluded that the dependence was first order. An inhibiting effect by $\text{Fe}(\text{CN})_6^{3-}$ was claimed, in direct contrast to the observations made here.

The variation in k_2 with $[\text{H}^+]$ is depicted in Figure 1. The decrease in the apparent order in $[\text{H}^+]$ with increasing $[\text{H}^+]$ can be accommodated by an equation of the form

$$k_2 = a[\text{H}^+]/(b + c[\text{H}^+] + d[\text{H}^+]^2 + [\text{H}^+]^3) \quad (9)$$

Values of the rate parameters were determined with a nonlinear least-squares computer program:²⁰ $a = (6.3 \pm 2.4) \times 10^3 M \text{sec}^{-1}$, $b = (1.04 \pm 0.42) \times 10^{-2} M^3$, $c = (4.4 \pm 1.5) \times 10^{-2} M^2$, and $d = -0.021 \pm 0.199 M$. These parameters reproduce the values of k_2 with an average deviation of 6.0% .

The reaction was also studied at $9.95 \times 10^{-3} M \text{H}^+$ with $[\text{HCrO}_4^-] > [\text{Fe}(\text{CN})_6^{4-}]$ in LiClO_4 media. Values of the rate constants are listed in the bottom section of Table II. The concentrations of HCrO_4^- listed are lower than the total $\text{Cr}(\text{VI})$ concentrations and were obtained from the relation²¹

$$K_d = [\text{Cr}_2\text{O}_7^{2-}]/[\text{HCrO}_4^-]^2 = 80 M^{-1} \quad (10)$$

Absorbance behavior in these experiments did not follow simple pseudo-first-order kinetics, but consisted of three subsequent and increasingly slower absorbance changes. The first was a decrease in absorbance at the same rate as observed when a $\text{Cr}(\text{VI})$ solution of the same concentration was mixed with $9.95 \times 10^{-3} M \text{H}^+$, $0.410 M \text{Li}^+$. The second change was an

(19) V. F. Stefanovskii, *Zh. Obshch. Khim.*, **11**, 963 (1941).

(20) The programs used are based on the reports from Los Alamos Scientific Laboratory, LASL-2367 + addenda, and were modified to operate on the IBM 360/65 computer.

(21) J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

Table III. Rate Constants for the Reaction of HCrO_4^- with $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ at $9.95 \times 10^{-3} M \text{H}^+$

$[\text{HCrO}_4^-]_0, M$	$[\text{Fe}(\text{bip})(\text{CN})_4^{2-}]_0, M$	$[\text{Fe}(\text{bip})(\text{CN})_4^-]_0, M$	$k_{\text{obsd}},^b \text{sec}^{-1}$	$10^{-3}k_2,^c M^{-1} \text{sec}^{-1}$
9.58×10^{-7}	2.01×10^{-5}	...	0.0917 ± 0.0122	4.55
1.92×10^{-6}	5.03×10^{-5}	...	0.242 ± 0.016	4.81
3.83×10^{-6}	1.01×10^{-4}	...	0.430 ± 0.016	4.27
7.66×10^{-6}	1.24×10^{-4}	...	0.533 ± 0.004	4.31
7.66×10^{-6}	1.24×10^{-4}	9.92×10^{-5}	0.551 ± 0.008	4.45
7.66×10^{-6}	1.24×10^{-4}	1.98×10^{-4}	0.540 ± 0.005	4.36
7.66×10^{-6}	1.24×10^{-4}	9.92×10^{-4}	0.615 ± 0.045	4.97
7.66×10^{-6}	2.01×10^{-4}	...	0.916 ± 0.026	4.55
1.92×10^{-5}	5.03×10^{-4}	...	2.08 ± 0.10	4.14
1.92×10^{-5}	5.03×10^{-4}	...	2.05 ± 0.03	4.08
				4.45 ± 0.21
$1.86 \times 10^{-3}^d$	1.24×10^{-5}	...	30.4 ± 1.4	6.60
$8.44 \times 10^{-4}^d$	1.24×10^{-5}	...	22.7 ± 0.3	8.97
$4.47 \times 10^{-4}^d$	1.24×10^{-5}	...	6.86 ± 0.07	5.12
$1.86 \times 10^{-4}^d$	1.24×10^{-5}	...	3.46 ± 0.08	6.20

^a Total initial $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ concentration ($[\text{Fe}(\text{bip})(\text{CN})_4^{2-}] + [\text{HFe}(\text{bip})(\text{CN})_4^-] + [\text{H}_2\text{Fe}(\text{bip})(\text{CN})_4]$). ^b Average of four or five experiments on the same solution. Uncertainties are average deviations. ^c When $[\text{Fe}(\text{II})] > [\text{Cr}(\text{VI})]$, $k_2 = k_{\text{obsd}}/[\text{Fe}(\text{II})]_0$; when $[\text{Cr}(\text{VI})] > [\text{Fe}(\text{II})]$, $k_2 = k_{\text{obsd}}/3[\text{HCrO}_4^-]$. ^d Concentration of $\text{Cr}(\text{VI})$ was corrected for dimerization, using eq 10.

increase in absorbance. Rate constants listed in Table II pertain to data obtained from this portion of the absorbance-time oscillograms, and were determined by the Guggenheim method.²² That this increase in absorbance indeed corresponds to the oxidation-reduction reaction is supported by the fact that the rate constant calculated by extrapolation of data to $[\text{Cr}(\text{VI})] = 0$ agrees well with that obtained from data with $\text{Fe}(\text{CN})_6^{4-}$ present in excess. The third absorbance change is again a decrease. It is postulated that this change corresponds to the relaxation to a new equilibrium position of the reaction



Since $\text{Fe}(\text{CN})_6^{4-}$ reacts with HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ at different rates, both of which are greater than the rate of relaxation of reaction 11,²³ the redox reaction will produce a net perturbation from equilibrium in eq 11. However, the above absorbance changes are also consistent with the formation and disappearance of an intermediate.

Although of low precision, the data in the bottom section of Table II indicate that the value of k_2 increases as $[\text{HCrO}_4^-]$ increases. This can be explained most simply by an equation of the form

$$k_2 = k_{\text{obsd}}/3[\text{HCrO}_4^-] = k_M + k_D[\text{HCrO}_4^-] \quad (12)$$

where k_M corresponds to the value of k_2 obtained with $\text{Fe}(\text{CN})_6^{4-}$ in excess. Values of the parameters at $9.95 \times 10^{-3} M \text{H}^+$ are $k_M = (5.61 \pm 0.22) \times 10^3 M^{-1} \text{sec}^{-1}$ and $k_D = (1.7 \pm 0.7) \times 10^7 M^{-2} \text{sec}^{-1}$.

The reaction of HCrO_4^- with $\text{Fe}(\text{CN})_6^{4-}$ was also studied in media where NaClO_4 was used to maintain constant ionic strength. Data at constant $[\text{H}^+]$ followed the same rate equation, eq 8. Except at low $[\text{H}^+]$ (see Figure 1), the average value of k_2 is not significantly different from that in LiClO_4 media. The deviation from first order at low $[\text{H}^+]$ is probably due to medium effects, which are expected to be greater in NaClO_4 than in LiClO_4 media.²⁴ The dependence of k_2 on $[\text{K}^+]$ was also examined. Within experimental error, values of

k_2 at 9.95×10^{-2} and $9.95 \times 10^{-3} M \text{H}^+$ did not vary over the range of $[\text{K}^+]$, 7.2×10^{-6} – $8.8 \times 10^{-2} M$.

Kinetics of the HCrO_4^- – $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ Reaction. The kinetics of the reduction of HCrO_4^- by $\text{Fe}(\text{bip})(\text{CN})_4^{2-}$ were studied at 25.0° and $0.50 M$ ionic strength (maintained with LiClO_4) over the following ranges of initial concentrations: 1×10^{-6} – $3 \times 10^{-5} M \text{Cr}(\text{VI})$, 2×10^{-5} – $5 \times 10^{-4} M \text{Fe}(\text{bip})(\text{CN})_4^{2-}$, 0 – $1 \times 10^{-3} M \text{Fe}(\text{bip})(\text{CN})_4^-$, and 5×10^{-4} – $0.5 M \text{H}^+$. Pseudo-first-order behavior was observed through $\geq 95\%$ reaction. Measurements were made primarily at $420 m\mu$, but results were independent of wavelength throughout the range 370 – $550 m\mu$. Data at $9.95 \times 10^{-3} M \text{H}^+$ are presented in Table III and are consistent with the rate equation given in eq 8, where $[\text{Fe}(\text{II})] = [\text{Fe}(\text{bip})(\text{CN})_4^{2-}] + [\text{HFe}(\text{bip})(\text{CN})_4^-] + [\text{H}_2\text{Fe}(\text{bip})(\text{CN})_4]$. Several experiments (Table III) were also carried out with $\text{Cr}(\text{VI})$ in excess. Although the treatment is rendered questionable by low precision, a fit of the data to eq 12 gives $k_M = (4.45 \pm 0.21) \times 10^3 M^{-1} \text{sec}^{-1}$ and $k_D = (4.5 \pm 3.0) \times 10^6 M^{-2} \text{sec}^{-1}$. The values of $[\text{HCrO}_4^-]$ were obtained from the total $\text{Cr}(\text{VI})$ concentration by correcting for $\text{Cr}_2\text{O}_7^{2-}$ formation according to eq 10.

The variation in k_2 with $[\text{H}^+]$, shown in Figure 2, is consistent with a rate equation of the form

$$k_2 = a[\text{H}^+]^2/(b + c[\text{H}^+] + [\text{H}^+]^2) \quad (13)$$

Values of the rate parameters, determined with a non-linear least-squares computer program,²⁰ are: $a = (1.23 \pm 0.22) \times 10^5 M^{-1} \text{sec}^{-1}$, $b = (3.59 \pm 0.72) \times 10^{-4} M^2$, and $c = 0.271 \pm 0.068 M$. This set of parameters reproduces the values of k_2 with an average deviation of 12.0%.

Kinetics of the HCrO_4^- – $\text{Fe}(\text{bip})_2(\text{CN})_2$ Reaction. The reduction of HCrO_4^- by $\text{Fe}(\text{bip})_2(\text{CN})_2$ was studied at 25.0° and $0.50 M$ ionic strength, maintained with LiClO_4 , over the initial concentration ranges: 2×10^{-6} – $2 \times 10^{-3} M \text{Cr}(\text{VI})$, 7×10^{-7} – $2 \times 10^{-4} M \text{Fe}(\text{bip})_2(\text{CN})_2$, and 5×10^{-4} – $0.5 M \text{H}^+$. Attempts to study the influence of added $[\text{Fe}(\text{bip})_2(\text{CN})_2]\text{ClO}_4$ on the rate of reaction failed because of the insolubility and instability of this substance. The material dissolved only very slowly in water, sufficiently slowly that significant portions of $\text{Fe}(\text{III})$ were reduced to $\text{Fe}(\text{II})$, consistent with the known instability in solutions of low

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(23) J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, 3, 278 (1964).

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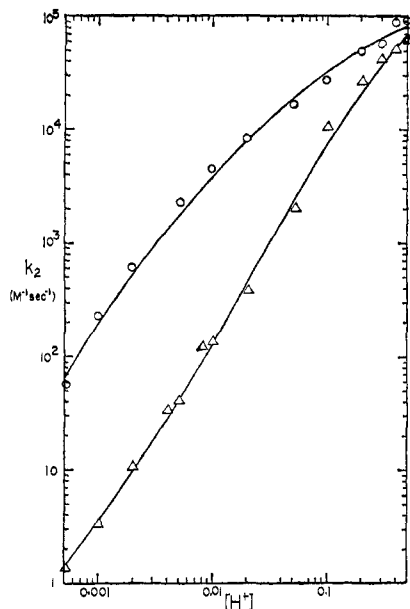


Figure 2. Plots of k_2 vs. $[H^+]$ on a log-log scale: O, $Fe(bip)(CN)_4^{2-}$ (line calculated from eq 13); Δ , $Fe(bip)_2(CN)_2$ (line calculated from eq 14).

acidity.⁷ In solutions sufficiently acidic to reduce the rate of reduction, the solubility of $[Fe(bip)_2(CN)_2]ClO_4$ was too low to allow meaningful variations in concentration. At high $[H^+]$, however, plots of $\log(D_t - D_\infty)$ vs. time (D = absorbance at the indicated time) were linear generally to $\geq 95\%$ completion, with either Fe(II) or Cr(VI) in excess. This indicates that changes in $[Fe(III)]$ from 0.0 to ca. $2 \times 10^{-5} M$ have no effect on the rate.

At low $[H^+]$ ($\leq 10^{-2} M$), absorbance-time traces did not follow pseudo-first-order kinetics throughout each experiment. These experiments were complicated by the reduction of the product $Fe(bip)_2(CN)_2^+$ by H_2O , which influenced the absorbance behavior even when Fe(II) was in excess, since the rates were measured by following the disappearance of Fe(II) at 530 m μ . In these experiments, data were treated by the Guggenheim method,²² which gave plots linear for 2-3 half-lives. Results of experiments at 9.95×10^{-2} and $9.81 \times 10^{-3} M H^+$ are presented in Table IV. Within experimental error, all data at $9.81 \times 10^{-3} M H^+$ and data at $9.95 \times 10^{-2} M H^+$ with Cr(VI) in excess appear to fit the rate equation given in eq 8, where $[Fe(II)] = [Fe(bip)_2(CN)_2] + [HFe(bip)_2(CN)_2^+] + [H_2Fe(bip)_2(CN)_2^{2+}]$. However, with Fe(II) in excess at $9.95 \times 10^{-2} M H^+$ (and indeed for all $[H^+] > 5 \times 10^{-2} M$), the rate constant k_2 decreases as $[Fe(II)]$ increases. This suggests a $[Fe(II)]$ dependence less than first order, according to a relation such as $k_{obsd} = a [Fe(II)] / (1 + b[Fe(II)])$, which could arise from the formation of a Cr(VI)-Fe(II) complex. The parameters a and b would be acid dependent. Such complex formation has been found for the reduction of $HCrO_4^-$ by As(III).²⁵ Since an analogous decrease in k_2 with increasing $[Cr(VI)]$ (when it is in excess) is not observed, complex formation is ruled out, but the data could possibly still be accommodated by an equation of the same form. Such a rate equation, barring complex formation, could arise only

(25) J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

in the case of a mechanism having a steady-state intermediate (e.g., conversion of Cr(VI) to a more reactive form, followed by reaction of this intermediate with Fe(II)).²⁶

A further observation is pertinent to this problem. When attempts were made to extend measurements at $9.95 \times 10^{-2} M H^+$ to $[Fe(II)]$ greater than those listed in Table IV, rapid formation of amorphous, colored precipitates was observed. Indeed, solutions of 2×10^{-6} to $1 \times 10^{-4} M Fe(II)$ in $9.95 \times 10^{-2} M H^+$ all formed such precipitates, which are most likely protonated species.²⁷ The time required to detect the precipitate increased with decreasing concentration, varying from several minutes for $\geq 10^{-4} M Fe(II)$ to ca. 40 hr for $2 \times 10^{-6} M Fe(II)$. It is suggested that Fe(II) is thus partially deactivated by the formation of insoluble protonated complexes, even though these complexes need not coagulate to such an extent that they are visible in order that they reduce the effective Fe(II) concentration. The rate equation given by eq 8 would thus be effective at all concentrations, provided the correct value of $[Fe(bip)_2(CN)_2]$ were used. This is supported by the fact that as $[Fe(II)]$ decreases, the value of k_2 approaches that observed with Cr(VI) in excess.

The dependence of k_2 on $[H^+]$ is shown in Figure 2. At high $[H^+]$, where there is a discrepancy between values determined with excess Cr(VI) or with excess Fe(II), the values used were determined with excess Cr(VI). Results are consistent with a rate equation of the form

$$k_2 = (a[H^+] + b[H^+]^2)/(c + [H^+]) \quad (14)$$

Values of the parameters were determined with a non-linear least-squares computer program²⁰ to be: $a = (3.3 \pm 1.1) \times 10^2 M^{-1} sec^{-1}$, $b = (1.82 \pm 0.26) \times 10^5 M^{-2} sec^{-1}$, and $c = 0.145 \pm 0.033 M$. This set of parameters reproduces the values of k_2 with an average deviation of 13.7%.

Kinetics of the $HCrO_4^-$ - $Fe(bip)_3^{2+}$ Reaction. The reaction of $HCrO_4^-$ with $Fe(bip)_3^{2+}$ was studied at 25.0° and 0.50 M ionic strength, maintained with $LiClO_4$, over the initial concentration ranges: 6.8×10^{-5} - $3.8 \times 10^{-3} M Cr(VI)$, 4×10^{-6} - $1 \times 10^{-4} M Fe(bip)_3^{2+}$, $0.4 \times 10^{-4} M Fe(bip)_3^{3+}$, and 2×10^{-3} - $0.5 M H^+$. In each experiment, with $[Cr(VI)] > [Fe(II)]$, the reaction deviated significantly from pseudo-first-order behavior. Treatment of the data by the Guggenheim method²² gave plots linear for only 1-2 half-lives. Similar deviations, although not so severe, were observed for the reduction of $HCrO_4^-$ by $Fe(phen)_3^{2+}$,³ and were interpreted in terms of a two-term rate equation: one term first order and the other second order in $[Fe(II)]$. Such an analysis would not be meaningful here, since in contrast to the situation with $Fe(phen)_3^{2+}$,³ the hydrolysis of $Fe(bip)_3^{2+}$ proceeds at rates comparable to that of the reduction of $HCrO_4^-$ throughout the range of $[H^+]$ studied.^{28,29} A further contribution to a deviation from first-order behavior arises at low $[H^+]$, where the reduction of the product $Fe(bip)_3^{3+}$ by water is

(26) The author is grateful to a referee for suggesting this possibility.

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(28) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(29) R. K. Murmann and E. A. Healy, *J. Am. Chem. Soc.*, **83**, 2092 (1961).

Table IV. Rate Constants for the Reaction of HCrO_4^- with $\text{Fe}(\text{bip})_2(\text{CN})_2$ at 9.95×10^{-2} and $9.81 \times 10^{-3} M \text{H}^+$

$[\text{HCrO}_4^-]_0, M^a$	$[\text{Fe}(\text{bip})_2(\text{CN})_2]_0, M^b$	$k_{\text{obsd}}, \text{sec}^{-1}{}^c$	$10^{-3}k_2, M^{-1} \text{sec}^{-1}{}^d$
$9.95 \times 10^{-2} M \text{H}^+$			
1.38×10^{-3}	1.42×10^{-5}	40.4 ± 0.4	9.77
7.94×10^{-4}	1.42×10^{-5}	24.1 ± 0.2	10.1
4.36×10^{-4}	1.06×10^{-5}	13.9 ± 0.2	10.6
1.88×10^{-4}	7.11×10^{-6}	5.43 ± 0.05	9.66
9.66×10^{-5}	7.11×10^{-6}	3.14 ± 0.07	10.8
4.97×10^{-5}	4.98×10^{-6}	1.67 ± 0.05	11.2
7.65×10^{-6}	7.11×10^{-7}	0.238 ± 0.004	10.4
10.4 ± 0.4			
1.92×10^{-7}	2.69×10^{-6}	0.0266 ± 0.0016	9.89
2.88×10^{-7}	5.02×10^{-6}	0.0453 ± 0.0019	9.02
2.88×10^{-7}	5.38×10^{-6}	0.0450 ± 0.0009	8.36
5.75×10^{-7}	1.00×10^{-5}	0.0799 ± 0.0026	7.99
3.84×10^{-7}	1.08×10^{-5}	0.0687 ± 0.0008	6.36
5.75×10^{-7}	1.08×10^{-5}	0.0770 ± 0.0012	7.13
9.56×10^{-7}	2.51×10^{-5}	0.167 ± 0.003	6.65
9.56×10^{-7}	2.69×10^{-5}	0.186 ± 0.005	6.91
9.56×10^{-7}	2.72×10^{-5}	0.179 ± 0.002	6.58
1.92×10^{-6}	5.38×10^{-5}	0.342 ± 0.003	6.36
1.92×10^{-6}	5.42×10^{-5}	0.333 ± 0.003	6.13
$9.81 \times 10^{-3} M \text{H}^+$			
1.05×10^{-3}	5.23×10^{-5}	0.301	0.095
6.22×10^{-4}	1.90×10^{-5}	0.193	0.103
6.22×10^{-4}	9.52×10^{-6}	0.187	0.100
5.53×10^{-4}	5.23×10^{-5}	0.217	0.130
3.25×10^{-4}	1.90×10^{-5}	0.151	0.153
3.25×10^{-4}	9.52×10^{-6}	0.144	0.148
2.88×10^{-4}	5.23×10^{-5}	0.126	0.146
2.88×10^{-4}	2.09×10^{-5}	0.126	0.146
1.34×10^{-4}	9.52×10^{-6}	0.0715	0.178
6.77×10^{-5}	9.52×10^{-6}	0.0304	0.149
0.135 ± 0.022			
1.36×10^{-6}	2.97×10^{-5}	0.00367	0.124
1.37×10^{-6}	3.80×10^{-5}	0.00598	0.157
3.42×10^{-6}	8.31×10^{-5}	0.00866	0.104
6.84×10^{-6}	1.66×10^{-4}	0.0262	0.158
6.84×10^{-6}	1.90×10^{-4}	0.0210	0.111
9.58×10^{-6}	2.09×10^{-4}	0.0308	0.147
0.134 ± 0.021			

^a Concentration was corrected for dimer formation using eq 10. ^b Total initial $\text{Fe}(\text{bip})_2(\text{CN})_2$ concentration ($[\text{Fe}(\text{bip})_2(\text{CN})_2] + [\text{HFe}(\text{bip})_2(\text{CN})_2^+]$ + $[\text{H}_2\text{Fe}(\text{bip})_2(\text{CN})_2^{2+}]$). ^c Where uncertainties are cited, these are average deviations for four or five determinations on the same solutions. ^d When $[\text{Fe}(\text{II})] > [\text{Cr}(\text{VI})]$, $k_2 = k_{\text{obsd}}/[\text{Fe}(\text{II})]_0$; when $[\text{Cr}(\text{VI})] > [\text{Fe}(\text{II})]$, $k_2 = k_{\text{obsd}}/3[\text{HCrO}_4^-]_0$.

Table V. Rate Constants for the Reaction of HCrO_4^- with $\text{Fe}(\text{bip})_3^{3+}$ at $9.95 \times 10^{-2} M \text{H}^+$

$[\text{HCrO}_4^-]_0, M^a$	$[\text{Fe}(\text{bip})_3^{3+}]_0, M$	$[\text{Fe}(\text{bip})_3^{3+}]_0, M$	$10^3 k_{\text{obsd}}, \text{sec}^{-1}$	$k_2^b, M^{-1} \text{sec}^{-1}$
2.68×10^{-3}	9.98×10^{-5}	...	43.9	5.44
2.06×10^{-3}	4.21×10^{-5}	...	25.3	4.10
1.59×10^{-3}	9.98×10^{-5}	...	22.6	4.73
1.16×10^{-3}	2.81×10^{-5}	...	9.56	2.75
8.74×10^{-4}	9.98×10^{-5}	...	10.9	4.16
6.22×10^{-4}	2.81×10^{-5}	...	3.41	1.83
4.64×10^{-4}	9.98×10^{-5}	...	5.59	4.02
2.63×10^{-4}	1.40×10^{-5}	...	1.65	2.09
2.22×10^{-4}	4.72×10^{-5}	...	1.80	2.69
1.34×10^{-4}	1.40×10^{-5}	...	1.37	3.33
1.13×10^{-4}	2.36×10^{-5}	...	2.10	6.20
6.77×10^{-5}	7.02×10^{-5}	...	1.12	5.50
				3.90 ± 0.99
1.16×10^{-3}	2.17×10^{-5}	...	6.13	1.76
1.16×10^{-3}	2.17×10^{-5}	2.99×10^{-5}	5.89	1.69
1.16×10^{-3}	2.17×10^{-5}	5.98×10^{-5}	5.64	1.62
1.16×10^{-3}	2.17×10^{-5}	1.20×10^{-4}	5.64	1.62
1.16×10^{-3}	2.17×10^{-5}	2.39×10^{-4}	5.89	1.69
1.16×10^{-3}	2.17×10^{-5}	4.19×10^{-4}	5.73	1.64
				1.67 ± 0.04

^a Corrected for dimer formation, using eq 10. ^b $k_2 = k_{\text{obsd}}/3[\text{HCrO}_4^-]_0$.

sufficiently rapid to be of importance. It was assumed in the treatment of data that these two reactions were alone responsible for the nonfirst order behavior. Representative data measured at $9.95 \times 10^{-2} M \text{H}^+$ are given in Table V. These data could not be reproduced to better than a factor of about 2, although in any series of experiments, variations in rate constant with $[\text{Cr}(\text{VI})]$ were of about the magnitude shown in Table V. The bottom section of the table demonstrates the lack of dependence of the rate on $[\text{Fe}(\text{bip})_3^{3+}]$. Although there is a slight decrease in rate on addition of $\text{Fe}(\text{bip})_3^{3+}$, the variations observed here are significantly smaller than those normally observed, and there is no apparent trend with $[\text{Fe}(\text{bip})_3^{3+}]$. Furthermore, deviations from pseudo-first-order behavior were not decreased on addition of $\text{Fe}(\text{bip})_3^{3+}$, so such deviations cannot be attributed to changes in $[\text{Fe}(\text{bip})_3^{3+}]$ during a reaction. There is no apparent trend in k_2 with $[\text{HCrO}_4^-]$, so the data can be accommodated reasonably well by the rate equation given in eq 8. The variation in rate constant k_2 with $[\text{H}^+]$ is given in Figure 1 for a series of experiments with $1.37 \times 10^{-3} M \text{Cr}(\text{VI})$. It should be noted again that these rate constants could not be reproduced exactly in other series of experiments, although qualitatively the behavior was identical in

each series. The reaction is first order in $[H^+]$ over most of the range studied with some indication of additional terms zero order and second order in $[H^+]$

$$k_2 = a + b[H^+] + c[H^+]^2 \quad (15)$$

Because of the nonreproducibility of the data, they were not treated in detail.

Discussion

The rate law for reduction of Cr(VI) by the iron(II) complexes, $Fe(bip)_{3-n}(CN)_{2n}^{(2-2n)+}$ ($n = 0, 1, 2, 3$), was in each case found to be that of eq 8 with an additional term second order in $[Cr(VI)]$, which is of decreasing importance as n decreases and which probably, but not necessarily, arises from a reaction with $Cr_2O_7^{2-}$. An alternative explanation for this path could involve a general acid catalysis by $HCrO_4^-$, as suggested by Edwards.³⁰ As discussed in the introductory section, this form of the rate equation is the limiting form of eq 4 which corresponds to the reduction of Cr(VI) to Cr(V) being rate determining ($k_2 = k_{65}$). It is interesting to speculate on the source of the difference in the form of the rate equation for the reactions studied here, compared to that found in all but one previous study, *i.e.*, the limiting form of eq 4 corresponding to a rate-determining reduction of Cr(V) to Cr(IV). The one-equivalent reducing agents which have been studied can be separated into two obvious categories—the substitution-inert species $Fe(CN)_6^{4-}$, $Fe(bip)(CN)_4^{2-}$, $Fe(bip)_2(CN)_2$, $Fe(bip)_3^{2+}$, and $Fe(phen)_3^{2+}$ and the relatively labile species Fe^{2+} , VO^{2+} , and NpO_2^+ (and the oxidizing agent $Ce(IV)$).

It is tempting then to assert that the difference in the form of the rate equation, which can also be separated into the above categories, is caused by the outer-sphere or inner-sphere character of the reducing agent. In a comparison of the rate equations observed for reductions by Fe^{2+} and $Fe(phen)_3^{2+}$, Espenson and King³ suggested that reduction of Cr(V) to Cr(IV) (with accompanying coordination number change¹) is slow relative to reduction of Cr(VI) to Cr(V) (with no change in coordination number) if the transition state involves an inner-sphere oxygen bridge such as $Fe-O-Cr$, and that the inverse order of rates is observed when the transition state is outer sphere. This ordering of rates would presumably be caused by an easier Cr(V) to Cr(IV) transformation if the reducing agent did not bridge to chromium in the transition state, since one of the immediate products of such a bridged transition state would necessarily be a species of reduced coordination number. These postulates appear to be quite reasonable and are supported, but not proved, by the results of the present study.

Examination of the products of the cyanoiron(II) reactions, which include Cr(III)–Fe(III) binuclear complexes, indicates that one cannot insist that these reactions occur by outer-sphere processes, in spite of the fact that the Fe(II) reductants are quite substitution inert. Since Cr(III) is very substitution inert, and Cr(IV) is presumably significantly more labile,³¹ either Fe(II) or Fe(III) must have been bonded to Cr(IV) at the time it was reduced. This could occur either by an inner-sphere reduction of Cr(IV) or by an outer-sphere

reduction of a Cr(IV)–Fe(III) complex. In the latter case, the binuclear complex would probably be the product of an inner-sphere reduction of Cr(V), since it is not likely that Cr(IV) would spontaneously complex with Fe(III) in the high yields observed. Since CN^- is known to act as a bridging ligand in electron-transfer reactions,^{32–34} it is not unreasonable to expect that one or more of the steps in the reduction of Cr(VI) will proceed by an inner-sphere process, as long as the rate of substitution on the Cr species involved is greater than the rate of the reduction reaction. At any rate, the formation of Cr(III) complexes of the oxidation products, apparently also observed in the Cr(VI) oxidation of H_2SO_3 ³⁵ and H_3PO_2 ³⁶ where two-electron transfer steps may occur, must be considered when postulating a mechanism for the reduction of Cr(VI).

These data also have important implications regarding the general mechanism of inner-sphere electron-transfer reactions. In most such reactions the relative labilities of the oxidizing and reducing agents are such that substitution occurs on the reducing agent; *i.e.*, the bridging ligand is originally bonded to the oxidizing agent. The present study apparently provides the first definite example of a system in which the bridging ligand is supplied by the reducing agent. This indicates that the usual situation in which the reducing agent is the more labile species is not an absolute requirement for the existence of an inner-sphere reaction.

The Marcus relation³⁷ for outer-sphere electron-transfer reactions, which has been discussed in some detail for the Ce(IV) oxidation of the series of Fe(II) complexes studied here,³⁸ is also relevant to the above discussion. With the exception of the $Fe(bip)_3^{2+}$ reaction, the rate constants for the $HCrO_4^-$ –Fe(II) reactions at constant $[H^+]$ correlate as well with the Fe(II) oxidation potential as did the rate constants for the Ce(IV) oxidations in 0.5 M H_2SO_4 .³⁸ One prediction of the Marcus theory is that the ratio of rate constants for the series of Fe(II) complexes by Ce(IV) (k_{Ce} , 0.5 M H_2SO_4) and by Cr(VI) (k_{Cr} , 0.5 M $HClO_4$) should be roughly independent of the identity of the Fe(II) complex.³⁹ As cyanides are replaced by bipyridines on Fe(II), the ratio k_{Ce}/k_{Cr} takes the values 86, 133, 135, and 1.43×10^4 . The discrepancy may indicate that the reduction of $HCrO_4^-$ by the cyanoiron(II) complexes is inner sphere, with rate constants greater than the expected outer-sphere values, while the $Fe(bip)_3^{2+}$ reduction is outer sphere. However, a failure of one of the other assumptions involved in the use of the Marcus relation may also be involved.^{37, 39}

It is possible that the difference in rate law between substitution-labile and -inert reducing agents arises from a difference in mechanism, *e.g.*, an initial two-electron transfer with the inert species, producing Fe(IV) and Cr(IV), followed by a rapid reaction of each of these intermediates with Fe(II). It is not clear, however, why the inert Fe(II) complexes, but not Fe^{2+} , should

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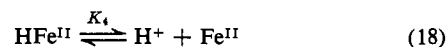
undergo two-electron oxidations, particularly since the HClO oxidation of Fe²⁺ apparently involves formation of an Fe(IV) species,⁴⁰ while no evidence was found for Fe(IV) in the oxidation of Fe(phen)₃²⁺.⁴¹ At any rate, the present study provides no evidence to distinguish between an initial one-electron or two-electron transfer.

Whatever the underlying reason, it should be emphasized again that there is apparently a correlation between the form of the rate equation and the substitution-inertness of one-equivalent reducing agents. In order to fully understand the mechanism of Cr(VI) oxidations, the above correlation and the formation of Cr(III)-Fe(III) binuclear complexes must be taken into account.

A frequent characteristic of redox reactions between ions of like charge is a catalysis by oppositely charged ions; e.g., the exchange reactions of Fe(CN)₆⁴⁻ with Fe(CN)₆³⁻,^{42,43} and MnO₄²⁻ with MnO₄⁻,^{44,45} and the reduction of S₂O₈²⁻ by Fe(CN)₆⁴⁻⁴⁶ are catalyzed by a number of cations, with various efficiencies. With respect to the present study, it is known that Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ form complexes⁴⁷⁻⁴⁹ with K⁺, so it is somewhat surprising that the reduction of HCrO₄⁻ by Fe(CN)₆⁴⁻ is independent of variations in [K⁺] over the

range 7 × 10⁻⁶ to 9 × 10⁻² M. Apparently if such catalytic activity is important in this case, K⁺, Na⁺, and Li⁺ are about equally as effective.

The [H⁺] dependence of the HCrO₄⁻-Fe(II) reactions can be explained in terms of activated complexes of composition {(HCrO₄⁻)(Fe(II))(H⁺)_n}[‡], where n = 1 (or possibly 2, depending on the value of K₄ below) for Fe(CN)₆⁴⁻, n = 2 for Fe(bip)(CN)₄²⁻, n = 1 and 2 for Fe(bip)₂(CN)₂, and n = 0, 1, and 2 for Fe(bip)₃²⁺. The denominator terms in the equations describing the [H⁺] dependence of the reactions of the cyanoiron(II) complexes presumably arise from variation in the predominant forms of the reactants with changes in [H⁺], and can be accommodated qualitatively by the equilibria



Although appropriate values of K₃ and K₄ have not been determined under the same conditions studied here, it is known that protonation of each of the cyanoiron(II) complexes occurs.^{7,8,27,50-52} Since the parameters used in the denominators of the various rate equations are composites of these unknown equilibrium constants, it is not possible to make any meaningful statements about the magnitude of these parameters at this time.

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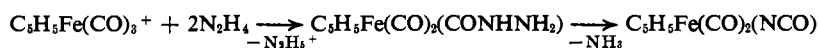
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Reactions of Cyclopentadienyliron Tricarbonyl Cation with Hydrazines and the Azide Ion

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Abstract: Hydrazine reacts with C₅H₅Fe(CO)₃⁺ to form first a carbazoyl intermediate which then loses NH₃ to give an isocyanate complex.



The reaction with some methyl-substituted hydrazines proceeds in the same manner. The isocyanate product may also be prepared by the reaction of C₅H₅Fe(CO)₃⁺ with N₃⁻ or NCO⁻. With CN⁻ and NCS⁻, the cationic carbonyl yields C₅H₅Fe(CO)₂(CN) and the N-bonded isomer of C₅H₅Fe(CO)₂(NCS), respectively. Mechanisms of these reactions are discussed.

Recently we have been interested in examining the reactions of cationic metal carbonyls with primary and secondary aliphatic amines. In two such studies,^{1,2} it was found that one carbonyl group in the

complex reacts with the amine to form a carboxamido group.

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