

shown in Fig. 10. These aggregates were obtained by mixing negative and positive sols. The positive sol was prepared by reversing the charge of deionized negative sol with poly-N-isopropyl-4-vinylpyridinium bromide. The experiments made by mixing 400 Å. negative sol with 200 Å. positive sol had shown that this kind of coagulation was not the result of simple interaction between oppositely charged particles, but the result of instant mutual neutralization of opposite charges. If one kind of charge exceeds the other by a small difference, the residual small charge may bring about coagulation of type III. Owing to imperfect mixing, however, some particles may get practically discharged, while others possessing a small charge of the same kind, for a short period of time during which the discharged particles coagulate rapidly, form compact aggregates of type I, and thus hinder further charge exchange through diffusion of ions. This process is followed by slow coagulation of the primary particles with the compact masses. This is believed to be the case in the formation shown in Fig. 10.

g. Conclusions.—It follows from this discussion that although the current theory of lyophobic colloids has been successful in explaining many aspects of the problem on semiquantitative basis, it fails to account for coagulation satisfactorily under ordinary circumstances. The reason for this failure lies in the fact that the simple picture of coagulation by compression of the double layer, which the theory is mainly concerned with, is frequently complicated. The complications arise from specific adsorbability of ions of both kinds. This conclusion parallels with the recent findings of Glazman, *et al.*,³⁰ and Mirnik, *et al.*³⁹ The introduction of the Stern correction in some explicit form will be an important refinement of the theory, as remarked by Overbeek (p. 312 of ref. 12). Also, the formulation of the stabilizing effect of the ions introduced (*cf.* subsection b), which appears to be a rate process, is another important and difficult problem to be tackled by the theoretical workers.

(39) M. J. Herak and M. Mirnik, *Kolloid-Z.*, **179**, 130 (1961); M. Mirnik, *Nature*, **190**, 689 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON, WIS.]

Kinetics and Mechanisms of Reactions of Chromium(VI) and Iron(II) Species in Acidic Solution¹

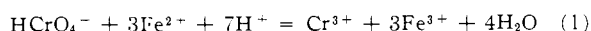
BY JAMES H. ESPENSON² AND EDWARD L. KING³

RECEIVED MAY 24, 1963

The rates of reaction of chromium(VI) with aquoiron(II) ion and tris-(1,10-phenanthroline)-iron(II) ion have been determined as a function of concentrations of reactants and products. The rate law for reaction of aquoiron(II) ion is $-d[\text{Fe}^{2+}]/dt = \{[\text{H}^+]^3[\text{Fe}^{2+}]^2/[\text{Fe}^{3+}]\}\{k_1[\text{HCrO}_4^-] + k_2[\text{HCrO}_4^-]^2\}$. In interpretation of kinetic data on this reaction, account was taken of interaction of iron(III) and chromium(VI); spectrophotometric data yield a value $Q_{36} = [\text{FeCrO}_4^+][\text{H}^+]/([\text{Fe}^{3+}][\text{HCrO}_4^-]) = 1.4$ at 0° in solutions of ionic strength 0.0839 *M*. The reaction of tris-(1,10-phenanthroline)-iron(II) ion and chromium(VI) is not retarded by tris-(1,10-phenanthroline)-iron(III) ion. Fewer mechanistic details of this latter reaction are revealed by the kinetic data.

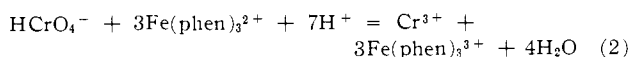
Chromium(IV) and chromium(V) may be unstable intermediates in reactions of stable +3 and +6 oxidation states of chromium with oxidizing and reducing agents, respectively. Reactions with one-equivalent reagents are particularly informative, and the kinetics of oxidation of chromium(III) by cerium(IV) indicate that reaction of cerium(IV) and chromium(IV) is rate determining.⁴ The present study deals with rates of reaction of chromium(VI) with two one-equivalent reducing agents, aquoiron(II) ion and tris-(1,10-phenanthroline)-iron(II) ion.

The first of these reactions



was studied by Benson,⁵ and her results have been discussed by Westheimer.⁶ The present work done at 0° using titrimetric and spectrophotometric procedures extends concentration ranges of the earlier work, characterizes the reaction order with respect to iron(III) ion more completely, and takes into account the interaction of iron(III) and chromium(VI) to form a relatively stable complex ion, FeCrO_4^+ .

The second of the reactions



the kinetics of which have not been studied previously,

(1) Taken from the Ph.D. Thesis of James H. Espenson, University of Wisconsin, 1962. This work was supported in part by the United States Atomic Energy Commission (Contract AT(11-1)-1168).

(2) Procter and Gamble Fellow, 1961-1962.

(3) Department of Chemistry, University of Colorado, Boulder, Colo.

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

(5) C. Benson, *J. Phys. Chem.*, **7**, 1 (1903); **7**, 356 (1903).

(6) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

was studied spectrophotometrically at temperature between 0 and 40°.

Experimental Details and Results

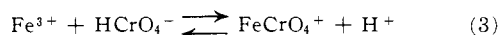
Reagents.—At least two independent sources of each reagent except tris-(1,10-phenanthroline)-iron(III) ion were used. Doubly distilled water was used in preparation of some solutions; the second distillation was from alkaline permanganate in a Barnstead still. A redistillation of this water from an all-glass still provided another source of water. Reagent grade potassium dichromate was used both without further purification and also after it was recrystallized two or three times from water and dried at 110°. Perchloric acid solutions were prepared by dilution of 60 and 72% reagent grade acids. Lithium perchlorate solutions were prepared either from twice-recrystallized reagent grade material or from material made by reaction of lithium carbonate and a slight excess of perchloric acid. Lithium perchlorate prepared in the latter way was recrystallized from water. Iron(III) perchlorate was prepared from both iron(III) chloride and iron(III) nitrate by prolonged fuming with perchloric acid. Hydrated iron(III) perchlorate was crystallized from this medium and once or twice more from 60% perchloric acid. These solids contained appreciable perchloric acid, the concentration of which was determined in each iron(III) stock solution as the difference between the total normality and the iron(III) normality. The former quantity was determined by titration of the perchloric acid solution resulting from passing an aliquot of stock solution through a column containing cation-exchange resin in the hydrogen ion form. Sources of aquoiron(II) ion used in reaction solutions were iron(II) sulfate heptahydrate, diammonium iron(II) disulfate, and iron(II) perchlorate. Stock solutions of the first two iron(II) compounds were prepared by dissolving reagent grade solids in dilute (*ca.* 0.01 *M*) perchloric acid. Iron(II) perchlorate solutions were prepared by dissolution of iron wire in *ca.* 0.5 *M* perchloric acid at temperatures below 80°. The absence of iron(III) and chloride ion in these solutions was proved by tests with thiocyanate ion and silver ion, respectively. The iron(II) stock solutions were stored under purified nitrogen in bottles equipped with self-sealing rubber disks; aliquots were removed by hypodermic needle and syringe. Aqueous solutions of tris-(1,10-phenanthroline)-iron(II) sulfate

were prepared by appropriate dilution of G. F. Smith 0.025 *M* solution. Solutions also were prepared with iron(II) sulfate heptahydrate and a very slight excess of 1,10-phenanthroline monohydrate which had been recrystallized from a mixture of water and ethanol. Dr. N. Sutin of Brookhaven National Laboratory generously supplied the solid tris-(1,10-phenanthroline)-iron(III) perchlorate⁷ used in these studies. Stock solutions in 9 *M* perchloric acid were stored in opaque containers at ca. 2°.

The substances used in the above-described preparations as well as all other chemicals used in this work were of reagent grade quality. Solutions were analyzed, if necessary, according to accepted procedures.

Spectrophotometric Experiments.—All spectrophotometric studies were made using a Cary Model 14 recording spectrophotometer equipped with a specially constructed 10-cm. quartz cell⁸ having a Liebig-type jacket of ca. 7-ml. volume through which thermostated water circulated at ~20 ml./sec. The temperature of solutions in the cell was probably constant to within 0.05°. In spectrophotometric studies of reaction rate, the chart paper was driven at 5 in./min. Concentrations were calculated from absorbance values read at points no more closely spaced than corresponded to 4-sec. intervals.

Spectrophotometric Study of Interaction of Aquoiron(III) Ion and Chromate Ion.—The concentration dependence of light absorption of perchloric acid-iron(III) perchlorate solutions containing potassium dichromate at low and variable concentration is consistent with occurrence of the reaction



Account must be taken of this equilibrium in formulation of a rate law for the reaction of aquoiron(II) ion and chromium(VI).

Each series of measurements at high and constant concentration of iron(III) perchlorate and perchloric acid and variable concentration of chromium(VI) gave a value of \bar{a}_6 , which is defined

$$\bar{a}_6 = \Delta(\log I_0/I)/b\Delta C_6$$

with b the cell length and C_6 the stoichiometric concentration of chromium(VI) expressed as monomers. Beer's law was obeyed, *i.e.*, \bar{a}_6 is not a function of C_6 ; this is expected since monomeric chromium(VI) species predominate at the low concentrations being studied ($C_6 < 7 \times 10^{-5}$ *M*).⁹ The dependence of \bar{a}_6 upon the concentration of aquoiron(III) ion is given by the two-parameter equation¹⁰

$$\bar{a}_6 - a_6 = s - \frac{\bar{a}_6 - a_6}{[\text{Fe}^{3+}]^r} \quad (4)$$

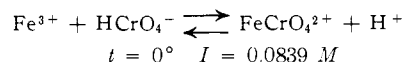
in which a_6 is the molar absorptivity index of hydrogen chromate ion.

At an ionic strength of 0.0839 *M* series of experiments were run at 1.27×10^{-2} , 2.43×10^{-2} , and 4.63×10^{-2} *M* hydrogen ion, but only at the intermediate acidity was the concentration of iron(III) varied. It was only at this acidity, therefore, that values of both r and s were obtained. The concentration of aquoiron(III) ion was slightly smaller than the stoichiometric concentration of iron(III); correction for the acid dissociation of aquoiron(III) ion was made using $Q_1 = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}] = 6.2 \times 10^{-4}$ estimated for ionic strength 0.0839 *M* and 0° from work by Milburn and Vosburgh.¹¹

The simplest interpretation of conformity to eq. 4 is the formation of a 1-1 species $\text{FeCrO}_4\text{H}_n^{1+n}$. If a particular value of n predominates in the acidity range studied, and if the absorptivity index of this species shows no medium effect with exchange of 0.034 *M* hydrogen ion for lithium ion, the value of s , interpreted as $(a_{36} - a_6)$ with a_{36} the absorptivity index of $\text{FeCrO}_4\text{H}_n^{1+n}$, obtained at the one acidity may be used to obtain r from data at other acidities. Values of r so obtained are proportional to the concentration of hydrogen ion, leading to the conclusion that one hydrogen ion is formed in the complex ion formation reaction. This conclusion is already implied in the balanced chemical eq. 3. A summary of the derived quantities $Q_{36} = [\text{H}^+][\text{FeCrO}_4^+]/[\text{Fe}^{3+}][\text{HCrO}_4^-] = [\text{H}^+]/r$ and $(a_{36} - a_6) = s$ is given in Table I. The value of Q_{36} derived from these data is 1.4 ± 0.2 . The maximum extent of formation of this 1-1 complex in the solutions of 0.0243 *M* hydrogen ion is calculated: $[\text{FeCrO}_4^+]/([\text{FeCrO}_4^+] + [\text{HCrO}_4^-]) = 1.4 \times 0.00915/(0.0243 + 1.4 \times 0.00915) = 0.35$.

The fit of the data to eq. 4 does not prove that a 1-1 complex is the only iron(III)-chromium(VI) species present in these solutions. Fortuitous combination of absorptivity indices and equilibrium quotient values can disguise the presence of ap-

TABLE I
SPECTROPHOTOMETRIC STUDY OF THE REACTION



$$t = 0^\circ \quad I = 0.0839 \text{ M}$$

[H ⁺] × 1. mole ⁻¹	10 ³ × [Fe ³⁺] × 1. mole ⁻¹	λ, mμ	10 ⁻³ × a ₃₆ ^a × mole l. ⁻¹ cm. ⁻¹	Q ₃₆
0.0127	6.00	410		1.40
		390		1.30
		380		1.29
		370		1.30
		410	3.21	1.53
0.0243	1.54-9.15	390	5.63	1.50
		380	6.23	1.40
		370	5.86	1.32
		410		1.52
0.0463	6.21	390		1.59
		380		1.47
		370		1.40
		410		1.40

^a At the two lower acidities, values of the absorptivity index of monomeric chromium(VI) are 235, 536, 816, and 1130 l. mole⁻¹ cm.⁻¹ at 410, 390, 380, and 370 mμ, respectively. At 0.0461 *M* hydrogen ion, the values are appreciably lower, being 215, 508, 791, and 1103 l. mole⁻¹ cm.⁻¹, respectively. The absorptivity of H_2CrO_4 in this spectral region is less than that of HCrO_4^- (J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953)).

preciable amounts of a second species.¹² Despite possible ambiguity, this simplest interpretation of the spectral data in terms of only a 1-1 complex with $Q_{36} = 1.4$ has been employed.

Using $Q_{36} = 1.4$, calculated values of the portion of chromium(VI) present as iron(III)-chromate complex range from ~8 to ~40% in the solutions in which rates of reaction were measured at an ionic strength of 0.0839 *M*.

Kinetics of Oxidation of Aquoiron(II) Ion by Chromium(VI).—This important reaction of analytical chemistry was studied at concentration conditions under which the predominant species of chromium(VI) were hydrogen chromate ion HCrO_4^- and iron(III)-chromate complex FeCrO_4^+ ; iron(III) was present largely as aquoiron(III) ion, although appreciable amounts of hydroxoiron(III) ion were also present.¹³ Whether chromium(III) was produced as hexaquoiron(III) ion or as dimeric species¹³ was not investigated in solutions of these compositions.¹⁴ The extent of reaction as a function of time was determined at 0° with both the titrimetric procedure used by Benson⁵ and a spectrophotometric procedure. Measurements were made on solutions of ionic strength 0.0839 and 0.200 *M*.

Benson's method of measuring the rate of reaction of aquoiron(II) ion and chromium(VI) involved oxidation of iodide ion induced by the iron(II)-chromium(VI) reaction.^{5,6,15} Under conditions employed in this work, the reaction of iodide ion with either iron(III) ion or chromium(VI) is slow. Therefore, the amount of iodine(0) produced when iodide ion is added to an iron(II)-chromium(VI) reaction mixture depends upon the amount of iron(II)-chromium(VI) reaction still to occur, that is, upon the amount of iron(II) and chromium(VI) unreacted at the time of addition of iodide ion. Appropriate calibration experiments were run to establish the relationship between the amount of iodine produced and the amount of iron(II) and chromium(VI) present. In calibration experiments, mixtures of iron(II) ion and iodide ion were added to solutions containing iron(III), chromium(VI), and chromium(III) prepared by prior reduction of chromium(VI) with insufficient iron(II). Immediately before addition of the iron(II) ion-iodide ion mixture, the concentration of aquoiron(III) ion was lowered by addition of 1.00 ml. of saturated disodium hydrogen phosphate per 500 ml. of calibration mixture, 500 ml. being the volume of solution used to obtain each point in experiments at ionic strength 0.0839 *M*. Experiments at ionic strength 0.200 *M* were carried out on a tenfold smaller scale. At the moment of addition of the iron(II) ion-iodide ion mixture, a calibration experiment was the same as a kinetic experiment at the moment of addition of iodide ion. In

(12) C. F. Baes, *J. Phys. Chem.*, **60**, 878 (1956); R. F. Kruh, *J. Am. Chem. Soc.*, **76**, 4865 (1954).

(13) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

(14) The violet color of hexaquoiron(III) ion does result, however, if the reaction is carried out in perchlorate solutions of sufficient concentration that the chromium(III) product is easily visible. Further, it seems unlikely that the pathway for production of dimer, namely, reaction of chromium(III) and chromium(IV), could be important in this reaction mixture.

(15) (a) R. A. Gortner, *J. Phys. Chem.*, **12**, 632 (1908); (b) C. Wagner and W. Preiss, *Z. anorg. Chem.*, **168**, 265 (1928).

(7) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 71 (1961).

(8) The spectrophotometer cells were purchased from the American Instrument Co. of Silver Spring, Md.

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

(10) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953); T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).

(11) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955); R. M. Milburn, *ibid.*, **79**, 537 (1957).

kinetic experiments, the 1.00 ml. of disodium hydrogen phosphate was added with the iodide ion.¹⁶ After exactly 2.00 min., the acidity was lowered by addition of ammonium hydrogen carbonate, and the iodine was titrated with arsenic(III) solution of known concentration. The lowered acidity effectively quenches the slow side reactions of iron(III) with iodide ion and of chromium(VI) with iodide ion; it also defines the time interval in which induced oxidation of iodide occurs. The color of iodine in an immiscible carbon tetrachloride phase was used as indicator. It was possible to determine the iron(II) ion concentration in reaction mixtures in the 10^{-4} to 10^{-5} *M* range. The calibration experiments obviate use of an assumed induction factor and need of correction for iodine-producing side reactions.

Titrimetric experiments at ionic strength 0.0839 *M* were run at nine sets of concentration conditions: 6×10^{-5} to 4×10^{-4} *M* chromium(VI) (expressed as monomers), 3×10^{-5} to 6×10^{-5} *M* iron(II), 0.0121 to 0.0483 *M* hydrogen ion, and 1.6×10^{-3} to 6.3×10^{-3} *M* iron(III). At ionic strength 0.200 *M*, experiments were run at six sets of concentration conditions: 2.6×10^{-4} *M* chromium(VI), 6×10^{-5} to 1.3×10^{-4} *M* iron(II), 0.0242 *M* hydrogen ion, and 3×10^{-3} to 2.5×10^{-2} *M* iron(III). In each set of experiments, the iron(II) concentration changed greatly, the chromium(VI) concentration changed slightly, and the hydrogen ion and iron(III) concentrations changed almost not at all. At each concentration, 3-7 calibration points were run; the results were consistent with a linear dependence of iron(II) concentration upon the concentration of iodine produced in the induced reaction. At each concentration, kinetic experiments were run with 2 to 14 different time intervals (average number 6) of from 4 sec. to 10 min.; the order of running points was random.

Twenty-six spectrophotometric experiments were run at an ionic strength of 0.0839 *M*, with measurement being made at 350, 370, 380, or 390 μ . The initial concentration of iron(II), the limiting reagent in all except two experiments, was 6.3×10^{-5} or 14.8×10^{-5} *M*. The initial concentration of chromium(VI) ranged from 3.2×10^{-5} to 9.6×10^{-5} *M*, and the initial concentration of iron(III) ranged from 1.6×10^{-3} to 9.5×10^{-3} *M*. The concentrations of hydrogen ion (0.0127, 0.0243, and 0.0463 *M*) were approximately the same as in the titrimetric experiments.

The light absorption of reaction solutions was due both to species present at significant concentrations (hydrogen chromate ion, aquoiron(III) ion, hydroxoiron(III) ion, and iron(III)-chromate complex) and also to dimeric iron(III) species which contribute appreciably to light absorption even though present at insignificant concentrations. Although the apparent molar absorptivity index of iron(III) was not constant, the change of iron(III) concentration in a single run was small, and, therefore, an absorptivity index appropriate for the average iron(III) concentration of each run was used. The equation used in calculation of the concentration of chromium(VI) from *A* the absorptivity

$$C_6 = \frac{A/b - \bar{a}_3(C_3 + 3C_6)}{\bar{a}_6 - 3\bar{a}_3} \quad (5)$$

in which *b* is the cell length, C_3 and C_6 are the initial stoichiometric concentrations of iron(III) and chromium(VI), \bar{a}_3 is the appropriate absorptivity index for iron(III), and \bar{a}_6 is the appropriate absorptivity index for chromium(VI)

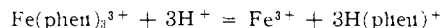
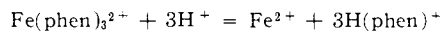
$$\bar{a}_6 = \frac{a_6[\text{H}^-] + a_{36}Q_{36}[\text{Fe}^{3+}]_{\text{av.}}}{[\text{H}^+] + Q_{36}[\text{Fe}^{3+}]_{\text{av.}}} \quad (6)$$

In eq. 5 account is taken of the very small change in iron(III) concentration during a run. To avoid a quadratic equation, the average concentration of aquoiron(III) ion for each particular experiment was used to calculate the appropriate value of \bar{a}_6 ; this does not introduce appreciable error into the calculated value of C_6 . At 370 μ , values of apparent absorptivity indices appropriate for the concentration ranges studied are: $\bar{a}_6 = 1.12 \times 10^3$ to 2.84×10^3 l. mole⁻¹ cm.⁻¹, depending upon the concentrations of aquoiron(III) ion and hydrogen ion, and $\bar{a}_3 = 6.2$ to 18.1 l. mole⁻¹ cm.⁻¹, depending upon the concentrations of aquoiron(III) ion and hydrogen ion. Calculation was made of the concentration of chromium(VI) at 8 to 22 points in an experiment, these points (*A*, *t*) being read from the chart paper of the spectrophotometer. From the reaction stoichiometry and initial concentration conditions other concentrations as a function of time were calculated.

Kinetics of Oxidation of Tris-(1,10-phenanthroline)-iron(II) Ion by Chromium(VI).—The extent of this reaction as a function of time was determined spectrophotometrically at temperatures 0°, 10°, 20°, 30°, and 40°. The absorptivity indices of tris-(1,10-phenanthroline)-iron(II) ion, tris-(1,10-phenanthroline)-iron(III) ion, and chromium(VI) at 510 μ , the wave length of

most measurements, are 1.11×10^4 , 292, and 30 l. mole⁻¹ cm.⁻¹, respectively. The absorptivity index of hexaquoiron(III) ion, the assumed chromium(III) product, is <10. That this reaction is essentially unidirectional under the acidity conditions studied, 0.25–1.5 *M* hydrogen ion, follows from consideration of oxidation potentials of the chromium(III)–chromium(VI) couple (–1.36 v.) and the tris-(1,10-phenanthroline)-iron(II)–tris-(1,10-phenanthroline)-iron(III) couple (–1.06 v.). It also was demonstrated that with the products at much higher concentrations, chromium(III) ion at 350-fold higher and tris-(1,10-phenanthroline)-iron(III) ion at 12-fold higher than existed in the kinetic experiments, the concentration of tris-(1,10-phenanthroline)-iron(II) ion was still decreasing after 98.7% of it had reacted.

The aquation reactions



are possible side reactions, but neither occurs at an appreciable rate.¹⁷

In experiments which went to completion, the absorptivity at all wave lengths in the visible region was close to the value predicted on the basis that tris-(1,10-phenanthroline)-iron(III) ion was the product.

The effect of tris-(1,10-phenanthroline)-iron(III) ion upon the rate of reaction was studied in five experiments at 0° in 1.5 *M* perchloric acid with an initial concentration of chromium(VI) of 4.8×10^{-4} *M*. In these experiments with initial concentrations of tris-(1,10-phenanthroline)-iron(II) ion of $\sim 10^{-5}$ *M* and tris-(1,10-phenanthroline)-iron(III) ion varied from zero to 3×10^{-4} *M*, the rates were the same within 10% at particular concentrations of tris-(1,10-phenanthroline)-iron(II) ion. At the points of comparison the concentration of tris-(1,10-phenanthroline)-iron(III) ion varied by a factor of $\sim 10^2$.

Experiments were carried out in perchloric acid–lithium perchlorate solutions of ionic strength 1.50 *M*; the concentrations of hydrogen ion were 0.25, 0.50, 1.00, and 1.50 *M*. The four concentrations of chromium(VI) were 2.4×10^{-4} , 4.8×10^{-4} , 7.1×10^{-4} , and 9.5×10^{-4} *M* (in monomeric chromium(VI)). The initial concentration of tris-(1,10-phenanthroline)-iron(II) ion was 1×10^{-5} to 2×10^{-5} *M*, and that of tris-(1,10-phenanthroline)-iron(III) ion varied from zero to 4.6×10^{-4} *M*. Of concentrations upon which the rate depends, only that of tris-(1,10-phenanthroline)-iron(II) ion varied appreciably during an experiment, and runs were generally followed to between 70 and 90% completion.

The data points ($[\text{Fe}(\text{phen})_3^{2+}]$, *t*) were obtained using the equation

$$[\text{Fe}(\text{phen})_3^{2+}] = (A - A_\infty)/b(a_{11} - a_{111}) \quad (7)$$

in which *A* and A_∞ are values of $\log I_0/I$ at the time in question and at infinite time, *b* is the cell length, and a_{11} and a_{111} are the molar absorptivity indices of tris-(1,10-phenanthroline)-iron(II) ion and tris-(1,10-phenanthroline)-iron(III) ion, respectively. The change in light absorption due to changing concentration of chromium species is negligible. From successive data points at intervals of concentration of $\sim 10^{-6}$ *M* iron(II), values of $\Delta \log [\text{Fe}(\text{phen})_3^{2+}]/\Delta t$ were calculated, and these quantities were correlated to obtain the rate law.

Interpretation of Kinetic Data

Chromium(VI)–Aquoiron(II) Ion Reaction.—Preliminary interpretation of both titrimetric and spectrophotometric data ($[\text{Fe}^{2+}]$, *t*) suggested a rate law of the form

$$-d[\text{Fe}^{2+}]/dt = k'[\text{Fe}^{2+}]^2C_6/C_3 \quad (8)$$

for reaction 1. In terms of the concentration of aquoiron(II) ion and initial stoichiometric concentrations (designated with zero subscripts or superscripts) this rate law is

$$-\frac{d[\text{Fe}^{2+}]}{dt} = \frac{k'[\text{Fe}^{2+}]^2(3C_6 - ([\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_t))}{3(C_3 + [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_t)} \quad (8')$$

which can be integrated to give

$$\frac{k't}{3} = \frac{2.303(3C_6 + C_3)}{(3C_6 - [\text{Fe}^{2+}]_0)^2} \log \frac{[\text{Fe}^{2+}]_t C_6 + C_3 + [\text{Fe}^{2+}]_0 \left\{ \frac{1}{[\text{Fe}^{2+}]_t} - \frac{1}{[\text{Fe}^{2+}]_0} \right\}}{[\text{Fe}^{2+}]_0 C_6} \quad (9)$$

Figure 1 shows data from one titrimetric experiment and one spectrophotometric experiment correlated with the integrated rate equation. The precision of

(16) Addition of phosphate, not made by Benson, was suggested by C. Wagner and W. Preiss, *Z. anorg. Chem.*, **168**, 265 (1928). By complexing iron(III) ion, it reduces the rate of the iron(III)-iodide reaction and increases the rate of the induced oxidation of iodide.

(17) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 3596 (1948).

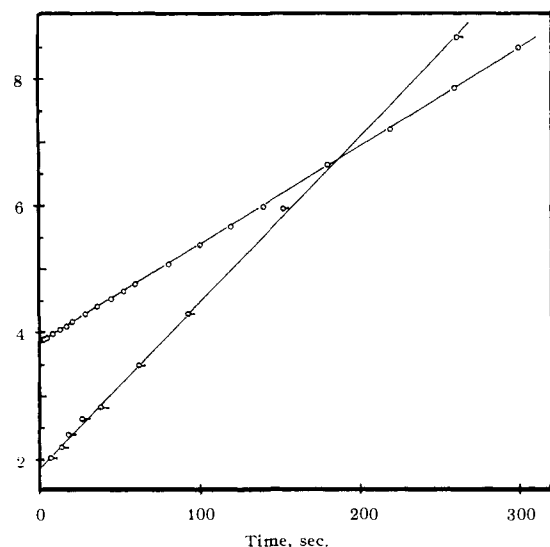


Fig. 1.—Correlation of rate data with integrated rate equation

$$\left\{ \frac{C_3^0 + [\text{Fe}^{2+}]_0}{3C_6^0 - [\text{Fe}^{2+}]_0} \times \frac{1}{[\text{Fe}^{2+}]} \right\} + \frac{2.303(3C_6^0 + C_3^0)}{(3C_6^0 - [\text{Fe}^{2+}]_0)^2} \log \left(\frac{[\text{Fe}^{2+}]}{C_6} \right)$$

vs. time. The slope of the line is $k'/3$. \circ , ordinate gives values $\times 10^{-6}$; spectrophotometric experiment; $[\text{H}^+] = 0.046 M$, $[\text{Fe}^{2+}]_0 = 1.48 \times 10^{-4} M$, $C_3^0 = 6.3 \times 10^{-3} M$, $C_6^0 = 6.4 \times 10^{-5} M$ (last point corresponds to 89% completion of reaction), $k' = 4.59 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. $\circ-$ ordinate gives values $\times 10^{-5}$; titrimetric experiment; $[\text{H}^+] = 0.024 M$, $[\text{Fe}^{2+}]_0 = 6.4 \times 10^{-5}$, $C_3^0 = 3.15 \times 10^{-3}$, $C_6^0 = 9.65 \times 10^{-5}$ (last point corresponds to 78% completion of reaction), $k' = 7.71 \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. (Both experiments at $I = 0.0839 M$.)

measurements may be judged from two sets of three identical spectrophotometric experiments for which values of $10^{-3} k'$ were 8.4, 8.8, and 9.6 $\text{l. mole}^{-1} \text{ sec.}^{-1}$ for the one set and 6.8, 6.8, and 7.2 $\text{l. mole}^{-1} \text{ sec.}^{-1}$ for the other set at a different concentration of chromium(VI). In a pair of duplicate titrimetric experiments using independent sets of reagents, values of $10^{-3} k'$ were 7.7 and 8.0 $\text{l. mole}^{-1} \text{ sec.}^{-1}$. For most experiments conformity to the integrated rate equation demonstrates only that reaction is second order with respect to iron(II). The principal evidence regarding reaction orders for hydrogen ion, chromium(VI), and iron(III) comes from correlation of values of k' from different experiments. At this point account must be taken of the presence of chromium(VI) and iron(III) in reaction solutions in more than one form. Use of the equations

$$[\text{HCrO}_4^-] = C_6 \frac{[\text{H}^+]}{[\text{H}^+] + Q_{36}[\text{Fe}^{3+}]}, \text{ and}$$

$$[\text{Fe}^{3+}] = C_3 \frac{[\text{H}^+]}{[\text{H}^+] + Q_1}$$

in which $Q_1 = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]$, relates the rate coefficient k of the rate law

$$-d[\text{Fe}^{2+}]/dt = k[\text{Fe}^{2+}]^2[\text{HCrO}_4^-][\text{H}^+]^3/[\text{Fe}^{3+}] \quad (10)$$

to the rate coefficient k'

$$k = k' \frac{[\text{H}^+] + Q_{36}[\text{Fe}^{3+}]}{([\text{H}^+] + Q_1)[\text{H}^+]^3} \quad (11)$$

Two series of experiments at 0.0242 M hydrogen ion are relevant to the reaction order for aquoiron(III) ion. In a series of titrimetric experiments at an initial concentration of chromium(VI) of $9.65 \times 10^{-5} M$ with 1.58×10^{-3} , 3.15×10^{-3} , and $6.30 \times 10^{-3} M$ iron(III), values of $10^{-8} k$ were 8.2, 8.6, and 6.2 $\text{l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$, respectively. In spectrophotometric experiments at $3.5 \times 10^{-5} M$ chromium(VI) with 3.15×10^{-3} , 6.30×10^{-3} , and $9.45 \times 10^{-3} M$ iron(III), values of $10^{-8} k$

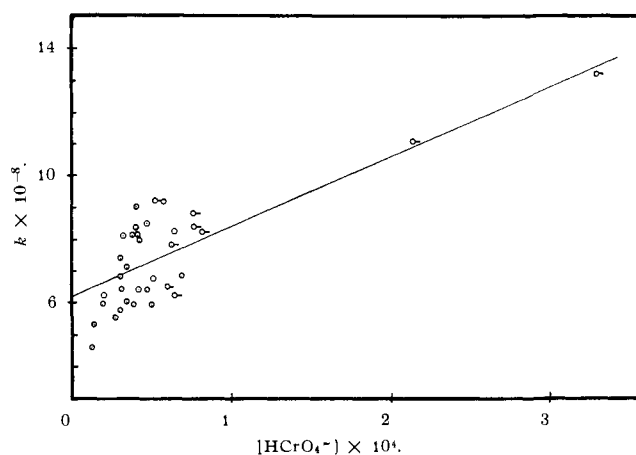


Fig. 2.—The dependence of k (defined by eq. 11) upon the average concentration of hydrogen chromate ion in each experiment: \circ , titrimetric experiments; $\circ-$, spectrophotometric experiments.

were 6.2, 7.8, and 5.8 $\text{l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$, respectively. Three series of experiments are relevant to the reaction order for hydrogen ion. At 0.0121, 0.0242, and 0.0483 M hydrogen ion, values of $10^{-8} k$ obtained in titrimetric experiments were 7.8, 8.6, and 6.5 $\text{l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$. At 0.0127, 0.0243, and 0.0463 M hydrogen ion, averaged values of $10^{-8} k$ obtained in two series of spectrophotometric experiments were 8.1, 7.7, and 6.0 $\text{l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$. Although there is scatter of the experimental values of k in these comparisons, they indicate that no other simple integral reaction orders would fit the data better.

There is an unmistakable trend in values of k from experiments with very different average concentrations of chromium(VI). A dependence

$$k = k_1 + k_2[\text{HCrO}_4^-] \quad (12)$$

corresponds to the straight line in Fig. 2 with $k_1 = 6.2 \times 10^8 \text{ l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$ and $k_2 = 2.2 \times 10^{12} \text{ l.}^5 \text{ mole}^{-5} \text{ sec.}^{-1}$.

The hydrogen ion dependence is not known for the rate law term which is second order in hydrogen chromate ion. The hydrogen ion concentration was not varied in experiments with the stoichiometric concentration of chromium(VI) larger than $9.6 \times 10^{-5} M$ because of the high rate of reaction, and it is only in experiments at higher concentrations of chromium(VI) that an appreciable fraction of reaction occurs by the pathway corresponding to this term.

Use of the integrated equation based on a first-order dependence upon chromium(VI) is not vitiated by this interpretation in terms of eq. 12. The quantity $(k_1 + k_2[\text{HCrO}_4^-])$ changed during an experiment by less than 10% in all except three titrimetric experiments (out of fourteen) and nine spectrophotometric experiments (out of twenty-six). Therefore, the provisional treatment in which first-order dependence upon chromium(VI) in a particular run was assumed is acceptable.

Spectrophotometric studies of interaction of iron(III) and chromium(VI) were not made at ionic strength 0.20 M . Since activity coefficients of many electrolytes do not vary greatly in the range of ionic strength 0.08 to 0.20 M , values of k' obtained at ionic strength 0.20 M were interpreted using $Q_{36} = 1.4$ obtained at ionic strength 0.0839 M . Values of $10^{-3} k'$ of 13.1, 11.4, 9.4, and 6.3 $\text{l. mole}^{-1} \text{ sec.}^{-1}$ obtained at concentration of aquoiron(III) ion of 3.1, 6.2, 12.1, and $24.7 \times 10^{-3} M$, respectively, are converted by eq. 11 to values of $10^{-9} k$, of 1.10, 1.13, 1.16, and 1.11 $\text{l.}^4 \text{ mole}^{-4} \text{ sec.}^{-1}$. The constancy of these calculated values is partly fortuitous

TABLE II
PARAMETERS FOR THE EQUATION $-2.3 \Delta \log [\text{Fe}(\text{phen})_3^{2+}] / \Delta t = k + k'[\text{Fe}(\text{phen})_3^{2+}]^a$, IONIC STRENGTH = 1.50 M

T, °C.	[H ⁺], M	[HCrO ₄ ⁻], ^d M							
		-2.38×10^{-4}		-4.77×10^{-4}		-7.15×10^{-4}		-9.53×10^{-4}	
		10 ^{2k}	10 ^{-2k'}	10 ^{2k}	10 ^{-2k'}	10 ^{2k}	10 ^{-2k'}	10 ^{2k}	10 ^{-2k'}
0	1.50	0.66	0.24	1.64	0.59	2.91	0.97	4.39	1.90
	1.00	.35	.099	0.83 ^c	.30 ^c	1.44	.69	2.52	1.09
	0.50	.069	.048	0.280	.111	0.52	.249	0.89	0.353
10	1.50	.78	.36	1.82	.96			4.98	3.70
	0.50	.117 ^b	.052 ^b	0.341 ^b	.144 ^b	0.704	0.292	1.23 ^b	0.53 ^b
20	0.50	.164	.065	0.44 ^b	.212 ^b	0.90	0.41	1.65 ^b	0.65 ^b
	1.00	.70 ^b	.28 ^b	1.79 ^c	.65 ^c	3.22 ^b	1.26 ^b	5.35 ^b	1.78 ^b
30	0.50	.211	.116	0.61	.31	1.19	0.50	1.87	0.93
	.25			.176	.144	0.353	.274	0.51	0.50
	.50	.362 ^b	.16 ^b	.83 ^b	.43 ^b	1.60	.82	2.34 ^b	1.43 ^b

^a Dimensions of $k = \text{sec.}^{-1}$, and of $k' = 1. \text{ mole}^{-1} \text{ sec.}^{-1}$. ^b The average of values obtained in two different runs. ^c The average of values obtained in three different runs. ^d Based upon assumption that only monomeric chromium(VI) species are present. At the highest concentration of chromium(VI) $\sim 20\%$ is present as dimeric species at 0°.

since with $Q_{36} = 1.4$ the concentration of hydrogen chromate ion in these solutions of constant stoichiometric concentration of chromium(VI) varies from 2.2×10^{-4} to 1.05×10^{-4} M as the concentration of aquoiron(III) ion increases, and, therefore, the relative importance of the two terms in eq. 12 varies. The data at ionic strength 0.200 M demonstrate, however, that an inverse dependence of reaction rate upon the concentration of aquoiron(III) ion is needed in experiments with relatively high chromium(VI) concentration. Values of $k'([\text{H}^+] + Q_{36}[\text{Fe}^{3+}]) / [\text{H}^+]^2 C_3$ at aquoiron(III) ion concentrations of 3.1, 6.2, 12.1, and 24.7×10^{-3} M vary by a factor of ~ 8 . Since the calculated concentration of hydrogen chromate ion varies by a factor of ~ 2 , it is reasonable to interpret these data in terms of eq. 10 and 12.

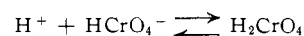
Benson's study⁵ of reaction 1 was carried out at higher concentrations of chromium(VI), lower concentrations of hydrogen ion, and lower concentration of iron(III) than in most of the experiments reported here. In addition, sulfate ion, not perchlorate ion, was present in solutions studied by Benson. These concentration changes favor complexing of iron(III) by chromium(VI), hydroxide ion, and sulfate ion, resulting in relatively little iron(III) being present as aquoiron(III) ion in the solutions studied by Benson ($\sim 25\%$ in a typical experiment). Benson mentions that a solid presumably iron(III) hydroxide, slowly precipitates from solution. Uncertainty in the nature of iron(III) makes obtaining a satisfactory rate law describing the dependence of rate upon the concentration of iron(III) impossible. By maintaining relatively constant total iron(III) concentration, Benson was able to obtain the second-power dependence of the rate upon the iron(II) concentration. Since relative amounts of chromium(VI) present as iron(II) complex and dichromate ion vary as the total chromium(VI) concentration changed, Benson's order of 1.7 with respect to chromium(VI) must be regarded as uncertain. In addition there is the possibility that a chromium(VI)-sulfur(VI) species,⁹ e.g., CrSO_4^{2-} , forms to an appreciable extent in these solutions.

Chromium(VI)-Tris-(1,10)-phenanthroline-iron(II) Reaction.—Values of $\Delta \log [\text{Fe}(\text{phen})_3^{2+}] / \Delta t$ depend upon the concentrations of tris-(1,10)-phenanthroline-iron(II) ion, chromium(VI), and hydrogen ion. Within each run only the concentration of tris-(1,10)-phenanthroline-iron(II) ion varied, and the concentration dependence is

$$-2.3 \times \frac{\Delta \log [\text{Fe}(\text{phen})_3^{2+}]}{\Delta t} = k + k'[\text{Fe}(\text{phen})_3^{2+}] \quad (13)$$

with the second-order term contributing from 20 to 50% at 10^{-5} M tris-(1,10)-phenanthroline-iron(II)

ion, the concentration at 50% reaction in most experiments. Values of k and k' were obtained by fitting the data to eq. 13 with the method of averages. The parameters so determined are presented in Table II, if used to recalculate values of $\Delta \log [\text{Fe}(\text{phen})_3^{2+}] / \Delta t$, they do so with an average deviation of 1-3%. The coefficients k and k' depend upon the concentrations of both chromium(VI) and hydrogen ion to powers between first and second. Interpretation of the dependence of rate upon hydrogen ion concentration is complicated by the equilibrium



which occurs to an appreciable extent in the activity range in question.⁹ The precision of the values of k and k' does not warrant their correlation to obtain four rate coefficients from each of them, *i.e.*

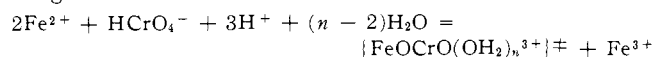
$$k = (k_1[\text{HCrO}_4^-] + k_2[\text{HCrO}_4^-]^2)(k_a[\text{H}^+] + k_b[\text{H}^+]^2)$$

$$k' = (k_1'[\text{HCrO}_4^-] + k_2'[\text{HCrO}_4^-]^2)(k_a'[\text{H}^+] + k_b'[\text{H}^+]^2)$$

Discussion

The stability of the iron(III)-chromium(VI) complex is high compared to the corresponding chromium(III)-chromium(VI) complex.¹⁸ Although the observed absorbancy enhancement in solutions containing chromium(III) and chromium(VI) did not allow evaluation of both equilibrium quotient and absorbancy index, the data set an upper limit on the equilibrium quotient corresponding to Q_{36} . This is $\sim 10^{-2}$, or approximately 10^2 -fold smaller than for the iron(III)-chromate complex. Ligand field stabilization contributes differently to the stability of complexes of chromium(III) which are stabilized and iron(III) which in the high spin state are not. In particular, if water as a ligand exerts a much greater ligand field stabilization than chromate ion, the lower stability of the chromium(III)-chromate complex relative to the iron(III)-chromate complex is rationalized.

The mechanism for reaction of hydrogen chromate ion and aquoiron(II) ion suggested by the empirical rate law is essentially that discussed by Westheimer involving a rate-determining reaction of aquoiron(II) ion and a species of chromium(V).⁶ The net activation process¹⁹ corresponding to the term first order in hydrogen chromate ion is



The transition state contains one iron(II) atom and one chromium(V) atom which are in the act of becoming iron(III) and chromium(IV). Corresponding to the term second order in hydrogen chromate ion, the transi-

(18) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

(19) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

tion state contains two chromium atoms with an average oxidation number of +5.5 and one iron(II) atom. Presumably the reactant in this rate-determining step is a dimeric species containing one chromium(V) atom and one chromium(VI) atom, *e.g.*, $\text{Cr}_2\text{O}_7\text{H}_n^{n-3}$.

The equation for the net reaction involves seven hydrogen ions on the reactant side. The positive reaction order with respect to hydrogen ion results from the economy in free energy of activation of adding some protons before formation of the transition state. A transition state containing one aquoiron(II) ion and one anionic chromium(V) species giving either aquoiron(III) ion or hydroxoiron(III) ion would also produce a species of chromium(IV) with a much more negative charge than that on the predominant chromium(IV) species at the acidity in question. This is avoided by involving protons in the net activation process.

The suggestion⁴ that the coordination number of chromium changes from four in chromium(V)²⁰ to six in chromium(IV) and that this is a factor in making the chromium(V) \leftrightarrow chromium(IV) transformation rate determining both in reactions of chromium(III) and one-equivalent oxidizing agents (*e.g.*, cerium(IV))⁴ and in reactions of chromium(VI) and one-equivalent reducing agents (*e.g.*, aquoiron(II) ion) remains appealing.

The reaction of chromium(VI) and tris-(1,10-phenanthroline)-iron(II) ion goes *via* transition states of four different compositions with respect to numbers of chromium atoms and iron atoms. With different degrees of protonation taken into account, there probably are even more than four independent transition states. The absence of retardation of reaction by tris-(1,10-phenanthroline)-iron(III) ion demonstrates that reduction of a species of chromium(V) is not rate determining in this reaction, so the appealing generalization of the last paragraph is not completely general. If, as seems reasonable, the transition state containing one tris-(1,10-phenanthroline)-iron(II) ion and one chromium(VI) atom gives chromium(V) and tris-(1,10-phenanthroline)-iron(III) ion, the concentration of chromium(V) does not build up to its equilibrium value; further reduction of chromium(V) must be rapid compared to re-oxidation to chromium(VI) by tris-(1,10-phenanthroline)-iron(III) ion. That in the competition between species of iron(II) and iron(III) for chromium(V), aquoiron(III) ion wins over aquoiron(II) ion but tris-(1,10-phenanthroline)-iron(II) ion wins over tris-(1,10-phenanthroline)-iron(III) ion is *not* what one would expect if there were a correlation of reaction rate and thermodynamic tendency for reaction to occur.²¹ Aquoiron(III) ion is a poorer oxidizing agent than tris-(1,10-phenanthroline)-iron(III) ion.²²

This lack of correlation of reaction rate and thermodynamic tendency for reaction to occur may be due to the different types of transition states accessible to the two iron(II) species. Reactions of tris-(1,10-phenanthroline)-iron(II) ion and tris-(1,10-phenanthroline)-iron(III) ion with chromium species necessarily occur by outer-sphere transition states,²³ but corresponding

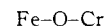
(20) However, the reflectance spectrum of $(\text{NH}_4)_2\text{CrOCl}_6$, a compound of chromium(V), has been interpreted in terms of an assumed octahedral configuration about chromium(V) (H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962)).

(21) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(22) The values of E° for the two half-reactions differ by 0.29 v.

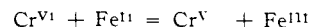
(23) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

reactions of aquoiron(II) ion and aquoiron(III) ion may occur by inner-sphere transition states²³ involving an oxygen bridge

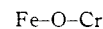


Reaction *via* the inner-sphere oxygen-bridged transition state appears to be faster if the coordination number of chromium does not change (the chromium(VI)-chromium(V) transformation), but reaction *via* the outer-sphere transition state appears to be faster if the coordination number of chromium changes (the chromium(V)-chromium(IV) transformation). Perhaps it is reasonable for the increase in coordination number in the chromium(V)-chromium(IV) transformation to be more easily accomplished with the reducing agent which does not insist on bridging to chromium. With tris-(1,10-phenanthroline)-iron(II) ion as reducing agent, solvent water molecules enter the coordination sphere of chromium(V) in the outer-sphere transition state by which chromium(V) is reduced to chromium(IV). The newly formed chromium(IV) can keep these water molecules. With aquoiron(II) ion as reducing agent, an oxygen atom shared between chromium and iron in an inner-sphere transition state does not necessarily build up the coordination number of chromium. After the transformation to chromium(IV) and iron(III), both metal atoms would like to keep the bridging oxygen. The break-up of an inner-sphere transition state in which each metal atom has its preferred coordination number necessarily leads to an immediate product having a lower coordination number.

It is not as straightforward to understand the greater facility of aquoiron ions in the reaction involving no change of coordination number for the chromium species. The postulation of such facility is, however, consistent with the greater rate of the chromium(VI)-aquoiron(II) ion reaction than the chromium(VI)-tris-(1,10-phenanthroline)-iron(II) ion reaction. Although exact quantitative comparisons are not possible because of differences of form of the rate laws, the composite second-order rate constant for reaction of aquoiron(II) ion with all forms of chromium(VI) is much larger than the corresponding quantity for reaction of tris-(1,10-phenanthroline)-iron(II) ion with all forms of chromium(VI). This comparison parallels the thermodynamic tendency for the reaction



to occur. Equilibrium in this first step is unfavorable for aquoiron(II) ion and is even less so for tris-(1,10-phenanthroline)-iron(II) ion, the difference in equilibrium constants being $\sim 10^6$. Perhaps this is all that is needed in an explanation of their relative rates. If additional "kinetic" rationalization is necessary, the accessibility of an inner-sphere transition state with the configuration



to aquoiron(II) ion which is not open to tris-(1,10-phenanthroline)-iron(II) ion may be part of the answer.

Relatively little can be said about the other pathways for reaction of chromium(VI) and tris-(1,10-phenanthroline)-iron(II) ion. Those containing two chromium(VI) atoms probably involve dichromate ion as reactant. Whether transition states involving two iron(II) atoms lead directly to chromium(IV) is not known.