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Article

Kinetics of the Reaction of Chromium(VI) with Tris(1,10-phenanthroline)iron(II) Ions in Acidic Solutions. Anion and Medium Effects: Perchlorate versus Triflate

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Reinvestigation of the reaction between title reagents in aqueous acidic triflate and perchlorate media revealed an unusual difference: the reaction is strictly first-order with respect to the concentration of $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) in the triflate medium but shows an additional, but we believe artifactual, higher-order term in the perchlorate medium. We postulate that the apparent orders with respect to $[Fe(phen)_3^{2+}]$ in $(H/Li)ClO_4$ do not indicate the actual chemical mechanism but, in whole or in part, the orders, particularly the higher-order component, reflect an interaction specific to $Fe(phen)_3^{2+}$ or $Fe(phen)_3^{3+}$ and ClO_4^- in solution. Data in $(H/Li)O_3SCF_3$ solutions indicate that, in the absence of added $Fe(phen)_3^{3+}$, the first of the three sequential electron-transfer steps is rate controlling. Reactions started in the presence of the product $Fe(phen)_3^{3+}$ occur somewhat more slowly, suggesting the first electron transfer is reversible. This finding allows the relative rate constants for Cr(V) oxidation and reduction to be evaluated, with limited precision, by two methods of analysis. The dependences on [Cr(VI)] can be resolved into contributions from the species $HCrO_4^-$ and $Cr_2O_7^{2-}$, each of which in turn depends on $[H^+]$. The reaction mechanism is discussed in light of the data obtained in the triflate medium. Further, the rate constants for certain steps can be considered in light of E^0 for the Cr(VI)/(V) couple.

Introduction

The reaction between chromium(VI) and tris(1,10-phenanthroline)iron(II), $Fe(phen)_3^{2+}$ (eq 1), was investigated decades ago[1] in perchloric acid solutions. In the presence of excess chromium(VI), the reaction rate showed deviations from a pseudo-first-order dependence on the $Fe(phen)_3^{2+}$ concentration in a direction that could be rationalized empirically in terms of an added higher-order term; no precision is lost by referring to the added term as having an apparent kinetic order of 2, but that statement is made with reservation, as will be made clear.

$$HCrO_4^- + 3Fe(phen)_3^{2+} + 7H^+ + 2H_2O = Cr(H_2O)_6^{3+} + 3Fe(phen)_3^{3+} \quad (1)$$
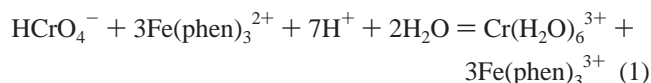
It is not clear why a "second-order" term should exist. Were the phenomenon to be taken literally, two $Fe(phen)_3^{2+}$

ions would be incorporated into the transition state to reduce a single chromium(VI) directly to chromium(IV), thus, circumventing a chromium(V) intermediate in that reaction pathway. However, other possibilities also exist: for example, it is suspected that presumably innocent perchlorate ions may interact in some manner with $Fe(phen)_3^{2+/3+}$ ions by outer-sphere complex formation[2] or by precipitation.[3] As a result, deviations from simple kinetics could be expected.

Here we present a reinvestigation of this reaction in a triflic acid medium. The results show that the higher-order dependence on $Fe(phen)_3^{2+}$ in perchlorate solutions no longer appears. The results in the perchlorate medium more likely arise from a special interaction, as suggested in the preceding paragraph, rather than as a representation of a genuine contribution from events related to the main electron-transfer chemistry. The reaction mechanism was further elucidated on the basis of kinetic behavior in the triflate medium where the data are entirely tractable.

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(1) Espenson, J. H.; King, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3328−3333.

(2) Johansson, L. *Chem. Scr.* **1976**, *9*, 30−35.

(3) Lednicky, L. A.; Stanbury, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3098−3101.

Experimental Section

Caution: Chromium(VI) is a known human carcinogen, and perchlorates are potentially explosive. Appropriate care should be taken in handling these substances.
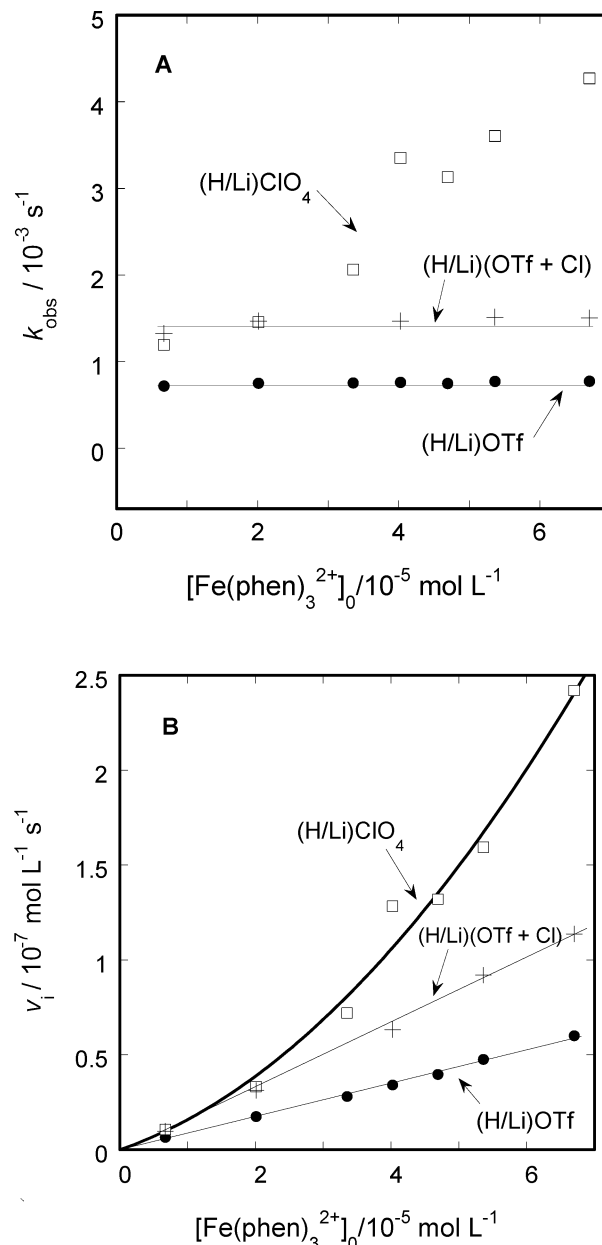
Materials. All the solutions were prepared with high purity water, which was obtained by passing laboratory distilled water through a Millipore Milli-Q water purification system. Reagent grade potassium dichromate was used to prepare chromium(VI) solutions. Solutions of trifluoromethanesulfonic acid (triflic acid, HOTf) were prepared by the dilution of the pure acid. Tris(1,10-phenanthroline)iron(II) solutions were made with iron(II) triflate and a stoichiometric amount of 1,10-phenanthroline in water. The "added" $Fe(phen)_3^{3+}$ referred to subsequently was, in fact, obtained by the use of spent reaction solutions as the solvent for the next kinetics experiment, often several times in succession; dilution effects were minimal owing to the volumes needed.

Instruments. Kinetics measurements were performed with conventional UV−visible spectrophotometers (Shimadzu UV-2101PC and 3101PC). Quartz cuvettes with 1−5 cm optical path lengths were used. The kinetics was studied at 25.0 ± 0.2 °C, maintained by either an electronic thermostatic holder or a circulating water thermostatic system.

Kinetics. The reaction progress was conveniently monitored by following the disappearance of $Fe(phen)_3^{2+}$ at 510 nm, where Fe-$(phen)_3^{2+}$ has an absorption maxima with $\epsilon = 1.11 \times 10^4$ L mol^{-1} cm^{-1}.[4] The absorbance−time data follow pseudo-first-order kinetics in triflic acid solutions. The same method, although rigorously incorrect, was used to gain approximate pseudo-first-order rate constants in perchloric acid solutions. Further, the absorbance data were transformed to concentration units, which were used in a sixth-order polynomial fit for initial rate (v_i) determinations, as in $[Fe^{II}]_t = [Fe^{II}]_0 - m_1t - m_2t^2 - ... - m_6t^6$, from which $v_i = m_1$.[5]

Results

Iron(II) Dependence. The first series of experiments was carried out in a $HClO_4$−$LiClO_4$ medium to verify the reported iron(II) dependence.[1] The conditions were as follows: 0.20 mmol L^{-1} Cr(VI), 0.0067−0.067 mmol L^{-1} $Fe(phen)_3^{2+}$ in 0.60 mol L^{-1} $HClO_4$ at 1.0 mol L^{-1} ionic strength, maintained with $LiClO_4$. The absorbance−time data were fitted to a single-exponential equation, although deviations from first-order kinetics were noted after about two half times. The values of k_{obs} in (H/Li)ClO_4 were comparable to those in the literature under similar conditions and clearly increased with increasing iron(II) concentration, as shown in Figure 1A, consistent with the literature.[1] An initial rate analysis gave the equivalent result, as presented in Figure 1B. The fitted curve for the initial rate data in perchlorate media, shown in Figure 1B, corresponds to the equation $v_i = ac + bc^2$, where $c = [Fe(phen)_3^{2+}]_0$, although this particular form is shown for empirical purposes only, not to define authentic reaction orders. Linear extrapolation of the perchlorate data in Figure 1A to $c = 0$ gives $k_{obs} = 6 \times 10^{-4}$ s^{-1}, not significantly different from the value 7.5×10^{-4} s^{-1} in (H/Li)OTf solutions.

(4) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830−1834.
(5) Hall, K. J.; Quickenden, T. I.; Watts, D. W. *J. Chem. Educ.* **1976**, *53*, 493−494.
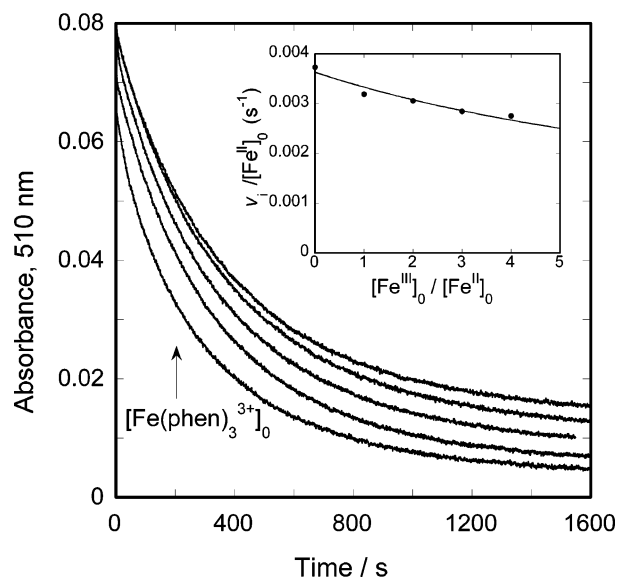(6) Ilcheva, L.; Bek, M.; Georgieva, M. *Khim. Ind.* **1980**, 28−32.

Figure 1. Plots showing the Fe(II) dependencies of the chromium(VI)−$Fe(phen)_3^{2+}$ reaction at 25 °C analyzed in terms of the pseudo-first-order kinetics (A) and in terms of the initial rates (B). The conditions are as follows: 0.20 mmol L^{-1} Cr(VI), 0.0067−0.067 mmol L^{-1} $Fe(phen)_3^{2+}$, 0.60 mol L^{-1} $HClO_4$ + 0.40 mol L^{-1} $LiClO_4$ (open squares), 0.60 mol L^{-1} HOTf + 0.40 mol L^{-1} LiOTf (closed circles), and 0.60 mol L^{-1} HOTf + 0.30 mol L^{-1} LiOTf + 0.10 mol L^{-1} LiCl (pluses). The fitted curve in panel **B**, in a perchlorate medium, is a fit to the empirical equation $v_i = ac + bc^2$, where $c = [Fe(phen)_3^{2+}]_0$.

A second series of experiments was carried out under similar conditions, except that a (H/Li)OTf medium was employed. It was somewhat surprising that the reaction was then slower than in the (H/Li)ClO_4 medium at finite values of $[Fe(phen)_3^{2+}]$. The values of k_{obs} remained essentially independent of $[Fe(phen)_3^{2+}]_0$, however, as shown in Figure 1A. This is just as one would normally expect when varying the concentration of the limiting reagent under pseudo-first-order conditions when the reaction is indeed first order with respect to the limiting concentration. Strictly speaking, however, a slight (ca. 7%) rate increase was noted when [Fe-

$(phen)_3^{2+}]_0$ was increased over the 10-fold concentration range investigated. Although this small deviation may signal other complications, we suggest that the validity of first-order kinetics is acceptable. Furthermore, the behavior in the $(H/Li)ClO_4$ medium is unreasonable, which is the principal point being made.

This difference in the $Fe(phen)_3^{2+}$ dependencies in the two media was also obvious when the initial rates were plotted against the initial iron(II) concentrations, as shown in Figure 1B. In HOTf, the plot shows a usual linear (first-order) dependence on $[Fe(phen)_3^{2+}]$, whereas in $HClO_4$, the higher-order dependence on $[Fe(phen)_3^{2+}]$ is evident. These results, taken together, clearly demonstrate that the perchlorate medium is not "innocent" in this particular system.

One possible source of complications is an outer-sphere complex formation between the tris(1,10-phenanthroline)-iron(II) and the perchlorate ions, which was shown to be quite strong in comparison with halides, acetate, and so forth.[2] The formation of an outer-sphere complex between $Fe(phen)_3^{2+}$ and OTf^- has not been reported, although OAc^- exerts such a weak effect that we surmise that its fluorinated analogue, being a weaker Lewis base, would exhibit an even weaker extent of outer-sphere complex formation with tris-(phenanthroline) complexes.[6] This explanation may not be the correct one. Lednicky and Stanbury reported that the oxidation of $Fe(phen)_3^{2+}$ by ClO_2 in $(H/Na)ClO_4$ solutions gave inconsistent data. In particular, the evaluated equilibrium constant "showed extreme sensitivity to an increase in ionic strength". These authors further stated the following: "The effects were ultimately traced to a virtually imperceptible precipitation of the perchlorate salt of the iron(III) complex."[3] They subsequently adopted a $(H/Na)OTf$ medium, which "gave much more reasonable results because of the high solubility of $[Fe(phen)_3^{3+}](CF_3SO_3)_3$".[7]
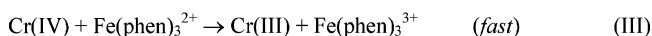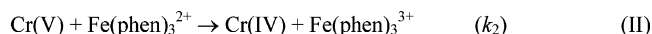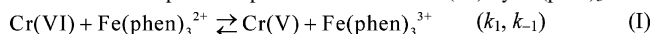
It is not clear why the formation of an outer-sphere complex or the precipitation of the product would exhibit its effect by increasing the reaction rate and raising the order with respect to $[Fe(phen)_3^{2+}]$ above unity. What is evident, however, is that $(H/Li)ClO_4$ solutions do not constitute a suitable medium for studies of this species.

Kinetics with Initially Added $Fe(phen)_3^{3+}$. A series of experiments was carried out by successively adding $Fe(phen)_3^{2+}$ to a spent reaction solution in $(H/Li)OTf$ solutions. In this way, a defined concentration of $Fe(phen)_3^{3+}$, in 0.067 mmol L^{-1} increments, was introduced at the beginning of the next reaction. A set of typical kinetic traces is shown in Figure 2. (The increase of the baseline simply reflects the accumulation of the oxidation product, $Fe(phen)_3^{3+}$, with $\epsilon_{510} = 292$ L mol^{-1} cm^{-1}; the agreement is some evidence in support of the 3:1 stoichiometry written in eq 1.) The value of k_{obs} decreased in each successive run, indicating that $Fe(phen)_3^{3+}$ inhibits the reaction. This observation is different from the earlier results in $(H/Li)ClO_4$ solutions, where the initial addition of the slightly soluble $[Fe(phen)_3^{3+}](ClO_4)_3$ showed little effect on the reaction rate.[1] Of course, as

(7) We are grateful to Professor D. M. Stanbury for calling our attention to these statements.

Figure 2. Time course of $Cr(VI)-Fe(phen)_3^{2+}$ reactions at 25 °C in 0.60 mol L^{-1} HOTf and 0.40 mol L^{-1} LiOTf. The conditions are as follows: 0.40 mmol L^{-1} Cr(VI) and 0.067 mmol L^{-1} $Fe(phen)_3^{2+}$. The Fe(II) reagent was added in successive 0.01 mL increments to 2.98 mL of solution, from bottom to top, as the means of increasing $[Fe(phen)_3^{3+}]$ at the start of the next run. The inset shows the retarding effect of $Fe(phen)_3^{3+}$ from the initial rate data, as fitted by the nonlinear form in eq 3.

Scheme 1. Proposed Stepwise Reduction of Cr(VI) by $Fe(phen)_3^{2+}$

$$Cr(VI) + Fe(phen)_3^{2+} \rightleftarrows Cr(V) + Fe(phen)_3^{3+} \qquad (k_1, k_{-1}) \qquad (I)$$

$$Cr(V) + Fe(phen)_3^{2+} \rightarrow Cr(IV) + Fe(phen)_3^{3+} \qquad (k_2) \qquad (II)$$

$$Cr(IV) + Fe(phen)_3^{2+} \rightarrow Cr(III) + Fe(phen)_3^{3+} \qquad (fast) \qquad (III)$$

remarked above, we have already discounted perchlorate solutions as an appropriate medium.

Although Cr(VI) is a strong oxidant in the overall three-electron transformation to Cr(III), its initial single-electron reduction to Cr(V) is much less exergonic. The Cr(VI) oxidation of the single-electron reducing agents has been suggested to proceed in three successive steps, as presented in Scheme 1.[8] At this point, a certain liberty has been taken in Scheme 1 and eq 2 in that Cr(VI) is represented as a single entity; individual effects of $HCrO_4^-$ and $Cr_2O_7^{2-}$ will be resolved in the next section.

The retarding effect of $Fe(phen)_3^{3+}$ on the reaction suggests that the rate-controlling step is usually step I of Scheme 1 but that, with added $Fe(phen)_3^{3+}$, step II can assume that role. The duality of the rate-controlling steps is expressed by eq 2,[9] in which the steady-state approximation has been made for the highly reactive Cr(V) intermediate.

$$v = -\frac{d[Fe(phen)_3^{2+}]}{dt} =$$

$$\frac{3k_1k_2[Fe(phen)_3^{2+}]^2[Cr(VI)]_T}{k_{-1}[Fe(phen)_3^{3+}] + k_2[Fe(phen)_3^{2+}]} \quad (2)$$

The reversibility of step I is not surprising because the thermodynamic data indicate that the equilibrium lies to the

(8) Westheimer, F. H. *Chem. Rev.* **1949**, *45*, 419−451.

left: the standard reduction potential for the Cr(VI)/(V) pair has been estimated to be $+0.55$ V,[10] whereas that of the Fe(phen)$_3^{3+/2+}$ couple is $+1.06$ V.[4] As the inset to Figure 2 illustrates, the rate-retarding effect of Fe(phen)$_3^{3+}$ is not particularly great over the concentration range the system permitted for investigation. Nonetheless, we have attempted to estimate the magnitude of k_2/k_{-1} by two methods. First, eq 2 can be rearranged as follows:
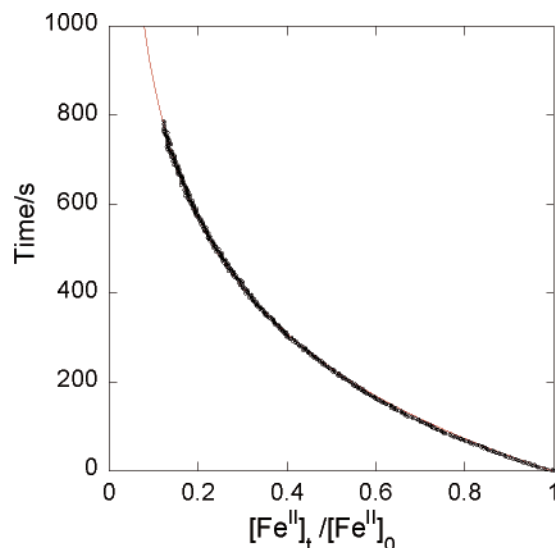
$$\frac{v_i}{[\text{Fe(phen)}_3^{2+}]_0} = \frac{3k_1k_2/k_{-1}}{\left(\dfrac{[\text{Fe(phen)}_3^{3+}]}{[\text{Fe(phen)}_3^{2+}]}\right) + \left(\dfrac{k_2}{k_{-1}}\right)} \times [\text{Cr(VI)}]_T \tag{3}$$

To implement this analysis, a plot of $v_i/[\text{Fe}^{II}]_0$ against $[\text{Fe}^{III}]_0/[\text{Fe}^{II}]_0$ was constructed; it is shown in the inset to Figure 2. From this plot, the ratio $k_2/k_{-1} = 11 \pm 2$ was evaluated by nonlinear least-squares fitting.[11] This result is consistent with the assumption that the reaction is generally first-order with respect to $[\text{Fe(phen)}_3^{2+}]$, that is, the reverse of step I is negligible in the kinetic fitting in the early stages and when Fe(phen)$_3^{3+}$ is not initially added, but that the denominator term, $k_{-1}[\text{Fe(phen)}_3^{3+}]$, gains force as Fe-(phen)$_3^{3+}$ accumulates.

The second method of analysis proceeds as follows. The literature[12] presents an expression for the integrated form of eq 2 as it applies to a scheme analogous to that in Scheme 1. The integrated rate law for this system is given by eq 4.

$$\left(1 - \frac{k_2}{k_{-1}}\right)\ln\left(\frac{[\text{Fe}^{II}]_t}{[\text{Fe}^{II}]_0}\right) - \left(1 + \frac{[\text{Fe}^{III}]_0}{[\text{Fe}^{II}]_0}\right)\left(1 - \frac{[\text{Fe}^{II}]_0}{[\text{Fe}^{II}]_t}\right) = \frac{3k_1k_2}{k_{-1}}[\text{Cr(VI)}]_T t \tag{4}$$

This is a transcendental equation, however, admitting no explicit solution for $[\text{Fe(phen)}_3^{2+}]_t$ as a function of time. We devised a different procedure for which we were unable to find a literature precedent. Rearrangement of eq 4 affords an expression for time as a function of concentration, as in eq 5. Although it is undesirable from a statistical viewpoint to reverse the roles of independent and dependent variables, necessity dictated that this method be attempted. Regression analysis of the individual traces according to this equation yields a k_2/k_{-1} ratio of about 20. A typical fit to eq 5 is shown in Figure 3. (It should be noted, however, that this treatment is not suitable, as a reviewer pointed out, for kinetic curves carried to high conversion because the extremely small
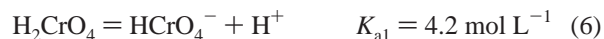
(9) At this stage, the rate is expressed in terms of the total concentration of chromium(VI), which, being present in large stoichiometric excess, is effectively constant in each experiment. Thus, $[\text{Cr(VI)}]_T$ is used in eqs 2–5, although the subsequent analysis presents a more complex factoring into the individual dependences on HCrO$_4^-$ and Cr$_2$O$_7^{2-}$.

(10) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985.

(11) That is, by fitting data to eq 9 with the program KaleidaGraph. The left-hand side (y) is the function $y = \{k_1M/[x + M)]\}[\text{Cr(VI)}]$, where x is the concentration ratio, where M is the fitted rate constant ratio, and with [Cr(VI)] held at a constant value, 0.40 mmol L^{-1}.

(12) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472–7482.

Figure 3. Typical fit to eq 5 of the data in Figure 2 with 0.067 mmol L^{-1} Fe(phen)$_3^{3+}$ initially added. Data display and analysis were terminated at 90% reaction (ca. 770 s in this experiment) because of errors introduced at high conversion, as described in the text. The fitted curve is shown as a thin line superimposed on the thicker points that represent the experimental data.

changes in concentration at the end correspond to huge differences in the reaction time.)

$$t = \left[\left(1 - \frac{k_2}{k_{-1}}\right)\ln\left(\frac{[\text{Fe}^{II}]_t}{[\text{Fe}^{II}]_0}\right) - \left(1 + \frac{[\text{Fe}^{III}]_0}{[\text{Fe}^{II}]_0}\right)\left(1 - \frac{[\text{Fe}^{II}]_0}{[\text{Fe}^{II}]_t}\right)\right] / 3[(k_1k_2)/k_{-1}][\text{Cr(VI)}]_T \tag{5}$$

Chromium(VI) and Hydrogen Ion Dependences. In aqueous acidic solution chromium(VI) exists in three principal forms, as described by eqs 6 and 7; note that [CrO$_4^{2-}$] is entirely negligible owing to the small value of K_{a2}, $(3.2-13) \times 10^{-7}$ mol L^{-1}

$$\text{H}_2\text{CrO}_4 = \text{HCrO}_4^- + \text{H}^+ \qquad K_{a1} = 4.2 \text{ mol L}^{-1} \tag{6}$$

$$2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \qquad K_d = 98 \text{ L mol}^{-1} \tag{7}$$

Various determinations of the equilibrium constants have been reported, with values varying in the range of $K_{a1} = 0.7-6.3$ mol L^{-1} and $K_d = 23-158$ L mol^{-1}.[10,13–17] The values listed in eqs 6 and 7 are the ones that we deem the most reliable[16,17] and have, thus, been used here to derive the HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ concentrations. The predominant species are HCrO$_4^-$ and H$_2$CrO$_4$, generally making up >90% of the total chromium. Although [Cr$_2$O$_7^{2-}$] is low, its effect on the kinetics cannot be ignored, as will be shown

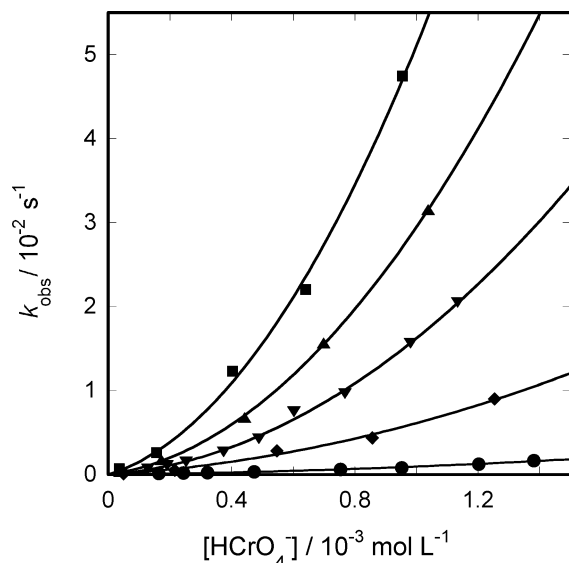(13) Davies, K. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 1884–1888.

(14) Buxton, G. V.; Djouider, F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4173–4176.

(15) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.

(16) Tong, J. Y.; King, E. L. *J. Am. Chem. Soc.* **1953**, *75*, 6180–6186.

(17) Tong, J. Y. *Inorg. Chem.* **1964**, *3*, 1804–1805.

Figure 4. Plots showing the variation of k_{obs} with [HCrO$_4^-$] at various [H$^+$]. The conditions are as follows: 0.020 mmol L^{-1} Fe(phen)$_3^{2+}$; HOTf concentrations decreasing downward, 0.20 (●), 0.40 (◆), 0.60 (▼), 0.80 (▲), and 1.0 (■) mol L^{-1}, at 25.0 °C; and an ionic strength of 1.0 mol L^{-1} (maintained with LiOTf). Values of [Cr(VI)]$_T$ were 0.067−2.0 mmol L^{-1}. Concentrations of HCrO$_4^-$ were calculated from eq 8. The lines depict the fitting to eq 9.

subsequently. From eqs 6 and 7, this expression follows for the concentration of the hydrogen chromate ion.[18]

$$[HCrO_4^-] = \frac{-A + \sqrt{A^2 + 8K_d[Cr(VI)]_T}}{4K_d},$$
$$\text{where } A = (K_{a1} + [H^+])/K_{a1} \quad (8)$$

The dependence on the total chromium(VI) concentration was assessed by varying [Cr(VI)]$_T$ in the range 0.067−2.0 mmol L^{-1} at a given [H$^+$] level, 0.2−1.0 mol L^{-1}, with both [Fe(phen)$_3^{2+}$] and ionic strength unchanged in a total of 33 determinations. Plots of k_{obs} against [HCrO$_4^-$] at each [H$^+$] are shown in Figure 4. The data at each [H$^+$] could be fit by eq 9.

$$k_{obs} = k_a'[HCrO_4^-] + k_b'[HCrO_4^-]^2 \quad (9)$$

It is not statistically reliable, however, to examine the fit first to one independent variable, [HCrO$_4^-$] in this instance, and then to a second, namely, [H$^+$]. We, therefore, used the program Scientist[19] to conduct a weighted least-squares fit to both variables simultaneously. The best fit, giving an overall standard deviation of 11% in 33 experiments, is given by eq 10, with the parameters k_a = 14.2 ± 1.3 L^3 mol^{-3} s^{-1} and k_b = (1.78 ± 0.27) × 10^4 L^4 mol^{-4} s^{-1}. The k_b term represents the contribution of Cr$_2$O$_7^{2-}$; its specific contribution is given as $k_c = k_b/K_d = 1.82 \times 10^2$ L^3 mol^{-3} s^{-1}. Several other attempted rate laws gave fits with negative parameters;

(18) Because the concentrations of the Cr(VI) species and that of H$^+$ are coupled, as in eqs 6 and 7, only the expressions for [HCrO$_4^-$] and [Cr$_2$O$_7^{2-}$] are material. A value of [H$_2$CrO$_4$] is immediately related to [HCrO$_4^-$] by eq 6, and, thus, any kinetic term for the former, such as [H$^+$]^n[HCrO$_4^-$], is indistinguishable from [H$^+$]$^{n-1}$[H$_2$CrO$_4$].

(19) *Scientist*, version 2.0.1; Micro-Math Scientific Software, Inc.: Salt Lake City, UT, 1995.
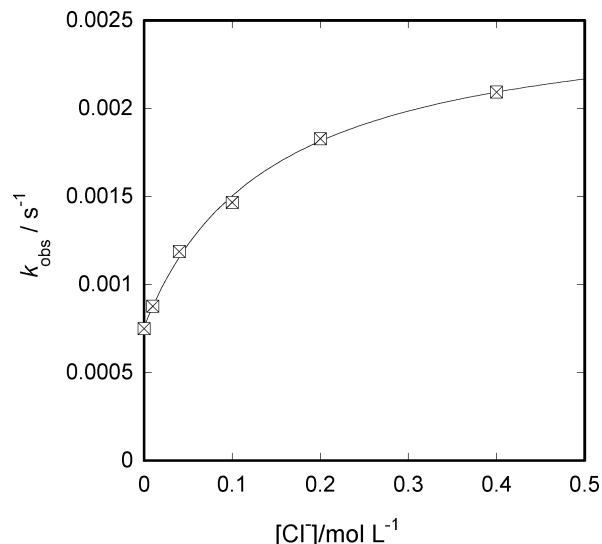
Figure 5. Plot showing the effect of chloride on the Cr(VI)−Fe(phen)$_3^{2+}$ reaction. The conditions are as follows: 0.20 mmol L^{-1} Cr(VI), 0.020 mmol L^{-1} Fe(phen)$_3^{2+}$, 0.60 mol L^{-1} HOTf, at 25 °C, and an ionic strength of 1.0 mol L^{-1} (maintained with LiOTf). The line depicts the fitting to eq 12 with K_{Cl} fixed at its established value.

others contained too many terms to be meaningful. The involvement of hydrogen ions in the transition state is certainly not unreasonable: protonation of a Brönsted base (or deprotonation of a Brönsted acid in the general case) is often energetically favorable.[20]

$$k_{obs} = k_a[HCrO_4^-][H^+]^2 + k_b[HCrO_4^-]^2[H^+]^2$$
$$= k_a[HCrO_4^-][H^+]^2 + k_c[Cr_2O_7^{2-}][H^+]^2 \quad (10)$$

Effect of Chloride Ions. One might inquire whether the unusual kinetic dependency on Fe(II) in perchlorate media might be due to the presence of trace adventitious chloride. Thus, varying concentrations of lithium chloride were added intentionally, and the rate constants were measured at otherwise identical conditions. It is obvious that chloride ions exhibit a significant accelerating effect. The plot of the measured rate constants versus [Cl$^-$] shows the saturation behavior, Figure 5. Similar experiments were carried out in triflate media with added HClO$_4$ (0−0.60 mol L^{-1}) or LiClO$_4$ (0−0.40 mol L^{-1}), keeping hydrogen and lithium ion concentrations constant. A smaller accelerating effect, which was linearly dependent on added [HClO$_4$] or [LiClO$_4$], was noticed in the concentration range investigated. The linear dependency was not in disagreement with the saturation kinetics by chloride, considering the concentration range. However, if the accelerating effect is to be attributed entirely

(20) We defend this generalization by noting that redox reactions of oxoanions often present multiterm hydrogen ion dependences, as do redox reactions of M(H$_2$O)$_n^{m+}$ ions, where M(H$_2$O)$_{n-1}$OH$^{(m-1)+}$ is often a participant. Further, ligand substitution reactions of aqua metal ions often proceed by parallel reactions of M(H$_2$O)$_n^{m+}$ and M(H$_2$O)$_{n-1}$OH$^{(m-1)+}$; indeed, the hydroxo complex, although not predominant, will often have the larger second-order rate constant. The cases of M = Fe and Cr are particularly well-established in this respect. Without citing specifics here, the reader is referred to the many examples presented in this citation: Wilkins, R. G. *Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH Publishers: New York, 1991.

to chloride, it would require the presence of 1−2% chloride in LiClO₄ and 6−8% chloride in HClO₄, which appear unreasonably high. Further, tests of LiClO₄ and HClO₄ solutions with silver nitrate revealed no detectable chloride. Another test is to run a series of reactions with added LiCl (0.10 mol L^{-1}) and varying the Fe(phen)$_3^{2+}$ concentration. The behavior, as shown in Figure 1, is much like that in a pure triflate medium and very different from that in a pure perchlorate medium.
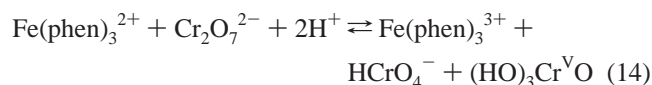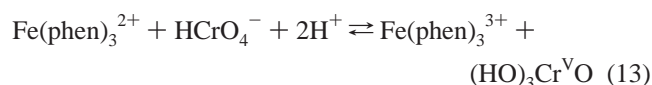
Could the accelerating effect of chloride come from the same effect as that of perchlorate, that is, by forming an outer-sphere complex with Fe(phen)$_3^{2+}$? The answer is probably not because the effect of chloride on the reaction rate is larger than that of perchlorate, whereas the Cl−Fe-(phen)$_3^{2+}$ interaction is weaker than the ClO₄−Fe(phen)$_3^{2+}$ interaction.[2] More likely, the formation of CrO₃Cl$^-$, eq 11, is responsible.[21] If this Cr(VI) species also oxidizes Fe-(phen)$_3^{2+}$ and provided eq 7 and 11 are maintained at equilibrium compared to the rate of the oxidation reaction (data for eq 7 have been reported),[22] then the rate law would take the form of eq 12. The data were fit well with this equation, and the calculated value of k' is about 3 times larger than that for HCrO₄$^-$. This result shows that CrO₃Cl$^-$ is itself reactive in oxidizing Fe(phen)$_3^{2+}$.

$$HCrO_4^- + Cl^- + H^+ = CrO_3Cl^- + H_2O$$
$$K_{Cl} = 17\ L^2\ mol^{-2}\ (\mu = 1.0)\quad (11)$$
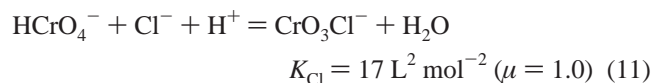
$$k_{obs} = \frac{k + k'K_{Cl}[H^+][Cl^-]}{1 + K_{Cl}[H^+][Cl^-]}[Cr(VI)]_T \quad (12)$$

Discussion

Net Activation Processes and Cr(V). From eq 10, these equations are the more specific representations of step I of Scheme 1:

$$Fe(phen)_3^{2+} + HCrO_4^- + 2H^+ \rightleftharpoons Fe(phen)_3^{3+} +$$
$$(HO)_3Cr^VO \quad (13)$$

$$Fe(phen)_3^{2+} + Cr_2O_7^{2-} + 2H^+ \rightleftharpoons Fe(phen)_3^{3+} +$$
$$HCrO_4^- + (HO)_3Cr^VO \quad (14)$$

These further comments are needed. Pulse radiolysis has independently confirmed the Cr(V) species;[14] it has a pK_a = 2.7 and, thus, exists without an ionic charge in the range 0.2−1.0 mol L^{-1} H$^+$, as in the current study. That is not to say, however, that its formula might not be (HO)CrO₂, as the extent of hydration cannot be determined from equilibrium or kinetics experiments in aqueous solution. Indeed, the dioxo formulation is not unlikely for a d^1 oxometal species in oxidation state five. It is gratifying that both Cr-(VI) reagents lead to the same Cr(V) species, so as to provide the optimal $\Delta G^\ddagger$ for each.

Analysis of k_{-1} and k_2. The equilibrium constant for eq 13, from the standard reduction potentials,[4,23] is $K = 2 \times 10^{-9}$, from which the rate constant for the reverse reaction is $k_{-1} = k_1/K = 6 \times 10^9$ L mol^{-1} s^{-1}, which is at or near the diffusion-controlled limit. The rate constant for the second step, k_2, is larger by a factor of about 10. These figures must be taken as quite approximate.

Specific Anion Effects. It has long been recognized that seemingly innocent counterions may have a significant effect on the reaction kinetics. For example, with sodium perchlorate as the substance used to maintain ionic strength, a number of redox reactions exhibit a *minor* acid-dependent kinetic term, which is absent in lithium perchlorate media.[24] Also, alkali metal ions are believed to be part of the transition state in the oxidation of Mo(CN)₈$^{4-}$ by S₂O₈$^{2-}$.[25] Perchlorate is widely used as a noncoordinating anion to maintain ionic strength, and there has rarely been a need to consider that it might exert a significant chemical effect. The present results clearly demonstrate the unusual effect of perchlorate on the chromium(VI)−Fe(phen)$_3^{2+}$ reaction kinetics, a point that was established earlier for this iron(II) complex.[3] It is probably more prudent to use a triflate medium for investigations of tris(phenanthroline) and tris(bipyridine) complexes.

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