ethylenediamine the addition of N-alkyl groups can significantly increase the exchange rate. The configuration of the ligand (tren *vs.* trien) and an increase to six-membered chelate rings (tn *vs.* en and *cis,cis*-tach *vs.* dien) also have significant effects. The presence of carboxylate groups in general does not lead to an increased exchange rate and in some cases appears to decrease the exchange rate.

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gen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969). The k^{-H_2O} value of 1.8×10^5 sec^{-1} (25°, 0.25 M $NaClO_4$) estimated from eq 6 for $Nien(H_2O)_4^{2+}$ is in reasonable agreement with the value of 4.4×10^5 sec^{-1} (25°, 0.52 M KNO_3) calculated from the nmr data. The latter data also show an increase in the water exchange rate as one, two, and four amine nitrogens are coordinated to nickel.

Rate Studies on the Primary Step of the Reduction of Chromium(VI) by Iron(II)[1a]

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Abstract: The oxidation of iron(II) to iron(III) in perchloric acid solution by chromium(VI) occurs in a sequence of three one-electron steps. The rate of the first of these has been studied by appropriate choice of concentration conditions and is first order with respect to the concentrations of Fe^{2+} and $HCrO_4^-$. The rate shows close to a second-order dependence upon $[H^+]$, although a more accurate description is given by the equation $-d[HCrO_4^-]/dt = (a[H^+] + b[H^+]^2)[Fe^{2+}][HCrO_4^-]$. Values of a and b are 4.4×10^3 M^{-2} sec^{-1} and 3.0×10^5 M^{-3} sec^{-1} at 25.0° and 0.084 M ionic strength in an $HClO_4$–$LiClO_4$ medium. The rate is essentially independent of temperature. At higher Fe^{2+} concentrations the absorbance change occurs in two steps, the second and slower stage corresponding to dissociation of an iron–chromium complex formed during the reaction. The rate of dissociation of the complex is proportional to $[H^+]$. Mechanisms consistent with these observations are proposed.

The oxidation of iron(II) by chromium(VI) in perchloric acid solution occurs as given in reaction

$$3Fe(H_2O)_6^{2+} + HCrO_4^- + 7H^+ + 2H_2O = 3Fe(H_2O)_6^{3+} + Cr(H_2O)_6^{3+} \quad \text{(I)}$$

I. This reaction has played an important part in the understanding of Cr(VI) oxidation mechanisms. Benson[2] carried out the first studies on the reaction rate; Westheimer[3] has reviewed her results. More recently, the rate behavior was studied under carefully controlled concentration conditions in a perchloric acid–lithium perchlorate medium.[4] The rate expression at low Cr(VI) concentrations[5] under the other conditions in that study was

$$\frac{-d[HCrO_4^-]}{dt} = k\frac{[Fe^{2+}]^2[HCrO_4^-][H^+]^3}{[Fe^{3+}]} \quad (1)$$

where k had the value 2.1×10^8 M^{-4} sec^{-1} at 0° and $\mu = 0.084$ M.

Among the important conditions of that study was the addition of high concentrations of Fe^{3+} to all reactant solutions to bring the rate into the region accessible to the conventional measurement techniques employed. The restriction to high Fe(III) concentrations limited the information obtained about the reaction in two important respects. First, the rate constant k of eq 1 represents a composite of values belonging to at least two reaction steps so that no rate constant for an elementary reaction in the mechanisms was evaluated. Second, the number of protons involved at different steps in the mechanism is not resolved by eq 1. The steps prior to and including the rate-determining step require three protons, but more detailed information is not available.

The mechanism suggested in accord with eq 1 can be represented *at constant* $[H^+]$ as follows

$$Fe^{2+} + HCrO_4^- \rightleftharpoons Fe^{3+} + Cr(V) \quad (k_1', k_2') \quad \text{(II)}$$

$$Fe^{2+} + Cr(V) \longrightarrow Fe^{3+} + Cr(IV) \quad (k_3') \quad \text{(III)}$$

$$Fe^{2+} + Cr(IV) = Fe^{3+} + Cr^{3+} \quad \text{fast} \quad \text{(IV)}$$

The primed rate constants refer to pseudo-second-order values that may depend upon $[H^+]$. According to this scheme the empirical rate parameter k is identified as $k_1'k_3'[H^+]^3/k_2'$, with the usual steady-state approximations made for Cr(V) and Cr(IV). The intermediacy of Cr(V) in the rate-determining step is supported by the scavenging effect toward iodide ion in which a limiting induction factor of 2.0 is achieved.[2,6]

A previous attempt[7] was made to learn the actual species involved in reaction steps II–IV. That attempt involved correlations of three independent results: rate studies on the oxidation of VO^{2+} by $HCrO_4^-$,[7]

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2626; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] C. Benson, *J. Phys. Chem.*, 7, 1, 356 (1903).

[3] F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

[4] J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963).

[5] A second rate term proportional to $[HCrO_4^-]^2$ is completely negligible under the lower Cr(VI) concentrations employed here and can be safely ignored in the present study.

[6] C. Wagner and W. Preiss, *Z. Anorg. Allg. Chem.*, **168**, 265 (1928).

[7] J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964).

the first-order hydrogen ion dependence of the oxidation of iodide ion induced by the VO^{2+} reaction,[6] and the zero-order hydrogen ion dependence of the induced oxidation of iodide in the Fe(II)–Cr(VI) reaction.[6] The reaction of VO^{2+} and $HCrO_4^-$ obeys a rate expression analogous to that in eq 1 except that the rate is independent of $[H^+]$; it was *assumed* that each term in the composite rate constant is independent of $[H^+]$. The inferences were drawn that k_3' is first order with respect to $[H^+]$ and k_1'/k_2' varies as $[H^+]^2$. With a further assumption that k_2' is independent of $[H^+]$, the following detailed mechanism for the first two steps was consequently proposed.[7]

$$Fe^{2+} + HCrO_4^- + 2H^+ \rightleftharpoons Fe^{3+} + H_3CrO_4 \quad (k_1, k_2) \qquad \text{(V)}$$

$$Fe^{2+} + H_3CrO_4 \longrightarrow Fe^{3+} + Cr(IV) \quad (k_3) \qquad \text{(VI)}$$

Associated with the sequence is the following rate expression

$$\frac{-d[HCrO_4^-]}{dt} = \frac{k_1[Fe^{2+}][HCrO_4^-][H^+]^2}{1 + \dfrac{k_2[Fe^{3+}]}{k_3[Fe^{2+}][H^+]}} \qquad (2)$$

which reduces to the expression in eq 1 in the limit of high Fe^{3+} concentrations.

In the present work, rate studies have been carried out without the addition of Fe^{3+} in an attempt to make dominant the first denominator term of eq 2 rather than the second.[8] These studies were undertaken to evaluate individual rate constants in the reaction sequence and to study directly the effect of hydrogen ion on the first step, thereby exploring the correctness of the assumptions made earlier.

During the course of these studies an intermediate, most probably a dinuclear Fe–Cr species formed in one of the steps II–IV, was discovered. Some studies were carried out to establish its identity and to study its role in the mechanism. The alternatives here have not yet been uniquely resolved.

Experimental Section

Materials. Hydrated iron(III) perchlorate, lithium perchlorate, and potassium dichromate were prepared, purified, and analyzed as described in earlier publications.[7,9] Reagent grade 72% perchloric acid was diluted and used without further purification. Iron(II) solutions were prepared immediately before use by reduction under a nitrogen atmosphere with amalgamated zinc. Conductivity water was used throughout.

Rate Procedures and Reaction Conditions. A Durrum stopped-flow instrument equipped with a Kel-F mixing block having a 2-cm optical path was used for most of the rate measurements. The most useful rate experiments were performed at λ 240 nm, where Fe^{3+} has an absorption maximum with $\epsilon \sim 4 \times 10^3\ M^{-1}\ cm^{-1}$. Some studies were also carried out at several wavelengths in the region 250–350 nm. A Cary Model 14 recording spectrophotometer, with a slide wire having a full-scale chart displacement of 0.1 absorbance unit was used to follow the reaction at 240 nm under certain conditions where the rate was lower.

In all the experiments the concentration of Fe^{2+} was in sufficient excess over that of $HCrO_4^-$ that pseudo-first-order rate plots and average Fe^{2+} concentrations could be employed. In most runs Fe^{3+} was not added initially. Lithium perchlorate was added to maintain ionic strength 0.084 *M*, which was effectively the same medium in which some of the earlier studies[4] were carried out.[10]

Results

Kinetics at λ 240 nm. The rate of the first stage of reaction I was studied at λ 240 nm because preliminary experiments indicated an absorbing intermediate interfered at wavelengths otherwise suitable (see below). The reaction exhibited a first-order dependence on $[HCrO_4^-]$, its initial concentration being varied in the range $0.25–1.0 \times 10^{-5}$ *M* without changes in the pseudo-first-order rate constants. Experiments were performed over the concentration range *ca.* $0.1–8 \times 10^{-3}$ *M* Fe^{2+}. At any particular $[H^+]$ the reaction appeared to be very close to first order with respect to $[Fe^{2+}]$, as seen from the average values of the experimental second-order rate constants given in Table I. A small but regular increase in the rate constant with $[Fe^{2+}]$ was noted over the 50-fold concentration variation. This appears not to be a meaningful variation, however, but one related to small effects arising from the reaction intermediate or from a slight change in medium[10] with progressively higher $[Fe^{2+}]$.

Table I. Apparent Second-Order Rate Constants for the Reaction of Fe^{2+} and $HCrO_4^-$ at Various Concentrations; 25.0°, μ = 0.084 *M*

	k_1' (M^{-1} sec^{-1})			
$10^3[Fe^{2+}]_{av}$	$[H^+]$ = 0.012	$[H^+]$ = 0.024	$[H^+]$ = 0.048	$[H^+]$ = 0.084
0.064	95	284		
0.098	93	284	900	2400
0.166	91	273	880	
0.385			1040	
0.785		309	990	2310
1.98		330	960	2230
3.98		341	1060	2560
7.98				2570

Table I also summarizes the effect of variation of $[H^+]$, a dependence slightly less than second order. The following equations describe the concentration dependencies

$$-d[HCrO_4]/dt = k_1'[Fe^{2+}][HCrO_4^-] \qquad (3)$$

$$k_1' = a[H^+] + b[H^+]^2 \qquad (4)$$

with the second-order $[H^+]$ dependence being the dominant term. A plot of $k_1'/[H^+]$ *vs.* $[H^+]$ is shown in Figure 1, from which the values are $10^{-3}a = 4.4 \pm 0.4\ M^{-2}\ sec^{-1}$ and $10^{-5}b = 3.0 \pm 0.1\ M^{-3}\ sec^{-1}$.

The reaction appears to be essentially independent of temperature; for example, in an experiment with 0.002 *M* Fe^{2+} at 0.084 *M* H^+ the apparent second-order rate constant was 2240 M^{-1} sec^{-1} at 15.0°.

The Reaction Intermediate. Under conditions of fairly high $[Fe^{2+}]$, >*ca.* 10^{-3} *M*, the apparent rate proved to be a function of the wavelength used to monitor the reaction. For example, an experiment at 0.048 *M* H^+ with initial concentrations of 2.00 × 10^{-3} *M* Fe^{3+}, and 5.0 × 10^{-6} *M* $HCrO_4^-$ is depicted in Figure 2. The increase in absorbance at λ 240 nm, corresponding to the production of Fe^{3+}, occurred with a pseudo-first-order rate constant of 2.15 sec^{-1}. On the other hand at λ 350 nm, where of the reactants

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[8] J. P. Birk, *J. Amer. Chem. Soc.*, 91, 3189 (1969).

[9] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, 6, 1370 (1967).

[10] Actually, $[H^+] + [Li^+]$ was maintained at 0.084 *M*; the presence of varying concentrations of Fe^{2+} raised the ionic strength as high as 0.1 *M* in the same runs. Separate experiments prove that the rate constant measured here was quite insensitive to changes of ionic strength in the range 0.08–0.15 *M*.

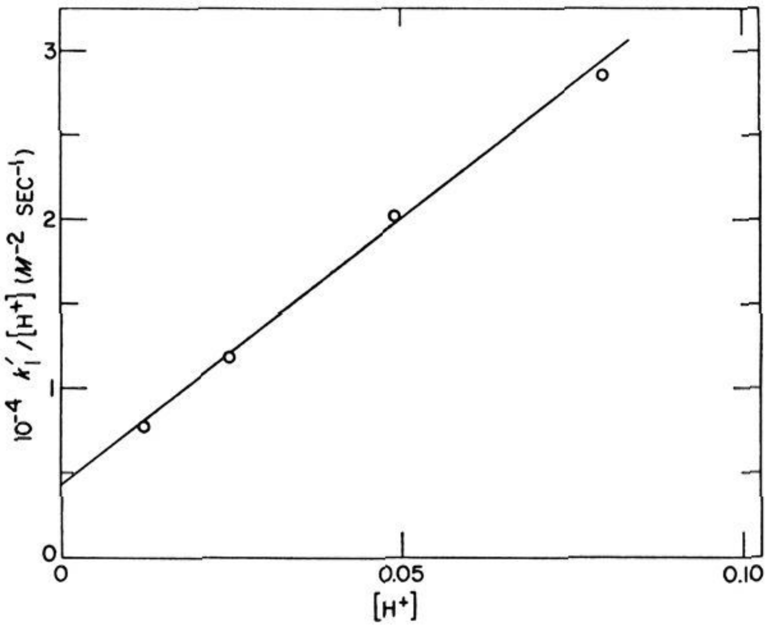

Figure 1. A plot of $k_1'/[H^+]$ *vs.* $[H^+]$ in accord with eq 4.

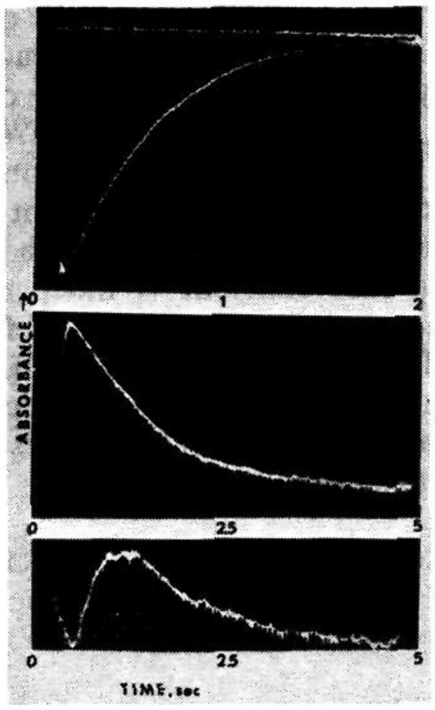

Figure 2. The absorbance–time oscillograms at various wavelengths for an experiment with the following initial concentrations: $5 \times 10^{-6}\ M\ HCrO_4^-$, $2 \times 10^{-3}\ M\ Fe^{2+}$, $0.048\ M\ H^+$; top, λ 240 nm; middle, λ 322; bottom, λ 290.

and products only the species $HCrO_4^-$ contributed to the absorbance, two separate absorbance changes occurred, the slower of which at a specific rate of *ca.* 1.1 sec^{-1}. At λ 322 nm, the effect of the intermediate was dominant; the reaction followed a pseudo-first-order expression with a rate constant of 1.01 sec^{-1}. In the range λ 270–300 nm, the absorbance passed through a maximum with time, confirming the existence of an intermediate. The rate constant for the second stage at λ 290 nm was 1.10 sec^{-1}, within experimental error of that at longer wavelengths.

In a similar experiment at twice the Fe^{2+} concentration, $4.00 \times 10^{-3}\ M$, the apparent rate constant evaluated at λ 240 nm doubled (4.2 sec^{-1}), whereas that evaluated at λ 322 nm remained invariant (1.05 sec^{-1}).

Addition of low concentrations of Fe^{3+}, comparable to the levels formed as product, changed neither of the values. For example, with $2.00 \times 10^{-3}\ M\ Fe^{2+}$ and $5.0 \times 10^{-6}\ M\ HCrO_4^-$ at $0.048\ M\ H^+$, the rate constants for the main reaction, evaluated at λ 240 nm, were 2.15, 2.10, and 2.22 sec^{-1} with $10^5[Fe^{3+}]_0 = 0$, 2.0, and 5.0, respectively. For the same three runs carried out at λ 322 nm, the rate constants were 1.01, 1.07, and 1.05 sec^{-1}.

These results establish that the intermediate does not react with Fe^{2+} or Fe^{3+}. As $[Fe^{2+}]$ becomes smaller, however, the rate of forming the intermediate comes more into competition with the rate of its decomposition. The plots become nearly linear, and the apparent rate constants evaluated at λ 320–350 are nearly in agreement with those evaluated at λ 240 nm.

The intermediate reacts at a rate dependent upon $[H^+]$. The pseudo-first-order rate constant (λ 322 nm) at $0.084\ M\ H^+$ is 1.53 sec^{-1}. The rate appears to be first order in $[H^+]$; the second-order rate constant is $20 \pm 3\ M^{-1}\ sec^{-1}$.

Interpretation and Discussion

Proposed Mechanism. The basic three-step reaction sequence II–IV appears consistent with the observations made here although in the form shown the reaction intermediate is not accounted for and the role of H^+ not defined. The important observation bearing on these questions are summarized as follows: (a) the main reaction under conditions of low $[Fe^{3+}]$ occurs according to the expression $-d[HCrO_4^-]/dt = b[Fe^{2+}]\cdot[HCrO_4^-][H^+]^2$, corresponding to a transition state $[FeCrO_4H_3^{3+}]^{\ddagger}$; (b) the reaction produces a metastable intermediate with uv absorption that reacts further at a rate proportional to $[H^+]$; (c) the reaction of the intermediate is not affected by moderate variations of $[Fe^{2+}]$ or $[Fe^{3+}]$ with the latter at low concentration, say $\leq 5 \times 10^{-5}\ M$; and (d) the rate under conditions of high $[Fe^{2+}]$, $> 2 \times 10^{-3}\ M$, varies as $[H^+]^3$ and as $[Fe^{3+}]^{-1}$, as given by eq 1.

The two mechanisms[11] shown in Scheme I both appear to account for all the evidence presently available. The intermediate proposed in A, $Fe(H_2CrO_4)^{2+}$, is a complex of Fe(III) and Cr(V) which can attain substantial concentrations when the rate of the first stage is high, as is the case at high $[Fe^{2+}]$. Proposal A involves the aquation of the complex in acid solution forming H_3CrO_4 as shown in reaction VIII. High concentrations of Fe^{3+} will, however, ensure the predominant Cr(V) species is the Fe(III) complex and not free H_3CrO_4, which latter form is the species that undergoes further reduction in this mechanism. In mechanism B

Scheme I

Mechanism A

$$Fe^{2+} + HCrO_4^- + 2H^+ \rightleftarrows Fe(H_2CrO_4)^{2+} + H^+ \qquad (k_1, k_4) \qquad \text{(VII)}$$

$$Fe(H_2CrO_4)^{2+} + H^+ \rightleftarrows Fe^{3+} + H_3CrO_4 \qquad (k_5, k_6) \qquad \text{(VIII)}$$

$$Fe^{2+} + H_3CrO_4 + H^+ \longrightarrow Fe^{3+} + Cr(IV) \qquad (k_3) \qquad \text{(IX)}$$

$$Fe^{2+} + Cr(IV) \longrightarrow Fe(III) + Cr(IV) \qquad \text{(fast)} \qquad \text{(IV)}$$

Mechanism B

$$Fe^{2+} + HCrO_4^- + 2H^+ \rightleftarrows Fe^{3+} + H_3CrO_4 \qquad (k_1, k_2) \qquad \text{(V)}$$

$$Fe^{2+} + H_3CrO_4 + H^+ \longrightarrow Fe^{3+} + Cr(IV) \qquad (k_3) \qquad \text{(VI)}$$

$$Fe^{2+} + Cr(IV) + nH^+ \longrightarrow FeOCr^{4+} \qquad \text{(fast)} \qquad \text{(X)}$$

$$FeOCr^{4+} + H^+ \longrightarrow Fe^{3+} + CrOH^{2+} \qquad (k_7) \qquad \text{(XI)}$$

$$CrOH^{2+} + H^+ = Cr^{3+} + H_2O \qquad \text{(fast)}$$

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(11) The author is grateful to a referee for the suggestions incorporated here as mechanism B.

the sequence is that referred to before except that the last step gives as a primary product a dinuclear Fe(III)–Cr(III) complex $FeOCr^{4+}$. The conversion of the dinuclear complex to Fe^{3+} and Cr^{3+} according to reaction XI is, in proposal B, the step responsible for the secondary reaction observed.

The experimental rate constant k of eq 1 is identified as $k_1k_3k_5/k_4k_6$ in A and as k_1k_3/k_2 in B; its value is 2.1 × 10^8 M^{-4} sec^{-1} ($\mu = 0.084$ M at 0°). In both mechanisms $b = k_1$; the value is 3.0 ± 0.1 × 10^5 M^{-3} sec^{-1} ($\mu = 0.084$ M, essentially independent of temperature). The rate constant for decay of the intermediate, k_5 in A or k_7 in B, is 20 ± 3 M^{-1} sec^{-1} ($\mu = 0.084$ M, 25.0°). To account for why the intermediate gives no interference at λ 240 nm it is necessary to have the absorbance decrease accompanying its decay balanced by the absorbance increase from Fe^{3+} formation. In A such a requirement gives the value $\epsilon(Fe(H_2CrO_4)^{2+})$ 1.2 × 10^4 and in B $\epsilon(FeOCr^{4+})$ 4 × 10^3 M^{-1} cm^{-1} at λ 240 nm. When the reaction conditions are such that the overall rate is much lower, as was the case in the earlier work when $[Fe^{3+}]$ was high and $[Fe^{2+}]$ low, the intermediate does not attain a significant concentration so that such studies[4] at λ 350 nm do correctly relate to reaction I.

Implications of the Proposed Mechanism. The verification that k_1' exhibits predominantly second-order $[H^+]$ dependence confirms the basis of the assumptions[7] that had been used earlier in drawing that tentative conclusion. Each of the proposed mechanisms involves a dinuclear Fe–Cr intermediate that decomposes to products (or to substances rapidly converted to products) at a rate proportional to $[H^+]$. The intermediate $Fe(H_2CrO_4)^{2+}$ in mechanism A is a reasonable formula considering the degree of protonation of other oxoanion complexes of iron(III).[12–16] Most notable as a model for the intermediate in mechanism A is a complex of Fe(III) and P(V), $Fe(H_2PO_4)^{2+}$, whose formula and stability[16] may well approximate that of $Fe(H_2CrO_4)^{2+}$. Moreover, the first-order dependence on $[H^+]$ in the decomposition reaction is also reasonable in view of the rate expression for similar reactions.[12–14,17] The spectral requirement for $Fe(H_2CrO_4)^{2+}$, ϵ_{240} 1.2 × 10^4, can be compared with ϵ_{240} 6 × 10^3 for $Fe(H_2PO_4)^{2+}$.

The intermediate $FeOCr^{4+}$ (or $Fe(OH)_2Cr^{4+}$) in mechanism B is formed from the reaction of Fe(II) with Cr(IV); it also is reasonable since analogous dinuclear complexes are produced in formally similar processes: the reactions[18] of Cr(II) with Cr(IV), Fe(II) with Fe(IV), V(II) with V(IV), Cr(II) with V(IV), and Cr(II) with V(III). Moreover, all these dinuclear complexes undergo decomposition at rates proportional to $[H^+]$ as found experimentally for the present intermediate.

In both formulations the rate constant for decay of the intermediate is reasonable. A value of $k_5 = 20$ M^{-1} sec^{-1} for $Fe(H_2CrO_4)^{2+}$ is consistent with the stability constant[16] of $Fe(H_2PO_4)^{2+}$ considering the generalizations[9,12,14,17] found applicable for the anation rate constants for Fe(III). On the other hand the rate constants for acid decomposition of the dinuclear MOM'^{4+} complexes have been found[18e] to correlate approximately with the solvent exchange rate of the more labile of the two metal ion constituents. Consequently, a value $k_7 = 20$ M^{-1} sec^{-1} is quite reasonable considering for instance the value[18c] 3.5 M^{-1} sec^{-1} for the reaction of $FeOFe^{4+}$ with H^+.

At the present time it is not possible to make a distinction between these two possible formulations for the intermediate, and perhaps others as well. Further experiments are in progress dealing directly with the nature and composition of the Fe–Cr intermediate.

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