

scale. We include the individual deviations and rms for each formula.

Finally in Tables VI and VII we display the values of $\Delta_1 = X_B - X_A$, $\Delta_2 = (X_B - X_A)/((X_B - X_A)/2)$, and $\Delta_3 = (X_B - X_A)/(X_B X_A)^{1/2}$, for the different molecules and electronegativity scales.

Discussion

Though the set of molecules studied is a little reduced, we believe that the range of dipole moment charges included is sufficiently broad to state some general conclusions.

Comparing the rms values obtained with eq 1-4 for the three scales, we concluded that eq 1 is incapable of producing reliable results of the dipole moment charge, in contrast with eq 2-4, which are of similar qualities. There is no advantage in using the more complex eq 2 and 3 instead of the much simpler eq 4. It may be seen that for the last equation there are many negative deviations; this suggests that if we include an empirical correction factor f in the expression for q

$$q_4 = f(X_B - X_A)/X_B \quad (5)$$

with $X_B > X_A$, we would obtain a better correlation between these values and those calculated from experimental values of μ and R_e . Indeed, that is so and the rms reduces to 0.054, 0.090, and 0.071 for each of the three scales (Pauling, Allred-Rochow, and Mande et al., respectively). The correction factors are 1.058,

1.119, and 1.021 for the three scales.

If we compare the electronegativity scales, we see that Mande et al.'s scale is nearly as good as Pauling's and perhaps a little better than Allred-Rochow's scale. This last observation is in agreement with the fact that Allred-Rochow's scale and Mande et al.'s scale have the same physical basis, but the latter calculates the effective charges in a more accurate fashion.

For the hydrides in Table V, we see that the results are worse than those obtained for the alkali-metal halides and the interhalogenides. The reason is in part due to the fact that electronegativity scales report values only for the most common oxidation states, and the great majority of molecules in the table do not fulfill this condition. As pointed out by Nethercot²⁹ and Barbe,³² each value of electronegativity must be corrected for this effect. To obtain an electronegativity scale for various oxidation states is a task that deserves more effort. Research along this line is being made in our laboratory, and results will be published in a forthcoming paper.

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Kinetics of Electron Transfer from Tris(picolinato)chromate(II) to Iron(III)

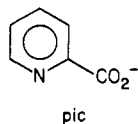
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The mechanism of the electron-transfer reaction from tris(picolinato)chromate(II) to iron(III) has been studied by spectrophotometry and stopped-flow techniques. The rate constants and the activation parameters for the inner-sphere process involving the formation and decay of the binuclear intermediate have been determined. The relevant thermodynamic and kinetic parameters for the formation of tris(picolinato)chromate(II), required for understanding the redox mechanism, have been determined from spectrophotometric and stopped-flow experiments. Some of the results were verified by T -jump measurements. All the values have been reported at 25 °C and ionic strength 2.3 M unless otherwise indicated. For the binuclear intermediate, the following rate constants were obtained: $k(\text{formation}) = 14.1 \text{ M}^{-1} \text{ s}^{-1}$; $k(\text{decay}) = 5.6 \times 10^{-4} \text{ s}^{-1}$.

Introduction

The corrosion products in nuclear reactors are mainly mixed-transition-metal oxides,¹ the major constituents being the oxides of Cr(III) and Fe(III). In order to facilitate their rapid removal, a practical method for their dissolution has to be devised.²⁻⁴ Recently, a method involving the use of $\text{V}(\text{pic})_3^-$, a powerful



reductant, was developed for dissolving metal oxides.⁵ It has been found that this process is inefficient in dissolving oxides that have

a high chromium content.¹ Consequently, tris(picolinato)chromate(II), which is a very stable complex,⁶⁻⁸ was tried as a possible decontaminating agent.

The mechanism of the homogeneous electron-transfer reaction between the complex, tris(picolinato)chromate(II), and Fe^{3+} was studied prior to investigating the heterogeneous reaction. This reaction, which is relatively slow, proceeds by an inner-sphere mechanism. Unlike the case of outer-sphere electron-transfer reactions, for which detailed theoretical studies are available and reasonably well supported by experimental evidence, quantitative theoretical predictions for inner-sphere reactions appear to be more elusive.⁹ The main focus of the investigations on this subject has been in detailing the actual mechanism of the electron-transfer process in complementary redox reactions between transition-metal ion complexes. The mechanism of these reactions depends upon the substitution properties of the reductant (usually the more labile reactant), the availability (or the unavailability) of a bridging

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ligand on the oxidant, and the thermodynamic driving force for electron transfer. These reactions are often accompanied by the transfer of the bridging ligand from the oxidant to reductant. Due to this reason investigations in this area have often focused on using a labile reductant that would become inert (to substitution) on oxidation and an inert oxidant. It has been generally found difficult to make the reductant inert to substitution so that the reaction would be governed by the substitution properties of the oxidant. The primary reason for this difficulty is that the reaction would proceed by an outer-sphere pathway if a suitable bridging ligand is not available on the reductant (as is the case with reactions using tris(bipyridyl)chromium(II)). In the present system, the reductant tris(picolinato)chromate(II) is relatively inert to substitution and has a suitable binding site (the carboxyl oxygen) for complexation with Fe^{3+} . Hence, the reaction proceeds by an inner-sphere pathway governed by the substitution properties of the oxidant. The binuclear intermediate that is formed has a half-life of about 20 min, enabling the kinetics of the formation and the decay of the intermediate to be studied independently. In this paper kinetic and thermodynamic results for the formation of tris(picolinato)chromate(II) and its oxidation by Fe^{3+} are presented. The application of these results in reductive dissolution is discussed.

Experimental Section

Solutions. Stock solutions of iron(III) perchlorate (G. F. Smith) and chromium(III) perchlorate (G. F. Smith) were prepared with a large excess of perchloric acid ($[\text{H}^+]/[\text{M}^{3+}] > 10$); these conditions ensured that the solutions were stable over an extended period of time.¹⁰ The total concentrations of both iron(III)¹¹ and chromium(III)¹² ions were determined spectrophotometrically. Perchloric acid (Baker), sodium perchlorate (G. F. Smith), picolinic acid (Aldrich), mossy zinc (Baker), and mercuric oxide (Fisher), all reagent grade, were used as supplied.

Chromium(II) perchlorate solutions were prepared by reducing chromium(III) perchlorate with amalgamated zinc, under a nitrogen atmosphere. The concentration of chromium(II) was determined spectrophotometrically.¹² The tris(picolinato)chromate(II) solutions were prepared by adding deaerated solutions of picolinic acid with a gastight Hamilton L005-LT syringe fitted with a Teflon tip to the standardized chromium(II) solutions. The solutions contained, in general, at least a 1% excess of picolinic acid. The solutions were stored under nitrogen at a pH around 2 (at room temperature) for a couple of hours. Then, they were made 1.0 M in perchloric acid and were stored at 4.0 °C in airtight glass bottles. Under these conditions the solutions were found to be stable for at least 1 month. The solutions used in the experiments were always less than 1 week old. The reducing power of the tris(picolinato)chromate(II) solution was determined by titrating it spectrophotometrically with acidified potassium permanganate ($[\text{H}^+] = 1.0 \text{ M}$, $\mu = 2.0 \text{ M}$, $[\text{H}^+]/[\text{complex}] > 100$). The concentrations determined from the titrations agreed very well (within 1%) with the concentration of the chromium(II) solution determined spectrophotometrically.

Sodium perchlorate was used to adjust the ionic strength. All the glassware was cleaned by using standard cleaning procedures—with alkaline potassium permanganate and hydroxylamine hydrochloride. Before use, each solution was passed through a qualitative filter paper (Sargent-Welch, Grade 800) and allowed to equilibrate overnight at ambient temperatures. The nitrogen gas was scrubbed by passing it through a chromium(II) perchlorate wash solution.

Methods. Potentiometry. A Chemtrix Type 60A pH meter, equipped with a digital readout, was used for the potentiometric titration of tris(picolinato)chromate(II) against potassium permanganate ($[\text{H}^+] = 1.0 \text{ M}$, $\mu = 2.0 \text{ M}$). The solutions were mixed with a magnetic stirrer, and the temperature of the system was measured at regular time intervals.

Spectrophotometry. Quantitative spectral measurements were made on a Perkin-Elmer 559A UV/vis spectrophotometer. This device permitted the determination of absorbance to three decimal places. The cell holder was thermostated to $\pm 0.1 \text{ }^\circ\text{C}$ with a Haake FK external circulating water bath. Matched 1-cm quartz cells were tightly stoppered to prevent evaporation. All the solutions were allowed to equilibrate for at least 5 min before measurements were made.

Kinetics. The kinetics of the formation of tris(picolinato)chromate(II) and the formation of the binuclear intermediate were studied with use

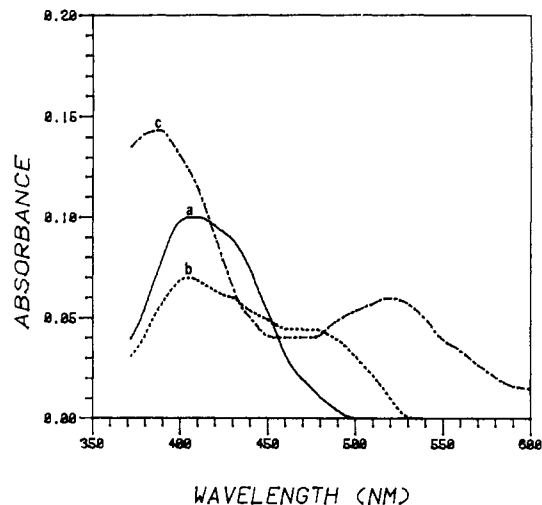


Figure 1. Visible spectrum of the chromium(II) picolinate complexes (pH 4.0, $\mu = 2.0 \text{ M}$, temperature 25 °C, $[\text{complex}] = 0.001 \text{ M}$): (a) picolinato)chromium(II); (b) bis(picolinato)chromium(II); (c) tris(picolinato)chromate(II).

of a combined stopped-flow and temperature-jump apparatus described elsewhere.¹³ The kinetics of the decay of the binuclear intermediate was studied on the Perkin-Elmer 559A UV/vis spectrophotometer by recording the absorbance from the digital readout at regular intervals of time.

Results and Discussion

Formation of Tris(picolinato)chromate(II). Complexes of Cr(II) and Cr(III) with picolinic acids have been studied by several investigators.^{6-8,14} Quantitative equilibrium data for the chromium(III) picolinate complexes have been reported in the literature,¹⁴ and the value of the stability constant ($\log \beta$) for $\text{Cr}(\text{pic})_3$ is 9.73 ± 0.05 . Although chromium(II) picolinate complexes have been the subject of several investigations,⁶⁻⁸ quantitative equilibrium data are not available in the literature except for the data (in a limited form) reported by Mercier and Paris.⁶

The spectra of the solution containing Cr(II) and picolinic acid show two absorption maxima; a sharp peak at 408 nm and a broad one at 520 nm. The peak at 408 nm increases in intensity and the 520-nm peak decreases as the acidity of the solution is increased. When the acidity of the solution is increased to above 1.0 M in HClO_4 , the peak at 520 nm essentially disappears. A modified Job method of equimolar solutions using a linear programming technique¹⁵ (for different $[\text{M}]/[\text{L}]$ ratios and wavelengths) applied to the absorbance data gave qualitative evidence for the presence of three different species with 1/1, 1/2, and 1/3 $[\text{M}]/[\text{L}]$ ratios. The spectra of the three species are shown in Figure 1. The stability of the complex increases as the metal to ligand ratio decreases (in accordance with the literature⁸). When the absorbance data for the solutions having a metal to ligand ratio less than 1/3 (to 1/40) were analyzed in a similar manner, it was found that only one species ($[\text{M}]/[\text{L}] = 1/3$) was present at significant concentrations, and this is the species that was used in this work. It must be mentioned that these solutions are likely to contain a mixture of various isomers of tris(picolinato)chromate(II) and that no experiments were performed to investigate this aspect. This complex was titrated against acidified KMnO_4 potentiometrically, and a value of $0.38 \pm 0.05 \text{ V}$ was obtained for the redox potential, which corresponds to a stability constant ($\log \beta$) of 23.1.

Oxidation of Tris(picolinato)chromate(II) by Iron(III). Since the standard redox potential of tris(picolinato)chromate(II) is much more positive than that of Cr^{2+} , it would not be a thermodynamically suitable reducing agent for dissolving chromium-

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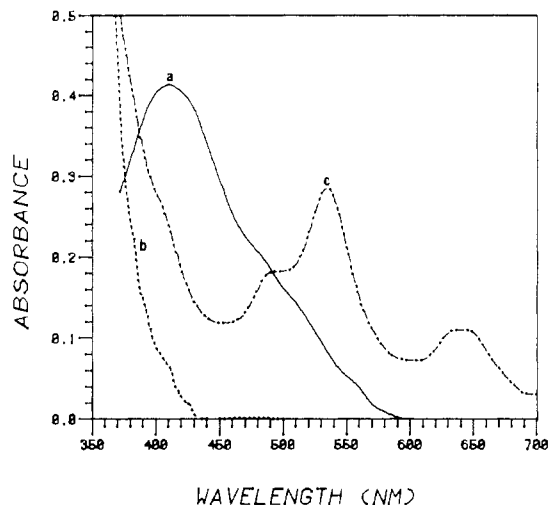


Figure 2. Visible spectra (pH 1.0, $\mu = 2.0$ M, temperature 25 °C): (a) tris(picolinato)chromate(II) (0.002 M); (b) Fe^{3+} (0.1 M); (c) $[\text{Cr}(\text{pic})_3\text{-Fe}]^{2+}$ (0.002 M).

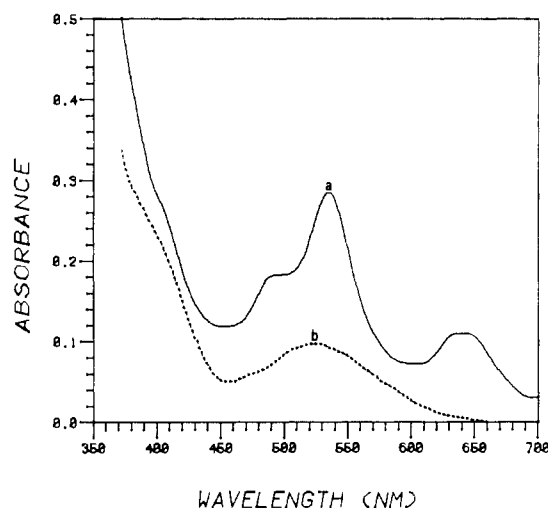


Figure 3. Spectra of the product of the reaction between Fe^{3+} and tris(picolinato)chromate(II) after two different time intervals (pH 1.0, $\mu = 2.0$ M, temperature 25 °C, $[\text{Cr}(\text{II})] = 0.002$ M, $[\text{Fe}^{3+}] = 0.1$ M): (a) time interval 1 min; (b) time interval 5 h.

(III) oxides. Instead, the feasibility of using it for dissolving Fe(III) oxides, which are also major constituents of the corrosion products from nuclear reactors, was investigated. ΔG° for this reaction ($\text{Cr}(\text{pic})_3^- + \text{Fe}^{3+} = \text{Cr}(\text{pic})_3 + \text{Fe}^{2+}$), calculated from the E^0 values, is 9.06 ± 0.05 kcal mol $^{-1}$. It should be noted that all the species mentioned in the chemical equations are aqueous unless otherwise mentioned.

Equilibrium Data. In all the experiments (except the pH-dependence studies) the acidity of the solutions was maintained at 1.0 M in HClO_4 and the maximum concentration of Fe(III) in any of the solutions was 0.1 M. These conditions were maintained in order to make the concentration of the hydrolyzed species of Fe(III) negligible.¹⁰

The spectra of Fe^{3+} , tris(picolinato)chromate(II), and the product of the reaction between the two (after a time interval of about 1 min) are shown in Figure 2. Figure 3 gives the spectrum of the product at two different times after mixing. The intermediate spectrum is assigned to the binuclear intermediate $[\text{Cr}(\text{pic})_3\text{-Fe}]^{2+}$. H_2O_2 and KMnO_4 react with tris(picolinato)chromate(II) vigorously, and the spectra of the products are similar to the spectrum of the final product of the reaction with Fe^{3+} (Figure 4). No stable intermediates are seen in the reactions with H_2O_2 and KMnO_4 .

The spectra of products of the reactions of tris(picolinato)chromate(II) with Fe^{3+} , H_2O_2 , and KMnO_4 (Figure 4) correspond to the spectrum of tris(picolinato)chromium(III).¹⁴ Moreover,

Table I. $[\text{Fe}^{3+}]$ Dependence of k_1' (Eq 5)^a

$[\text{Fe}^{3+}]$, M	k_1' , s $^{-1}$	$[\text{Fe}^{3+}]$, M	k_1' , s $^{-1}$
0.0398	0.7	0.0100	0.2
0.0298	0.5	0.0050	0.1
0.0199	0.4		

^a Conditions: $[\text{H}^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25 °C.

Table II. Temperature Dependence of $k_1'^*$ ^a

temp, °C	$k_1'^*$, M $^{-1}$ s $^{-1}$	temp, °C	$k_1'^*$, M $^{-1}$ s $^{-1}$
10.0	6.6	35.0	33.3
15.0	7.7	45.0	54.5
25.0	15.4		

^a Conditions: $[\text{H}^+] = 1.0$ M, $\mu = 2.3$ M.

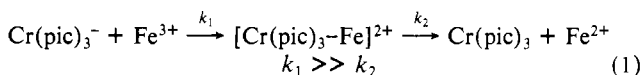
Table III. $[\text{H}^+]$ Dependence of $k_1'^*$ (Eq 6)^a

$[\text{H}^+]$, M	$k_1'^*$, M $^{-1}$ s $^{-1}$	$[\text{H}^+]$, M	$k_1'^*$, M $^{-1}$ s $^{-1}$
1.0	15.4	0.3	47.5
0.5	21.0	0.1	137

^a Conditions: $\mu = 2.3$ M, temperature 25 °C.

green chromium(III) hydroxide is precipitated on making the solution alkaline. The Fe^{2+} produced from the reduction of Fe^{3+} was identified quantitatively by complexing it with 2,2'-bipyridyl.¹⁶

Kinetic Data. The formation of the binuclear intermediate is very rapid (time scale of milliseconds), and the decay of the intermediate is much slower (time scale of minutes):



Due to this reason the kinetics of the two processes (the formation and the decay of the intermediate) were studied independently. The first process was studied in a stopped-flow instrument¹³ and the second in a conventional spectrophotometer.

Formation of the Intermediate. Parts a and b of Figure 5 are the kinetic curves obtained for the first step at 408 and 640 nm. Part a represents the decrease in concentration of tris(picolinato)chromate(II) and part b the increase in the concentration of the intermediate as a function of time. Since the absorbance changes obtained at 408 nm were significantly larger than the corresponding ones at 640 nm, the former wavelength was used in the kinetic study. The results obtained at the two wavelengths agreed to within 1%. The reaction was studied under pseudo-first-order conditions with use of excess of Fe^{3+} . Under these conditions the rate equation representing the reaction is

$$X = A + B e^{-k_1' t} \quad (2)$$

where X is the absorbance at 408 nm, A and B are constants that include terms involving the amplitude of the reaction, k_1' is the pseudo-first-order rate constant, and t is the time in seconds.

This equation is valid for any first-order or pseudo-first-order process irrespective of whether the change in concentration of a reactant or a product is observed and accounts for the absorbance of any other substance in the solution, as well as the dead time of the instrument. The equation was tested numerically on simulated data for the correlation between the three variable parameters by fitting them with use of the Marquardt NLIN procedure available on SAS.¹⁷ The absolute values of the correlation¹⁸ between the three parameters were always less than 0.75, which is excellent for experimental data.

In this case the pseudo-first-order rate constant, k_1' , is a function of k_1 , $[\text{H}^+]$, $[\text{Fe}^{3+}]$, and T ; i.e.

$$k_1' = f(k_1, [\text{H}^+], [\text{Fe}^{3+}], T) \quad (3)$$

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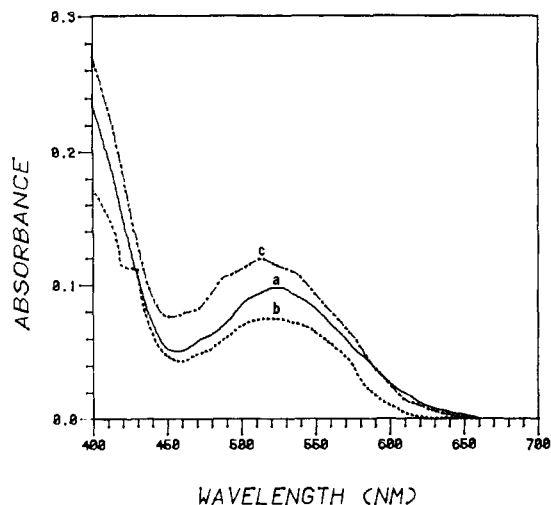


Figure 4. Spectra of the products of the reaction of tris(picolinato)chromate(II) with Fe^{3+} , H_2O_2 , and KMnO_4 (pH 1.0, $\mu = 2.0$ M, temperature 25 °C, $[\text{Cr}(\text{II})] = 0.002$ M, $[\text{oxidants}] = 0.1$ M): (a) reaction with H_2O_2 ; (b) reaction with KMnO_4 ; (c) reaction with Fe^{3+} .

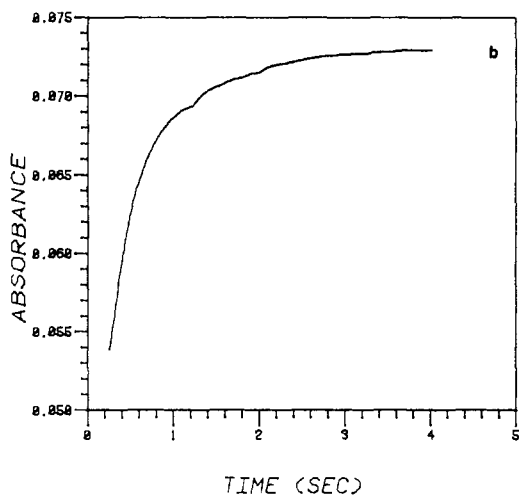
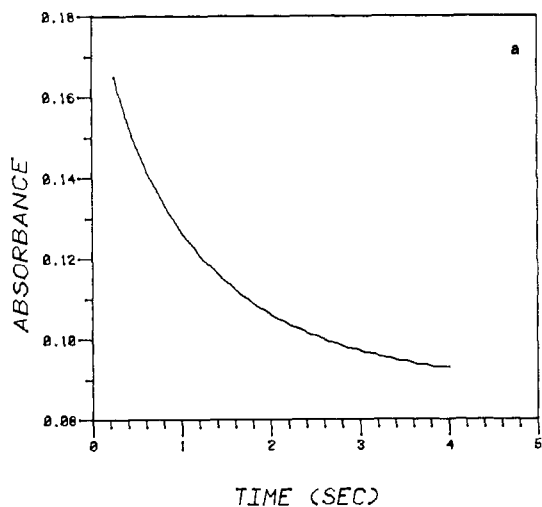


Figure 5. (a) Kinetic curve for step 1, eq 4 (decay of tris(picolinato)chromate(II)) at 408 nm ($[\text{H}^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25 °C). (b) Kinetic curve for step 1 (formation of the binuclear intermediate) at 640 nm ($[\text{H}^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25 °C).

When the three variable parameters were varied independently, the contribution of each one of the terms in the above equation to the rate law was determined. Table I is a list of the pseudo-first-order rate constant (k_1') at different values of $[\text{Fe}^{3+}]$ at 25 °C, Table II a list of k_1^* ($k_1^* = k_1'/[\text{Fe}^{3+}]$) values at various

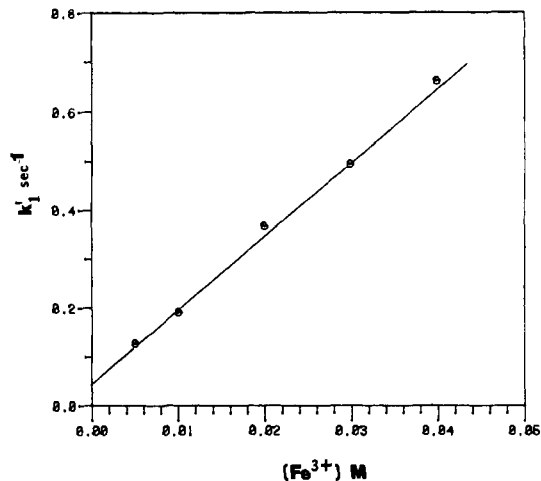


Figure 6. Plot of the pseudo-first-order rate constant (k_1') as a function of $[\text{Fe}^{3+}]$ ($[\text{H}^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25 °C).

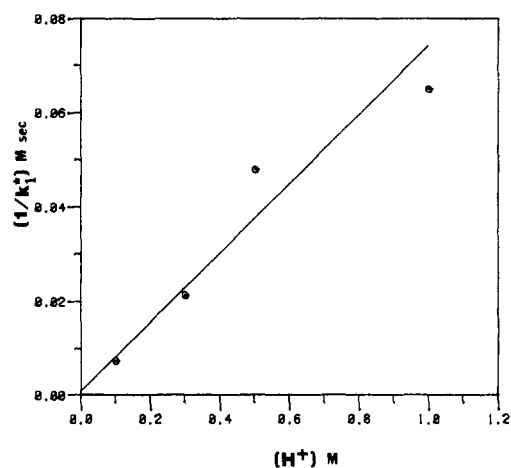
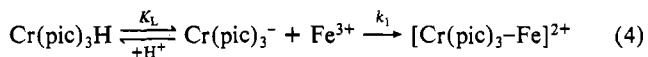


Figure 7. Plot of $(1/k_1^*)$ vs. $[\text{H}^+]$ (eq 6) ($\mu = 2.3$ M, temperature 25 °C).

temperatures, and Table III a list of k_1^* values at various $[\text{H}^+]$ values.

1. **Contribution of $[\text{Fe}^{3+}]$.** A plot of k_1' vs. $[\text{Fe}^{3+}]$ is a straight line (Figure 6). The standard deviation of the intercept of this line has the same magnitude as the intercept itself, and the latter does not show any temperature dependence, indicating that the reaction is irreversible under the experimental conditions. The electron-transfer reaction following the formation of the intermediate has a relatively high activation enthalpy and is the predominant reaction. Hence, a reverse reaction with a zero activation enthalpy seems unlikely.

2. **Contribution of $[\text{H}^+]$.** The reaction showed an inverse dependence on $[\text{H}^+]$, which can be attributed to the acid-base equilibrium of tris(picolinato)chromate(II) in accordance with the mechanism



The pseudo-first-order rate constant, k_1' (for the formation of the binuclear intermediate), is given by

$$k_1' = \frac{k_1[\text{Fe}^{3+}]K_L}{K_L + [\text{H}^+]} \quad (5)$$

Rearrangement of eq 5 using k_1^* gives

$$\frac{1}{k_1^*} = \frac{1}{k_1} + \frac{[\text{H}^+]}{k_1K_L} \quad (6)$$

Figure 7 is a plot of $1/k_1^*$ vs. $[\text{H}^+]$, from which the values of $k_1 = 2.15 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $K_L = 7.20 \times 10^{-2} \text{ M}$ ($\text{p}K_L = 1.14$) are

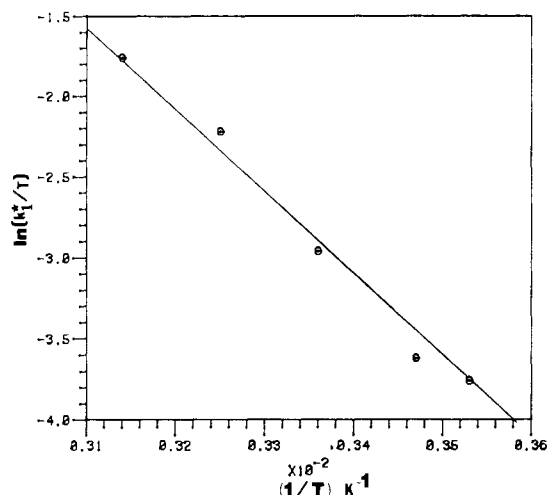


Figure 8. Eyring plot for step 1 of eq 4 ($[H^+] = 1.0$ M, $\mu = 2.3$ M).

obtained. The value of pK_L is significantly smaller than the pK_a of Fe(III) (pK_a for Fe(III) $> 2.8^{19}$), and it is unlikely that the hydrolyzed form of Fe(III) is the reactive species. Further, the value of k_1 is more consistent with the rate constants for the substitution reactions of Fe^{3+} than with the substitution reactions of $Fe(OH)^{2+}$, which are much faster (of the order of 10^4).²⁰ It is also important to note that the value reported here is very much smaller than the value of the pK_a for the carboxyl oxygen of picolinic acid (4.66),¹⁴ as one would expect. This is understandable since the positive charge originally on the central metal ion is distributed over the whole complex, and the resultant neutralization of the negative charge at the ligand center makes it more positive.²⁰ It is already known^{11,20} that Fe^{3+} prefers the carboxyl oxygen to the nitrogen on the pyridine ring. The possibility of any pathway involving the protonated form of tris(picolinato)chromate(II) can also be ruled out because this would give rise to a finite, positive intercept²⁰ in a plot of k_1^* vs. $1/[H^+]$, contrary to experimental observation. Also, from a skeletal model representing the structure of tris(picolinato)chromate(II), it can be seen that no site would be available for chelation when the complex is protonated. This reasoning is also supported by the fact that the decay of the binuclear intermediate is not pH dependent.

3. Temperature Dependence. Figure 8 represents the Eyring plot of k_1^* and is linear with an absolute value of the correlation coefficient of 0.98. From this plot the following results were obtained:

$$\Delta H^* = 10.8 \pm 0.1 \text{ kcal mol}^{-1} \quad (7)$$

$$\Delta S^* = -16.7 \pm 0.1 \text{ cal mol}^{-1} \text{ K}^{-1} \quad (8)$$

In the limiting case of $[H^+] \gg K_L$ and with $[Fe^{3+}]$ in large excess, it can be shown that

$$\frac{d \ln k_1^*}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln K_L}{dT} \quad (9)$$

Hence, the following equations are valid:

$$\Delta H^* = \Delta H^\circ + \Delta H^\ddagger \quad (10)$$

$$\Delta S^* = \Delta S^\circ + \Delta S^\ddagger \quad (11)$$

Even though the literature information on the enthalpy values for the acid-base equilibria of metal complexes is limited, there is sufficient evidence indicating that they are quite large.¹⁹ A lower limit of $5.0 \text{ kcal mol}^{-1}$ can be placed on the value of the enthalpy change for the protonation equilibrium of tris(picolinato)chromate(II), which would give a value of $5.8 \text{ kcal mol}^{-1}$ as the upper

Table IV. $[Cr(pic)_3^-]$ Dependence of $k_1'^a$

$[Cr(pic)_3^-]$, M	k_1' , s^{-1}	$[Cr(pic)_3^-]$, M	k_1' , s^{-1}
0.004	0.9	0.001	1.0
0.002	0.9		

^a $[H^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25°C , $[Fe^{3+}] = 0.05$ M.

Table V. Thermodynamic and Kinetic Data for the Formation of Tris(picolinato)chromate(II) from Bis(picolinato)chromium(II) (Eq 11)^a

t , $^\circ\text{C}$	K , M^{-1}	k_f , $M^{-1} s^{-1}$	k_b , s^{-1}	ΔH° , kcal M^{-1}
20	8×10^2			
25	9×10^2	436	0.5	5.3
30	1×10^3			

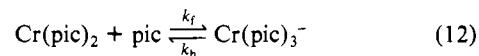
^a Conditions: pH 4.5, $\mu = 2.3$ M, 25°C .

limit for the activation energy for the substitution reaction. The effect of ionic strength on the rate constant was not studied, and this would affect the absolute value of the activation entropy but would not affect the value of the activation enthalpy.²⁰

4. Effect of $[Cr(pic)_3^-]$. In order to obtain more information on the actual mechanism of the formation of the intermediate (a substitution reaction of Fe^{3+}), experiments were performed with variation of the concentration of tris(picolinato)chromate(II) (Table IV). The values of k_1' in Table IV suggest a slight inverse dependence on the initial concentration of tris(picolinato)chromate(II). However, the effect is too small to enable one to draw any definite conclusions. Moreover, the negative value of the activation entropy for the formation of the intermediate (eq 4) suggests an associative mechanism.²⁰ As a result of the uncertainties associated with the data (arising from ionic strength effects and the entropy for the acid-base equilibrium of tris(picolinato)chromate(II)), only a qualitative emphasis should be placed on this aspect.

In order to determine the effect of any free picolinic acid present in the solution, a few runs were made where the concentration of the free picolinic acid in the tris(picolinato)chromate(II) solution was varied. This did not affect the rate of the reaction, which is not surprising considering the fact that the rate constant for the formation of (picolinato)ferrate(III)¹¹ is only $29 \text{ M}^{-1} \text{ s}^{-1}$ under these conditions. However, the concentrations of free picolinic acid in the tris(picolinato)chromate(II) solutions used in the kinetic runs were always negligible ($< 1\%$ of the concentration of tris(picolinato)chromate(II)).

It should be noted here that the bridging ligand is supplied by the reducing agent, which is a rare occurrence. In order to confirm that the kinetics of this reaction is governed by the substitution properties of Fe^{3+} , the following reaction was studied:



The equilibrium constant (k_f/k_b) for the reaction was determined by conventional spectrophotometry at three temperatures (20, 25, and 30°C) and at pH 4.5 by using the method of Siddal and Vosburgh.²¹ Due to the high overall stability constant for the tris complex the absorbance changes involved were small, which led to fairly large uncertainties. The forward rate constant was determined by stopped-flow experiments at 25°C and was additionally confirmed by a T -jump experiment (the uncertainties that are associated with the equilibrium measurements do not affect the kinetic measurements ($k_f \gg k_b$), and the forward rate constant is precise to $\pm 5\%$). The values reported in Table V represent the lower limits for the equilibrium constant and hence the upper limit for the backward rate constant. The upper limit for the backward rate constant k_b is definitely smaller than k_1 , which supports the reasoning that k_1 is determined by the substitution properties of Fe^{3+} . The true value of the equilibrium constant is expected to be higher by at least 1 order of magnitude.

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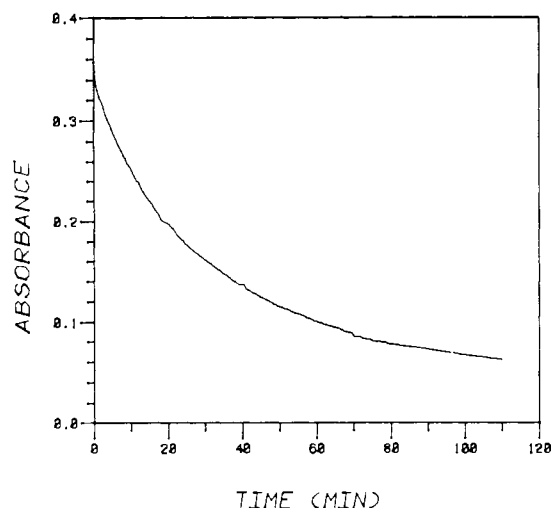


Figure 9. Kinetic curve for step 2 (decay of the binuclear intermediate) of eq 12 at 640 nm ($[H^+] = 1.0$ M, $\mu = 2.3$ M, temperature 25 °C).

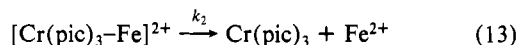
Table VI. Rate Constants for Step 2 of Eq 12^a

temp, °C	k_2, s^{-1}	temp, °C	k_2, s^{-1}
25	5.6×10^{-4}	45	4.9×10^{-3}
35	1.9×10^{-3}		

^a Conditions: $[H^+] = 1.0$ M, $\mu = 2.3$ M.

The uncertainty in the equilibrium constant arises from the uncertainty in the intercept in the method of Siddall and Vosburgh.²¹ Since only the slope of this relationship is required for the van't Hoff plot, the value of ΔH° reported here should be very accurate. It should be noted that the value of the enthalpy change for this reaction (eq 12) is comparable to the activation enthalpy for the first step (formation of the binuclear intermediate, eq 4).

Decay of the Intermediate (Eq 13). The decay of the intermediate was followed in a conventional double-beam spectrophotometer by recording the absorbance at 640 nm manually at regular intervals of time:



the data were fitted to eq 2 by the Marquardt NLIN procedure as before. The rate law representing the formation and decay of the intermediate is

$$\frac{d[\text{intermediate}]}{dt} = k_1[Fe^{3+}] - k_2[\text{intermediate}] \quad (14)$$

Since the formation of the intermediate is very rapid and is essentially irreversible, the equation reduces to a simple first-order equation of the form

$$\frac{d[\text{intermediate}]}{dt} = -k_2[\text{intermediate}] \quad (15)$$

When this equation is integrated, it takes the form of eq 2. Figure 9 is a kinetic curve obtained for the decay of the intermediate (a plot of absorbance (at 640 nm) vs. time in minutes), and Table VI lists values of k_2 at various temperatures. Figure 10 is the Eyring plot of k_2 and yields the results

$$\Delta H^\ddagger = 20.9 \pm 0.1 \text{ kcal mol}^{-1} \quad (16)$$

$$\Delta S^\ddagger = -4.5 \pm 0.1 \text{ cal K}^{-1} \text{ mol}^{-1} \quad (17)$$

The rate-determining step in the decay of the intermediate should be the transfer of the electron from Cr(II) to Fe(III) since Fe(II) is labile to substitution. The substitution rates for Fe(II)²² (of the order of 8×10^6 s⁻¹) are much higher than the value of k_2 . This is also substantiated by the unusual inertness of tris(picolinato)chromate(II) to air oxidation.^{6,7} On the basis of the

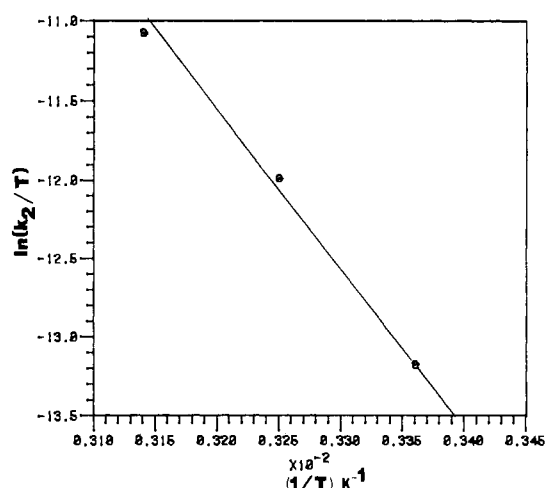


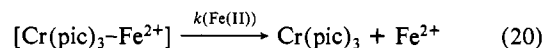
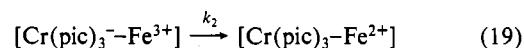
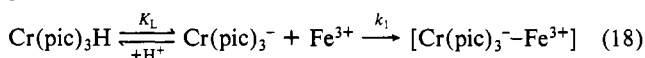
Figure 10. Eyring plot for step 2 of eq 13 ($[H^+] = 1.0$ M, $\mu = 2.3$ M).

Table VII. k_{obsd} for the Dissolution of Magnetite (Eq 20)^a

temp, °C	$[Cr(pic)_3^-], M$	$k_{\text{obsd}}, \text{min}^{-1}$
30	0.00	0.2
30	0.01	0.3

^a Conditions: pH 2.5, $\mu = 2.3$ M.

evidence presented above, the following mechanism can be proposed for the overall reaction:



Heterogeneous Electron Transfer. The heterogeneous electron-transfer reaction between $Cr(pic)_3^-(aq)$ and $Fe^{III}(s)$ was investigated by studying the dissolution of magnetite in the presence and the absence of $Cr(pic)_3^-$ in water. Uniform, spherical magnetite particles were prepared as described in the literature²³ and dispersed in water at pH values ranging from 1.0 to 6.0 by using an ultrasonic bath. Nitrogen was passed through the slurry continuously, and the temperature of the system was measured every 5 min with a mercury thermometer. Small volumes of the reaction mixture were pipetted out at regular intervals of time and were filtered and tested for dissolved Fe^{2+} with use of 2,2'-bipyridyl, and electron micrographs of the particles were taken. The experiments were repeated in the presence of $Cr(pic)_3^-$ at various concentrations. The average temperature of the reaction mixture was 30 ± 1 °C. The data were plotted according to the equation⁵

$$(1 - C_t/C_\infty)^{1/3} = 1 - (k/\rho r_0)t \quad (21)$$

where C_t is the concentration of dissolved Fe^{2+} at time t , C_∞ is the concentration of dissolved Fe^{2+} as $t \rightarrow \infty$, r_0 is the initial radius of the particles, ρ is the density of the particles, and k is the rate constant for dissolution.

A plot of $(1 - C_t/C_\infty)^{1/3}$ vs. t should be linear for monodispersed particles since r_0 and ρ are constant for a particular batch of particles. In practice this equation held good for about 75% of the reaction since the particles tend to get polydispersed toward the latter part of the reaction.⁵ The slope of this plot is a good indication of the rate constant for dissolution when applied to particles with a narrow size distribution (from the same batch). The value of $k_{\text{obsd}} (=k/r_0\rho)$ for the dissolution of magnetite (Table VII) does not show significant variation in the presence and absence of $Cr(pic)_3^-$. Considering the relatively large errors in these sampling methods,⁵ these two values can be considered to be essentially the same, indicating that tris(picolinato)chromate(II)

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does not contribute appreciably to the dissolution of magnetite (at least at this temperature). This is not totally surprising considering that the rate constant for the homogeneous electron transfer is rather small ($1.9 \times 10^{-3} \text{ s}^{-1}$ at 35°C). On the other hand, the rather high activation enthalpy for electron transfer suggests that the reductive dissolution of magnetite at higher temperatures would proceed at useful rates (k_2 (extrapolated to 80°C) = $1.2 \times 10^{-1} \text{ s}^{-1}$). Due to experimental difficulties this aspect was not pursued at the present time.

Conclusions

There are several important observations resulting from this work:

(1) Until now Cr(II) has been studied mainly for its redox behavior,⁹ although some of the other properties (such as hydrolysis in aqueous solutions²⁴) have been studied indirectly. We now have a species of Cr(II) that is relatively stable to air oxidation and hence can be used to study its substitution chemistry relatively easily.

(2) This is probably the first instance when significantly high concentrations of a relatively long-lived precursor complex (involving Cr(II)) has been produced by mixing an oxidant and a reductant directly.^{25,26} An interesting aspect of this study is that the spectrum of the inner-sphere complex can be obtained at various stages of the reaction. Further studies are being directed toward obtaining the visible and Raman spectra of this intermediate at various stages of the formation and decay by rapid data acquisition using photodiode arrays. We believe that this would give further insight regarding the detailed mechanism of electron transfer by providing information about the structure of the intermediate at various stages of the reaction. Redox reactions involving transition-metal oxidants and tris(picolinato)chromate(II) will probably follow an inner-sphere mechanism similar to this reaction with Fe^{3+} , and this system should provide an

excellent experimental model for future studies on intramolecular electron transfer. The unusual stability of tris(picolinato)chromate(II) can be explained by the following two reasons:

(1) The pyridine ring is able to withdraw electrons, which is supported by the fact that the complex of Cr(II) with isonicotinic acid²⁷ is also stable with respect to oxidation (though not to the same extent as the complex with picolinic acid).

(2) From a skeletal molecular model for tris(picolinato)chromate(II) it can be seen that Cr(II) can form a chelate by using both the carboxyl oxygen and the nitrogen on the pyridine ring to form a sterically stable closed five-membered ring structure. Since the nitrogen and the carboxyl oxygen on picolinic acid are part of a conjugated structure,²⁵ the complex is extremely stable with respect to oxidation. Even though the nitrogen and the carboxyl oxygen are part of a conjugated system in isonicotinic acid, the complex is not as stable due to the fact that it is not possible for the metal ion to be bonded to both the nitrogen and the oxygen.

Finally, certain guidelines regarding the suitability of a reducing agent for dissolving oxides having a high chromium content can be formulated. In order to prepare a complex of Cr(II) that would have a thermodynamically favorable redox potential for reducing Cr(III), one would have to use a ligand that is not strongly electron withdrawing. A rule of thumb would be to use a ligand that would complex Cr(III) more strongly than Cr(II). It appears that complexes of oxalic acid or ethylenediaminetetraacetic acid (EDTA) with Cr(II) would be suitable for this purpose. Since the dissolution of corrosion products in nuclear reactors is usually carried out at high temperatures, chromium(II) oxalate should be more suitable than the chromium(II) EDTA complex. Further work along these lines should provide definitive answers.

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Chemistry of Highly Reduced Polypyridyl-Metal Complexes. Anion Substitution Induced by Ligand-Based Reduction

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For a series of complexes of the type *cis*-[M(bpy)₂(L)Cl]ⁿ⁺ (bpy = 2,2'-bipyridine), where M is Ru^{II} or Os^{II} and L is a variety of ligands that range from σ and π donors such as Cl⁻ to σ donors and π acceptors such as pyridine or tertiary phosphines to π acceptors such as CO, bpy-based electrochemical reduction causes rapid loss of Cl⁻. Cyclic voltammetric and bulk electrolysis studies in CH₃CN show that two sequential, one-electron reductions (each bpy based) followed by reoxidation lead to exchange of CH₃CN for Cl⁻ at the metal center. The results of differential-pulse polarographic experiments show that the rate of Cl⁻ loss is retarded as the ligand L is made more electron withdrawing. Likewise, using complexes containing the better electron-accepting anions NO₂⁻ and CN⁻ instead of Cl⁻ leads to stabilization of the bpy-reduced product and slower loss of the anionic ligand.

Metal complexes containing polypyridyl ligands such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), or their substituted derivatives show distinctive electrochemical properties that derive from both metal- and ligand-based redox processes. In the majority of cases the complexes show at least one electrochemically reversible, one-electron reduction for each of the polypyridyl ligands present in the coordination sphere. For complexes like [M(bpy)₃]²⁺ (M = Fe, Ru, Os)¹⁻⁴ or [Ru(bpy)₂(PR₃)Cl]⁺⁵ the

reduction processes occur at potentials more negative than -1.2 V (vs. SCE) although the exact potential depends upon a number of factors such as the σ -donor and π -acceptor abilities of the ancillary ligands and the overall charge on the complex.⁵

An important aspect of the reactivity of the reduced complexes is their implied ability to act as multiple-electron reservoirs, which may have important applications in chemical reductions. Thus, [Ru^{II}(bpy⁻)₂(bpy)]⁰ will produce H₂ from aqueous acetonitrile

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