

TiCl₄-CH₃C(CH₂AsMe₂)₃ and the tungsten complex shows that all of the peaks in the former, including that due to C-CH₃, lie at 0.13–0.4 ppm to lower field than those in the latter. It should be noted that the C-CH₃ and uncomplexed -AsCH₂- resonances for the tungsten complex

(and for Re(CO)₃CH₃C(CH₂AsMe₂)₃Cl, in which the ligand is bidentate) have been misassigned in the original publication.³⁷
(37) R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6564 (1965).

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Linear Free Energy Relationship for Some Inner-Sphere Electron-Transfer Reactions

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Received August 7, 1975

AIC50593G

Second-order rate constants k_2 have been measured for the reactions by which various chromous complexes, Cr^{II}L, are oxidized to corresponding chromic complexes, Cr^{III}L, by Cr(NH₃)₅Cl²⁺ acting as oxidant. Reversible reduction potentials, \mathcal{E}° , of the Cr^{III}L complexes have also been studied. At 25 °C, in 1 M NaClO₄, values of k_2 , M⁻¹ s⁻¹ ($-\mathcal{E}^\circ$, V vs. SCE), for various ligands L are as follows: EDDaDp, 7.1×10^4 (1.42); EDTA, 1.2×10^3 (1.23); HEDA, 3.4×10^3 (1.22); MIDA, 3.15 (0.82). These data and previously measured values for L = H₂O follow the linear free energy relationship $\Delta \log k_2 = 0.48 \Delta \mathcal{E}^\circ$. There is firm evidence that the reactions of the aquo ion and the MIDA complex follow the inner-sphere electron-transfer mechanism and the same mechanism is probable for the other reactions. The enthalpies of activation (kJ mol⁻¹) for the EDTA and EDDaDp reactions are 54 and 32. Entropies of activation (J deg⁻¹ mol⁻¹) for the same reactions are -6 and -44. These results are interpreted in terms of rate-determining electron transfer in a binuclear intermediate.

Introduction

Reversible electrode potentials (\mathcal{E}°) for Fe(III)-Fe(II) couples vary over a wide range, depending on the nature of the ligands coordinated to iron. In particular, the series of tris(orthophenanthroline) complexes¹ (with various substituents on the ligand rings) has been used a number of years ago to demonstrate that simple outer-sphere electron-transfer reactions² and also more complex reactions, probably initiated by outer-sphere electron transfer,³ follow linear free energy relationships. For such reactions, changes in free energy of activation directly parallel changes in overall free energy of reaction, measured by changes in the reduction potential of the Fe(III) complexes involved. This result is consistent with Marcus' theory⁴ as well as with less elaborate rationalizations⁵.

The effectiveness of changes in ligands on Co(III) complexes in causing changes in rate of reaction depends on the reducing agent, being large for Fe(II)-Co(III) reactions⁶ but small for Cr(II)-Co(III)⁷ reactions. Guenther and Linck⁸ demonstrated that linear free energy relationships existed between log rates of reduction of a series of common oxidants, by Fe²⁺ on the one hand and either Ru(NH₃)₆²⁺ or V²⁺ on the other hand. The order of sensitivity to changes in the nonbridging ligands on Co(III) was Fe²⁺ > Ru(NH₃)₆²⁺ > V²⁺. The authors interpreted this order on the basis that lower reducing power (Fe²⁺) corresponds to a transition state which more closely resembles the reactants but that more powerful reductants (as V²⁺) give rise to a transition state more like the products. This version of the maxim "the more reactive, the less selective" has also been expressed in a more formal way.⁹

Shortly after the elucidation of the inner-sphere electron-transfer mechanism, Taube¹⁰ suggested that reactions following this mechanism should follow linear free energy relationships. Characteristics which favor the bridged electron-transfer mechanism are not conducive to measurement of free energy data. Bustin and Earley¹¹ studied polarographic reductions of various chromium(III)-amino acid complexes and demonstrated that these Cr(III)-Cr(II) systems covered a wide range of potentials. Using these data, Earley¹² summarized evidence¹³ that Cr(II)-Cr(III) electron-transfer reactions (involving OH⁻ as bridging ligand) followed a linear

free energy relationship over many orders of magnitude. We now present more detailed results of a related study of Cr(II)-Cr(III) electron transfers, in this case involving chloride ion as bridging group.

Experimental Section

Materials. The compound [Cr(NH₃)₅Cl]Cl₂ was prepared according to the method of Schlessinger.¹⁴ The perchlorate salt was precipitated from solutions of the chloride by slow addition of a solution of perchloric acid and cooling. The precipitate was washed with ice-cold water, ethanol, and ether and was air-dried. The complex was stored in the dark to prevent photochemical decomposition. The visible and ultraviolet absorption spectra of the complex showed maxima at λ 513 (ϵ 35.6) and 376 nm (ϵ 36.8 M⁻¹ cm⁻¹) in good agreement with published data.¹⁵

Deionized water that had been doubly distilled through a quartz apparatus was used throughout. Sodium perchlorate was prepared by neutralization of analytical grade HClO₄ with Na₂CO₃ and was recrystallized twice from distilled water. Stock solutions of chromium(II) perchlorate were obtained by allowing excess Cr metal (99.999%) to react with HClO₄ for about 1 week. The resultant solution, after filtration from the excess Cr metal, showed a pH of ~3. It was standardized by oxidation with potassium dichromate, the excess chromium(VI) being determined iodometrically. "Analyzed reagent" disodium ethylenediaminetetraacetate dihydrate (J. T. Baker), recrystallized from ethanol-water mixtures, was used as the source of the ligand EDTA. Standard solutions were made up by weight. *N*-(2-Hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and *N*-methyliminodiacetic acid (MIDA) obtained from the Aldrich Chemical Co. (99%) were twice recrystallized from water and standardized by pH titration. The ligand ethylenediamine-*N,N'*-diacetic-*N,N'*-di-3-propionic acid (EDDaDp) (LaMont Laboratories) was further purified prior to use by treating weighed aliquots of the acid with 2 equiv of NaOH to effect solution, followed by the addition of HClO₄ to precipitate the free acid. The solid obtained, after drying in air, analyzed as the trihydrate C₁₂H₂₀O₈N₂·3H₂O. Anal. Calcd: C, 38.5; H, 6.95; N, 7.49. Found: C, 38.0; H, 7.06; N, 7.23. It underwent a 14.6% loss in weight (\equiv 3 H₂O) on heating at 110 °C for 1 h. A further check on the ligand EDDaDp was obtained from its pH titration in 0.1 M KCl solution. Titration data in good agreement with those reported earlier by Chaberek and Martell¹⁶ were obtained.

Kinetic Measurements. Many of the rate constant determinations were made using a Durrum stopped-flow instrument with a 2-cm

optical path, coupled to a Biomation transient recorder and a Hewlett-Packard X-Y recorder with time base. Slower rate measurements involving the reductants Cr^{II}MIDA and Cr(H₂O)₆²⁺ were obtained on a Gilford 240 spectrophotometer equipped with a thermostated 10-cm cell compartment and a fast-scanning recorder. The reactions were followed by monitoring the increase in absorbance at or near the wavelength of maximum absorbance of the Cr^{III}L product (λ 540–560 nm). In some cases, a continuing small increase in absorbance, following the main absorbance change due to the formation of Cr^{III}L, was noted. This latter change, which was attributed to the reduction of water by the strongly reducing Cr^{II}L species, did not seriously affect the kinetic measurements being made. Pseudo-first-order rate constants calculated by the Guggenheim method¹⁷ were always found to be linear to at least 2 and usually 3–4 half-times.

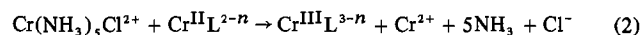
All kinetic measurements were made with excess ligand as buffer using sodium perchlorate to maintain the ionic strength at 1.0 M. In a typical experiment, a mixture of Cr(NH₃)₅Cl²⁺, ligand, and sodium perchlorate was adjusted to the appropriate pH with sodium hydroxide. For slower reactions, this solution was introduced into a two-necked 10-cm optical absorption cell in the thermostated cell compartment of the Gilford spectrophotometer. After deoxygenation of the solution with O₂-free nitrogen, the reaction was initiated by injection of thermostated chromium(II) perchlorate. In experiments requiring the stopped-flow method, the buffered solution was mixed with a chromium(II) solution which had also been adjusted to an ionic strength of 1.0 M with NaClO₄. It was established in separate experiments that the pH of the medium was not significantly affected by the addition of the chromium(II) solution.

Potential Measurements. Cyclic voltammetric measurements were made using a three-electrode polarographic cell and standard operational amplifiers adapted from the instrumentation described elsewhere.¹⁸ Potentials were obtained mostly using a commercially available (Brinkman Instruments, Inc.) hanging mercury drop electrode. Some difficulty was encountered with this method in measurements involving ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid as ligand. The solution appeared to exhibit a detergency effect causing loss of adhesion by the drop. For this reason, measurements were also made using a dropping mercury electrode with a slow flow rate maintained by a small Hg column. No differences were noted in the potentials obtained by the two methods. Potentials were measured with respect to a calomel electrode saturated with NaCl, which has a potential 5 mV more negative than the SCE, but are reported with respect to the latter. Voltammograms were recorded on a storage oscilloscope at 3–4 V/s, the voltage calibration being made with an NLS digital voltmeter.

In a particular measurement, a solution containing the appropriate ligand and sodium perchlorate concentrations adjusted to the required pH with NaOH was deoxygenated in the polarographic cell. The chromium(II)-chelate complex was then generated by addition of chromium(II) perchlorate from a calibrated syringe, and the potential measurements were made on the fresh chromium(II)-ligand solution.

Results

Table I summarizes kinetic data obtained for reactions of the Cr^{II}-EDTA, Cr^{II}-HEDTA, and Cr^{II}-EDDaDp complexes with Cr(NH₃)₅Cl²⁺ between pH 3.3 and 6.1. The reaction followed in each case is in effect the Cr²⁺-catalyzed conversion of Cr(NH₃)₅Cl²⁺ to the corresponding chromium(III) chelate complex, as in eq 1 and 2. Spectra of the final reaction



products showed maxima at λ 544 and 392 nm for the Cr^{III}-EDTA complex and at λ 545 and 388 nm for the Cr^{III}-HEDTA complex in agreement with published data for the quinquadentate species Cr(H₂O)EDTA⁻ and Cr(H₂O)-HEDTA⁰.^{11,19} The nature of the chelate complex formed with the ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid ligand is less well established. A spectrum with λ_{max} 397 and 547 nm was recorded for this complex. With such strongly chelating ligands, it is expected that the chromium(II) present during the reaction will be entirely in the complexed form under the experimental conditions employed. The calculated

Table I. Kinetic Data for the Reaction of Cr(NH₃)₅Cl²⁺ with Cr^{II}L at 1.0 M Ionic Strength (NaClO₄)^a

[L] _T , mM	[Cr(II)] _T , mM	pH	Temp, °C	<i>k</i> _{obsd} , s ⁻¹	10 ⁻³ <i>k</i> ₂ , M ⁻¹ s ⁻¹
(a) L = EDTA					
50	1.03	5.6	25.0	1.27	1.23
50	1.03	3.3	25.0	1.47	1.43
50	1.03	4.5	25.0	1.28	1.24
25	1.03	4.5	25.0	1.15	1.12
50	2.06	4.5	25.0	2.63	1.29
50	1.02	4.2	25.0	1.18	1.15
50	1.02	4.2	32.2	1.69	1.64
50	1.02	4.2	15.0	0.468	0.457
50	1.02	4.2	7.0	0.265	0.259
(b) L = HEDTA					
50	1.04	4.4	25.0	3.56	3.42
50	1.04	5.2	25.0	3.50	3.37
50	1.04	5.1	25.0	3.62	3.48
50	1.04	3.4	25.0	3.08	2.96
(c) L = EDDaDp					
43.6	0.933	6.1	25.0	62.1	66.6
43.6	0.933	4.4	25.0	74.7	80.1
34.2	0.933	4.5	25.0	72.7	77.9
34.2	0.933	5.7	25.0	51.5	55.2
34.2	0.933	5.7	25.0	50.4	54.0
41.1	1.20	5.7	25.0	78.5	65.4
41.1	1.20	5.7	34.5	135.1	113
41.1	1.20	5.7	15.8	57.6	48.0
41.1	1.20	5.7	6.4	34.5	28.8

$$^a [\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}] = (1.4\text{--}1.6) \times 10^{-3} \text{ M.}$$

second-order rate constants, $k_2 = k_{\text{obsd}}(\text{s}^{-1})/[\text{Cr}(\text{II})]_{\text{T}}$, are seen to be independent of both ligand concentration and pH, consistent with this expectation. The data also establish a first-order dependence on [Cr(II)] and [Cr(NH₃)₅Cl²⁺] indicating a rate expression

$$d[\text{Cr}^{\text{III}}\text{L}]/dt = k_2 [\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}] [\text{Cr}^{\text{II}}\text{L}] \quad (3)$$

The specific rate constants obtained with Cr^{II}EDTA, Cr^{II}-HEDTA, and Cr^{II}EDDaDp as reductants were $(1.24 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $(3.42 \pm 0.17) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, and $(7.12 \pm 0.85) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 25.0 °C. Rate measurements were also made at temperatures other than 25 °C with two of the complexes, and activation parameters were calculated from plots of $\log(k_2/T)$ vs. $1/T$. The values of the parameters so obtained are $\Delta H^\ddagger = 54.0 \pm 11.3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -5.9 \pm 23.4 \text{ J deg}^{-1} \text{ mol}^{-1}$ for Cr^{II}EDTA and $\Delta H^\ddagger = 32.2 \pm 4.6 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -43.5 \pm 15.9 \text{ J deg}^{-1} \text{ mol}^{-1}$ for Cr^{II}-EDDaDp.

Ogino and Tanaka²⁰ have previously determined a value of $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for the rate of electron transfer between Cr(NH₃)₅Cl²⁺ and the ethylenediaminetetraacetatochromium(II) complex at 25.0 °C. They reported activation parameters $\Delta H^\ddagger = 38.1 \pm 4.2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -54 \pm 13 \text{ J deg}^{-1} \text{ mol}^{-1}$ for the same reaction, though details of the rate constants at temperatures other than 25 °C are not provided. Though there is some discrepancy between their activation parameters and those determined in this work, we suggest that this is possibly due to limitations imposed in the measurement of such a rapid reaction with their experimental method. The mixing of reactants directly in an optical cell and the recording of absorbance changes within 5 s of mixing are expected to result in lack of precision in their data compared to measurements made in this work by the stopped-flow method (mixing time of a few milliseconds).

Kinetic data were also obtained for the reduction of Cr(NH₃)₅Cl²⁺ by the chromium(II)-*N*-methyliminodiacetic acid²¹ complex, Cr(MIDA)(H₃O)₃ (Table II). Rate measurements in this case were made at pH 2.5 to avoid the formation of higher bis complexes which are known to exist.²² Under these conditions, only a fraction of the total chromi-

Table II. Kinetic Data for the Reaction of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ with $\text{Cr}(\text{MIDA})(\text{H}_2\text{O})_3$ at 25.0° and 1.0 M Ionic Strength (NaClO_4)^a

[MI-DA], M	$10^4 k_{\text{obsd}}$, s ⁻¹	$10k_2',^b$ M ⁻¹ s ⁻¹	[MI-DA], M	$10^4 k_{\text{obsd}}$, s ⁻¹	$10k_2',^b$ M ⁻¹ s ⁻¹
0.029	2.00	1.89	0.154	8.55	8.07
0.050	3.32	3.13	0.175	9.17	8.65
0.080	5.67	5.35	0.200	10.3	9.65
0.100	6.42	6.06	0.250	11.3	10.7
0.120	6.22	5.87	0.269	11.5	10.9
0.150	7.27	6.86			

^a $[\text{Cr}(\text{II})]_{\text{T}} = 1.06 \times 10^{-3}$ M; $[\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}] = 8.7 \times 10^{-4}$ to 1.54×10^{-3} M; pH 2.5. ^b $k_2' = k_{\text{obsd}}/[\text{Cr}(\text{II})]_{\text{T}}$.

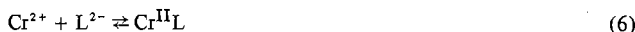
um(II) was present in the complexed form and the measured pseudo-first-order rate constants showed a dependence on the ligand concentration of the form $k = a[\text{L}]/(b + [\text{L}])$. The observed rates are sufficiently high that contribution due to reduction of Cr(III) by uncomplexed Cr^{2+} is negligible.

Under the experimental conditions employed, where the total chromium(II) is distributed between complexed and uncomplexed forms and where the *N*-methyliminodiacetic acid is present as a mixture of protonated, unprotonated, and coordinated ligand, the relationships

$$[\text{Cr}^{\text{II}}\text{L}] = \frac{K[\text{L}^{2-}][\text{Cr}(\text{II})]_{\text{T}}}{1 + K[\text{L}^{2-}]} \quad (4)$$

$$[\text{L}]_{\text{T}} = \left\{ \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1 \right\} [\text{L}^{2-}] + [\text{Cr}^{\text{II}}\text{L}] \quad (5)$$

can be shown to hold, where K is the chelate formation constant for the reaction



K_1 and K_2 are the two acid dissociation constants for *N*-methyliminodiacetic acid,²³ and $[\text{Cr}(\text{II})]_{\text{T}}$ and $[\text{L}]_{\text{T}}$ represent the total analytical concentration of chromium(II) and ligand present during the reaction.

If the reduction is carried wholly by the chelated chromium(II) species $\text{Cr}(\text{MIDA})(\text{H}_2\text{O})_3$ according to the rate expression given in eq 3, provided $[\text{L}]_{\text{T}} \gg [\text{Cr}^{\text{II}}\text{L}]$, elimination of $[\text{L}^{2-}]$ and $[\text{Cr}^{\text{II}}\text{L}]$ from eq 3–5 leads to the expression

$$\frac{1}{k_2'} = \left\{ \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1 \right\} \frac{1}{K k_2 [\text{L}]_{\text{T}}} + \frac{1}{k_2} \quad (7)$$

where $k_2' (=k_{\text{obsd}}(\text{s}^{-1})/[\text{Cr}(\text{II})]_{\text{T}})$ is the apparent second-order rate constant.

A test of this relation can be made in a plot of $1/k_2'$ vs. $1/[\text{L}]_{\text{T}}$ which should be a straight line having $1/k$ as intercept and

$$\left\{ \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1 \right\} \frac{1}{K k_2}$$

as slope. Treatment of the data in this manner, shown in Figure 1, leads to the values of $k_2 = 3.15 \text{ M}^{-1} \text{ s}^{-1}$ and $K = 1.84 \times 10^7 \text{ M}^{-1}$, using $K_1 = 10^{-1.95}$ and $K_2 = 10^{-9.3}$. The value of K , derived from this treatment, is in line with values reported for the complexation of other first-row divalent transition metal ions by the same ligand.²³ Visible spectra recorded on a Cary 14 spectrophotometer at the end of the reaction with MIDA as ligand were not consistent with $\text{Cr}(\text{MIDA})(\text{H}_2\text{O})_3^{3+}$ as the chromium(III) product. Hamm and Weyh²² reported a spectrum for this complex with maxima at 393 (ϵ 48) and 553 nm (ϵ 60 $\text{M}^{-1} \text{ cm}^{-1}$). The immediate product of our reaction showed absorption bands shifted appreciably toward higher

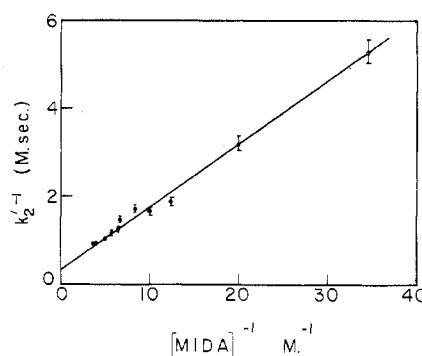
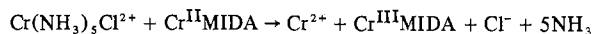


Figure 1. Plot of the reciprocal of the apparent second-order rate constant k_2' against $[\text{MIDA}]^{-1}$ showing conformity to eq 7.

wavelengths: λ_{max} 405 (ϵ 53) and 565 nm (ϵ 63). The spectrum obtained from product solutions left to stand overnight, however, resembled that of $\text{Cr}(\text{MIDA})(\text{H}_2\text{O})_3^{3+}$ quite closely with λ_{max} 395 (ϵ 47) and 554 nm (ϵ 59). Experiments were also carried out to monitor the release of Cl^- into solution during the reaction. The turbidity resulting on addition of Ag^+ to quenched reaction solutions at various times ($t < t_{1/2}$) was compared to the turbidity obtained with standard Cl^- solutions under similar conditions. The rate of Cl^- buildup was found to be slower than the rate of reduction of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. At reaction times $t_{1/4}$ – $t_{1/3}$ the free chloride ion in solution was only 25–40% of that expected for an outer-sphere reaction



though at the end of the reaction near-quantitative release of Cl^- was found.

The rate of electron transfer between $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ and Cr^{2+} in the absence of complexing ligands has also been measured. An average value of $k_2 = 4.95 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, independent of acidity, was obtained from three experiments at 25.0 °C and 1.0 M ionic strength, in good agreement with the value of $5.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ reported by Ogard and Taube.²⁴

Formal redox potentials for the $\text{Cr}^{\text{II}}\text{L}$ – $\text{Cr}^{\text{III}}\text{L}$ couples, where $\text{L} = \text{EDTA}$, EDDAp , and MIDA , were determined by cyclic voltammetry using both hanging mercury drop and dropping mercury electrode methods. Measurements were made in the presence of excess ligand at an ionic strength of 1.0 M maintained with NaClO_4 as in the kinetic experiments. For the $\text{Cr}^{\text{II}}\text{EDTA}$ complex, the reversible voltammogram recorded at pH 5.9 was in agreement with earlier findings.^{11,25} Reversible voltammograms were also recorded for the chromium(II)–ethylenediamine-*N,N'*-diacetic-*N,N'*-di-propionic acid system, though the respective anodic and cathodic peaks in this case were found at more negative potentials than was the case for the EDTA complex. In light of this unexpected result, measurements were made at several pH values and with variation in the excess ligand concentration. From six such measurements (Table III) between pH 4.1 and 5.4, which showed no systematic trend, an average value of \mathcal{E}° of $-1.424 \pm 0.017 \text{ V}$ was obtained. The formal potential was obtained from the average of the anodic and cathodic peaks, which showed a separation of some $76 \pm 4 \text{ mV}$ in the six determinations made. Though at the very negative potentials involved the cathodic peak was found close to the hydrogen wave with which it merged, the two were always sufficiently separated for measurement of the cathodic peak potential to be possible.

In the *N*-methyliminodiacetic acid case, a different approach was adopted since it was not possible to work with the chromium(II) entirely in the complexed form. The cyclic

Table III. Data on the Formal Potential^a of the Cr^{II}EDDaDp-Cr^{III}EDDaDp Couple at $\mu = 1.0$ M and 22 °C

pH	[EDDaDp], mM	[Cr(II)] _T , mM	-E°, V vs. SCE
4.1	10.2	2.05	1.420 ^b
4.7	20.4	2.05	1.407 ^b
4.8	7.4	2.05	1.455 ^c
5.1	11.0	2.23	1.447 ^c
5.3	11.2	2.05	1.415 ^c
5.3	22.4	2.05	1.410 ^c
Av			1.42 ± 0.02

^a The values reported are the arithmetic average of the cathodic and anodic peak potentials. ^b Measured using a dropping mercury electrode. ^c Measured using a hanging mercury drop electrode.

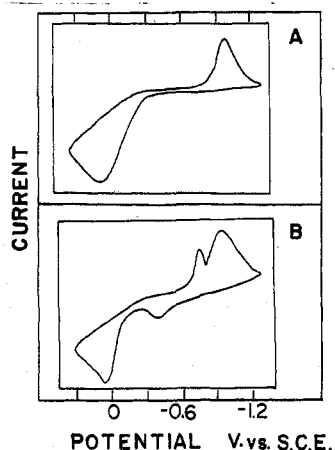


Figure 2. Cyclic voltammograms of 4 mM chromium(II) solutions at pH 2.5, 22 °C, and 1.0 M ionic strength (NaClO₄); scan rate 3.3 V/s: (A) [Cr(H₂O)₆](ClO₄)₂ = 4 × 10⁻³ M; (B) [Cr(II)]_T = 4 × 10⁻³ M, [MIDA] = 10⁻³ M.

voltammogram obtained for a 4 × 10⁻³ M solution of chromium(II) perchlorate at pH 2.5 in the absence of complexing ligands is shown in Figure 2. It shows typically irreversible oscillographic waves with a large separation between the cathodic and anodic peaks. For a similar solution containing additional 10⁻³ M *N*-methyliminodiacetic acid, further maxima were observed between the Cr³⁺ and Cr²⁺ waves in both the anodic and cathodic phases of the cycle. These are due to the Cr^{II}-MIDA and Cr^{III}-MIDA complexes generated in the ligand solution. With increase in the ligand concentration, a shift in the potential of the anodic peak due to oxidation of Cr(MIDA)(H₂O)₃ was noted toward more negative values, while the position of the cathodic maximum due to the reduction of Cr(MIDA)(H₂O)₃⁺ remained relatively unchanged. This potential dependence on the ligand concentration due to the changing fraction of the chromium(II) present in the complexed form is shown in Figure 3. The limiting potential at high [MIDA], obtained from a reciprocal plot of 1/E_{anodic} vs. 1/[MIDA] when averaged with the cathodic potential of Cr^{III}MIDA, afforded a value of -0.819 V vs. SCE for the formal potential of the Cr^{II}MIDA-Cr^{III}MIDA couple at pH 2.5. The value of *Q*, the formal equilibrium quotient for the Cr^{II}-MIDA complex, derived from these data is 4 × 10⁸, which deviates from the value of the equilibrium constant *K* measured spectrophotometrically by 1 order of magnitude. Such deviations between polarographic and spectrophotometric measurements of equilibrium constants are usually ascribed to kinetic complications on the electrode reactions,¹¹ and the optical value is preferred.

Discussion

The finding that the ligand ethylenediamine-*N,N'*-di-propionic acid, EDDaDp, gave a more negative reduction potential with chromium(II) than did EDTA suggests greater

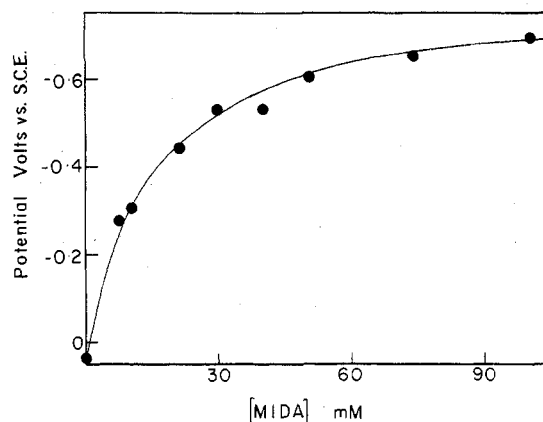


Figure 3. Dependence of the anodic Cr^{II}MIDA peak potential on [MIDA]_T at pH 2.5, [chromium(II)]_T = 4 × 10⁻³ M, and 1.0 M ionic strength.

Table IV. Summary of Data on the Reaction of Cr(NH₃)₅Cl²⁺ with Cr^{III}L Reductants

L	<i>k</i> ₂ , M ⁻¹ s ⁻¹	-E°[Cr ^{II} L-Cr ^{III} L], V vs. SCE
EDDaDp	7.12 × 10 ⁴	1.424 ^a
EDTA	1.24 × 10 ³	1.227 ^b
HEDTA	3.42 × 10 ³	1.22 ^c
MIDA	3.15	0.819 ^d
H ₂ O	4.95 × 10 ⁻²	0.656 ^e

^a This work at 22 ± 1 °C and $\mu = 1.0$ M (NaClO₄). ^b At 20 °C and $\mu = 0.10$ M (KCl): R. L. Pecsok, L. D. Shields, and W. P. Schaefer, *Inorg. Chem.*, **3**, 114 (1964). A value of -1.20 V was obtained in this work by cyclic voltammetry at 22 °C and $\mu = 1.0$ M (NaClO₄). ^c At 22 °C and $\mu = 0.2$ M (NaClO₄): D. I. Bustin and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 1818 (1967). ^d This work at 22 °C, $\mu = 1.0$ M (NaClO₄), and pH 2.5. ^e At 19 °C: G. Grube and A. Breitingner, *Z. Elektrochem.*, **33**, 112 (1927).

stabilization of the oxidized form through chelation in the case of EDDaDp.

In the chromium(III) complex Cr(EDTA)(H₂O)⁻, EDTA behaves as a quinque-dentate chelating ligand, and its inability to achieve closure of the fifth chelate ring (compared to Co(EDTA)⁻ in which it is hexadentate) has been attributed both to the larger size of chromium(III) ion²⁵ and to the different repulsions between the t_{2g} electrons of the ions and the methylene group of the ring in the two cases.¹⁹

With EDDaDp as ligand the ability of the larger propionate group to form six-membered rings should enable the Cr^{III}-EDDaDp complex to avoid the strain present in the corresponding EDTA complex. Consistent with this, Douglas and Radanovic²⁶ have recently reported the preparation of a Cr^{III}-EDDaDp complex in which EDDaDp acts as a hexadentate ligand. They have characterized the complex through its infrared, electronic absorption, and CD spectra and have shown that of three possible geometrical isomers, the trans (O₅) isomer with two six-membered rings in the plane of the diamine ring is formed preferentially. This isomer is preferred since it avoids the strain associated with five-membered glycinate rings in the "equatorial" girdle plane. Bond length and bond angle data²⁷ have shown that even in the hexadentate Co(EDTA)⁻ complex the five-membered glycinate rings in the girdle plane are considerably more strained than the two glycinate rings bonded in the "axial" positions. Greater stabilization of the chromium(III) ion in Cr(EDDaDp)⁻ through increased chelation, compared to the corresponding EDTA complex, is consistent with the greater reducing power of Cr^{II}EDDaDp noted in this study.

Tables IV and V contain summaries of kinetic data that we have obtained on the Cr(II)-catalyzed formation of Cr(III)

Table V. Kinetic Parameters for the Reaction of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ with Chromium(II) Reductants

Reductant	$k_2(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J deg}^{-1} \text{mol}^{-1}$
$\text{Cr}(\text{H}_2\text{O})_6^{2+}$	4.95×10^{-1}	46 ^a	-113 ^b
$\text{Cr}(\text{EDTA})^{2-}$	1.24×10^3	54	-6
$\text{Cr}(\text{EDDaDp})^{2-}$	7.12×10^4	32	-44

^a Reference 26. ^b The value $-96 \text{ J deg}^{-1} \text{ mol}^{-1}$ reported in error in ref 24 is corrected to $-113 \text{ J deg}^{-1} \text{ mol}^{-1}$ in ref 37.

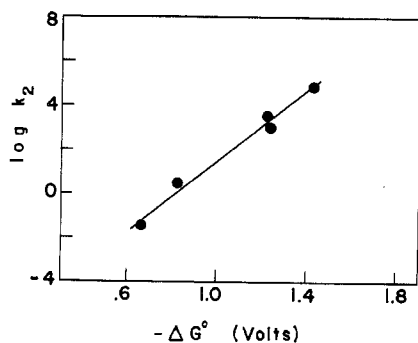


Figure 4. Variation of rate of Cr(II)-Cr(III) electron transfer ($\log k_2$) with free energy of reaction (ΔG° , $\text{Cr}^{\text{II}}\text{L}-\text{Cr}^{\text{III}}\text{L}$).

complexes from $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. Of particular interest is the very considerable increase in the rate of the electron transfer brought about by changing the nonbridging ligands on the chromium(II) reductant, a rate enhancement factor of up to 10^6 being effected with some of the ligands tested. How this marked sensitivity to the change in nonbridging ligands correlated with the overall free energy of the reactions is illustrated in Figure 4. The logarithm of the second-order rate constant shows a linear dependence on the formal redox potential of the particular chromium(II) reducing agent used, with formal potentials ranging from -0.66 to -1.42 V . The data clearly demonstrate a linear free energy relationship between the variation of free energy of activation ($\Delta\Delta G^\ddagger$) of the bulk phase redox process and the free energy difference ($\Delta\Delta G_e^\circ$) between oxidized and reduced chromium species in the environment of the ligand used. The slope ($\Delta\Delta G^\ddagger/\Delta\Delta G_e^\circ$) is 0.48.

Interpretation of this result requires that one consider the detailed mechanism of these redox processes. The inner-sphere mechanism is unambiguously established for the reaction between $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ and Cr^{2+} by the isolation of CrCl^{2+} as Cr(III) product.²⁴ With the $\text{Cr}^{\text{II}}\text{-MIDA}$ complex as reductant, the observation that the rate of loss of Cl^- into the solution is slower than the rate of reduction of Cr(III) demonstrates an inner-sphere mechanism for reduction and is consistent with the formation of $\text{Cr}(\text{MIDA})\text{Cl}(\text{H}_2\text{O})_n$ as the initial product. As is the case in the reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ by the pyrophosphato complex of Cr^{2+} ,²⁸ the initial product rather rapidly loses Cl^- . The slower spectral change which follows the main reaction appears to be due to conversion of a $\text{Cr}^{\text{III}}\text{-MIDA}$ complex in which the ligand is bidentate to a more stable form in which the ligand is tridentate.²²

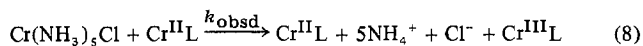
Sykes²⁹ previously concluded that reactions between $\text{Cr}^{\text{II}}\text{EDTA}$ and oxidants containing potential halide bridges are probably of the outer-sphere type, since no halide was found in the final Cr(III) product. This reasoning depends on the assumption that Cr(III) complexes are nonlabile, but there is much evidence that many Cr(III) complexes (particularly those containing nonbonded carboxylate groups)^{30,31} are quite labile to substitution. Iodide,³² O-bonded sulfite,³³ nitrite,³⁴ and nitrate ligands all bring about lability in Cr(III)

substitution reactions. No $\text{Cr}^{\text{III}}(\text{EDTA})\text{X}$ complexes ($\text{X} = \text{halide}$) are known although the corresponding Co(III) species are known. Carbonates stabilize^{35,36} Cr(III) [but not Co(III)] and replacement of water by a carboxylate group of $\text{Cr}^{\text{III}}(\text{EDTA})(\text{H}_2\text{O})_2^-$ is rapid.¹⁹ All of this evidence leads to the conclusion that product analysis of $\text{Cr}^{\text{II}}\text{EDTA}$ oxidations is not a criterion of mechanism since chloride would rapidly be lost from the product of an inner-sphere mechanism.

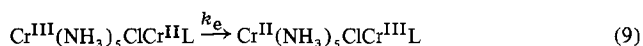
On the other hand, positive evidence for the inner-sphere mechanism for $\text{Cr}^{\text{II}}\text{EDTA}$ oxidations does exist. Tanaka²⁰ has measured the rate of oxidation of $\text{Cr}^{\text{II}}\text{EDTA}$ by $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{NCS}^-$) and has found that the variation of rate with the nature of X indicates an inner-sphere not an outer-sphere path. In the reaction of $\text{Cr}^{\text{II}}\text{EDTA}$ with $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$, isotope fractionation effects³⁷ demonstrate that an inner-sphere mechanism obtains.

There is direct experimental evidence in the Cr^{2+} and $\text{Cr}^{\text{II}}\text{MIDA}$ cases that electron transfer involves a bridged electron-transfer mechanism. The best available evidence for other systems favors a bridged mechanism for $\text{Cr}^{\text{II}}\text{EDTA}$ oxidations and the data of Figure 4 reinforce that interpretation, since a rate discontinuity would be expected to accompany a change in mechanism, but none is observed. The following discussion will be based on the conclusion that all the reactions studied are inner-sphere redox reactions.

The course of an inner-sphere redox process may be broken down into formation of the precursor complex, electron exchange within this complex, and then dissociation of the initial product thus formed to give, via subsequent reactions, species which are stable in the prevailing environment. Since our medium is buffered and contains excess ligand, the overall process being studied in this work is



Since substitution reactions of Cr(II) are rapid, the rate-determining step is electron transfer within the assembled precursor complex



Since steps subsequent to (9) are rapid, the overall rate is $k_{\text{obsd}} \approx Kk_e$, where K is an overall equilibrium constant for rapid steps prior to (9). Variation in the nature of L will cause changes in K although in high ionic strength media such changes should be small. The effect of variation in the nature of L on the step represented by (9) occurs only on the reductant side since the same chloropentaammine oxidant is used for all reactions. The variation of free energy of reaction for step 9 should, therefore, be the same as the variation in the Cr(III)-Cr(II) potential caused by variation in L. The affinity of Cr(III) for H_2O is not greatly different from the affinity of Cr(III) for Cl^- and the affinity difference for Cr(II) is still smaller; therefore the difference caused by the presence of the bridgehead Cl^- should be small. The linear free energy relationship shown in Figure 4 may therefore be interpreted to indicate that $\Delta\Delta G^\ddagger/\Delta\Delta G_e^\circ$ for electron transfer between Cr(II) and Cr(III) within a Cl-bridged binuclear complex is nearly $1/2$.

The prototype of linear free energy relationships is the Bronsted³⁸ relationship which notes that the logarithm of the rate constant for catalysis of decomposition of nitramide, by a basic anion, is proportional to the equilibrium constant for protonation of the same basic anion, the proportionality constant being $1/2$. For many years, this result was discussed in terms of a simple proton-transfer reaction being rate determining. Bronsted, however, had pointed out real difficulties with this explanation in his original paper and more recently

Eigen³⁹ showed that systems for which simple proton transfer was in fact rate determining yield curved, rather than linear, free energy relationships, and that a $\Delta\Delta G^\ddagger/\Delta\Delta G^\circ$ of nearly $1/2$ does not persist for even a single order of magnitude of change in rate constant.

A useful model for discussing electron-transfer reactions involves two hypothetical potential energy (U) surfaces in nuclear configuration space, one (U_r) corresponding to the reactants and the other (U_p) to the products. It is customary to approximate the shape of such surfaces by parabolic potential wells

$$U_r = a(x^2 + U^\circ) \quad (10)$$

$$U_p = b(x - R)^2$$

where x is a displacement and R is a distance between minima of the wells, along the reaction coordinate. It is usually assumed that both wells have the same shape; that is, $a = b = 1$. At the intersection of the two surfaces, x is x^* and U is U^\ddagger . Assuming that R is a constant, x^* can be eliminated between U_r and U_p to give

$$U^\ddagger = \frac{R^2}{4} - \frac{U^\circ}{2} + \frac{(U^\circ)^2}{4R^2} \quad (11)$$

$$\frac{\delta U^\ddagger}{\delta U^\circ} = \frac{1}{2} + \frac{U^\circ}{8R^2} \quad (12)$$

For all constant values of R , this model predicts a linear relationship between U^\ddagger and U° , with a proportionality constant of $1/2$, but only for $U^\circ \ll 4R^2$. Any large variation in U° would be expected to give rise to a nonconstant $\delta U^\ddagger/U^\circ$ and hence curvature of the free energy relationship. Equation 12 has some similarities to the final equation of Marcus' theory,⁴ and Newton⁴⁰ has shown that the assumption of harmonic oscillator potential wells and more elaborate arguments than given here do yield the full form of the Marcus equation. The assumptions made here ($a = b = 1$ and $R = \text{constant}$) are also made in the more elaborate treatments, if less obviously. It appears that no such model can adequately account for the wide span of the linear free energy relationship and that these redox reactions, like the proton transfers originally studied by Bronsted and later discussed by Eigen, require a more complete model for adequate discussion.

Cr(II) is subject to severe Jahn-Teller distortion whereas Cr(III) is not. The Franck-Condon restriction requires that the long axial Cr^{II}-H₂O bonds be compressed and the corresponding bonds of Cr^{III} be extended, prior to the transfer of the electron between chromium atoms. Motions of this type would necessarily involve considerable alteration in secondary solvation sheaths of both ions and corresponding entropy variations. Nearly half of the activation barrier to oxidation of Cr²⁺ by Cr(NH₃)₅Cl²⁺ resides in the $T\Delta S$ term and our present data indicate that the more rapid rate of reaction of the Cr^{II}-EDTA complex is to be ascribed to a less unfavorable entropy of activation rather than to a lower enthalpy of activation. Conversely, the reaction of the Cr^{II}-EDDaDp complex does appear to show decreased ΔH^\ddagger . The greater thermodynamic and kinetic reducing power of the Cr(II) complex indicates that intraligand interactions in the equatorial plane of this Cr(II) complex are more unfavorable than those in the corresponding Cr(III) complex and that this is apparently an enthalpy effect.

A noncooperative one-step mechanism would suggest either zero or unity for $\Delta\Delta G^\ddagger/\Delta\Delta G^\circ$ (reaction being diffusion controlled in one direction or the other). The simple double-harmonic-oscillator model predicts a more complicated variation of ΔG^\ddagger and ΔG° than is observed.

In the case of general-base catalysis, Eigen invoked highly cooperative proton transfers involving many molecules; a related rationale can be given for our result. As ΔG° changes from zero to a more negative value, any treatment will predict that U^\ddagger will decrease from a maximum. The relative influence of geometric changes (variation in R , say) and of entropy effects will increase. Variations in these should be less than variation in U^\ddagger and $\Delta\Delta G^\ddagger/\Delta\Delta G^\circ$ should be reduced below the value predicted by eq 12.

Our result may be phrased as follows: the nexus of factors which influences the magnitude of the Cr(III)-Cr(II) redox potential also determines the rate of bulk-phase electron transfer, which proceeds through the inner-sphere (bridged) electron-transfer mechanism. The measured value of $\Delta\Delta G^\ddagger/\Delta\Delta G^\circ$ pertains to the electron transition and is consistent with a transition state partaking of both product and reactant character; however, as in the hoary case of the Bronsted reaction, it appears that an understanding of this phenomenon based on an explicit microscopic model will have to include a significant contribution from the action of many molecules.

Acknowledgment. This research was supported, in part, by the National Science Foundation under Grant GP 32188.

Registry No. Cr(NH₃)₅Cl²⁺, 14482-76-9; EDTA, 60-00-4; HEDTA, 150-39-0; EDDaDp, 32701-19-2; Cr, 7440-47-3; Cr-(MIDA)(H₂O)₃, 58384-15-9.

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Reduction of Azidochromium(III) Complexes by Vanadium(II)

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Received September 22, 1975

AIC50699B

The kinetics of the reduction of $(\text{H}_2\text{O})_5\text{CrN}_3^{2+}$, *cis*- $(\text{H}_2\text{O})_4\text{Cr}(\text{N}_3)_2^+$, and $(\text{H}_2\text{O})_3\text{Cr}(\text{N}_3)_3$ by V^{2+} have been measured. The respective activation parameters at 25 °C, $I = 0.97 \text{ M}$ (LiClO_4), are as follows [ΔH^\ddagger (kcal/mol), ΔS^\ddagger (cal/(deg mol))]: 12.9, -13.0; 12.4, -12.9; 14.1, -6.5. These results and data from experiments with added Cr^{2+} are consistent with an inner-sphere pathway with electron transfer through a single azide bridge to the Cr(III) center for all three systems. The rate of reduction of VN_3^{2+} by Cr^{2+} was determined indirectly; $\Delta H^\ddagger = 3.85 \text{ kcal/mol}$ and $\Delta S^\ddagger = -27.3 \text{ cal/(deg mol)}$. Cr^{2+} was concluded to reduce $(\text{H}_2\text{O})_3\text{Cr}(\text{N}_3)_3$ via a doubled-bridged activated complex; the rate constant is $112 \pm 7 \text{ M}^{-1} \text{ s}^{-1}$ at 4.8 °C. The implications of these kinetic results are discussed and reaction schemes are proposed.

Introduction

Hydrazoic acid has been used in a number of kinetic studies both as an oxidant and as a reductant, and the results have revealed a rich chemistry.¹ Attempts to investigate the redox properties of the azide ion when coordinated to a substitution-inert metal ion center, however, have met with difficulty. Nitrous acid is the most notable exception; it reacts with many azido complexes and hydrazoic acid with analogous stoichiometry and similar rates.² Generally, though, the coordinated azide ion serves as an effective bridging ligand and either undergoes no net oxidation or reduction or does so in a subsequent step after the primary electron-transfer process. For example, although chromium(II) reduces hydrazoic acid rapidly,^{1g} the only detectable reaction in the chromium(II)-azidochromium(III)³ system is isotopic exchange.⁴ When azidopentaamminecobalt(II) is treated with excess vanadium(II), an inner-sphere reaction occurs producing cobalt(II) and azidovanadium(III);⁵ the latter species aquates rapidly in acidic solution,⁶ and the hydrazoic acid released is reduced by the excess vanadium(II). Since vanadium(II) reduces hydrazoic acid at a moderate rate^{1g} but reacts very slowly with chromium(III),⁷ we thought it was conceivable that vanadium(II) would directly reduce the ligand when allowed to react with azidochromium(III) complexes. This does not occur; in every case the reaction proceeds via an inner-sphere pathway with electron transfer through a single azide bridge to the chromium(III) center. The results of our kinetic studies of these systems are presented in this article.

Experimental Section

Reagents. Azidochromium(III) solutions were isolated by ion-exchange separation at 5 °C of an equilibrated chromium(III)-hydrazoic acid, azide buffer mixture.⁸ A minor modification utilized potassium azide instead of sodium azide in the equilibrium solution; the precipitation and separation of potassium perchlorate significantly lowered the electrolyte concentration and minimized smearing in the ion-exchange procedure. *cis*-Diazidochromium(III) solutions were purified by ion-exchange methods at 5 °C after allowing excess *cis*-diazidobis(ethylenediamine)cobalt(III) to react with chromium(II).⁹ Triazidochromium(III) solutions were isolated from equilibrated chromium(III)-azide solutions by ion-exchange procedures at 5 °C after first removing excess hydrazoic acid by acidification, extraction with cold ether, and aeration. Diazidochromium(III) was retained by the long column of Dowex 50W-X12 resin used in the separation provided the potassium azide procedure was used in preparing the equilibrated solution. All of the separated azidochromium(III) solutions were stored at -78 °C. Triazidochromium(III) aquates rather rapidly; in the kinetic experiments individual

aliquots were thawed just prior to initiation of the reaction.

A number of procedures were used in an attempt to prepare a diazidochromium(III) solution containing appreciable amounts of the *trans* isomer.

Method A. The middle fraction of diazidochromium(III) in an equilibrated chromium(III)-azide solution was collected.

Method B. The first 30% of the diazidochromium(III) fraction was collected following a slow elution (4 h) with 0.2 M HClO_4 or 0.2 M NaClO_4 - 10^{-3} M HClO_4 at 5 °C. Longer elution times (24 h) as used previously¹⁰ to separate *cis*- and *trans*-dichlorochromium(III) were unsuccessful due to aquation of diazidochromium(III), even at 5 °C.

Method C. The final 30% of the diazidochromium(III) fraction described in method B was collected.

Method D. A solution of triazidochromium(III) was allowed to aquate, and the predominantly diazidochromium(III) product was isolated by ion exchange.

Method E. Chromium(II) was oxidized with excess hydrazoic acid-azide buffer and the diazidochromium(III) product was separated by ion exchange.¹¹ The first 30% was collected.

Method F. The last 30% of the diazidochromium(III) fraction described in method E was collected.

Method G. An equilibrated chromium(III)-azide solution was slowly (ca. 4 h) eluted, and the first 40% of the diazidochromium(II) fraction was collected. This eluent was allowed to react with half of its concentration of nitrous acid, and the remaining diazidochromium(III) was separated from the predominantly azidochromium(III) product by ion exchange (first 40% collected). It is not clear that any of these procedures resulted in a diazidochromium(III) solution containing an appreciable amount of the *trans* isomer (vide infra).

Vanadium(II) and chromium(II) solutions were prepared at 0 °C in the absence of oxygen by reduction of oxovanadium(IV) perchlorate and chromium(III) perchlorate, respectively, over a pool of mercury containing dissolved granulated zinc. These solutions were prepared freshly just prior to a series of kinetic or stoichiometric experiments. Total vanadium in the reaction mixtures were determined spectrophotometrically as vanadium(V) after addition of excess bromate ion.¹² Total chromium was determined as chromate ion.¹³

Stoichiometric Studies. When azidochromium(III) and excess vanadium(II) are allowed to react completely, 94-97% of the chromium(III) originally present in the complex ion is converted to amminechromium(III). For example, a solution originally containing 0.239 mmol of CrN_3^{2+} and 0.78 mmol of V^{2+} in 25 ml of 2 M HClO_4 was allowed to react for 40 min in the absence of oxygen at 25 °C. The ion-exchange separation of the reaction products, after addition of excess chlorate ion to convert the vanadium to a mixture of VO_2^+ and VO_2^+ , yielded 0.226 mmol of CrNH_3^{3+} . Similarly, a solution originally containing 0.257 mmol of CrN_3^{2+} , 0.737 mmol of V^{2+} , and 6.80 mmol Cr^{2+} in 25 ml of 2 M HClO_4 yielded 0.250 mmol of CrNH_3^{3+} . Blank experiments showed negligible net chemical reaction