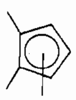
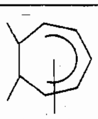
Table VIII. Downfield Shifts of ^{13}CO Resonances for **2** and **3** from **1** for the Two Possible Assignments of **1**

Assign- ment for **1**	 -Mo(CO)$_3$			 -Mo(CO)$_3$		
	δ_i	$\delta_2-\delta_1$	$\delta_3-\delta_1$	δ_i	$\delta_2-\delta_1$	$\delta_3-\delta_1$
A	32.6			27.4		
	40.0	7.4		32.2	4.8	
	34.4		1.8	38.1		11.7
B	27.4			32.6		
	40.0	12.6		32.2	−0.4	
	34.4		7.0	38.1		5.5

singlets observed in the fast-exchange limits. These comparisons are set out in Table VIII. The two possible assignments, A and B, are defined as follows. A: the "fast" Mo(CO)$_3$ group, 32.6 ppm, is assigned to the cyclopentadienyl ring B: the "slow" Mo(CO)$_3$ group, 27.4 ppm, is assigned to the cyclopentadienyl ring.

It is evident that only the results for assignment A are in agreement with the two empirical rules. For assignment B the rules are violated for both **2** and **3**. For **2**, one of the shifts is slightly upfield (−0.4) instead of downfield. For **3**, the relative magnitudes of the shifts for the two sets of CO groups are the inverse of what they should be, i.e., greater for those on the *un*substituted atom.

Since assignment A is correct, we conclude that it is the Mo(CO)$_3$ group bonded to the cyclopentadienyl ring which has the lower activation energy for internal CO scrambling in the parent molecule, **1**.

In our earlier study[3] of $C_{10}H_{12}Fe_2(CO)_5PEt_3$ we observed that when a CO group on one Fe(CO)$_3$ unit was replaced by PEt$_3$, the coalescence temperature for scrambling of the CO groups on the other Fe(CO)$_3$ moiety was substantially lowered, namely by about 45 °C. We did not know whether an effect of this sort would be general. The results for compounds **1**, **2**, and **3** presented here leave this point still somewhat ambiguous. A comparison of compounds **1** and **2** reveals the same effect observed with the iron compound; the coalescence temperature for the Mo(CO)$_3$ group attached to the seven-membered ring drops from about −35 to about −95 °C, an even greater drop than the one observed earlier. On the other hand, for compound **3** the coalescence temperature for the Mo(CO)$_3$ group attached to the five-membered ring appears to be around −110 °C, which is not lower, and possibly a little higher than the corresponding one in compound **1**. The nature of these neighboring substituent effects thus remains puzzling and not even empirically predictable.

Another effect observed here (see Figure 3 and Table VII) is the large chemical shift difference between the two CO groups remaining on the substituted Mo atom. These differences are 4.8 and 3.5 ppm in compounds **2** and **3**, respectively. We find this surprising and do not have a ready explanation for it.

Acknowledgment. We thank Dr. Douglas L. Hunter for his contributions to the earlier phases of this study and Dr. Douglas M. Collins for some discussions concerning the crystallography. Financial support was provided in part by the National Science Foundation (Grant No. 33142X) and by the Commission on Cultural Exchange between Spain and the United States of America through a fellowship to P.L.

Registry No. 1, 59414-35-6; **2**, 59350-36-6; **3**, 59350-35-5; triethylphosphine, 554-70-1; ^{13}C, 14762-74-4.

Supplementary Material Available: Tables of the observed and calculated structure factor amplitudes for compounds **2** and **3** (29 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Organomet. Chem.*, **87**, C42 (1975).

(2) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Am. Chem. Soc.*, **97**, 1046 (1975).

(3) F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, **97**, 5739 (1975).

(4) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(5) Programs for data reduction as well as those used subsequently in the structure analysis are as follows: DATARED by Frenz was used for data reduction. AGNOST, used for the absorption correction, is a modification by Frenz of Cohen's AGNOST. The Fourier program JIMDAP by Ibers is a version of Zalkin's FORDAP. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\sum w(|F_o| - |F_c|)^2$. ORTEP by Johnson was used for drawing illustrations on a Gerber plotter. Atomic distances, angles, and errors were calculated using program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen. Final structural refinement of compound 3 was conducted using a PDP 11/45 computer and the Enraf Nonius SDP computer programs at the Molecular Structure Corporation, College Station, Texas.

(6) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 7, 1545 (1968).

(7) These data are from unpublished studies in this laboratory by Dr. John R. Kolb.

(8) H. Mahnke, R. K. Sheline, and H. W. Spiess, *J. Chem. Phys.*, **61**, 55 (1974).

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Distinguishing between Inner- and Outer-Sphere Electrode Reactions. Reactivity Patterns for Some Chromium(III)–Chromium(II) Electron-Transfer Reactions at Mercury Electrodes

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Two methods for distinguishing between inner- and outer-sphere electrode reaction mechanisms for a certain class of metal complexes are described and applied to several complexes of Cr(III). One method is based on the response of the reaction rate to the addition of strongly adsorbed but chemically inactive anions. The second method depends upon differences in the potential dependence of the reaction rate for inner- and outer-sphere pathways. Electrochemical reactivity differences spanning eight orders of magnitude were measured for a series of eight complexes of Cr(III) of the type $Cr(OH_2)_5X$. The origin of the large range of reactivities is discussed in terms of "intrinsic" and "thermodynamic driving force" differences. It is suggested that the latter factor is dominant with outer-sphere reactants whereas both factors can contribute significantly to the relative reactivities of inner-sphere reactants.

Introduction

Efforts directed toward the identification of the electrode reaction mechanisms of simple, one-electron redox reactions of transition metal ion complexes have been both less extensive and less successful than is true for the analogous homogeneous redox reactions. A primary factor contributing to the greater

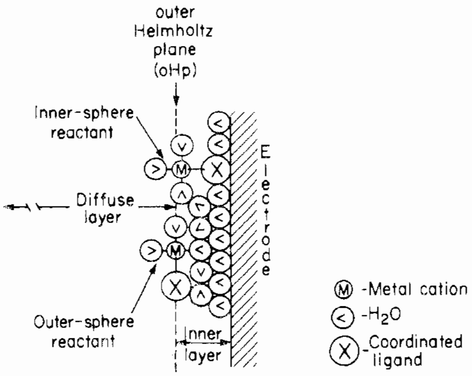

Figure 1. Schematic representation of the double layer at electrode surfaces and the reaction sites of inner-sphere and outer-sphere reactants.

interpretative difficulties in the case of electrode reactions has been the lack of reliable means for distinguishing between inner-sphere and outer-sphere reactions with the same confidence that this distinction can be made for many homogeneous redox reactions.[1]

Figure 1 illustrates the essential differences between inner-sphere and outer-sphere electrode reactions for substitutionally inert metal complexes. Electron transfer during outer-sphere reactions takes place with the reactant center located at the so-called "outer Helmholtz plane" (oHp)[2] which is the plane of closest approach for reactants whose coordination spheres do not penetrate the layer of solvent molecules that are specifically adsorbed on[3] (i.e., "coordinated" to) the electrode surface. The situation is closely analogous to that involved in homogeneous outer-sphere reactions between two ions in which the coordination spheres of both reactants remain intact in the transition state.[1] During electrode reactions that proceed by inner-sphere pathways, one (or more) of the ligands in the reactant's primary coordination sphere penetrates the oHp and is attached to the electrode surface in the transition state as shown in Figure 1. The solvent (and most other) molecules and ions coordinated to the mercury surface are readily replaceable, and this substitutional lability of the electrode surface (whether it serves as an oxidant or a reductant) vitiates the use of the classical tactics introduced by Taube[4] for demonstrating inner-sphere reaction pathways during homogeneous reactions by observing the transfer of a bridging ligand from one substitutionally inert metal center to another. The appearance of anions that are known to be specifically adsorbed on mercury electrodes in the coordination sphere of the inert chromium(III) complexes produced by the oxidation of chromium(II) at mercury electrodes in supporting electrolytes containing the adsorbing anions has been cited as evidence that the electrooxidation of chromium(II) follows an inner-sphere pathway in these electrolytes.[5-7] However, the possibility of outer-sphere electron transfer to a chromium(II)–anion complex formed homogeneously and located at the oHp usually cannot be completely ruled out.

Inner-sphere electrode reaction mechanisms have been established unambiguously for several isothiocyanatochromium(III) complexes which spontaneously adsorb on mercury electrodes via the exposed sulfur atom of the ligand sufficiently strongly so that the kinetics of their reduction in the specifically adsorbed state can be measured without significant interference from any parallel reduction of the unadsorbed complex by an outer-sphere pathway.[8,9] The kinetic behavior exhibited by these complexes is sufficiently different and intriguing compared with that of unadsorbed complexes that it seemed worthwhile to determine if the contrasting kinetics could be used to identify inner-sphere reaction pathways for the many chromium(III) complexes whose adsorption on mercury is too weak to measure but which might, nevertheless, undergo inner-sphere reduction at the electrode. Some success has been realized in this attempt[10] with a series of complexes from the class $Cr(OH_2)_5X^{(3-p)+}$ (where X^{p-} is a simple anionic ligand) whose reductions at mercury electrodes have been identified as following inner-sphere or outer-sphere pathways. The purposes of this report are to expose the methods and reasoning employed in arriving at the mechanistic classifications and to consider the ways in which the nature of X^{p-} affects the relative electrochemical reactivities of the Cr(III)–Cr(II) reactions for both mechanisms. The latter topic has been extensively investigated for homogeneous redox reactions[1] but the corresponding heterogenous processes have been subjected to remarkably little systematic study since the initial work of Aikens and Ross,[5] and sufficient quantitative kinetic data to support detailed reactivity comparisons have not previously been available.

Experimental Section

Materials. Analytical grade reagents were used without further purification and all solutions were prepared from triply distilled water. Chromium(III) perchlorate solutions were prepared by reducing CrO_3 with excess H_2O_2 in perchloric acid. The resulting stock solutions of Cr(III) were made 0.5–1 M in $HClO_4$ in order to minimize the formation of Cr(III) polymers. The preparation of solutions of Eu(III) has been described.[11]

Cation-exchange columns were prepared from Bio-Rad AG 50W-X8 resin, 100–200 mesh, and were usually used in their acid forms.

Published procedures were followed to prepare $Cr(OH_2)_5NCS^{2+}$,[12] $Cr(OH_2)_5N_3^{2+}$,[13] and $Cr(OH_2)_5NO_3^{2+}$.[14] (The nitrato complex was stored for a few months at −195 °C without detectable decomposition.) Preparations of the other five complexes involved slight modification of published procedures.

$Cr(OH_2)_5F^{2+}$.[15] To facilitate studies of this complex over a range of pH values, one batch was prepared in 1.5 M $NaClO_4$ + 0.01 M $HClO_4$ by employing the cation-exchange column in the Na^+ form and eluting with suitably acidic solutions of sodium perchlorate.

$Cr(OH_2)_5OSO_3^+$.[16] The ion was isolated from reagent grade hydrated chromic sulfate (J. T. Baker Chemical Co.) by elution from the cation-exchange column with 0.15 M $HClO_4$.

$Cr(OH_2)_5Cl^{2+}$. A solution containing 0.05 M Cr^{3+}, 0.1 M Cl^-, and 0.05 M H^+ was electrolyzed under nitrogen with a stirred mercury pool electrode at −1200 mV vs. SCE. The resulting solution was then reoxidized at the pool electrode by adjusting its potential to −200 mV vs. SCE. The resulting $Cr(OH_2)_5Cl^{2+}$ was separated from the excess chloride and the small amount of $Cr(OH_2)_6^{3+}$ also formed by means of cation exchange.[15] (Elution of the desired complex as a green band was accomplished with 1.3 M $HClO_4$.)

$Cr(OH_2)_5Br^{2+}$. This complex was prepared by an electrolytic procedure similar to that used to obtain the chloro complex. The ion-exchange column was maintained at 5 °C during isolation of the complex to minimize its aquation. Frozen solutions of both the chloro and bromo complexes were stored at −25 °C and were used within a few days after preparation.

The concentrations of the solutions of the complexes were determined spectrophotometrically[17] following oxidation of the Cr(III) to chromate with alkaline peroxide.

Apparatus and Techniques. Conventional two-compartment electrochemical cells were employed for kinetic measurements with a hanging mercury drop electrode (Brinkman Instruments, Inc.) serving as the indicator electrode. The electronic potentiostat and computer-based data acquisition and analysis system have been previously described.[18] Measurements were made with solutions that had been deoxygenated by bubbling with a stream of prepurified nitrogen which had passed through a solution of vanadium(II) and then over bright copper turnings at 450 °C. Measurements were made at 24.0 ± 0.25 °C. Potentials were measured with respect to a sodium chloride saturated calomel reference electrode but are reported with respect to the usual potassium chloride saturated calomel electrode (SCE). The heterogenous electron-transfer rates were determined by both conventional dc polarography[19] and chronocoulometry.[20] The latter technique allowed rate constants as large as ca. 2×10^{-1} cm s^{-1} to be measured with a reproducibility of ±5%. The experimental procedures employed in kinetic measurements have been previously described.[11,20]

For measurements of the oxidation kinetics of Cr^{2+} (or Eu^{2+}) test solutions of Cr^{3+} (or Eu^{3+}) were employed and the reduced forms of the reactants were generated in the solution near the electrode surface by adjusting its potential to an appropriate value (−1200 mV for Cr^{2+}; −900 mV for Eu^{2+}) for ca. 10–15 s before a brief anodic potential step was applied in a standard chronocoulometric kinetic measurement. Kinetic responses in experiments conducted in this way were indistinguishable from those in homogeneous solutions of Cr^{2+} (or Eu^{2+}) so long as the chronocoulometric measurements were restricted to times shorter than ca. 100 ms.

The reduction of a few $Cr(OH_2)_5X^{2+}$ complexes proceeded close enough to the reversible equilibrium potential for the measured current to be influenced by a significant contribution from an anodic back-reaction. The situation at the electrode surface is complicated in such cases by the fact that two species are involved in the back-reaction, Cr^{2+} and X^-, so that in the absence of an excess of the latter the back-reaction may exhibit overall second-order kinetics. To avoid this complication the kinetic measurements of the reduction of all complexes were restricted to potentials and observation times where contributions from anodic back-reactions were calculated to be negligible on the basis of the effective formal potentials for the half-cell reaction $Cr(OH_2)_5X^{2+} + e^- \rightleftharpoons Cr(OH_2)_6{}^{2+} + X^-$. The appropriate formal potentials were estimated from the standard potential for $Cr(OH_2)_6{}^{3+}$–$Cr(OH_2)_6{}^{2+}$ (−655 mV) and the reported equilibrium constants for the binding of X^{p-} to $Cr(OH_2)_6{}^{3+}$. These restrictions meant that only the chronocoulometric technique was acceptable with the most rapidly reduced complexes ($Cr(OH_2)_5Br^{2+}$, $Cr(OH_2)_5NCS^{2+}$) as kinetic observation times no greater than 5 ms were sometimes required to avoid significant back-reaction corrections.

Negative contributions to measured currents from the first-order anodic back-reaction $Cr(OH_2)_6{}^{2+} - e^- \rightarrow Cr(OH_2)_6{}^{3+}$ were calculated to be negligible under most conditions for both chronocoulometry and dc polarography.[20] In any case, the regression analysis used to analyze the chronocoulometric data[11] allows for the presence of such effects.

To avoid complications resulting from the chemical reaction[21] between the Cr^{2+} and HN_3 generated when $Cr(OH_2)_5N_3{}^{2+}$ is reduced in acidic solutions, polarographic measurements with this complex were confined to the foot of its wave in dilute solutions of Cr(III) where the concentrations of Cr^{2+} and HN_3 released were low enough to ensure a negligible extent of reaction. In chronocoulometric measurements where higher concentrations were generated the problem was avoided by restricting measurement times to 40 ms or less.

The aquation rates of several of the Cr(III) complexes employed are known to be enhanced by Cr^{2+}.[22,23] However, calculations based on the known rate constants for the Cr(II)-catalyzed pathways showed that no significant aquation would be induced by the Cr^{2+} generated at the electrode surface on the time scale of the electrode kinetic measurements.

The reduction rates of all the complexes studied showed no dependence on pH in the range from 1 to 3. Experiments were usually carried out at pH 2 (Cr(III)) or pH 3 (Eu(III)).

Results

The kinetics of reaction 1 were examined in both the forward

$$Cr(OH_2)_5X^{(3-p)+} + e^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr(OH_2)_6{}^{2+} + X^{p-} \qquad (1)$$

and the reverse directions. The oxidation of Cr(II) in electrolytes containing potential ligands, X^{p-}, often leads to a mixture of Cr(III) complexes[5-7] because of the presence of more than a single accessible reaction pathway. This feature can severely complicate the quantitative analysis of the oxidation kinetics. In addition, while the kinetics of reduction of the Cr(III) complexes of basic ligands such as $N_3{}^-$, F^-, and $SO_4{}^{2-}$ can be studied in acidic electrolytes without difficulty, these ligands are present primarily in their protonated forms in the acidic electrolytes compatible with studies of the oxidation of Cr(II) which introduces an additional source of complexity. For these reasons the reduction of the well-characterized $Cr(OH_2)_5X^{(3-p)+}$ complexes was given primary emphasis in this study, although some measurements of the oxidation rates for Cr(II) were conducted in order to cover as wide a range of electrode potentials as possible.

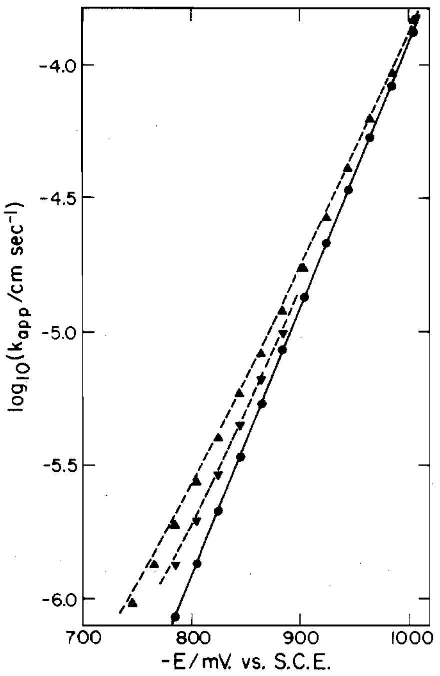

Figure 2. Rate–potential data for the reduction of $Cr(OH_2)_5F^{2+}$ at unit ionic strength. Supporting electrolytes: ●, 1 M $NaClO_4$; ▼, 0.9 M $NaClO_4$ + 0.1 M NaI; ▲, 0.67 M $NaClO_4$ + 0.33 M NaI. Reactant concentrations were 2–10 mM (the larger concentrations were used only at the most positive potentials) and all solutions were adjusted to pH ~2 with $HClO_4$. The solid line is drawn through the experimental points for $NaClO_4$. The dashed lines give the rates calculated from the solid line and (modified) diffuse layer theory as explained in the text and ref 26.

Distinguishing between Mechanisms. Our first desire was to determine if a systematic basis could be found for determining whether any particular chromium(III) complex was reduced at the electrode by an inner-sphere or an outer-sphere mechanism. The distinction being sought is between the two reaction sequences shown in eq 2 and 3.

Inner-sphere electroreduction

$$Cr(OH_2)_5X^{(3-p)+}\ (Hg(e^-) \rightleftharpoons Cr(OH_2)_5X^{(3-p)+} \cdots (Hg(e^-) \qquad (2a)$$

$$Cr(OH_2)_5X^{(3-p)+} \cdots (Hg(e^-) \xrightarrow[\text{slow}]{} Cr(OH_2)_5X^{(2-p)+} \cdots (Hg \qquad (2b)$$

$$Cr(OH_2)_5X^{(2-p)+} \cdots (Hg \xrightarrow[\text{fast}]{H_2O} Cr(OH_2)_6{}^{2+} + X^{p-} + (Hg \qquad (2c)$$

Outer-sphere electroreduction

$$Cr(OH_2)_5X^{(3-p)+} \rightleftharpoons [Cr(OH_2)_5X^{(3-p)+}]_{OHp} \qquad (3a)$$

$$[Cr(OH_2)_5X^{(3-p)+}]_{OHp} \xrightarrow[\text{slow}]{+e^-} [Cr(OH_2)_5X^{(2-p)+}]_{OHp} \qquad (3b)$$

$$[Cr(OH_2)_5X^{(2-p)+}]_{OHp} \xrightarrow[\text{fast}]{H_2O} Cr(OH_2)_6{}^{2+} + X^{p-} \qquad (3c)$$

It proved possible to assign each complex investigated to one of these mechanistic pathways on the basis of two criteria: (i) the response of the reaction rate to additions of iodide anions which are strongly adsorbed on mercury; (ii) the dependence of the electrode reaction rate on the electrode potential, i.e., the slope of plots of the logarithm of the apparent electron-transfer rate constant, k_{app}, vs. the electrode potential. The behavior of eight chromium(III) complexes was examined in terms of these two characteristics and the results are summarized in Table I.

Outer-Sphere Reactions. Figure 2 shows a set of rate–potential data for $Cr(OH_2)_5F^{2+}$ whose behavior is representative of those complexes which we believe follow outer-

Table I. Apparent Transfer Coefficients, Responses to Iodide Adsorption, and Mechanistic Diagonoses for the Reduction of Some Cr(III) Complexes at Mercury Electrodes

X^{P-} in $Cr(OH_2)_5X^{(3-P)+}$	Potential range, $-E$, mV vs. SCE	α_{app}[a]	Response to iodide[b]	Likely mechanism
H_2O	750-1100	0.58	+	Outer sphere
F^-	700-1200	0.58	+	Outer sphere
SO_4^{2-}	600-1150	0.56	+	Outer sphere
Cl^-	550-900	0.37	–	Inner sphere
Br^-	200-450	0.43	–	Inner sphere
NCS^-	650-900	0.38	–	Inner sphere
N_3^-	650-1100	0.42	–	Inner sphere
NO_3^-	700-1000	0.41	–	Inner sphere

[a] From eq 4. Kinetic measurements were carried out in 1 M $NaClO_4$ at pH values between 1 and 3 where the rates showed no pH dependence. [b] The supporting electrolyte was changed from 1 M $NaClO_4$ + 0.01 M $HClO_4$ to $1 - x$ M $NaClO_4$ + x M NaI + 0.01 M $HClO_4$ with $x = 0.1$ and 0.33. The resulting changes in the reduction rates of the complexes at constant potential are indicated: + = rate increase; – = rate decrease.

sphere reaction pathways. The solid line drawn through the circles in Figure 2 gives the rate–potential dependence for reduction of $Cr(OH_2)_5F^{2+}$ in 1 M $NaClO_4$ as supporting electrolyte. The data points all fall on a straight line whose slope, $\partial \log k_{app}/\partial E$, is related to the apparent transfer coefficient, α_{app}, by the relation given in eq 4.[24] All of the

$$\alpha_{app} = \frac{-2.3\,RT}{F}\left(\frac{\partial \log k_{app}}{\partial E}\right) \tag{4}$$

complexes investigated yielded essentially linear plots from which the values of α_{app} listed in Table I were calculated.

The triangular points in Figure 2 show how the reaction rate at constant potential was increased by addition of 0.1 and 0.33 M sodium iodide while maintaining the total ionic strength at 1 M. The dashed lines are the calculated rate–potential behavior expected for a dipositive reactant undergoing an outer-sphere reaction whose rate increases when negative ions are adsorbed on the electrode surface because of the resulting Coulombic enhancement of the concentration of reactant at the outer Helmholtz plane (Figure 1).[25] (The procedure used to calculate the dashed lines is described in the Discussion.) Essentially similar responses to iodide adsorption are also exhibited by $Cr(OH_2)_6^{3+}$ and $Cr(OH_2)_5OSO_3^{+}$, the only difference being that quantitatively smaller rate enhancements are obtained with the less highly charged sulfato complex while larger enhancements result with the tripositive hexaaquochromium(III) cation.

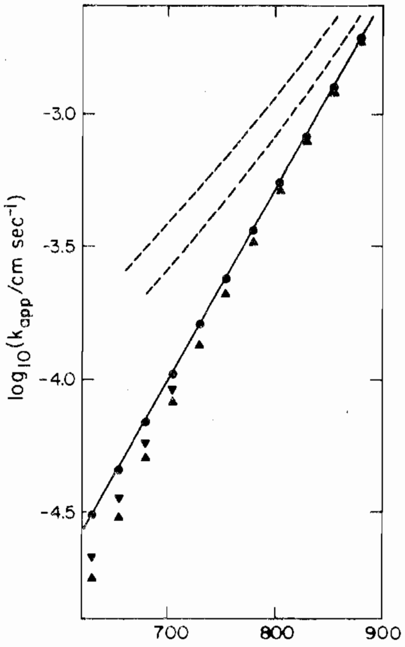

Figure 3. Rate–potential data for the reduction of $Cr(OH_2)_5N_3^{2+}$ at unit ionic strength. The symbols and lines have the same significance as in Figure 2.

Inner-Sphere Reactants. Rate–potential data for the reduction of $Cr(OH_2)_5N_3^{2+}$, a typical complex from the class which is believed to undergo inner-sphere reductions, are shown in Figure 3. These data contrast markedly with those for the complexes whose reductions are believed to proceed by outer-sphere pathways such as $Cr(OH_2)_5F^{2+}$ in Figure 2. The reduction rate of the azido complex in 1 M $NaClO_4$ is considerably larger than that of the fluoro complex within the measured potential range and the addition of iodide produces small decreases in the measured rates instead of the large increases that were observed in Figure 2. The dashed lines in Figure 3 were calculated in the same way as were those in Figure 2. They give the rates that would be expected if the only effect of iodide adsorption were to enhance the concentration of $Cr(OH_2)_5N_3^{2+}$ and alter the potential at the oHp as was the case with $Cr(OH_2)_5F^{2+}$ (Figure 2). Instead, a decline in reduction rate results despite the fact that the concentration of $Cr(OH_2)_5N_3^{2+}$ at the oHp is enhanced by the adsorption of the added iodide anions. This last assertion was verified by inspecting the kinetic responses of both $Cr(OH_2)_5N_3^{2+}$ and $Cr(OH_2)_5F^{2+}$ when the potential at the oHp was made more negative by decreasing the ionic strength of the sodium perchlorate supporting electrolyte rather than by adsorbing iodide anions. The results, given in Figure 4, show that decreases in ionic strength cause the reduction rates of both complexes to increase by amounts which are in reasonably good accord with those calculated from slightly modified[20,26] diffuse layer parameters[25] (the dashed and dotted lines in Figure 4). All eight of the complexes listed in Table I showed essentially similar responses to changes in ionic strength which is good evidence that the concentrations at the oHp of both the inner- and outer-sphere reactants will be enhanced when the potential at this plane, ϕ_2, becomes more negative. The fact (Table I, Figure 3) that the reduction rates of one set of reactants decrease despite this concentration enhancement when the change in the value of ϕ_2 is achieved by means of iodide adsorption strongly indicates the presence of an additional kinetic factor (e.g., an inner-sphere mechanism) for this set of the reactants. Complexes whose responses to iodide adsorption match that of $Cr(OH_2)_5N_3^{2+}$ (i.e., small decreases in reduction rates) include the chloro, bromo, nitrato, and isothiocyanato complexes. The data are summarized in Table I from which it may also be noted that those complexes which exhibited rate decreases in the iodide addition experiments also yielded rate–potential plots with slopes corresponding to values of α_{app} smaller than 0.5. By contrast, the three complexes whose reduction rates were increased by adsorbed iodide all gave values of α_{app} larger than 0.5.

Oxidation of Cr^{2+}. Rate–potential data for the oxidation of Cr^{2+} in pure perchlorate or chloride supporting electrolytes are plotted in Figure 5A. These data are similar to those of Aikens and Ross[5] but are for a higher concentration of chloride and cover a wider range of potentials. Corresponding data for the oxidation of Eu^{2+}, which falls within the same potential

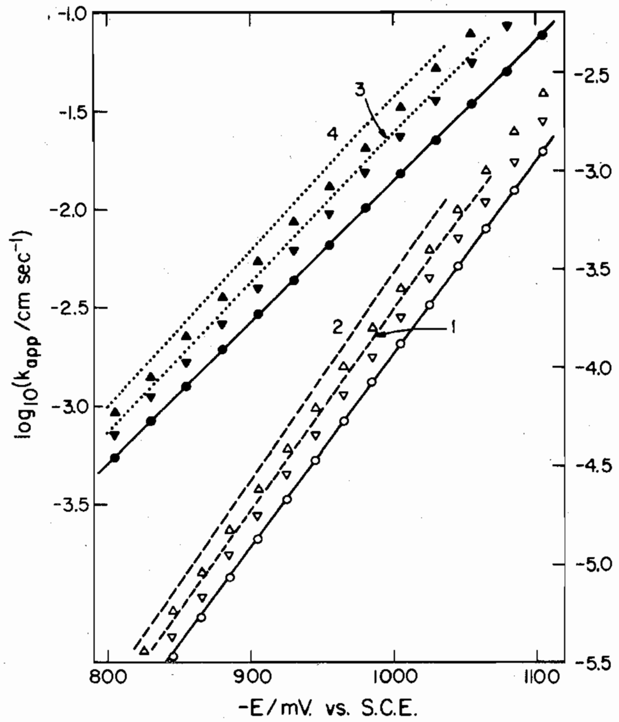

Figure 4. Rate-potential data for the reduction of $Cr(OH_2)_5F^{2+}$ (open points, right-hand ordinate axis) and $Cr(OH_2)N_3^{2+}$ (solid points, left-hand ordinate axis), at varying ionic strengths. Supporting electrolytes: ○, ●, 1 M $NaClO_4$; ▽, ▼, 0.5 M $NaClO_4$; △, ▲, 0.3 M $NaClO_4$. Reactant concentrations were 2–10 mM and all solutions were adjusted to pH ~2 with $HClO_4$. The solid lines are drawn through the experimental points for 1 M $NaClO_4$. The dashed and dotted lines give the rates calculated from the solid lines and modified diffuse layer theory as explained in the text and ref 20. Curves 1 and 3 are for 0.5 M $NaClO_4$; curves 2 and 4 are for 0.3 M $NaClO_4$.

range and appears to behave as an outer-sphere reactant in both electrolytes,[26] are shown in Figure 5B for comparison. Note that the substitution of chloride for perchlorate produces a much greater increase in rate for Cr^{2+} than for Eu^{2+}.

The addition of iodide to perchlorate supporting electrolytes increases the oxidation rates of both Cr^{2+} [5] and Eu^{2+}.[27] However when iodide ion is added to the chloride supporting electrolytes in Figure 5, the oxidation rates of the two cations respond in opposite directions: the rate of oxidation of Eu^{2+} increases while that of Cr^{2+} decreases. This difference in response will be featured in arguments presented in the Discussion to show that Cr^{2+} follows an inner-sphere electrooxidation pathway in chloride electrolytes.

Discussion

A number of general theoretical treatments of electrode kinetics for both outer-sphere and inner-sphere reactants have been presented. Rate laws for outer-sphere electrode reactions are classical and well established.[24,28] Some corresponding expressions for inner-sphere reactions have been proposed[29–31] although experimental tests of the derived rate laws have been less extensive. A general form of a rate law which can be written for both classes of reduction reaction is given in eq 5.[31]

$$\log \frac{i}{FC^{b}} \equiv \log k_{\mathrm{app}} = \log k + \log \gamma^{b} - \log \gamma^{\ddagger} - \frac{1}{2.3RT}\left[\alpha(\Delta G^{\circ}_{\mathrm{A_P}} - \Delta G^{\circ}_{\mathrm{A_R}} + FE) + \Delta G^{\circ}_{\mathrm{A_R}}\right] \qquad (5)$$

A single-electron reduction is assumed which results in a current density, i, corrected for any concentration changes produced at the electrode surface by the occurrence of the reaction. F is the Faraday constant, C^b is the bulk concentration of the reactant, k is a rate constant which is independent of electrode potential and the composition of the supporting electrolyte, γ^b and $\gamma^\ddagger$ are the activity coefficients of the bulk reactant and the transition state, respectively, α is the ("true", intrinsic[32]) electrochemical transfer coefficient expressing the symmetry properties of the elementary barrier to electron transfer (i.e., $\alpha = 0.5$ for a symmetrical barrier), E is the electrode potential, and $\Delta G^\circ_{\mathrm{A_R}}$ and $\Delta G^\circ_{\mathrm{A_P}}$ are the standard free energies of adsorption of the reactant and product, respectively.[33] It is convenient to regard the two activity coefficients in eq 5 as measures of the interactions of

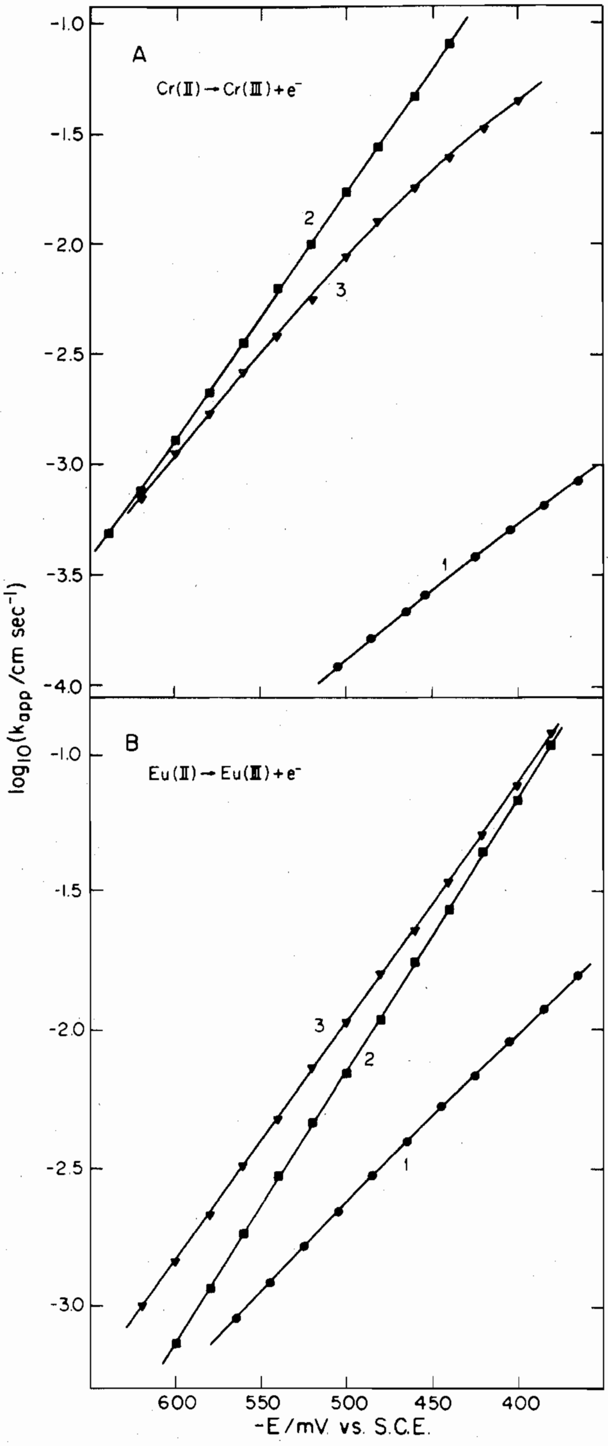

Figure 5. Rate-potential data for the oxidations of (A) Cr^{2+} and (B) Eu^{2+} in perchlorate, chloride, and iodide electrolytes. Supporting electrolytes: 1, 1 M $NaClO_4$; 2, 1 M KCl; 3, 1 M KCl + 0.01 M KI. Reactant concentrations were 1–8 mM and solutions were adjusted to pH 2 (Cr^{2+}) or pH 3 (Eu^{2+}) with $HClO_4$.

reactant molecules with themselves and with the activated complex, respectively. Interactions of both particles with the electrode surface and other, nonreacting species that may be present are then accounted for in terms of their contributions to the standard free energies of adsorption in eq 5. One advantage of this separation of the sources of nonideality is that the activity coefficient terms in eq 5 vanish for cases such as those at hand in which the quantity of reactant adsorbed on the electrode is extremely small.

Equation 5 can potentially serve as the basis for the diagnosis of reaction mechanisms by determining the dependence of k_{app} upon changes in electrode potential or supporting electrolyte composition. Thus, at constant bulk concentration of reactant and of the supporting electrolyte, slopes of plots of log k_{app} vs. E (such as those in Figures 2–5) should be given by eq 6. Substituting the apparent transfer coefficient, α_{app},

$$\frac{\partial \log k_{app}}{\partial E} = -\frac{\alpha}{2.3RT}\left(\frac{\partial \Delta G^{\circ}{}_{A_P}}{\partial E} + F\right) - \frac{1-\alpha}{2.3RT}\left(\frac{\partial \Delta G^{\circ}{}_{A_R}}{\partial E}\right) \tag{6}$$

as defined by eq 4, into eq 6 leads to eq 7.

$$\alpha_{app} = \frac{\alpha}{F}\left(\frac{\partial \Delta G^{\circ}{}_{A_P}}{\partial E}\right) + \frac{1-\alpha}{F}\left(\frac{\partial \Delta G^{\circ}{}_{A_R}}{\partial E}\right) + \alpha \tag{7}$$

It is clear from eq 7 that α_{app} will differ from the intrinsic transfer coefficient, α, to an extent which is determined by the potential dependence of the standard free energies of adsorption for both the reactant and the product. The magnitude and even the signs of the differential free energy terms in eq 7 will differ significantly during the inner-sphere or outer-sphere reactions reactions of related complexes and these differences offer one possible means for characterizing the reaction pathways.

Inferring Mechanisms from the Values of α_{app}. For outer-sphere reactions the two free energies of adsorption in eq 5 are simply the electrostatic energies required to bring the reactant and product from the bulk of the solution to the oHp across the potential difference, ϕ_2. For a reaction involving the reduction of a reactant bearing the charge Z_R by one electron these energies will be equal to $Z_RF\phi_2$ and $(Z_R - 1)F\phi_2$, respectively. The derivatives of these free energies with respect to the electrode potential can be substituted in eq 7 to obtain the well-known[20,25] relationship given in eq 8, where

$$\alpha_{app} = \alpha - (\alpha - Z_R)\left(\frac{\partial \phi_2}{\partial E}\right)_{\mu} \tag{8}$$

α_{app} is the observed transfer coefficient for the outer-sphere pathway and $(\partial\phi_2/\partial E)_{\mu}$ is the indicated derivative at constant composition of the supporting electrolyte.

In nonadsorbing supporting electrolytes at ionic strengths of 0.5–1 M typical values of $(\partial\phi_2/\partial E)_{\mu}$ (measured experimentally[20,26]) are 0.02–0.05 so that α_{app} should be greater than α for the reduction of reactants (such as $Cr(OH_2)_5X^{2+}$) with $Z_R \geq 1$. There is evidence that α is close to 0.5 for a number of simple outer-sphere reactants[20,34] so that experimental values of α_{app} which significantly exceed 0.5 with multiply charged cationic reactants are suggestive of an outer-sphere mechanism.

For inner-sphere reactions the experimental evaluation of the differential terms in eq 7 requires information on the equilibrium adsorption isotherms for the reactants and products which is usually unavailable because the spontaneous adsorption of both species is too weak to measure. Theoretical estimates of the coefficients are also very difficult to provide even when the interactions of the adsorbed species with the electrode are assumed (rather unrealistically) to be entirely electrostatic.[35] However, a number of isothiocyanate complexes of chromium(III) are adsorbed in easily measurable quantities and the potential dependence of the standard free energies of adsorption for a group of these complexes was determined in some recent experiments.[9] In every case, regardless of the net charge of the complex ion, these complexes exhibited negative values of $\partial\Delta G^{\circ}{}_A/\partial E$ throughout the range of potentials where coadsorption of components of the supporting electrolyte was unimportant. This result may seem somewhat surprising for cationic complexes whose free energies of adsorption might have been expected to become more negative as the negative charge on the electrode surface increased. The contrary result can be understood by noting that the isothiocyanate ligands which hold the complexes on the mercury surface are likely to retain at least part of their anionic character and would therefore be expected to be less strongly adsorbed at more negative potentials. The cationic centers of both inner- and outer-sphere reactants will lie near the oHp (Figure 1) where they are affected less strongly by changes in electrode potential.

Similar behavior does not seem unlikely with the less strongly adsorbing chromium(III) complexes examined in this study. If the two differential terms in eq 7 are indeed negative for most anion-bridged inner-sphere electrode reactions, it follows that the apparent transfer coefficient for the reduction of such inner-sphere reactants, α_{app}, will be smaller than the intrinsic transfer coefficient, α. Values of α close to 0.5 were obtained[9] for most of the strongly adsorbing isothiocyanato complexes of chromium(III) which are clearly reduced by inner-sphere mechanisms. If these results are accepted as typical, then α_{app} values significantly below 0.5 can be regarded as a sign of an inner-sphere reaction mechanism.

Some indication of the possible usefulness of values of α_{app} in mechanistic diagnoses can be judged from the data of Table I. Note that the eight complexes studied can be clearly divided into two classes on the basis of their values of α_{app} and it is encouraging to find that the three complexes which would be classified as outer-sphere reactants on this basis (i.e., $\alpha_{app} > 0.5$) are those containing sixth ligands which bind less strongly to mercury surfaces than do the ligands present in the remaining five complexes which also yield values of $\alpha_{app} < 0.5$, consistent with inner-sphere reaction pathways.

Inferring Mechanisms from Kinetic Responses to Iodide Adsorption. To analyze the results of the iodide addition experiments summarized in Table I, it is useful to refer again to eq 5 to consider the ways in which the adsorption of iodide ions on the electrode surface may affect the reaction rate at constant electrode potential and ionic strength. The terms on the right-hand side of eq 5 which will be altered by the adsorption of iodide anions under these conditions are $\Delta G^{\circ}{}_{A_R}$ and $\Delta G^{\circ}{}_{A_P}$. (Note that the definition chosen earlier for $\gamma^{\ddagger}$ excludes its being affected by the adsorption of nonreacting ions. The ln k term would be altered if the chromium(III) complexes were anated by the added iodide ions but this is not a thermodynamically favorable process under the conditions of the experiments.) For the outer-sphere reactions the changes in $\Delta G^{\circ}{}_{A_R}$ or $\Delta G^{\circ}{}_{A_P}$ caused by iodide adsorption should arise entirely from the resulting changes in the electrostatic work involved in transporting the reactant or the product from the bulk of the solution to the oHp. These changes can be calculated from the changes in the potential at the oHp, ϕ_2, just as was done earlier in connection with eq 8. Thus, the changes in $\Delta G^{\circ}{}_{A_R}$ and $\Delta G^{\circ}{}_{A_P}$ are $Z_RF\Delta\phi_2$ and $(Z_R - 1)F\Delta\phi_2$, respectively, for a one-electron reduction. Inserting these values into eq 5 leads to eq 9, whose left-hand side represents the change in log k_{app} at any constant electrode potential, E,

$$(\Delta \log k_{\mathrm{app}})_E = (\alpha - Z_{\mathrm{R}})\frac{F}{2.3RT}(\Delta\phi_2)_E \qquad (9)$$

resulting from the change in the potential at the oHp, $(\Delta\phi_2)_E$, caused by the adsorption of iodide ions. Equation 9 was used to calculate the dashed lines in Figures 2 and 3. The necessary values of $(\Delta\phi_2)_E$ were evaluated from the iodide adsorption data in ref 26 and a diffuse layer capacitance of 520 μF cm^{-2} at all potentials rather than the values predicted by conventional diffuse layer theory[3] because this larger and potential-independent value has been shown experimentally to be the appropriate value in uni-univalent electrolytes at unit ionic strength.[20,26] The adsorption of iodide produces negative values of $(\Delta\phi_2)_E$ so that the reaction rates of cationic reactants undergoing outer-sphere reductions will be enhanced by iodide adsorption. Note that the measured rate enhancements shown in Figure 2 in the case of $Cr(OH_2)_5F^{2+}$ are in quite good agreement with the changes calculated from eq 9. Similar good agreement is also obtained with $Cr(OH_2)_6{}^{3+}$ and $Cr(OH_2)_5OSO_3{}^{+}$ which is consistent with the same three complexes having been classified as outer-sphere reactants in Table I on the basis of their α_{app} values. If the substitutionally labile water molecules coordinated to the electrode surface (Figure 1) were displaceable by a water molecule in the inner coordination sphere of Cr(III), an inner-sphere reaction pathway in which a water molecule served as a bridging ligand could conceivably be followed by these three complexes. This possibility seems remote, particularly in view of the good agreement between the observed and calculated rate enhancements for these complexes in the iodide-addition experiments (Figure 2), but it could not be absolutely ruled out. However, the absence of a water-bridged pathway in related homogenous charge-transfer reactions[36] also argues against its likelihood in these electrode reactions. Thus, on the basis of both of the test criteria, the complexes $Cr(OH_2)_6{}^{3+}$, $Cr(OH_2)_5F^{2+}$, and $Cr(OH_2)_5OSO_3{}^{+}$ can be identified as outer-sphere reactants with reasonable confidence.

For complexes that follow inner-sphere pathways the two free energies of adsorption in eq 5 contain an additional component. Cationic complexes will experience the same electrostatic attraction from adsorbed iodide ions as do outer-sphere reactants but, in addition, the free energy required to move the reactant and product from the oHp to the reaction site where the bridging ligand is bound to the electrode surface must be included. The anionic bridging ligands are expected to interact strongly and repulsively with adsorbed iodide anions because all simple anions are known to obey adsorption isotherms on mercury which correspond to large, repulsive interactions between the adsorbed ions.[37] (The interactions are much stronger between ions present in the inner portion of the double layer than between those in the diffuse layer because dielectric saturation in the inner layer results in a much lower effective dielectric constant within this region.[38]) Thus, the two contributions to the free energies of adsorption of inner-sphere cationic reactants act in opposing directions and the net effect of iodide adsorption on the reaction rate is difficult to predict quantitatively. In fact, the reduction rates of $Cr(OH_2)_5N_3{}^{2+}$ (Figure 2) and the other four complexes classified as inner-sphere reactants in Table I all exhibit a decrease in reaction rate in the presence of adsorbed iodide anions. This implies that interionic repulsions within the inner layer dominate over the electrostatic attraction between the negative electrode surface and the positive, but more remote, cationic centers of the complexes. Thus, the same five complexes which gave α_{app} values consistent with inner-sphere reaction mechanisms also respond to iodide adsorption as expected for inner-sphere reactants.

The latter test provides somewhat more persuasive evidence because it does not require that a value of the intrinsic transfer coefficient be known. However, the consistent pattern of behavior exhibited by the five complexes in both tests appears to be a clear indicator of inner-sphere reactions.

The diagnostic usefulness of the methods described will be least ambiguous with net cationic complexes containing anionic ligands but extension of the tests to neutral or even net anionic complexes may prove possible on the basis of quantitative measurements of relative reaction rates in the presence and absence of adsorbed anions. For example, Guidelli and coworkers[39] have recently reported that the addition of adsorbing anions produces decreases in the rates of reduction of perbromate and dithionate anions which are larger than those predicted from conventional diffuse layer theory for outer-sphere reactions. On this basis they argue that the reaction site for these two anions must be closer to the electrode surface than the oHp although the possibility that these anions might follow inner-sphere reaction pathways was not considered explicitly.

Mechanisms of Oxidation of Cr^{2+}. The oxidation of Cr^{2+} in perchlorate supporting electrolytes appears to proceed along the same pathway employed by Eu^{2+} in this electrolyte: both ions respond to changes in ionic strength[40] and give (oxidation) rate–potential plots that correspond to almost identical apparent anodic transfer coefficients. It seems virtually certain that both ions behave as outer-sphere reactants in perchlorate electrolytes. The rate–potential plots for their oxidations intersect the corresponding plots for the reduction of $Cr(OH_2)_6{}^{3+}$ and Eu^{3+} at the independently measured formal potentials for each couple.[20]

The modest increase in the rate of oxidation of Eu^{2+} when 1 M KCl is substituted for 1 M $NaClO_4$ as supporting electrolyte (Figure 5) can be satisfactorily accounted for by means of the standard Frumkin correction[25] and the more negative values of ϕ_2 resulting from the specific adsorption of chloride anions (bearing in mind the observed inadequacies of the Gouy–Chapman–Stern model[20,26]). By contrast, the much larger increase in the rate of oxidation of Cr^{2+} in 1 M KCl suggests that a more efficient reaction pathway is provided for Cr^{2+} by the presence of chloride anions. Since it is known[5] that $Cr(OH_2)_5Cl^{2+}$ rather than $Cr(OH_2)_6{}^{3+}$ constitutes almost all of the reaction product in 1 M chloride electrolytes, it seems quite reasonable to attribute the large increase in the rate of oxidation of Cr^{2+} to a chloride-bridged, inner-sphere pathway.

Note that microscopic reversibility cannot be invoked to argue that an inner-sphere pathway for the electrooxidation of Cr^{2+} to $Cr(OH_2)_5Cl^{2+}$ in chloride electrolytes requires that the reduction of $Cr(OH_2)_5Cl^{2+}$ must also be inner sphere. The reason is that the kinetics of the two reactions must be measured at quite different electrode potentials in order to obtain observable rates of reaction. Thus, it is usually necessary to examine the kinetic behavior of the electrode reaction separately in both the reduction and oxidation direction in order to identify the reaction pathway for each case. Only with complexes which are sufficiently reactive to yield measurable currents in both directions at potentials in the vicinity of the equilibrium potential does the principle of microscopic reversibility render kinetic measurements in both directions redundant.

The slopes of the anodic rate–potential plots for the chloride electrolyte in Figure 5 correspond to apparent anodic transfer coefficients which are greater than 0.5 for both reactants. (The apparent transfer coefficients are 0.67 and 0.58 for Cr^{2+} and Eu^{2+}, respectively.) Thus, an apparent transfer coefficient that exceeds 0.5 for these oxidation reactions is not indicative of an outer-sphere reactant as it was for the reduction reactions in Table I. The fact that Cr^{2+} and Eu^{2+} exhibit different apparent transfer coefficients suggests that these two cations follow different reaction mechanisms in chloride electrolytes.

Table II. Formation Quotients and Electrode Reaction Rate Constants for $Cr^{III}(OH_2)_5X^{(3-p)+}$ Complexes

Complex no.	X^{p-} in $Cr(OH_2)_5$-$X^{(3-p)+}$	Likely mechanism	Q_{III},[a] M^{-1}	Q_{II},[b] M^{-1}	$-E^f{}_X$,[c] mV	10^5k_{app},[d] cm s^{-1}	$10^5k^s{}_{cor}$,[e] cm s^{-1}	$k^{s'}{}_{cor}$,[f] s^{-1}	$10^5k^{700}{}_{app}$,[g] cm s^{-1}
1	H_2O	Outer sphere			655	0.75	0.25		2.2
2	F^-	Outer sphere	2.1×10^4	7.1	859	0.60	0.21		0.012
3	$SO_4{}^{2-}$	Outer sphere	22	3.2	704	0.46	0.36		0.42
4	Cl^-	Inner sphere	0.11	1.4	589	120		4×10^4	560
5	Br^-	Inner sphere	2.2×10^{-3}	0.20	539	7×10^4		1.5×10^6	11×10^5
6	NCS^-	Inner sphere	1.8×10^2	13	722	420		4×10^3	290
7	$N_3{}^-$	Inner sphere	$\sim10^3$	~70	~723	12		5×10^3	9.5
8	$NO_3{}^-$	Inner sphere	9.3×10^{-3}						35

[a] Equilibrium quotient for $Cr(OH_2)_6{}^{3+} + X^{p-} \rightleftharpoons Cr(OH_2)_5X^{(3-p)+} + H_2O$ at unit ionic strength. Sources for Q_{III} values: **3**, ref 16; **2**, **4–6**, **8**, ref 51; 7, estimated from product distribution data in ref 13. [b] Equilibrium quotient for $Cr(OH_2)_6{}^{2+} + X^{p-} \rightleftharpoons Cr(OH_2)_5X^{(2-p)-} + H_2O$ at unit ionic strength. Complex numbers and sources for Q_{II} values: **2–5**, ref 49; **6**, quoted in ref 52;7, estimated by assuming the same Q_{II}/Q_{III} ratio as for NCS^-. [c] Calculated from eq 13. [d] The apparent rate constant at $E^f{}_X$. [e] $k^s{}_{cor} = k^s{}_{app} \exp(Z_R - 0.5)F\phi_2$; ϕ_2 values are from ref 20; see text. [f] $k^{s'}{}_{cor} = k^s{}_{app}(C_{ss}/\Gamma_{ss}) \exp(\Delta G_{AX}/RT)$; $\Gamma_{ss} = 1$ mol cm^{-2}; $C_{ss} = 10^{-3}$ mol cm^{-3}; values of ΔG_{AX} were taken (or estimated using data) from the following: for $X = Cl^-$, R. Payne, *Trans. Faraday Soc.*, **64**, 1638 (1968); D. C. Grahame and R. Parsons, *J. Am. Chem. Soc.*, **83**, 1291 (1961); for $X = Br^-$, J. Lawrence, R. Parsons, and R. Payne, *J. Electroanal. Chem. Interfacial Electrochem.*, **16**, 193 (1968); A. R. Sears and P. A Lyons, *ibid.*, **42**, 69 (1973). For $X = NCS^-$, ref 43; for $X = N_3{}^-$, C. V. D'Alkaine, E. R. Gonzalez, and R. Parsons, *J. Electroanal. Chem. Interfacial Electrochem.*, **32**, 57 (1971). [g] The apparent rate constant evaluated at −700 mV vs. SCE.

(The corresponding two transfer coefficients in 1 M $NaClO_4$ are both 0.37 ± 0.01.) The larger apparent transfer coefficient of Cr^{2+} is consistent with its preferring an inner-sphere pathway which features anion bridging because this pathway would be expected to become relatively more favorable as the electrode potential is made more positive and anion adsorption becomes more extensive.

Unfortunately, a more quantitative analysis of the kinetic data for these anodic processes is not feasible because adsorbed chloride anions increase the rates of both inner- and outer-sphere reactions and the differences in the potential dependences for the two cases are quite small. On the other hand, the effect of iodide anion adsorption on the oxidation rates of Eu^{2+} and Cr^{2+} in chloride supporting electrolytes (Figure 5) provides very clear additional evidence that these two reactants follow different mechanisms. The marked increase in the rate of oxidation of Eu^{2+} is to be expected for an outer-sphere reactant whose concentration at the oHp is enhanced by the increased electrostatic attraction provided by the adsorbed anions. By contrast, the decrease in rate for Cr^{2+} seems a certain indication that the more strongly adsorbing iodide anions displace some of the initially adsorbed chloride anions which are required for the more rapid, inner-sphere oxidation of the Cr^{2+}. The adsorbed iodide anions cannot substitute for chloride in an inner-sphere oxidation reaction within the range of electrode potentials examined in Figure 5 because the formal potential for half-reaction 10 can be calculated from the

$$Cr(OH_2)_5I^{2+} + e^- \rightleftharpoons Cr(OH_2)_6{}^{2+} + I^- \qquad (10)$$

equilibrium formation quotient of $Cr(OH_2)_5I^{2+}$ [41] (and the formal potential for the two aquo cations) to be −240 mV vs. SCE in 10 mM iodide.[42]

Thus, the iodide-addition test can also prove diagnostically useful in distinguishing between inner- and outer-sphere reactions with substitutionally labile reactants such as Cr^{2+} and Eu^{2+}. In fact, we have recently employed this test in studies of the reduction kinetics of Eu^{3+} in thiocyanate supporting electrolytes.[43] Iodide addition leads to a decrease in reaction rate which was taken as an indication that Eu^{3+} reduction proceeds by an inner-sphere, anion-bridged pathway in thiocyanate electrolytes.

Reactivity Patterns. Table II contains a summary of the kinetic data for the reduction of the eight complexes in 1 M $NaClO_4$. The various complexes exhibit a very wide range of reactivity toward electrochemical reduction just as do these and related complexes in homogeneous redox reactions.[22,44] A useful formalism for exposing the various factors which may contribute to differences in reactivity is that due to Marcus[45] as embodied in eq 11. $\Delta G_\ddagger°$ is the standard free energy of

$$\Delta G_\ddagger° = \frac{F(E - E°)}{2} + \frac{w^R + w^P}{2} + \frac{\lambda el}{4} \qquad (11)$$

activation for an electroreduction process which is related to the measured values of k_{app} (Figures 2–5) by $k_{app} = Z \exp(-\Delta G_\ddagger°/RT)$, where Z is the collision frequency of the reactant with the electrode surface and the other terms in eq 11 have their customary[45] significance. (The term involving a quadratic potential dependence has been omitted from eq 11 because experiments have shown[46,47] that including it leads to poorer agreement with log k_{app} vs. E data for the reduction of several Cr(III) complexes.)

Although eq 11 was originally derived for outer-sphere reactions,[45] the same general formalism should also apply to inner-sphere reactions.[48] The first two terms on the right-hand side of eq 11 can be regarded[49] as the "thermodynamic" (or "driving force") contributions to $\Delta G_\ddagger°$, while the final term represents the free energy required to form the activated complex when the preceding and succeeding ground states are of equal energy.[48,49] Thus, the final term constitutes the "intrinsic" energy barrier opposing the reaction.

To understand the differences in reactivity represented by the various rate constants in Table II, it is useful to calculate the contributions of each of the terms on the right-hand side of eq 11 to the free energies of activation and hence to the measured rate constants. The first term can be eliminated if the rate constant for each complex is evaluated at the corresponding standard potential. In practice, electrode kinetic measurements require the presence of significant supporting electrolyte concentrations so that is is appropriate to employ the formal potential for each complex in the supporting electrolyte employed rather than $E°$. The relevant formal potential, $E^f{}_X$, is that corresponding to half-reaction 12 in

$$Cr(OH_2)_5X^{(3-p)+} + e^- \rightleftharpoons Cr(OH_2)_5X^{(2-p)+} \qquad (12)$$

which the anionic ligand, X^{p-}, is coordinated to the chromium center in both oxidation states. $E^f{}_X$ is related to the formal potential for the $Cr(OH_2)_6{}^{3+}$–$Cr(OH_2)_6{}^{2+}$ couple, $E^f{}_{aq}$, according to eq 13, where Q_{III} and Q_{II} are the equilibrium

$$E^f{}_X = E^f{}_{aq} - \frac{RT}{F} \ln \frac{Q_{III}}{Q_{II}} \qquad (13)$$

quotients for the formation of complexes between X and Cr(III) and Cr(II), respectively. Although values of Q_{III} have been measured for all but one of the complexes studied, Q_{II}

is much more difficult to measure and estimates are sparse. The values of Q_{II} listed in Table II are essentially the only values in the literature. Most of these quotients were obtained indirectly from the measured effects of the added ligands on the kinetics of some homogeneous chromous reductions.[50] They are not likely to be as reliable as the values of Q_{III}. The values of E^f_X given in the sixth column of Table II were calculated from eq 13 for all of the complexes for which Q_{II} and Q_{III} could be estimated. Values of the standard apparent rate constants, k^s_{app}, were then evaluated for each complex at the corresponding value of E^f_X in order to eliminate the contributions of the first term in eq 11 to $\Delta G_{\ddagger}°$ and k_{app}.

The second term in eq 11 represents the average of the work required to bring the reactant and product species to the reaction site. For outer-sphere reactions this quantity should be comprised entirely of the electrostatic work required for each species to move across the diffuse layer to the oHp where the potential is ϕ_2 with respect to the bulk of the solution. For one-electron reactions having intrinsic transfer coefficients, α, of 0.5, $(w^R + w^P)/2 = (Z_R - 0.5)F\phi_2$, where Z_R is the charge of the reactant.[25] For the three outer-sphere reactants in Table II the listed values of k^s_{cor} were obtained by multiplying k^s_{app} by $\exp(Z_R - 0.5)F\phi_2$ with the values of ϕ_2 at E^f_X obtained from the estimates in ref 20.

Remaining differences in the resulting values of k^s_{cor} should reflect only the differences in the final term of eq 11 which may arise from differences in the intrinsic reorganizational energy barrier faced by each of the reactants. The fact that the values of k^s_{cor} for the three outer-sphere reactants (Table II, column 7) differ by less than a factor of 2 is consistent with their following a common mechanism in which the reorganization energy in each case is expended primarily in adjusting the outer solvation sheath to accommodate a net charge that is diminished by one unit and in stretching the pair of axial ligands in the incipient Cr(II) product. The latter contribution might well be nearly constant among the three complexes considering the proximity of H_2O, F^-, and SO_4^{2-} in the spectrochemical series.[51]

A comparison of the reduction rates for the inner-sphere reactants also requires values of E^f_X from eq 13 but measured values of Q_{II} are available only for the cases $X = Cl^-$, Br^-, and NCS^- (and an estimated value for N_3^-). Moreover, the reported values[49] of Q_{II} for Cl^- and Br^- correspond to greater stabilities of the Cr(II) than of the Cr(III) complexes, which seems unlikely. (Fortunately, the values of Q_{II} appear to vary much less with the nature of X^- than do those for Q_{III} (Table II) so that the variation of E^f_X as X^- is changed will be dominated by the changes in Q_{III} for which more reliable values are available.) Despite the possible quantitative uncertainties involved, k_{app} was evaluated for each inner-sphere complex at the values of E^f_X shown in Table II. Our hope was that the resulting values of k^s_{app} would be sufficiently different to permit qualitative distinctions in reactivity to be made among the complexes in spite of the uncertainties about the formal potentials at which the rate constants were evaluated.

The values of k^s_{app} for these inner-sphere reactants do indeed span a greater range and are individually larger than those of the outer-sphere reactants (Table II, column 6). However, in order to correct for differences in the work terms in eq 11 before making rate comparisons, it is necessary to evaluate the equivalent of k^s_{cor} for these inner-sphere reactants. The work involved in bringing an inner-sphere reactant or product to the reaction site on the electrode surface is given by the corresponding free energy of adsorption $\Delta G°_A$, introduced earlier in eq 5. Thus, the work term in eq 11 can be written as $(\Delta G°_{A_R} + \Delta G°_{A_P})/2$. Unfortunately, none of the inner-sphere complexes in Table II are adsorbed strongly enough on mercury to allow their adsorption isotherms to be measured so that it is necessary to estimate the free energies of adsorption. For present purposes it was assumed that both of these free energies could be approximated by those of the corresponding uncoordinated anion at the same potential, $\Delta G°_{A_X}$. (Even though these anion free energies of adsorption are likely to be more negative than those of the chromium–anion complexes, the relative values of both sets are likely to be comparable.[53]) Corrected standard rate constants for the inner-sphere reactants in Table II were then obtained by multiplying the k^s_{app} values by $(C_{ss}/\Gamma_{ss}) \exp(\Delta G°_{A_X}/RT)$, where C_{ss} and Γ_{ss} are the standard state values used in defining $\Delta G°_{A_X}$ (note that the values obtained for k^s_{cor} are independent of the particular standard states selected).

The resulting values of $k^{s'}_{cor}$ (Table II, column 9) have the units of s^{-1} because they correspond to the reduction of the complexes while they are attached to the electrode surface. In contrast with the small variation in the corresponding values of k^s_{cor} for the outer-sphere reactants (Table II, column 7), the inner-sphere corrected rate constants, $k^{s'}_{cor}$ (column 8), show differences approaching 10^3. Although unavoidable uncertainties were introduced into the absolute values of $k^{s'}_{cor}$ in the process of correcting for the first two ("driving force") terms in eq 11, we believe the relative ordering of these rate constants probably gives a qualitatively correct reactivity sequence; that is, reactivity increases in the order $X^{p-} = N_3^- \sim NCS^- < Cl^- < Br^-$. The reactivity difference between the two halo complexes and the two pseudohalo complexes is very likely to be even greater than is indicated from the values of $k^{s'}_{cor}$ in Table II because the approximate method used to correct for the work terms in eq 11 almost certainly underestimates the strength of the adsorption of the pseudohalo complexes compared with that of the halo complexes.[54] The observed reactivity order matches that of the inner-sphere reaction of each of the $Cr(OH_2)_5X^{(3-p)+}$ complexes with $Cr(OH_2)_6^{2+}$.[22,25] This suggests that similar factors contribute to the intrinsic reorganizational energy barriers faced by the reaction in both the homogeneous and heterogeneous cases. The relative ease of stretching the bonds to the bridging ligands as well as the relative abilities of heteroligands to mediate electron transfer between metal centers or from the electrode surface to the metal center (i.e., the "permeability" of the heteroligand to electron flow[1a]) may be included among such common factors.

The lower reactivity of the isothiocyanate complex contrasts with the widespread ability of this anion to catalyze the electrode reactions of a number of metal cations,[56] usually more strongly than do bromide or chloride ions. The implication is that bromide and chloride are intrinsically better bridging ligands for facilitating inner-sphere electron transfer and the greater net effectiveness of isothiocyanate is entirely attributable to its ability to bind the complex to the mercury surface. That is, the "precursor complex" formation constant is sufficiently greater for isothiocyanate complexes to more than compensate for their intrinsically lower reactivity.

The nearly equal reactivity of the isothiocyanato and azido complexes contrasts with the much greater reactivity of the latter complex in its homogeneous reactions with Cr^{2+}.[22] This difference is not unexpected inasmuch as the homogeneous reaction of the isothiocyanate complex leads to an unstable, sulfur-bonded, linkage isomer of chromium(III) thiocyanate[22,57] while the binding of thiocyanate anions to mercury electrode surfaces by a sulfur–mercury bond is the stable configuration.[58]

Rate Comparisons at Constant Potential. In studies of homogeneous charge-transfer reactions, comparisons of observed second-order rate constants are often made without applying corrections for differences in thermodynamic driving forces or for the work of bringing the reactants together (i.e., for the first and second terms in eq 11). So long as the limitations inherent in comparisons among such uncorrected rate constants are kept in mind, the same approach can be used with electrochemical rate constants by comparing their values at a constant potential. The final column in Table II shows the apparent rate constants that result if the reduction rate of each of the complexes is evaluated at −700 mV, where all complexes have measurable rates of reaction.

The great span of reactivities among the set of complexes remains evident when the rates are compared on this basis as does the very high reactivity of the bromo and chloro complexes. However, the finer distinctions which are reflected by smaller differences in reaction rates are lost. Comparisons among rate constants at a common potential are thus best confined to discussions of gross trends rather than subtle differences. For this reason, some of the conclusions reached in previous work where this source of difficulty was largely ignored[59] deserve to be regarded with some skepticism.

Comparisons among the apparent, corrected, or fixed-potential rate constants in Table II all show the outer-sphere reactants to be significantly less reactive. It is tempting to suggest that comparably low reactivity might be taken as a general indication of an outer-sphere reactant but kinetic data for many additional complexes are needed before drawing such a generalization would be warranted. The serious problems encountered in the present study in establishing the appropriate formal potentials at which to compare rate constants emphasize the desirability in future studies of selecting complexes which are stable enough in both oxidation states to permit reliable estimates of the metal–ligand formation quotients to be measured.

Conclusions

The primary result of this study has been the establishment of a general and systematic basis for analyzing the electrode kinetics of certain types of metal ion complexes to permit the identification of their electrode reaction mechanisms as inner or outer sphere. The two diagnostic criteria that are proposed are applicable to both inert and labile complexes although fewer tests of the reliability of the criteria with the latter type of complexes have been made. Comparisons of the relative electrochemical reactivities of the complexes studied (though impeded by inadequacies of the available equilibrium stability data) reveal trends which resemble those for the homogeneous reductions for some of the complexes but which contrast with their homogeneous counterparts in other cases because of the particular coordination chemistry exhibited by the surfaces of mercury electrodes.

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References and Notes

(1) (a) H. Taube, "Electron Transfer Reactions of Complex Ion in Solution", Academic Press, New York, N.Y., 1970; (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, N.Y., 1966.
(2) P. Delahay, "Double Layer and Electrode Kinetics", Interscience, New York, N.Y., 1965, Chapter 3.
(3) Reference 2, Chapter 4.
(4) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953).
(5) D. A. Aikens and J. W. Ross, *J. Phys. Chem.*, **65**, 1213 (1961).
(6) J. J. Ulrich and F. C. Anson, *Inorg. Chem.*, **8**, 195 (1969).
(7) D. J. Barclay, E. Passeron, and F. C. Anson, *Inorg. Chem.*, **9**, 1024 (1970).
(8) F. C. Anson and R. S. Rodgers, *J. Electroanal. Chem. Interfacial Electrochem.*, **47**, 287 (1973).
(9) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **58**, 95 (1975).
(10) M. J. Weaver and F. C. Anson, *J. Am. Chem. Soc.*, **97**, 4403 (1975).
(11) R. S. Rodgers and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **42**, 381 (1973).
(12) E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).
(13) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).
(14) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).
(15) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).
(16) N. Fogel, J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962). The monodenticity of the sulfate ligand in this complex has been demonstrated: J. E. Finholt, T. W. Anderson, J. A. Fyfe, and K. G. Caulton, *Inorg. Chem.*, **4**, 43 (1965).
(17) G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 2331 (1952).
(18) G. Lauer, R. Abel, and F. C. Anson, *Anal. Chem.*, **39**, 765 (1967).
(19) J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York, N.Y., 1966, Chapter XIV.
(20) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **65**, 711 (1975).
(21) R. G. Linck, *Inorg. Chem.*, **11**, 61 (1972).
(22) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).
(23) (a) A. Adin and A. G. Sykes, *J. Chem. Soc. A*, 1518 (1966); (b) A. Adin, J. Doyle, and A. G. Sykes, *ibid.*, 1504 (1967); (c) J. Doyle, A. G. Sykes, and A. Adin, *ibid.*, 1314 (1968).
(24) Reference 2, Chapter 7.
(25) Reference 2, Chapter 9.
(26) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **65**, 737 (1975).
(27) L. Gierst and R. Cornelissen, *Collect. Czech. Chem. Commun.*, **25**, 3005 (1960).
(28) R. Parsons, *Trans. Faraday Soc.*, **47**, 1332 (1951).
(29) D. M. Mohilner and P. Delahay, *J. Phys. Chem.*, **67**, 588 (1963).
(30) D. M. Mohilner, *J. Phys. Chem.*, **73**, 2652 (1969).
(31) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **58**, 81 (1975).
(32) R. Parsons, *Croat. Chem. Acta*, **42**, 281 (1970).
(33) Equation 5 is somewhat reminiscent of eq 15 of ref 31, but the two equations differ significantly because the latter gives the rate in terms of the surface concentration of an adsorbed reactant while eq 5 expresses the rate more conventionally in terms of the bulk concentration of the reactant, C^b.
(34) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).
(35) W. R. Fawcett, *J. Chem. Phys.*, **61**, 3842 (1974).
(36) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).
(37) R. Parsons, *Trans. Faraday Soc.*, **51**, 1518 (1955).
(38) C. A. Barlow and J. R. MacDonald, *Adv. Electrochem. Electrochem. Eng.*, **6** (1967).
(39) M. L. Foresti and R. Guidelli, *J. Electroanal. Chem. Interfacial Electrochem.*, **53**, 219 (1974); M. L. Foresti, D. Cozzi, and R. Guidelli, *ibid.*, **53**, 235 (1974).
(40) R. Cornelissen, Thesis, Free University of Brussels, 1962.
(41) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).
(42) The thermodynamic instability of $Cr(OH_2)_5I^{2+}$, which is the origin of the very positive value of the formal potential for half-reaction 10, means that the oxidation of $Cr(OH_2)_6^{2+}$ in iodide electrolytes cannot produce $Cr(OH_2)_5I^{2+}$ at potentials significantly more negative than this formal potential. Any $Cr(OH_2)_5I^{2+}$ somehow produced near the electrode would be rapidly reduced. For this reason it is erroneous to point to increases in the rate of oxidation of Cr^{2+} at potentials negative of −350 mV with iodide concentrations in the millimolar range as an indication that an iodide-bridged, inner-sphere mechanism obtains.[5] At these more negative potentials the rate enhancements caused by iodide additions are almost certainly the result of increases in the rate of formation of $Cr(OH_2)_6^{3+}$ via an outer-sphere pathway that responds to the changes in ϕ_2 resulting from iodide adsorption.[26] Similar limitations on allowable mechanistic inferences also pertain to measurements of yields of anated chromium(III) complexes during controlled-potential electrolyses of $Cr(OH_2)_6^{2+}$.[6,7] Unless such electrolyses are confined to potentials well positive of the formal potential for the corresponding Cr(III)–Cr(II) couple, increases in yields of anated products as the potentials are made more positive are more likely to reflect shifts in Nernstian equilibria than changes in the relative dominance of competing inner-sphere and outer-sphere reaction mechanisms.
(43) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, **65**, 759 (1975).
(44) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1967, p 475.
(45) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).
(46) F. C. Anson, N. Rathjen, and R. D. Frisbee, *J. Electrochem. Soc.*, **117**, 477 (1970).
(47) M. J. Weaver and F. C. Anson, *J. Phys. Chem.*, in press.
(48) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
(49) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).
(50) C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 1568 (1968).
(51) Reference 44, p 67.
(52) J. E. Earley and R. D. Cannon, *Transition Met. Chem.*, **1**, 33 (1966).
(53) Values of $\Delta G°_A$ have been measured for a few chromium(III) isothiocyanate complexes.[9] They were typically ca. 2 kcal mol^{-1} less negative than that for free thiocyanate anions.
(54) F. C. Anson, *Acc. Chem. Res.*, **8**, 400 (1975).

(55) R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288, (1964).
(56) R. DeLevie, *J. Electrochem. Soc.*, **118**, 185c (1971).
(57) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).
(58) R. Parsons and P. C. Symons, *Trans. Faraday Soc.*, **64**, 1077 (1968).
(59) For example, A. A. Vlček in "Advances in the Chemistry of Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, N.Y., 1971, p 590; *Prog. Inorg. Chem.*, **5**, 211 (1963); *Discuss. Faraday*, **26**, 164 (1958).

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Substitution at Chromium(III) Centers in Aprotic Solvents. Ion Pairing, Anation, and Solvent Exchange in *N*,*N*-Dimethylformamide

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Rate coefficients and enthalpies and entropies of activation have been obtained for anation of $Cr(DMF)_6^{3+}$ in DMF by Br^-, NCS^-, and N_3^- and for DMF solvent exchange with $Cr(DMF)_6^{3+}$ in the presence of Br^-, Cl^-, and ClO_4^-, as well as exchange rate data at single temperatures in the presence of NCS^- and N_3^-. Ion-pair formation quotients were also estimated from the kinetics of one or both reactions for Br^-, Cl^-, NCS^-, N_3^-, and ClO_4^-, the last result superseding an earlier inaccurate estimate. Solvent-exchange rates were depressed by ion pairing, but only slightly so, and to roughly the same extent for all of the above anions. These and previously published data confirm the validity of the interchange model of substitution in octahedral cations in solution and indicate an associative interchange mechanism for all of the foregoing reactions. The nucleophilicities of anions X^- toward the Cr(III) complex are simply related to the pK_a of the aqueous acids HX.

Introduction

The experimental data presently available on the kinetics of simple anation reactions of cationic octahedral transition metal complexes[1]

$$ML_5(solvent)^{n+} + X^{x-} \xrightarrow{k_{obsd}} ML_5X^{(n-x)+} + solvent \qquad (1)$$

are generally consistent with, but do not necessarily require, a model known as the interchange mechanism[1,2] according to which the rapid initial formation of an ion pair (encounter complex)

$$ML_5(solvent)^{n+} + X^{x-} \overset{K_{IP}}{\rightleftharpoons} \{ML_5(solvent)^{n+},X^{x-}\} \qquad (2)$$

precedes rate-determining entry of X^{x-} into the first coordination sphere of the complex

$$\{ML_5(solvent)^{n+},X^{x-}\} \xrightarrow{k_i} ML_5X^{(n-x)+} + solvent \qquad (3)$$

In the case of a dissociative interchange (I_d) mechanism,[2] the fission of the metal–solvent bond is rate determining, and consequently k_i will in general[3] be less than the rate coefficient k_{ex} for the exchange of complexed and uncomplexed solvent

$$ML_5(solvent^*)^{n+} + solvent \xrightarrow{k_{ex}} ML_5(solvent)^{n+} + solvent^* \qquad (4)$$

and k_i would be expected to vary only slightly from one ligand X^{x-} to another. These requirements seem to be realized for M = Co(III), L = NH_3, and solvent = H_2O[4] and for M = Co(III), L = en and NO_2^-, and solvent = dimethyl sulfoxide.[5] Conversely, when M–X^{x-} bond making initiates the interchange process, bringing about essentially simultaneous metal–solvent bond breaking, k_i may exceed k_{ex} if X^{x-} is a sufficiently good nucleophile toward ML_5, and in any event k_i can be expected to vary strongly with the nature of X^{x-}.[1] These phenomena characterize simple substitution reactions of many Cr(III) complexes,[1] $Rh(NH_3)_5OH_2^{3+}$,[6,7] and $Ir(NH_3)_5OH_2^{3+}$,[8,9] to which an I_a mechanism may therefore be assigned.

A major weakness of this model lies in the fact that the reactivity of $ML_5(solvent)^{n+}$ within the ion pair could conceivably be quite different from that of the free complex ion. Watts, in particular, has stressed[10] that the free energy of formation of ion pairs from the constituent ions can be so large (e.g., -20 kJ mol^{-1} for $\{Cr(DMF)_6^{3+},Cl^-\}$ in DMF at 70 °C, as reported below) that a complex ion within an ion pair might justifiably be regarded as a species chemically different from the free complex ion. Thus, for a complex within an ion pair, the value of k_{ex} (hereinafter called k_1) might well be considerably greater or less than that for the free complex (k_2), and accordingly Monacelli,[6] in his study of the anation of $Rh(NH_3)_5OH_2^{3+}$ by chloride, was careful to establish that k_{ex} was not greatly affected by the presence of chloride ion (cf. Duffy and Earley's work[11] with $Cr(NH_3)_5OH_2^{3+}$). Unfortunately, ion-pair formation constants K_{IP} for 3:1 electrolytes in water are small, so that k_i and k_1 are measurable only by extrapolation, and so, because k_i for chloride anation of $Rh(NH_3)_5OH_2^{3+}$ and $Ir(NH_3)_5OH_2^{3+}$ was found[6–9] to be only marginally (2–3 times) greater than the free-ion value of k_{ex}, there is some room for skepticism over the assignment of an I_a mechanism on the sole basis of the above data, while for anation of $Cr(NH_3)_5OH_2^{3+}$ in water k_i is much less than k_{ex},[11] even though there is other evidence[1] that the mechanism is indeed I_a. We have therefore completed a detailed study of the title reactions, which, in the interchange model, are represented by reactions 5–8 with *N*,*N*-dimethylformamide

$$Cr(DMF)_6^{3+} + X^- \overset{K_{IP}}{\rightleftharpoons} \{Cr(DMF)_6^{3+},X^-\} \qquad (5)$$

$$\{Cr(DMF)_6^{3+},X^-\} \xrightarrow{k_i} Cr(DMF)_5X^{2+} + DMF \qquad (6)$$

$$\{Cr(DMF\text{-}d_7)_6^{3+},X^-\} + 6DMF\text{-}h_7 \xrightarrow{k_1} \{Cr(DMF\text{-}h_7)_6^{3+},X^-\} + 6DMF\text{-}d_7 \qquad (7)$$

$$Cr(DMF\text{-}d_7)_6^{3+} + 6DMF\text{-}h_7 \xrightarrow{k_2} Cr(DMF\text{-}h_7)_6^{3+} + 6DMF\text{-}d_7 \qquad (8)$$

(DMF) as solvent. Here, X^- was Br^-, NCS^-, and N_3^-, and measurements of k_1 for X^- = Cl^- were also made to utilize the corresponding k_i data reported previously.[12] These systems were chosen because the relatively low dielectric constant of DMF leads to high values of K_{IP}, so that k_i can be measured directly and with satisfactory accuracy. Furthermore, as noted previously,[13] the use of perdeuterated DMF permits relatively high precision to be attained in k_{ex} measurements. Finally, the use of the aprotic solvent DMF and the hexakis(solvent) substrate $Cr(DMF)_6^{3+}$ allows the apparently high nucleophilicity toward chromium(III) of Bronsted bases such as