

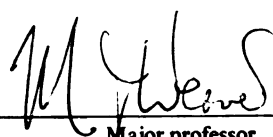


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ELECTRODE KINETICS AND DOUBLE LAYER
STRUCTURE AT PLATINUM AND GOLD ELECTRODES

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ELECTRODE KINETICS AND DOUBLE LAYER STRUCTURE
AT PLATINUM AND GOLD ELECTRODES

By

Stephen Wayne Barr

A DISSERTATION

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ABSTRACT

ELECTRODE KINETICS AND DOUBLE LAYER STRUCTURE AT PLATINUM AND GOLD ELECTRODES

By

Stephen Wayne Barr

The interaction between the reactant and the electrode surface is explored for simple heterogeneous electron transfer reactions at platinum and gold electrodes in aqueous solutions. The electroreductions of cobalt(III) ammine complexes were of primary interest. The ligands in the primary coordination sphere for these complexes could be varied and the effect of various ligands on reaction mechanisms or electrocatalysis could be determined. The reactivity of some complexes was employed to deduce the nature of the interphasial environment at the electrode surface. The heterogeneous electron transfer rates were determined by rotating disk voltammetry or cyclic voltammetry at platinum and gold electrodes, and by d.c. polarography at mercury electrodes. Reactant adsorption was determined by fast cyclic voltammetry, by reduction

rate shifts in probe reactions sensitive to surface charge, and by measurements of the overall reaction order for electron transfer. Chronocoulometry was used for adsorption measurements at mercury electrodes.

Electron transfer rates and reactant adsorption were also found for iodide-treated platinum and gold electrodes. Adsorbed iodide was found to block reactant adsorption at these surfaces. The iodide layer was found to have only a small effect upon the double layer charge which indicates that the metal-iodide bond is fairly covalent. The iodide-treated electrode results were instrumental in determining the degree of catalysis caused by reactant adsorption.

Several types of ligands were found to promote the adsorption of the cobalt(III) complexes. Among these are the chloro-, bromo-, isothiocyanato-, and pyridyl ligands. Significant catalysis of the electroreduction rates was noted for the chloro- and bromo- complexes. This catalysis was attributed to a lowering of the intrinsic barrier to electron transfer. It was also proposed that the intrinsic barrier to electron transfer was increased by certain ligands such as isothiocyanate.

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Several people deserve a share of the credit for the execution and completion of this research. Dr. Weaver's abundant suggestions and assistance kept the author from becoming hopelessly lost amidst a virtual quagmire of electrochemistry. The support and interest of the Weaver Group was greatly appreciated. Visiwanathan Srinivasan and Dr. David Larkin performed several mercury experiments included herein. Ken Guyer's work with silver electrodes offered many stimulating discussions when contrasted with platinum and gold, which often led to useful ideas for further work. Much of this research was supported by the Air Force Office of Scientific Research, which I gratefully acknowledge. The Chemistry Department may be credited with providing the atmosphere and financial support conducive to research, that made this work possible.

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INTRODUCTION

A central and fundamental problem in electrochemical kinetics is understanding the means by which the interphasial environment at an electrode surface influences heterogeneous electron transfer. That such influences are important is shown by the many and varied uses found for electrodes in industrial syntheses, electroplating, analyses and in the production of electricity. However, the basic understanding of these processes is quite limited even among specialists. Indeed, the term "black magic" often arises in connection with these electrochemical processes. The empirical formulae developed by such workers are often jealously guarded secrets. The empirical nature of much of this work is mainly the fault of the chemistry involved rather than the scientists. The mechanisms of many of the most useful applications are very complex, and those processes which exhibit the most simple and understandable mechanisms generally have no practical applications.

It was my aim in the research presented here to examine an electrochemical system which had the potential for yielding fundamental information about heterogeneous electron transfer at electrode surfaces which have in the past

been widely used in electrochemical catalyses. Platinum and gold were chosen as electrodes. Although mercury electrodes would be a more tractable choice, platinum and gold are more catalytic and hence a better choice to investigate heterogeneous catalysis. The electrode is only one half of the electron transfer process. The choice of an appropriate reactant is equally important. For reasons which are discussed in some detail in Chapter I, cobalt (III) ammine complexes were chosen.

The goal of the research was then to understand as well as possible the effect of the interphasial environment at platinum and gold electrodes upon the electrochemical reduction of cobalt (III) ammine complexes. In many cases much was revealed by comparison to their reduction at mercury electrodes or to their homogeneous reduction.

This research can be roughly divided into two parts: the determination of reactant adsorption and the electron transfer kinetics. This latter part includes studies of reaction mechanisms and rates. The contributions of the reactant and the electrode surface to electrocatalysis are discussed.

CHAPTER I

BACKGROUND AND HISTORICAL ASPECTS

A. Heterogeneous Electron Transfer

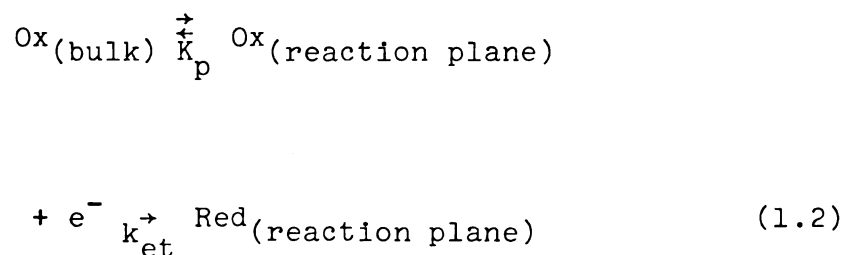
It is useful to divide heterogeneous electron transfer mechanisms into inner- and outer-sphere categories, depending on whether the reactant or its coordinated ligands does or does not penetrate the layer of adsorbed solvent molecules at the electrode surface.^{1,2} The inner-sphere transition metal complex undergoes electron transfer via an adsorbed intermediate where one or more of the coordinated ligands is bound to the electrode surface. The outer-sphere complex undergoes electron transfer at a more distant reaction plane, separated from the surface by at least one solvent layer. These definitions for heterogeneous reaction pathways are analogous to their homogeneous counterparts for electron transfer reactions.³

The electron transfer reaction,



where Ox and Red denote some species in its oxidized and reduced forms, can be described by the so-called

pre-equilibrium model.^{4,5} According to this model the overall electron transfer reaction (Equation 1.1) can be divided into two discrete steps:



The bulk reactant is in equilibrium with the reactant at a plane near or at the electrode surface depending on the type of mechanism. The reactant at this plane corresponds to the "precursor" state for the elementary electron transfer process. Some degree of reactant orbital overlap with surface metal orbitals is achieved in this state. Thermal activation of the precursor leads to the proper bond/orbital orientation for electron transfer in the activated complex at which point electron transfer occurs. The product thus formed represents the "successor" state. This product at the reaction plane is in equilibrium with the bulk product.^{4,5}

The free energy surfaces are depicted in Figure 1 for this process for both inner- and outer-sphere pathways. The overall process can be treated more formally by a consideration of the free energy barriers between states. The bulk reactant-to-precursor and successor-to-bulk

Figure 1. Free energy-reaction coordinate plot proposed for heterogeneous electron transfer.

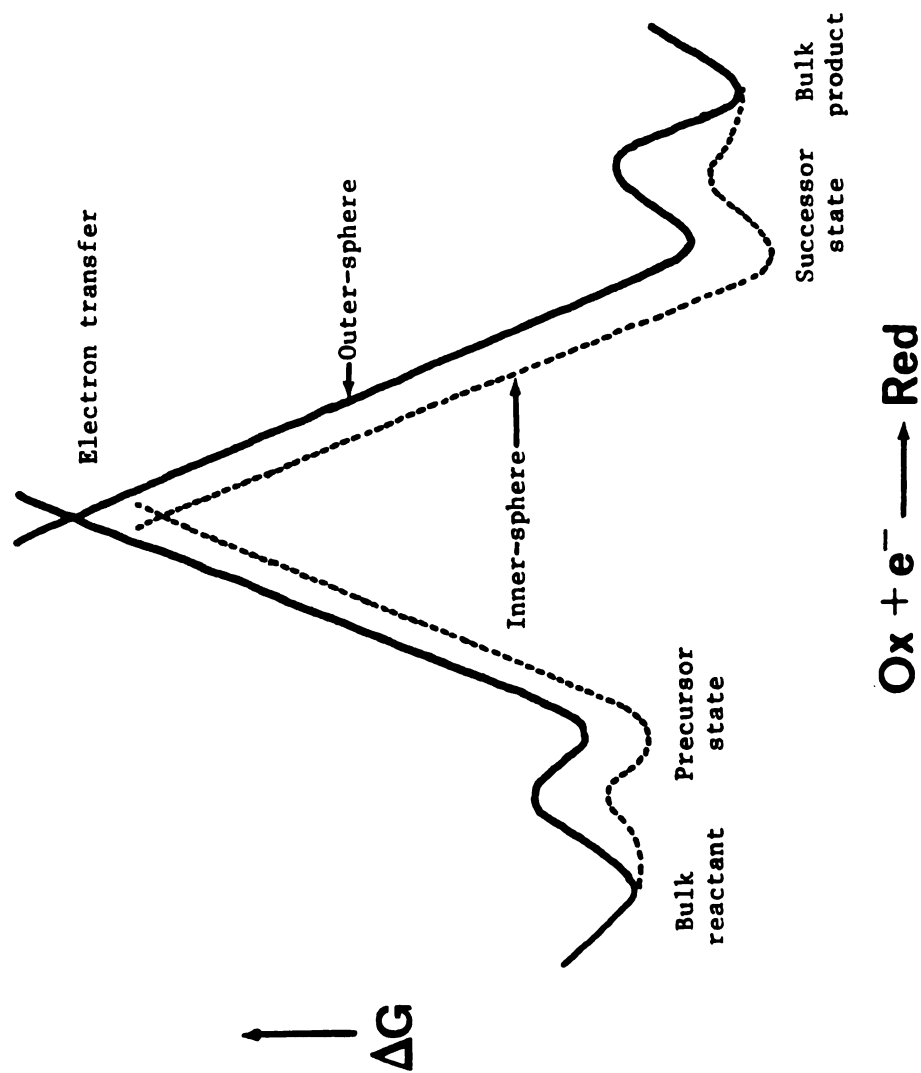


Figure 1

product equilibria can be described by the equilibrium constants K_p and K_s , respectively. The type of mechanism determines the nature of these equilibria. In an outer-sphere mechanism the reactant diffuses to the reaction plane through a potential gradient at a rate controlled by the magnitude of the potential, charge on the reactant ion, and the nature of the supporting electrolyte ions. The constant K_p is then given by⁶

$$K_p = r \exp(-z_r F \phi_r / RT) \quad (1.3)$$

where r is the reactant radius, z_r its ionic charge number, and ϕ_r the potential at the plane of reaction. The radius r is included as a statistical factor which converts a three-dimensional reactant concentration to an effective two-dimensional concentration on the reaction plane, i.e., the average surface concentration of reactant point charges in a layer centered at the reaction plane and extending $\frac{1}{2}r$ in either direction. For an inner-sphere mechanism K_p is equivalent to a more conventional adsorption equilibrium constant and is expressed as¹¹

$$K_p = \Gamma / C_b \quad (1.4)$$

the ratio of the surface concentration to the bulk concentration. Equation 1.4 could be separated into two

contributions, an electrostatic work term similar to Equation 1.3 and an adsorption term, but is most conveniently given as the concentration ratio. The rate constant for electron transfer from the precursor state is shown as k_{et} in Equation 1.2 and is related to the overall rate constant by¹¹

$$k_{app} = K_p k_{et} \quad (1.5)$$

The measured, overall electrochemical rate constant for either pathway can also be given as^{6,7}

$$\ln k_{app}^E = \ln K_p + \ln \kappa v_p - (\Delta G^*)^E / RT \quad (1.6)$$

at a specified electrode potential E , where $(\Delta G^*)^E$ and v_p are the reorganization energy and frequency factor for activation from the precursor state, and κ is the probability of the electron tunneling from one free energy surface to the other in the activated state (generally taken to be unity for adiabatic mechanisms^{8,9}). The pre-equilibrium represented by K_p corresponds to a thermodynamic contribution to the overall rate.

The activation represented by $(\Delta G^*)^E$ can be more precisely defined as⁸

$$(\Delta G^*)^E = (\Delta G^\ddagger)^1 - 0.5 RT (\ln K_s - \ln K_p) + 0.5 F(E - E^\circ) \quad (1.7)$$

Here $(\Delta G^\ddagger)^1$ is the intrinsic free energy of reorganization and the remaining two terms on the right hand side of Equation 1.7 represent the thermodynamic contributions of relative precursor and successor state stabilities and the "driving force" from the potential difference from the standard potential. The term $(\Delta G^\ddagger)^1$ has been called the "intrinsic barrier to electron transfer".^{6,10-12} The intrinsic barrier is equivalent to $\Delta G^\ddagger$ when the driving force for the elementary electron transfer reaction (i.e., precursor to successor) is equal to zero.^{6,11} One may expect $K_s \approx K_p$ for many simple reactions, which would eliminate the second term on the r.h.s. of Equation 1.7. The final term in that equation (a driving force term) is less easily taken into account. Values of E° for cobalt (III) complexes are usually not available. However, by comparing relative rates of similar complexes or the same complex reacting by different mechanisms, one can obtain estimates of $\Delta(\Delta G^\ddagger)^1$ from $\Delta(\Delta G^*)^E$.^{6,10} The use of relative rates accounts for any driving force differences. With adsorption or double layer data, values for K_p can be calculated and the intrinsic barrier to electron transfer evaluated from Equation 1.6 and relative apparent rate constants.¹¹ The intrinsic barrier is expected to be of greatest importance for inner-sphere reactions which can exhibit significant catalysis. A determination of the intrinsic barrier for a variety of reactants could aid in

the understanding of the mechanisms and controlling factors in heterogeneous catalysis.

B. Kinetics at Platinum and Gold Surfaces

The first electrochemical studies were performed near the beginning of the twentieth century and featured primarily platinum and gold electrodes.¹³⁻¹⁵ Work proceeded with electrolysis of metal ions and oxidation of anions at these surfaces until about 1930 when the advantages of working with dropping mercury electrodes became apparent.¹⁶ From that time on studies at solid electrodes ran parallel to those at mercury except for the "special" electrocatalytic area involving organic molecule oxidations at noble metal surfaces.³⁴ The generally less reproducible solid electrode studies at first did not lend themselves to theoretical treatment as well as results obtained at mercury. However, the reliability of solid electrode results has greatly improved as better methods of assuring solution purity and surface pretreatments have been developed.

Recent interest in platinum and gold electrodes can be divided into two major areas: kinetic studies of solution redox systems, and fundamental investigations of electrode surface processes such as oxide formation. The latter area has always been important in studies of electrode kinetics as well as in the "activation" of electrode surfaces by electrochemical pretreatments.^{17,20}

Conway and coworkers have recently studied the oxide formation, reduction and hydrogen evolution processes in some detail for platinum.¹⁷⁻¹⁹ Analogous studies for gold electrodes are reviewed by Woods.²⁰ The potentials of interest in these experiments usually lie outside the potential range appropriate for solution redox kinetics experiments, where currents due to oxide or hydrogen processes only serve to complicate the analysis of kinetics parameters. In order that such interferences may be avoided, all kinetics studies must involve some determination of underlying surface phenomena for the appropriate experimental conditions of pH, electrolyte, potential and surface pretreatment.

Kinetics studies of redox systems are much more prevalent for mercury than for solid electrodes, mainly due to the effort applied to polarographic analysis and the advantages of a continually regenerated clean electrode surface at a dropping mercury electrode.¹⁶ The large body of work involving platinum catalysts in organic molecule oxidation illustrates its ability to assist oxidation through chemical catalysis in addition to electrocatalysis.³⁴ For the most part these reactions proceed by complicated multi-step mechanisms which are not well suited to a fundamental study. A summary of recent kinetics studies at platinum or gold electrodes follows.

Transition metal ions have been investigated by

Oldham and Parry for Pb(II) at Pt²¹ and by Angell and Dickinson for Fe(III)/(II) at Pt and Au.²² In these studies the inner-coordination sphere can be readily altered by complex formation with anionic contaminants in solution.³³ Dissolved gases such as SO₂ have been studied at Au²³ and their oxidations also involve multiple steps of more than one electron per molecule.²³ Probably the most popular redox couple studied at these surfaces (apart from the Co(III) complexes used in this study), is the ferri-ferrocyanide (Fe(CN)₆^{3-/4-}) couple. Kinetics of electron transfer for this couple have been determined by rotating disk voltammetry at Pt and Au.^{22,24,25} The influence of adsorbed cations upon the kinetics at Au has been measured.²⁶ Kuta and Yeager²⁶ found Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ to exhibit more complicated charge transfer than previously suspected, and claim it is an inappropriate couple for checking the properties of new electrodes. In a similar study Müller and Prumke²⁷ encountered mechanistic complications for the Fe(edta)^{-/-2} couple on Pt, which may indicate that iron (III)/(II) couples in general are not the best choice of redox systems.³⁹ The other class of reactants receiving some attention are the inorganic anions such as I⁻,^{28,29} S₂O₈²⁻ and S₄O₆⁴⁻.^{27,30-32} The extremely strong bond formed between iodide and platinum²⁹ or gold is interesting and unusual.¹⁰ The reduction of iodide is also quite interesting, but hardly a model of typical

redox chemistry at these surfaces.²⁹ The $S_2O_8^{2-}$ and $S_4O_6^{2-}$ reduction have been found to be extremely sensitive to the supporting electrolyte cations in much the same manner as $Fe(CN)_6^{3-/4-}$.³¹

The suitability of Co(III) ammine complexes for kinetic studies has been amply demonstrated by Weaver and coworkers.^{6,35-38} Although Cr(III) complexes were also well-suited for mercury experiments,¹ they almost always reduce too slowly (i.e., at potentials too negative) to be used with either platinum or gold electrodes. The Co(III) complexes are recommended by several features:

(i) Co(III) complexes are "substitutionally inert". They have stable, low spin t_{2g}^6 , configurations which allow the inner coordination sphere to be varied independently of the solution composition, and to remain intact until electron transfer occurs.

(ii) They undergo one-electron reductions which are chemically irreversible in aqueous solution due to rapid aquation of the Co(II) reduction product to form $Co(OH_2)_6^{2+}$. This product is not oxidized until a very positive potential is reached (the formal potential of $Co(OH_2)_6^{3+/2+}$ is +1.65 V versus SCE).³⁶ The irreversible nature of the electron transfer reaction makes the determination of electrode kinetics straightforward since no back reaction correction is necessary.³⁸

(iii) The electroreduction proceeds relatively slowly as a consequence of the metal-ligand bond alterations necessary to accommodate the reducing electron in an e_g orbital.

(iv) The Co(III) complexes can be reduced by inner- or outer-sphere mechanisms depending on the ability of coordinated ligands to bond to the electrode surface.^{10,39,40}

(v) Much homogeneous redox information has been accumulated for these complexes, for both inner- and outer-sphere mechanisms.^{3,41}

Other advantages and disadvantages are more dependent upon the type of electrochemical technique employed. The electroreduction of some Co(III) complexes are observable on silver, mercury, platinum and gold electrodes. A comparison with electrode kinetics at mercury surfaces is especially useful.^{10,11,39}

C. Adsorption on Platinum and Gold in Aqueous Solution

As previously noted, most of the adsorption studies at these surfaces have been concerned with O_2 , or H^+ and H_2 .^{17,18,20} The adsorption/deposition of metal ions has been extensively investigated by the Russian school with radiotracer techniques.⁶⁰⁻⁶³ The adsorption of organic molecules and simple inorganic ions has been examined by capacitance measurements² with most success at gold

electrodes.⁴²⁻⁴⁹ The adsorption of alcohols,⁴² pyridine,⁴³ chloride,⁴⁴⁻⁴⁶ iodide,^{46,47} bromide,^{46,48} and perchlorate⁴⁹ on polycrystalline gold was determined from analyses of differential capacitance curves. The adsorption of bromide on gold has also been detected by specular reflectance.^{50,51} Isotherms for the adsorption of chloride, bromide, iodide and H_2PO_4^- were obtained from their effects upon the reversible hydrogen adsorption/desorption cyclic voltammetry peaks.⁵² The adsorption of cesium and sodium cations on platinum was found by capacitance measurements.⁵³ In nearly all of these studies of adsorption some difficulty in obtaining results in agreement with other investigators was noted. Most of these adsorbates are electroinactive at platinum and gold; notable exceptions are iodide and some small molecular weight alcohols which can be electroactive at extreme positive potentials.^{29,42}

Electroactive complex ions have been considerably less studied at platinum and gold. Hubbard and coworkers have examined the adsorption and kinetics of Pt(II)/(IV) complexes at platinum electrodes by thin layer voltammetry.⁵⁴⁻⁵⁷ They found the reduction of Pt(IV) complexes to proceed by halide bridged mechanisms which were sensitive to other adsorbed species. The reduction of the octahedral Pt(IV) goes through an unstable Pt(III) intermediate to produce a square planar Pt(II) complex. The

two-electron reduction or oxidation was used to investigate various olefinic surfactants on platinum and their effect upon the double layer potential.⁵⁷

D. Related Kinetics and Adsorption at Mercury Electrodes

Several aspects of the kinetics of Co(III) ammine complexes have been detailed by Weaver and coworkers at mercury electrodes in aqueous solutions. The rates of reduction and the effect of anion adsorption upon these rates were measured and compared to contemporary double layer theory with excellent agreement.^{35,36} The outer-sphere (non-bridging) complexes such as $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ were found to be sensitive kinetic probes of the mercury-aqueous double layer structure, i.e., their electroreduction rates were systematically altered as adsorbed anions changed the double layer potential at the reaction plane.^{35,36} The mechanism of electroreduction was found to be inner-sphere (ligand-surface bridging) for Co(III) complexes containing N_3^- or NCS^- ligands.^{6,36} The comparison of the heterogeneous electrochemical reduction rates to the corresponding homogeneous reductions with known outer-sphere reducing agents as treated by the Marcus electron transfer theory,^{8,58} was suggested by Weaver as a further means of identifying mechanisms for heterogeneous electron transfer reactions.³⁶ The temperature dependence of the reduction rates for a few

Co(III) ammine complexes allowed the thermodynamic activation parameters to be calculated for mercury electrodes.⁵⁹

Adsorption measurements for the Co(III) complexes at the mercury-aqueous interface are not available, at least partly because the reduction potentials of adsorbed Co(III) complexes are positive enough to make measurements difficult if not impossible.^{10,11} Cr(III) analogs have been used to estimate Co(III) complex adsorption.⁶

The mercury experiments demonstrated the utility and versatility of Co(III) complexes in electron transfer and double layer studies. The amount of double layer data available for mercury experiments exceeds that at solid electrodes. On the other hand the most interesting catalytic behavior occurs on solid electrodes rather than mercury. This compensates for the more difficult and less precise nature of solid electrode experiments. The success encountered with the cobalt (III) amines at mercury makes an extension of these studies to include platinum and gold electrodes desirable. Such studies can yield in situ information about factors controlling catalysis and double layer structure at these electrode surfaces.

CHAPTER II

EXPERIMENTAL

A. General Apparatus

Electrochemical cells employed for most kinetic measurements were of the conventional two-compartment type. The working and reference compartments were separated by an "ultra-fine" glass frit (0.9 to 1.4 μm pore size) specially ordered from Corning, Inc. This frit was found to allow good electrical conductivity while preventing the separate solutions from mixing over the timescale of a typical experiment ($\sim 2-4$ hrs). The cells had working compartments of two general shapes depending on whether they would be used for rotating-disk voltammetry. The regular working compartment was cylindrical with a diameter of ~ 1.5 cm, joined to a 24/40 female joint at the top, and a Teflon stopcock at the bottom. Typical solution volumes were 5 ml. The working compartments for the rotating-disk cells were also cylindrical but had a larger diameter (~ 3 cm) to accommodate a rotating-disk electrode (RDE). The compartment bottom was flat to insure the proper hydrodynamic solution flow. The cell top was constructed to fit a Teflon plug which closely fitted the RDE body. Typical solution volumes

for these cells were 7 to 10 ml.

A special type of cell was made to allow bulk electrolysis by a mercury pool followed by rotating-disk voltammetry without transfer of the electrolyzed solution. The working compartment was similar to that of a RDE cell with a stopcock attached at the bottom to allow the mercury pool to be drained after use. Some of these cells included a platinum wire contact to the mercury pool through the cell wall. In addition to the reference compartment a frit separated the counter electrode from the working compartment. This frit was more porous to minimize cell resistance as much as possible without allowing free exchange of anodic and cathodic electrolysis products.

Reference electrodes were aqueous saturated calomel reference electrodes (SCE). When perchlorate media were used the standard fill solution of saturated KCl was replaced by saturated NaCl to make a sodium calomel electrode (NaSCE). This was necessary to avoid the precipitation of KClO_4 in the reference electrode junction which would give rise to erroneous potentials. The NaSCE differs from the SCE by only -5 mV. Counter electrodes were simply lengths of platinum wire. Occasionally in electrolyses longer lengths of wire were submerged in the counter electrode compartment to give a larger electrode area and allow a higher current flow.

The solid electrodes used (several of both platinum

and gold) were fabricated from high purity (99.999%) polycrystalline metal rods. These rods were enclosed in a cylindrical Teflon sheath and attached to a stainless steel shaft which fit into the electrode rotator. The sheath radius was about 0.6 cm and the exposed electrode disk radii were either 0.200 or 0.125 cm. A model ASR2 rotator (Pine Instruments Company) was employed for the RDE experiments. Rotation speeds up to 10,000 rpm were possible.

B. Solution Preparation

Solid electrodes have proven to be very sensitive to solution impurities, both organic and inorganic. These impurities have a strong tendency to be adsorbed at the surface. Sensitivity to impurities was especially noticeable in RDE experiments where their transport to the surface is assisted by the convection caused by the rotating electrode. Consequently, (and unfortunately) extreme measures were required to obtain pure water and supporting electrolytes for solid electrode experiments.

Water for solution preparation and electrode pretreatments was produced from two sources. The first step in both purifications was distillation of tap water from alkaline KMnO_4 to oxidize most of any organic impurities to O_2 and CO_2 . While this procedure previously had been adequate, many organic contaminants present in more

recent times are steam volatile and hence not removed in this distillation step.⁶⁴ This permanganate feed water was then either pyrodistilled or fed into a quartz sub-boiling still.⁶⁵ In pyrodistillation water vapor in an O_2 stream is passed through a quartz column heated to $750^\circ C$ to cause combustion of the remaining organic impurities. The quartz subboiling still employs infrared heaters to evaporate water which is condensed on a cold finger and collected. The subboiling still is most effective in the removal of inorganic impurities. The purity of the water is evidenced by the shape of the hydrogen evolution and adsorption peaks on platinum as well as by capacitance measurements on mercury.

The supporting electrolytes (primarily $NaClO_4$ and KPF_6) were obtained at the best purity commercially available and recrystallized two or three times from pyrodistilled water. $NaClO_4$ was usually obtained as reagent grade from G. Frederick Smith Chemical Company. KPF_6 came from Pfaltz and Bauer, Inc. as 96% purity. $HClO_4$ (also from G. F. Smith) was used from 70% ACS reagent grade without further purification. HPF_6 was prepared from concentrated $HClO_4$ and KPF_6 (taking advantage of the low solubility of $KClO_4$) and stored frozen to prevent acid catalyzed hydrolysis to form fluoride. The concentration of HPF_6 was determined by titration with standard $NaOH$.

Although $LiClO_4$ is normally employed at mercury

electrodes (the conductance of Li^+ being closest to H^+), NaClO_4 was preferred for solid electrode experiments since it proved to be more easily purified. Concentrations of supporting electrolytes on solid electrodes were generally kept to about 0.1 M to reduce the effect of any residual impurities in these electrolytes.

Solutions for mercury experiments, except for those involving chronocoulometry, used tap distilled water passed through a Milli-Q Reagent-Grade Water System (Millipore Corp.), which proved adequate for the generally less stringent purity requirements at mercury. Chronocoulometry experiments at mercury employed the same water as solid electrodes.

All solutions required deaeration to remove dissolved oxygen before use in electrochemical measurements. This was achieved by bubbling the solutions with a stream of deoxygenated purified nitrogen for 15 minutes after which a stream of nitrogen was passed over the solution during the experiment. Oxygen and residual organic contaminants were removed from the prepurified nitrogen stream by a solid catalyst train. The catalyst (BASF, R3-11 copper based pellets from Chemical Dynamics Corp.) was packed in a glass cylinder (5 x 28 cm, volume $\sim 500 \text{ cm}^3$) heated to $\sim 150^\circ\text{C}$. The gas stream was subsequently passed through a gas scrubbing bottle containing pyrodistilled water to humidify the nitrogen and prevent evaporation of the

working solution by a dry gas.

Supporting electrolyte solutions were usually prepared before each experiment and not stored, in order to reduce the formation of hydrolysis products such as fluoride or chloride.

C. Preparation of Electroactive Complexes

Most of the transition metal complexes used were already available and required only recrystallization as ClO_4^- salts. However, the following complexes were synthesized following literature procedures: $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$,⁶⁶ cis- $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2](\text{ClO}_4)_3$,^{66,67} $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$,⁶⁸ cis- and trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{ClO}_4$,⁶⁹ and cis- $[\text{Co}(\text{en})_2(\text{NCS})_2]\text{ClO}_4$.⁷⁰ Several attempts to synthesize cis- $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{NO}_3$ by Böhm's method⁷¹ and a few modifications failed. $\text{Cr}(\text{OH}_2)_6^{2+}$ was synthesized by electrolysis of 3 mM Cr^{3+} in 0.5 M NaClO_4 + 20 mM HClO_4 over a mercury pool potentiostatted at -1100 mV versus NaSCE for 30 min. Solutions of $\text{Ru}(\text{OH}_2)_6^{3+}$ were prepared by electrolyzing a 4 mM solution of RuCl_3 (Alpha Inorganics) in 0.18 M KPF_6 + 0.02 M HPF_6 over a stirred pool of mercury at -600 mV under an argon atmosphere. Then 20 mM AgPF_6 prepared from Ag_2O and HPF_6 was added to precipitate the liberated chloride as AgCl . The solution was cooled, filtered and electrolyzed at 50 mV to electrodeposit the excess Ag^+ and oxidize the $\text{Ru}(\text{OH}_2)_6^{2+}$ to $\text{Ru}(\text{OH}_2)_6^{3+}$. Both $\text{Cr}_{\text{aq}}^{2+}$ and

$\text{Ru}_{\text{aq}}^{3+}$ were stored in liquid nitrogen prior to use. $\text{V}_{\text{aq}}^{3+}$ was prepared by electrolysis of V(V) from V_2O_5 over mercury at -1100 mV; the $\text{V}_{\text{aq}}^{2+}$ product then being oxidized to $\text{V}_{\text{aq}}^{3+}$ at -300 mV versus SCE. The synthesis of the cobalt (III) ammine complexes incorporating carboxylate and pyridine-related ligands by Visiwanathan Srinivasan is gratefully acknowledged.

The solutions of cobalt (III) complexes were not stored for long periods since the complexes eventually are hydrolyzed. The ClO_4^- salts were kept in a dessicator in the refrigerator to reduce the chances of photolysis and explosion of dry ClO_4^- salts.

D. Electrochemical Techniques

1. Cyclic Voltammetry

A PAR (Princeton Applied Research) 174 or 174A potentiostat was usually employed to generate a triangular-wave potential sweep at a rate of 20 to 500 mV per second during which the current at a stationary electrode was monitored. The current-potential profile was recorded with a Hewlett-Packard HP7045A x-y recorder. The RDE or small area flag electrodes prepared from the appropriate metal foil were used for platinum and gold. A hanging mercury drop electrode (HMDE) (Metrohm Model E410, Brinkman Instrum.) was used for mercury. Cyclic voltammetry

was usually employed prior to rotating disk voltammetry to determine the potential range most suited for the rotating disk experiment. However, the apparent heterogeneous rate constant, k_{app} , can be obtained if necessary by methods described by Nicholson and Shain⁷² (for quasi-reversible) or Galus⁷³ (for totally irreversible) electron transfer reactions.

2. D.C. and Pulse Polarography

The apparatus used for these techniques were usually the same as described for cyclic voltammetry. A dropping mercury electrode (DME) with a mercury flow rate of 1-2 mg s^{-1} and column height of 50 cm was employed. Drop times of 0.5, 1.0 or 2.0 s were obtained by means of a PAR 174/70 mechanical drop timer. The potential was usually scanned at a rate of 2 mV s^{-1} . Kinetic parameters were obtained by Koutecky analysis⁷⁴⁻⁷⁶ (for d.c. polarography) and by equations derived by Oldham and Parry⁴⁴ (for pulse techniques).

3. Fast-Cyclic Voltammetry

For cyclic voltammetry at sweep rates above 500 mV s^{-1} (which is the fastest attainable on a PAR 174), a combination of a fast-potential ramp generator (Michigan State University prototype built by Marty Rabb) and a

PAR 173 potentiostat as used to obtain sweep rates of up to 50 V s^{-1} . The cyclic voltammograms were recorded and photographed from a Tektronix 7623A storage oscilloscope.

4. Rotating-Disk Voltammetry

The large majority of kinetic measurements at platinum and gold were performed using this technique. The reactants typically exhibited irreversible electron-transfer waves³⁶ which considerably simplifies extraction of the kinetic parameters. The voltammetric waves were analyzed by determining the effective reactant concentration just outside the double layer, C_r , from $C_r = C_b[1 - i/i_1]$ where C_b is the bulk reactant concentration, i the measured current in the kinetically-controlled portion of the reduction wave, and i_1 is the limiting current.⁷⁸ The apparent rate constant k_{app}^E at a given electrode potential E was then calculated from $k_{\text{app}}^E = i/FAC_r^m$, where m is the reaction order, and A is the geometrical electrode area. The use of rotation speeds in the range of 100-2,000 rpm allowed values of k_{app} in the range 10^{-4} to $10^{-1} \text{ cm s}^{-1}$ to be determined. Tafel plots³⁶ of $\log k_{\text{app}}$ versus E were typically linear for potentials in the kinetically controlled region of the waves. In most cases the reaction order m was found to be unity by determining the slope of a plot of $\log i$ against $\log C_r$ at a given potential. C_r was varied by changing the rotation speed of the electrode as well as the bulk

concentration C_b . Diffusion coefficients for the reactants could be determined from the limiting current using the Levich equation.⁷⁹ Normal pulse polarography was also attempted at solid electrodes. A range of rotation speeds (200 to 1000 rpm) was found to provide enough replenishment of the reactant by convection to compensate for the depletion of reactant which occurs on a potential step into the reduction wave.²¹ This technique offered the possible advantage of having less current through the solid electrode-solution interface than in a conventional RDE experiment. The same potentiostat-recorder combination as used for cyclic voltammetry was employed for rotating-disk voltammetry. Most kinetics parameters are an average of at least four determinations on different days.

E. Solid Electrode Pretreatments

Undoubtedly one of the primary advantages of the DME as an electrode is that surface effects relating to the history of the electrode surface can usually be ignored; each falling drop renews the electrode surface. This is, of course, not true for solid electrodes. Electrode history, pretreatment and contamination are serious and sometimes severely limiting considerations with solid electrodes.

Since the electrode pretreatment, be it chemical, mechanical or a combination of these, is critical in any kinetics data obtained with these electrodes, a standard

operating procedure must be adopted. Reproducible kinetics results are almost always obtained provided the pretreatment is duplicated each time.⁸⁰ However, the absolute values of any kinetics parameters are expected to depend on the electrode pretreatment.

A rather extensive review of the platinum pretreatments has been made by Gilman⁸¹ which is current to 1965. More recent pretreatments described by Hamelin⁸² and Woods⁸³ are variations on some general principles described in the Gilman review.⁸¹ According to Gilman,⁸¹ pretreatments involve three steps: (1) mechanical polishing, (2) chemical or electrochemical oxidation of the surface, and (3) reduction of the oxidized surface.

Some criterion appropriate to the specific application must be found to judge the effectiveness of the pretreatment. For platinum and gold in this work the hysteresis in the rate of reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ measured by rotating-disk voltammetry served as this criterion. Rotating-disk voltammetry is a steady-state technique so any change (i.e., hysteresis) in forward and reverse scans of a reduction wave indicates a change in the state of the electrode surface. The reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, for poorly understood reasons, appears most sensitive. Such time-dependent "activation" of solid electrodes is common.⁸¹ The deactivation is usually attributed to either adsorption of solution impurities (which is especially rapid at the

highly convective RDE) or to formation of a surface oxide layer.⁸⁰ The pretreatments of platinum and gold described below were found to give the least hysteresis for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$.

1. Platinum Electrodes

The electrode was first mechanically polished with successively finer grades of 1.0, 0.3 and 0.05 μm alpha alumina (Micropolish grades C, B and A, Buehler, Ltd.) on Buehler Microcloth. A two-speed polishing wheel (Buehler 44-1502-160) was employed. Pyrodistilled water was used to wet the polishing cloth and to rinse the electrode.

Mechanical polishing was followed by immersion of the electrode in hot ($\sim 80^\circ\text{C}$) 1:1 nitric acid to oxidize the surface and strip any organic film which may be present.⁸¹ The electrode was then transferred to a cell containing deoxygenated 0.1 M perchloric acid and potentially cycled between +900 mV and -100 mV for about 2,000 cycles. Finally, the electrode was rinsed and transferred to the test solution where the potential was held at +100 mV to strip any remaining oxide. Cycling of the electrode potential was found to give a fairly stable, activated surface. A similar, but not identical, method has been described by Woods.⁸³ A more roughened platinum electrode was obtained by polishing with an abrasive disk (Carbimet, Buehler,

Ltd.) before pretreating.

2. Gold Electrodes

The mechanical polishing was exactly as for platinum. This was followed by immersion in concentrated sulfuric acid for 30 s, rinsing and cycling the potential in 0.1 M perchloric acid between +1000 mV and -200 mV. The potential was held at -100 mV in the test solution to strip residual oxide. An alternative pretreatment⁸² using cyanide to strip the oxide was found to offer no improvement over that described above.

3. Iodide Treated Electrodes

To prepare the iodide treated electrodes the freshly pretreated platinum or gold electrodes were placed in a deoxygenated solution of 5 mM NaI in pyrodistilled water for one minute. The surface was then rinsed with supporting electrolyte and transferred to the test solution. For some experiments, where the adsorbed iodide could possibly be displaced, 5 mM NaI was added to the test solution to maintain an adsorbed iodide layer. Such iodide treatment always improved the reproducibility of kinetics measurements. The iodide layer remained intact at potentials below +700 mV on gold and platinum. Oxidation of the adsorbed iodide to iodate occurs at more positive

potentials.⁸⁴ The iodide was in fact so tenaciously adsorbed that it could only be completely removed by mechanical polishing. Cells used for iodide experiments were reserved for this function alone to avoid iodide contamination of "clean" surfaces. The nature of the adsorbed iodide layer will be discussed in more detail in regard to its effect on electron-transfer rates in Chapter V.

CHAPTER III

DIRECT MEASUREMENT OF REACTANT ADSORPTION

The adsorption of ions at electrode surfaces can be determined by various means. The nonfaradaic methods for measuring adsorption of electroinactive ions have received the most attention, since they seem most appropriate in tests of double layer theory at mercury electrodes.^{2,85} The adsorption of electroactive ions or neutral substances (including transition metal complexes) can be determined by either nonfaradaic or faradaic methods, although the latter is usually more appropriate as the effect of adsorption upon the faradaic process is of fundamental value in electrocatalysis studies.^{6,10}

The nonfaradaic methods include electrocapillary measurements based on a relation of surface tension to the surface excess of adsorbed ions, double layer capacitance measurements,⁴²⁻⁴⁹ radiotracer techniques,⁶⁰⁻⁶³ ellipsometry (which measures the change in refractive index of an adsorbed film by reflection of plane-polarized light), and surface tension measurements at solid electrode surfaces.⁸⁷ Of these techniques double layer capacitance is probably the method of choice for routine adsorption

measurements,^{2,64} although the thermodynamic analyses required to obtain the specifically adsorbed charge can be rather involved.^{88,89} Generally, it is fair to say that these techniques suffer additional complications at solid electrodes relative to mercury, as a result of surface roughness and the nonrenewable surface structure. Reflectance and radiotracer techniques are especially limited by these factors. Uncertainty in the assignment of real electrode area affects all measurements at solid electrodes. The application of double layer capacitance measurements to determine reactant adsorption is confined to potential regions where no faradaic process occurs. This is partly because new species (the oxidation or reduction products) are formed at the electrode surface and can then competitively adsorb with the bulk reactant. With solid electrodes the faradaic current can perturb the double layer by altering the metal surface structure in some irreversible fashion, and hence cause the capacitance to be changed in an uncertain and irreproducible way. Such a situation is proposed at platinum and gold electrodes.^{10,11}

Of more immediate importance in this work is the determination of reactant adsorption at potentials just preceding reactant oxidation or reduction, i.e., the determination of the concentration of the reactant in the precursor state to electron transfer. Under appropriate conditions several faradaic techniques (chronopotentiometry, chronocoulometry, voltammetry, etc.) can yield information

related to reactant adsorption. The faradaic techniques have the advantage of being sensitive only to electroactive adsorbates, presuming that a correction for the nonfaradaic effects of the supporting electrolyte can be made, which is sometimes an unreasonable presumption.

In this study single-step chronocoulometry and fast cyclic voltammetry were employed to determine reactant adsorption at platinum and gold surfaces. A novel method for the measurement of double layer capacitance relying on chronocoulometry is also described and is used to illustrate some problems with single-step chronocoulometry and an advantage of fast cyclic voltammetry at solid electrodes. The succeeding chapter will deal with an indirect method of detecting complex ion adsorption with outer-sphere kinetics probe reactions.

A. Single-step Chronocoulometry

As the name implies, in chronocoulometry the charge is monitored as a function of time after a potential step is applied to the electrode-solution interface. Usually the current is most easily recorded and then integrated numerically, or as in this case electronically, to obtain the charge. In single-step chronocoulometry the potential is held initially at a point where the reactant is adsorbed but not reduced or oxidized (where no faradaic current is present). The potential is then stepped to a point at

which the faradaic reaction is entirely diffusion controlled. The charge in the presence of an adsorbed reactant is then given by⁹⁰

$$q(t) = 2nFAC(Dt)^{1/2}\pi^{-1/2} + q_{dl} + nFA\Gamma' \quad (3.1)$$

where C and D denote reactant concentration and diffusion coefficient, q_{dl} , the charge consumed in charging the electrode-electrolyte solution double layer, A, the "real" electrode area, n, the number of electrons required in the faradaic reaction of one reactant molecule or ion, and Γ' , the apparent reactant surface concentration in moles cm^{-2} . The true surface concentration is related to Γ' by

$$\Gamma = \Gamma' - (1/F)(\Delta q^m)_E \quad (3.2)$$

where Δq^m is the change in the electronic charge density on the electrode produced by the adsorption of the reactant at a constant potential E.^{91,92} The quantity Δq^m has been measured for a few Cr(III) complexes adsorbed at mercury surfaces,^{91,93,94} but the techniques such as charge measurements at an expanding mercury drop are not applicable to solid electrodes. In the absence of Δq^m values, Γ' can serve as an upper limit for the reactant surface concentration.

Equation 3.1 requires a plot of q as a function of

$t^{1/2}$ to be linear with a slope proportional to the reactant concentration and an intercept equal to the sum of the double layer charge and the charge due to the faradaic reaction of the adsorbate, $nFA\Gamma'$. The charges acquired at later times ($>1 \times 10^{-3}$ s) are extrapolated back to $t^{1/2} = 0$. This is necessary to avoid interference by reactant kinetics occurring at less than diffusion controlled rates. The extrapolation to zero time allows the adsorption at the initial potential to be found. The correction for the double layer charge (nonfaradaic charge) can theoretically be obtained as the q versus $t^{1/2}$ intercept for the same potential step in a solution of supporting electrolyte alone. In practice the value of q_{dl} obtained in the absence of the adsorbed reactant provides a good estimate of the value obtained in the presence of the reactant only if the product of the faradaic process is not adsorbed at the final potential.¹¹ An underlying assumption is that the electrode is ideally polarizable. As will be seen in the following discussion, this may not be the case at platinum and gold electrodes.

An on-line chronocoulometric data acquisition and analysis system based on an LSI-11 microcomputer was adapted from its previous incarnation as an on-line pulse polarograph.⁹⁵ The major modification involved the insertion of a variable scale integrator between the potentiostat current output and the analog-to-digital converter

(ADC) input to the computer.⁹⁶ The charge points were acquired at 5×10^{-5} s intervals for a total of 200 points. Electrodes and cells were the same as used in kinetics measurements. Since single-step chronocoulometry had been used quite successfully at mercury electrodes,^{90,91,93,94} this surface was chosen to characterize the on-line system.

1. Adsorption Isotherm for $\text{Cr}(\text{NCS})_6^{3-}$ at Mercury

A determination of the adsorption isotherm for $\text{Cr}(\text{NCS})_6^{3-}$ on mercury was deemed an appropriate test as this would test the sensitivity as well as the accuracy of our system. The supporting electrolyte was 1 M NaClO_4 , and the potential was stepped from -300 to -1100 mV. Concentrations of $\text{Cr}(\text{NCS})_6^{3-}$ in the range 5 to 370 μM were obtained by addition from a concentrated $\text{Cr}(\text{NCS})_6^{3-}$ stock solution. An HMDE with a drop area of 0.032 cm^2 was used for the working electrode. Each new mercury drop was allowed ~30 sec to achieve adsorption equilibrium before the potential step was applied. Figure 2 depicts the q versus $t^{1/2}$ data points for several bulk concentrations of $\text{Cr}(\text{NCS})_6^{3-}$. The adsorbed charge density, q , was found by subtracting the blank (0 μM complex) intercept at $t^{1/2} = 0$ from the observed intercept for a given complex concentration and then dividing by the electrode area. When these charge densities were plotted against the logarithm of the bulk complex concentration the adsorption isotherm represented by triangles

Figure 2. Chronocoulometric data for various $\text{Cr}(\text{NCS})_6^{3-}$ concentrations (μM). The supporting electrolyte was 1M NaClO_4 . The potential was stepped from -300 to -1100 mV at an HMDE (Area= 0.032 cm^2).

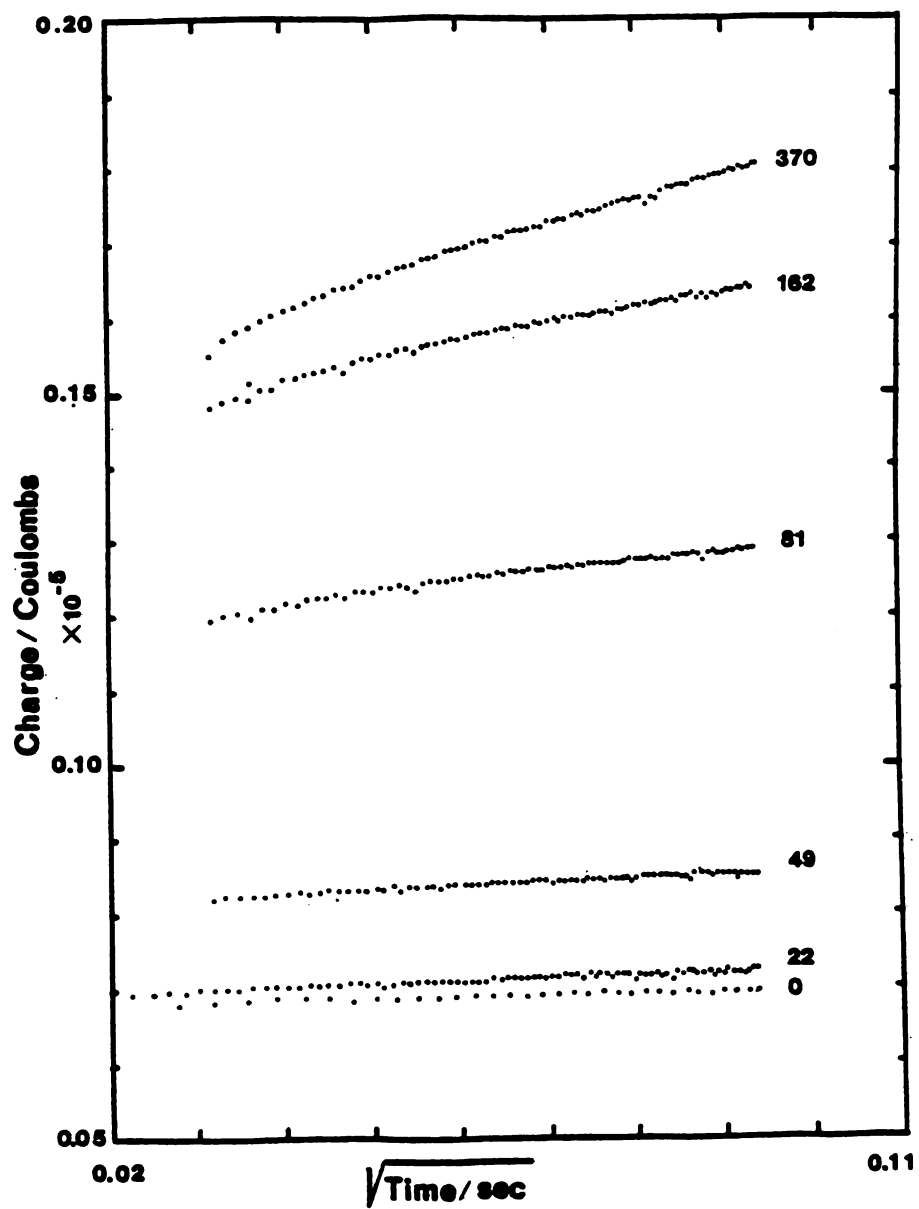


Figure 2

in Figure 3 was obtained. The circles in Figure 3 represent the literature values for FF' reported by Weaver and Anson⁹¹ for the same initial potential. The agreement is fairly good, especially at the extremes of high and low bulk concentrations. The deviations at intermediate concentrations may be a result of errors in measuring such small concentrations. In addition to this result several other chronocoulometry experiments at mercury (related to kinetic probe work) were sufficiently in accord with expectations to inspire some confidence in the system. Unfortunately, application of this technique to solid electrodes (platinum, gold and silver) proved to be considerably less useful than anticipated in the determination of reactant adsorption.^{11,96}

2. Single-step Chronocoulometry at Platinum and Gold

Several of the Co(III) ammine complexes were suspected to be specifically adsorbed at these surfaces.¹⁰ Complexes containing adsorbing ligands such as chloride, bromide and isothiocyanate fall into this category. It was therefore of interest to determine the extent of specific adsorption for these complexes by single-step chronocoulometry. However, the values obtained for the apparent adsorbed charge density, FF' , were always found to be very small ($\leq 2 \mu\text{C cm}^{-2}$) or negative for these complexes at platinum and gold surfaces. Since their specific adsorption is

Figure 3. Adsorption Isotherms for $\text{Cr}(\text{NCS})_6^{3-}$ from chronocoulometric data at an HMDE in 1M NaClO_4 . Circles represent data reported by Weaver and Anson.⁹¹ The line and triangles are the isotherm from data like that in Figure 2.

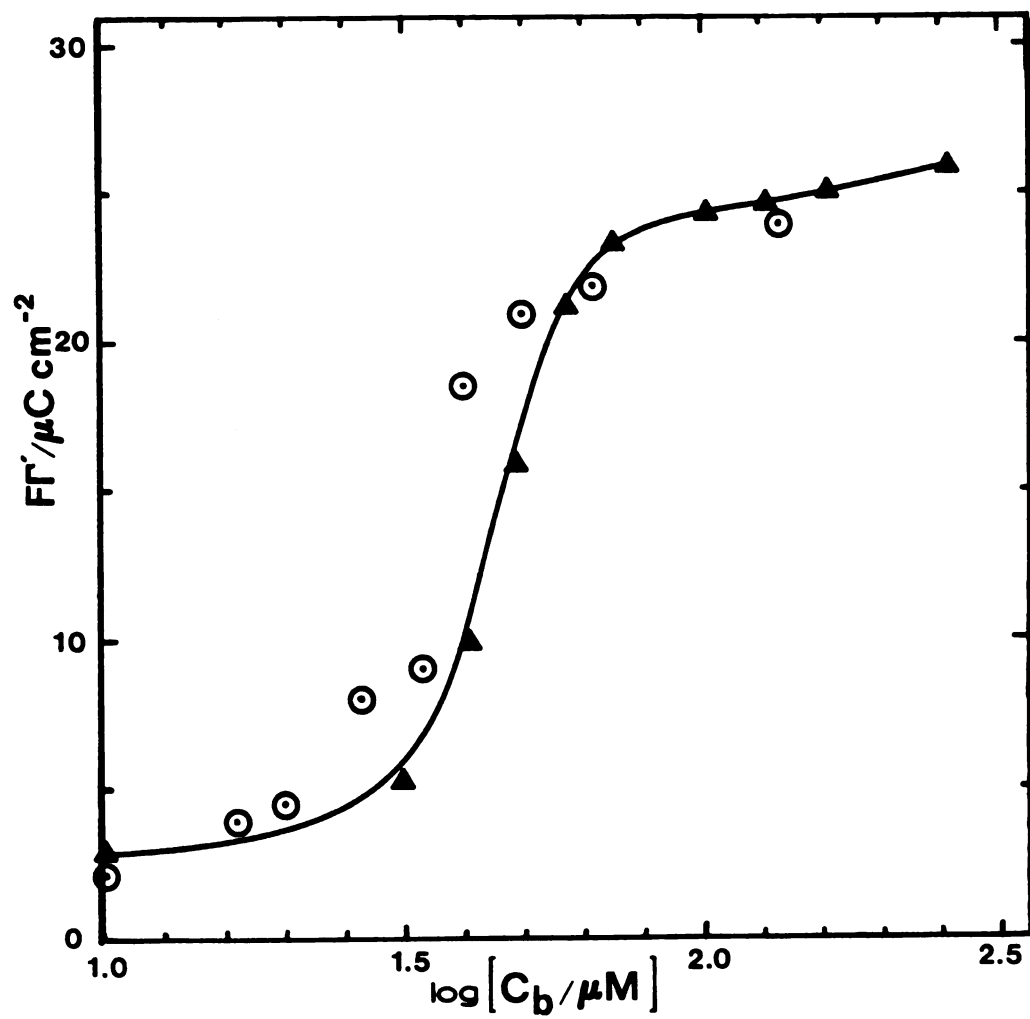


Figure 3

indicated by kinetics measurements¹⁰ and by mercury experiments,⁶ this result was clearly in error. Adsorption isotherm experiments for $\text{Co(en)}_2(\text{NCS})_2^+$, and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ showed large, negative changes in the q versus $t^{1/2}$ intercepts for the first small ($\sim 1 \mu\text{M}$) addition of complex, and further additions had relatively little effect. The addition of thiocyanate anions had a similar effect, which indicated that the adsorption of reduction products (i.e., the ligands formerly bound to Co(III)) was interfering in the analysis.

The strong adsorption of faradaic reaction products at the final potential invalidates the assumption that q_{dl} in the absence of the adsorbed reactant is the same as q_{dl} in the presence of the adsorbed reactant. On mercury electrodes this problem can be avoided by choosing a final potential sufficiently negative of the potential of zero charge (PZC) to assure that anionic reaction products are not adsorbed.^{70,72} Negative surface charges of this magnitude are not accessible with gold, or especially platinum, since hydrogen evolution or proton reduction occurs at potentials only slightly more negative than the potentials of zero charge. The PZC of platinum and gold are the subject of some controversy⁷⁶ but are probably near -50 mV versus SCE for both surfaces in 0.1 M NaClO_4 .^{49,97} The evolution of hydrogen from the surface can indeed cause anions to be desorbed, but it also makes a large contribution

to the chronocoulometric charge. Charges for hydrogen evolution can exceed those for monolayer complex reduction by orders of magnitude.¹⁸⁻²⁰ While it may seem possible to bypass the problem of unequal values for q_{dl} by adding an excess of the free adsorbing anions and thereby minimizing the effect of the anions released by the complex, this is impractical for two reasons. First, the anions will adsorb competitively and are capable of blocking complex adsorption.¹⁰ Secondly, the hydrogen evolution and proton reduction processes are highly sensitive to adsorbed anions which can cause substantial catalysis of proton reduction.¹⁷⁻¹⁹ Since proton reduction consumes so much more charge, it is likely that a very large excess of anions would be needed to make the contribution due to released anions negligible.

The adsorption of released anions can be circumvented by using a complex such as $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$ which is substitutionally inert in both oxidation states.^{98,99} An adsorption isotherm was determined for this complex at a gold electrode. Limiting coverage was apparently reached by $\sim 4 \mu\text{M}$ where Γ' was $4 \mu\text{C cm}^{-2}$. This corresponds to about 20% of monolayer coverage, when in all probability the actual limiting coverage is a monolayer. This result can also be explained by product adsorption, although in this case the product is $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$ rather than free anions.

The basis of the erroneous behavior can be found in electrode capacitance measurements. A description of the effect of anions on the double layer capacitance follows as a digression to explain the technique used to measure the capacitance.

3. Staircase Chronocoulometry

The concept of obtaining the nonfaradaic charge from chronocoulometric intercepts was applied to the determination of capacitance. Software modifications of the single-step chronocoulometry system allowed the electrode capacitance over a one volt range to be found in one or two minutes as opposed to the 15 or 20 minutes needed to perform the same measurement by conventional a.c. bridge techniques. The faster measurements are desirable since solid-metal surfaces are not easily renewable and are known to adsorb solution impurities readily. The technique actually consists of several single-step chronocoulometric experiments performed in succession for small, fixed potential steps with the initial potential being incremented by the step size until the final potential is reached. A provision for a poor data set (a poor q versus $t^{1/2}$ linear regression fit) permitted steps to be repeated at the same initial potential until the designated regression test was met. Figure 4 is a plot of the potential-time function for staircase chronocoulometry. The potential step

Figure 4. Potential-time function for staircase chronocoulometry. E_i , E_f , and E_s are the initial, final and step potentials. t_w , t_p , and t_d are the wait time, pulse time and delay time respectively. Typical values are given in the text.

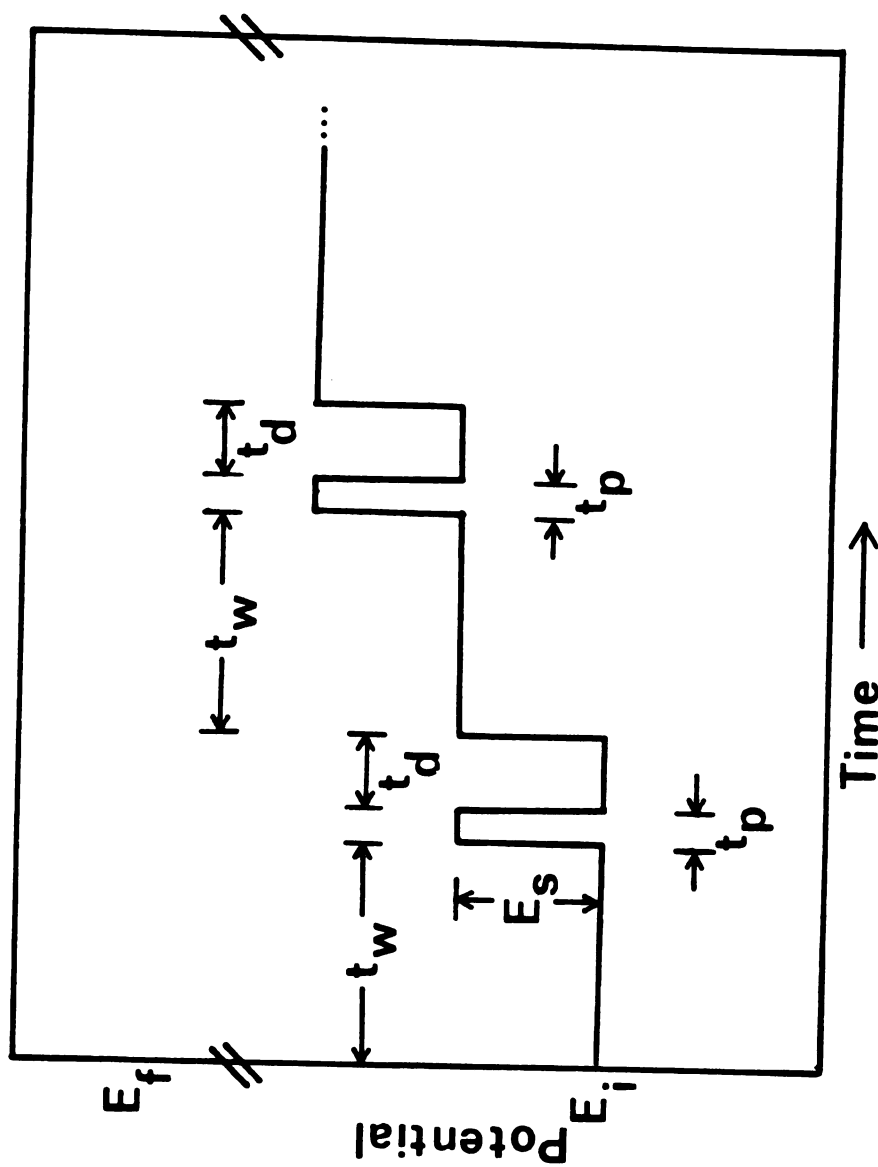


Figure 4

size E_s was usually between 10 and 100 mV. The wait time, pulse time and delay time are denoted by t_w , t_p and t_d , respectively. The sum of these three intervals corresponds to one cycle of the program, i.e., one single-step chronocoulometric determination. The wait time (typically, 5 s) allows the double layer to reach an equilibrium condition at some initial potential. The current is monitored, integrated and stored during the pulse time (typically, 1 ms). The delay time (typically, 1 s) allows time for the linear regression and the test for goodness of fit. An integral capacitance is calculated for each step by dividing the charge intercept q_{dl} by the potential step E_s .

Figure 5 shows the capacitance of a mercury electrode in 0.115 M NaClO_4 obtained by staircase chronocoulometry (triangles) and by a.c. bridge measurements (circles and line)¹⁰⁰ as a function of the electrode potential. The agreement is fairly close except for a slight accentuation of the extrema at more positive potentials. This may be the result of some perchlorate adsorption which is given less equilibration time in the chronocoulometric technique, or more likely it is a consequence of the larger perturbations inherent in staircase chronocoulometry. The two trials with the staircase technique show the capacitance to be reproducibly measured to $\pm 0.3 \mu\text{F cm}^{-2}$ for different mercury drops.

Figure 5. Comparison of capacitance curves from a.c. bridge and staircase chronocoulometry at mercury electrodes. The supporting electrolyte was 0.115 M NaClO_4 . Triangles represent two trials of staircase chronocoulometry with $E_s = +100$ mV. The line and circles are the a.c. bridge result.

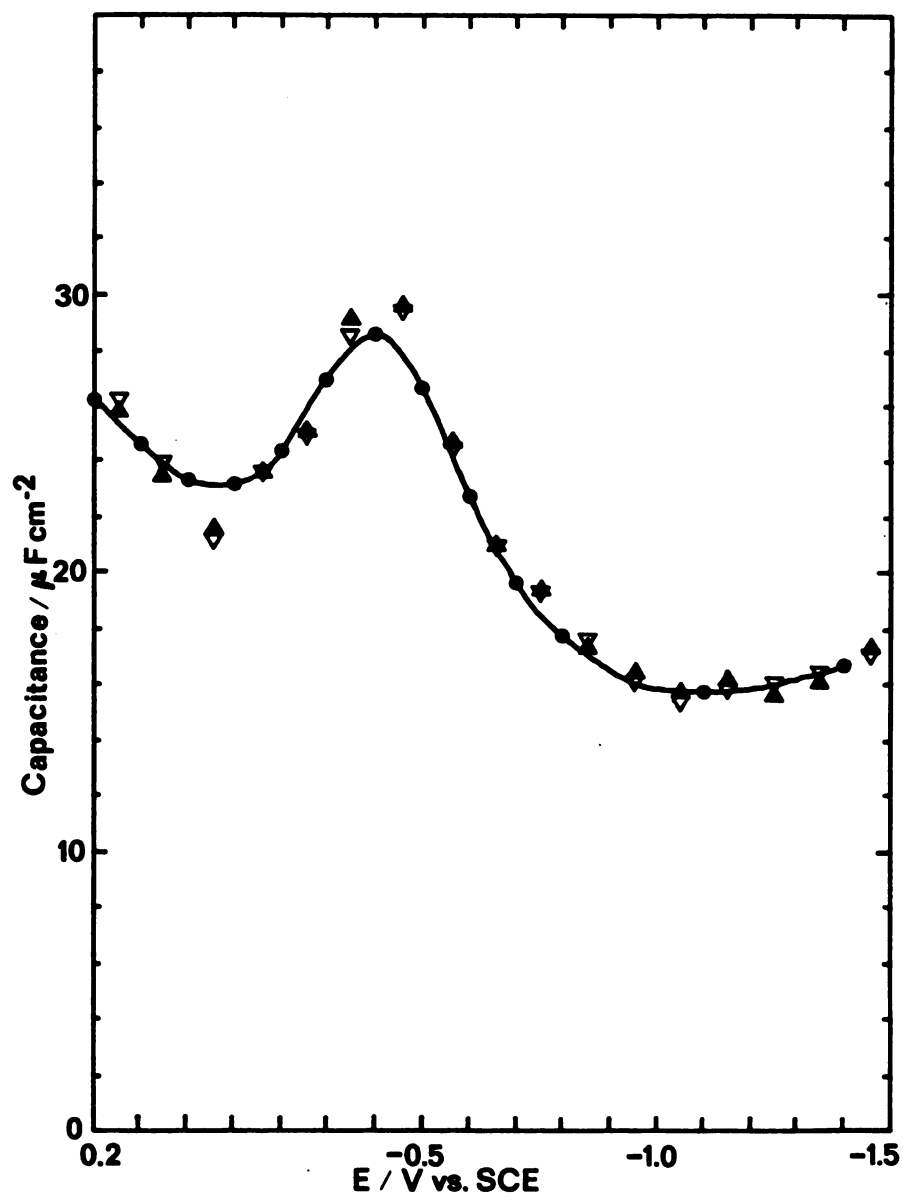


Figure 5

4. Capacitance-related Errors in Single-step Chronocoulometry

The capacitance curve for a gold electrode in 0.5 M NaClO_4 by staircase chronocoulometry is given in Figure 6. The curve clearly has a minimum at -50 mV which is in agreement with published results found with a capacitance bridge.^{42,29} The rapid rise in capacitance at potentials more negative than -250 mV is caused by the adsorption and subsequent reduction of protons.⁴⁹ In order to explain the behavior noted for single-step chronocoulometry the effect of adsorbing anions on the electrode capacitance of gold was investigated. The effect of added thiocyanate anions upon the gold electrode capacitance in 0.5 M NaClO_4 at a constant potential can be seen in Figure 7. This curve shows the apparent change in electrode capacitance at +200 mV for a -500 mV step (typical of single-step chronocoulometry experiments) as a function of thiocyanate concentration. This behavior, the rapid decline and partial recovery, of the capacitance was also noted for chloride and for adsorbing complexes such as $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. Kinetic probe experiments have shown thiocyanate to be strongly adsorbed on platinum and gold surfaces (Chapter IV). The concentration required to reach limiting adsorption on gold was found to be $\sim 4 \mu\text{M}$. A similar decrease in capacitance has been noted by others at platinum,¹⁰¹ gold^{42,46} and

Figure 6. Capacitance curve from staircase chrono-
coulometry at a gold electrode in 0.5 M NaClO₄.

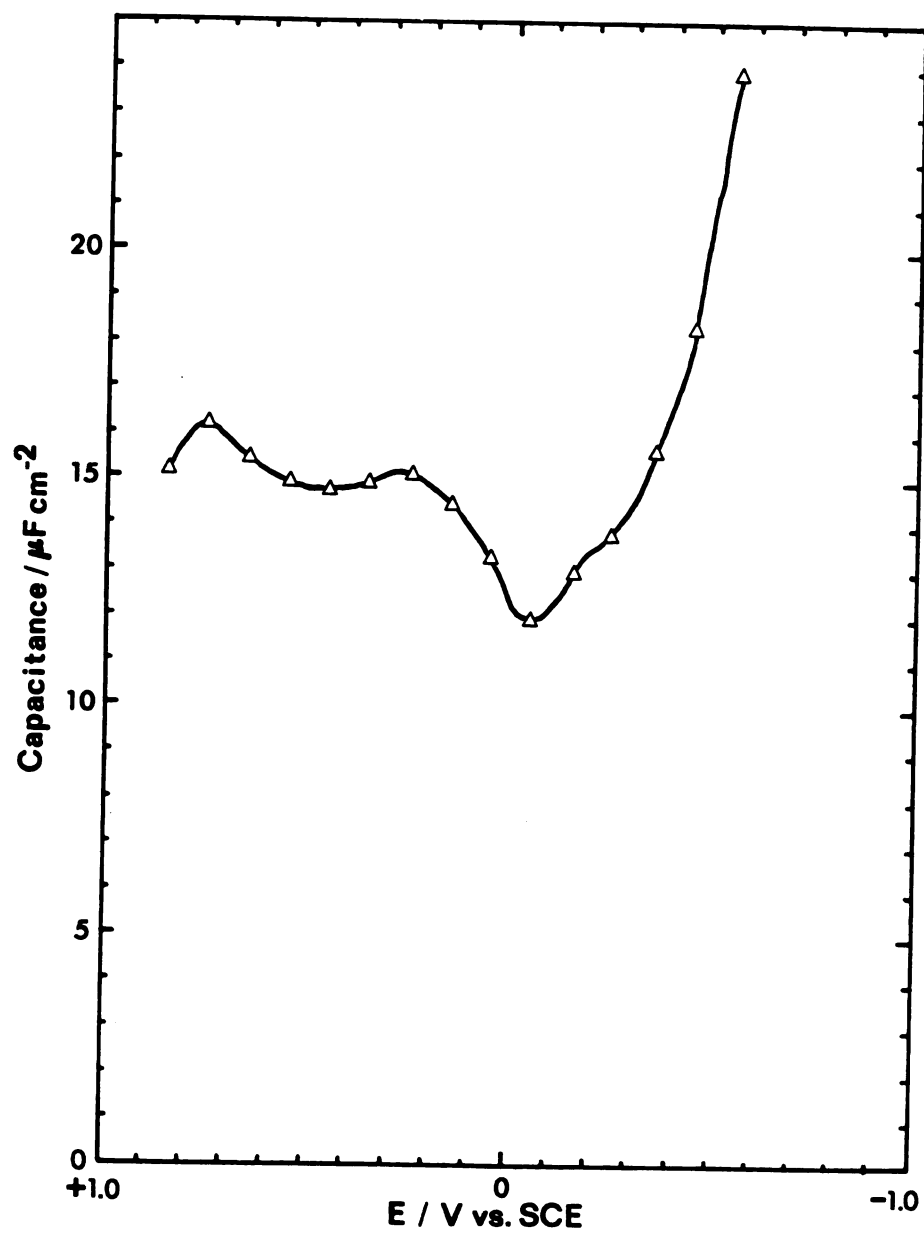


Figure 6

Figure 7. Capacitance of a gold electrode as a function of NCS^- concentration from single-step chronocoulometric data. The potential was stepped from +200 to -300 mV in 0.5 M NaClO_4 .

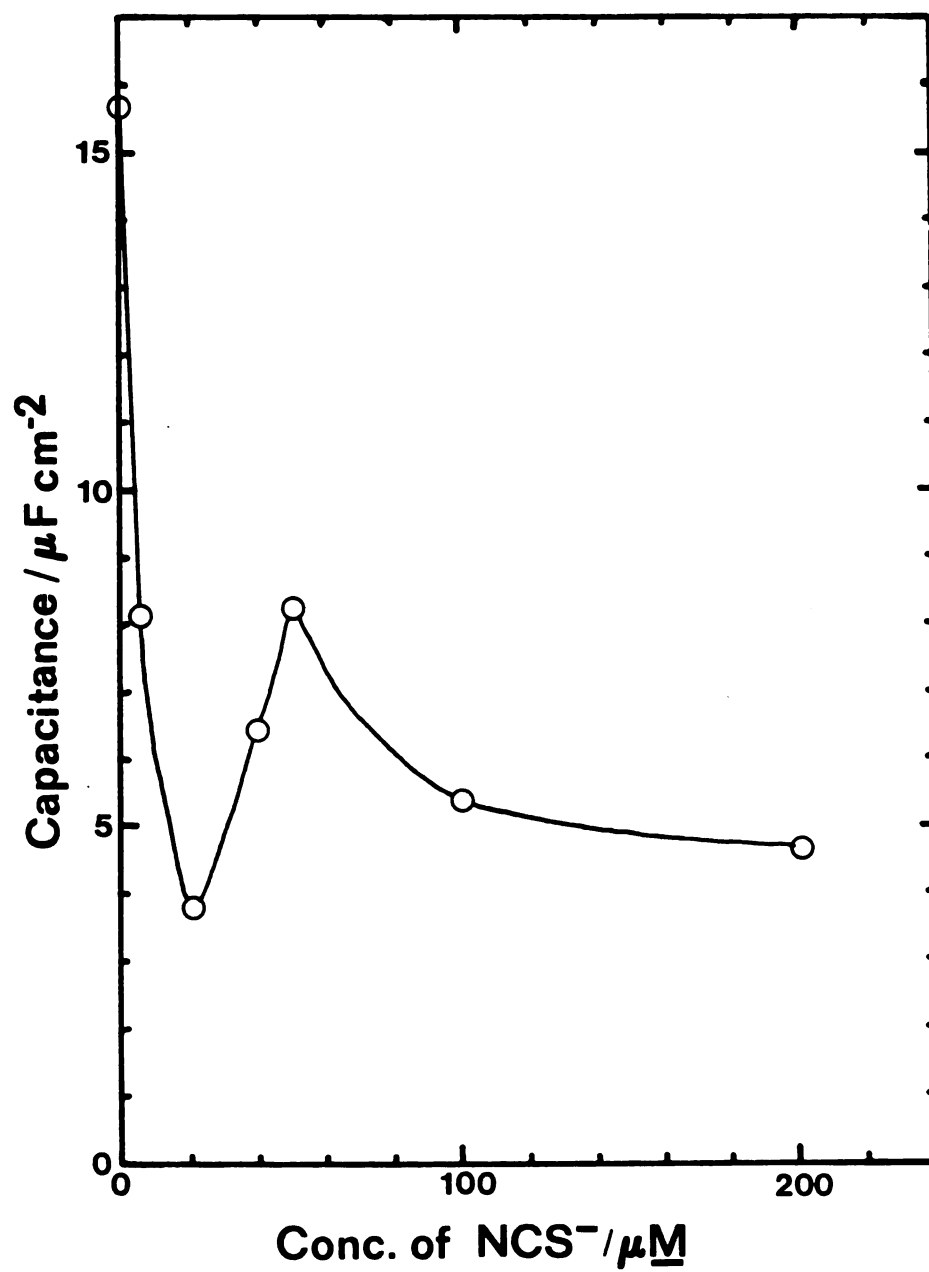


Figure 7

silver.⁹⁶ Capacity measurements are complicated by hydrogen and oxygen adsorption and show strong pH dependencies for platinum and gold.^{101,102} However, the decrease depicted in Figure 7 is at an essentially constant pH and surface roughness. This decrease in nonfaradaic charge is the major source of erroneous chronocoulometric adsorption measurements at platinum, gold and silver electrodes.

Several explanations for this behavior are possible. Adsorbed anions may facilitate reorganization of surface atoms to produce a greater degree of orientation for surface atoms and water dipoles. Water dipoles at the surface are replaced by adsorbed anions which can form covalent bonds to the surface thereby donating some electronic charge to the metal surface.⁹¹ Once monolayer adsorption has been reached further, more ionic layers might be formed which could explain the "recovery" of the capacitance beyond 20 μM thiocyanate in Figure 7. An alternative explanation is that uncharged substances are adsorbed on the supposedly clean surface and then displaced by the adsorbing anions. As much care as possible was used to assure the purity of electrolytes and cleanliness of the cells and electrodes (Chapter II).

B. Determination of Reactant Adsorption by Fast Cyclic Voltammetry

1. Introduction

Linear sweep or cyclic voltammetry is a useful faradaic means of determining reactant or product adsorption and has been extensively employed for this purpose at mercury and solid electrodes.¹⁰³⁻¹⁰⁷ The rate of electron transfer of an adsorbed reactant can also be deduced^{19,107} (see also Chapter V). Probably the most advantageous feature of cyclic voltammetry is the ease by which a correction for nonfaradaic charge can be made, even in the presence of the reaction products.

Nonfaradaic charge arising from the charging of the double layer is simply accounted for by extrapolating the i - E curve from in front of the faradaic peak to a point beyond the faradaic peak and integrating the current above this line to obtain the adsorbed faradaic charge. This "baseline" method is conventionally used to find peak currents.^{108,109} The adsorbed faradaic charge $nF\Gamma_1$ can then yield a value for the initial surface concentration of the reactant Γ_1 . Adsorption of the reactant causes the nonfaradaic current to decrease but also lowers the faradaic peak by the same amount. Hence, this method is much better suited than single-step chronocoulometry to accurately correct for the large changes in nonfaradaic

charge typically encountered at solid electrodes.¹¹

The peak current for irreversible electron transfer for an adsorbed reactant is given by¹⁰⁹

$$i_p^{ad} = \frac{n\alpha n_a F^2 A v \Gamma_1}{2.718 RT} \quad (3.3)$$

where α is the transfer coefficient, n_a , the number of electrons in the rate determining step, v , the potential sweep rate in $V s^{-1}$; the other symbols have been previously defined. Here it is clear that i_p depends on v and that the initial surface concentration could be calculated from i_p^{ad} . The integration of the current to determine Γ_1 is preferred over the use of Equation 3.3 because the shape of the faradaic peak is assumed to be constant in the derivation of Equation 3.3,¹⁰⁹ when in fact the peak may change shape as a result of adsorbate-adsorbate interactions.^{105,107}

The interference by reactant current as a result of reactant diffusion to the surface becomes more important as the bulk reactant concentration increases, especially at slower sweep rates. This becomes evident from the following analysis. The peak current due to diffusion of the reactant undergoing irreversible electron transfer is described by¹⁰⁸

$$i_p^{dif} = 3.01 \times 10^5 n[\alpha n_a]^{1/2} A D^{1/2} C_b v^{1/2} \quad (3.4)$$

at 25°C, where C_b is the bulk reactant concentration in mol cm⁻³. The current for the diffusing reactant is proportional to $v^{1/2}$; so at faster potential sweep rates the current for the adsorbed reactant is favored. This has some practical limitations in that the current due to double layer charging is also proportional to the sweep rate and double layer capacitance¹²¹

$$i_{dl} = C_{dl}v \quad (3.5)$$

The nonfaradaic "background" current becomes an increasingly larger fraction of the measured current at faster sweep rates since the adsorbed, faradaic current is limited by Γ_1 (Equation 3.3), which typically does not exceed the value for monolayer coverage ($\sim 3 \times 10^{-10}$ mol cm⁻²). The effect of uncompensated cell resistance becomes more apparent at faster sweep rates (for our cells at $v > 50$ V s⁻¹). Equation 3.4 also indicates that the diffusion current is proportional to the bulk reactant concentration. This suggests that some optimum conditions of sweep rate and bulk concentration exist for accurate determinations of adsorbed reactant concentrations.

If currents for adsorbed and diffusing reactants are compared directly, i.e., assuming they appear at the same electrode potential, where the interference of diffusion current in the integration of the faradaic peak is greatest, then the optimal ranges of C_b and v can be calculated from

Equations 3.3 and 3.4. If the interference is limited to 5%, then

$$i_p^{\text{dif}} \leq 0.05 i_p^{\text{ad}} \quad (3.6)$$

and from Equations 3.3 and 3.4 with $\alpha = 0.5$, $T = 25^\circ\text{C}$, $n = n_a = 1$ and $D = 7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ Equation 3.6 becomes

$$C_b \leq (63.8 \text{ cm}^{-1} \text{ V}^{-1/2} \text{ s}^{1/2}) \Gamma_1 v^{1/2} \quad (3.7)$$

A plot of $\log C_b$ against the sweep rate is shown in Figure 8 for two surface concentrations of 3×10^{-10} and $5 \times 10^{-11} \text{ mol cm}^{-2}$ corresponding to monolayer coverage and the minimum detection limit, respectively. The area between these lines then indicates the conditions for adsorption determination by linear sweep or cyclic voltammetry. Figure 8 illustrates several interesting aspects. Sweep rates greater than about 2 V s^{-1} are necessary to observe an adsorption peak with C_b in the range 4-25 μM . This range includes reactants with adsorption coefficients, K_p , greater than $2 \times 10^{-3} \text{ cm}$, which can be obtained by very strongly adsorbing complexes at solid electrode surfaces.¹¹ The use of even faster sweep rates up to about 30 V s^{-1} allows less strongly adsorbed reactants to be studied at higher bulk concentrations. Beyond 30 V s^{-1} relatively little is gained in detection limit or maximum bulk

Figure 8. Useful range of experimental parameters for reactant adsorption measurements by fast cyclic voltammetry. The numbers on the curves are the surface concentrations of reactant in mol cm^{-2} . The useful range lies between the curves.

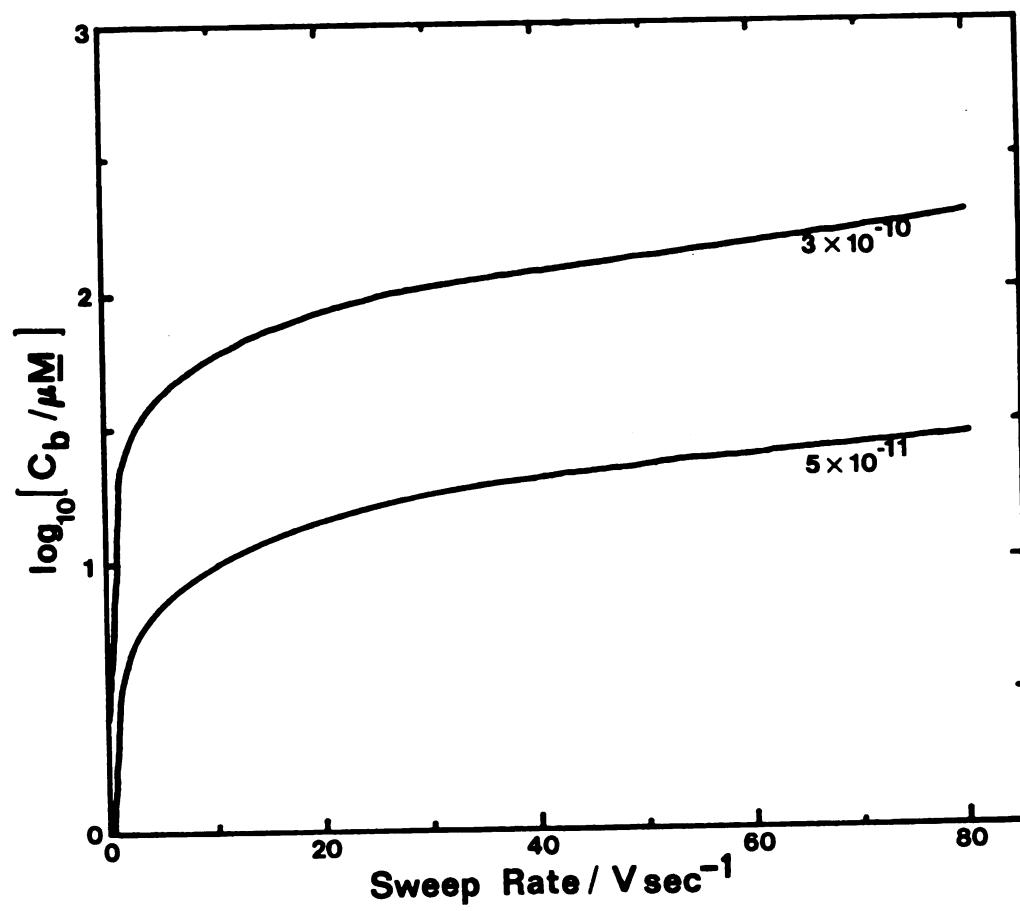


Figure 8

concentration by increasing the sweep rate, while the contributions of double layer charging and uncompensated resistance become increasingly important.¹⁰⁹

The practical ranges are summarized as

$$2 \leq v \leq 30 \quad (\text{V s}^{-1}) \quad (3.8)$$

$$4 \leq C_b \leq 100 \quad (\mu\text{M}) \quad (3.9)$$

for

$$K_p \geq 4.5 \times 10^{-4} \quad (\text{cm}) \quad (3.10)$$

2. Adsorption of Transition Metal Complexes Determined by Fast Cyclic Voltammetry

The results of adsorption measurements by fast cyclic voltammetry are listed in Table I for those complexes for which a reduction peak was observed under the experimental conditions set by Equations 3.8 and 3.9. E_p is the reduction peak potential for the adsorbed reactant. All of the complexes with the exception of $\text{Co}(\text{NH}_3)_5\text{pyrazine}^{3+}$ were found to have reached maximum adsorption at bulk concentrations of $100 \mu\text{M}$ or less. An uncertainty of about $\pm 1 \times 10^{-11} \text{ mol cm}^{-2}$ is present in the Γ_1 values. This uncertainty is primarily a result of errors in the assignment of a "baseline" and in the reading of faradaic currents from photographs of the oscilloscope display. The $\text{Co}(\text{NH}_3)_5\text{pyz}^{3+}$ result is near the detection limit for this

Table I. Fast Cyclic Voltammetry Results at Platinum and Gold.^a

Complex	C _b (μ M)	Electrode	v (V s ⁻¹)	$\Gamma_1 \times 10^{11}$ (mol cm ⁻²)	E _p (mV)
$\underline{c}\text{-Co(en)}_2(\text{NCS})_2^+$	10	Au	10	17.6	-305
	10		20	20.6	-305
	20		10	27.5	-285
	50		20	23.6	-295
	100		20	25.9	-300
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	30	Au	10	18.8	-145
	40		10	19.4	-140
$\text{Co}(\text{NH}_3)_5\text{pyz}^{3+}$	100	Au	10	6.9	0
	100		20	5.8	- 45
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	20	Pt	10	38.5	+ 95
	80		10	40.6	+145
$\text{Co}(\text{NH}_3)_5\text{SO}_4^+$	80	Au	5	22.6	-150
$\text{Cr}(\text{OH}_2)_5\text{Br}^{2+}$	48	Au	2	58.8	+ 70
	48		10	65.5	- 30
	72		10	77.1	- 50
	100		10	78.8	- 50

^aMeasurements were made in 0.1M NaClO₄ + 5 mM HClO₄ at 25°C.^ben = ethylenediamine, pyz = pyrazine.

technique. As expected, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, a known outer-sphere complex,³⁹ gave no peak under these experimental conditions. Other complexes which failed to exhibit adsorption peaks are as follows: for gold; $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, for platinum; $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$, $\text{c-Co}(\text{en})_2(\text{NCS})_2^+$, $\text{Co}(\text{NH}_3)_5\text{pyz}^{3+}$, and $\text{Cr}(\text{OH}_2)_5\text{Br}^{2+}$; for neither surface; $\text{t-Co}(\text{en})_2\text{Cl}_2^+$, $\text{c-Co}(\text{NH}_3)_4\text{Cl}_2^+$, $\text{Co}(\text{NH}_3)_5\text{pyridine}^{3+}$, and $\text{Cr}(\text{OH}_2)_5\text{Cl}^{2+}$. There is other evidence of adsorption for some of these complexes (Chapters IV, V and VI). Reactant adsorption has therefore been found to be a necessary, but not sufficient, condition for the appearance of an adsorption peak.

A qualitative difference between the halide-bridged and thiocyanate-bridged complexes is noted in the much smaller values of limiting surface concentrations for the latter complexes. For a smooth electrode surface (roughness factor of 1.2, see Chapter II) there are approximately 2×10^{-9} moles of surface metal atoms per square centimeter.¹¹⁰ Apportioning surface atoms equally between adsorbed complexes yields 4, 5 and 9 surface atoms for each $\text{Cr}(\text{OH}_2)_5\text{Br}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ adsorbed ion, respectively. Either the thiocyanate and sulfate complexes require more surface area or the types of surface sites needed for adsorption of these two groups of complexes are different. This latter conclusion seems more likely since the morphology of the complexes are not so different. However, the argument for different adsorption sites is

not a strong one from such a small number of results.

The values for Γ_1 in Table I are used later to determine the amount of adsorbed reactant present for inner-sphere electron transfer kinetics measurements (Chapters V and VI). The cyclic voltammograms were also analyzed in order to calculate the rate of electron transfer for the adsorbed reactant. This aspect is discussed in Chapter V.

CHAPTER IV

KINETIC PROBES OF COMPLEX ION ADSORPTION

A. Introduction

The most interesting catalytic behavior is expected for those reactants which are reduced (or oxidized) via inner-sphere mechanisms at solid electrodes. In heterogeneous electron transfer involving transition metal complexes this requires that the reactant be bound to the electrode surface by one or more of its coordinated ligands when electron transfer occurs. Experimental detection of reactant adsorption (or equivalently, of an inner-sphere mechanism) is achieved by various means in this work. This chapter describes the use of outer-sphere "probe" reactions in the detection of Cr(III) complex adsorption at mercury, platinum and gold electrode surfaces.

Outer-sphere reactants are known to exhibit kinetic shifts with changes in surface charge due to various amounts of adsorbed simple anions, such as chloride and thiocyanate, on mercury electrodes.^{35,36,112} The kinetic effects of adsorbed tetra-alkylammonium ions have been studied for vanadium(III)¹¹³ and europium(III)¹¹⁴ reductions. It has generally been found that small amounts of large ions such

as the tetra-alkylammonium ions retard cation reductions as anticipated from a simple electrostatic model.¹¹⁵ At higher adsorbed ion concentrations blocking effects and ion-ion association become more significant.^{113,115} For the adsorption of simple anions on mercury electrodes the observed kinetic shifts in the "probe" reduction rate were shown to be in accordance with the Gouy-Chapman-Stern-Frumkin (GCSF) model of the double layer.^{35,36} This work is an extension of that study to include complex ion adsorption at mercury, platinum and gold electrodes.

The probes chosen were $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. These reactants are known to be reduced via outer-sphere mechanisms at mercury³⁶ and also at platinum and gold electrodes (Chapter V).³⁹ They have been used successfully as probes of anion adsorption at mercury.^{35,36,112} The reduction products ($\text{Co}(\text{OH}_2)_6^{2+}$, F^- , H_2O , and NH_4^+) are not likely to be adsorbed and therefore should not interfere with the probe kinetics. A series of chromium(III) isothiocyanato complexes were chosen as adsorbates to characterize the technique at mercury electrodes. These complexes are substitutionally inert and are reduced at fairly negative potentials on mercury. These two factors are important since they allow these complexes to be adsorbed but not reduced at potentials where the probes are reduced. The adsorption of many chromium(III) isothiocyanato complexes has previously been determined at

mercury by single-step chronocoulometry.^{91,93,94,116}

Chronocoulometry was also used in this study to determine adsorption under the appropriate experimental conditions.

B. Results

The kinetic probe results at a dropping mercury electrode (DME) are summarized in Table II. The reduction kinetics of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ were monitored in the presence and absence of the indicated chromium complex by d.c. polarography. Values for the apparent heterogeneous rate constant, k_{app} , were calculated from the conventional Koutecky analysis,^{74,75} and tabulated as logarithms of the rate shift at constant electrode potential (in this case, -400 mV against the saturated calomel electrode, SCE). All charge densities in Table II were also reported for $E = -400$ mV. The supporting electrolyte was 0.1 M KPF_6 in order to minimize supporting electrolyte ion adsorption.¹¹⁷

The change in the diffuse layer charge density as a consequence of chromium complex ion adsorption was found from^{91,92}

$$-\Delta q^d = z_{\text{Cr}} F \Gamma_{\text{Cr}} + \Delta q^m \quad (4.1)$$

where z_{Cr} refers to the net ionic charge of the chromium complex, and Γ_{Cr} to its surface concentration in mol cm^{-2} . The change in the electrode electronic charge density as

Table II. Kinetic Probe Results at a DME.^a

Adsorbed Complex	Conc. (mM)	Γ_{Cr}^*	Δq^m	$(\frac{\Delta q^m}{\Delta F})^m$	Δq^d	$Co(NH_3)_6^{3+}$ $\Delta \log k_{calc}$	$Co(NH_3)_5F^{2+}$ $\Delta \log k_{calc}$	reduc. $\Delta \log k_{app}$
$Cr(NH_3)_6^{3+}$	0.5	~ 0				0		0
$f-Cr(OH_2)_3(NCS)_3$	0.8	16.3	5.2	0.32 ^b	-5.2	-2.48	-1.49	-0.25
$Cr(NH_3)_5NCS^{2+}$	0.8	2.8	0.3	$\sim 0.1^b$	-5.3	-2.52	-1.52	-0.10
$t-Cr(en)_2(NCS)_2^+$	0.3	3.0	0.3	$\sim 0.1^b$	-3.0	-1.62	-0.98	-0.15
$c-Cr(OH_2)_4(NCS)_2^+$	0.5	8.4	1.3	0.15 ^b	-8.4	-3.38	-2.04	-0.40
$c-Cr(NH_3)_4(NCS)_2^+$	0.5	11.5	1.7	0.15 ^b	-11.5	-4.02	-2.42	-1.00
$c-Cr(en)_2(NCS)_2^+$	0.8	11.7	1.2	0.10 ^b	-11.7	-4.06	-2.45	-1.60
$Cr(NCS)_6^{3-}$	0.5	26.0	10.4	0.40 ^c	+36.4	6.52	3.93	>2.2

* ($\mu C/cm^2$)

^a In 0.1 M KPF₆ at 25°C, drop time = 2 sec., E = -400 mV vs SCE.

^b From Reference 93.

^c From Reference 91.

a result of the bonding of an adsorbate, Δq^m , can be calculated from $F\Gamma_{Cr}$ and $(\Delta q^m/F\Gamma_{Cr})$ coefficients reported by Weaver and Anson.^{91,92} The values of these parameters are also given in Table II. The adsorbed charge density due to the chromium complex, $F\Gamma_{Cr}$, is given by

$$F\Gamma_{Cr} = F\Gamma'_{Cr} - \Delta q^m \quad (4.2)$$

where Γ'_{Cr} is the apparent surface concentration as measured by chronocoulometry.^{91,92} The apparent adsorbed charge density was determined at the same DME and at the same drop time that was used for the kinetics measurements. Substitution of Equation 4.2 into Equation 4.1 yields

$$-\Delta q^d = -z_{Cr}F\Gamma'_{Cr} + (z_{Cr} - 1)\Delta q^m \quad (4.3)$$

Examination of this relationship reveals that Δq^m need not be known for an adsorbate which has a net ionic charge of +1. This could be valuable for solid electrode experiments where Δq^m is usually not known. At $E = -400$ mV, $q^d(0.1 \text{ M KPF}_6) \approx 0$.¹¹⁸ Under these conditions $\Delta q^d = q^d$.

A study by Frank, et al.¹¹⁹ indicated that multiligand-bridged isothiocyanato complex adsorption was slow, but that the monobridged complex adsorption rate was limited only by diffusion of the adsorbate to the electrode surface. The time required to reach limiting adsorption

under diffusion control can be calculated, and is found to be less than 5×10^{-6} s.¹²⁰ As a consequence of this, the adsorption of mono-bridged isothiocyanato complexes is not expected to exhibit any time-dependent adsorption behavior in DME experiments. The much slower adsorption of the multi-bridged complexes could cause substantial deviations in adsorbed charge density measurements on the timescale of DME measurement times (20-50 msec). The adsorption and kinetics measurements were performed at the same drop times. The charge densities obtained at a DME are noted to be less than those reported by Frank¹¹⁹ at an HMDE where long equilibration times are possible.

The change in the potential across the diffuse layer corresponding to the change in charge density can be calculated according to the Gouy-Chapman theory for a symmetrical (+z:-z) electrolyte as¹²¹

$$\Delta\phi_d = \frac{2kT}{ze} \sinh^{-1}(\Delta q^d / (8kT\epsilon\epsilon_0 n)^{1/2}) \quad (4.4)$$

which for dilute aqueous solutions at 25°C simplifies to

$$\Delta\phi_d = (19.5z_e)^{-1} \sinh^{-1}(\Delta q^d / 11.7C^{1/2}) \quad (4.4a)$$

Here z_e is the magnitude of the electrolyte ionic charge (unity for KPF₆), Δq^d is in $\mu C \text{ cm}^{-2}$, and C is the concentration in moles liter⁻¹ of the supporting electrolyte. From

these potential changes the theoretical changes in the electron transfer rate constants may be calculated employing the Frumkin double layer correction:¹²²

$$\Delta \log k_{\text{calc}} = \frac{(\alpha n - z_r)F}{2.303RT} \Delta \phi_d \quad (4.5)$$

where α is the intrinsic transfer coefficient (assumed to be 0.5 for the outer-sphere probes³⁹), n is the number of electrons transferred and z_r is the net ionic charge for the reactant. The experimental values of $\log k_{\text{app}}$ (Table II) were found to be reproducible to within about 0.05 log units by repetitive measurements.

The sensitivity of a kinetic probe reaction for a single adsorbate at various concentrations was determined with $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ as a probe of cis- $\text{Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ adsorption on a DME. The results of this experiment are plotted in Figure 9 as the rate shifts versus adsorbed charge density from chronocoulometry at -200 mV against the NaSCE. An electrode potential of -200 mV was chosen rather than -400 mV (as for the results in Table II) to compensate for the faster reduction kinetics of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ relative to the hexaammine and fluoro complexes. The supporting electrolyte was 98 mM NaClO_4 + 2 mM HClO_4 . The kinetic response is observed to be linear with respect to adsorbed charge density in the measured range corresponding to

Figure 9. Change in the rate constant for reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ as a function of apparent surface charge density of cis- $\text{Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ at a DME. Rate constants were found by d.c. polarography. Adsorbed charge density was determined by single-step chronocoulometry at -200 mV.

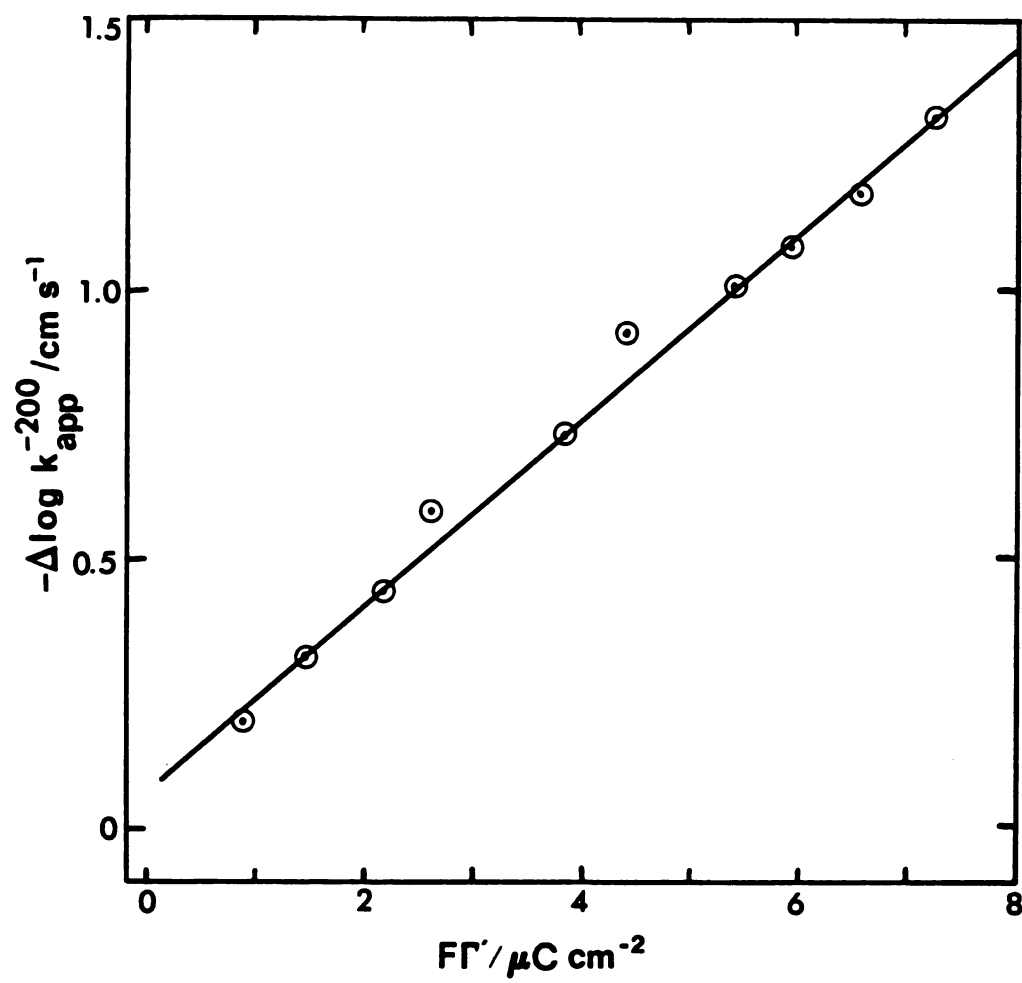


Figure 9

bulk chromium complex concentrations from 8 to 240 μM .

The line is given by $-\Delta \log k_{\text{app}} = 0.172 F \Gamma'_{\text{Cr}} + 0.05$.

Table III contains the rate shifts for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ reduction at 0 mV against the NaSCE for various chromium-(III) complexes at platinum and gold electrodes. The use of $\text{Co}(\text{NH}_3)_6^{3+}$ or $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ as probes on these surfaces is precluded by the proximity of their reduction waves to the negative potential limit. The reduction rate constants were found from rotating-disk voltammetric data for the solid electrodes. The chromium complexes are not reduced on platinum or gold electrodes in the useful potential range, i.e., between the potentials for electrode surface oxidation and hydrogen evolution. Chronocoulometric data would therefore be unobtainable (apart from the difficulties described in Chapter III for chronocoulometry at solid electrodes).

A Gouy-Chapman calculation (employing Equation 4.4a) was performed to determine whether the bulk concentration of nonadsorbed chromium complex would significantly contribute to the double layer potential and thereby affect the observed kinetic shift. For all bulk concentrations employed ($< 1 \text{ mM}$) this contribution was found to be less than one percent of the potential drop across the diffuse layer, $\Delta\phi_d$, and hence essentially negligible in $\Delta \log k_{\text{calc}}$ determinations (Equation 4.5).

Table III. Kinetic Probes of Adsorption at Platinum and Gold: $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ Reduction at 0 mV vs NaSCE.^a

Adsorbed Complex	Conc. (mM)	$\Delta \log k$ Pt	$\Delta \log k$ Au
$\text{Cr}(\text{NH}_3)_6^{3+}$	0.5	+0.10	-0.10
$\text{c-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$	0.5	-0.40	-2.40
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$	0.5	-1.00	-1.60
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	0.5	-1.00	-0.80
$\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$	0.5	~ -3	~ -3

^aIn 0.1 M NaClO_4 + 2 mM HClO_4 at $23 \pm 1^\circ\text{C}$, measured by rotating disk voltammetry.

C. Discussion

The linear response depicted in Figure 9 justifies the experimental method by which rate shifts and adsorbed charges were obtained, especially since cis-Cr(NH₃)₄(NCS)₂⁺ is probably di-bridged and may be expected to be sensitive to any time-dependent adsorption effects.¹¹⁹ If the outer-sphere probes interact with their environment in a purely electrostatic fashion, rate decreases would be expected for cationic probes of cationic adsorbates. The magnitude of the rate decrease is larger for higher cationic adsorption. There is no indication of coverage-related effects other than that for adsorbed charge. Blocking of the reactant by a large adsorbate to force a more distant reaction plane would be one such effect. This would attenuate the kinetic double layer effects at higher adsorbate coverages.¹¹³⁻¹¹⁵ This situation has been noted by others¹¹³⁻¹¹⁵ for tetra-alkylammonium ion adsorption, but is not observed here for the chromium complexes. Blocking effects may, however, occur at higher adsorbate concentrations than were obtained in this experiment.

The experimental values for the rate shifts reported in Table II are at least qualitatively correct in that cationic adsorbates cause rate decreases, and the anionic adsorbate Cr(NCS)₆³⁻ causes a rate increase. The rate enhancement by Cr(NCS)₆³⁻ is large enough to shift the probe reductions into the mercury dissolution(positive potential)

limit, and could only be evaluated as a minimum value. The actual rate shift would probably not be much larger in any case, since ion pairing would act to decrease the enhancement. As expected from the double layer calculations the presence of $0.5 \text{ mM } \text{Cr}(\text{NH}_3)_6^{3+}$, which is not adsorbed, does not measurably influence the probe reduction rates. The neutral adsorbate, fac- $\text{Cr}(\text{OH}_2)_3(\text{NCS})_3$ was adsorbed, and gave a value of $\text{FF}'_{\text{Cr}} = 16.3 \text{ } \mu\text{C cm}^{-2}$, but because z_{Cr} is zero, $\Delta q^{\text{d}} = \Delta q^{\text{m}}$ (from Equation 4.3).

The experimental rate shifts seem to be only tenuously related to the adsorbate net ionic charge z_{Cr} . This is apparent in the large discrepancy between observed and calculated values for $\Delta \log k$. In every case the calculated values for the rate shifts are found to be of much greater magnitude than those found experimentally. There may be several reasons for this discrepancy. It is probably naive to ignore the internal charge distributions of the chromium adsorbates, especially since the chromium complexes must extend about $6.8 \text{ } \text{\AA}$ into the solution from the electrode surface.¹²³ The diffuse layer itself is approximately $10 \text{ } \text{\AA}$ thick in 0.1 M electrolyte. The reaction plane of the outer-sphere probes probably lies within or near the $6.8 \text{ } \text{\AA}$ distance, and they would experience a very different electrostatic environment than a uniform layer of adsorbed charge. Such discrete charge effects are difficult to isolate or treat theoretically. Another possible cause

of the discrepancy is that the Gouy-Chapman theory may be inadequate when dealing with relatively large adsorbed charges.^{2,121}

The plane of closest approach could be more distant in the presence of the adsorbed complex. The extra distance required to diminish the double layer effect to the point where experimental and calculated rate shifts agree can be found from¹²⁴

$$x = - \frac{1}{\kappa_D} \ln \left(\frac{\tanh(z_e f \phi_{app}/4)}{\tanh(z_e f \phi_d/4)} \right) \quad (4.6)$$

where κ_D , the Debye-Huckel reciprocal length is

$$\kappa_D = (8\pi z_e^2 F f C / \epsilon)^{1/2} = (3.29 \times 10^7) z_e C^{1/2} \quad (4.7)$$

for dilute solutions at 25°C. The notations are: $f = F/RT$, ϕ_{app} and ϕ_d are the apparent and calculated (from Equation 4.4a) diffuse layer potentials, ϵ is the bulk dielectric constant, and C is the bulk electrolyte concentration in mol l⁻¹. $\Delta\phi_{app}$ is obtained from $\Delta \log k_{app}$ values and Equation 4.5. $\Delta\phi_d$ and $\Delta\phi_{app}$ give ϕ_d and ϕ_{app} respectively when the contribution to the potential due to the supporting electrolyte is zero. The distance x that the reaction plane would need to move for the various chromium complexes with $\text{Co}(\text{NH}_3)_6^{3+}$ as the outer-sphere probe are

listed in Table IV. A glance at these x values indicates that the discrepancy between theory and experiment cannot be entirely due to a more distant reaction plane, as the distances required would put the outer-sphere reactant an unreasonably long distance beyond the diffuse layer. The actual cause or causes are likely to be a good deal more complex than suggested here and actually are not the primary goal of this study. Several striking and useful results were nevertheless observed.

It is clear that the kinetic probes actually can detect the adsorption of complex ions, and thereby aid in the identification of inner-sphere electron transfer mechanisms. For isothiocyanato complexes this method is most satisfactory for those complexes capable of forming multiple ligand-surface bonds, and marginally successful for the mono-bridged complexes. As indicated by Figure 9 the probe is sensitive to very small amounts ($\sim 1 \mu\text{C cm}^{-2}$) of adsorbed charge for the di-bridged cis- $\text{Cr}(\text{NH}_3)_4(\text{NCS})_2^+$ complex. Even though the magnitudes of the probe kinetics shifts differ for different adsorbed complexes present at nearly the same amount of adsorbed charge; the shifts for each individual adsorbate are probably simply related to its adsorbed charge density. If this is the case the technique could be made more quantitative with calibration plots similar to Figure 9.

Table III shows that the results at platinum and gold

Table IV. Apparent Change in the Reaction Plane of $\text{Co}(\text{NH}_3)_6^{3+}$.

Adsorbed Complex	ϕ_d^a (mV)	ϕ_{app}^b (mV)	x^c (Å)
$\underline{t}\text{-Cr}(\text{OH}_2)_3(\text{NCS})_3$	58	18	10
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$	59	4	24
$\underline{t}\text{-Cr}(\text{en})_2(\text{NCS})_2^+$	38	2	28
$\underline{c}\text{-Cr}(\text{OH}_2)_4(\text{NCS})_2^+$	79	15	14
$\underline{c}\text{-Cr}(\text{NH}_3)_4(\text{NCS})_2^+$	94	31	8.7
$\underline{c}\text{-Cr}(\text{en})_2(\text{NCS})_2^+$	95	47	5.1
$\text{Cr}(\text{NCS})_6^{3-}$	-153	-52	6.3

^aFrom Equation (4.4a).

^bFrom Equation (4.5) and $\Delta \log k_{\text{app}}$ values.

^cFrom Equation (4.6).

electrodes are about the same as at mercury. The $\text{Cr}(\text{NH}_3)_6^{3+}$ complex is again employed to gauge the response of the probe to a nonadsorbed species. The observed probe response of ± 0.1 log units is probably not significant in light of the less reproducible rate measurements at solid electrodes (relative standard deviations for k_{app} are 20-50% for platinum and gold by rotating disk voltammetry). The considerably larger kinetics shifts observed for the remaining chromium complexes in Table III are quite significant, and in most cases larger than obtained at mercury electrodes. In fact, the reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ is almost completely suppressed by the adsorption of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$. The lesser response for mono-bridged complex adsorption seen for mercury is not evident for platinum and gold electrodes. The larger magnitude of response on the solid electrodes may be due in part to the replacement of adsorbed supporting electrolyte anions by the adsorbing chromium cations. The contribution to the diffuse layer potential for 0.1 M NaClO_4 can be estimated to be about -60 mV on platinum and gold at $E = 0$. (Estimates of outer-sphere reaction plane potentials are given in Table VI, Chapter V.) This potential corresponds to $\sim 5 \mu\text{C cm}^{-2}$ of adsorbed charge. The complete loss of adsorbed anions would cause a rate shift in the probe reaction of ~ 2.6 log units (from Equation 4.5). This is sufficient to account for even the largest shifts obtained at solid electrodes. The replacement of adsorbed

anions is as valid a criterion for complex adsorption as the electrostatic repulsion between the adsorbate and the probe complexes. The kinetic shift actually becomes more sensitive to cationic adsorption under these conditions. (The probe experiences the extreme electrostatic environments of attraction by anions and repulsion by cations as the adsorption of the cationic complex increases.) One may conclude from the results listed in Table III that the isothiocyanato, chloro and bromo chromium complexes are adsorbed on platinum and gold electrode surfaces. If the adsorption is "ligand-induced", then the cobalt complexes containing these anionic ligands should also be adsorbed. Evidence supporting this assertion is presented in Chapters III and V.

The kinetic probe technique, although beset with complicating nuances, is shown to be useful in the detection of complex ion adsorption and offers some advantages over other methods. It employs simple steady-state electrochemical techniques which do not require the reduction or oxidation of the adsorbed complex. The release of adsorbing ligands is avoided. Outer-sphere probes with a range of reduction rates could be used to detect adsorption at different electrode potentials. Perhaps further investigation could determine the effects of adsorbate morphology and discreteness-of-charge on the outer-sphere probes.

CHAPTER V

KINETICS OF ELECTRON TRANSFER AT PLATINUM AND GOLD ELECTRODES

A. Introduction

This chapter presents the kinetics results for several electron transfer reactions at platinum and gold electrodes in aqueous solutions. Most of these results are for the one electron reductions of cobalt(III) ammine complexes containing aquo, halide or pseudo-halide ligands. The modification of the electrode surfaces by the adsorption of iodide was found to be useful in identifying reaction mechanisms. Additional evidence for inner-sphere mechanisms was extracted from apparent reaction orders obtained by rotating disk voltammetry. The reactant adsorption data described in the preceding chapters are used to separate the overall electron transfer rate into intrinsic and thermodynamic contributions.^{10,11} The reduction rates of simple outer-sphere reactants are employed to probe the double layer structure at these surfaces and to determine the effect of electrode material upon heterogeneous electron transfer.³⁹ Taking all of these aspects of the kinetics into account allows one to determine the factors

important for heterogeneous electrocatalysis.

B. Reaction Orders

As was mentioned earlier (Chapter II) the reaction order for the overall electron transfer reaction (Equation 1.1) at a constant electrode potential and solution composition can be determined by rotating disk voltammetry. The reaction order m is given by

$$m_{E,u} = \left(\frac{\partial \log i}{\partial \log C_r} \right)_{E,u} \quad (5.1)$$

A value for m can be calculated by measuring the current density at a constant electrode potential for various reactant concentrations. The reactant concentration near the surface, $C_r (=C_b(1 - i/i_{lim}))$, can be varied by either altering the RDE rotation speed or by changing the reactant bulk concentration C_b . If the latter method is used, care must be taken to insure that the changes in reactant concentration do not significantly affect the double layer composition. This is easily accomplished by keeping the reactant concentrations in a relatively low range, $\sim 10^{-3}$ M, in an excess of supporting electrolyte $\sim 10^{-1}$ M. The value of $\log C_r$ changed by only ~ 0.3 as the rotation speed was varied from 300 to 2500 rpm. This is not large enough to give an accurate value for the reaction order. Consequently,

C_b was also altered from 0.5 to 3 mM, extending the range of $\log C_r$ by ~ 0.8 log units. Figure 10 illustrates a reaction order plot for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ on platinum at an electrode potential of +250 mV. The reaction order obtained from the slope of the linear regression line was equal to 0.35 ± 0.05 .

A summary of the reaction order results is presented in Table V for a few complexes at both clean and iodide-treated platinum and gold surfaces. The precision of the reaction orders reported in Table V is ± 0.05 or better, as determined from the standard deviations of linear regression slopes. The reaction orders are for potentials near the kinetic-controlled reduction of the complex. All of the values (except $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ on Pt and Au) were independent of potential within a range of about 100 mV of the indicated potential. A lower reaction order at more positive potentials was obtained for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. The complexes, $\underline{c}\text{-Co}(\text{en})_2(\text{NCS})_2^+$ and $\underline{t}\text{-Co}(\text{en})_2\text{Cl}_2^+$, gave such scattered reaction order plots for iodide-treated platinum and gold that no reasonable linear regression fit could be made. Reaction orders for outer-sphere complexes such as $\text{Co}(\text{NH}_3)_6^{3+}$ were typically very near unity, as expected since such reactants should obey Henry's Law.¹²⁵ Such is the case for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ in Table V at both clean and iodide-treated surfaces. The iodide-treated surfaces lend credence to the assignment of "forced outer-sphere" mechanisms.

Figure 10. Reaction order plot for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ reduction on platinum in 0.1 M NaClO_4 at +400 mV. Reactant bulk concentrations were 0.5, 1, and 3 mM for circles, triangles and squares, respectively. Points are labeled with the rotation speed in rpm.

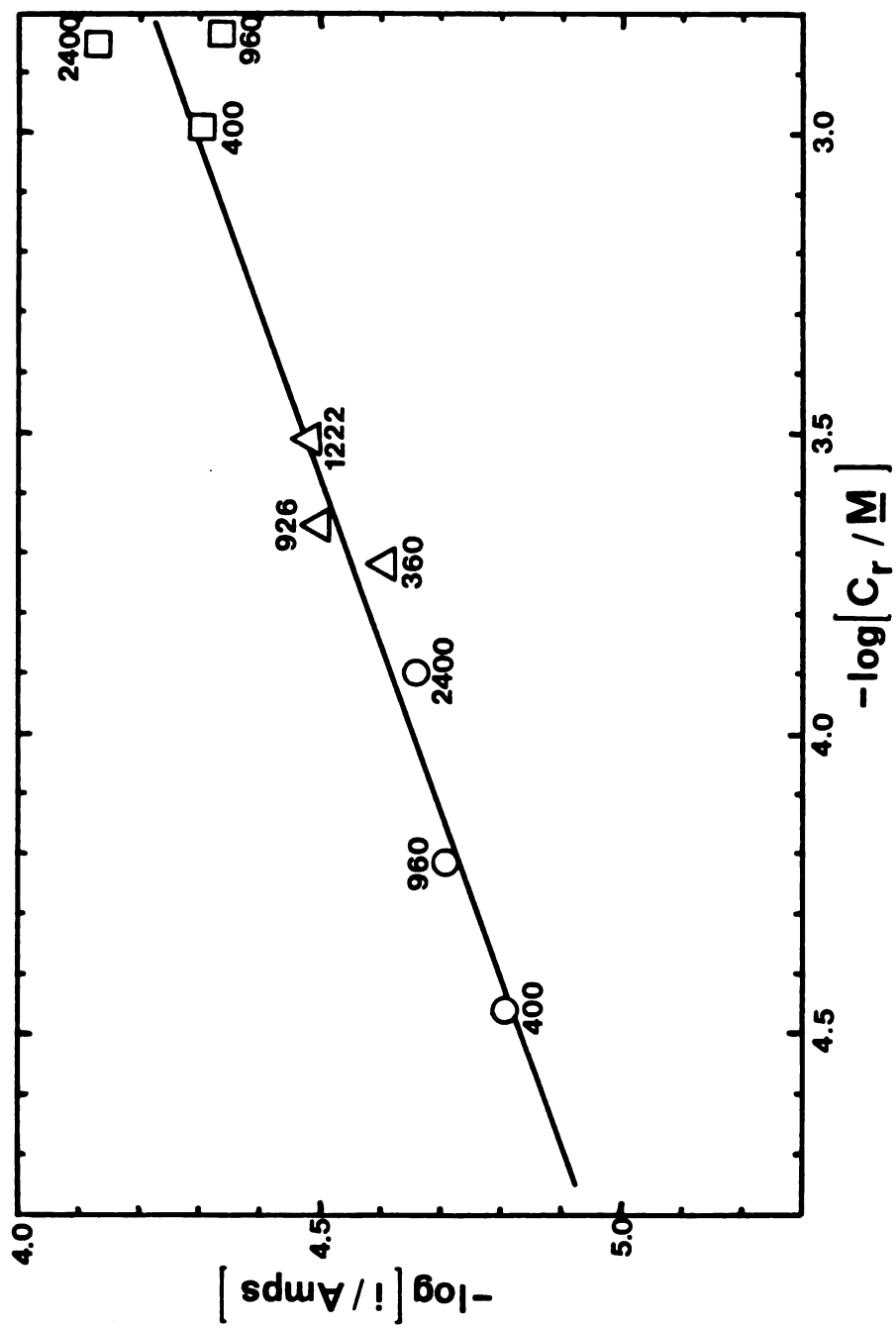


Figure 10

Table V. Reaction Orders.

Complex	Pt	Reaction Order		
		Pt(I) ^c	Au	Au(I) ^c
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	0.35 ^a	1.00	0.10 ^a	1.05
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	0.40 ^a	0.85	0.40 ^a	1.00
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	0.40 ^c	0.90	0.35 ^c	0.85
$\underline{\text{c}}\text{-Co}(\text{en})_2(\text{NCS})_2^+$	0.50 ^c		0.25 ^c	
$\underline{\text{t}}\text{-Co}(\text{en})_2\text{Cl}_2^+$	0.50 ^b		0.30 ^b	
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$	1.05 ^c	0.90	0.90 ^c	0.95

^aAt +400 mV.^bAt +250 mV.^cAt 0 mV, (I) denotes an iodide-treated surface.

The conclusion is that the iodide, present as a monolayer, blocks all surface adsorption sites for otherwise inner-sphere reactants.¹⁰ The evidence supporting the adsorption of iodide to a monolayer, and its likely effects upon electrode kinetics is discussed in more detail later in this chapter.

The observation of reaction orders significantly smaller than unity on the clean electrode surfaces may be taken as an indication of a strongly adsorbed intermediate in the overall electron transfer process. This conclusion is supported by the following analysis.

For the overall process given in Equation 1.1 the most simple mechanism involving an adsorbed intermediate is



where M denotes a metal surface adsorption site. OM and RM represent the adsorbed oxidized and reduced species. If 5.3 is rate limiting, and k_2 is small compared to K_1 then at a constant electrode potential

$$i \propto k_2 C_{OM} \quad (5.5)$$

and

$$C_{OM} = K_1 C_O C_M \quad (5.6)$$

The concentration of free metal sites can be found from

$$C_M = C_M^{\text{tot}} - C_{OM} \quad (5.7)$$

where C_M^{tot} represents the total concentration of surface sites. Substituting for C_{OM} in Equation 5.7 from Equation 5.6 gives

$$C_M = C_M^{\text{tot}} / (1 + K_1 C_O) \quad (5.8)$$

Combining Equations 5.5, 5.6 and 5.8 gives

$$i \propto k_2 K_1 C_M^{\text{tot}} C_O (1 + K_1 C_O)^{-1} . \quad (5.9)$$

so,

$$\log i \propto \log (k_2 K_1 C_M^{\text{tot}}) + \log C_O - \log (1 + K_1 C_O) \quad (5.10)$$

In order to differentiate Equation 5.10 with respect to $\log C_O$ it is useful to expand the last term as

$$\log (1 + K_1 C_O) = K_1 C_O - \frac{(K_1 C_O)^2}{2} + \frac{(K_1 C_O)^3}{3} \dots \quad (5.11)$$

which is valid for $-1 < K_1 C_0 \leq 1$, then 5.10 can be written as

$$\begin{aligned} \log i \approx \log (\text{const}) + \log C_0 - K_1 \exp(\log C_0) \\ + \frac{1}{2} K_1^2 \exp(\log C_0^2) - \dots \end{aligned} \quad (5.12)$$

Now Equation 5.12 is easily differentiated by $\log C_0$ to yield

$$\left(\frac{\partial \log i}{\partial \log C_0} \right)_{E,\mu} = m_{E,\mu} = 1 - K_1 C_0 + (K_1 C_0)^2 - \dots \quad (5.13)$$

In terms of surface coverages of 0,

$$K_1 C_0 = \left(\frac{\theta}{1-\theta} \right) \quad (5.14)$$

To meet the requirement for the log expansion, the surface coverage is limited to the range $0 \leq \theta \leq 0.5$.

Substitution of Equation 5.14 into 5.13 yields the interesting result of

$$m_{E,\mu} \approx 1 - \theta \quad (0 \leq \theta \leq 0.5) \quad (5.15)$$

Thus in the absence of adsorbate interactions, under steady-state conditions, at a constant electrode potential, the overall reaction order is simply and directly related

to the surface coverage of the adsorbed intermediate by Equation 5.15. Adsorbate-adsorbate interactions are neglected. Such interaction can be either attractive or repulsive.^{105,107} Since these interactions are not known at platinum or gold, their inclusion into the analysis would have little purpose. Equation 5.15 is not meant to show more than the fact that an adsorbed intermediate can lead to lower overall reaction orders. While reactant adsorption is certainly not the sole possible cause of depressed reaction orders, it seems a very probable one for the cobalt(III) ammine complexes which offer few mechanistic tricks.

Because they exhibit reaction orders of 0.5 or lower (Table V), the complexes $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (where $\text{X} = \text{Br}^-$, Cl^- , NCS^-), $\underline{\text{t}}\text{-Co}(\text{en})_2\text{Cl}_2^+$ and $\underline{\text{c}}\text{-Co}(\text{en})_2(\text{NCS})_2^+$ are probably adsorbed to half coverage or greater on clean platinum and gold surfaces. By the same reasoning an inner-sphere mechanism appears to be blocked by iodide on the iodide-treated surfaces, where reaction orders near unity are observed.

C. Outer-Sphere Kinetics of Co(III) Ammines

In heterogeneous outer-sphere electron transfer the reactant is expected to interact only weakly with the electrode surface.^{35,39,125} The plane of reaction is by definition at least one solvent molecule diameter plus a

reactant radius from the surface.³⁵ This does not mean that the kinetics for electron transfer are insensitive to the electrode condition. On the contrary, outer-sphere reactants are quite responsive to electrode charge and structure.^{39,125}

The sensitivity of the outer-sphere reduction of cobalt(III) ammines to the charge on the electrode has been used to determine double layer potentials at mercury electrodes.³⁵ These potentials were found to compare favorably to those predicted on the basis of the Gouy-Chapman-Stern-Frumkin theory.^{35,121} The observed (apparent) rate constant can then be corrected for the effect of the ionic double layer.³⁶ The corrected rate constant for a one-electron reaction is related to the apparent rate constant by³⁶

$$\log k_{\text{corr}}^E = \log k_{\text{app}}^E + (F/2.303 RT) (z_r \pm \alpha_I) \phi_r^E \quad (5.16)$$

where α_I is the intrinsic transfer coefficient, which is probably close to 0.5 for these reactants.^{35,36} The term ϕ_r^E is the average potential at the reaction plane for the given electrode potential E .¹²⁶ (The plus/minus signs refer to electrooxidation and electroreduction reactions respectively.) The plots of $\log k_{\text{corr}}$ for the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ at mercury are depicted in Figure 11 as dashed and dotted-dashed lines, respectively.^{36,39}

Figure 11. Rate-potential (Tafel) plots for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ reductions at platinum and mercury in 0.1 M NaClO_4 . Solid lines refer to platinum rate constants. Dashed lines are double layer corrected rate constants at mercury electrodes.

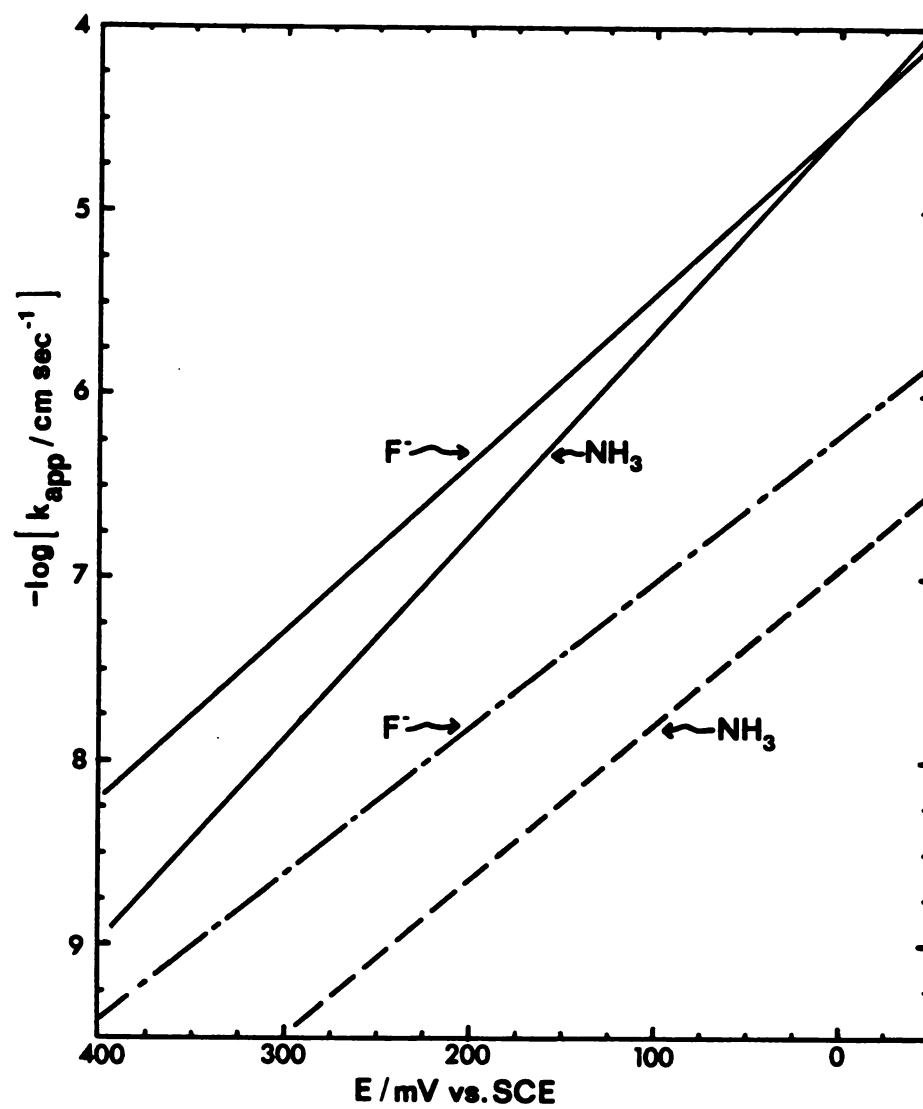


Figure 11

The linear regression lines of $\log k_{\text{app}}$ for these two complexes at platinum electrodes are shown as the solid lines. These are linear regression lines representing averages of six to eight rate determinations at platinum. The slowest measurable RDE rate constant is about $10^{-5} \text{ cm s}^{-1}$. The rates in Figure 11 correspond to an extrapolation of the data to more positive potentials, where most of the rate data for the other cobalt complexes are measured.^{10,11}

The comparison of solid electrode rates to those at mercury can be used to calculate double layer potentials at the solid electrodes.¹⁰ Rate comparisons between different types of electrode material must be made with care. There are a number of ways in which the nature of the electrode material can affect the rates and mechanisms of electrode reactions.^{10,39,125} These effects may be relatively small if the reactions occur by an outer-sphere mechanism on both surfaces.^{39,125,127} In such reactions, the variation of electrode material may lead to a change in the ionic double layer effect,^{125,127} a change in the tunneling probability in the transition state (κ in Equation 1.6),^{128,129} or a different solvent structure at the metal-solution interface.^{128,130} All of these factors have some influence upon the apparent rate constant.³⁹ The variation of k_{app} with electrode material for a one-electron reaction at a given electrode potential can be expressed as^{10,39}

$$(\Delta \log k_{\text{app}})_E = -(F/2.303RT)(z_r \pm \alpha_I)\Delta\phi_r^E + M \quad (5.17)$$

where $\Delta\phi_r^E$ is the change in the average potential at the reaction plane at a constant electrode potential. The first term is a form of the conventional Frumkin double layer correction^{2,130} as it was applied in Equation 5.16. The M term contains any variation in the "specific" effects^{128,130} brought about by changes in the electrode material. These specific effects include those due to tunneling surface roughness and solvent interfacial structure. By comparing values of $(\Delta \log k_{\text{app}})_E$ for two complexes having different values of z_r and similar ligand structure, we can eliminate the M term from Equation 5.17. It is assumed that outer-sphere reactants of similar structure, such as $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, would experience similar reaction environments, i.e., M for $\text{Co}(\text{NH}_3)_6^{3+}$ is the same as for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$.^{35,39} The resulting value of ϕ_r^E can then be used to calculate M from Equation 5.17. Values of M found by this method were near zero (± 0.1) for Pt, Pt(I) and Au(I) surfaces when compared to mercury. On gold M was found to be +0.3 relative to mercury. The assumption of M = 0 for these complexes seems reasonable for Pt, Pt(I) and Au(I) surfaces. Even for gold surfaces this assumption would only cause an error of about 10 mV in the value of $\Delta\phi_r^E$ obtained (as calculated for $\text{Co}(\text{NH}_3)_6^{3+}$ at $E \leq 100$ mV).

Instead of comparing apparent rate constants at both surfaces, k_{app}^E at the solid electrode can be compared to k_{corr}^E at mercury. Since k_{corr} values represent the condition of $\phi_r^E = 0$, Equation 5.17 becomes

$$(\log k_{\text{app}} - \log k_{\text{corr}}^{\text{Hg}})_E = -(F/2.303RT)(z_r \pm \alpha_I)\phi_r^E \quad (5.18)$$

The value of ϕ_r^E from Equation 5.18 is the average reaction plane potential for the solid electrode. From data like those in Figure 11 for all four surfaces (Pt, Au, Pt(I), and Au(I)), ϕ_r^E was calculated using Equation 5.18. These values are listed in Table VI for various electrode potentials. It can be seen that ϕ_r is more negative at these solid surfaces than at mercury. The differences between values of ϕ_r calculated from $\text{Co}(\text{NH}_3)_6^{3+}$ reduction and those obtained from the reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ are attributed to nonzero values for M in Equation 5.17 or to slightly different reaction planes for these two reactants at solid electrodes.³⁹ To fit this latter explanation the reaction plane for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ would have to be closer to the surface than for $\text{Co}(\text{NH}_3)_6^{3+}$. The distance required is small, as can be calculated from Equation 4.6. For example, at platinum for $E = 0$, the $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ reaction site would need to lie 0.6 Å closer than that for $\text{Co}(\text{NH}_3)_6^{3+}$.

The absolute magnitudes of ϕ_r on solid electrodes are considerably larger than on mercury electrodes at the same

Table VI: ϕ_r^E in 0.1 M NaClO₄ at Various Electrode Potentials E.^a

Reactant	Surface	E (mV)			
		-100	0	+250 ^c	+400 ^c
Co(NH ₃) ₆ ³⁺	Pt	-61	-55	-41	-32
	Au	-67	-57	-32	-18
	Pt(I)	-62	-56	-39	-29
	Au(I)	-69	-53	-12	+11
	Hg ^b	-25	-19	- 4	
Co(NH ₃) ₅ F ²⁺	Pt	-63	-60	-54	-50
	Au	-78	-69	-46	-33
	Pt(I)	-73	-65	-46	-40
	Au(I)	-81	-63	-19	+ 9
	Hg ^b	-24	-18	- 3	

^aUnits of ϕ_r^E are in mV.

^bCalculated from data presented in References 35 and 39 using Equation 5.18.

^cThese ϕ_r values are from extrapolated Tafel plots of the reactant reduction rates.

electrode potential. This difference is primarily due to the different potentials of zero charge (PZC). The PZC for mercury in 0.1 M NaClO_4 is -457 mV.¹³¹ On solid electrodes PZC values are less easily obtained.⁹⁷ Values of PZC for polycrystalline platinum in 0.1 M NaClO_4 have been reported as -110,¹³² -50,¹³³ and 0 mV.^{18,134,135} For polycrystalline gold electrodes in the same electrolyte -250,¹³⁶ -200,¹⁸ -80,⁸⁷ -40,⁴⁹ and 0 mV¹³³ are given for the PZC in the literature. Despite the diversity of these values, it is clear that the PZC for mercury lies at least 300 to 400 mV more negative than for platinum and gold. The potentials at which ϕ_r is reported in Table VI for the solid surfaces are all near or positive of the PZC, while at the same potentials ϕ_r for mercury is several hundred millivolts more positive of the PZC. It is known that ϕ_r for mercury becomes increasingly negative as the electrode potential approaches the PZC from the positive direction.^{35,131} Compared at the same potential difference with respect to the PZC, the values of ϕ_r for platinum and gold would be much closer to the value of ϕ_r for mercury.

The implication is that ClO_4^- adsorption on platinum and gold is similar to mercury. Adsorption studies support this conclusion.^{18,49,86} The adsorption of ClO_4^- from 0.2 M HClO_4 on gold and platinum has been reported to be too low to be detected by ellipsometry.⁸⁶ Capacitance measurements in 50 mM KClO_4 have shown no specific adsorption

of ClO_4^- on gold near the PZC ($-40 \text{ mV} \pm 10 \text{ mV}$).⁴⁹ Perchlorate is found to be weakly adsorbed on platinum and gold at potentials in the vicinity of the potential for oxide reduction ($E \approx +400 \text{ mV}$) by cyclic voltammetry.¹⁸ It therefore seems reasonable to assume weak or no ClO_4^- adsorption at $E = 0$, with perhaps slightly more adsorption at more positive potentials from 0.1 M NaClO_4 .

The cobalt ammine outer-sphere kinetics results are summarized in Tables VII and VIII for platinum and gold electrodes in 0.1 M acidified NaClO_4 . The rate parameters for each complex are given for the clean surface, iodide-treated surface and for mercury. The apparent rate constants were measured by rotating disk voltammetry at the listed electrode potential E . For these complexes, excepting $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$, at least four rate determinations have been averaged to obtain the listed values. (The nitrate complex exhibited a large hysteresis in the "steady-state" kinetics at gold electrodes and is not reported. The results for this complex in Table VIII are averages of only two experiments.) The standard deviations for these averages are less than 20% of k_{app} , except for those rate constants marked by an asterisk, which had a precision $\leq 50\%$ of k_{app} . Tables VII and VIII also list values for the apparent transfer coefficient α_{app} , defined by

$$\alpha_{\text{app}} = -(2.303 \text{ RT/F})(\partial \log k_{\text{app}} / \partial E)_{\mu} \quad (5.19)$$

Table VII. Reduction Rate Parameters for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ at $E = 0$.

Complex	Electrode	k_{app}^c (cm sec^{-1})	α_{app}	K_p (cm)	k_{et} (sec^{-1})
$\text{Co}(\text{NH}_3)_6^{3+}$	Pt	2.7×10^{-5}	0.65	2.6×10^{-5}	1.0
	Pt(I)	2.8×10^{-5}	0.67	2.7×10^{-5}	"
	Au	3.2×10^{-5}	0.75	3.2×10^{-5}	"
	Au(I)	2.0×10^{-5}	0.91	1.9×10^{-5}	"
	Hg ^b	7.1×10^{-7}	0.67	3.3×10^{-7}	"
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	Pt	2.8×10^{-5}	0.54	4.0×10^{-6}	7.0
	Pt(I)	3.8×10^{-5}	0.62	5.9×10^{-6}	"
	Au	$4.9 \times 10^{-5*}$	0.64	8.4×10^{-6}	"
	Au(I)	3.3×10^{-5}	0.77	5.2×10^{-6}	"
	Hg ^b	2.2×10^{-6}	0.59	1.4×10^{-7}	"

^aIn 0.1 M NaClO_4 + 5 mM HClO_4 .

^bFrom Reference 39.

^cAn asterisk indicates a precision of 50%-20%, all other rate constants have precisions better than 20%.

Table VIII. Reduction Rate Parameters for Other Outer-sphere Cobalt(III) Complexes.^a

Complex	Electrode	E (mV)	k _{app} ^d (cm s ⁻¹)	α _{app}	K _p ^b (cm)	k _{et} (s ⁻¹)	k _{et} (E=0) (s ⁻¹)
Co(NH ₃) ₅ OH ₂ ³⁺	Pt	0	1.1x10 ^{-3*}	0.53	2.6x10 ⁻⁵	42	42
	Pt(I)	0	2.3x10 ⁻³	0.69	2.7x10 ⁻⁵	85	85
	Au	0	8.1x10 ^{-3*}	0.74	3.2x10 ⁻⁵	250	250
	Au(I)	0	6.5x10 ⁻³	0.84	1.9x10 ⁻⁵	340	340
	Hg ^c	0	1.0x10 ⁻⁴	0.56	3.3x10 ⁻⁷	300	300
Co(NH ₃) ₅ NO ₃ ²⁺	Pt	0	3.0x10 ⁻⁴	0.57	4.0x10 ⁻⁶	75	75
	Pt(I)	0	2.5x10 ^{-4*}	0.56	5.9x10 ⁻⁶	42	42
c-Co(NH ₃) ₄ (OH ₂) ₂ ³⁺	Pt	250	7.4x10 ⁻⁴	0.52	4.4x10 ⁻⁶	170	1.5x10 ⁴
	Pt(I)	250	2.7x10 ^{-3*}	0.68	3.5x10 ⁻⁶	770	6.9x10 ⁴
	Au	250	3.6x10 ⁻³	0.73	1.6x10 ⁻⁶	2.3x10 ³	1.9x10 ⁵
	Au(I)	250	1.6x10 ^{-3*}	0.68	1.4x10 ⁻⁷	1.1x10 ⁴	6.7x10 ⁵

^aIn 0.1 M NaClO₄ + 5 mM HClO₄, at 23±1°C. ^bEstimated from Co(NH₃)₆³⁺ or Co(NH₃)₅F²⁺ values for φ_r, depending on whether the reactant charge was 3+ or 2+, respectively.

^cFrom Reference 39. ^dAn asterisk indicates a precision of 50-20%, all other rate constants have precisions better than 20%.

The partial derivative is the slope of the $\log k_{\text{app}}$ versus potential plot (as in Figure 11) at constant solution composition. The equilibrium constant for precursor state formation K_p was described and defined (by Equation 1.3) for outer-sphere reactions in Chapter I. The ϕ_r^E values in Table VI were used to calculate K_p from Equation 1.3 (with $r = 3.4 \times 10^{-8}$ cm).¹²³ Complexes of the same charge z_r were assumed to experience the same reaction plane potential ϕ_r .^{36,127} The rate constant for electron transfer from the precursor state k_{et} was calculated from the ratio of k_{app} to K_p (Equation 1.5). The final column lists the values of k_{et} measured or extrapolated to an electrode potential of 0 mV. The rate constants are reported at potentials positive of, or into, the potential range for the kinetically controlled reduction of complexes. The constant K_p can be more accurately estimated when the reactant concentration at the reaction plane is controlled by RDE hydrodynamics and kinetics rather than by diffusion and kinetics. Once k_{et} is found, α_{et} can be used to extrapolate k_{et} to some common potential for comparison. The slope ($\partial \log k_{\text{et}} / \partial E$) and α_{et} were found from the $\text{Co}(\text{NH}_3)_6^{3+}$ rate constants at 0 and +250 mV. α_{et} was determined to be 0.46, 0.45, 0.46 and 0.42 for Pt, Au, Pt(I) and Au(I) surfaces, respectively. These values were used in the extrapolation of k_{et} .

The k_{et} values for $\text{Co}(\text{NH}_3)_6^{3+}$ are all found to be quite close to 1.0 sec^{-1} . At first glance this seems to be an

artifact of the calculation for k_{et} . However, by combining Equations 1.3, 1.5 and 5.18 one can arrive at the following relationship for k_{et} :

$$k_{et} = \frac{1}{r}[k_{app}^M]^{(1-\lambda)}[k_{corr}^{Hg}]^\lambda \quad (5.20)$$

where $\lambda = z_r/(z_r \pm \alpha_I)$, and k_{app}^M is the rate constant measured at the solid metal electrode. From Equation 5.20 it is clear that k_{et} maintains a dependence on the apparent rate constant. It can be noted that k_{et} values are fairly similar for the same complex regardless of the electrode material. The relatively small differences can be attributed to uncertainties in k_{app} . The $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ complex shows the largest relative differences in k_{et} as electrode material is varied, but it also exhibits the least reproducible values for k_{app} . The lack of any strong dependence on electrode material for these complexes reinforces the use of such complexes as probes of double layer structure. The different values of k_{et} for different complexes are expected, if the complexes have different standard potentials. Equations 1.5 and 1.6 indicate that k_{et} depends on the reorganization energy $(\Delta G^*)^E$, which in turn is dependent upon $(E - E^\circ)$ (from Equation 1.7). Driving force differences are more easily illustrated in the comparisons of heterogeneous and homogeneous reduction rates which are presented later in this chapter.

D. Unusual Aspects of Iodide-Treated Platinum and Gold Electrodes

The interesting character of the iodide-treated electrodes is evident in Tables VII and VIII. It is noted that at $E = 0$, $k_{\text{app}}(\text{clean}) \approx k_{\text{app}}(\text{I})$. Nearly equivalent apparent rate constants lead to similar ϕ_r values from Equation 5.18. Under these conditions the adsorbed iodide does little to perturb the reaction plane potentials. Scrutiny of Table VI shows this remains the case for platinum over the potential range $-100 \leq E \leq 400$ mV. The diffuse layer charge for the iodide monolayer^{84,137} must be nearly the same as that due to any perchlorate adsorption in the absence of iodide. This is also true for gold, but only for $E \leq 0$.

Considerable electronic charge appears to be transferred from the iodide monolayer to the platinum surface, resulting in a practically covalent Pt-I bond.⁸⁴ Low energy electron diffraction (LEED) studies have confirmed the chemically irreversible adsorption of iodide on platinum in a ratio of one iodine atom per two platinum surface atoms.¹³⁷ Bagotzky, et al. find a 1:1 ratio from 1 mM I^- .⁵² Radiotracer⁶⁰ and chronocoulometry¹³⁸ experiments indicate a maximum iodide coverage of 1.5 and 1.6×10^{-9} g ion cm^{-2} , respectively. (A smooth platinum surface has 2.1×10^{-9} g atom Pt cm^{-2} .)¹³⁷ The covalent "iodine atom" layer may explain the insensitivity of ϕ_r^E to E as observed

for Pt(I) surfaces.

The nature of iodide on gold has been less thoroughly studied. The monolayer adsorption of iodide on gold has been proposed from differential capacitance data.⁴⁷ Specular reflectance studies have supported this conclusion over a wide (-0.4 to 1.0 V) potential range.⁵⁰ The qualitative behavior of the cobalt ammine complexes at Au(I) for $E = 0$ is not much different from Pt(I) where monolayer adsorption is present. However, there is not any evidence for the covalency of an Au-I bond. The capacitance data of Hamelin⁴⁷ is consistent with conventional anion specific adsorption.² The estimated values for ϕ_r^E on Au(I) in Table IV clearly diverge from those on the clean Au surface as the electrode potential becomes more positive. Increasing iodide adsorption may be occurring. The fact that Au(I) appears to affect outer-sphere kinetics similarly to Pt(I) around $E = 0$ may be coincidental. Alternatively, a covalent layer of iodine atoms may be adsorbed followed by further ionic iodide adsorption at positive potentials. Multilayer adsorption of iodide proceeds by this mechanism at platinum,²⁹ but at present there is not enough evidence to support this explanation at gold surfaces.

The strength of the iodide bond to both clean platinum and gold surfaces is sufficiently great to block other adsorbing species, as is evident from the reaction orders

seen in Table V for normally ligand-bridged reactants. Evidence of a more qualitative nature was noted in the enhanced reproducibility experienced in kinetics measurements at iodide-treated surfaces. The steady-state kinetics remained stable for at least an hour without any repretreatment of the electrode. Typically, clean surfaces required a pretreatment after each RDE determination (about every 10 min) to "re-activate" the electrode surface (see Chapter II for a more detailed discussion of pretreatments). Such behavior may be ascribed to an iodide layer blocking the adsorption of solution impurities which deactivate the electrode surface.

Iodide-treated platinum electrodes have perhaps been inadvertently used in some previous platinum studies. R. N. Adams⁸⁰ describes a pretreatment used to form a "reduced platinum surface" which consists of immersing an oxidized platinum electrode in an iodide solution to strip off surface oxide. He calls such a surface "stripped Pt". This treatment is followed by a water rinse. In light of later work,^{60,84,137,138} once the oxide is stripped off, iodide adsorbs as a monolayer and cannot be removed by simply rinsing with water.^{84,137} Adams gives no specific references to work employing "stripped Pt", but they undoubtedly exist.⁸⁰ The unusual nature of the Pt(I) surface (i.e., covalent adsorption), and the lack of effect on double layer potentials tend to make the iodide adsorption nearly

undetectable by kinetics measurements over the usual platinum potential region ($-100 < E < 400$ mV). Without more sophisticated surface analysis techniques,^{60,137} Pt(I) could easily be mistaken for an unusually stable reduced Pt surface.⁸⁰

E. Transition-Metal Aquo Reactants

After finding that the electrode material had only a minor influence upon the electroreduction of the cobalt-(III) ammine complexes, it might be expected that this would prove to be true for other simple cationic redox couples as well. However, quite different behavior was obtained for the one-electron oxidations of $\text{Cr}_{\text{aq}}^{2+}$, $\text{V}_{\text{aq}}^{2+}$, $\text{Ru}_{\text{aq}}^{2+}$ on platinum, gold and mercury surfaces.³⁹ The rate data are summarized in Table IX for these surfaces. An examination of k_{app} for $\text{Cr}_{\text{aq}}^{2+}$ oxidation reveals striking differences between platinum or gold and mercury. The oxidation of $\text{Cr}_{\text{aq}}^{2+}$ was found to occur on these solid electrodes at very positive electrode potentials (+700 to +1000 mV). The rate constants listed were determined by both cyclic voltammetry and rotating disk voltammetry. In order to compare the rates at platinum and gold to mercury at the same electrode potential, long linear extrapolations of the $\log k_{\text{app}}$ versus E (Tafel) plots were necessary. Even though some inaccuracy is probably introduced by this technique, it is clear that the rate constants at -100 mV are at least

Table IX. Oxidation Rate Parameters of Various Aquo Complexes.

Reactant	E_f^a (mV)	Electrode	Electrolyte ^b	E (mV)	k_{app}^c (cm s ⁻¹)	α_{app}^d
Cr_{aq}^{2+}	-655	Hg	0.4M $\overline{KPF}_6$	-100	2.0×10^{-2}	0.25
				-100	(3×10^{-3})	(0.20)
		Pt	0.1M $\overline{NaClO}_4$	800	1×10^{-3}	~ 0.4
				-100	$\sim 10^{-9}$	
				800	6×10^{-3}	~ 0.4
				-100	$\sim 10^{-8}$	
V_{aq}^{2+}	-480	Au	0.1M $\overline{NaClO}_4$	800	7×10^{-4}	~ 0.5
				800	1.5×10^{-3}	~ 0.5
		Hg	0.4M $\overline{KPF}_6$	-100	$\sim 10^{-10}$	
				-100	7×10^{-2}	
				-100	(9×10^{-2})	(0.23)
				-200	> 0.1	
Ru_{aq}^{2+}	-20	Pt	0.2M $\overline{NaClO}_4$ +1 mM $\overline{Cr}^{2+}$	-100	1.5×10^{-5}	~ 0.3
				-300	> 0.1	
		Au	0.2M $\overline{NaClO}_4$ +1 mM $\overline{Cr}^{2+}$	-100	5.5×10^{-5}	~ 0.4
				-20	5×10^{-3}	
				-20	(2×10^{-2})	

Table IX. Continued.

Reactant	E_f^a (mV)	Electrode	Electrolyte ^b	E (mV)	k_{app}^c (cm s ⁻¹)	α_{app}^d
Ru_{aq}^{2+}		Pt	0.2M KPF ₆	- 20	$>5 \times 10^{-2}$	
		Au	0.2M KPF ₆	- 20	$>5 \times 10^{-2}$	
			+1 mM Cr ²⁺	- 20	5×10^{-5}	~ 0.45

^aFormal redox potential from Reference 34.

^bElectrolyte contained either 5 mM HClO₄ or HPF₆, +1 mM Cr²⁺ indicates that the experiment was repeated after 1 mM Cr²⁺ had been added.

^cValues in parentheses indicate double layer corrected rates as determined by Equation 5.16 from Reference 2.

^dValues in parentheses are for double layer corrected α .

several orders of magnitude slower than for mercury ($\sim 10^6$ to 10^7 -fold). Such a large depression of the oxidation rate at platinum and gold cannot be explained by a simple ionic double layer effect.³⁹ The rate differences are not only too large, but of the opposite sign to those observed for the cobalt(III) ammine reactants. Table VI shows the double layer potentials on platinum and gold are favorable for cationic reactants for $-100 \leq E \leq +400$ mV, and yet $\text{Cr}_{\text{aq}}^{2+}$ oxidation is not noted until $E \geq 700$ mV. Oxidation of $\text{Cr}_{\text{aq}}^{2+}$ was also found to be immeasurably slow on silver electrodes (no oxidation up to the positive potential limit at +250 mV).^{39,96} The conclusion is that this reaction exhibits a large, specific metal effect in contrast to the cobalt(III) ammine reductions.³⁹

The electrooxidations of $\text{V}_{\text{aq}}^{2+}$ and $\text{Ru}_{\text{aq}}^{2+}$ were also studied and their rate constants are also given in Table IX. The kinetics of the $\text{Ru}_{\text{aq}}^{3+/2+}$ couple are more rapid (quasi-reversible), which limits the $\text{Ru}_{\text{aq}}^{2+}$ oxidation rate determinations to cyclic voltammetry at the formal potential ($E_f = -20$ mV).⁷² For these two reactions the rates are found to be faster on platinum and gold than on mercury (contrasting sharply with $\text{Cr}_{\text{aq}}^{2+}$ oxidation). These three electrooxidations occur at similar rates on mercury electrodes (Table IX).

It seemed possible that trace anionic impurities might be catalyzing the oxidation of $\text{V}_{\text{aq}}^{2+}$ through an inner-sphere,

ligand-bridged mechanism. Because both V_{aq}^{2+} and V_{aq}^{3+} are substitution-labile, a small amount of an anionic impurity (e.g., chloride) could participate in the catalysis of a much larger quantity of V_{aq}^{2+} , since the bridging ligand can be rapidly released after electron transfer.³⁹ Such catalysis is not possible for Cr_{aq}^{2+} oxidation, since Cr(III) is substitutionally inert and would "trap" the trace amounts of impurity in the Cr(III) product.³ The $Ru_{aq}^{2+/3+}$ couple is substitutionally inert in both oxidation states on the time scale of cyclic voltammetry.^{39,98,99} The use of Cr_{aq}^{2+} to remove these hypothetically catalytic impurities suggests a means of testing the mechanism of electrooxidation. The Cr_{aq}^{2+} will ligand-bridge with, and incorporate the impurities, into the Cr(III) product; thereby drastically reducing their participation in other catalytic processes.³⁹ The electrooxidation rate for substitution-labile V_{aq}^{2+} should be decreased, while that for substitution-inert Ru_{aq}^{2+} should remain unchanged. The addition of 1 mM Cr_{aq}^{2+} did not significantly affect electrooxidation rates of aquo couples at mercury, or the electroreduction rates of $Co(NH_3)_6^{3+}$ at platinum, gold, silver⁹⁶ or mercury.³⁹ This indicates that 1 mM Cr_{aq}^{2+} does not significantly affect the ionic double layer (i.e., is not specifically adsorbed, and does not perturb the double layer potentials through some interaction with the supporting electrolyte). Consequently, double layer effects are not likely to complicate

this test of mechanism. The addition of $\text{Cr}_{\text{aq}}^{2+}$ was found to decrease the rate of electrooxidation of $\text{V}_{\text{aq}}^{2+}$ on platinum and gold as predicted. Table IX shows the rate constant to be decreased by $\sim 10^3$ -fold. However, the rate constant for $\text{Ru}_{\text{aq}}^{2+}$ oxidation also decreases by about this same amount on gold. By this result, the ligand bridging hypothesis is invalidated.

The $\text{V}_{\text{aq}}^{2+}$ and $\text{Ru}_{\text{aq}}^{2+}$ rates in the presence of $\text{Cr}_{\text{aq}}^{2+}$ were substantially slower on platinum and gold than on mercury, just as was $\text{Cr}_{\text{aq}}^{2+}$ itself. The original rates (no Cr^{2+}) at platinum and gold seemed more reasonable, because they were near or larger than the mercury rates, in accordance with the predicted double layer effect. Hence, it is the behavior of $\text{Cr}_{\text{aq}}^{2+}$ that appears most unusual. The depression of the $\text{Ru}_{\text{aq}}^{2+}$ rate is particularly problematical. It seems clear that some specific interaction between $\text{Cr}_{\text{aq}}^{2+}$ and the solid metal surface is depressing the oxidation rates, (and probably acts to suppress its own oxidation as well). One may speculate that active surface sites important for aquo reactants, but not for $\text{Co}(\text{NH}_3)_6^{3+}$, are adversely affected by $\text{Cr}_{\text{aq}}^{2+}$.³⁹

The most likely difference between aquo and ammine reactants is in their relative abilities to form hydrogen bonds with the solvent, or adsorbed solvent on electrode surfaces.³⁹ Reaction entropies for the aquo couples indicate that considerable hydrogen bonding is present between

aquo ligands and solvent water molecules.¹³⁹ The reaction plane for reduction of Cr(III) aquo complexes was proposed to be more distant from the electrode than for Cr(III) ammine complexes, presumably due to an additional water molecule diameter.³⁶ The surfaces of platinum^{83,128,140,141} and gold^{83,142} probably are covered by a layer of specifically adsorbed water molecules. (Trassatti has determined that water is not preferentially oriented at gold near the PZC).^{128,140} If water molecules at these solid electrode surfaces are adsorbed "oxygen down",¹⁴³ then hydrogen bonding with aquo ligands is disfavored. The electrostatic effect of the cationic reactant adjacent to the inner-layer water molecules is uncertain.³⁹ In order to explain the observed reactivity, water molecules would need to be more "oxygen down" on the solid electrodes than on mercury. The evidence for this is inconclusive at present.^{39,128,140,143}

F. Inner-Sphere Kinetics of Co(III) Ammines

The cobalt(III) ammine complexes containing chloride, bromide, or pseudo-halide ligands have been found to be reduced by ligand-bridged mechanisms at platinum and gold.^{10,11} An inner-sphere mechanism can be assigned on the basis of adsorption measurements (Chapters III and IV) or on the observation of substantially depressed reaction orders (Section B, this chapter).¹¹ Because these complexes are capable of large catalyses relative to their

corresponding outer-sphere pathways, it is desirable to understand the cause of their enhanced reactivity on platinum and gold.

Tables X and XI summarize the kinetics data for the reduction of the inner-sphere complexes at platinum and gold. The format of these tables are similar to that described for Tables VII and VIII for the outer-sphere complexes. A notable difference is the inclusion of values for C_r and Γ_p , the reactant concentration near the surface and surface concentration, respectively. These are needed to calculate the equilibrium constant for precursor formation, K_p , from Equation 1.4. Under the "Complex" column the kinetics parameters are reported first for the clean surface, then for the iodide-treated surface (marked as (I)), followed by a row giving the ratio of the clean/(I) parameters when appropriate (marked as Δ). Surface concentrations were determined either by fast cyclic voltammetry (Chapter III), or they were estimated from the reaction order. As before (Section C, this chapter), k_{et} was found from the ratio of k_{app} to K_p .

In a few cases k_{et} could be directly determined from fast cyclic voltammetry. Chapter III described the use of this technique to determine Γ_p . The same data can also be used to calculate k_{et} .¹¹ Under the conditions for fast cyclic voltammetry given in Chapter III, the observed current is proportional to the adsorbed reactant concentration.

Table X. Kinetics Data for Inner-Sphere Electron Transfer at Platinum Electrodes.^a

Complex	C_r (10^6 mol cm^{-3})	Γ_p^b (10^{11} mol cm^{-2})	E (mV)	k_{app} ($cm\ s^{-1}$)	α_{app}	K_p^c (cm)	k_{et}^d (s^{-1})	$k_{et}(E=0)^e$ (s^{-1})
$Co(NH_3)_5Br^{2+}$ (I)	0.07	30	250	8.6×10^{-2}	0.62	4.3×10^{-3}	20	1.0×10^3
Δ	1.0		250	1.8×10^{-7}	0.68	1.3×10^{-6}	0.14	7.0
				4.8×10^5		3.3×10^3	140	
$Co(NH_3)_5Cl^{2+}$ (I)	0.13	40	250	2.3×10^{-2}	0.59	3.1×10^{-3}	7.4(29)	370(200)
Δ	1.0		250	6.6×10^{-7}	0.66	1.3×10^{-6}	0.51	26
				3.5×10^4		2.4×10^3	15	
$t-Co(en)_2Cl_2^+$ (I)	0.48	30	250	7.2×10^{-3}	0.59	6.3×10^{-4}	11	550
Δ	1.0		250	9.9×10^{-5}	0.57	2.1×10^{-7}	470	2.4×10^4
				73		2.0×10^3	2.4×10^{-2}	
$c-Co(en)_2Cl_2^+$ (I)	0.75	30	250	9.6×10^{-4}	0.58	4.0×10^{-4}	2.4	120
Δ	1.0		250	9.0×10^{-6}	0.40	2.1×10^{-7}	43	2.2×10^3
				1.1×10^2		1.9×10^3	5.6×10^{-2}	
$c-Co(NH_3)_4Cl_2^+$ (I)	0.07	30	250	6.3×10^{-2}	0.48	4.3×10^{-3}	15	730
Δ	1.0		250	2.7×10^{-5}	0.57	2.1×10^{-7}	130	6.5×10^3
				2.3×10^3		2.0×10^4	0.12	

Table X. Continued.

Complex	C_r (10^6 mol cm^{-3})	Γ_p^b (10^{11} mol cm^{-2})	E (mV)	k_{app} (cm s^{-1})	α_{app}	K_p^c (cm)	k_{et}^d (s^{-1})	$k_{et}(E=0)^e$ (s^{-1})
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	0.92	30	0	3.9×10^{-4}	0.36	3.3×10^{-4}	1.2	1.2
(I)	0.96		0	2.4×10^{-4}	0.38	6.1×10^{-6}	39	39
Δ				1.6		54	3.1×10^{-2}	
$\text{e-Co(en)}_2(\text{NCS})_2^+$	0.98	30	0	1.1×10^{-4}	0.58	3.1×10^{-4}	0.35	0.35
(I)	0.96		0	1.9×10^{-4}	0.58	4.6×10^{-7}	410	410
Δ				0.58		6.7×10^2	8.5×10^{-4}	

^aAll rate data are for 0.1 M NaClO_4 + 5 mM HClO_4 at $24 \pm 0.5^\circ\text{C}$.

^b Γ_p estimated from fast cyclic voltammetry results (Table I), or from apparent reaction orders (Table V) and Equation 5.15.

^c K_p for the clean surfaces calculated from Equation 1.4, for iodide-treated surfaces from ϕ_r^E values in Table VI and Equation 1.3.

^dValues in parentheses are directly measured by fast cyclic voltammetry and calculated from Equation 5.21.

^e k_{et} was extrapolated to $E=0$ assuming $\alpha_{et}=0.40$.

Table XI. Kinetics Data for Inner-Sphere Electron Transfer at Gold Electrodes.^a

Complex	C_r		Γ_p ^b	$(10^{11} \text{ mol cm}^{-2})$	E (mV)	k_{app} (cm s ⁻¹)	α_{app}	K_p^c (cm)	k_{et}^d (s ⁻¹)	$k_{et}(E=0)^e$ (s ⁻¹)
	$(10^6 \text{ mol cm}^{-3})$	$(10^{11} \text{ mol cm}^{-2})$								
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (I) Δ	0.17	80	400	1.8×10^{-2}	0.75	4.7×10^{-3}	3.8	2.0×10^3		
	1.0		400	2.8×10^{-8}	0.66	1.7×10^{-8}	1.6	840		
				6.3×10^5		2.8×10^5	2.3			
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (I) Δ	0.18	40	400	1.1×10^{-2}	0.60	2.2×10^{-3}	5.0	2.6×10^3		
	1.0		400	6.8×10^{-9}	0.63	1.7×10^{-8}	0.40	210		
				1.6×10^6		1.3×10^5	13			
$\text{t-Co(en)}_2\text{Cl}^+$ (I) Δ	0.18	20	250	1.3×10^{-2}	0.63	1.1×10^{-3}	12	600		
	1.0		250	7.1×10^{-6}	0.54	7.1×10^{-8}	100	5.0×10^3		
				1.8×10^3		1.6×10^4	0.12			
$\text{c-Co}(\text{NH}_3)_4\text{Cl}^+$ (I) Δ	0.18	20	250	1.3×10^{-2}	0.63	1.1×10^{-3}	12	600		
	1.0		250	2.7×10^{-5}	0.57	7.1×10^{-8}	380	1.9×10^4		
				4.9×10^2		1.6×10^4	3.1×10^{-2}			
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ (I) Δ	0.06	25	0	5.1×10^{-2}	0.58	4.2×10^{-3}	12(35)	12(35)		
	0.12		0	2.5×10^{-2}	0.54	5.2×10^{-6}	4.8×10^3	4.8×10^3		
				2.1		8.0×10^2	2.5×10^{-3}			

Table XI. Continued.

Complex	C_r (10^6 mol cm^{-3})	Γ_p ^b (10^{11} mol cm^{-2})	E (mV)	k_{app} (cm s^{-1})	α_{app}	K_p ^c (cm)	k_{et} ^d (s^{-1})	$k_{\text{et}}(E=0)$ ^e (s^{-1})
$\underline{\text{c-Co(en)}}_2(\text{NCS})_2^+$	0.89	30	0	6.6×10^{-4}	0.64	3.4×10^{-4}	1.9(4.8)	1.9(4.8)
	0.98		0	1.2×10^{-4}	0.50	4.6×10^{-7}	260	260
				5.6		7.4×10^2	7.3×10^{-3}	

^aAll rate data are for 0.1 M $\underline{\text{NaClO}}_4$ + 5 mM $\underline{\text{HClO}}_4$ at $24 \pm 0.5^\circ\text{C}$.

^b Γ_p estimated from fast cyclic voltammetry results (Table I), or from apparent reaction orders (Table V) and Equation 5.15.

^c K_p for the clean surfaces calculated from Equation 1.4, for iodide-treated surfaces from ϕ_r^E values in Table VI and Equation 1.3.

^dValues in parentheses are directly measured by fast cyclic voltammetry and calculated from Equation 5.21.

^e k_{et} was extrapolated to $E=0$ assuming $\alpha_{\text{et}}=0.40$.

When the potential sweep is rapid ($>2 \text{ V s}^{-1}$) the change in the current as a function of time can be used to calculate k_{et} from¹¹

$$k_{\text{et}} = 1/nF\Lambda\Gamma_i \quad (5.21)$$

Here Γ_i is the surface concentration that remains unreacted at the potential where i is measured. Values of Γ_i were obtained by partial integration of the cyclic peaks. This calculation assumes that k_{et} is first-order with respect to the concentration of adsorbed reactant. The values of k_{et} calculated from fast cyclic voltammetry data are given in parentheses in Tables X and XI. The directly measured values were in qualitative agreement with those calculated from steady-state measurements. The final column in these tables reports the values of k_{et} when extrapolated to $E = 0$ for an $\alpha_{\text{et}} = 0.40$. (α_{et} was measured for several complexes with cyclic voltammetry and found to be $0.35 \leq \alpha_{\text{et}} \leq 0.45$). K_p values for the iodide-treated surfaces (corresponding to "forced outer-sphere" mechanisms) were calculated from Equation 1.3 and ϕ_r values listed in Table VI.

If one compares the apparent rate constants for these inner-sphere complexes on the clean electrode surface to that on the iodide-treated surface, striking effects are noted.¹⁰ For the chloro- and bromo-complexes the ratio

of $k_{\text{app}}(\text{clean})/k_{\text{app}}(\text{I})$ is as large as 10^6 for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ on gold and 10^5 for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ on platinum electrodes.

The iodide treatment of these surfaces caused relatively minor rate changes for normally outer-sphere complexes.³⁹

Reaction order measurements (Table V) support the idea that iodide blocks inner-sphere mechanisms for this group of complexes. The large rate decreases are therefore the probable result of a mechanistic change from inner-sphere on clean surfaces to outer-sphere on the iodide-treated surfaces.

An inner-sphere pathway can enhance the rate of electron transfer (relative to the outer-sphere pathway) by several possible means. For convenience these have been grouped into thermodynamic and intrinsic effects as described in Chapter I. One obvious thermodynamic effect is the relatively higher reactant (more properly, "precursor") concentration present for an inner-sphere reaction.

When a favorable adsorption equilibrium precedes the electron transfer step the concentration of reactant at the surface can be greatly enhanced relative to the bulk.^{11,144} This is the case for the cobalt(III) complexes containing chloride, bromide or isothiocyanate anions as can be seen from Tables X and XI. Examination of the ratios for $K_p(\text{clean})/K_p(\text{I})$ (given in the rows marked " Δ ") shows the inner-sphere pathway enhances the formation of the precursor state. Because all of these complexes are at

or near monolayer adsorption from ~ 1 mM bulk concentrations, the K_p ratios for inner-sphere versus forced outer-sphere are much greater than one. At electrode potentials where the electroreduction rates are kinetically controlled (e.g., those given in Tables X and XI), reactant adsorption can cause 10^2 to 10^5 -fold increases in the overall electron transfer rates depending on the type of bridging ligand. The complexes exhibiting faster overall electron transfer rates on the clean surfaces ($\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, for instance) are reduced at electrode potentials where diffuse layer adsorption³⁵ is less favorable as a result of less negative values of ϕ_r^E (Table VI). A smaller value of K_p for the outer-sphere mechanism indicates that the concentration of reactant at the reaction plane is lower relative to the bulk concentration. From an electrostatic standpoint a less negative ϕ_r^E offers less attraction for cationic reactants. The larger ratios of $K_p(\text{clean})/K_p(\text{I})$ for the faster reacting complexes are therefore mainly due to double layer effects upon $K_p(\text{I})$.

An interesting point is illustrated when the effect of the double layer upon reactant adsorption is considered. The complexes which exhibit the largest extents of adsorption (highest values for $K_p(\text{clean})$) are adsorbed at electrode potentials where the double layer effect favors cationic adsorption the least. However, the adsorption of anions is increasingly favored as the electrode potential

becomes more positive. Adsorption of these complexes then appears to be dominated by the character of the ligands rather than the overall ionic character. That is, the adsorption can be said to be "ligand-induced", and might be anticipated to parallel the adsorptive behavior of the free anion.^{11,96} The bridging ligand character then is expected to strongly influence both the thermodynamic and intrinsic behavior for an inner-sphere reaction.¹ Ligands affect the outer-sphere reactions primarily through thermodynamic "driving force" differences (i.e., differences in formal potentials). Under these assumptions a comparison of inner-sphere k_{et} values to outer-sphere k_{et} values for the same complex at the same electrode potential should reflect primarily the intrinsic effect of the inner-sphere mechanism.

When such a comparison of $k_{et}(\text{clean})$ to $k_{et}(\text{I})$ is made, only $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ show a catalytic intrinsic effect (Chapter I). For $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ on platinum the inner-sphere rate is 140 times faster than the outer-sphere rate. Although $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is only 15 times faster on this surface by an inner-sphere route, this is still a substantial degree of catalysis. On gold electrodes the $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ complex is catalyzed to a greater degree than the $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by an inner-sphere mechanism. The other chloro complexes have large values of k_{et} but they do not have higher k_{et} values for the inner-sphere mechanism relative to the outer-sphere. In fact,

the results indicate that for these complexes the outer-sphere pathway is favored for equal concentrations in the precursor state. The outer-sphere route is even more favorable for the isothiocyanate complexes.

Intrinsic effects arise from specific influences upon the transition state for electron transfer.¹ For inner-sphere heterogeneous electron transfer these effects are probably caused by the presence of the ligand-surface bond. For the monoatomic-bridged complexes, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, a halide-surface bond can markedly influence the transition state.¹⁰ The cobalt center is connected through only a single ligand p orbital to the metal electrode orbitals, which may facilitate the transfer of the electron. The formation of the bond between the bridging ligand and the electrode surface weakens the cobalt-ligand bond. The lower force constant of this bond then could serve to diminish the reorganization energy necessary for electron transfer.

The isothiocyanate complexes are intrinsically decatalyzed for inner-sphere electron transfer. The isothiocyanate ligand differs from the halide ligands in two major features. The polyatomic bridge does not offer as intimate a connection between the cobalt center and the electrode surface. Secondly, the orbitals conducting the transferring electron are more likely π orbitals than σ as for the halides. The sulfur-metal bond will have

relatively little effect upon the force constant of the more distant cobalt-nitrogen bond. A back-donation of π electron density from platinum or gold surface atoms may strengthen the thiocyanate π system.^{145,146} The back-donation of π electrons is known to stabilize t_{2g} orbitals like those in cobalt(III).^{145,147} And the back-donation of π electron density has been proposed for isothiocyanate transition metal complexes.¹⁴⁵ This explanation is also consistent with the observation of more pronounced decatalysis for the cis-Co(en)₂(NCS)₂⁺ complex, which is expected to be di-bridged.

In summary, the mono-bridged complexes have been found to be intrinsically catalyzed for chloride and bromide ligands, but decatalyzed for isothiocyanate ligands relative to their outer-sphere reductions at platinum and gold electrodes. The proposed explanation has two points. First, that monoatomic bridges promote intrinsic catalysis through a more intimate connection between redox centers. Second, that platinum and gold surfaces may act as "sigma-withdrawing" and "pi-donating" reactants for the adsorbed complexes.¹⁴⁶ The "sigma-withdrawing" property leads to strong adsorption and a weakening of the transition metal-ligand bond for chloro and bromo mono-bridged complexes. The same would be true for isothiocyanate but for this ligand the π character is more dominant. The cobalt(III) t_{2g} orbitals are stabilized as a result of back-bonding

from the isothiocyanate ligand.¹⁴⁵ When adsorbed at the platinum or gold surfaces additional π electron density is acquired through filled t_{2g} orbitals on platinum and gold surface atoms,¹⁴⁶ which tends to further strengthen the isothiocyanate-Co(III) π system. The adsorbed isothiocyanate complex then is stabilized and exhibits a larger force constant for the cobalt-nitrogen bond, causing the electron transfer to be intrinsically decatalyzed relative to the outer-sphere pathway.

G. Heterogeneous-Homogeneous Rate Correlations

The comparison of the observed heterogeneous reduction rates with the rates of corresponding outer-sphere homogeneous reactions can provide additional evidence for the identification of ligand-bridged electrode reactions.^{10,36,38,148} According to the Marcus theory for outer-sphere electron transfer,⁸ the ratios of the rate constants k_h for homogeneous electron transfer of a series of reactants by a given reagent will be approximately independent of the reagent chosen. These rate constant ratios are also expected to be the same as the ratios of the rate constants for the corresponding heterogeneous electron transfer reactions at a fixed electrode potential.^{8,10,58} So the following relationship should be valid:

$$\log \left(\frac{k_h^X}{k_h^R} \right)_A \cong \log \left(\frac{k_{app}^X}{k_{app}^R} \right)_E \quad (5.22)$$

where X and R superscripts denote the given reactant and the reference reactant. Subscripts A and E refer to constant homogeneous reducing (or oxidizing) agent and constant electrode potential, respectively. A plot of the two ratios in Equation 5.22 can be seen in Figures 12 and 13 for platinum and gold electrodes. The apparent rate constants were taken at an electrode potential of 0 mV. The homogeneous reducing agent was $\text{Ru}(\text{NH}_3)_6^{2+}$. The rate ratios are all relative to the $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ rate constants for the appropriate reaction. The straight line in these two figures mark the location for a perfect correlation, i.e., unit slope through the origin. Circles mark the outer-sphere complexes and triangles mark inner-sphere complexes. The filled symbols represent the ratios for an iodide-treated surface.

Figures 12 and 13 are similar in many respects. The outer-sphere complexes always appear above, but near, the correlation line for both clean and iodide-treated surfaces. The iodide-treated ratios are very near the clean surface ratios for the outer-sphere complexes, which is indicative of the similar reaction plane potentials (as noted earlier in Sections C and D in this Chapter). The $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$

Figure 12. Heterogeneous-homogeneous correlation at platinum electrodes. The heterogeneous data were extracted from Tables VII, VIII, X and XI. Circles and triangles denote outer- and inner-sphere mechanisms, respectively. The homogeneous data are for reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$ and are from Reference 160, and R. C. Patel and J. F. Endicott, J. Am. Chem. Soc., 90, 6364 (1968). The solid symbols correspond to iodide-treated surfaces. All of the ratios are relative to the reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. The points are labeled with the X ligand in $\text{Co}(\text{III})(\text{NH}_3)_5\text{X}$. The symbols $\underline{\text{c}}-(\text{OH}_2)_2$, and $\underline{\text{c}}$ and $\underline{\text{t}}-(\text{en})_2\text{Cl}_2$ refer to $\underline{\text{c}}-\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ and $\underline{\text{c}}$ and $\underline{\text{t}}-\text{Co}(\text{en})_2\text{Cl}_2^+$ complexes, respectively.

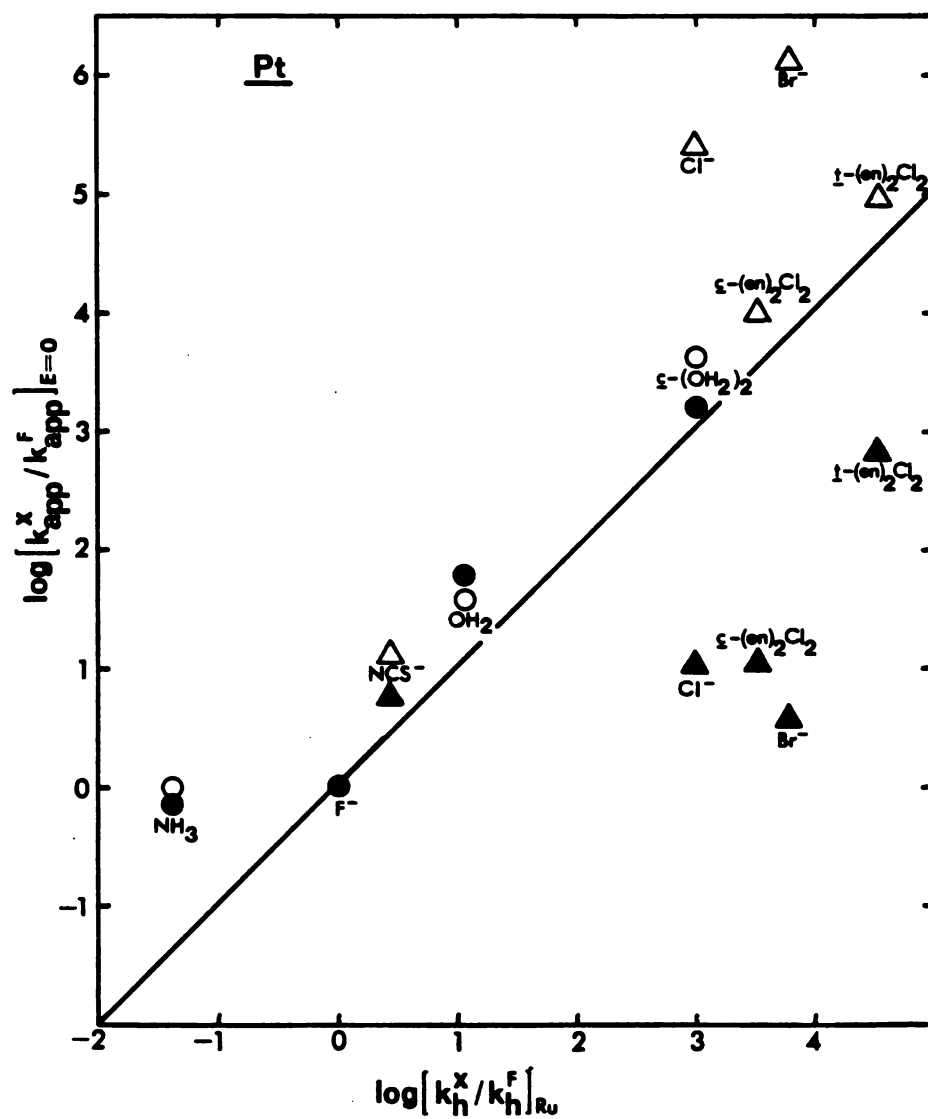


Figure 12

Figure 13. Heterogeneous-homogeneous correlation at gold electrodes. The heterogeneous data were extracted from Tables VII, VIII, X and XI. Circles and triangles denote outer- and inner-sphere mechanisms, respectively. The homogeneous data are for reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$ and are from Reference 160, and R. C. Patel and J. F. Endicott, J. Am. Chem. Soc., 90, 6364 (1968). The solid symbols correspond to iodide-treated surfaces. All of the ratios are relative to the reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$. The points are labeled with the X ligand in $\text{Co}(\text{III})(\text{NH}_3)_5\text{X}$. The symbols $\underline{\text{c}}-(\text{OH}_2)_2$, and $\underline{\text{c}}$ and $\underline{\text{t}}-(\text{en})_2\text{Cl}_2$ refer to $\underline{\text{c}}-\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ and $\underline{\text{c}}$ and $\underline{\text{t}}-\text{Co}(\text{en})_2\text{Cl}_2^+$ complexes, respectively.

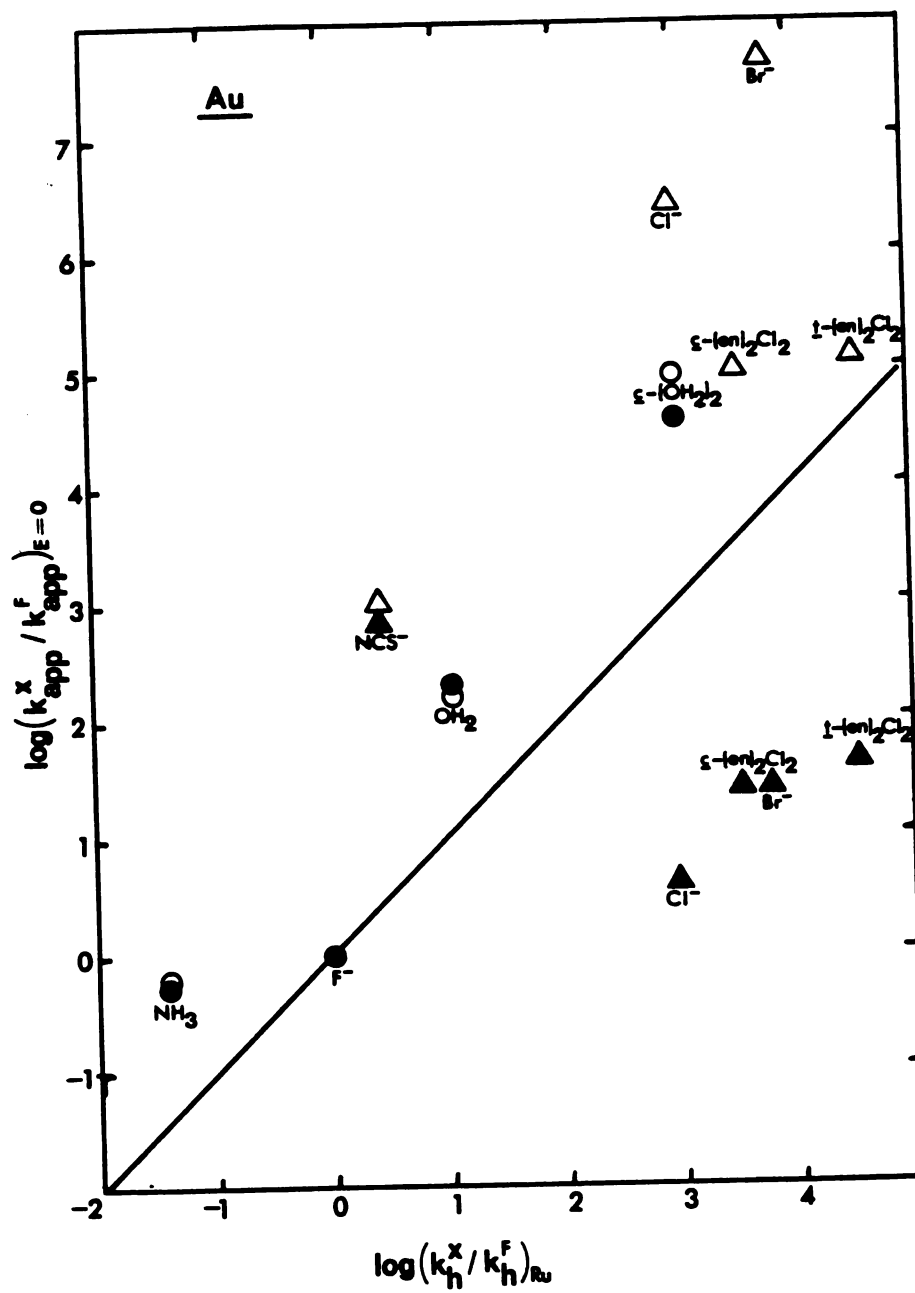


Figure 13

ion appears to mimic the outer-sphere behavior, even though it is known to be adsorbed strongly on clean platinum and gold.¹¹ The remaining inner-sphere complexes all have heterogeneous rate ratios which lie above the correlation line on clean surfaces and below it on iodide-treated surfaces. The $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ions have ratios substantially greater than predicted from Equation 5.22, which is reasonable in light of the probable intrinsic catalysis which they experience by an inner-sphere mechanism.^{10,11} The generally higher values for the heterogeneous ratios at gold electrodes may be a result of an erroneously low rate constant for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ at this surface. (As was noted in Table VII, k_{app} for this complex could only be determined to within ~50% of the average value on gold electrodes.)

The use of such correlations as diagnostic tools for mechanism identification^{10,36,38} must be seen as a risky business at best. The assignment of an inner-sphere mechanism is only possible when substantial inner-sphere catalysis is present. In such a circumstance the rate response to adsorbed iodide seems at least as good a test. The assignment of an outer-sphere mechanism on the basis of a correlation with homogeneous rates can lead to errors, as it would for the $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ complex on platinum. Even the rate response to adsorbed iodide gives the faulty impression that this complex reacts by an outer-sphere

route. Only the determination of reactant adsorption can unambiguously verify an inner-sphere pathway. The absence of such adsorption and a reaction order near unity are the best indications that the mechanism is outer-sphere.

CHAPTER VI

ELECTRON TRANSFER WITH CARBOXYLIC OR AROMATIC LIGANDS AT PLATINUM AND GOLD ELECTRODES

The use of the cobalt(III) pentaammine complexes with simple anionic and neutral ligands has revealed much about the double layer structure and reactivity at platinum and gold surfaces.^{10,11,39,40} With the background of this work and the techniques developed (to distinguish between different electron transfer mechanisms, for instance), it would be interesting to examine a slightly more complicated group of reactants. To this end, cobalt(III) pentaammine complexes with various aromatic and carboxylic ligands were studied.¹⁴⁹

A. Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing 4,4'-Bipyridine and Related Ligands

The electroreduction kinetics of $\text{Co}(\text{NH}_3)_5\text{L}^{3+}$ complexes containing 4,4'-bipyridine (BP), 1,2-bis(4-pyridyl)ethane (BPA), trans-1,2-bis(4-pyridyl)ethylene (BPE), pyridine (py), or pyrazine (pyz) ligands were studied at mercury-, platinum-, and gold-aqueous interfaces in order to explore the ability

of such nitrogen heterocycles to mediate heterogeneous electron transfer reactions.¹⁴⁹ These reactants have the potential to be adsorbed at these surfaces and thereby to act as extended ligand bridges. The possibility of ligand π orbital overlap with surface orbitals is especially interesting in view of the previous results obtained for the isothiocyanate-bridged complexes in Chapter V.

The electrochemical rate parameters for the reduction of the above mentioned $\text{Co}(\text{NH}_3)_5\text{L}^{3+}$ complexes in perchlorate electrolytes at mercury, platinum and gold electrodes are summarized in Table XII as values of k_{app} at 0 mV and the apparent transfer coefficient α_{app} . Data for $\text{Co}(\text{NH}_3)_5\text{DMSO}^{3+}$, which was the synthetic precursor to many of these complexes, are also tabulated. The rate parameters for the outer-sphere reactant $\text{Co}(\text{NH}_3)_6^{3+}$ are restated here for comparison purposes. (They also appear in Table VII.) The choice of 0 mV was made to minimize the extrapolation of Tafel plots,³⁶ which was sometimes necessary in order to compare rate constants at a constant electrode potential. The electrolyte solutions were acidified (to pH = 3, with HClO_4) 0.5 M LiClO_4 and 0.1 M NaClO_4 for mercury and solid electrode measurements, respectively. All experiments were performed at 24 ± 0.5 °C. The kinetics of most reactions were independent of pH in the range $1 \leq \text{pH} \leq 3$ at all surfaces. The exception was $\text{Co}(\text{NH}_3)_5\text{BP}^{3+}$ which exhibited decreasing rates of reduction as the pH was lowered to

Table XII. Electrochemical Rate Parameters for the Reduction of Various Co(III)-
(NH₃)₅X Complexes at Mercury, Platinum and Gold Electrodes in Perchlorate
Electrolytes.

Complex ^a	k_{app} (cm s ⁻¹) at 0 mV versus SCE					α_{app}	
	Hg ^{b,e}	Pt ^{c,e}	Au ^{c,e}	Pt(I ⁻) ^{d,e}	Au(I ⁻) ^{d,e}	Hg ^{b,e}	Pt ^{c,e} Au ^{c,e}
R-NH ₃ ³⁺	3x10 ⁻⁷	2.7x10 ⁻⁵	3.2x10 ⁻⁴	2.8x10 ⁻⁵	2.0x10 ⁻⁴	0.80	0.65 0.75
R-DMSO ³⁺	1.6x10 ⁻³	8.4x10 ⁻⁴	1.1x10 ⁻²	6.0x10 ⁻²	0.16	0.63	0.56 0.58
R-py ³⁺	1.9x10 ⁻³	2.2x10 ⁻²	2.7x10 ⁻²	1.9x10 ⁻²	3.6x10 ⁻²	0.81	0.71 0.73
R-pyz ³⁺	5.0x10 ⁻³	2.6x10 ⁻³	9.2x10 ⁻²	0.11	0.81	0.66	0.51 0.57
R-BP ³⁺	~0.3	~0.5	~1.9	~0.5	~1.3	0.95	0.67 0.66
R-BPH ⁴⁺	1.9x10 ⁻²	1.7x10 ⁻²	4.2x10 ⁻²	4.3x10 ⁻³	1.4x10 ⁻²	0.85	0.60 0.66
R-BPAH ⁴⁺	7.5x10 ⁻³	5.2x10 ⁻³	6.5x10 ⁻³	6.5x10 ⁻³	9.2x10 ⁻⁴	0.75	0.61 0.67
R-BPEH ⁴⁺	8.2x10 ⁻²	2.4x10 ⁻²	2.2x10 ⁻²	2.4x10 ⁻²	3.7x10 ⁻²	0.9	0.61 0.62

^aR=Co(III)(NH₃)₅; DMSO=dimethylsulfoxide; py = pyridine; pyz = pyrazine; BP = 4,4'-bipyridine; BPA = 1,2-bis(4-pyridyl)ethane; BPE = t-1,2-bis(4-pyridyl)ethylene. BPH, BPAH, and BPEH refer to the corresponding monoprotonated ligands.

^bDetermined in 0.5 M LiClO₄ containing 1 mM HClO₄. These experiments were performed by Visiwanathan Srinivasan. 149

Table XII. Continued.

^cDetermined in 0.1 M $\underline{\text{NaClO}}_4$ containing 1 mM $\underline{\text{HClO}}_4$.
^dValues of k_{app} after the addition of 5 mM $\underline{\text{NaI}}$.
^eValues of k_{app} and α_{app} for reduction of R-Bp^{3+} and corresponding protonated species
 R-BpH^{4+} determined from rate-pH dependence combined with pK_a for complex (see text).

pH $\approx$ 2, after which the rates become pH-independent.

The pH dependence is probably due to the protonation of the uncoordinated end of the 4,4'-bipyridine ligand to form $\text{Co}(\text{NH}_3)_5\text{BPH}^{4+}$, which is then reduced at a slower rate than $\text{Co}(\text{NH}_3)_5\text{BP}^{3+}$.¹⁴⁹ The pK_a for the protonated complex was determined by the titration of 1 mM $\{\text{Co}(\text{NH}_3)_5\text{BP}\}(\text{ClO}_4)_3$ in 0.5 M LiClO_4 with HClO_4 . This pK_a was found to be 4.0 ± 0.2 . The analogous pK_a values for $\text{Co}(\text{NH}_3)_5\text{BPAH}^{4+}$ and $\text{Co}(\text{NH}_3)_5\text{BPEH}^{4+}$ were too large ($\text{pK}_a > 5.0$) to be accurately determined by this technique. Under the experimental conditions for kinetics measurements (pH = 3), these latter two complexes are almost entirely in their protonated forms. If it is assumed that the observed rate for the bipyridine complex is the result of the parallel reductions of the protonated and unprotonated forms, the pK_a can be used to calculate individual kinetics parameters for the two forms. These values are also listed in Table XII.

Reactant adsorption measurements for these complexes yielded sparse results. The results indicated that relatively small amounts ($2\text{--}3 \mu\text{C cm}^{-2}$) of adsorbed complex were obtained from 1 mM solutions (i.e., low values for K_p). Single-step chronocoulometry experiments for hanging mercury drop electrodes (HMDE) at +200 mV failed to detect the adsorption of any complexes, except $\text{Co}(\text{NH}_3)_5\text{BPH}^{4+}$ and somewhat surprisingly $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$. From 1 mM bulk concentrations the apparent surface concentrations, Γ' ,

were $5 \times 10^{-11} \text{ mol cm}^{-2}$ and $2.0 \times 10^{-10} \text{ mol cm}^{-2}$ for the BPH⁺ and py complexes respectively. On gold electrodes Co(NH₃)₅-pyz³⁺ was the only complex detectably adsorbed. From a 100 μM bulk concentration, Γ' was $\sim 7 \times 10^{-11} \text{ mol cm}^{-2}$ as determined from fast cyclic voltammetry (Chapter III, Table I). The addition of 5 mM NaI caused this fast cyclic adsorption peak to disappear, as expected, if iodide blocks the specific adsorption of this complex.¹¹ Adsorption measurements at platinum electrodes were not possible due to the proximity of hydrogen reduction current to the reduction waves (or cyclic peaks) for these complexes. Fast cyclic voltammetry on mercury electrodes confirmed the adsorption of the pyridine complex to at least a monolayer.

A cursory examination of Table XII shows the rate constants for the heterocyclic complexes to be larger than the rate constant for Co(NH₃)₆³⁺ on any electrode surface. The substitution of an ammonia ligand in the hexaammine by a nitrogen-ligating heterocycle yields substantial increases in some cases. For example, the rate constant for the 4,4'-bipyridine complex is a factor of 10^5 faster than that for the hexaammine. The most striking result is that the rate constants for reduction of a given heterocyclic complex are relatively insensitive to the nature of the electrode surface. This is better illustrated by the plot of the rate constants in Figure 14. The iodide-treated electrode rate constants are not drastically lower as was the case

Figure 14. Reduction rate constants for $\text{Co(III)(NH}_3)_5\text{L}$ at various electrodes. The supporting electrolytes were 0.5 M LiClO_4 for Hg or 0.1 M NaClO_4 for Pt and Au electrodes. The pH was adjusted to $\text{pH} = 3$ with HClO_4 .

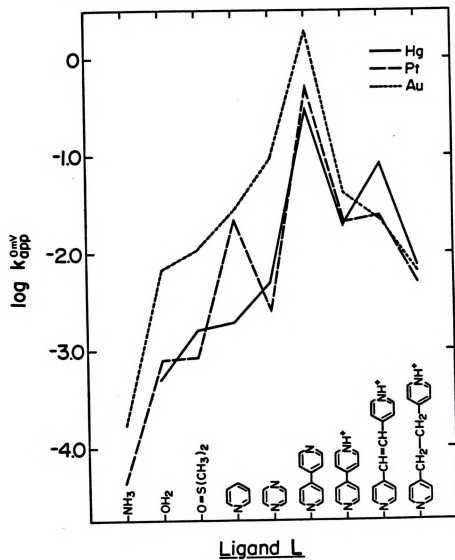


Figure 14

for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (Chapter V). Evidently these heterocyclic ligands do not promote the kind of intrinsic catalysis noted for the two halide-bridged reactants.

A correlation to homogeneous reductions (Table XIII) shows that the nitrogen heterocycle-containing complexes are catalyzed in their heterogeneous reductions at mercury, platinum, and gold surfaces.¹⁴⁹ The outer-sphere homogeneous reductions (for $\text{Ru}(\text{NH}_3)_6^{2+}$, for instance) have not been extensively investigated for this group of reactants. One outer-sphere reducing agent which has been studied is $\text{Fe}(\text{CN})_6^{4-}$.^{153,154} The reduction rate constants for this reducing agent refer to outer-sphere electron transfer within a precursor (collision) complex.¹⁵⁴ The homogeneous reduction rate constants are used to calculate rate constant ratios relative to the outer-sphere reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$,^{10,39} by the procedure used in Chapter V for such conditions. The analogous heterogeneous rate constant ratios can be calculated from data in Table XII and those for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ given in Table VIII. Table XIII lists these ratios. The heterogeneous ratios are much larger (~50-5000-fold) than the corresponding homogeneous ratios. In Chapter V, rate enhancements as much as 10^4 were seen to result from reactant adsorption.^{10,11} This same factor could account for the rate enhancement here. This result together with the adsorption measurements indicates that

Table XIII. Relative Heterogeneous and Homogeneous Rate Comparisons for Nitrogen Heterocycle-Containing $\text{Co(III)(NH}_3)_5\text{L}$ Complexes.

Ligand L	$k_{\text{app}}/k_{\text{app}}^{\text{OH}_2^{\text{a}}}$			$k_{\text{h}}/k_{\text{h}}^{\text{OH}_2^{\text{b}}}$
	Hg	Pt	Au	Fe(CN)_6^{4-}
Py	3.8	28	4.0	0.083
BP	600	640	280	0.13
BPAH ^{+c}	15	4.7	0.80	0.056
BPEH ^{+c}	165	22	3.0	0.055

^aRate constants from Table XII relative to $\text{Co(NH}_3)_5\text{OH}_2^{3+}$ from Table IIX.

^bFrom References 153 and 154, for homogeneous reducing agent Fe(CN)_6^{4-} . [$k_{\text{h}} = 0.18 \text{ s}^{-1}$ for $\text{Co(NH}_3)_5\text{OH}_2^{3+}$].

^cDenotes protonated ligands.

the enhanced reactivity of the heterocyclic complexes relative to simple outer-sphere reactants is probably a result of reactant adsorption, i.e., an enhanced reactant concentration at the electrode surface.

The similarities in rate constants for the homogeneous reductions of the BPA and BPE complexes have been taken (in the literature¹⁵⁵) as evidence that these ligands serve to keep reacting centers in close proximity for outer-sphere electron transfer, and are not being utilized to mediate the electron transfer through orbital coupling.¹⁵⁵ (BPA has a saturated linkage between pyridine rings, while BPE is conjugated.) The heterogeneous rate constant ratios indicate that the reduction of the BPE complex is favored over the BPA complex by at least a factor of 4. Perhaps the more extensive π orbital structure of the former complex leads to a greater extent of adsorption at electrode surfaces.

In comparison to the previous kinetics studies,^{10,11,39} these heterocycle-containing reactants exhibit behavior similar to the isothiocyanate complexes discussed in Chapter V. That is, rates on all surfaces are nearly the same, even though evidence for reactant adsorption exists. The reactant adsorption is not nearly as well documented for these complexes as it was for the isothiocyanate complexes. Only $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ appears to be strongly adsorbed on mercury and probably platinum and gold. The assumption that the complex is also strongly adsorbed on the solid

electrodes is supported by evidence of strong adsorption of pyridine at these surfaces.^{43,150} The 4,4'-bipyridine and pyrazine complexes were also detectably adsorbed, but not to the same extent as the pyridine or isothiocyanate complexes. The adsorption of the reactant leads to a "surface thermodynamic" lowering of the overall free energy barrier to electron transfer as a result of the increase in the concentration of the precursor complex for electron transfer (Chapter I).^{11,149} The close similarity between inner-sphere and forced outer-sphere (iodide-blocked) rate constants requires the inner-sphere rates to be intrinsically decatalyzed to compensate for the reactant concentration differences (just as it did for the NCS^- complexes in Chapter V). The other alternative is that these complexes are adsorbed on iodide-treated electrodes. The fast cyclic voltammetry results for the pyrazine complex on Au and Au(I) indicate that iodide is effective in blocking the adsorption of $\text{Co}(\text{NH}_3)_5\text{pyz}^{3+}$ (Chapter III).

Although similar to the isothiocyanate complexes in many respects, the heterocycle-containing complexes achieve the same pattern of reactivity by different means. Isothiocyanate complexes are undoubtedly bound to the electrode surface by a sulfur-electrode bond.^{11,36,93,94} While most of the heterocyclic ligands have an exposed nitrogen lone pair capable of forming a surface bond, the pyridine complex does not. Because the pyridine complex is adsorbed

to the greatest extent, the availability of a nitrogen lone pair is not the primary consideration for strong reactant-surface interaction. The heterocyclic ligand-surface interactions for the pyridine complex (and probably the other complexes as well) must almost certainly result from π orbital overlap or van der Waals forces.¹⁴⁹ This result is somewhat surprising, since it does not seem likely that the pyridine can attain a high degree of π orbital overlap when bound to cobalt(III) pentaammine. The pyridine ligand extends only slightly (~ 1 Å) beyond the ammine ligand "sphere" and consequently cannot lie flat on the electrode surface. Pyridine and BPE are known to be strongly adsorbed on mercury surfaces, either through the nitrogen lone pair or through the π system, i.e., end-on or flat.^{105,151,152} As far as I know, this is the first time adsorption of pyridine through the "opposite end" (opposing the nitrogen) has been observed.

The inner-sphere mechanism for these complexes is subtly different from that defined for more simple complexes (Chapter I).¹¹ Rather than the formation of a bond to the surface, the interaction here is more delocalized, involving the ligand π orbitals or non-bonding van der Waals effects. The d- π back bonding explanation (Chapter V) is still applicable to the apparent intrinsic decatalysis observed for these complexes. The pyrazine and 4,4'-bipyridine ligands appear to be most effective in increasing the rate

of electron transfer (Figure 14). These ligands can offer a nitrogen-electrode surface bond and a more conventional inner-sphere mechanism.

B. Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing Carboxylic Acid Ligands

Homogeneous electron transfer studies by Fan and Gould^{156,157} have found that carboxylate anions tend to be effective mediators for electron transfer. They concluded that the $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ complexes are reduced mainly by inner-sphere mechanisms by $\text{Cr}_{\text{aq}}^{2+}$, $\text{V}_{\text{aq}}^{2+}$,¹⁵⁶ and $\text{Eu}_{\text{aq}}^{2+}$.¹⁵⁷ Through homogeneous rate correlations with known outer-sphere reactants, they were able to determine the rate constants for outer-sphere homogeneous reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$.¹⁵⁶ The electron supply by the ligand was more important for the outer-sphere reactivity (the $\text{Ru}(\text{NH}_3)_6^{2+}$ rates), while non-bonding, steric effects governed the inner-sphere ($\text{Eu}_{\text{aq}}^{2+}$, $\text{V}_{\text{aq}}^{2+}$ and $\text{Cr}_{\text{aq}}^{2+}$) reduction rates.¹⁵⁶ The inner-sphere mechanism proceeds through the carbonyl functional group.¹⁵⁷ This section describes the heterogeneous kinetics for electron transfer of these carboxylate-containing complexes.

The heterogeneous kinetics were studied for the reductions of various $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ complexes, where the X ligand was an anion of a carboxylic acid. These ligands are bound to the cobalt center by a carboxylate oxygen. The reduction

rate parameters are given in Table XIV for mercury, platinum, and gold electrodes at 0 mV in 0.5 M LiClO_4 for mercury, and 0.1 M NaClO_4 for solid electrode experiments. For the rate constants reported here, the pH was adjusted to pH = 3 with HClO_4 . Rate constants were determined by d.c. polarography or rotating-disk voltammetry. The mercury results were obtained by V. Srinivasan. A plot of the rate constants as a function of the ligand X is depicted in Figure 15. This figure shows that these reactants are relatively insensitive to the type of electrode material. Unlike the pyridine complexes, reactant adsorption was not detected for any of the carboxylate-containing complexes by fast cyclic voltammetry at mercury or gold electrodes. These complexes are reduced at rates near or slower than the reduction rate for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, a simple outer-sphere reactant.³⁹ (The aquo complex is used for comparison since it also features an oxygen-ligating ligand.) These observations would be consistent with an outer-sphere mechanism for reduction.^{10,39}

The effect of the electron supply to the carbonyl group from the attached R group (e.g., CH_3 for acetic) may be expected to be reflected in the pK_a values of the appropriate carboxylic acids. Electron-withdrawing R groups should stabilize the acid anion, giving a lower value for the pK_a . If the heterogeneous reaction is indeed outer-sphere, then a correlation between the ligand pK_a and the reduction rate constant might be anticipated. If, on the other hand,

Table XIV. Reduction Rate Parameters for Carboxylic Cobalt(III) Complexes.

Complex	k_{app} (cm s ⁻¹ at 0 mV)						α_{app}	
	Hg	Pt	Au	Pt(I)	Au(I)	Hg	Pt	Au
R-formate	1.1×10^{-5}	1.7×10^{-4}	1.9×10^{-4}	2.7×10^{-5}	2.7×10^{-4}	.63	.59	.65
R-acetate	5.2×10^{-6}	1.1×10^{-4}	1.4×10^{-4}	5.1×10^{-5}	2.9×10^{-4}	.60	.45	.66
R-F ₃ acetate	2.8×10^{-5}	3.0×10^{-4}	1.0×10^{-3}	1.8×10^{-4}	2.7×10^{-3}	.56	.55	.73
R-Cl ₃ acetate	7.5×10^{-4}	8.4×10^{-4}	5.6×10^{-3}	1.5×10^{-3}	4.3×10^{-3}	.62	.45	.62
R-pivalate	1.2×10^{-5}	2.1×10^{-5}	1.9×10^{-4}	1.9×10^{-5}	4.1×10^{-5}	.59	.70	.83
R-benzoate	1.2×10^{-3}	5.6×10^{-5}	1.4×10^{-3}	1.1×10^{-4}	4.6×10^{-4}	.62	.45	.63

Figure 15. $\text{Co(III)(NH}_3)_5\text{X}$ electroreduction rates at 0 mV at various electrodes. The supporting electrolytes were 0.5 M LiClO_4 for Hg or 0.1 M NaClO_4 for solid electrodes.

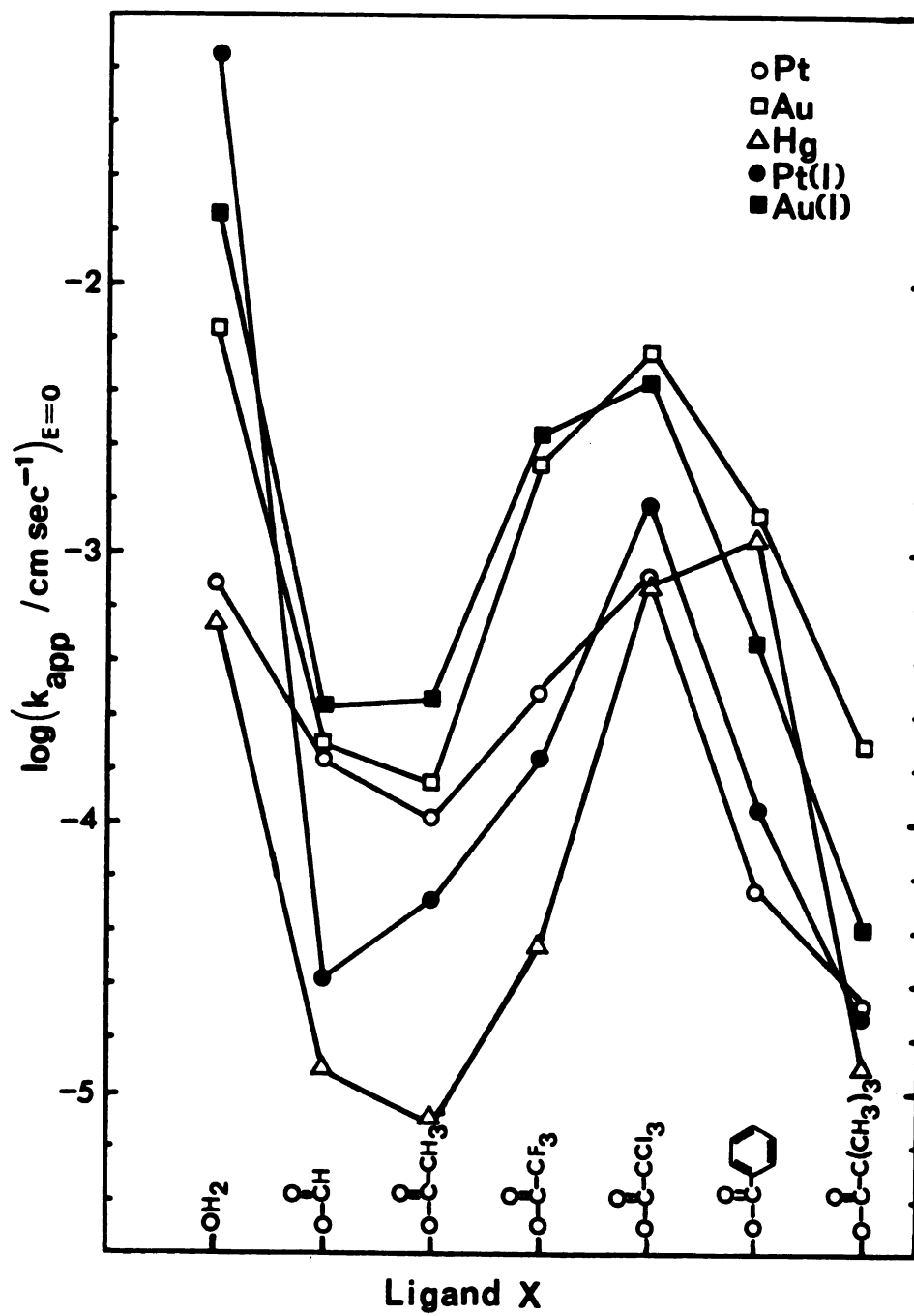


Figure 15

Figure 16. Homogeneous and heterogeneous reduction rate constants of $\text{Co(III)(NH}_3)_5\text{X}$ as a function of the X ligand pK_a .

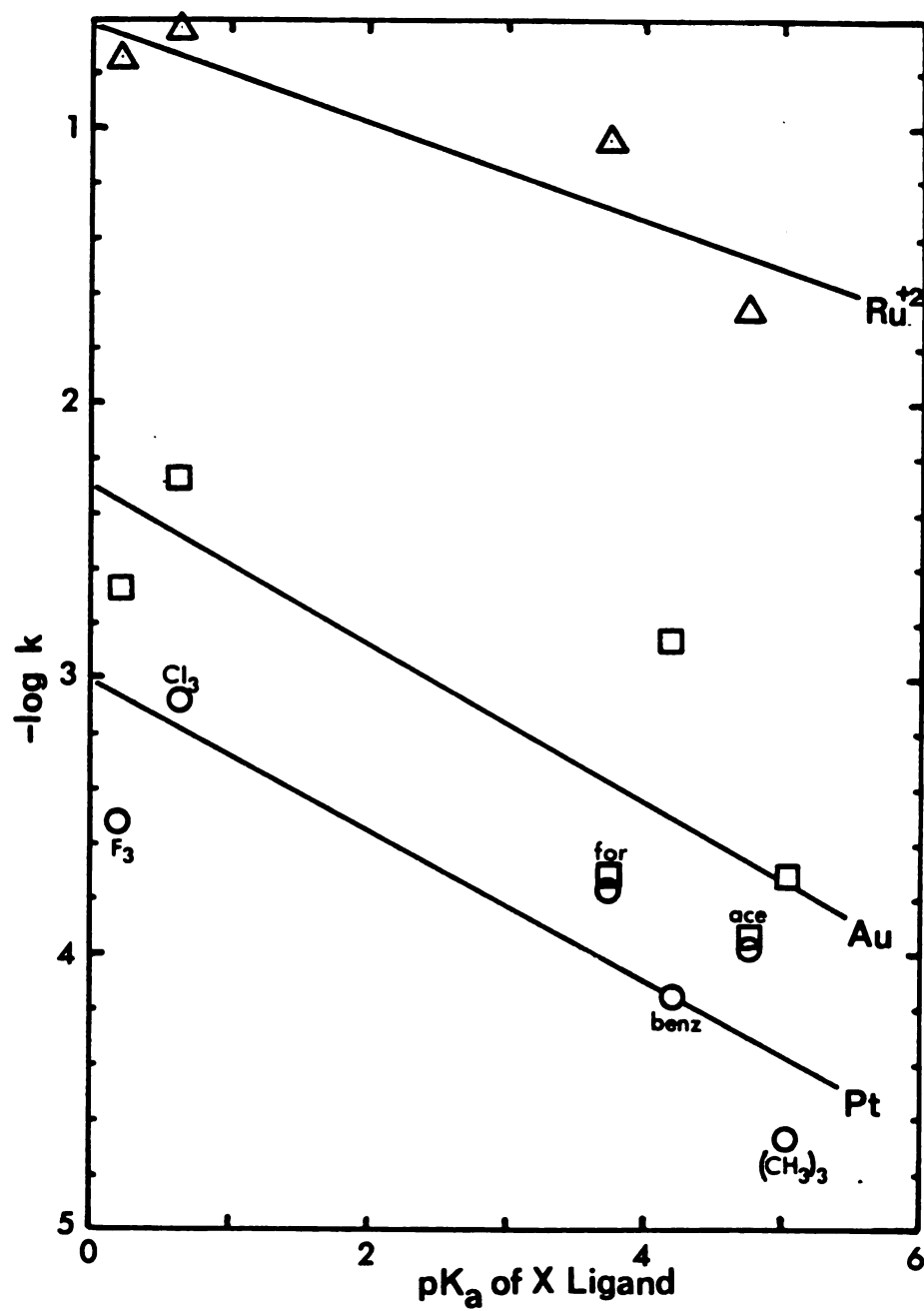


Figure 16

the reaction were to proceed via an inner-sphere mechanism, then this correlation should be disrupted by steric effects of the carboxylate R groups. Figure 16 shows the results of such a correlation for the reductions by $\text{Ru}(\text{NH}_3)_6^{2+}$,¹⁵⁶ and platinum and gold electrodes (Table XIV). The rate constants are observed to correlate reasonably well with the pK_a of the ligand, with slightly stronger dependence for the heterogeneous reductions. Steric effects do not appear to affect the correlation. This result also supports the assignment of outer-sphere mechanisms to the heterogeneous reductions. The generally higher rates at gold than at platinum probably result from the double layer potential differences that favor outer-sphere cation reductions at the former surface (Table VI).

The contrast between homogeneous and heterogeneous reductions for the carboxylate-containing complexes is unusual. The mechanisms for the simple complexes (Chapter V) and the pyridyl complexes for reduction by $\text{Eu}_{\text{aq}}^{2+}$ and $\text{V}_{\text{aq}}^{2+}$ are usually the same as for heterogeneous reductions at platinum and gold. Perhaps these metal electrodes have less affinity for oxygen-bridging than for nitrogen or halogen-bridging. The rates of outer-sphere reductions in Figure 15 do not exhibit any steric effects that would suggest a more distant reaction plane for the larger ligands. The reactant may be oriented with the carboxylate ligand pointing away from the electrode surface.

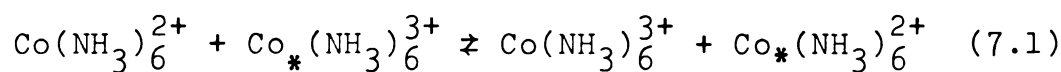
CHAPTER VII

MISCELLANEOUS EXPERIMENTS

A. The Standard Potential for $\text{Co}(\text{NH}_3)_6^{3+/2+}$

1. Introduction

The electron transfer reaction represented by Equation 7.1 has been of fundamental interest in theories of homogeneous electron transfer.^{58,159,160,162} The very slow rate constant usually assigned



for the electron exchange rate, k_{ex} , has provoked considerable commentary^{58,159-166} and some revision of electron transfer theory.^{159,162,168} Stranks¹⁶¹ determined an upper limit of $k_{\text{ex}} < 8 \times 10^{-10} \text{ M}^{-1}\text{s}^{-1}$ at 64.5°C. This limit is undoubtedly lower at 25°C,^{58,160,167} and was estimated to be $\sim 3 \times 10^{-12} \text{ M}^{-1}\text{s}^{-1}$ at this temperature.¹⁶⁰ This contrasts sharply with k_{ex} for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, which has been measured to be about $10^3 \text{ M}^{-1}\text{s}^{-1}$ at 25°C.^{169,170} The large difference in electron exchange rate constants for these two couples has been attributed to high internal

reorganization energies for Co(III/II)-N bond length changes,^{161,164} quantum effects,¹⁶³ electron tunneling effects,¹⁵⁹ and the work required to achieve the necessary reactant orbital overlap when donor and acceptor orbitals are both e_g^* .¹⁶⁸ The fact is, k_{ex} for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ is such an anomalous value that it requires an extraordinary explanation. Up until now most investigators have chosen to trust the experimental result reported by Stranks.^{161,164} Actually Stranks' value and the consequent discussion generated by it, can be traced to measurements of the stability constants for cobalt ammines first performed by Lamb and Larson¹⁷¹ followed by more extensive measurements by Bjerrum.¹⁷²

The electron exchange rate for Equation 7.1 is not a directly measurable quantity. The standard rate constant for heterogeneous electron transfer, k_s , is presumably (see later discussion) measurable by some form of voltammetry. Once k_s is known, k_{ex} can be calculated from the Marcus relation,⁵⁸

$$(k_{ex}/Z)^{1/2} = k_s/Z_{el} \quad (7.2)$$

for outer-sphere electron transfer, where Z and Z_{el} are the collision frequencies of the homogeneous and heterogeneous processes. In Marcus' treatment Z and Z_{el} are taken to be 10^{11} and 10^4 , when k_{ex} and k_s have the units

of $\text{M}^{-1}\text{s}^{-1}$ and cm s^{-1} , respectively.⁵⁸ The standard rate constant is the rate constant for heterogeneous electron transfer that is measured at the standard potential E° for the particular redox couple. Hence a determination of k_{ex} from Equation 7.2 depends on accurate measurements of electron transfer rates and a determination of E° . It is this latter value that is cast into doubt by the present work.

The stability of $\text{Co}(\text{NH}_3)_6^{2+}$ as determined by Bjerrum¹⁷² indicates that high concentrations of ammonia (6 N) are needed for this complex to be favored (>50%) over other cobalt(II) mixed aquo, ammine complexes. Measurements of k_s and E° have consequently been performed under conditions of high pH and high ammonia concentrations.^{161,164-166,172} In all of these measurements the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration is presumed to be that given by Bjerrum's stability constants. Bartlett and Landazury¹⁶⁵ have reported platinum RDE data for the $\text{Co}(\text{NH}_3)_6^{3+/2+}$ redox couple in 2 N NH_4Cl and concentrated NH_3 , that seem to be in agreement with Bjerrum's estimate of the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration for these conditions (~70% of all Co(II) species). They also find the same value (± 2 mV) for the standard potential, $E^\circ = -182$ mV versus SCE.^{165,172} On the other hand, Laitinen and Kivalo¹⁷⁷ performed platinum RDE experiments with $\text{Co}(\text{NH}_3)_6^{3+}$ in 12.7 M NH_3 and 1 M NH_4NO_3 and found the anodic current to be about 1% of the value expected on the basis

of Bjerrum's stability data for $\text{Co}(\text{NH}_3)_6^{2+}$. This stability constant has also been employed in determinations of the $\text{Co}(\text{OH}_2)_6^{3+/2+}$ electron exchange rate,¹⁷³ in spectroscopic studies of $\text{Co}(\text{II})$ complexes,¹⁷⁴ and in radiotracer exchange experiments for $\text{Co}(\text{NH}_3)_6^{2+}$.^{175,176}

The importance and widespread use of Bjerrum's result prompted us to take another look at the chemistry and electrochemistry for the $\text{Co}(\text{NH}_3)_6^{3+/2+}$ redox system. We chose to examine this system with cyclic and rotating disk voltammetry at gold electrodes in alkaline aqueous solutions. Cyclic voltammetry offers the opportunity of obtaining both E° and k_s values. It also is especially useful in monitoring preceding or succeeding chemical steps to electron transfer. Rotating disk voltammetry was employed in an attempt to duplicate the results of Bartlet¹⁶⁶ at gold electrodes instead of platinum. The formation of $\text{Co}(\text{NH}_3)_6^{2+}$ in solution and its electrooxidation to $\text{Co}(\text{NH}_3)_6^{3+}$ were of primary interest in our work. The value of k_{ex} is probably less certain than formerly believed,^{161,164} as we have observed considerable reason to doubt previously reported values for the standard potential^{165,166,172} and the stability constant for $\text{Co}(\text{NH}_3)_6^{2+}$.¹⁷²

2. Experimental

The following data were obtained with a gold RDE or a gold "flag" electrode constructed from a small portion of

gold foil. These electrodes were pretreated in the normal fashion (Chapter II) with one exception; the gold flag electrode was not mechanically polished. Electrolyte solutions were deaerated for two hours with prepurified nitrogen passed through a gas scrubbing bottle containing the same concentration of NH_3 to reduce the loss of NH_3 . Measurements of solution pH with an Orion glass electrode (Model 91-02) were in close agreement with the calculated pH, indicating that loss of NH_3 was minimal during the deaeration process. The electrolyte solutions were stored in sealed glass vessels under a nitrogen atmosphere until needed. The appropriate cobalt complex was added to a portion of this electrolyte and dissolved by the bubbling of nitrogen through the electrochemical cell. Unless otherwise noted, the electrochemical measurements were made as soon as possible (as soon as the cobalt complex had completely dissolved). The UV-Visible spectra were obtained with a Beckman DB-GT Spectrophotometer. The effective electrode areas were calculated from cyclic voltammetry peak heights for the reversible $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple as 0.127 and 0.210 cm^2 for the RDE and flag electrodes, respectively.

3. Results

Figure 17 illustrates the possible electrochemical and chemical processes that may be observed in an

Figure 17. The possible reaction scheme for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ in aqueous ammonia solutions.

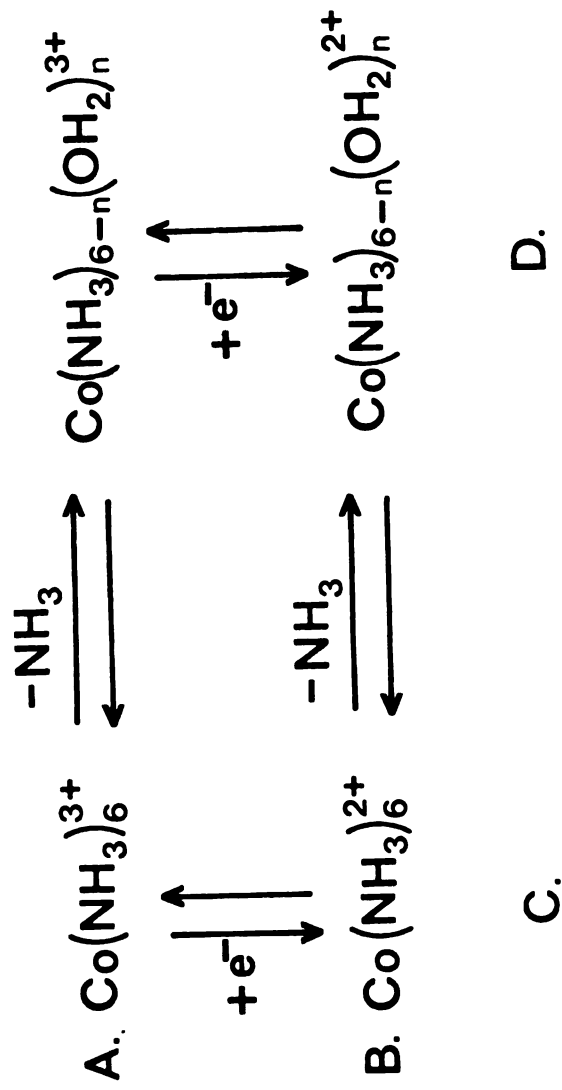


Figure 17

investigation of the redox behavior of $\text{Co}(\text{NH}_3)_6^{3+/2+}$. This figure represents the electron transfer reactions possible for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ and its partially solvent-substituted ($n > 0$) congeners. Knowledge of processes B and C is essential in a determination of k_{ex} , while processes A and D constitute possible interferences. High concentrations of NH_3 presumably favor the hexaammine species in processes A and B. It is known that $\text{Co}(\text{NH}_3)_6^{3+}$ is substitution inert over a reasonable time period (a few hours),¹⁰ so process A heavily favors the hexaammine species. Cobalt(II) complexes are substitution labile, so exchange of aquo and ammine ligands occurs rapidly, and process B may be expected to be sensitive to the NH_3 concentration. The solution pH becomes important for longer time scale experiments; at $\text{pH} > 10$ the precipitation of $\text{Co}(\text{OH})_2$ on the electrode surface can interfere with electrochemical measurements.¹⁷⁶ The latter point is a more serious complication in electrolyses than it is for cyclic voltammetry experiments. For the typical pH in this study (~ 10), process D more likely involves hydroxyl-substituted complexes (i.e., aquo ligands are deprotonated).

Table XV lists the cyclic voltammetry results at gold electrodes for 5 mM CoCl_2 in 6 and 14.8 M NH_3 , where the solution pH was varied at constant ionic strength in the mixed electrolyte $(2.5 - x)\text{M KCl} + x\text{M NH}_4\text{Cl}$. The results are separated with respect to the direction of potential

Table XV. Cyclic Voltammetry Results for 5 mM CoCl_2 in $\text{NH}_3/\text{NH}_4\text{Cl}$ Solution ($\mu = 2.5 \text{ M}$) at Gold Electrodes.^a

Conc. NH_3 (<u>M</u>)	pH	E_f (mV)	$E_{p,a}$ (mV)	$i_{p,a}$ (mA cm^{-2})	C_a^b (mM)
Anodic-Cathodic					
6	10.80	-275	-200	1.30	1.10
	10.25	-325	-275	1.10	0.93
	10.02	-330	-267	0.98	0.83
14.8	11.40	-388	-345	0.66	0.56
	10.50	-384	-354	0.88	0.74
	10.03	-391	-357	0.72	0.61
Cathodic-Anodic					
6	10.80	-291	-197	1.02	0.86
	10.25	-304	-234	0.63	0.53
	10.02	-302	-229	0.43	0.37
14.8	11.40	-392	-335	0.67	0.56
	10.50	-380	-337	0.71	0.60
	10.03	-375	-325	0.64	0.54

^a200 mVs^{-1} at 25.0°C .

^bThe equivalent concentration of $i_{p,a}$ assuming one electron oxidation, calculated from Equation 3.4.

scan (i.e., "anodic-cathodic" indicates the potential was scanned positive first then negative, causing oxidation followed by reduction). The apparent formal potential E_f was the median potential between the anodic and cathodic peak potentials, $E_{p,a}$ and $E_{p,c}$, respectively. The anodic peak current density $i_{p,a}$ was the background corrected current density at $E_{p,a}$. All of these results refer to a potential sweep rate of 200 mV s^{-1} and 25.0°C . The concentration of oxidizable species C_a was calculated from $i_{p,a}$ from Equation 3.4, and C_a was always observed to be substantially smaller than 5 mM (the bulk concentration of CoCl_2 added). A typical cyclic voltammogram is shown in Figure 18. This cyclic was for the anodic-cathodic potential scan in 14.8 M NH_3 at $\text{pH} = 10.50$.

Cyclic and rotating-disk voltammetric measurements were also made for solutions of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in $1 \text{ M NH}_4\text{Cl}$ and 14.8 M NH_3 at platinum and gold electrodes. The rotating disk results were similar to those of Laitinen and Kivalo,¹⁷⁷ i.e., the anodic limiting current was between 1 and 10% of the cathodic limiting current. (Bjerrum's data indicates that $\text{Co}(\text{NH}_3)_6^{2+}$ should comprise greater than 90% of all $\text{Co}(\text{II})$ species under these conditions.)¹⁷² Cyclic voltammetry of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in the same solution at gold electrodes yielded some unusual results, some of which are shown in Figure 19. The formal potential E_f appeared to be around $-210 \pm 5 \text{ mV}$ which is near the -182 mV value

Figure 18. The cyclic voltammogram for CoCl_2 in 14.8 M NH_3 + 1.5 M KCl + 1 M NH_4Cl at a gold electrode. The potential was scanned in the positive direction first. This is an example of an anodic-cathodic scan. The potential sweep rate was 200 mV s^{-1} . $\text{pH} = 10.50$.

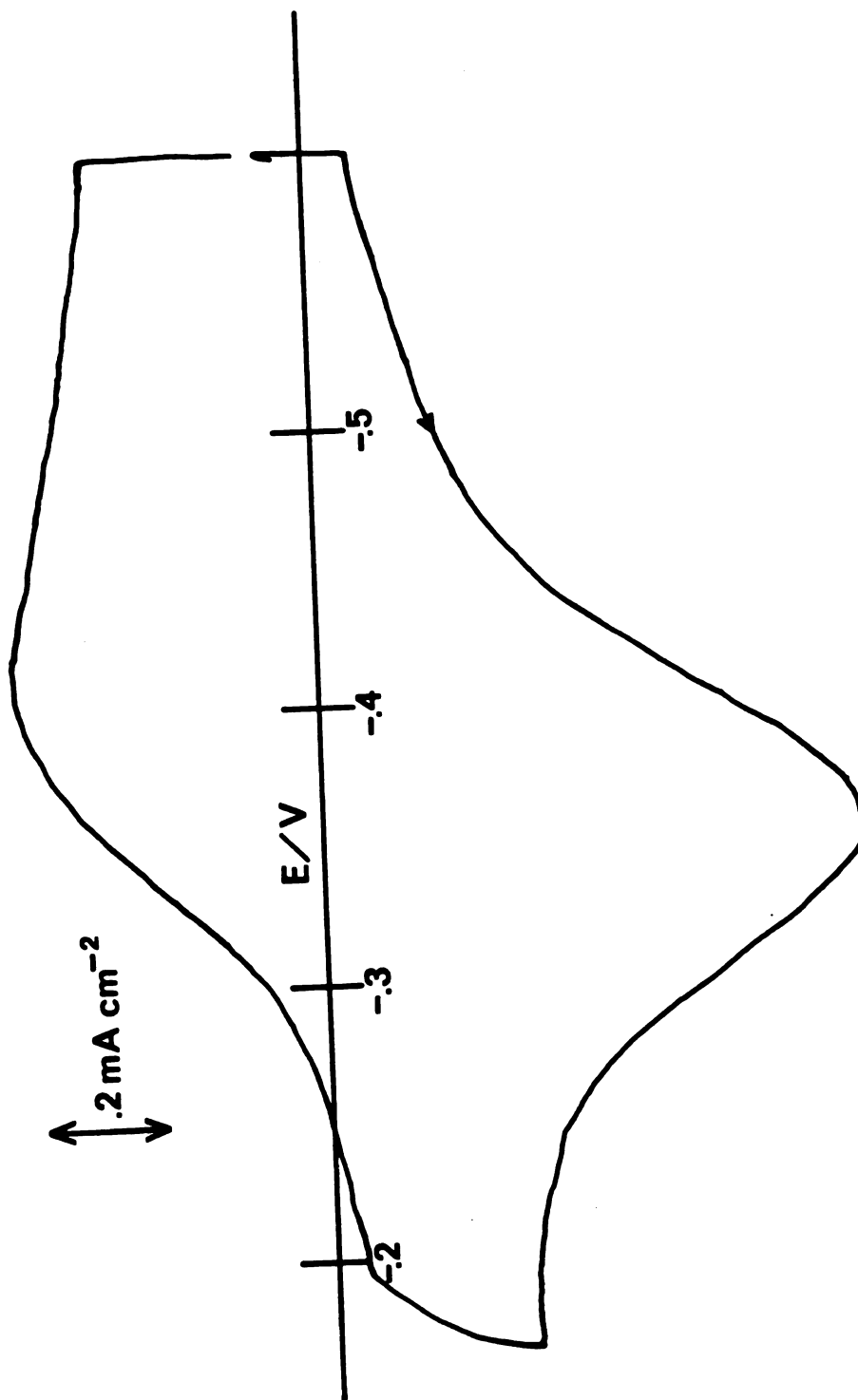


Figure 18

3 M
electrode.
direction
was

Figure 19. The cyclic voltammograms for $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in $14.8 \text{ M NH}_3 + 1 \text{ M NH}_4\text{Cl}$ at a gold electrode. The anodic-cathodic scans for various electrolysis times (a-c) at -500 mV . The potential sweep rate was 200 mV s^{-1} . $\text{pH} = 10.50$.

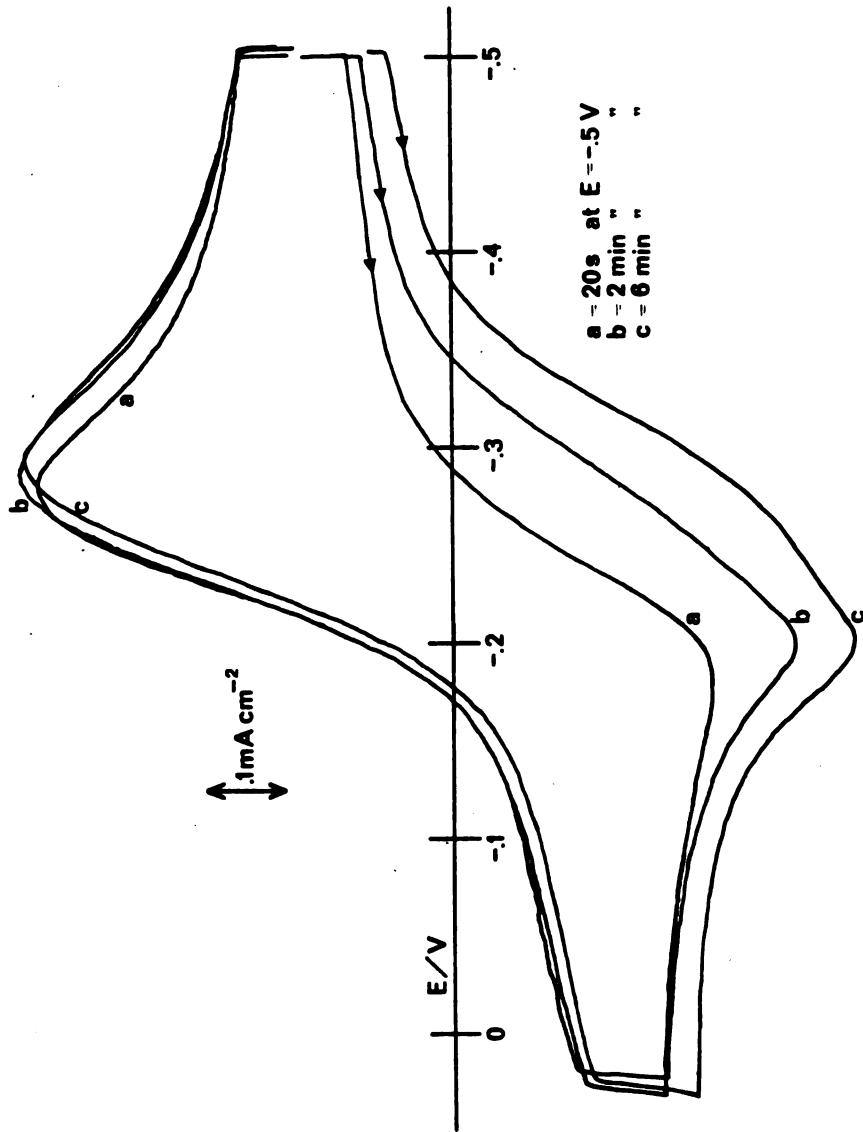


Figure 19

reported by Bjerrum¹⁷² and Bartelt^{165,166}, but is on the average 170 mV more positive than E_f for the CoCl_2 solutions listed in Table XV and shown in Figure 18.

A time-sweep rate dependence was noted in these $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ experiments. The cathodic peak for reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ was not affected, but the anodic peak current was found to depend on the time that the potential was held at -500 mV (where $\text{Co}(\text{NH}_3)_6^{3+}$ is reduced at a diffusion-limited rate). At longer electrolysis times at -500 mV the anodic peak current increased. From 20 s to 6 min the current was seen to increase by about 60%; (this is illustrated by cyclics a to c in Figure 19). The same type of behavior was noted in cathodic-anodic scans, but to a lesser degree. In these scans the anodic peak was proportionally larger (relative to the cathodic peak) as the sweep rate decreased from 500 to 20 mV s^{-1} . This is opposite to what one might expect, if $\text{Co}(\text{NH}_3)_6^{2+}$ is the source of anodic current. If $\text{Co}(\text{NH}_3)_6^{2+}$ undergoes a fairly slow aquation, more anodic current for $\text{Co}(\text{NH}_3)_6^{2+}$ should be present at faster sweep rates. The reduction peak seemed to be for $\text{Co}(\text{NH}_3)_6^{3+}$, as it was noted to increase when more $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ was added. The reductions of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ and cis- $\text{Co}(\text{NH}_3)_4(\text{OH})_2^+$ occurred at distinctly different (>50 mV) potentials than $\text{Co}(\text{NH}_3)_6^{3+}$.

The bulk electrolysis of CoCl_2 in 14.8 M + 1 M NH_4Cl at a gold electrode (area $\approx 10 \text{ cm}^2$) potentiostatted at

-100 mV for 9 hours at 10°C produced a yellow solution with an absorbance maximum at $478 \pm 4 \text{ } \mu\text{m}$. A solution of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in the same electrolyte gave an identical absorbance maximum. The wavelengths of maximum absorbance for $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ and cis- $\text{Co}(\text{NH}_3)_4(\text{OH})_2^+$ solutions were 505 and 525 μm respectively.

4. Discussion

The cyclic voltammetry results have been found to be distinctly different for solutions of CoCl_2 and $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ in 1 M NH_4Cl and 14.8 M NH_3 (Figures 18 and 19). For the latter reactant one can be reasonably certain that the observed reduction peak is for the hexaammine species. The subsequent oxidation of the reduction products produced a much smaller current than was expected (from Bjerrum's data)¹⁷² for $\text{Co}(\text{NH}_3)_6^{2+}$. The larger anodic peaks at slower sweep rates are indicative of at least one chemical step following the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$. This process is probably similar to B in Figure 17, although other processes such as formation of hydroxyl-bridged surface species are possible. In any case, it seems that some electroactive species is formed rapidly from $\text{Co}(\text{NH}_3)_6^{2+}$, which can then be oxidized to a Co(III) complex. This Co(III) complex, which is most likely not $\text{Co}(\text{NH}_3)_6^{3+}$ (only process C, Figure 17 could account for direct oxidation to the hexaammine), is not observable as a separate peak on a subsequent

cathodic scan. The formal potential is therefore probably not the E° for $\text{Co}(\text{NH}_3)_6^{3+/2+}$, but is a mixed potential for $\text{Co}(\text{NH}_3)_6^{3+}$ and some $\text{Co}(\text{II})$ complex other than $\text{Co}(\text{NH}_3)_6^{2+}$. The amount of this $\text{Co}(\text{II})$ complex is much less (1%) than was expected on the basis of Bjerrum's stability constants.¹⁷²

The experiments with CoCl_2 approach the problem from the opposite end. When $\text{Co}(\text{II})$ is added to a solution of concentrated aqueous ammonia, it may be reasonably assumed that it rapidly achieves an equilibrium between the various possible $\text{Co}(\text{II})$ aquo, hydroxyl, and ammine complexes. The observation of an apparent formal potential for this solution that is 170 mV more negative than for the $\text{Co}(\text{NH}_3)_6^{3+}$ solution is a strong indication that $\text{Co}(\text{NH}_3)_6^{3+}$ is not being formed. The redox behavior may then represent something similar to process D in Figure 17. Eventually the CoCl_2 solution forms $\text{Co}(\text{NH}_3)_6^{3+}$ by electrolysis, as was determined from the spectroscopic measurements. However, this only occurs after several hours. It may be that a very small amount of $\text{Co}(\text{NH}_3)_6^{2+}$ is continuously electrolyzed to the thermodynamically stable $\text{Co}(\text{NH}_3)_6^{3+}$. This could explain the long time required for electrolysis.

The results in Table XV show the apparent formal potential to be fairly pH-independent in 14.8 M NH_3 . The differences between E_f values at 6 and 14.8 M NH_3 can be attributed to medium effects (e.g., junction potential differences). These factors argue against a mixed potential

for this system, although pH-independence of a process like D in Figure 17 is difficult to rationalize.

As a consequence of this work, the stability of $\text{Co}(\text{NH}_3)_6^{2+}$ appears to be much lower than previously reported.^{165,166,172} The experimental result of Bartelt¹⁶⁵ on a platinum RDE could not be duplicated. The E° for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ was, in fact, not observed. A mixed potential, however, was determined to be near previously reported values of the standard potential. It is our opinion that this mixed potential could easily be mistaken for the standard potential in potentiometric measurements, such as those done by Bjerrum.¹⁷² The dubious nature of the actual value for the standard potential would seem to preclude extensive speculation regarding the anomalous value of k_{ex} for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ electron exchange.

B. Activation Parameters for Heterogeneous Electron Transfer Reactions

1. Introduction

The measurement of the rate constant for electron transfer in the adsorbed state, k_{et} , by fast cyclic voltammetry (Chapter V) allows a determination of the thermodynamic activation parameters for an adsorbed reactant. If Equations 1.5 and 1.6 are combined the following relationship is obtained,

$$\ln k_{et} = \ln \kappa v_p - (\Delta G^*)^E/RT \quad (7.3)$$

Substituting for $(\Delta G^*)^E$ gives

$$\ln k_{et} = \ln \kappa v_p + (\Delta S^*)^E/R = (\Delta H^*)^E/RT \quad (7.4)$$

It is clear from Equation 7.4 that the temperature dependence of k_{et} can be used to find the enthalpy of activation from the precursor state $(\Delta H^*)^E$ from the slope of a plot of $\ln k_{et}$ versus T^{-1} . If one knows or assumes a value for κv_p , the activation entropy for the precursor state $(\Delta S^*)^E$ can be determined from the intercept of such a plot. For a rigorous treatment the activation parameters should be evaluated at a fixed coverage (or surface concentration) of the adsorbed reactant to eliminate the effect of adsorbate-adsorbate interactions. Consequently, k_{et} must be determined for a fixed adsorbate coverage and electrode potential as a function of temperature.

2. Results

The complexes $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ and cis- $\text{Co}(\text{en})_2(\text{NCS})^+$ were chosen for this study. They exhibited reproducible fast cyclic peaks with gold electrodes that occurred at sufficiently positive electrode potentials to minimize

the interference of proton reduction current. The rate constant for electron transfer could be evaluated at different coverages from a single fast cyclic peak. Equation 5.21 gives the dependence of k_{et} on the surface concentration of the reactant at various points on the cyclic voltammetric peak. These different coverages were necessarily at different electrode potentials. (Different points on the cyclic peak correspond to different electrode potentials as well as different adsorbate concentrations.)

The procedure used to obtain values of k_{et} at constant potential and constant surface concentration was as follows:

- (i) Calculate k_{et} at several electrode potentials from Equation 5.21 for several temperatures.
- (ii) Interpolate values for $\ln k_{et}$ and E for a fixed surface concentration of the reactant.
- (iii) From knowledge of the Tafel slope $(\partial \ln k_{et} / \partial E)_\Gamma$ extrapolate the $\ln k_{et}$ values to a single electrode potential.

The necessary Tafel slope was determined from plots of $\log (i)_{F\Gamma}$ against $E_{F\Gamma}$, where $F\Gamma$ signifies the reactant surface charge density. Variation of $(i)_{F\Gamma}$ with $E_{F\Gamma}$ was achieved by changing the potential sweep rate from 2 to 50 V s^{-1} . Figure 20 shows an example of this type of plot for $80 \text{ } \mu\text{M Co(NH}_3)_5\text{NCS}^{2+}$ on gold for various surface charge densities at 25.0°C . Because $(i)_{F\Gamma}$ is proportional

Figure 20. Tafel plots from fast cyclic voltammetry at various surface charge densities of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ on a gold electrode at 25.0°C. The supporting electrolyte was 0.1 M NaClO_4 . Triangles, squares, and circles represent sweep rates of 20, 10, and 5 V s^{-1} , respectively.

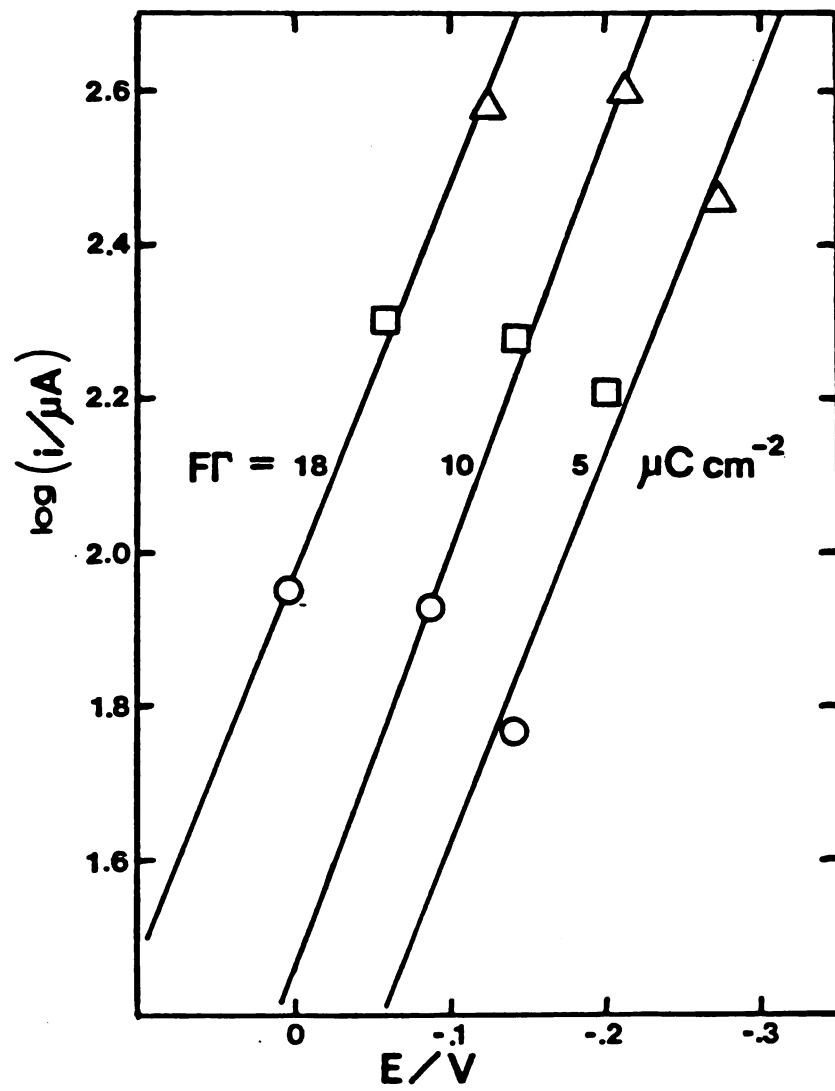


Figure 20

to $(k_{\text{et}})_{\text{FR}}$ (from Equation 5.21), the slopes of these lines give the Tafel slopes that were required. Tafel slopes for various coverages were found for each temperature. The average Tafel slope for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ was $14.3 \pm 0.1 \text{ V}^{-1}$. These slopes seemed to be fairly independent of coverage and temperature.

The results for the activation plots of $\ln(k_{\text{et}})_{\text{E,FR}}$ against T^{-1} are listed in Table XVI for both $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ and cis- $\text{Co}(\text{en})_2(\text{NCS})_2^+$. The rate constants were measured with a non-isothermal cell arrangement, where the reference electrode compartment was maintained at 25.0°C regardless of the temperature in the working compartment. Cyclic voltammograms were recorded at six different temperatures in the range $6 - 60^\circ\text{C}$. The quantity κv_p was assumed to be 10^{13} s^{-1} .^{8,59} As Table XVI shows, the enthalpy and entropy of activation from the precursor state are not very dependent on the surface concentration of the reactant (precursor). The difference noted for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ with $\text{FR} = 5 \mu\text{C cm}^{-2}$ may result from a less certain value of k_{et} at this low coverage ($\sim 20\%$ of maximum coverage). In this case, $\text{FR} = 5$ corresponds to the trailing edge of the fast cyclic reduction peak. This portion of the peak appears at more negative potentials, where the background correction for proton reduction current is less certain. Apart from this one result, fairly good agreement is obtained between activation parameters determined at surface

Table XVI. Activation Plot Results at a Gold Electrode.^a

Complex	C _b (μM)	FR (μC cm ⁻²)	Slope	Inter- cept	r ^{2b}	ΔH* (kJmol ⁻¹)	ΔS* ^c (Jmol ⁻¹ deg ⁻¹)
Co(NH ₃) ₅ NCS ²⁺	80	18	-6950	26.5	0.996	+57.8	-28
		10	-7220	26.9	0.950	+59.8	-25
		5	-7880	28.6	0.974	+65.6	-11
c-Co(en) ₂ (NCS) ₂ ⁺	20	20	-2240	9.72	0.984	+18.4	-170
		10	-2430	10.2	0.952	+20.1	-160

^aThe supporting electrolyte was 0.1 M NaClO₄ + 2 mM HClO₄. Plots were for ln k_{et} against T⁻¹, for k_{et} evaluated at 0 mV and 10 Vs⁻¹ and 6 temperatures ranging from 6 to 60°C.

^bThe coefficient of linear regression; r² = 1 for a perfect fit.

^cSimilarly large negative values of ΔS* were found at silver and mercury electrodes for these complexes.⁹⁶

concentrations which differ by as much as a factor of 2. A striking difference is observed between activation parameters for these two complexes.

3. Discussion

Both of these complexes are strongly adsorbed at gold electrodes (Chapter III), and exhibit nearly zero-order overall reaction orders for reduction (Chapter V).¹¹ Kinetics probe results for analogous chromium complexes indicated that the cis-diisothiocyanate complexes were more strongly adsorbed than the monoisothiocyanate complexes (Chapter IV). The difference between mono- and di-bridged complexes is readily apparent from the activation parameter results in Table XVI. Although these results may be in error by as much as 20-30% because of the great deal of derivation employed; clearly, the two complexes are different both enthalpically and entropically. This result is somewhat unexpected for activation from the precursor state.

The activation from the precursor state might be expected to have only a small entropic contribution. The structure of (and around) the adsorbed precursor should be similar to the adsorbed transition state. Metal-ligand bonds must stretch, but no solvent should be displaced or significantly reorganized in the activation process. The large, negative entropies (especially for the cis complex)

are therefore surprising. It is possible that the orientation of the adsorbed reactant is substantially different from that of the activated complex. The isothiocyanate ligands could prefer to be adsorbed at an angle to the electrode surface,¹⁴⁶ and then reorient perpendicular to the electrode surface in the activated complex. For the cis complex this could even entail the transformation from a di-bridged precursor to a mono-bridged activated complex. However, from such a small amount of data these speculations are not well supported although measurements at silver and mercury surfaces had similar results.⁹⁶

C. Maxima in Pulse Voltammetry at an RDE

As was mentioned in Chapter II, pulse voltammetry at an RDE was occasionally used to determine the electron transfer rate constants. This necessarily required some characterization of the technique under various conditions. At slow electrode rotation speeds (<200 rpm) maxima were invariably obtained in the voltammetric waves. The apparent limiting currents were also observed to be lower than expected on the basis of the Cottrell Equation.⁷⁹ These effects were initially attributed to a reactant depletion effect, which results from the inability of reactant and product diffusion to keep pace with the electrochemical reaction. The reactant depletion can also result from the adsorption of the reactant.^{178,179} The maximum arises

for nernstian reactions because the rate of reduction of an adsorbed reactant is limited by the diffusion of the product away from the surface.¹⁷⁸ As a result, the additional current for the reduction of the adsorbed reactant is present when the current is sampled in normal pulse voltammetry.¹⁷⁹ Maxima for outer-sphere complexes such as $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, and cis- $\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ were typically smaller than for inner-sphere complexes such as $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ and cis- $\text{Co}(\text{en})_2(\text{NCS})_2^+$. The depletion effect was thought to result from different causes for outer- and inner-sphere reactants.

At rotation speeds in the range 300 - 1000 rpm the depletion effect was overcome for the outer-sphere complexes. No maxima were observed at platinum or gold electrodes, and the limiting current was as expected for pulse voltammetry. The time after the application of the potential pulse at which the current was sampled was 48 ms for these experiments (with a PAR 174 potentiostat). On-line normal pulse experiments indicated that faster rotation speeds over a smaller range were required to obtain correct kinetics parameters with shorter pulse measurement times. For example, with $\text{Co}(\text{NH}_3)_6^{3+}$ the appropriate rotation speed range was ~500 - 750 rpm for a pulse measurement time of 20 ms. The upper limit was determined by the point at which the limiting current is no longer correct for pulse voltammetry.⁷⁹

Because some inner-sphere complexes at platinum and gold exhibited persistent maxima at any rotation speed, it was thought that this behavior could be used as another criterion for an inner-sphere mechanism. Figure 21 shows a typical result for the pulse voltammetric wave of 0.5 mM $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ in 0.1 M NaClO_4 + 2 mM HClO_4 at a gold RDE. The rotation speed was 540 rpm, and the potential was scanned at 2 mV s^{-1} . This maximum was still observed at a rotation speed of 1000 rpm. With digital simulation¹⁷⁸ and curve fitting, perhaps the extent of adsorption could be found from the shape of the maximum. By using such simulations the kinetics and adsorption might be determined from a single experiment, which would be a great advantage for solid electrode experiments.

Figure 21. Pulse voltammogram for 0.5 mM $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ at a gold RDE in 0.1 M NaClO_4 + 2 mM HClO_4 . The rotation speed was 540 rpm. The potential was scanned at 2 mV s⁻¹.

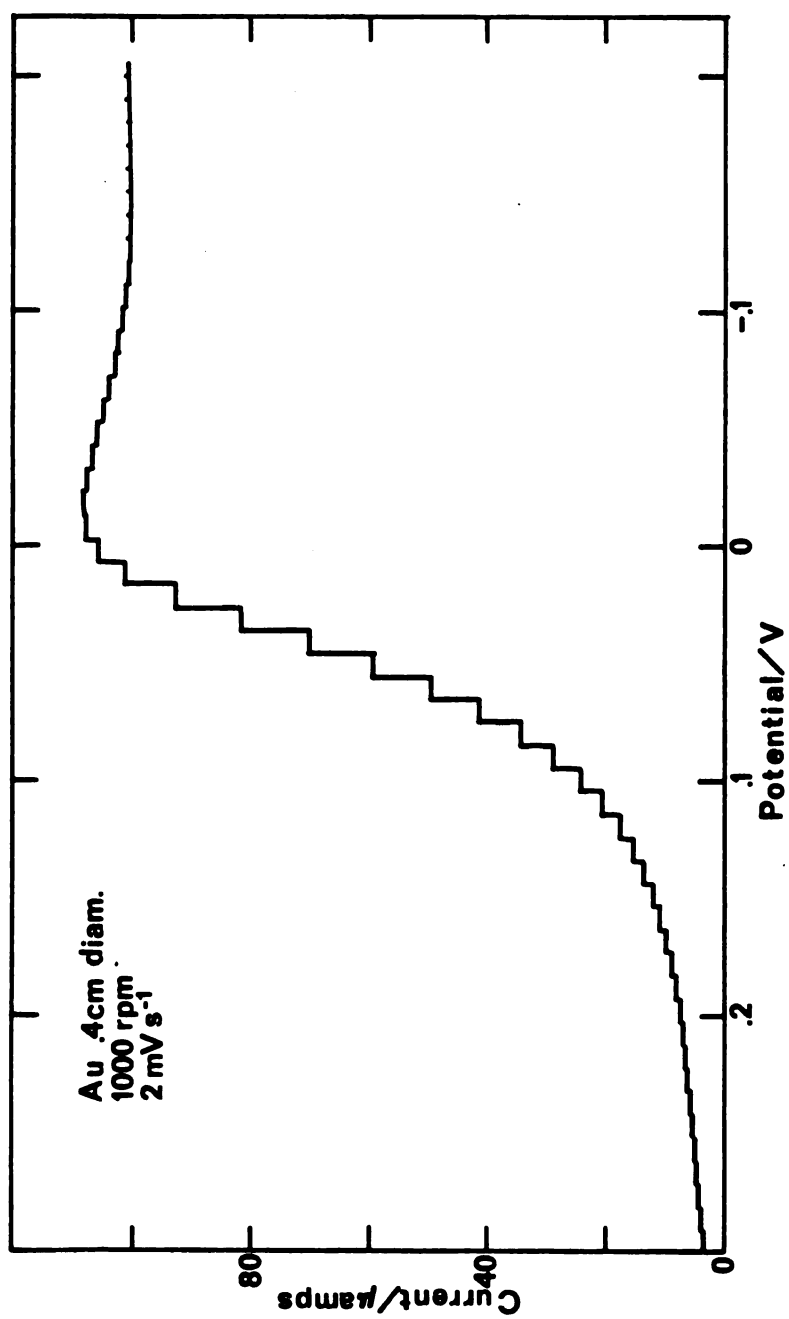


Figure 21

CHAPTER VIII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The cobalt(III) ammines proved to be a versatile group of reactants for the investigation of kinetics and double layer structure at platinum and gold electrode surfaces. Their reactivity was found, for the most part, to depend on the types and arrangement of the coordinated ligands. Complex adsorption and inner-sphere catalysis were strongly dependent upon the nature of the bridging ligand. Some generalizations with regard to ligand types and reactivity at platinum and gold are possible. Fluoro, ammine, and aquo ligands do not induce adsorption or inner-sphere mechanisms.^{10,39} Chloro and bromo ligands induce reactant adsorption and intrinsic catalysis of the electron transfer reaction.^{11,40} Mono-bridged halide complexes are catalyzed the most of all complexes investigated, showing an overall catalysis (inner- versus outer-sphere) of up to 10^7 -fold and an intrinsic catalysis as high as 200-fold (Chapter V). Isothiocyanato ligands induce strong adsorption of the reactant, but cause the electron transfer rate to be intrinsically decatalyzed by an inner-sphere mechanism.^{11,40} Pyridine and pyridyl ligands induce reactant adsorption

through π orbitals or van der Waals interactions, but are not effective as mediators of the electron transfer.¹⁴⁹

Adsorbed iodide was very effective in blocking inner-sphere electron transfer mechanisms.^{10,11,40} The covalent nature of the iodide layer allowed outer-sphere rates of reduction to be easily determined for normally inner-sphere complexes. This greatly simplifies the task of assessing inner-sphere catalysis. Iodide-treated electrodes were also less susceptible to deactivation by solution impurities. The adsorbed iodide apparently renders platinum and gold surfaces inert with respect to further adsorption.

The measurement of reactant adsorption was more difficult than anticipated. Single-step chronocoulometry gave erroneous results for platinum and gold electrodes. This technique could not account for substantial changes in the electrode capacitance caused by reactant and product adsorption.¹¹ The apparent overall reaction order for the electron transfer reaction was used to roughly quantify the amount of reactant adsorbed.¹⁰ The use of outer-sphere reactions to "probe" for adsorbed nonreacting species offered a means to determine complex ion adsorption without interference from adsorbing anions produced by reduction of the adsorbed complex. By far the most useful and accurate technique was fast cyclic voltammetry.¹¹ The capacitance changes that gave erroneous chronocoulometry results were easily accounted for by integrating fast cyclic

peaks over a baseline corresponding to the nonfaradaic capacitance.¹¹ The electron transfer rate from the precursor state could also be calculated from these peaks. However, not all adsorbed complexes produced fast cyclic peaks.

Intrinsic catalysis at platinum and gold surfaces seems to be limited to mono-atomic, mono-bridged complexes, such as $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. Other complexes that are as strongly adsorbed, but involve multi-bridged intermediates or poly-atomic bridges, do not exhibit a lowering of the intrinsic barrier to electron transfer. In fact these latter complexes appear to be intrinsically decatalyzed as a result of their adsorption. These results indicate that the catalysis is to a large degree determined by the vibrational freedom of the cobalt-ligand bond. The short mono-atomic chloro- and bromo-bridged complexes weaken the cobalt-ligand bond through donation of σ electron density to the electrode surface. The weaker force constant causes a decrease in the reorganization energy ΔG^* for electron transfer. The weakening of the cobalt-ligand bond is attenuated for poly-atomic bridging ligands. It was proposed that for some ligands with substantial π orbitals the cobalt-ligand bond may actually be strengthened through additional π orbital electron density acquired from the electrode surface, which would also stabilize the adsorbed reactant by d- π back-bonding (Chapter V).

Platinum and gold have been observed to be generally more catalytic than mercury electrodes. Much, but not all, of this catalysis is a result of a greater extent of reactant adsorption on the solid metal surfaces. The catalysis of outer-sphere complexes is probably caused by more anion adsorption on platinum and gold than on mercury. The solid electrode results are less reproducible and more difficult to obtain than similar results at mercury electrodes.³⁹

Suggestions for Further Work

The intramolecular electron transfer reactions for cobalt-ligand-platinum complexes could be used to test many of the above conclusions, especially since vibrational spectroscopy might be used. Surface enhanced Raman spectroscopy (SERS) could possibly be effective in determining the same kind of information. The reproducibility and unusual characteristics of iodide-treated platinum and gold electrodes make them suitable for use in other (perhaps, analytical) applications. The reactivity of complexes containing sulfur heterocyclic ligands might prove interesting in comparison to the nitrogen heterocycle results of Chapter VI.

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