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CORRELATION OF ELECTRODE KINETICS WITH SURFACE STRUCTURE.(U)
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Correlation of Electrode Kinetics
with Surface Structure

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Michigan State University

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Abstract

The overall objective of this research ~~program~~ is to develop ~~our~~ [illegible] understanding of the relationships between the kinetics and mechanisms of some simple heterogeneous electron-transfer reactions and the molecular structure of the reactant and the electrode-solution interface. Emphasis is being placed on studies of transition-metal redox couples involving substitutionally inert complexes in aqueous media at a number of solid metals as well as at mercury electrodes. These reactions provide excellent model systems for studying structural effects in electron transfer, since they are mechanistically simple and either inner- or outer-sphere reaction mechanisms can be induced, depending on the ability of the coordinated ligands to bind to the electrode surface. Problems that were addressed included: (1) the effects of varying the nature of the metal surface upon the rates of inner- and outer-sphere reactions, (2) the influence of ionic specific adsorption upon the reactivities of outer-sphere pathways, (3) determination of the influence of reactant specific adsorption to the reorganization energy barrier for electron transfer, and (4) elucidation of the role of reactant-solvent interactions in redox kinetics and thermodynamics.

Introduction

The central unifying theme of this research program is to develop our fundamental understanding of the ways in which the rates and mechanisms of electrode reactions depend upon the structural properties of the reactant and the interphasial region where the reaction occurs. Emphasis has been placed on experimental studies of the electrochemical kinetics and thermodynamics of simple transition-metal redox couples in aqueous media, primarily Co(III)/(II) and Cr(III)/(II), on a variety of solid metal substrates. These reactions provide especially suitable "model systems" with which to explore reactivity-structure relationships. Thus either "outer-sphere" or "inner-sphere" electrode reactions can provide the predominant electron transfer pathway, depending upon the ability of the coordinated ligands to bind to the electrode surface. Outer-sphere pathways (i.e. where there is only a weak nonspecific interaction between the reactant and the electrode within the transition-state) are of particular theoretical interest since they have the unique feature that no chemical bonds are required to be broken or formed during the reaction. Inner-sphere pathways (i.e. where the reactant is bound directly to the electrode, usually via a coordinated ligand, in the transition state) usually correspond to cases where the electrode surface exerts a direct "electrocatalytic" [illegible] interactions between the reactant and electrode surface act to decrease the activation energy to electron transfer compared with that for the corresponding alternative outer-sphere route. The primary aim of the research program is to gain fundamental new insights into how the structural properties of electrochemical systems, in particular the electrode material and the reactant, influence the extent of this electrocatalysis for mechanistically simple electrode reactions.

Three chief types of experimental quantities have been evaluated: (i) heterogeneous electron transfer kinetic parameters, (ii) thermodynamics of adsorption, particularly for electrochemical reactants, (iii) redox thermodynamics. Although (i) provides the direct kinetic information with which to explore electron transfer processes, (ii) and (iii) provide essential thermodynamic information which allows the structural factors influencing this reactivity to be assessed.

Recently, we have initiated a fourth type of measurement: surface-enhanced Raman spectroscopy (SERS) of adsorbed reactant molecules. This should allow microscopic insight to be obtained into the nature of adsorbate-electrode interactions and how these affect electrochemical reactivity.

The major segments of these research activities will now be described in turn. References are given, where appropriate, to the publications resulting so far from this program wich are listed in pages 18-19. These sources can be consulted for further details.

I. Redox Thermodynamics: "Half-Cell" Parameters

For a number of reasons, it is very desirable to evaluate the formal electrode potential E_f for redox couples for which electrode kinetic parameters are being obtained. This potential corresponds to the point where the free energy driving force ΔG^o_{rc} for the redox couple $[= F(F-E_f)]$ equals zero. In addition, it is desirable to evaluate the individual enthalpic and entropic components of ΔG^o_{rc}: ΔH^o_{rc} and ΔS^o_{rc}, respectively. We have shown that the "reaction entropy" ΔS^o_{rc} is a particularly instructive quantity since it is essentially equal to the difference between the ionic entropies of the reduced and oxidized species $(\overline{S}^o_{red}-\overline{S}^o_{ox})$.[1] For redox couples that involve no major structural differences between the reduced and oxidized forms, ΔS^o_{rc} should reflect the changes in the extent of solvent polarization ("ordering") around the reacting species brought about by electron transfer. Although ΔS^{o}_{rc} is an "extrathermodynamic" (half-cell) quantity, we have pointed out that estimates can be obtained to a very good approximation from the temperature dependence of the formal potential using a nonisothermal cell arrangement with the reference electrode held at a fixed temperature.[1] We have evaluated reaction entropies for a wide range of transition-metal couples of the type M(III)/(II) in aqueous solution.[1-3] It was found that ΔS^{o}_{rc} is extremely sensitive to the chemical structure as well as the charge of the coordinated ligands, indicating the importance of specific, short-range solvation to the thermodynamics of such redox processes. Publication 1 represents the first systematic study of reaction entropies for a range of systems of interest to fundamental redox kinetics. Since reaction entropies provide a direct monitor of the changes in solvent polarization necessary for electron transfer to occur involving an isolated redox center, they are of particular significance to outer-sphere electron-transfer processes in both homogenous and heterogeneous environments. The utilization of our measurements in redox kinetics so far has included: (i) the detection of a contribution from short-range solvent reorganization to the Franck-Condon barrier to outer-sphere electron transfer,[1,4] (ii) the demonstration of a relationship between the free-energy barriers to outer-sphere electron self-exchange with reaction entropies, (iii) the elucidation of ion-solvent interactions in the transition-state for outer-sphere electrochemical reactions,[5] (see below), and (iv) the resolution of anomalies between experiment and theory for highly exothermic homogeneous redox processes.[6]

Another recent study which has provided strong evidence of the importance of short-range solvent polarization to redox thermodynamics has involved the effect upon E_f of substituting heavy water (D_2O) for H_2O solvent.[7] Although a number of redox couples not containing replaceable protons (e.g. ferrocinium/ferrocene, $Ru(bpy)_3^{3+/2}$, $Ru(NH_3)_6^{3+/2+}$(at low pH) exhibit essentially identical formal potentials in H_2O and D_2O (against an aqueous s.c.e.), couples containing aquo ligands were found to yield values of E_f in D_2O that were substantially (up to 50 mV) more positive than in H_2O.[7] These potential differences were found to be porportional to the corresponding values of ΔS_{rc}, and were ascertained to be chiefly due to values of ΔS_{rc} that are greater in D_2O than H_2O. These results are in harmony with the known greater "hydrogen bonding" capability of D_2O yielding a greater degree of field-assisted solvent ordering induced by the aquo ligands in the higher oxidation state.

II. Electrochemical Activation Parameters

In view of the useful information on the thermodynamics of redox processes obtained by evaluating the entropic component ΔS^o_{rc} of the bulk thermodynamic driving force, it is also desirable to separate the electrochemical free energy of activation for the redox couple $\Delta G^{\ddagger}_{rc}$ into its entropic and enthalpic components $\Delta S^{\ddagger}_{rc}$ and $\Delta H^{\ddagger}_{rc}$. The measurement and theoretical significance of electrochemical activation parameters has given rise to a good deal of confusion over the years, as a result of the ambiguity of how to control the electrical variable as the temperature is altered. However, following a detailed analysis of the problem we have concluded that electrochemical activation parameters can be determined that allow a good deal of insight into the physical nature of the activation process.[5,8] For the present systems, the most instructive are the so-called "ideal" activation parameters which are obtained from the temperature dependence of the electrochemical rate constant at a constant electrode potential using a nonisothermal cell arrangement.[5] Since it is very likely that these conditions maintain the Galvani potential difference essentially constant, the "ideal" parameters are essentially equal to the entropy and enthalpy of activation $\Delta S^{\ddagger}_{rc}$ and $\Delta H^{\ddagger}_{rc}$ at that electrode potential.[5,8] Similarly to ΔS^{o}_{rc}, the activation entropy $\Delta S^{\ddagger}_{rc}$ is of particular interest since it reflects the changes in solvent structure necessary to form the transition state from the bulk reactant. Additionally, the apparent values of $\Delta S^{\ddagger}_{rc}$ will be influenced by values of the electron tunneling probability that are substantially less than unity (i.e. by nonadiabaticity).

We have found that the large variations in the outer-sphere electroreduction rates of Cr(III) and Co(III) complexes at the mercury-aqueous interface brought about by varying the nature of the coordinated ligands are due to substantial differences in $\Delta S^{\ddagger}_{rc}$ as well as $\Delta H^{\ddagger}_{rc}$.[5] These variations in $\Delta S^{\ddagger}_{rc}$ closely parallel those in ΔS^{o}_{rc} and suggest that such electrode reactions are adiabatic, or nearly so, and the proximity of the mercury electrode does not exert a major influence upon the solute-solvent interactions in the transition state for outer-sphere electron transfer.[5]

III. Environmental ("Double-Layer") Effects upon Electrode Kinetics

A. Distinction between Inner-Sphere and Outer-Sphere Pathways

In principle, studies of the response of the measured (apparent) rate constant k^{E}_{app} to changes in the interphasial composition can yield valuable information on the geometry of the transition state in the interphasial region,[8] and in particular provide diagnostic criteria for distinguishing between inner- and outer-sphere pathways.

Some time ago, Weaver and Anson [Inorg. Chem. 15, 1871 (1976)] noted that the addition of specifically adsorbing iodide anions to perchlorate electrolytes at a constant total ionic strength induced *decreases* in k^E_{app} for the electroreduction of a number of cationic Cr(III) aquo complexes containing adsorbing anions, instead of the large increases in k^E_{app} that are expected from the attraction between the reactant and the adsorbed anions. However, for otherwise similar Cr(III) complexes not containing adsorbing anions, rate *increases* in reasonable agreement with expectations were observed. The qualitative explanation offered for the former result was that the presence of co-adsorbed iodide destabilizes the inner-sphere transition states by means of repulsive interactions between adsorbed nonreacting I^- and the bridging anion. This repulsion outweighs the attraction between the I^- and the more distant Cr(III) center. More recent experiments for the electroreduction of Cr(III) and Co(III) ammine complexes at mercury electrodes in conjunction with other diagnostic criteria of mechanism have so far verified the validity of these early assertions and shown that inner-sphere pathways are frequently favored over the ever-present outer-sphere route even at a poor electrocatalyst such as mercury.[9]

We have recently found that a related but more striking distinction between reactions following inner- and outer-sphere pathways can be made at some solid electrode-aqueous interfaces.[10] It has been found that iodide adsorption at platinum and gold electrodes is sufficiently strong so that monolayers are formed upon contact even with small (millimolar) bulk iodide concentrations. Moderate rate increases upon the addition of iodide were obtained for reactions such as $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5F^{2+}$ reduction that are expected to follow outer-sphere pathways at Pt and Au in perchlorate electrolytes. In contrast, the reduction rates of $Co(NH_3)_5Cl^{2+}$ on both surfaces were decreased by factors of ca 10^4-10^5 upon iodide addition.[10] Marked rate decreases were also observed for other Co(III) reactants containing halide and pseudohalide anions which are expected to act as bridging ligands.[10] It was concluded that Co(III) halide complexes are reduced via strongly favored inner-sphere pathways on "clean" Pt and Au surfaces that are eliminated on the iodide-covered surfaces.[10] Similar though less striking results were also obtained for the reduction of Co(III) and Cr(III) complexes at silver electrodes.

These findings are important because they demonstrate that systematic variations in inner-layer composition can be employed to provide a firm experimental basis for the distinction between inner- and outer-sphere electrode reaction pathways without recourse to involved (and perhaps untrustworthy) double-layer models. This is an essential first step towards unraveling the connections between surface structure and reactivity in a manner analogous to that achieved with homogeneous redox systems.[8]

B. Tests of Coulombic Double-Layer Models for Outer-Sphere Reactions

Aside from employing double-layer effects as mechanistic criteria, it is also of considerable interest to test the quantitative applicability of simple electrostatic models such as the Frumkin model[8] to the description of double-layer effects upon the kinetics of outer-sphere reactions. These double-layer influences can be extremely large (often a factor of 10^2-10^3 in k^E_{app}), particularly at solid electrodes where extensive specific adsorption of the supporting electrolyte ions can result in large values of the average potential at the reaction plane ϕ_{rp}. Although a considerable number of experimental tests of the simple Frumkin model have been made over the years, the effects of specific ionic adsorption of the supporting electrolyte upon electrode kinetics have only recently begun to be studied systematically.

We have been comparing the influence of specifically adsorbed anions upon the outer-sphere reduction rates of various Co(III) and Cr(III) complexes at the mercury-aqueous interface with the predictions of the simple Frumkin model (eqn. (5)).[9,11] Two types of experimental conditions have been employed to coincide with the available double-layer compositional data: (i) mixed electrolytes at constant ionic strength (usually 1 M) containing various ratios of the specifically adsorbing anion (e.g. I^-, Br^-, Cl^-, NO_3^-, N_3^-, NCS^-, etc.) with a weakly or nonadsorbing anion (F^- or ClO_4^-), using double-layer data obtained from capacitance measurements via the Hurwitz-Parsons analysis;[9] (ii) single electrolytes of varying ionic strengths, using double-layer data obtained from surface tension and capacitance measurements using the classical Grahame analysis.[11] For the reduction of Co(III) ammines for which the effect of a variety of anionic adsorbates could be scrutinized, the variations in $\log k^E_{app}$, $\Delta\log k^E_{app}$, observed upon altering the electrolyte composition were consistently found to be similar (±10%) to the corresponding quantities calculated from the Frumkin equation.[9,11] We have consistently observed that for a given outer-sphere reaction the effect of discrete adsorbed charge q' is very similar to the effect of the electrode charge q^m itself, in harmony with the simple Frumkin model.[9,11,12] This conclusion, although perhaps surprising, applies quite generally to all the outer-sphere reactions involving metal complexes that we have studied so far at the mercury-aqueous interface (including Cr(III)/(II), Co(III)/(II), $Eu^{3+/2+}$, and $V^{3+/2+}$ redox couples). This behavioral simplicity has important implications to the current research program because it indicates that quantitative electrostatic double-layer corrections can be applied to outer-sphere rates even in the presence of extensive anionic adsorption as is commonly encountered at electrocatalytic solid-aqueous interfaces. The application of such corrections enables the possible additional influence of the electrode surface upon electrochemical reactivity, arising from such factors as inefficient electron tunneling (i.e. nonadiabaticity) and nonelectrostatic reactant-electrode interactions, arising for example from hydrogen bonding between reacting species and adsorbed water molecules.

There has been some controversy over the applicability of eqn. (5) to oxyanion reductions, particularly perbromate [R. deLevie, M.Nemes, J. Electroanal. Chem. 58, 123 (1975); R. Guidelli, M. L. Foresti, ibid, 67, 231 (1976)]. In view of our success in applying eqn. (5) to Co(III) ammine reductions, we have recently undertaken a series of parallel measurements of the kinetics of perbromate reduction in the same mixed and single electrolytes in which we have previously scrutinized double-layer effects upon transition-metal complexes (E. W. Schindler, M. J. Weaver, to be published). The results indicate that the kinetics of perbromate reduction exhibit noticeably greater discrepancies with the predictions of the Frumkin model than seen for Co(III) ammine reductions, although the extent of these discrepancies at mercury electrodes is not enormous.

C. Influence of Electrode Material on Outer-Sphere Electrochemical Reactivities

It is expected from theoretical considerations that the chemical nature of the electrode material should influence the measured rate constant for outer-sphere pathways only via the electrostatic work terms embodied in the Frumkin equation for double layer effects. Consequently, if these work terms arise only from averaged coulombic forces the only variations in k_{app}^{E} brought about by altering the electrode material at a given electrode potential E will arise from variations in ϕ_{rp}. As a first step in exploring the electrocatalytic activity of solid metal surfaces towards transition-metal reactants, we have monitored the effects of altering the electrode material from mercury to silver, platinum, and gold upon the (apparently) outer-sphere electroreduction of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5F^{2+}$, and $Co(NH_3)_5OH_2^{3+}$ and the electro-oxidation of Cr^{2+}, Eu^{2+}, V^{2+}, and Ru^{2+} in noncomplexing electrolytes (KPF_6 and $NaClO_4$).[13] It was found that the variations in k^E_{app} with the electrode material for the Co(III) ammines were relatively small and approximately in accordance with the expected variations from the Frumkin model.[13] However, the values of k^E_{app} for the aquo reactants were less reproducible and generally much smaller (by factors up to 10^8) on the solid surfaces compared with mercury electrodes. We have speculated that these dramatically and unexpectedly large substrate effects for the aquo reactants arise from the influence of the inner-layer water structure on the reactant-solvent interactions experienced by these reactants at their plane of closest approach.[13] Aquo complexes appear to engage in extensive hydrogen-bonding with the surrounding solvent. Therefore it is possible that the more "hydrophilic" solid metals (Ag, Pt, and possibly Au) may prevent the aquo reactants from engaging in stabilizing hydrogen bonding with interphasial water, at least not to the same extent as in the bulk solution or at the weakly hydrophilic mercury surface, rendering the work terms extremely unfavorable at Ag, Pt, and Au. On the other hand, cationic ammine complexes are known to be relatively weakly solvated so that the insensitivity of the Co(III) ammine systems to the interphasial solvent structure is not surprising.

Although these interpretations are unsubstantiated at the present time, it seems quite likely that the nature of the metal substrate could profoundly influence the reactivity of those outer-sphere electrode processes for which the reactant interacts intimately with the interphasial solvent. These may be termed solvent "structure-demanding" processes. We have also observed that the electrode kinetics for perbromate reduction are strikingly different at silver compared to mercury electrodes, suggesting that this reaction may also be of the "structure-demanding" type (E. Schindler, K. Guyer, M. J. Weaver, unpublished results). In contrast, the especially simple "Frumkin-like" behavior of the ammine complexes at all the metal substrates studied so far suggests that they could provide valuable "kinetic probes" for evaluating the ionic composition of metal-electrolyte interfaces from rate measurements using the Frumkin model.[10,11]

D. Relative Rates of Inner- and Outer-Sphere Pathways

As noted above, an important objective of this research program is to unravel the factors that favor inner-sphere ("catalytic") over outer-sphere ("noncatalytic") pathways. The simplest way to consider such environmental influences upon redox reactivity is to treat the overall reaction as a two-stage process involving the formation from the bulk reactant of a stable precursor intermediate in a geometrical configuration suitable for electron transfer, followed by a separate activation step (Franck-Condon barrier).[14] The measured electrochemical rate constant is then given by $k_{app} = K_{ad}\ \nu \exp(-\Delta G^{\ddagger}_{rc}/RT)$, where K_{ad} is the equilibrium constant ("work term") for the formation of the precursor intermediate, ν is a frequency factor describing the rate of passage over the activation barrier, and $\Delta G^{\ddagger}_{rc}$ is the free energy of reorganization from the precursor to the activated states. Differences in the rate constants k^{is}_{app} and k^{os}_{app} for a given overall reaction occurring via inner- and outer-sphere reaction pathways may therefore be due to differences between $(\Delta G^{\ddagger}_{rc})_{is}$ and

$(\Delta G^{\ddagger}_{rc})_{os}$, and/or between K^{is}_{ad} and K^{os}_{ad}. Since the inner- and outer-sphere routes provide parallel reaction pathways for a given overall reaction, only k^{is}_{app} or k^{os}_{app} can be determined directly at a given surface, whichever is the larger. However, we have shown that semiquantitative estimates of k^{os}_{app} [and $(\Delta G^{\ddagger}_{rc})_{os}$] can often be obtained either from an experimental value of k^{os}_{app} for a structurally similar reactant coupled with the relative rates of a pair of outer-sphere homogeneous reactions involving the same reactant pair,[9,10,14] or from the measured kinetics at an electrode surface covered with a monolayer of a tightly bound adsorbate (e.g. I^- on Pt) so that the inner-sphere pathway is eliminated.[10]

Our initial efforts concerned the analysis of the reduction kinetics of $Cr^{III}(NH_3)_5X$, $Cr^{III}(OH_2)_5X$, and $Co^{III}(NH_3)_5X$ complexes (where the bridging ligand X = NCS^-, N_3^-, Cl^-, Br^-) at mercury electrodes.[14] These systems are of particular interest because some reactant specific adsorption data (values of K_{ad}) are avilable so that estimates of $\Delta G^{\ddagger}_{rc}$ for inner- as well as outer-sphere pathways can be obtained from the experimental values of k_{app}. It was found for these systems that $(k^{is}_{app}/k^{os}_{app})^E \lesssim 10^2$ and $(\Delta G^{\ddagger}_{rc})^E_{is} \approx (\Delta G^{\ddagger}_{rc})^E_{os}$; i.e. the attachment of these bridging ligands to the electrode surface (i.e. the occurrence of inner-sphere pathways) accelerated the reaction rates simply by providing a larger reactant concentration at the electrode surface and had little influence on the height of the reorganizational barrier to electron transfer.[14]

However, we have found strikingly different behavior for the reduction of $Co^{III}(NH_3)_5X$ and $Co^{III}(en)_2X_2$ at platinum and gold electrodes.[10] For halide bridging ligands ($X=Cl^-$, Br^-), $(k^{is}_{app}/k^{os}_{spp})^E$ is of the order of 10^4-10^6.

We have recently devoted considerable attention to obtaining estimates of K_{ad} for these systems. Although the method of choice, potential-step chronocoulometry turned out to be unsuitable, rough estimates of K_{ad} were obtained using a "kinetic probe" technique which involved monitoring the effect of the adsorbed reactants within a potential region prior to their reduction upon the kinetics of simple outer-sphere reactions such as $Co(NH_3)_5F^{2+}$ reduction (S. W. Barr, M. J. Weaver, to be published). Using these estimates of K_{ad}, we have concluded that a substantial part of 10^4- to 10^6-fold preferences of the reactions for the halide-bridged versus outer-sphere route arise because $(\Delta G^{\ddagger}_{rc})^E_{is} < (\Delta G^{\ddagger}_{rc})^E_{os}$. On the other hand, for X = NCS^- and N_3^-, $(k^{is}_{app}/k^{os}_{app})^E \approx 10 - 10^2$, which suggests that $(\Delta G^{\ddagger}_{rc})_{is} \approx (\Delta G^{\ddagger}_{rc})_{os}$.[10] These reactivity ratios are intriguing since they suggest that the monoatomic bridges Cl^- and Br^-, when attached to catalytically active metals such as Pt and Au where strong covalent bonding is probably involved, are capable of substantially diminishing the reorganization barrier to electron transfer. Similar conclusions have also been reached for the ligand-bridged reduction of Cr(III) complexes at silver electrodes (K. L. Guyer, M. J. Weaver, unpublished experiments).

We have also initiated studies of heterogeneous electron transfer mediated via organic ligands with an examination of the electroreduction kinetics of various Co(III) pentaammine complexes containing pyridine and 4,4'-bibpyridine ligands.[15] It was found that substantially (10^2- to 10^3-fold) faster rates were found for pyridine-containing complexes than for structurally similar complexes not containing aromatic functional groups. These catalyses were traced to the strong specific adsorption of the aromatic ligands on the electrode surface. Parallel adsorption measurements at mercury electrodes using chronocoulometry suggest that the aromatic rings be either flat or edgewise on the surface, presumably as a result of π-ligand-metal interactions. Such "delocalized" electron mediation by aromatic bridging ligands constitutes an interesting new class of inner-sphere electrode reactions.

IV. Other Experiments

Although the emphasis in this research program is on electrode reactions at solid metal-aqueous interfaces, kinetic studies at mercury electrodes also play an important role, particularly in unraveling the details of outer-sphere electron transfer. Some of this work has been summarized above. Four other examples are briefly noted below.

(i) We have compared the corresponding heterogeneous and homogeneous outer-sphere reactivities for a number of transition metal aquo and ammine redox couples (including $Eu^{3+/2+}$, $Cr^{3+/2+}$, $V^{3+.2+}$, $Ru^{3+/2+}$, $Co(NH_3)_6^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$) with the theoretical predictions of the Marcus model, using rate constants corrected for the coulombic work terms (i.e. for diffuse-layer and "primary salt" effects).[16] The application of diffuse-layer corrections was facilitated by employing acidified potassium hexafluorophosphate supporting electrolytes: the PF_6^- anion is relatively noncomplexing and is only very weakly adsorbed at mercury electrodes, even at the potential of zero charge so that $\phi_{rp} \simeq 0$ at this potential. Following these corrections, significant differences were found between the relative free energies and especially enthalpies of activation for corresponding electrochemical and homogeneous processes and the predictions obtained from the usual form of the Marcus model. For reactions involving aquo complexes, the electrochemical activation free energies were somewhat (2-3 kcal $mole^{-1}$) larger than expected, whereas the opposite was found to be true for ammine complexes. These behavioral differences are compatible with the known differences in the planes of closest approach at mercury electrodes for aquo and ammine complexes, and suggest that the closer approach of the more weakly solvated ammine complexes leads to stabilization of the transition state via imaging interactions with the electrode.

(ii) The finding that KPF_6 electrolytes provide a suitably noncomplexing supporting electrolyte that exhibits only very weak PF_6^- specific adsorption even at positive electrode charges and high ionic strengths ($\mu \sim$ 0.1-0.5) opened up the possibility that outer-sphere electrochemical rate constants could be reliably corrected for double-layer effects over a wide range of positive as well as negative electrode charge densities. We have exploited this situation to evaluate plots of double layer-corrected rate constants $\ell n k_{corr}$ versus E for $Cr^{3+/2+}$, $V^{3+/2+}$, and $Eu^{3+/2+}$ aquo couples over wide ranges (0-850 mV) of anodic as well as cathodic overpotentials η, in order to test the prediction of contemporary electron transfer models that the transfer coefficient α should depend upon η.[12] In contrast to the relative constancy of α with varying cathodic overpotential, α for all three couples was found to decrease with increasing anodic overpotential to a much greater extent than predicted by conventional theory. It was concluded that this unexpected result probably arises from strongly anharmonic potential energy surfaces due to major differences in short-range solvent polarization between the oxidized and reduced aquo complexes.[12]

(iii) Following our observation that the substitution of D_2O and H_2O solvent produces dramatic changes in the redox thermodynamics for aquo redox couples, we have explored the corresponding effects upon the outer-sphere electrochemical redox reactivity of transition-metal complexes. Similarly large solvent isotope effects were observed upon the electrode kinetics of aquo complexes, which were found to include unexpectedly large differences in the intrinsic barriers $\Delta G_i^{\ddagger}$ between D_2O and H_2O.[17]

These experiments, as well as those discussed above, are allowing us to assemble an increasingly detailed picture of the nature of such outer-sphere electrode reactions. In particular, they illustrate the importance of the ligand composition in determining the structure of the surrounding solvent and the contribution of short-range solvent polarization to the electrochemical activation process.

(iv) We have recently monitored the reduction rates of $Cr(OH_2)_6^{3+}$ and $Cr(NH_3)_6^{3+}$ at mercury electrodes in electrolytes containing univalent, divalent, or trivalent cations with systematically varying atomic number in order to explore the role of the supporting electrolyte cation in the electrode kinetics of these archetypically simple outer-sphere reactions.[18] Comparison between the rate responses to changes in the supporting electrolyte cation for these two reactions can shed considerable light upon the cation effects upon the potential profile in the double-layer. Thus it appears very likely that $Cr(OH_2)_6^{3+}$ reacts significantly further away from the electrode surface than $Cr(NH_3)_6^{3+}$ as a result of the greater extent of hydration around the former reactant.[17] The results are considered to provide a distinction between two alternative double-layer models that have been extensively debated: that the observed sensitivity of both electrode kinetics and the double-layer thermodynamics to the nature of the supporting electrolyte cation are due to (a) cation specific adsorption or (b) variations in the position of the outer Helmholtz plane due to cation size effects. We found that the kinetic data strongly supported (b), and indicated that specific adsorption was very weak or even absent at negative electrode potentials for most monoatomic cations.[18]

V. Experimental Aspects

Although the main purpose of this report is to provide a summary of the chief results obtained and interpretations made during the funding period, mention should be made of some important experimental details.

The question of the reliability of rate and equilibrium parameters obtained at solid metal surfaces has been pursued throughout this work. The selection of solid metals has been determined partly by the likely availability of pretreatment methods by which clean and reproducible surfaces can be obtained. Considerable effort has been expended in preparing electrode surfaces which yield reproducible kinetic behavior. At some surfaces, particularly polycrystalline silver and lead, remarkably stable rate parameters can be obtained for both inner- and outer-sphere electrode reactions (precision of k_{app} within ca 20%) which allow truly quantitative experiments to be conducted.[10,13]

Several of these and other types of electrochemical experiments have utilized the on-line microprocessor data acquisition and analysis system which we have constructed. In particular, this system allows us to gather and store transient signals in real time at rates up to 40 μsecs between data points. So far, it has proved to be valuable for performing potential step chronocoulometric measurements of reactant adsorption, and for rapid normal pulse polarography.

Further details of the experimental methods employed in this research program are given in the resulting publications cited below.

Publications Resulting from AFOSR Grant

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The overall objective of this research program was to develop the understanding of the relationships between the kinetics and mechanisms of some simple heterogeneous electron-transfer reactions and the molecular structure of the reactant and the electrode-solution interface. Emphasis was placed on studies of transition-metal redox couples involving substitutionally inert complexes in aqueous media at a number of solid metals as well as at mercury electrodes. These reactions provide excellent model systems for studying structural effects in electron transfer, since they are

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mechanistically simple and either inner- or outer-sphere reaction mechanisms can be induced, depending on the ability of the coordinated ligands to bind to the electrode surface. Problems that were addressed included: (1) the effects of varying the nature of the metal surface upon the rates of inner- and outer-sphere reactions, (2) the influence of ionic specific adsorption upon the reactivities of outer-sphere pathways, (3) determination of the influence of reactant specific adsorption to the reorganization energy barrier for electron transfer, and (4) elucidation of the role of reactant-solvent interactions in redox kinetics and thermodynamics.

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