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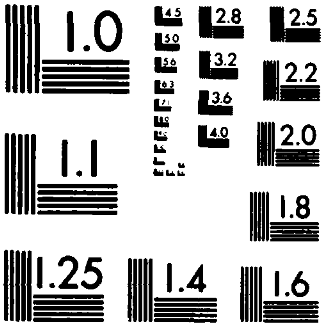

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Electrochemical Activation Parameters for Surface-Attached Reactants
Evaluation of Unimolecular Frequency Factors for Representative Ligand-Bridged Reactions

by

T. T-T. Li, K. L. Guyer, S. W. Barr,
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electron-transfer step to be evaluated. Values of A_{et} close to 10^{13} sec^{-1} were obtained in this manner for the thiocyanate-bridged reactions at mercury, indicating that the electronic transmission coefficient, κ_{el}, approaches unity, i.e. the reactions are adiabatic. Although a comparable value of A_{et} was obtained for Co(III) reduction via a thiophenecarboxylate bridge featuring uninterrupted conjugation, substantially smaller A_{et} values were observed with bridges containing one or more saturated carbon atoms, suggesting that $\kappa_{el} << 1$ under the latter conditions.

ELECTROCHEMICAL ACTIVATION PARAMETERS FOR SURFACE-ATTACHED REACTANTS. EVALUATION OF UNIMOLECULAR FREQUENCY FACTORS FOR REPRESENTATIVE LIGAND-BRIDGED REACTIONS

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Abstract

The temperature dependence of unimolecular rate constants are reported for the one-electron reduction of various Co(III) and Cr(III) reactants attached to mercury or silver surfaces via either thiocyanate or various thiophenecarboxylate ligands. Combining the "ideal" activation enthalpies obtained at a constant electrode potential using a nonisothermal cell arrangement with the corresponding activation entropies estimated from reaction entropy data enables values of the unimolecular frequency factor, A_{et}, for the elementary electron-transfer step to be evaluated. Values of A_{et} close to 10^{13} sec^{-1} were obtained in this manner for the thiocyanate-bridged reactions at mercury, indicating that the electronic transmission coefficient, κ_{el}, approaches unity, i.e. the reactions are adiabatic. Although a comparable value of A_{et} was obtained for Co(III) reduction via a thiophenecarboxylate bridge featuring uninterrupted conjugation, substantially smaller A_{et} values were observed with bridges containing one or more saturated carbon atoms, suggesting that $\kappa_{el} << 1$ under the latter conditions.

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Introduction

Studies of the temperature dependence of electrochemical reaction rates, as for redox processes in solution, are of fundamental importance since they can provide detailed information on the nature of the activation process leading to electron transfer.[1,2] In contract to widespread belief, their interpretation contains no more ambiguities than for the more commonly encountered activation parameters for ordinary bulk-phase reactions.[1-6] However, relatively few measurements of electrochemical activation parameters have been made, at least under well-defined conditions. Nevertheless, we have demonstrated that electrochemical activation parameters for solution reactants can yield useful information on the nature of the solvation environment in the interfacial region with respect to the bulk solution.[3]

The evaluation of electrochemical rate parameters for mechanistically uncomplicated single electron transfer processes involving specifically adsorbed (or "surface-attached") reactants offer important advantages over rate data gathered for solution reactants since the former provide direct information on the energetics of the elementary electron-transfer step. The situation is entirely analogous to the well-documented advantages of studying the kinetics of homogeneous intramolecular, rather than biomolecular, redox processes.[7] We have recently outlined the virtues of evaluating electrochemical activation parameters for surface-attached reactants, especially for detecting nonadiabatic reaction pathways from the measured frequency factor.[6] Nevertheless, presumably due in part to the continuing confusion surrounding their interpretation, virtually no measurements of this type have been undertaken.

There are two distinct types of electrochemical activation parameters for adsorbed as well as solution-phase reactants. Most commonly, so-called "real" enthalpies and entropies of activation, ΔH^*_r and ΔS^*_r, respectively, are determined from the temperature dependence of the "standard" rate constant, k_s, i.e. that measured at the standard (or formal) potential <u>at each temperature</u>.[1] For adsorbed reactants, ΔH^*_r and ΔS^*_r determined at the formal potential for the surface-attached redox couple can be identified with the "intrinsic" enthalpies and entropies of activation, respectively. These are the components of ΔH^* and ΔS^* that remain after correction for the enthalpic and entropic driving forces, ΔH°_{et} and ΔS°_{et} respectively, for the elementary electron-transfer step.

Such activation parameters are clearly inaccessible for chemically irreversible redox couples for which the formal potential and hence k_s cannot be determined. However, fundamentally useful information may still be obtained for such systems from the so-called "ideal" enthalpies and entropies of activation, ΔH_i^* and ΔS_i^*, respectively. These are determined from the temperature dependence of the rate constant for the reduction (or oxidation) of the reactant measured at a fixed electrode potential using a nonisothermal cell arrangement.[1,2] Since this strategy maintains the Galvani metal-solution potential difference essentially constant, ΔH_i^* and ΔS_i^* may be identified directly with the enthalpic and entropic barriers to electron transfer at this potential.

The measurement of such activation parameters in principle enables the rate constant to be partitioned into a frequency factor and a Franck-Condon barrier. The relationship between the experimental quantities and these fundamental variables is especially direct for surface-attached reactants.[6] Thus the unimolecular rate constant for a one-electron transfer reaction, k_{et}, can be expressed as

$$k_{et} = A_{et} \exp(\Delta S_{i,a}^*/R) \exp(-\Delta H_{i,a}^*/RT) \qquad (1a)$$

$$= A_{et} \exp(\Delta S_{int}^*/R) \exp(-\Delta H_{r,a}^*/RT) \qquad (1b)$$

where $\Delta S_{i,a}^*$ and $\Delta H_{i,a}^*$ and $\Delta H_{r,a}^*$ are "ideal" and "real" activation parameters for surface-attached reactants, ΔS_{int}^* (=$\Delta S_{r,a}^*$) is the "intrinsic" activation entropy, and A_{et} is the unimolecular frequency factor for the elementary electron-transfer step. The "ideal" activation entropy is related to ΔS_{int}^* by[6]

$$\Delta S_{i,a}^* = \Delta S_{int}^* + \alpha_{et}\Delta S_{et}^\circ \qquad (2)$$

where α_{et} is the transfer coefficient for the electron-transfer step, obtained from $\alpha_{et} = -(RT/F)(d\ln k_{et}/dE)$. The last term in Eq (2) describes the contribution to the activation entropy that arises from the thermodynamic entropy change accompanying electron transfer, ΔS_{et}^o.

The frequency factor A_{et} can be expressed as[6,8]

$$A_{et} = \kappa_{el}\Gamma_n\nu_n \qquad (3)$$

where κ_{el} is an electronic transmission coefficient, Γ_n is a nuclear tunneling factor, and ν_n is the nuclear frequency factor. (It is important to distinguish between A_{et} and the more usual frequency factor for electron-transfer involving solution-phase reactants. The latter also contains a statistical term associated with forming the precursor state within the double layer.[8])

Since $\Gamma_n \sim 1$ and ν_n is expected to be around 10^{13} $\sec^{-1}$ for many reactions,* the evaluation of A_{et} enables κ_{el} to be estimated, i.e. the fractional probability that electron transfer will occur each time the nuclear transition state is attained. In view of Eqs (1) - (3) κ_{el} may be obtained from measurements of either $\Delta H^*_{i,a}$ or $\Delta H^*_{r,a}$. Although the latter route is preferred since an estimate of ΔS^o_{et} is not required [Eq (1b)], the evaluation of such "real" parameters is limited to the rare cases where the adsorbed redox couple is chemically reversible yet exhibits measurable values of k_{et}.[6] Strictly speaking, values of ΔS^o_{et} cannot be determined for chemically irreversible electrochemical reactions for which values of k_{et} can often be reliably determined. Fortunately, however, approximate estimates of ΔS^o_{et} can often be obtained for such reactions from data for structurally similar redox couples (vide infra), enabling estimates of A_{et} to be obtained from $\Delta H^*_{i,a}$ using Eqs. (1a) and (2).

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*The value of ν_n is determined by a weighted mean of the frequencies of the various reactant vibrations and solvent reorientations which are required to surmount the free energy barrier ΔG^*.[8,9] Provided that the inner-shell (metal-ligand vibrational) component of ΔG^* is at least comparable to the outer-shell component associated with lower frequency solvent reorientation (as for the present systems) ν_n is essentially equal to the effective metal-ligand stretching frequency ν_i. For the simple ammine and aquo reactants considered here, $\nu_i \approx 1 \times 10^{13}$ $\sec^{-1}$.[9]

Although Eq (3) applies to outer- as well as inner-sphere pathways,[8] k_{et} and hence A_{et} cannot usually be measured directly for the former type since the "precursor state" preceding the electron-transfer step is usually insufficiently stable to be analytically detected.[8] The measurement of electrochemical activation parameters for surface-attached reactants therefore offers a unique opportunity for evaluating this fundamentally important parameter. It is often implicitly assumed that electrochemical reactions are adiabatic (i.e. $\kappa_{el} \simeq 1$). However, there are good reasons to suspect that nonadiabatic pathways ($\kappa_{el} << 1$) are commonly encountered at electrode surfaces[10] as well as in homogeneous solution.[11]

We present here experimental activation parameters for the one-electron reduction of a number of Co(III) and Cr(III) reactants bound to mercury electrodes via either isothiocyanate or thiophenecarboxylate bridging ligands. Some additional data are also given for thiocyanate-bridged reactions at silver electrodes. We have recently studied these reactions in detail.[12-17] They are chemically irreversible on account of the instability and substitution lability of the Co(II) and Cr(II) products. Approximate values of A_{et} and hence κ_{el} were extracted via Eqs (1a) and (2) from measurements of k_{et} and $\Delta H^{*}_{i,a}$ along with suitable estimates of ΔS^{o}_{et}. The thiophenecarboxylate ligands are of particular interest since the ligand structure between the thiophene surface binding group and the carboxylate Co(III) coordination site can be altered by the insertion of saturated or unsaturated carbon linkages.[12] This enables the influence of ligand conjugation upon the frequency factor, and hence κ_{el}, to be assessed. The results described therein appear to represent the first systematic evaluation of A_{et} for heterogeneous electron-transfer processes.

Experimental

The various carboxylatopentaamminecobalt(III) complexes used here were synthesized as solid perchlorate salts as described in ref. 12. c-[Co(en)$_2$(NCS)$_2$]ClO$_4$ (en = ethylenediamine) was prepared using a literature procedure.[18] Stock solutions of c-Cr(OH$_2$)$_4$(NCS)$_2^+$ and f-Cr(OH$_2$)$_3$(NCS)$_3$ were prepared as described in ref. 19. The sodium perchlorate used as supporting electrolyte was twice recrystallized from water. All solutions were prepared using water that was purified by double distillation from alkaline permanganate.

Measurements of rate constants, k_{et} (sec^{-1}), for the reduction of the various adsorbed complexes as a function of electrode potential at various temperatures in the range 0-55°C were mostly obtained using rapid linear sweep voltammetry.[12-14] These employed sufficiently dilute reactant solutions (usually $\lesssim 50\ \mu M$) and rapid sweep rates ($\gtrsim 10$ V sec^{-1}) so that the observed current-potential peak arose almost entirely from the initially adsorbed, rather than the diffusing, reactant. The surface reactant concentrations, Γ, corresponding to each point on the current-potential curves were obtained from the charge required to reduce the remaining adsorbate. Plots of reduction rate as a function of reactant surface concentration and electrode potential were obtained by performing this procedure for a set of voltammograms obtained for sweep rates from 10 to 100 V $\sec^{-1}$. Kinetic parameters were usually evaluated for surface concentrations $\Gamma \lesssim 1 \times 10^{-10}$ mole cm^{-2} where the reaction rate was approximately first order in the surface reactant concentration; i.e. k_{et} was independent of Γ (cf ref. 19). Further details are given in refs. 12-14. Some measurements of k_{et} at mercury electrodes were also made using the potential-step chronocoulometric technique as described in ref. 19. Similar results were generally obtained using these two methods. However, chronocoulometry was found to be unsuitable both for eval[illegible] the extent of reactant adsorption and rate parameters for adsorbed reactants at silver and several other solid electrodes.[13,14,16]

Kinetic measurements at the mercury-aqueous interface employed a commercial hanging mercury drop electrode (Brinkman Instruments). The silver electrode was fabricated so to minimize any heat loss from the metal surface to the connecting wire. The electrode, of rotating disk construction, featured thermal insulation from the steel shaft by using a copper contact spring encased in nylon.[16] The silver surface was pretreated by means of the cyanide electropolishing procedure described elsewhere.[20,21]

Potential sweeps were made mostly by means of a PAR 173 potentiostat and a PAR 175 potential programmer, and the current-potential curves recorded by using a Nicolet Explorer I oscilloscope with a Houston 2000 X-Y recorder, or by using a Tektronix 7623A storage oscilloscope with a Polaroid camera. The chronocoulometric measurements utilized on on-line data acquisition and analysis system based on a LSI-11 microcomputer, along with a fast potentiostat of in-house design. Thermostatic control of the portion of the nonisothermal electrochemical cell containing the working electrode was achieved by circulating water through a surrounding jacket using a Braun Melsungen circulating thermostat. This controlled the variable temperature of the working compartment and frit to the adjoining reference compartment to within ± 0.05 deg C. The reference compartment containing the reference electrode was maintained at ambient temperature. The virtues of such nonisothermal cells are described in refs. 2 and 22, along with further pertinent experimental details. All electrode potentials are quoted versus the saturated calomel electrode (s.c.e.).

Results

Representative values of k_{et} and $\Delta H^{*}_{i,a}$ for the reduction of three isothiocyanate-bridged Cr(III) and Co(III) reactants, and four thiophenecarboxylate-bridged Co(III) reactants at mercury- and silver-aqueous interfaces are summarized in Table I. These complexes were selected for the present study since they are sufficiently strongly adsorbed ($\Gamma \gtrsim 5 \times 10^{-11}$ moles cm^{-2}), at dilute bulk concentrations ($C_b \leq 50$ $\mu\underline{M}$) to yield values of k_{et} with sufficient accuracy to enable reliable activation enthalpies to be obtained from $\Delta H^{*}_{i,a} = -R[\partial \ln k_{et}/\partial(1/T)]_E$. The electrode potentials, E, were also chosen so to optimize the data reliability. At least at the well-defined mercury-aqeuous interface, the resulting values of k_{et} are estimated to be accurate to within ca 20%, and those of $\Delta H^{*}_{i,a}$ to ca. 0.7 - 1 k J. mol^{-1}. Although the data reproducibility at silver electrodes was not markedly inferior, the reliability of the resulting $\Delta H^{*}_{i,a}$ values is called into question by the surprisingly broad linear sweep voltammograms obtained for adsorbate reduction at this and other solid metals (vide infra).[13,16]

In order to extract values of A_{et} from k_{et} and $\Delta H^{*}_{i,a}$, it is necessary to know both ΔS^{*}_{int} and ΔS°_{et}. The former term is expected to be close to zero (within ca. 5 J. deg^{-1} mol^{-1}) on the basis of the classical model of electron transfer since the entropy of the transition state is expected to be approximately midway between that for the "precursor" and "successor" states that immediately precede and follow it on the potential-energy surface.[2] However, a significant contribution to the effective value of ΔS^{*}_{int} can be viewed as arising from the decrease of the nuclear tunneling factor Γ_n with increasing temperature.[23] (This factor can be viewed as a quantum mechanical correction to the classical free energy barrier arising from the small, yet significant probability that molecules can react without entirely surmounting the classical barrier.[8,23]) Although the quantitative calculation of the temperature dependence of Γ_n requires a detailed knowledge of the intrinsic free energy barrier and the thermodynamic driving force (i.e. the overpotential) under the experimental conditions, from the relationships available in the literature[23] ΔS^{*}_{int} is calculated to be about -15 J. deg^{-1} mol^{-1} for the present reactions.*

A somewhat larger uncertainty surrounds the estimates of the entropic driving force ΔS^{o}_{et} for the electron-transfer step. Since the surface attachment sites for the thiophenecarboxylate-bridged reactants are relatively distant from the metal redox center, ΔS°_{et} is expected to be similar to the corresponding "reaction entropies", ΔS°_{rc} (i.e. the entropy difference between the reduced and oxidized forms of the bulk-solution redox couple.[22]) Indeed similar values of ΔS°_{et} and ΔS°_{rc} have been obtained

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*Almost all literature discussions of these points concern homogeneous rather than electrochemical reactions.[23,24] However these arguments can be directly transposed to electrochemical reactions bearing in mind that only a single redox center undergoes reorganization in this case, rather than a reactant pair as for homogeneous reactions. Therefore values of ΔS^{*}_{int} for electrochemical reactions are calculated to be one half of those for the corresponding homogeneous processes.

for a surface-attached ferricinium-ferrocene couple in several solvents.[25] Reaction entropies cannot be determined for the present redox couples on account of their chemical irreversibility. However, approximate estimates can still be obtained by examining experimental values for structurally related couples. The most extensive ΔS°_{rc} values are available for Ru(III)/(II) couples on account of their chemical and electrochemical reversibility. Ru(III)/(II) ammine couples containing one or two anionic ligands exhibit ΔS°_{rc} values in the range ca 45 to 65 J. deg^{-1} mol^{-1}, somewhat smaller than for $Ru(NH_3)_6^{3+/2+}$ (75 J. deg^{-1} mol^{-1}), consistent with their smaller charge.[22,26] Although such information for Co(III)/(II) ammine couples is unavailable, ΔS°_{rc} for the closely related couple $Co(en)_3^{3+/2+}$ (en = ethylenediamine) is 155 J. deg^{-1} mol^{-1}, markedly larger than that for $Ru(en)_3^{3+/2+}$ (55 J. deg^{-1} mol^{-1}).[22] Such larger ΔS°_{rc} values for Co(III)/(II) and Cr(III)/(II) couples are commonly observed, and are consistent with the greater changes in the ligand-solvent interactions caused by the addition of an e_g electron, as compared to a t_{2g} electron in Ru(III)/(II). Bearing in mind these differences, we estimate that the values of ΔS°_{rc} for the present $Co(NH_3)_5X^{2+/+}$ couples (X^- is a carboxylate) lie around 100-120 J deg^{-1} mol^{-1}.

The estimation of ΔS^o_{et} for the isothiocyanate-bridged reactants is more complicated since the anionic charge on the NCS^- ligands is located partly on the surface-bound sulfur atoms. In view of the above, ΔS°_{rc} for $c\text{-}Co(en)_2(NCS)_2^{+/o}$ is estimated to lie around 80-120 J deg^{-1} mol^{-1}. A slightly larger value is expected for $c\text{-}Cr(OH_2)_4(NCS)_2^{+/o}$ in view of the greater ΔS°_{rc} values for corresponding aquo versus ammine couples.[22] On the other hand, ΔS°_{rc} for $f\text{-}Cr(OH_2)_3(NCS)_3^{o/-}$ is expected to be much smaller in view of the negative charge of the reduced form.[26]

The resulting values of $\Delta S^*_{i,a}$ determined from the above estimates of ΔS^*_{int} and ΔS^o_{et} along with the experimental values of α_{et} using Eq (2) are given in Table I. Fortunately, the uncertainties in $\Delta S^*_{i,a}$ are substantially smaller than those in ΔS^o_{et} due to the fractional α_{et} term in Eq (2). Given these uncertainties in ΔS^o_{et}, the resulting values of A_{et} at mercury electrodes may be as much as 5 to 10-fold in error. However, at least the *relative* values of A_{et} for reduction of the various Co(III) thiophenecarboxylates are rather more reliable since the values of ΔS^o_{et} are likely to be closely similar for all these reactions.

Discussion

The estimates of A_{et} obtained for the three thiocyanate-bridged reactions at the mercury-aqueous interface, around 10^{13} sec^{-1}, are consistent with the value, 1×10^{13} sec^{-1}, expected from Eq (3) for adiabatic pathways, i.e. for $\kappa_{el} \simeq 1$. This indicates that surface attachment of Cr(III) or Co(III) via thiocyanate ligands induces sufficient coupling between the mercury donor and metal redox acceptor orbitals to yield efficient electron tunneling once the nuclear activation barrier to electron transfer has been surmounted. On the basis of crystallographic bond length data for bridged thiocyanate complexes,[27] the metal redox centers are estimated to lie 5-6 Å from the electrode surface. Some recent electron-tunneling calculations for homogeneous electron transfer between $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{2+}$ indicate that κ_{el} can approach unity for internuclear separations around 5 Å, although κ_{el} decreases very sharply for larger separations.[9] Such tunneling probabilities are expected to be sensitive to the nature of the donor and acceptor orbitals and the intervening medium. Nevertheless, comparable electron-tunneling distances are inferred for some outer-sphere Cr(III) reductions at mercury from an analysis of the relative reactivities of corresponding outer-sphere and ligand-bridged electrochemical pathways.[28]

Surface attachment via relatively small unsaturated bridging ligands such as thiocyanate therefore may well enhance the reactant-surface electronic coupling so to yield essentially adiabatic pathways. However, the variations in the A_{et} values for the thiophenecarboxylate-bridged Co(III) reductions indicates that the degree to which this coupling is achieved is sensitive to the bridging ligand structure. Whereas $2TP\text{-}CH{=}CHCOORo^{2+}$ [where $Ro{=}Co(NH_3)_5$, TP = thiophene,"2"denotes substitution in the 2-position)] features uninterrupted conjugated double bonds between the thiophene sulfur atom and the carboxylate group, this conjugation is interrupted for the last three reactants (V - VII) in Table I by the insertion of one, two, or three methylene groups between the thiophene and carboxylate moities. This structural modification is reflected in substantial decreases in k_{et}; these are associated chiefly with decreases in A_{et}. The value of A_{et} for $2TP\text{-}CH{=}CHCOORo^{2+}$, $\sim 2 \times 10^{12}$ sec^{-1}, (Table I) indicates that this reaction is close to adiabatic, and may indeed be adiabatic ($\kappa_{el} \sim 1$) given the uncertainty in evaluating A_{et}. However, $2TP\text{-}(CH_2)_2COORo^{2+}$ (which differs only in the hydrogenation of the central carbon-carbon double bond) exhibits a 20-fold smaller value of k_{et} and a ca. 100-fold smaller frequency factor, $\sim 3 \times 10^{10}$ sec^{-1}. The latter value of A_{et} clearly indicates that $\kappa_{el} << 1$.

This result provides direct evidence that electron tunneling is greatly facilitated by bond conjugation between the electron donor and acceptor sites. This observation appears to be the first of its kind for heterogeneous electron transfer. However, the present results are strongly reminiscent of activation parameter data gathered for the intramolecular reduction of Co(III) by Ru(II) mediated by 4,4'bipyridine and related ligands.[29] Thus the interposition of saturated carbons between the two pyridine rings yields a ca 20-fold decrease in k_{et} and a correspondingly substantial decrease in the frequency factor.[29,30]

(We have recently analyzed these homogeneous activation parameter data with a view towards providing quantitative estimates of A_{et}.[30] Although the intramolecular systems are charge symmetric since they feature $Co^{3+/2+}$ and $Ru^{3+/2+}$ reacting partners, similarly to the present electrode reactions they involve significantly positive values of ΔS°_{et} since the entropy increase for Co(III) reduction is not entirely compensated by a corresponding decrease for Ru(II) oxidation. Indeed the estimation of A_{et} for homogeneous intramolecular processes features an entirely similar analysis to that employed for the present heterogeneous systems[30]).

One interesting feature of both the heterogeneous and the Ru(II) intramolecular reduction of pentaamminecobalt(III) is that interposition of further saturated carbons in the bridging ligand yields only minor additional decreases in k_{et} and A_{et} beyond that caused by a single methylene group.[12,29] The most likely explanation is that an alternative electron-tunneling pathway involving direct "through space" transfer rather than via the bridging ligand is operative under these conditions, probably involving close approach of the donor and acceptor sites via contortion of the bridging ligand. This seems especially likely for the electrochemical reactions where the Co(III) redox center may approach a number of other surface sites than that occupied by the thiophene ligand. This mechanistic change may also be responsible for the slightly smaller values of $\Delta H^{*}_{i,a}$, expecially for $2TP-(CH_2)_3COORo^{2+}$, observed in comparison with that for $2TP-CH=CHCOORo^{2+}$ (Table I).

The relatively small frequency factors, ca $10^{8}-10^{10}$ sec^{-1}, obtained for the thiocyanate-bridged reduction of Cr(III) and Co(III) at silver electrodes might be taken as evidence of nonadiabatic pathways for these reactions. However, this is considered unlikely since the values of k_{et} are comparable to or larger than those for the same reactions at mercury electrodes. It seems feasible that this behavior arises from an artifact associated with the polycrystalline nature of the silver surface. Thus although the voltammetric peak shapes for the adsorbate reduction at mercury electrodes are close to that expected for first-order kinetics, those obtained at silver electrodes are markedly broader.[13,14,16] This behavior is consistent with the presence of a variety of interacting adsorption sites on the polycrystalline surface. The kinetic parameters are determined in the vicinity of the voltammetric peaks which reflect the properties of the predominant adsorption sites. However, systematic structural redistributions may occur with varying temperature which could yield artifactually small values of $\Delta H^*_{i,a}$. Anomalously small values of $\Delta H^*_{i,a}$ have also been observed for some adsorbed reactants at polycrystalline gold electrodes.[17] We plan temperature-dependent rate measurements for adsorbed reactants at oriented single-crystal surfaces in order to examine this question further.

Conclusions

The present results demonstrate the virtues of evaluating electrochemical activation parameters for surface-attached reactants for gaining hitherto unavailable information of the dynamics of the electron-transfer step. The analysis can be applied to chemically irreversible, as well as reversible processes provided that the electron-transfer step is rate determining and occurs prior to any coupled chemical steps. The evaluation of A_{et} for such irreversible processes is dependent on the satisfactory estimation of the entropic driving force for the electron-transfer step. However, it is important to note that the evaluation of A_{et} from "ideal" activation parameters does not rely on the validity of any extrathermodynamic assumption associated with nonisothermal cell measurements[2,22] since this will cancel when the individual values of $\Delta H^*_{i,a}$ and ΔS°_{et} are inserted into Eq (1a). Although the determination of the "real" activation enthalpy is in a sense preferable as this enables A_{et} to be determined without a separate evaluation of ΔS°_{et} [Eq (1b)][6], such measurements are limited to the few adsorbed redox couples that are chemically reversible yet display measurably slow heterogeneous electron-transfer kinetics. A similar limitation applies to the analogous intramolecular reactions in homogeneous solution for which the evaluation of <u>thermal</u> electron-transfer kinetics for any chemically reversible binuclear redox reaction has apparently yet to be made.[7,29]

Most importantly, the interpretation of electrochemical activation parameters for such chemically-bound systems at electrodes as well as in bulk solution are free from the ambiguities that beset the interpretation of such quantities for outer-sphere reactions associated with uncertainties in the magnitude and temperature dependence of work terms.[6] In addition, the relatively well-defined transition-state geometry for the former, combined with the ability to systematically alter the bridging ligand structure, provides unique opportunities to examine the sensitivity of heterogeneous electron-transfer energetics to molecular structure. Further measurements of this type, involving a variety of organic bridging ligands, are underway in our laboratory.

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TABLE I. Activation Parameters for Reduction of Representative Adsorbed Co(III) and Cr(III) Reactants at Mercury and Silver Electrodes in 0.1 M $NaClO_4$.

	Reactant[a]	Surface	E mV vs sce	k_{et}[b] sec^{-1}	α_{et}[c]	$\Delta H^{*}_{i,a}$[d] k J. mol^{-1}	$\Delta S^{*}_{i,a}$[e] J $deg^{-1} mol^{-1}$	A_{et}[f] sec^{-1}
I	$c\text{-}Cr(OH_2)_4(NCS)_2^+$	Hg	-600	70	0.4	80	~ 50	$\sim 1x10^{13}$
		Ag	-600	50	0.35	50	~45	$\sim 1x10^{8}$
II	$f\text{-}Cr(OH_2)_3(NCS)_3$	Hg	-600	70	0.35	68	~0	$\sim 4x10^{13}$
		Ag	-600	100	0.4	45	~0	$\sim 1x10^{10}$
III	$c\text{-}Co(en)_2(NCS)_2^+$	Hg	-200	1.5	0.6	82	~40	$\sim 2x10^{12}$
		Ag	-200	300	0.5	50	~35	$\sim 3x10^{9}$
IV	$2TP\text{-}CH{=}CHCOORo^{2+}$	Hg	-200	$4x10^{3}$	0.6	65	~55	$\sim 2x10^{12}$
V	$2TP\text{-}CH_2COORo^{2+}$	Hg	-200	260	0.6	60	~55	$\sim 1x10^{10}$
VI	$2TP\text{-}(CH_2)_2COORo^{2+}$	Hg	-200	290	0.6	62	~55	$\sim 3x10^{10}$
VII	$2TP\text{-}(CH_2)_3COORo^{2+}$	Hg	-200	230	0.6	55	~55	$\sim 1x10^{9}$

[a] en = ethylenediamine, Ro = $Co^{III}(NH_3)_5$-, TP = Thiophene. Prefix "2" designates substitution at the 2-position of the thiophene ring.

[b] Unimolecular rate constant for one-electron reduction of given surface-attached reactant. See text and refs. 12-14 for details.

[c] Transfer coefficient for electron-transfer step, determined from $\alpha_{et} = -(RT/F)(d\ln k_{et}/dE)$. See refs. 12-15.

[d] "Ideal" enthalpy of activation for surface-attached reactant, determined from $\Delta H^{*}_{i,a} = -R[\partial \ln k_{et}/\partial(1/T)]_E$, at the indicated fixed value of E using a nonisothermal cell arrangement.[2,22]

[e] "Ideal" entropy of activation, estimated by using Eq (2) using listed values of α_{et} and assuming that $\Delta S^{\ddagger}_{int} = -15$ J. deg^{-1} mol^{-1}; values of ΔS^{o}_{et} taken as follows: I, 150; II, 0, III, 100; IV-VII, 110 J. deg^{-1} mol^{-1} (see text for details).

[f] Unimolecular frequency factor for electron-transfer step, determined from listed values of k_{et}, $\Delta S^{\ddagger}_{i,a}$, and $\Delta H^{\ddagger}_{i,a}$ using Eq (1a). Uncertainties in A_{et} values estimated to be ca 5-fold, determined largely by uncertainties in corresponding estimates of ΔS^{o}_{et} and hence $\Delta S^{*}_{i,a}$ (see text).

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