The isotope effects appear as the deviation and unsymmetrization of the potential profile along the IRC in the mass-weighted Cartesian coordinate system, whereas in the ordinary non-mass-weighted Cartesian coordinate system they appear as the differences of the effective mass. The analysis of tunneling probability has shown that the difference in the effective mass which is greatest in the vicinity of the transition state extends to the considerably extended region along the IRC. In such a case where a light species transfers as a proton exchange, the tunneling process is significant. Several authors[1b,8] have noted that the tunneling paths "cut the corner" rather than pass through the saddle point. Reduction of the multidimensional motion of the constituting atoms to the one-dimensional motion along the reaction coordinates, *s*, has enabled us to analyze the complicated nature of chemically reacting systems, in particular attending the isotope effects.

In the future, the tracing of the reaction pathway using the concept of the IRC will be profitable in applications to more complicated biochemical systems.

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Experimental Estimate of the Electron-Tunneling Distance for Some Outer-Sphere Electrochemical Reactions

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Estimates of the reaction zone thickness over which electron tunneling can effectively occur for the outer-sphere electrochemical reduction of some Cr(III) complexes are obtained by comparing the observed work-corrected rate constants with unimolecular rate constants for the electroreduction of structurally similar surface-bound Cr(III) reactants. Effective reaction zone thicknesses of ca. 0.1–0.3 and ca. 5 Å are obtained for outer-sphere electron transfer with Cr(III) reactants containing predominantly aquo or ammine ligands, respectively. This indicates that the former reactions are marginally nonadiabatic whereas the latter are decidedly adiabatic at their respective planes of closest approach. These findings are compatible with the greater reactant–electrode separation distances previously noted for Cr(III) aquo relative to ammine complexes resulting from the more extensive hydration sheath surrounding the former reactants. Comparisons with recent calculations performed for some outer-sphere homogeneous reactions suggest that efficient electron tunneling takes place over roughly comparable distances at metal–electrolyte interfaces and in bulk solution.

An important question in the treatment of electron-transfer reactions concerns the magnitude of the preexponential factor, *A*, in the expression

$$k_{\text{obsd}} = A \exp(-w_p/RT) \exp(-\Delta G_{\text{et}}^*/RT) \qquad (1)$$

where k_{obsd} is the observed rate constant, w_p is the work required to bring the reactants together (or the reactant to the electrode surface), and ΔG_{et}^* is the free-energy barrier for the elementary electron-transfer step. Although sophisticated theoretical methods have been developed for evaluating ΔG_{et}^* from structural and thermodynamic information, there remains considerable uncertainty as to the numerical values of the preexponential factor for outer-sphere pathways.[1,2]

In the recent literature it has been emphasized that outer- as well as inner-sphere redox reactions in homogeneous solution and at electrode surfaces can usually be viewed as involving formation of a reactive precursor complex from initially separated reactants followed by the rate-determining transfer step.[1–5] Thus, the observed rate constant can be formulated as

$$k_{\text{obsd}} = K_p k_{\text{et}} \qquad (2)$$

where K_p is the equilibrium constant for forming the precursor state and k_{et} is the rate constant describing the elementary electron-transfer step. When applied to outer-sphere pathways, this approach can be termed an "encounter-preequilibrium" treatment. It views the reaction as taking place via the unimolecular activation of a weakly interacting reactant pair having a suitably close proximity and geometrical configuration to enable electron transfer to occur once the appropriate nonequilibrium nuclear configuration has been achieved.[1b,c 2b,5c]

According to the encounter-preequilibrium treatment, the preexponential factor can be expressed as[1b,c,5c]

$$A = \Gamma_n \nu_n \kappa_{\text{el}}^0 K_0 \qquad (3)$$

where Γ_n is the nuclear tunneling factor, ν_n is the effective frequency for activating nuclear reorganization modes, κ_{el}^0 is the electronic transmission coefficient at the distance of closest approach of the reactants, and K_0 is the statistical part of the precursor stability constant K_p where

$$K_p = K_0 \exp(-w_p/RT) \qquad (4)$$

For electrochemical reactions the statistical factor K_0^e can be expressed simply as[5c]

$$K_0^e = \delta r_e \qquad (5)$$

where δr_e is the thickness of a "reaction zone" beyond the plane of closest approach within which the reactant must reside in order to contribute significantly to the overall reaction rate. The value of δr_e is determined by the need for the reactant and surface to be in sufficiently close proximity to achieve significant overlap

(1) (a) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979,** *101,* 883. (b) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, M. *ibid.* **1980,** *102,* 5798. (c) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982,** *198,* 105. (d) Brunschwig, B. S.; Creutz, C.; McCartney, D. H.; Sham, T.-K.; Sutin, N. *Discuss. Faraday Soc.,* in press. (e) Sutin, N. *Prog. Inorg. Chem.* **1983,** *30,* 441.

(2) (a) Newton, M. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980,** *14,* 363. (b) Tembe, B. L.; Friedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982,** *76,* 1490. (c) Newton, M. D. *ACS Symp. Ser.* **1982,** *198,* 255.

(3) Marcus, R. A. *Int. J. Chem. Kinet.* **1981,** *13,* 865.

(4) Li, T. T.-T.; Weaver, M. J.; Brubaker, C. H., Jr. *J. Am. Chem. Soc.* **1982,** *104,* 2381.

(5) (a) Weaver, M. J. *Inorg. Chem.* **1979,** *18,* 402. (b) Weaver, M. J. In "Inorganic Reactions and Methods"; Zuckerman, J. J., Ed.; Verlag Chemie, in press. (c) Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983,** *152,* 1.

TABLE I: Kinetic and Thermodynamic Data for the One-Electron Reduction of Cr(III) Complexes at the Mercury–Aqueous Interface at 25 °C

reactant	pathway[a]	$-E$, mV vs. SCE	k_{obsd},[b] cm s^{-1}	k_{cor}^{os},[c] cm s^{-1}	K_p,[d] cm	k_{et}^{is},[e] s^{-1}	k_{cor}^{os}/k_{et}^{is}, Å
Cr(NH$_3$)$_5$NCS^{2+}	is	600	1×10^{-5}		2×10^{-5}	0.5	
Cr(NH$_3$)$_5$N$_3$$^{2+}$	os	600	6×10^{-7}	1×10^{-7}			5–10
	is	600	$\sim 5 \times 10^{-7}$		5×10^{-7}	~ 1	
Cr(NH$_3$)$_5$Cl^{2+}	os	600	3×10^{-6}	6×10^{-7}			
	is	600	1×10^{-5}		$\sim 1 \times 10^{-6}$	~ 10	~ 5
Cr(OH$_2$)$_6$$^{3+}$	os	655	7.5×10^{-6}	2.5×10^{-6}			
Cr(OH$_2$)$_5$SO$_4$$^+$	os	705	4.6×10^{-6}	3.5×10^{-6}			
Cr(OH$_2$)$_5$F^{2+}	os	860	6×10^{-6}	2×10^{-6}			~ 0.1–0.3
Cr(OH$_2$)$_5$NCS^{2+}	is	720	4×10^{-3}		$\sim 4 \times 10^{-6}$	1×10^3	
Cr(OH$_2$)$_5$N$_3$$^{2+}$	is	~ 720	1.2×10^{-4}		$\sim 2 \times 10^{-7}$	2×10^3	

[a] is = inner-sphere (ligand-bridged) pathway; os = outer-sphere pathway. [b] Observed rate constant for overall electrode reaction following is or os pathway indicated at electrode potential, E, listed in adjacent column. Values of k_{obsd} for Cr(III) aquo complexes determined at formal potential for Cr(III)/(II) couple. Data taken from ref 5a, 6, and 7. [c] Work-corrected rate constant for outer-sphere pathway. Determined from corresponding value of k_{obsd} by using $k_{cor}^{os} = \exp[(Z - 0.5)\phi_{rp}]$, where Z is the reactant charge number, and ϕ_{rp} is the average potential at the reaction plane (see ref 6 and 7 for details). [d] Stability constant for the inner-sphere precursor state, determined from eq 7; taken from ref 5a. [e] Unimolecular rate constant for electron-transfer step involving ligand-bridged intermediate. Obtained from listed values of k_{obsd} and K_p using eq 2.

of donor and acceptor orbitals, and hence nonzero values of the transmission coefficient κ_{el} for a given reactant orientation (vide infra). The composite term $\kappa_{el}^0 K_0^e$ ($\equiv \kappa_{el}^0 \delta r_e$) appearing in eq 3 for electrochemical reactions can therefore be considered to be an "effective reaction zone thickness." If $\kappa_{el}^0 < 1$, the reaction is termed "nonadiabatic", whereas "adiabatic" processes are those for which $\kappa_{el}^0 \sim 1$. Since the magnitude of δr_e is determined by the dependence of κ_{el} upon the donor–acceptor separation distance, markedly smaller values of $\kappa_{el}^0 \delta r_e$ are anticipated for the former compared to the latter processes as a result of smaller values of δr_e as well as κ_{el}^0.

The statistical factor for homogeneous reactions, K_0^h, is more complex than K_0^e yet entirely analogous, corresponding to the probability of finding one reactant within a reaction zone of thickness δr_h beyond the bimolecular contact distance. This term can be estimated approximately from[1c,e,2b,c]

$$K_0^h = 4\pi N \bar{r}^2 \delta r_h \qquad (6)$$

where N is the Avogadro number, and $\bar{r}$ is the distance between the reacting centers when in contact.

Recent ab initio calculations for some homogeneous outer-sphere reactions[2] indicate that κ_{el} can be substantially below unity even at a relatively small internuclear separation r, decreasing sharply with increasing r. This corresponds to relatively small values of $\kappa_{el}^0 \delta r_h$ (<1 Å, vide infra).[1c,e] It would be extremely desirable to obtain an experimental measure of such quantities. In the approach described here, estimates of $\kappa_{el}^0 \delta r_e$ for several outer-sphere electrochemical processes are obtained by a relatively direct method involving the comparison of rate constants for these pathways with those for structurally related electrochemical reactions occurring via geometrically well-defined ligand-bridged transition states. The results provide evidence that heterogeneous, as well as homogeneous, electron-transfer processes can be significantly nonadiabatic.

Data Analysis

The virtue of comparing rate parameters for corresponding electrochemical reactions occurring via outer- and inner-sphere (ligand-bridged) pathways can be seen by noting that, in contrast to the former, unimolecular rate contants for the electron-transfer step involving a ligand-bridged precursor state, k_{et}^{is} (s^{-1}), can be determined directly from the overall rate constant, k_{obsd}^{is}, by using eq 2 since K_p can be found from[5a,c]

$$K_p = \Gamma_p / C_b \qquad (7)$$

where Γ_p is the measured reactant surface concentration (mol cm^{-2}) corresponding to a given bulk reactant concentration C_b. The values of k_{et}^{is} can be expressed as

$$k_{et}^{is} = \Gamma_n \nu_n \kappa_{el}^{is} \exp(-\Delta G_{et}^* / RT) \qquad (8)$$

where κ_{el}^{is} is the electronic transmission coefficient for the ligand-bridged reaction pathway. In view of eq 1 and 3–5, the work-corrected rate constant for the corresponding outer-sphere electrochemical pathway, k_{cor}^{os}, can be expressed as

$$k_{cor}^{os} = \Gamma_n \nu_n \kappa_{el}^{os} \delta r_e \exp(-\Delta G_{et}^* / RT) \qquad (9)$$

Provided that ΔG_{et}^*, Γ_n, and ν_n are unaffected by surface attachment at a given electrode potential (vide infra), evaluation of the rate ratios k_{cor}^{os}/k_{et}^{is} enables estimates of $\kappa_{el}^{os} \delta r_e$, at least relative to κ_{el}^{is}, to be obtained. This procedure will now be utilized to estimate the effective electron-tunneling distances for some outer-sphere Cr(III) reductions at the mercury–aqueous interface.

Pertinent kinetic and thermodynamic data are assembled in Table I for the electroreduction of three Cr^{III}(NH$_3$)$_5$X complexes, where X = NCS$^-$, N$_3$$^-$, and Cl$^-$, and five Cr^{III}(OH$_2$)$_5$X complexes, where X = OH$_2$, SO$_4$$^{2-}$, F$^-$, NCS$^-$, and N$_3$$^-$. The data were extracted from ref 5a, 6, and 7. These reactions where chosen because rate constants corresponding to both inner- and outer-sphere pathways, k_{et}^{is} and k_{cor}^{os}, respectively, can be obtained directly or estimated from experimental data.[5c] Several of these reactions have been examined previously in a related discussion of the relative energetics of inner- and outer-sphere pathways.[5a]

The work-corrected rate constants, k_{cor}^{os}, were determined from the corresponding observed rate constants, k_{obsd}^{os}, by using the electrostatic double-layer corrections as outlined in ref 6 (see footnotes to Table I). Of the three Cr(III) ammine reactants, Cr(NH$_3$)$_5$N$_3$$^{2+}$ and Cr(NH$_3$)$_5$Cl^{2+} exhibit mixed electroreduction kinetics which enable both k_{obsd}^{os} and k_{obsd}^{is} to be obtained.[5a,6] The latter values are combined with estimates of K_p obtained under the same conditions from kinetic probe measurements[5a,8] to yield values of k_{et}^{is} by using eq 2. The common electrode potential of -600 mV vs. the saturated calomel electrode (SCE) was chosen so to minimize the extent of data extrapolation that is involved. The estimate of k_{et}^{is} for Cr(NH$_3$)$_5$N$_3$$^{2+}$ reduction (1 s^{-1}) is close to that observed for Cr(NH$_3$)$_5$NCS^{2+} reduction (0.5 s^{-1}); this supports the validity of the former estimate in view of the closely similar coordination properties of $-$N$_3$$^-$ and $-$NCS$^-$.[5a]

Each of the five Cr(III) aquo reactants in Table I undergoes electroreduction via sufficiently rate-dominating outer- or inner-sphere pathways so that only k_{obsd}^{os} or k_{et}^{is} can be evaluated for each reactant. Nevertheless, an approximate estimate of k_{cor}^{os}/k_{et}^{is} for these structurally related reactions can still be obtained as follows. As we have noted previously,[7] the values of k_{cor}^{os} for Cr(OH$_2$)$_6$$^{3+}$, Cr(OH$_2$)$_5SO_4$$^+$, and Cr(OH$_2$)$_5$F^{2+} reduction are closely similar when evaluated at their respective formal potentials. This indicates that the intrinsic electron-transfer barrier is ap-

(6) Weaver, M. J.; Satterberg, T. L. *J. Phys. Chem.* **1977**, *81*, 1772.

(7) Weaver, M. J.; Anson, F. C. *Inorg. Chem.* **1976**, *15*, 1871.

(8) Guyer, K. L.; Satterberg, T. L.; Weaver, M. J., unpublished experiments.

proximately independent of the nature of the sixth ligand, even though the coordinating properties of OH_2, SO_4^{2-}, and F^- differ widely. These values of k_{cor}^{os}, listed in Table I, are therefore also likely to be close to those for $Cr(OH_2)_5NCS^{2+/+}$ and $Cr(OH_2)_5N_3^{2+/+}$ which cannot be measured but for which the corresponding values of k_{et}^{is} are known, enabling the desired estimate of k_{cor}^{os}/k_{et}^{is} to be obtained (Table I).

Discussion

Inspection of Table I shows that the resulting values of k_{cor}^{os}/k_{et}^{is} for Cr(III) aquo reduction, ca. 0.2 Å, are ca. 10–30-fold smaller than those for the Cr(III) ammine reductions, ca. 5 Å. Quantitative interpretation of these results can be made by referring to eq 8 and 9. Of the various terms, ν_n and Γ_n will almost certainly have the same values for the corresponding inner- and outer-sphere pathways. Thus, ν_n is determined chiefly by the metal–ligand stretching frequencies[5c] and Γ_n is usually close to unity, being dependent upon the magnitude of ΔG_{et}^* rather than the transition-state geometry.[1b] The reorganization energy ΔG_{et}^* may differ significantly for corresponding inner- and outer-sphere pathways, arising from differences in both the inner-shell (metal–ligand) and outer-shell (solvent) reorganization terms. Ligand bridging may yield some decreases in the inner-shell component of ΔG_{et}^* arising from the influence of surface attachment on the Cr(III)–ligand bonding. However, we have found scant evidence for such catalyses with Cr(III)/(II) and Co(III)/(II) electrode reactions, even at surfaces such as platinum and gold that bind inorganic ligand bridges much more strongly than does mercury.[9]

Surface attachment may yield an alteration in the outer-shell component of ΔG_{et}^* since this is predicted to diminish as the distance between the redox center and the surface decreases, as a result of greater image stabilization of the transition state.[11] With the azido and isothiocyanato bridges, the redox center is estimated to lie about 5–6 Å from the surface.[10] Provided that the outer-sphere transition state is formed with the reactant in contact with a monolayer of inner-layer water molecules (vide infra), the redox center will be about 6.5 Å from the surface, based on a reactant crystallographic radius of 3.5 Å and a water molecule diameter of 3 Å.[6] On the basis of the well-known relation for the outer-shell component of ΔG_{et}^* due to Marcus,[11,12] k_{cor}^{os} is predicted to increase by only ca. 50% upon decreasing the reactant–electrode separation from 7 to 6 Å, and by only ca. 3-fold from 7 to 5 Å. It therefore appears likely that ΔG_{et}^* only differs to a small extent between corresponding outer- and inner-sphere pathways involving thiocyanate or azide bridges. The similar values of k_{cor}^{os}/k_{et}^{is} seen for $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5N_3^{2+}$ reduction (Table I), even though the Cr(III)–surface distance is expected to be ca. 2 Å smaller for the former reaction, lend support to this assertion.

To a first approximation, then, from eq 8 and 9 the rate ratios k_{cor}^{os}/k_{et}^{is} for the present system can be related to the effective reaction zone thickness for the outer-sphere pathways, $\kappa_{el}^0 \delta r_e$, simply by

$$k_{cor}^{os}/k_{et}^{is} \approx \kappa_{el}^0 \delta r_e / \kappa_{el}^{is} \tag{10}$$

Since the ligand bridge should facilitate overlap between the surface donor and Cr(III) acceptor orbitals, it is anticipated that the inner-sphere pathways are adiabatic, i.e. $\kappa_{el}^{is} \sim 1$. If indeed $\kappa_{el}^{is} \sim 1$, then the values of k_{cor}^{os}/k_{et}^{is}, ca. 5 and 0.2 Å, can be identified directly with the effective reaction zone thickness $\kappa_{el}^0 \delta r_e$ for the ammine and aquo reactants, respectively. Even if $\kappa_{el}^{is} < 1$, it is likely to have essentially the same value for both penta-

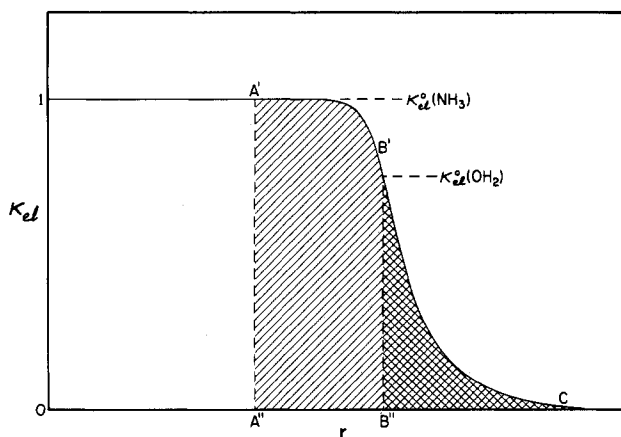**Figure 1.** Schematic plot of electronic transmission coefficient κ_{el} for an outer-sphere electrochemical reaction against the reactant–electrode separation distance r. A'A'' and B'B'' represent anticipated planes of closest approach for Cr(III) ammine and aquo, reactants, respectively. The shaded and cross-hatched areas represent the corresponding values of the "effective reaction zone thickness" $\kappa_{el}^0 \delta r_e$ for these reactants.

ammine and pentaaquo Cr(III) reductions bridged by azide and isothiocyanato ligands since the Cr(III)–surface distance and hence the degree of orbital overlap should be determined by the bridging ligand. It therefore appears certain that $\kappa_{el}^0 \delta r_e$ is markedly larger for the ammine compared to the aquo reactants.

A persuasive explanation for this striking result is to be found in the differences in the location of the outer-sphere reaction sites that have been noted previously for these reactions.[6,12,13] Thus, the reduction rates of $Cr(OH_2)_6^{3+}$ and other Cr(III) aquo complexes are markedly less sensitive to variations in the double-layer potential profile than are the reduction rates of $Cr(NH_3)_6^{3+}$ and related Cr(III) ammines.[6] These results provide evidence that the Cr(III) aquo reaction sites are constrained to lie significantly further from the electrode surface. This is consistent with the larger hydrated radii for aquo vs. ammine reactants due to the more extensive ligand–solvent hydrogen bonding exhibited by the former complexes.[6,14] From an analysis of the observed double-layer effects, we have estimated that the reaction site for $Cr(OH_2)_6^{3+}$ reduction lies 6–7 Å from the surface, whereas that for $Cr(NH_3)_6^{3+}$ reduction is about 1.5 Å closer.[6] (Although the absolute reactant–electrode distances are subject to as much as 1–1.5 Å uncertainty, the relative distances for the aquo vs. ammine reactants are rather more reliable.) It is therefore to be expected that κ_{el}^0 will be larger for the ammine than for the aquo reactants unless the reactant–surface electronic coupling is sufficient to provide adiabatic pathways ($\kappa_{el}^0 \approx 1$) in both cases.

In order to interpret the individual values of $\kappa_{el}^0 \delta r_e$, it is advantageous to consider the encounter-preequilibrium treatment in a little more detail. Since κ_{el} will depend upon the donor–acceptor separation distance within the reaction zone of thickness δr_e, strictly speaking one should express the overall observed rate constant in terms of an integral of "local" values of k_{et}, each being associated with a particular spatial position and orientation of the reactant and hence individual values of κ_{el}, w_p, and ΔG_{et}^*.[2b] The dependence of κ_{el} upon the separation distance, r, for nonadiabatic pathways can be approximated by [2a,c]

$$\kappa_{el}(r) = \kappa_{el}^0 \exp[-\alpha(r - \sigma)] \tag{11}$$

where σ is the separation distance corresponding to closest approach, and α is a constant which is typically estimated to lie in the range ca. 1–2 Å^{-1}.[2c,15] Consequently, if $\kappa_{el}^0 < 1$ (i.e., the reaction is nonadiabatic at the plane of closest approach), the effective value of δr_e will equal α^{-1}. On the other hand, if σ is

(9) Barr, S. W.; Guyer, K. L.; Li, T. T.-T.; Liu, H. Y.; Weaver, M. J. In "The Chemistry and Physics of Electrocatalysis"; McIntyre, J. D. E., Weaver, M. J., Yeager, E., Eds.; The Electrochemical Society: Pennington, NJ, in press. Barr, S. W.; Weaver, M. J., submitted for publication.

(10) On the basis of crystallographic data for bridging azide and thiocyanate (Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford 1975; pp 648, 746) Cr^{III}–surface bond distances of 6.5–7 Å are obtained. However, the N_3^-–Hg and NCS^-–Hg bond angles are likely to be less than 180°, thereby decreasing somewhat the Cr^{III}–surface separation.

(11) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(12) Weaver, M. J. *J. Phys. Chem.* **1980**, *84*, 568.

(13) Weaver, M. J.; Liu, H. Y.; Kim, Y. *Can. J. Chem.* **1981**, *59*, 1944.

(14) (a) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (b) Weaver, M. J.; Nettles, S. M. *Inorg. Chem.* **1980**, *19*, 1641.

(15) Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78* (Part II), 4086.

sufficiently small so that $\kappa_{el} \approx 1$ not only at the distance of closest approach but also for a significant distance, χ, beyond it, we expect that roughly

$$\delta r_e = \chi + \alpha^{-1} \qquad (12)$$

Equation 12 therefore provides a general relationship where $\chi = 0$ if $\kappa_{el}^0 < 1$, and $\chi > 0$ if $\kappa_{el}^0 \approx 1$.

Figure 1 is a schematic representation of the dependence of κ_{el} upon r. The magnitude of $\kappa_{el}^0 \delta r_e$ will equal the area under the curve bounded by the distance of closest approach, for example, the shaded area A′A″C. Taking $\alpha \approx 1.5$ Å^{-1}, it follows that $\kappa_{el}^0 \delta r_e < 0.5$ Å if $\kappa_{el}^0 < 1$, whereas $\kappa_{el}^0 \delta r_e > 0.5$ Å if $\kappa_{el}^0 \approx 1$. The above estimate of $\kappa_{el}^0 \delta r_e$ for the Cr(III) aquo reactions, ca. 0.1–0.3 Å, therefore suggests that $\kappa_{el}^0 < 1$ at the plane of closest approach for the aquo cations, so that $\chi \approx 0$. However, this estimate of $\kappa_{el}^0 \delta r_e$ may be ca. 1.5–2-fold too small as a result of the likely differences in ΔG_{et}^* between the inner- and outer-sphere pathways noted above, although it may be too large if $\kappa_{el}^{is} < 1$. Another factor which would decrease the apparent value of $\kappa_{el}^0 \delta r_e$ is the possibility that a specific reactant orientation is required either to enable the reactant to approach the electrode more closely or to provide more effective coupling of the surface donor and Cr(III) acceptor orbitals. Such factors have recently been considered in detail for $Fe(OH_2)_6^{3+/2+}$ self-exchange.[2] In any case, we conclude that outer-sphere electron transfer involving the Cr(III) aquo reactants only approaches adiabaticity for electron-tunneling distances very close to the plane of closest approach of these cations (represented by B′B″ in Figure 1), around 6–7 Å from the electrode surface.

On the other hand, the estimate of $\kappa_{el}^0 \delta r_e$ for the Cr(III) ammines, ca. 5 Å, suggests that electron transfer to these reactants remains adiabatic even for reaction sites several angstroms from the plane of closest approach (represented by A′A″ in Figure 1). The exact value of $\kappa_{el}^0 \delta r_e$ for the amine reactants is in one respect subject to greater uncertainty than for the aquo reactants in that the magnitude of the work-term ("double-layer") correction upon k_{obsd} is somewhat greater for the former.[6] Moreover, the work-term correction employed assumes that the reaction occurs only at the outer Helmholtz plane (oHp), whereas the large value of $\kappa_{el}^0 \delta r_e$ suggests that the effective reaction zone is relatively thick. Given that the ammine reactants can probably penetrate inside the oHp, this work-term correction may well be an underestimate, so that k_{cor}^{os} and hence $\kappa_{el}^0 \delta r_e$ are actually smaller than the present values. Given that the aquo reactants are marginally adiabatic at their plane of closest approach, from the reaction site differences noted above it would be expected that $\chi \sim 2$ Å for the ammines, yielding $\kappa_{el}^0 \delta r_e \sim 2$–3 Å. One factor which may enhance $\kappa_{el}^0 \delta r_e$ for the ammine vs. the aquo complexes is the likely greater ligand character of the acceptor orbital on the former reactants,[2c] leading to greater electrode–reactant orbital overlap at a given electrode–reactant separation distance. The difference in the effective reaction zone thickness between the aquo and ammine reactants is therefore roughly compatible with the likely differences in the reaction sites if the dependence of κ_{el} upon the surface–reactant separation is similar for these reactants, with κ_{el} decreasing below unity for surface–reactant separations greater than ca. 6 Å.

Taking $\Gamma_n = 2.5$ and $\nu_n = 1.2 \times 10^{13}$ s^{-1} for the present reactions,[16] we deduce from eq 3 and 5 that the overall preexponential factor A is ca. 6×10^4 and 1.5×10^6 cm s^{-1} for the aquo and ammine reactants, respectively. Both these values are somewhat larger than the preexponential factor, ca. 5×10^3 cm s^{-1}, derived from the conventional collisional model assuming adiabatic behavior.[5c,17] It should be noted that the encounter-preequilibrium treatment employed here represents a departure from the collisional model since the latter views the reaction as being consum-

mated only by collisions between the reactant and the electrode surface (or a coreactant).[5c]

It is of interest to compare the above estimate of A for the Cr(III) aquo reactants with that obtained for $Cr(OH_2)_6^{3+}$ reduction under the same conditions from the temperature dependence of k_{cor}^{os}. We can write[17]

$$k_{cor}^{os} = (A/\Gamma_n) \exp(\Delta S_i^*/R) \exp(-\Delta H_i^*/RT) \qquad (13)$$

where ΔS_i^* and ΔH_i^* are the work-corrected "ideal" entropies and enthalpies of activation which form the components of ΔG_{et}^* at the particular electrode potential at which k_{cor}^{os} is obtained.[17,18] The activation enthalpy ΔH_i^* can be obtained directly from the Arrhenius slope of ln k_{cor}^{os} vs. $1/T$, being measured at a constant electrode potential using a nonisothermal cell arrangement.[18] The value of ΔS_i^* can be obtained from[1,19]

$$\Delta S_i^* = \alpha_{cor} \Delta S_{rc}^0 + \Delta S_{int}^* \qquad (14)$$

where α_{cor} is the work-corrected transfer coefficient, ΔS_{rc}^0 is the so-called reaction entropy of the redox couple concerned,[14a] and ΔS_{int}^* is the intrinsic activation entropy.[20] From the data given in ref 17, at −800 mV vs SCE, $k_{cor}^{os} = 5.5 \times 10^{-5}$ cm s^{-1} (25 °C), $\Delta H_i^* = 17.5$ kcal mol^{-1},[21] $\alpha_{cor} = 0.50$, $\Delta S_{rc}^0 = 49$ cal deg^{-1} mol^{-1}, and $\Delta S_{int}^* = -3.5$ cal deg^{-1} mol^{-1}.[20] Inserting these data into eq 13 and 14 yields $A = 2 \times 10^4$ cm s^{-1}. (This calculation cannot be performed for Cr(III) ammine reductions since the ΔS_{rc}^0 values are not known with sufficient accuracy.)

The ca. 3-fold discrepancy between this and the above estimate of A probably arises in part from the very approximate nature of eq 14. This relation presumes that the transition-state entropy is unaffected by the proximity of the reacting ions to the electrode surface, whereas it is likely that ΔS_i^* and ΔH_i^* are much more sensitive than is the overall barrier ΔG_{et}^* to the solvating environment at the interface and the bulk solution. Indeed, we have found that the activation parameters for these and other reactions are rather more sensitive than is k_{cor}^{os} to the nature of the electrode material, surprisingly small frequency factors being typically obtained at solid metal surfaces.[22]

Conclusions

The foregoing treatment provides a relatively direct, albeit approximate, experimental method for evaluating the effective electron-tunneling distances for outer-sphere electrochemical reactions. It exploits both the close relationship between the energetics of corresponding inner- and outer-sphere electrode reactions and the information that can be derived[6,13] on the reactant–electrode separation distance from the magnitude of the double-layer effects in electrochemical kinetics. A strictly analogous approach cannot be employed for homogeneous processes due to the inevitable changes in reactant coordination between otherwise related inner- and outer-sphere pathways and the lack of a means for subtly altering the electrostatic interactions between ionic reactants in solution.

Although it would not be surprising if similar differences in the internuclear distances and hence $\kappa_{el}^0 \delta r$ also arise between aquo

(16) Γ_n was calculated from the nuclear tunneling factor, Γ_n^h, for the $Cr(OH_2)_6^{3+/2+}$ self-exchange reaction (6.0) given in ref 1d using $\Gamma_n = (\Gamma_n^h)^{1/2}$ (ref 5c); ν_n equals the corresponding value for the self-exchange reaction.[1d]

(17) Equation 13 contains the prefactor A/Γ_n rather than A, since *experimentally* any nuclear tunneling contributions will appear directly in the measured activation parameters (cf. ref 20). Although confusing, this formulation maintains consistency with the preceding definitions. Note that ΔG_{et}^* as defined by eq 1 will equal $\Delta H_i^* - T\Delta S_i^* - RT$ ln Γ_n.

(18) Equivalently, A can be determined by evaluating the so-called "real" activation enthalpy from the temperature dependence of k_{cor}^{os} measured at a fixed overpotential, and assuming that the "real" activation entropy (i.e., the activation entropy corrected for the entropic driving force ΔS_{rc}^0) equals ΔS_{int}^*.[17,19,20]

(19) Weaver, M. J. *J. Phys. Chem.* **1976**, *80*, 2645; **1979**, *83*, 1748.

(20) The major component of ΔS_{int}^* is associated with the temperature dependence of Γ_n; a value of ca. −3.5 cal deg mol^{-1} is obtained from the corresponding quantity determined for self-exchange reactions, $\Delta S_{int}^*{}_h$, using the relations in ref 1b, given that $\Delta S_{int}^* = 0.5 \Delta S_{int}^*{}_h$. (The factor 0.5 arises because only one redox center has to be activated for the electrochemical reaction, rather than two as in the homogeneous case.) Recent work indicates that specific reactant–solvent interactions may provide an additional contribution of about 3 cal deg^{-1} mol^{-1} to ΔS_{int}^*.[28]

(21) The effective value of ΔH_i^* is slightly (0.3 kcal mol^{-1}) larger than the values given in ref 18 since these were determined by assuming that the frequency factor is slightly temperature dependent as expected from the collision model utilized in ref 18.

(22) Hupp, J. T.; Liu, H. Y.; Weaver, M. J., submitted for publication. Liu, H. Y. Ph.D. Thesis, Michigan State University, East Lansing, MI, 1982.

and ammine complexes in homogeneous electron-transfer reactions, the solvating environments may be sufficiently different from that pertaining to the present electrochemical reactions[23] to bring other factors to the fore. Indeed, the larger rate ratios for Co(III) ammine vs. aquo reactants observed at mercury electrodes relative to that obtained with a given reductant in homogeneous solution[12] suggest that these differences in $\kappa_{el}^0 \delta r$ may well be smaller in the latter environment. Nevertheless, the present finding that outer-sphere electrochemical reactions can be at least marginally nonadiabatic bears a close resemblance to the interpretation of some anion catalytic effects upon homogeneous outer-sphere reactions between cationic complexes[25] as well as to the results of the recent ab initio calculations noted above.[2] Similar calculations have yet to be performed for electron-transfer processes at metal surfaces; they would provide an invaluable guide to the further interpretation of the experimental data.

The present results therefore are at variance with a previous suggestion that the effective electron-tunneling probabilities should be much larger at metal surfaces due to the multitude of electronic energy states in the vicinity of the Fermi level that are available for coupling with the reactant orbitals.[26] Further support to the present findings is given by our observation that both the unimolecular rate constants and frequency factors for the electro-reduction of pentaamminecobalt(III) bound to a mercury surface via organic bridges are decreased markedly upon interruption of bond conjugation in the bridging ligand.[9,27] These observations serve to highlight the previously neglected role of nonadiabatic electron tunneling in influencing electron-transfer reactivity at electrode surfaces as well as in homogeneous solution.

(23) Evidence supporting such differences in the reactant solvation at mercury electrodes and in homogeneous solution is provided by the markedly different solvent deuterium isotope effects observed for aquo complexes in these reaction environments.[24]

(24) Weaver, M. J.; Tyma, P. D.; Nettles, S. M. *J. Electroanal. Chem.* **1980,** *114,* 53. Weaver, M. J.; Li, T. T.-T. *J. Phys. Chem.* **1983,** *87,* 1153.

(25) Endicott, J. F.; Ramasami, T. *J. Am. Chem. Soc.* **1982,** *104,* 5252.

(26) (a) Hale, J. M. "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Interscience: New York, 1971; Chapter 4. (b) Hale, J M. *J. Electroanal. Chem.* **1968,** *19,* 315.

(27) Li, T. T.-T.; Liu, H. Y.; Weaver, M. J., submitted for publication.

(28) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.,* in press.

Comparative Molecular Orbital Study of the Singlet State of *o*-Benzyne and Molecules with Similar Structural Elements

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We have carried out calculations at the 6-31G and 6-31G*(5D) levels on *o*-benzyne, benzene, *trans*-1,3-butadiene, ethane, ethylene, acetylene, and methane, and at the 6-31G level on butatriene and 1-buten-3-yne, with full geometry optimization. The ring geometry of *o*-benzyne is very similar to that reported in the literature using the STO-3G and 4-31G basis sets, but the optimization of the carbon–hydrogen bonding shows the C–H bonds nearer the dehydro bond to be tilted away from it and to be somewhat shorter than the farther C–H bonds. From a comparison of experimental and calculated bond lengths for acetylene, ethylene, and benzene an experimental geometry has been predicted for *o*-benzyne. Comparisons of calculated bond lengths, π-charge transfer, and π-electron overlap populations for *o*-benzyne, benzene, and the acyclic molecules add further support to the widely held view that *o*-benzyne is aromatic in character. Calculations at the 6-31G level, like those with the STO-3G and 4-31G basis sets, find an alternation in the π-electron overlap population going round the ring but, unlike these other calculations, also find an alternation in the σ-electron overlap population. Energetic aspects of the bonding in *o*-benzyne are studied in terms of isodesmic bond separation and homodesmotic group separation reactions for both aryne-like and cumulene-like valence bond structures. Whereas the isodesmic reaction energies are either positive or only slightly negative, giving no indication of significant ring strain, the homodesmotic reaction energies are large and negative, indicative of a highly strained structure.

Introduction

The participation of *o*-benzyne (1,2-dehydrobenzene) as an intermediate in many reactions is well established,[1] and it is generally accepted that the ground state is a closed-shell singlet.[2–5] But its transient nature and high reactivity have made the experimental investigation of its structure quite difficult. Utilizing normal-coordinate analysis in conjunction with observed matrix-infrared vibration frequencies, Laing and Berry[6] concluded that an aryne-like structure (Figure 1a) gives a better fit than either a cumulene-like structure (Figure 1b) or the type of structure having no bond length alternation predicted by the

majority of the semiempirical calculations, MINDO/2,[7] MINDO/3,[3] MNDOC,[8] and MNDO-CI,[5] and the ab initio calculations, STO-3G[9,10] and 4-31G,[4] reported in the literature (see

(1) Hoffman, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press: New York, 1967.

(2) (a) Wittig, G.; Peiper, G.; Fuhrmann, G. *Ber. Dtsch. Chem. Ges.* **1940,** *73,* 1193. (b) Wittig, G. *Naturwissenschaften* **1942,** *30,* 696.

(3) Dewar, M. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974,** *97,* 5569.

(4) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979,** *101,* 51.

(5) Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983,** *105,* 3162.

(6) Laing, J. W.; Berry, R. S. *J. Am. Chem. Soc.* **1976,** *98,* 660.

(7) Haselbach, E. *Helv. Chim. Acta* **1971,** *54,* 1987.

(8) Thiel, W. *J. Am. Chem. Soc.* **1981,** *103,* 1420.

(9) Newton, M. D.; Fraenkel, H. A. *Chem. Phys. Lett.* **1973,** *18,* 244.

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