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J T HUPP ET AL. FEB 83 TR-12 N00014-83-K-0086
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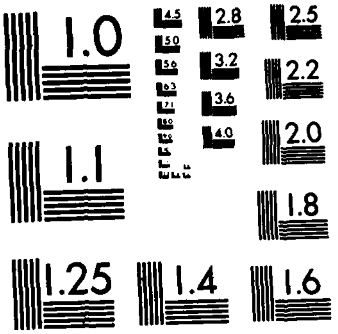
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Contract N00014-83-K-0086

TECHNICAL REPORT NO. 12

The Frequency Factor For Outer-Sphere Electrochemical Reactions

by

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Prepared for Publication

in the

Journal of Electroanalytical and Interfacial Electrochemistry

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February 1983

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 12	2. GOVT ACCESSION NO. A126722	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (*and Subtitle*) The Frequency Factor for Outer-Sphere Electrochemical Reactions		5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 12
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(*s*) Joseph T. Hupp and Michael J. Weaver		8. CONTRACT OR GRANT NUMBER(*s*) N00014-83-K-0086
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Purdue University West Lafayette, IN 47907		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE February, 1983
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)		15. SECURITY CLASS. (*of this report*) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for Public Release; distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Frequency factor, electrochemical kinetics, outer-sphere electron transfer

A sub(n)(e)

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The conventional formulation of the frequency factor A_n^e for outer-sphere electrochemical reactions based on a "collisional" model is compared with an alternative "encounter preequilibrium" treatment whereby A_n is determined by the effective frequency of surmounting the free energy barrier within a previously assembled precursor state. The latter model is shown to provide a more appropriate description for electrochemical reactions under most conditions, in harmony with analogous considerations for homogeneous redox

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A sub n(e)

processes. Noticeably (ca. 20-fold) larger values of A_n^e are derived from the encounter preequilibrium as compared to the collisional model. Numerical relationships between the kinetics of corresponding electrochemical and homogeneous reactions and of competing inner- and outer-sphere electrochemical pathways that are significantly different from the conventional relations are also predicted on the basis of the encounter preequilibrium model. The relationships between A_n^e and experimental frequency factors obtained from the temperature dependence of electrochemical rate constants are also considered in the light of these considerations.

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The observed rate constant, k_{ob} (cm sec^{-1}), for heterogeneous outer-sphere electron transfer is usually related to the overall free energy barrier $\Delta G^{\ddagger}$, by[1]:

$$k_{ob} = \kappa_{el} A_n \exp(-\Delta G^{\ddagger}/RT) \qquad (1)$$

where κ_{el} is the electronic transmission coefficient, and A_n is the nuclear frequency factor (cm sec^{-1}). The latter term equals the effective frequency at which the transition state is approached from the reacting species via rearrangement of the appropriate nuclear coordinates, whereas κ_{el} describes the probability with which electron transfer will occur once the transition state has been formed. For so-called adiabatic processes, $\kappa_{el} \approx 1$, whereas for nonadiabatic processes, $\kappa_{el} << 1$. Essentially equivalent approaches can be employed for both homogeneous and electrochemical electron-transfer processes. Knowledge of A_n and κ_{el} is required in order to extract estimates of $\Delta G^{\ddagger}$ from experimental rate constants, thereby providing the link with theoretical treatments of electron transfer which are generally expressed in terms of Franck-Condon barriers. The value of the frequency factor is also closely related to questions concerning the theoretical upper limits to electrochemical rate constants.

Although A_n has conventionally been assumed to correspond to a collision frequency Z, there are good reasons to prefer a somewhat different formulation based on an "encounter preequilibrium" model whereby the frequency factor is determined by the vibrational activation of a binuclear "encounter (or precursor) complex" having a suitable geometric configuration for electron transfer.[2-8] Such a model has received a good deal of recent attention for homogeneous redox processes.[2-6] We have suggested that a similar preequilibrium, rather than a collisional, description is also appropriate for outer-sphere electrochemical reactions.[7,8] In this communication, we critically compare such collisional and encounter preequilibrium formulations of the electrochemical frequency factor, and consider the consequences of employing the latter formalism upon some theoretical expressions for electrochemical kinetics and their relationship to those for homogeneous redox processes.

The Collisional Model

As already noted, the nuclear frequency factor for electrochemical reactions, A_n^e, has conventionally been assumed to equal the rate, Z_e (cm. $\sec^{-1}$), at which unit bulk concentration of reactant molecules strike unit area of a two-dimensional "reaction plane" at (or suitably close to) the electrode surface, leading to reaction. This is usually taken to be equal to the collision number for gas-phase heterogeneous collisions involving hard spheres given by[1]:

$$Z_e = (k_B T/2\pi m)^{\frac{1}{2}} \tag{2}$$

where k_B is the Boltzmann constant and m is the mass of the reactant. The corresponding expression for the collision frequency, Z_h($\underline{M}^{-1}$ $\sec^{-1}$), commonly used for electron-transfer reactions in homogeneous solution is[1]

$$Z_h = 10^{-3} N r_h^{\,2} (8\pi k_B T/m_r)^{\frac{1}{2}} \tag{3}$$

where N is Avogadro's number, and m_r and r_h are the effective reduced mass and the distance between the reacting centers, respectively, for the collision complex.

Such expressions are not strictly applicable to condensed-phase reactions since collisions involving solute molecules are expected to occur within solvent cages ("encounters") having average lifetimes that are long compared to the collisions themselves. Expressions for the rate of diffusion-controlled encounter formation have been given for homogeneous reactions,[9,10] the best known being the Smoluchowski equation.[9] An analogous expression for the rate of diffusion-controlled encounters between a spherical reactant and a plane surface has been given as[11]

$$Z_e = 3D/2\lambda \quad (4)$$

where D is the diffusion coefficient of the reactant and λ is the average distance over which the reactant is required to move between adjacent "lattice positions" in the solvent. Somewhat smaller estimates of Z_e are obtained using Eq (4) than from Eq (2); thus inserting the typical values $D = 10^{-5}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$ and $\lambda = 3 \times 10^{-8}$ cm into Eq (4) yields $Z_e = 5 \times 10^2\ \mathrm{cm\ sec}^{-1}$, whereas $Z_e = 5 \times 10^3\ \mathrm{cm\ sec}^{-1}$ from Eq (2) at ambient temperatures taking $N_m = 200$. Similarly smaller estimates of Z_h are obtained using the Smoluchowski equation in place of Eq (3).[9] A number of collisions are nevertheless expected to occur during each diffusive encounter, so that Eqs (2) and (3) may predict roughly the correct order of magnitude of the collision frequencies in solution. Values of Z_h that are somewhat larger than given by Eq (3) result from a detailed consideration of such "solvent cage" effects.[10]

However, there are two difficulties with such collisional formulations for electrochemical as well as homogeneous electron-transfer reactions. By extending the analogy with gas-phase reactions the model seems to imply that the collisions themselves are responsible for activating the reactant molecules; in other words, a portion of the translational momentum of the reactant is converted to an activation energy. In contrast, contemporary theories of electron transfer maintain that reactants are activated through solvent polaron fluctuations (outer-shell modes) and by energy transfer from solvent phonons to inner-shell vibrational modes.[12] This problem can be circumvented by noting that the collision model applied to electrochemical reactions requires only that *suitably activated* reactants strike the electrode at a certain frequency. Unlike gas-phase reactions, activation in solution need not occur simultaneously with the collisions. Thus the usual formulation of the collision model for electron-transfer processes in solution represents an anomalous situation in chemical kinetics, namely that the chosen frequency factor for the elementary reaction does not correspond to the frequency of passage across the barrier.

A more serious difficulty concerns the implication that charge transfer involves only those reactants striking the collision plane, presumably the outer Helmholtz plane for outer-sphere electrode reactions. Actually, since outer-sphere reactions involve only electron tunneling which in principle can occur between essentially isolated donor and acceptor orbitals, reactivity is not confined to the collision plane but instead can involve any reactant molecules located within a range of distances from the electrode surface.[6] The collisional model may therefore underestimate the number of molecules contributing to the observed reaction rate, yielding a falsely small value of the frequency factor A_n.

The Encounter Preequilibrium Model

These difficulties suggest that a more appropriate description of the frequency factor for outer-sphere electron-transfer is in terms of activation via solvent-reactant energy transfer of isolated reactant molecules that nevertheless are located so to allow electron transfer to occur with reasonable probability once the appropriate configuration of the nuclear coordinates has been achieved. The probability of electron tunneling, κ_{el}, between the reactant and electrode, as between a pair of reactants in homogeneous solution,[3,5,6] will be sensitive to the degree of overlap between the donor and acceptor orbitals. It is therefore useful to conceive of a "reaction zone" of thickness δr_e that encompasses those molecules that lie sufficiently close to the surface to contribute importantly to the observed reaction rate. This enables the observed rate constant k_{ob} (cm. sec^{-1}) to be related to a unimolecular rate constant, k_{et} (sec^{-1}), for electron transfer within this reaction zone ("precursor state"):

$$k_{ob} = K_p^e k_{et} \qquad (5)$$

The effective "equilibrium constant" for forming the precursor state, K_p^e (cm), is given by[7,8]

$$K_p^e = \delta r_e \exp(-w_p^e/RT) \qquad (6)$$

where w_p^e is the average free energy required to transport the reactant from the bulk solution to the reaction zone. Approximate estimates of w_p^e may be obtained for outer-sphere reactions using the Gouy-Chapman or more sophisticated electrostatic models. This work term describes the modification to the effective "cross-sectional" reactant concentration (mole cm^{-2}) within the precursor state caused by differences in the environment around the reacting species in the reaction zone and that in the bulk solution.

The corresponding statistical model that describes the stability constant, K_p^h ($\underline{M}^{-1}$), for formation of the precursor complex involving a pair of spherical reactants in homogeneous solution* is[4,13-15] [cf. Eq. (6)]:

$$K_p = 10^{-3} 4\pi N r_h^2 \delta r_h \exp(-w_p^h/RT) \qquad (7)$$

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*Estimates of K_p for homogeneous reactions have also been obtained[2] using the related expression $K_p^h = (4\pi N r_h^3/3000)\exp(-w_p^h/RT)$, which refers to the probability of forming contact pairs between two spherical species. However, Eq. (7) or closely related expressions[15] provide a more appropriate description of the probability that one reactant is present within a given inclusion volume surrounding the coreactant.[5,13,15]

where δr_h (cm) is the thickness of the reaction layer that lies beyond the distance, r_h, that separates the reactant pair when they are in contact, and w_p^h is the average free energy work expended in forming this precursor complex. The quantities δr_e and δr_h are determined by the effective electron tunneling distances in heterogeneous and homogeneous environments, respectively. More precise treatments can be formulated for both electrochemical and homogeneous processes whereby the rate is expressed in terms of an integral of incremental reactant separations multiplied by the respective transition probabilities (*vide infra*).[14] For nonsymmetrical reactants the necessary orbital overlap may only be achieved by attaining a particular molecular orientation at the reaction site, requiring the inclusion of a fractional "steric factor" in Eqs. (5) and (6).[15] Nevertheless, the simple treatment given here is adequate for the present purposes, especially *in lieu* of information on the dependence of κ_{el} upon δr_e and orbital symmetry for electrochemical reactions.

Equation (5) treats the overall reaction as a two-step process involving the *unimolecular* activation of reactant within the precursor state that is in quasi-equilibrium with respect to the bulk reactant state. A similar "encounter preequilibrium" model was advocated some time ago for bimolecular solution reactions in general.[13] It is expected that the rate-determining step commonly involves activation within an "encounter complex" formed with a solvent cage, although the effective frequency factor for ordinary chemical reactions (eg atom, group transfers) refers to "vibrational collisions" between the reactants within this cage.[13] The unimolecular rate constant k_{et} for an elementary electron-transfer step can be expressed as[3]

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

where Γ_n is a nuclear tunneling factor, ν_n is a nuclear frequency factor (sec^{-1}), and ΔG^* is the electrochemical free energy for activation from the precursor state. The nuclear tunneling term is a quantum-mechanical correction which adjusts the rate expression to account for the contribution from molecules which react without entirely surmounting the classical free energy barrier.[3] The nuclear frequency factor ν_n corresponds to the effective frequency with which the configuration of the various nuclear coordinates appropriate for electron transfer is reached from the precursor state. Since such activation results from a combination of solvent reorientation, polarized solvent vibrations and inner-shell (reactant bond) vibrations bond lengths,[3,6] ν_n can be taken as an appropriately weighted mean[16] of the characteristic frequencies for these processes.[6] The major contributions to these manifold motions arise from solvent reorientation and symmetric stretching vibrations of the reactant. Thus[3]:

$$\nu_n^2 = \frac{\nu_{os}^2 \Delta G_{os}^* + \nu_{is}^2 \Delta G_{is}^*}{\Delta G_{os}^* + \Delta G_{is}^*} \qquad (9)$$

where ν_{os} and ΔG_{os}^* are the characteristic frequency and free energy of activation associated with outer-shell (solvent) reorganization, and ν_{is} and ΔG_{is}^* are the corresponding quantities associated with inner-shell bond vibrations.

The preequilibrium formalism for electrode reactions embodied in Eqs. (5), (6), (8), and (9) can be placed in the same format as Eq. (1) by noting that the free-energy barrier for the overall reaction, $\Delta G^{\ddagger}$, and that for the elementary step within the precursor state, ΔG^{*}, are related by $\Delta G^{\ddagger} = \Delta G^{*} + w_p^e$. Therefore from Eqs. (5),(6), and (8), the electrochemical frequency factor A_n^e is given by

$$A_n^e = \delta r_e \Gamma_n \nu_n \tag{10}$$

Similarly, in view of Eq (7) the corresponding frequency factor A_n^h for homogeneous reactions is given by

$$A_n^h = 10^{-3} 4\pi N r_h^2 \delta r_h \Gamma_n \nu_n \tag{11}$$

Although Γ_n is calculated to be substantially greater than unity at low temperatures for reactions having large inner-shell barriers ΔG_{is}^{*},[3] it typically approaches unity ($\Gamma_n \approx$ 1-2) at ambient temperatures.** Typical values of ν_n may be obtained from Eq. (9) by noting that $\nu_{os} \approx 10^{11}$ sec^{-1} in water and $\nu_{is} \approx 10^{13}$ sec^{-1} for a typical metal-ligand stretching frequency.[3] Although the numerical value of ν_n also depends somewhat on the relative values of ΔG_{is}^{*} and ΔG_{os}^{*} for the common situation where $\Delta G_{is}^{*} \gtrsim 0.25\ \Delta G_{os}^{*}$, $\nu_n \approx 0.5$ to 1×10^{13} sec^{-1}. (For some organic compounds ν_{is} may approach 10^{14} sec^{-1}, yielding correspondingly larger values of ν_n).

**The values of Γ_n for electrode reactions, Γ_n^e, will generally be smaller than those for homogeneous reactions, Γ_n^h, since only one reactant center is activated in the former processes. Thus for exchange reactions $\Gamma_n^e = (\Gamma_n)^{1/2}$. Also, Γ_n^h and hence Γ_n^e will gradually approach unity as the driving force is progressively increased.[18]

There is some uncertainty regarding the magnitude of δr_e. In an early discussion it was speculated that $\delta r_e \sim 1\mathrm{x}10^{-8}$ cm.[17] We suggested that δr_e could be set equal to the reactant radius, since reactants within this distance of the plane of closest approach might be expected to have a roughly equal chance of undergoing electron transfer.[7] In order to deduce a more quantitative estimate of δr_e it is necessary to know how κ_{el} varies with the reactant-electrode separation distance. In the adiabatic limit there will be some range of distances beyond the plane of closest approach wherein $\kappa_{el} \approx 1$, beyond which κ_{el} diminishes to negligibly small values. It has been suggested that electrode reactions at metal surfaces are much more likely to be adiabatic than are homogeneous redox processes.[19] Satisfactory calculations have yet to be performed. However, outer-sphere electrode reactions are believed to involve a plane of closest approach separated from the electrode surface by a layer of solvent molecules.[20] By analogy with the results of recent *ab initio* calculations for homogeneous outer-sphere reactions[5,21,22] one therefore might anticipate that outer-sphere electrode reactions are weakly adiabatic or even nonadiabatic. In this case κ_{el} is expected to vary with separation distance, r, according to:

$$\kappa_{el}(r) = \kappa_o \exp[-\alpha(r-\sigma)] \qquad (12)$$

where κ_o is the value of $\kappa_{el}(r)$ at the plane of closest approach, and σ is the value of r at this point. The coefficient α has been variously estimated between 1.8×10^8 cm^{-1} and 1.4×10^8 cm^{-1} for reactions between metal ions.[6,22,23] Taking $\alpha = 1.6 \times 10^8$ cm^{-1}, it is found that $\kappa_{el}(r)$ drops to only 20% of κ_o at $(r-\sigma) = 1 \times 10^{-8}$ cm. Comparable values of α might be expected for related electrochemical processes. Consequently, for electrode reactions that are either weakly adiabatic or nonadiabatic it is reasonable to assume that $\delta r_e \sim 1 \times 10^{-8}$ cm.

If the former is the case, then effectively $\kappa_{el} \simeq 1$ in Eq. (8); for the latter, then $\kappa_{el} < 1$, the magnitude of κ_{el} depending on the degree of overlap between the surface and reactant orbitals at the plane of closest approach. One factor that may diminish the effective value of δr_e is the expectation that the activation energy ΔG^* will be somewhat smaller for transition states formed closer to the electrode as a result of stabilizing imaging interactions with the metal surface.[1,24]

Assuming then that $\delta r_e = 1 \times 10^{-8}$ cm, along with $\nu_n = 1 \times 10^{13}$ sec^{-1} and $\Gamma_n = 1$ leads from Eq (10) to a "typical" value of $A_n^e = 1 \times 10^5$ cm sec^{-1}, to be compared with the typical value 5×10^3 cm sec^{-1} obtained using the collision formulation [Eq (2)] that was noted above. It also appears likely that $\delta r_h \sim 1 \times 10^{-8}$ cm[4]; inserting this estimate into Eq. (11) along with the typical values $r_h = 7 \times 10^{-8}$ cm, $\nu_n = 1 \times 10^{13}$ sec^{-1}, and $\Gamma_n = 1$ yields $A_n^h = 3.5 \times 10^{12}$ $\underline{M}^{-1}$ sec^{-1}. As for the heterogeneous case, this estimate of A_n^h is noticeably larger than the values of Z_h obtained from Eq (3); thus if $Nm_r = 100$ and $r_h = 7 \times 10^{-8}$cm, $A_h = 2.5 \times 10^{11}$ $\underline{M}^{-1}$ sec^{-1}.

Comparisons of Models

These different values of A_n predicted using the collisional and encounter preequilibrium formalisms reflect the disparate physical models upon which they are based. Comparision between these two models for electrochemical reactions is facilitated by noting that the collision frequency can be viewed naively as the velocity with which reactants from bulk solution "pass through" the reaction zone. Taking a collision "velocity" to be 5×10^3 cm sec^{-1} along with an effective reaction zone thickness of 1×10^{-8} cm., each reactant molecule is estimated to remain in the zone for about 2×10^{-12} sec. On the basis of the preequilibrium formulation, during this period reacting molecules would be activated about 20 times if $\nu_n = 1 \times 10^{13}$ sec^{-1}. Therefore the encounter preequilibrium model yields an appropriately larger frequency factor accounting for the additional opportunities for a molecule to undergo electron transfer while within the reaction zone that is prescribed by the effective electron tunneling distance.

Under typical experimental conditions the encounter preequilibrium model therefore seems to provide a more appropriate description for electrochemical as well as homogeneous reactions. However, there may be circumstances in which the collisional model applies. Thus for small reactants Z_e estimated from Eq (2) can be greater than 10^4 cm sec^{-1}, while ν_n can be as small as ca. 10^{11} sec^{-1} for reactions that require little or no inner-shell reorganization [i.e. $\Delta G^*_{is} = 0$ in Eq. (9)]. Characterizing Z_e again as a velocity, under these circumstances the reactant could pass through the prescribed ca. 1×10^{-8}cm reaction zone in less than one tenth the time required for unimolecular activation, whereupon Z_e would provide the appropriate frequency at which the reaction could be consummated. Another situation where the preequilibrium model will clearly fail is when the rate of the elementary electron-transfer step becomes sufficiently large so that the preceding step involving precursor state formation is no longer in quasi-equilibrium, ultimately becoming the rate-determining step. In this case the effective frequency factor will equal Z_e given by Eq (4) since it refers to the transport-controlled formation of the precursor state.

Nevertheless, the onset of rate control by precursor state formation should only occur for outer-sphere electrochemical reactions having rate constants approaching ca. 10^2 cm sec^{-1}, which are beyond the range of experimental accessibility using conventional methods. It should be noted that the onset of partial rate control by diffusion polarization that is commonly encountered in electrochemical kinetics will not vitiate the applicability of the preequilibrium formalism since quasi-equilibrium will normally be maintained throughout the diffusion-depletion layer. This allows the reactant concentration immediately outside the double layer that is required for the evaluation of k_{ob} to be determined using Fick's Laws of diffusion.

The appearance of the precursor work terms w_p^e in Eq. (6) suggests that the evaluation of k_{et} using the preequilibrium formulation also accounts for the influence of the double-layer structure upon k_{ob}. That this is only partly correct can be seen by recalling the general form of the double-layer effect upon k_{ob}[7,8,20]:

$$\ln k_{corr} = \ln k_{ob} + (1/RT)\ w_p^e + \alpha_I (w_s^e - w_p^e) \qquad (13)$$

where w_s^e is the work of transporting the *product* from the bulk solution to the interfacial reaction site (the "successor state"), and α_I is the intrinsic transfer coefficient ("symmetry factor", ≈ 0.5). The "corrected" rate constant k_{corr} is the value of k_{ob} that would be observed at a given electrode potential in the absence of the double layer. By comparison, from Eqs. (5) and (6):

$$\ln k_{et} = \ln k_{ob} - \ln \delta r_e + (1/RT) w_p^e \qquad (14)$$

The difference between Eqs. (13) and (14) is that the latter corrects only for the effect of the double layer upon the stability of the *precursor* state, whereas the former, via the additional term $\alpha_I (w_s^e - w_p^e)$, accounts also for the double-layer effect upon the elementary electron-transfer step.[8] Nevertheless, a rate constant corresponding to k_{corr}, k_{et}^{corr}, may also be defined using the preequilibrium formulation, whereby:

$$k_{et}^{corr} = k_{corr} / \delta r_e \qquad (15)$$

Relation between Electrochemical and Homogeneous Rate Constants

According to the model of Marcus based on a weak adiabatic treatment, the (work-corrected) rate constant for electrochemical exchange of a given redox couple, k_{ex}^{e}, (i.e. the "standard" rate constant), is related to the (work-corrected) rate constant for the corresponding homogeneous self exchange reaction, k_{ex}^{h}, by[1,25]

$$(k_{ex}^{e}/Z_e)^2 \leqslant k_{ex}^{h}/Z_h \qquad (16)$$

where Z_e and Z_h are given by Eqs. (2) and (3), respectively.

Equation (16) arises from the theoretically expected relationship between the corresponding intrinsic free energy barriers to electrochemical exchange and homogeneous self exchange, $\Delta G^{*}_{ex,e}$ and $\Delta G^{*}_{ex,h}$, respectively. It is generally expected that

$$2\Delta G^{*}_{is,e} = \Delta G^{*}_{is,h} \qquad (17)$$

where $\Delta G^{*}_{is,e}$ and $\Delta G^{*}_{is,h}$ are the components of these intrinsic barriers associated with inner-shell (usually metal-ligand) reorganization. The relation between the outer-shell (solvent reorganization) components of the intrinsic barriers, $\Delta G^{*}_{os,e}$ and $\Delta G^{*}_{os,h}$, is more complicated (and tenuous), being dependent on the relative distances between the reacting centers for the homogeneous process and between the reactant and its image in the electrode for the electrochemical process, R_h and R_e, respectively.[1,25] From the Marcus treatment[1,25]

$$2\Delta G^{*}_{os,e} = \Delta G^{*}_{os,h} + \frac{e^2}{4}\left(\frac{1}{R_h} - \frac{1}{R_e}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \qquad (18a)$$

$$= \Delta G^{*}_{os,h} + C \qquad (18b)$$

where e is the electronic charge, and ε_{op} and ε_s are the optical and static dielectric constants, respectively.

In view of Eqs. (1), (15), and (16), we can write

$$2 \log (k^e_{ex}/\kappa^e_{el}A^e_n) = \log (k^h_{ex}/\kappa^h_{el}A^h_n) - C/2.303RT \qquad (19)$$

where κ^e_{el} and κ^h_{el} are the effective transmission coefficents for the electrochemical and homogeneous exchange reactions, respectively.

Equation (19) represents a more complete version of the conventional relation Eq (16). Since for outer-sphere reactions it is generally expected that $R_e > R_h$ then from Eq (18), $C > 0$; this is responsible for the inequality sign in Eq (16). Commonly, however, an equality sign is employed in Eq (16), and the frequency factors are presumed to be given by Eqs (2) and (3). In view of the above discussion, it is deemed more appropriate to employ Eq (19) with A^e_n and A^h_n estimated using the encounter preequilibrium formulation [Eqs (10), (11)] rather than Eq (16).

Noticeably different numerical relationships between k^e_{ex} and k^h_{ex} are predicted by Eqs. (16) and (19). In the limiting case where $C = 0$ (i.e. $2\ \Delta G^*_{ex,e} = \Delta G^*_{ex,h}$), using the typical numerical values $Nm = 200$, $Nm_r = 100$, $T = 298^oK$, $r_h = 7 \times 10^{-8}$cm, $\delta r_e = \delta r_h = 1 \times 10^{-8}$ cm, $\kappa^e_{el} = \kappa^h_{el} = 1$, yields from Eq (16)

$$(k^e_{ex})^2 = 8.5 \times 10^{-5}\ k^h_{ex} \qquad (20)$$

whereas from Eq (19)

$$(k^e_{ex})^2 = 2.5 \times 10^{-3}\ k^h_{ex} \qquad (21)$$

with k^e_{ex} in cm sec^{-1} and k^h_{ex} in $\underline{M}^{-1}$ sec^{-1}. The common observation[26] that $(k^e_{ex})^2 \lesssim 10^{-4}\ k^h_{ex}$ therefore indicates that the inequality $\Delta G^*_{ex,e} > \Delta 0.5\ G^*_{ex,h}$ is rather larger than previously suspected on the basis of the collisional formulation [Eq (20)]. However, taking into account the likely magnitude of the inequality $2\Delta G^*_{ex,e} > \Delta G^*_{ex,h}$ by estimating C as in Eq (18a) leads to very good agreement between Eq (19) and experimental rate data for a number of transition-metal couples.[27]

One recent discussion of the relationship between electrochemical and homogeneous rate constants also employs a preequilibrium model for the frequency factors.[28] A relation was derived that is numerically the same as that conventionally obtained using the collisional treatment, resulting from an apparent identity of $\nu_n \cdot \delta r_e$ with Z_e. However, this numerical agreement is fortuitous, resulting from the assumptions $\delta r_e = 10^{-7}$ cm and $\nu_n = 10^{11}$ sec^{-1}.[28] The latter choice was prompted by the presumption[28] that ν_n approximates the frequency of solvent reorientation when ΔG^*_{os} provides the major part of ΔG^*. As noted above, typically $\nu_n \approx \nu_{is} \sim 10^{13}$ sec^{-1} even when $\Delta G^*_{os} > \Delta G^*_{is}$.

Comparison between the Kinetics of Corresponding Inner- and Outer-Sphere Pathways

Besides the inherent virtues of the preequilibrium model, it is clearly also applicable to inner-sphere electrode reactions since these involve the formation of a specifically adsorbed intermediate of well-defined structure, analogous to the binuclear "precursor complexes" formed with homogeneous inner-sphere reactions. Although K_p^e cannot normally be estimated theoretically for inner-sphere pathways, it can be measured directly for reactions for which the precursor intermediates are sufficiently stable to be analytically detected. Thus $K_p^e = \Gamma_p/C_b$, where Γ_p is the concentration of the (adsorbed) precursor intermediate and C_b is the bulk reactant concentration.[7] Values of k_{et} can therefore be determined from k_{ob} and K_p^e using Eq (5), or directly from the current required to reduce or oxidize a known concentration of adsorbed reactant.[29]

Since Eq. (8) is expected to apply equally well to precursor states involving surface-attached or unattached reactants, the comparison between corresponding values of k_{et} for a given electrode reaction proceeding via inner- and outer-sphere pathways provides fundamental information on the influence of reactant-surface binding upon the energetics of the elementary electron-transfer step.[7] We have made such a comparison for a number of reactions involving transition-metal complexes at both mercury and solid electrodes; the results are described in detail elsewhere.[7,30,31] In particular, it appears that the overall catalyses (i.e. larger values of k_{ob}) often observed for inner-sphere reactions, especially at solid metal surfaces, are frequently influenced by alterations in the elementary free-energy barrier ΔG^* as well as by larger values of K_p brought about by surface attachment.[30,31] In the context of the present discussion, it is important to note that ΔG^* for outer- as well as inner-sphere electron transfer should be estimated using Eqs. (5), (6), and (8), rather than the conventional use of Eqs. (1) and (10) assuming that A_n equals Z_e [Eq. (2)].

The Apparent Frequency Factor from the Temperature Dependence of Electrochemical Kinetics

The principle, direct information on the magnitude of the frequency factor for electrochemical reactions can be obtained from measurements of the dependence of electrochemical rate constants upon temperature. Despite the early seminal work of Randles[17,32] relatively few measurements of electrochemical Arrhenius parameters have been reported,
at least under well-defined conditions. This is due in part to a widespread doubt as to their theoretical significance arising from an apparent ambiguity in how to control the electrical variable as the temperature is altered. We have recently discussed the matter in detail for mechanistically simple electrode processes involving both solution-phase[33-35] and surface-attached reactants.[36]

Conventionally:

$$k_{corr} = A' \exp(-\Delta H^{\ddagger}/RT) \qquad (22)$$

where $\Delta H^{\ddagger}$ and A' are the activation enthalpy and apparent frequency factor, respectively, obtained from an Arrhenius plot.

Two different types of activation enthalpies should be distinguished.[33-35] The so-called "ideal" activation enthalpies $\Delta H_i^{\ddagger}$, are derived from the temperature dependence of the rate constant measured at a constant metal-solution (Galvani) potential difference. So-called "real" activation enthalpies, $\Delta H_r^{\ddagger}$, are obtained from the temperature dependence of the standard rate constant; i.e., of the rate constant measured at the standard potential *at each temperature*. The former approximate the actual enthalpic barrier at the electrode potential at which it is measured,[33-35] whereas the latter equal the enthalpic barrier that remains in the absence of an enthalpic driving force, i.e. under "thermoneutral" conditions.[17,33]

The frequency factor A_i' obtained from $\Delta H_i^{\ddagger}$ and k_{corr} will differ markedly from the "true" frequency factor A_n [Eq. (1)] since A_i' will contain a contribution from the entropic driving force.[33-35] However, the frequency factor A_r' extracted from $\Delta H_r^{\ddagger}$ and k_{corr} is closely related to A_n since[33-35]

$$\begin{aligned} k_{corr} &= A_r' \exp(-\Delta H_r^{\ddagger}/RT) \\ &= \kappa_{el}^{e} A_n^{e} \exp(\Delta S_{int}^{\ddagger}/R) \exp(-\Delta H_r^{\ddagger}/RT) \qquad (23) \end{aligned}$$

where $\Delta S_{int}^{\ddagger}$ is the "intrinsic" activation entropy, i.e. the activation entropy that remains after correction for the entropic driving force. Providing that the outer-sphere transition state is formed in a similar solvent environment to that experienced by the bulk reactant and product, $\Delta S_{int}^{\ddagger}$ will be close to zero (± 10 J deg^{-1} mol^{-1}),[36] so that $A_r' \approx A_n$ providing that $\kappa_{el}^{e} \sim 1$ and the appropriate double-layer corrections upon the rate constants have been made.

Experimental values of A_r' (or equivalently, apparent activation entropies obtained assuming a value of A_n) are not abundant, especially for conditions where the electrostatic double-layer corrections are known with confidence. At metal-aqueous interfaces, it appears that $A_r' \lesssim 10^3$ cm sec^{-1} for most transition-metal redox couples.[32-35,37] Since these values are closer to that predicted from the collisional than from the encounter preequilibrium formulation (*vide supra*) it might be argued that the former model is more appropriate. However, it seems likely that these disparities arise in part from a breakdown in the assumption $\Delta S_{int}^{\ddagger} = 0$ as a result of differences in the solvating environment at the electrode surface and in the bulk solution.

Smaller (ca. 5- to 10-fold) values of A_r relative to A_n can also result for reactions having large inner-shell barriers since then Γ_n and therefore A_n will decrease significantly with increasing temperature.[3] In addition, the observation $A_r << A_n$ could result from $\kappa_{el} << 1$ [Eq. (23)], i.e. from nonadiabaticity effects. However, values of A'_r determined in aprotic solvents are typically close to those predicted by the encounter preequilibrium model, ca. 10^5 to 10^6 cm sec^{-1}.[38]

More Sophisticated Treatments

Although the treatment based on the simple encounter preequilibrium model that is described above represents a decided improvement over the conventional collisional approach, it is somewhat oversimplified. A more sophisticated treatment applicable to homogeneous reactions between metal complexes has recently been outlined.[5] Instead of regarding the reacting ions as hard spheres the likelihood that the ligand envelopes may interpenetrate, leading to better overlap between the donor and acceptor orbitals, has been recognized.[5] Rather than considering a uniform "reaction zone", the rate is treated in terms of an integral of different reactant configurations averaged over spherical coordinates with a corresponding distribution of local values of κ_{el}, ΔH^*, ΔS^*, and hence rate constants to yield an integral value of k_{et}. In addition, the interaction between the reactants are treated using contemporary ion-ion pair correlation functions rather than the usual Debye-Huckel model.[5] Although comparable values of K_p to the simplified treatment result from this approach, it does provide much better agreement with the experimental activation entropies as a function of ionic strength.[5]

In principle, a similar treatment could be developed for electrochemical reactions. Recent statistical treatments of the diffuse double layer provide a more realistic picture of interfacial ionic distributions than given by the usual Gouy-Chapman model.[39] In particular, these treatments demonstrate that the ionic surface excess (or deficiency) is contained within a noticeably smaller distance from the surface at high ionic strengths than deduced from the Gouy-Chapman model.[39] Such approaches will therefore yield different local reactant concentrations and hence K_p^e [Eq (6)]. Another significant development is the inclusion of a (albeit crude) molecular model for the solvent.[40] It is expected that the solvent ordering induced by hydrophilic surfaces, in particular,[41] will profoundly influence the local probability distribution of charged reactants.

Conclusions

Despite the approximations and numerical uncertainities in the parameters involved, the encounter preequilibrium formulation provides a description of the frequency factor for outer-sphere electrochemical reactions that is more appropriate than the collisional formulation which has usually been employed for this purpose. Most importantly, the former model describes the nuclear frequency factor for the elementary electron-transfer step in terms of an appropriate combination of unimolecular reorganization modes. The collisional model infers that the motion along the reactant coordinate arises from the translational motion of the reactant(s). In actuality, the ability of electrons to tunnel between the reacting centers and the unimolecular activation of the reactant via energy transfer with the surrounding solvent obviates the need for any such momentum transfer, in contrast to chemical reactions involving atom or group transfer. In addition, the electron tunneling probability appears as an integral part of the preequilibrium formalism by determining the appropriate size of the "reaction zone" within which the electronic transmission probability is sufficiently large for a given internuclear geometry to contribute significantly to the overall reaction rate. A similar electronic transmission coefficient is often contained in the collisional formulation, but as an arbitrary added component.

These considerations highlight the need for theoretical treatments of electron tunneling and associated molecular dynamics at electrode surfaces along similar lines to the important developments that are being made for electron transfer between metal ions in homogeneous solution.[5,21,22] The combination of such theoretical work with further detailed experimental studies, especially comparisons between apparent frequency factors as well as rate constants for corresponding electrochemical and homogeneous reactions, will provide a firm basis upon which to develop our understanding of the factors that influence electrochemical reactivity.

Acknowledgments

We acknowledge helpful discussions with Dr. Norman Sutin and Professor Dennis Evans. This work is supported in part by the Office of Naval Research and the Air Force Office of Scientific Research. Michael J. Weaver acknowledges a fellowship from the Alfred P. Sloan Foundation.

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