

Linear Free Energy Relations for Multielectron Transfer Kinetics: A Brief Look at the Brønsted/Tafel Analogy

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A comparison is made between electrochemical and homogeneous redox reactivity for species involving the transfer of multiple electrons at a single thermodynamic potential. In the electrochemical case the coreactant is the electrode; in the homogeneous case it is any of several members of a homologous series of one-electron reagents. In the latter case it is shown that the slope of a plot of the observed pseudo-first-order rate constant (one-electron reagent in excess) versus the thermodynamic driving force can be used to identify the cross reaction's rate-determining step. It is noted that the proposed use of a homogeneous linear free energy relation (Brønsted plot) for mechanistic purposes is closely analogous to the well-known Tafel approach (log current versus potential) in electrochemical kinetics.

Introduction

One of the recurring themes in kinetic studies of single-electron-transfer (ET) reactions at electrochemical interfaces is that much can be learned by simple analogy to related reactions in homogeneous solution.¹ Electrochemists, at least, also like to believe that the converse is true: insights regarding homogeneous electron-transfer reactivity can be derived from electrochemical investigations. We are seeking to apply both principles in our emerging studies of multielectron-transfer kinetics. In this paper we explore one particular aspect of multi-ET reactivity—the dependence on thermodynamic driving force. Starting from an electrochemical perspective, we develop a fairly simple homogeneous analogue. We then collect the observations and reflect briefly on the possible broader significance of linear free energy relations for multi-ET processes.

In the area of electrochemical kinetics there exists a long and successful history of utilizing linear free energy relations to ascertain the mechanistic details of interfacial rate processes.² Experimentally these relations take the form of so-called “Tafel plots”, i.e., plots of $\ln i$ (or sometimes $\ln k$) versus the electrochemical potential, E . In the plots, i is the diffusion-corrected and back-reaction-corrected current, in other words the net electrochemical rate. Alternatively, k is the first-order heterogeneous rate constant (cm s^{-1}). In either case the slope of the plot is $\pm \alpha F/RT$, where α is the transfer coefficient and F is the Faraday constant. Perhaps the most significant point is that α behaves as an electrochemical “Brønsted coefficient”;^{2a} within the context of transition-state theory, therefore, α can be identified approximately as $n\Delta G^*/\partial \Delta G$. (Here ΔG^* is the experimental activation free energy, while ΔG is the overall (n electron) thermodynamic driving force. The driving force is equivalently given by $\pm nF(E - E_f)$, where E_f is the formal reduction potential and the sign distinguishes oxidation from reduction.)

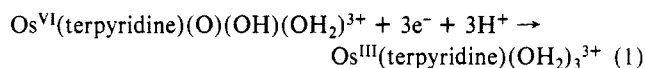
In electrochemical studies the Tafel approach is particularly helpful when a reaction requires the transfer of multiple electrons at a single thermodynamic potential, but in kinetically distinct one-electron steps. It is well-known that under these conditions the value of α precisely prescribes the integral number of electrons transferred in any rapid equilibria preceding the rate-determining step. For example, if no electrons precede the slowest step (i.e., the first electron is rate determining), α will equal roughly 0.5.³

If one electron transfer precedes the rate-determining ET step (i.e., the second electron is rate determining), α will equal approximately 1.5. If two electron transfers precede the rate-determining step (i.e., the third electron is rate determining) α will equal 2.5 and so on. Furthermore, from the principle of microscopic reversibility the sum of α values in the forward and reverse directions at any given electrochemical potential should equal the total number of electrons transferred.

Tafel measurements clearly are powerful diagnostic tools in electrochemical kinetic studies. We were interested, therefore, in ascertaining whether a complementary method might exist for homogeneous processes. We find that indeed one does. What follows is an informal derivation. For concreteness the derivation is presented in terms of specific (hypothetical) homogeneous cross reaction. In general, however, the reactions of interest are those involving a multielectron redox couple and a homologous series of one-electron coreactants.

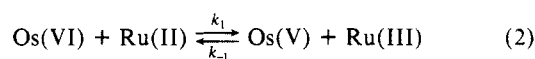
Derivation of Homogeneous Driving Force Relationships

Consider the three-electron, three-proton reduction of chelated Os(VI):⁴



Although eq 1 can be driven electrochemically, it should also be possible to effect the reduction homogeneously with a one-electron reagent. If a series of closely related reagents is prepared (say, $\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{pyridine-X})^{2+}$, where $\text{X} = \text{H}, \text{CH}_3, \text{Br}, \text{NO}_2$, etc.) the members of the series will likely display different redox potentials but similar self-exchange rates. From a series of rate measurements, one should be able to construct a “Brønsted” plot of log rate versus driving force (by analogy to similar plots for Brønsted acid catalysis) and perhaps derive mechanistic information.

The reduction of Os(VI) by any particular member of the series presumably occurs sequentially as follows:



Defining E_1 as the reduction potential of the Os(VI/V) couple, E_{Ru} as the potential for the Ru(III/II) couple, and K_1 as the equilibrium constant for eq 2, we find that

$$E_1 - E_{\text{Ru}} = (RT/F) \ln K_1 \quad (3)$$

and

$$K_1 = k_1/k_{-1} \quad (4)$$

where k_1 and k_{-1} are the second-order rate constants for the

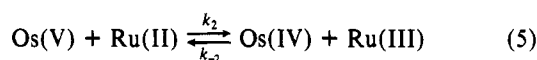
(1) See, for example: Weaver, M. J. In *Comprehensive Chemical Kinetics*; Compton, R. G., Ed.; Elsevier: Amsterdam, 1988; Vol. 27.

(2) (a) Albery, W. J. *Electrode Kinetics*; Oxford University Press: Oxford, UK, 1975. (b) Vetter, K. J. *Electrochemical Kinetics*; Academic Press: New York, 1967. (c) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum Press: New York, 1970; Vol. 2, Chapters 9 and 10.

(3) In principle, α (or β) for a one-electron transfer can differ substantially from 0.5 when the reaction is extremely exothermic ($\alpha \rightarrow 0$), extremely endothermic ($\alpha \rightarrow 1$), when large work terms exist, or when force constants for internal-coordinate displacements are strongly oxidation-state dependent.

(4) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 4042.

forward and reverse reactions in eq 1. Similarly, if we assume



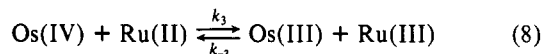
we obtain

$$E_2 - E_{\text{Ru}} = (RT/F) \ln K_2 \quad (6)$$

and

$$K_2 = k_2/k_{-2} \quad (7)$$

where E_2 is the Os(V/IV) redox potential and K_2 , k_2 , and k_{-2} are the respective equilibrium and rate constants. Finally, we may write

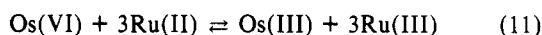


$$E_3 - E_{\text{Ru}} = (RT/F) \ln K_3 \quad (9)$$

and

$$K_3 = k_3/k_{-3} \quad (10)$$

where E_3 is the Os(IV/III) redox potential and K_3 , k_3 , and k_{-3} are the respective equilibrium and rate constants. The net process thus is



By applying a steady-state approximation to the unstable intermediates (Os(V) and Os(IV)) we can obtain several rate expressions. When eq 2 is rate determining

$$d[\text{Os(III)}]/dt = (1/3) d[\text{Ru(III)}]/dt = k_1[\text{Os(VI)}][\text{Ru(II)}] \quad (12)$$

When eq 5 is rate determining

$$d[\text{Os(III)}]/dt = (1/3) d[\text{Ru(III)}]/dt = \frac{k_1 k_2 [\text{Os(VI)}][\text{Ru(II)}]^2}{k_{-1}[\text{Ru(III)}] + k_2[\text{Ru(II)}]} \quad (13)$$

When eq 8 is rate determining

$$d[\text{Os(III)}]/dt = (1/3) d[\text{Ru(III)}]/dt = \frac{k_1 k_2 k_3 [\text{Os(VI)}][\text{Ru(II)}]^3}{k_{-1}[\text{Ru(III)}] + k_{-1} k_{-2} [\text{Ru(III)}]^2 + k_3 [\text{Ru(II)}]^2} \quad (14)$$

If Ru(II) were used in great excess over Os(VI) and if all steps preceding the rate-determining step were in rapid equilibrium, then the following expressions for the observed pseudo-first-order rate constant would apply. When eq 2 is rate determining

$$k_{\text{obs}} = k_1[\text{Ru(II)}] \quad (15)$$

When eq 5 is rate determining

$$k_{\text{obs}} = K_1 k_2 [\text{Ru(II)}]^2 / [\text{Ru(III)}] \quad (16)$$

When eq 8 is rate determining

$$k_{\text{obs}} = K_1 K_2 k_3 [\text{Ru(II)}]^3 / [\text{Ru(III)}]^2 \quad (17)$$

where $k_{\text{obs}} = -(1/[\text{Os(VI)}])(d[\text{Os(VI)}]/dt)$ and $-d[\text{Os(VI)}]/dt = d[\text{Os(III)}]/dt$ in eqs 15–17.⁵

Experimentally, any fractional order with respect to Ru(II) would suggest that the equilibria prior to the rate-determining step are not rapid and that some steps occur concurrently. It is also worth considering the reverse experimental condition. If Os(VI) were used in pseudo-first-order excess instead of Ru(II), and if eq 2 were rate determining, k_{obs} would equal $3k_1[\text{Os(VI)}]$. On the other hand, if either eq 5 or 8 were slow, non-pseudo-first-order kinetics with respect to [Ru(II)] would be expected,

despite the large excess of Os(VI) (cf. eqs 12–14.)

In general, when m one-electron steps precede the rate-determining step

$$k_{\text{obs}} = K_1 K_2 \dots K_m k_{\text{rds}} [\text{R}]^{m+1} / [\text{O}]^m \quad (18)$$

where R and O represent the reduced and oxidized forms of the one-electron reductant. In fact, under the assumption that all steps prior to the rate-determining step are occurring as rapid pre-equilibrium processes, and with excess added O (such that its concentration is essentially constant), the order with respect to R will indicate which step in the multielectron transfer is rate determining.

If we assume that a linear free energy relationship (eq 19) can be applied to the rate-determining step (analogous, in a sense, to a Brønsted acid catalysis expression), then eq 20 can be obtained by combining eqs 18 and 19:

$$\ln k_{\text{rds}} = \beta \ln (K_{m+1}) + \gamma \quad (19)$$

$$\ln k_{\text{obs}} = (E_1 - E_{\text{R}})F/RT + (E_2 - E_{\text{R}})F/RT + \dots + (E_m - E_{\text{R}})F/RT + \beta(E_{m+1} - E_{\text{R}})F/RT + (m+1) \ln [\text{R}] - m \ln [\text{O}] + \ln k_{\text{rds}}^0 \quad (20)$$

(In eq 20, k_{rds}^0 is the value of k_{rds} when the overall free energy driving force is zero. Also, it is assumed that the dimensions of the last three terms are chosen so as to render the composite logarithmic term unitless.) Thus, if we have a series of one-electron reductants whose potentials (E_{R}) vary, a plot of $(RT/F) \ln k_{\text{obs}}$ versus E_{R} should be linear with a slope of $m + \beta$ (for a fixed concentration of the reductant and with enough added oxidized form such that [O] is effectively constant during the course of the reaction). This type of experiment is a precise homogeneous analogue of the electrochemical Tafel experiment ($\ln i$ versus E) and for a multielectron transfer reaction yields the same information (m and α values). If Marcus-type behavior were obeyed for the rate-determining step in the homogeneous reaction, the value of β would generally be close to 0.5.³ Thus from the slope of the Brønsted plot the value of m would be obtained, where $m + 1$ would designate the slow step in the overall kinetic process.

When the reverse of eq 11 can be studied with the same reagents and a second Brønsted plot constructed, the slope can be shown (by microscopic reversibility) to equal $n - m - 1 + \beta'$, where $\beta' = 1 - \beta$ and m is determined from the forward kinetics (see above). It also follows that the two Brønsted plots will intersect at the overall formal potential for the multielectron couple⁶ (provided that any stoichiometric factors implicit in the plots have been handled in a consistent way).

Potential Limitations

It should be noted that in the derivation several assumptions have been made, including the following: (1) All steps prior to the rate-determining step occur as rapid pre-equilibria. (2) With a series of one-electron-transfer reagents, only the potential of the reagent varies, but not its intrinsic reactivity (i.e., self-exchange rate). (3) The rate-determining step in the multi-ET cross reaction remains constant throughout the series. (4) A steady-state approximation is acceptable for the concentrations of species in unstable intermediate oxidation states. (5) Whenever the first step is not rate determining, both the oxidized and reduced forms of the one-electron reagent are present in sufficient amounts that their concentrations remain effectively constant throughout the reaction. (6) Extraneous parameters such as pH, ionic strength, and temperature remain fixed for a given reaction series. Obviously in any particular experiment one or more of the assumptions might be invalid and suitable corrections would need to be applied. Nevertheless the framework of assumptions is not really very much more restrictive than in electrochemical Tafel studies.

Following on from the above, we find in particular that two of the more obvious chemical complications, disproportionation

(5) We note that up to this point the derivation is fairly routine and that rate laws analogous to eqs 12, 13, 15, and 16 can be found, in particular, in the extensive literature on Cr(VI) redox chemistry. See, for example: (a) Espenson, J. H. *Acc. Chem. Res.* 1970, 3, 347. (b) Beattie, J. K.; Haight, J. P. *Prog. Inorg. Chem.* 1972, 17, 93.

(6) This is just a statement, of course, that the forward rate constant must equal the reverse when $\prod_{i=1}^{m+1} K_i$ is unity.

of redox intermediates (e.g., Os(V) or Os(IV) in the example above)⁷ and "square scheme" coupling of electron transfer to proton transfer,⁸ do not necessarily vitiate the multielectron Brønsted analysis. However, a third possible complication, the occurrence of inner-sphere pathways, is more problematic. Just as with the Marcus one-electron cross relationship,^{9,10} there is no reason to believe a priori that the multielectron driving-force analysis will be applicable when reactions proceed by ligand-bridged pathways. In fact, in many such instances it may not even be useful to view the reaction in terms of sequential one-electron steps. Such limitations obviously will circumscribe to a large extent the applicability of the analysis to true catalytic reactions. On the other hand, the same is true of the Marcus cross relationship. The Brønsted analysis still might prove useful, however, as a benchmark against which catalytic multielectron redox reactivity could be evaluated.

Possible Applications

Ideally one would like to illustrate the above analysis with kinetic data for a "real" system. Unfortunately we have been unable to identify a suitable reaction series. [A significant number of examples do exist for the sequential one-electron reduction (or oxidation) of multielectron redox species (most notably, chromate) by isolated single-electron reagents.^{5b} Unfortunately, in almost no instance (to our knowledge) has the identity of the single-electron reagent been varied in a systematic fashion.^{11,12} This should perhaps not be too surprising since, in the absence of the present analysis, there would be no compelling reason to pursue such an investigation.] Also, preliminary studies in our laboratory¹³ of a three-electron osmium/ruthenium series (comparable to the one described above) were thwarted by an inability to monitor adequately (by stopped-flow methods) the relatively rapid ET kinetics. Nevertheless, given the recent proliferation of both synthetic and mechanistic activity involving related transition-metal oxo/aquo species¹⁴ it seems reasonable to suppose that many examples of Brønsted-type multielectron reactivity will eventually become available.

Despite the shortage of existing illustrative examples, it may be worth speculating briefly on what other kinds of redox studies might possibly be facilitated by the proposed analysis. Two examples come to mind, based on our own current research interests. The first involves the electrochemical oxidation and reduction of solution species by hydrous oxide surfaces.¹⁵ These surfaces can

display both univalent (e.g., Ir(III/IV)) and divalent (e.g., Ir(IV/V) or Ru(IV/V)) redox phase transformations. Whether these transformations correspond to the discrete (i.e., localized) oxidation and reduction of an array of metal sites or, alternatively, to electrochemical band depletion and filling is, at present, a point of controversy. (Indeed, some evidence suggests that both types of electronic behavior may exist, the determining chemical factor being the extent of metal oxide hydration.¹⁵) Regardless of the details, if the oxide surface were to function as a redox mediator¹⁶ (i.e., if electron transfer to and from solution species were to entail repetitive cycling between different oxide valence states) the reaction kinetics would be formally analogous to those for homogeneous processes. In attempting to unravel the kinetics, however, there could be substantial difficulties in usefully varying the metal oxide concentration and thereby determining an oxide reaction order. On the other hand, a Brønsted-type analysis of oxide reactivity (based on a homologous series of solution species) might provide an alternative route to the desired information. The second example is closely related. It would involve hybrid reactions between solution redox species and species immobilized in a polymeric film, at an electrode surface.¹⁷ Depending on just how the immobilization were carried out, there might again be difficulties in achieving systematic variations in concentration for the incorporated species and, therefore, in ascertaining a reaction order in the conventional fashion. The proposed driving-force analysis, however, might well provide a viable route to the same information.

Concluding Comments: An Implication for Heterogeneous Systems

As indicated above, a homogeneous analogue of the electrochemical Tafel analysis can be formulated for multielectron reagents. The simple derivation offered here¹⁸ highlights the relation between Brønsted slopes and reaction orders. From the derivation one might reasonably conclude that a suitable alternative interpretation for the transfer coefficient in the corresponding heterogeneous (electrochemical) experiment would be in terms of an effective reaction order in the electron.¹⁹ Although the usual preference in electrochemical kinetics is to express reactivity exclusively in terms of potentials and currents (i.e., without specific regard for the electron itself as a reactant) the reaction-order analogy offered by the multielectron Brønsted analysis is (at least in a formal sense) very appealing. We hope to explore the concept further in ongoing experimental studies.

Acknowledgment. This work was supported by a grant from the Office of Naval Research.

(7) Obviously, however, very rapid disproportionation would modify and complicate the overall scheme for multielectron transfer. Nonetheless, the proposed Brønsted analysis should still prove successful, in many instances, in identifying the slow single-electron-transfer step preceding disproportionation.

(8) For a succinct description of square scheme kinetics in the context of electrochemical reactions see ref 2a, Chapter 5.

(9) Marcus, R. A. *J. Chem. Phys.* **1965**, *45*, 679.

(10) Newton, T. W. *J. Chem. Educ.* **1968**, *45*, 571.

(11) An exception apparently is the sequential conversion of oxygen to hydrogen peroxide by a series of bis(phenanthroline)copper(I) complexes (Goldstein, S.; Czapski, G. *Inorg. Chem.* **1985**, *24*, 1087). Here, however, the second one-electron reduction ($\text{CuL}_2^+ + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{CuL}_2^{2+} + \text{H}_2\text{O}_2$) fails to display Marcus-type behavior, thereby ruling out "simple" electron transfer (or proton coupled electron transfer) as the redox mechanism.

(12) A system which comes close to fulfilling the criteria we would find ideal for application of the Brønsted analysis is the two-electron oxidation of a series of phenols by $\text{Fe}(\text{phenanthroline})_3^{3+}$ (Kimura, M.; Kaneko, Y. *J. Chem. Soc., Dalton Trans.* **1984**, 341). Unfortunately, in this system it is the potential of the multielectron reagent (rather than FeL_3^{3+}) that is systematically varied. Furthermore, the available evidence indicates that the oxidation proceeds by a relatively uninteresting mechanism (from our perspective) that is illustrated here (albeit, in the reverse direction) by eq 2 (i.e. in the two-electron phenol oxidation the first electron transfer is rate determining).

(13) Ram, M. S., unpublished work.

(14) For an excellent (but already somewhat dated) review, see: Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C.

(15) Burke, L. D. In *Modern Aspects of Electrochemistry*, White, R. E., Bockris, J. O'M., Conway, B. E., Eds.; Plenum Press: New York, 1986; Vol. 18.

(16) Burke, L. D.; Healy, J. F.; O'Dwyer, K. J.; O'Leary, W. A. *J. Electrochem. Soc.* **1989**, *136*, 1015.

(17) For a representative report involving a single electron transfer, see: Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1606.

(18) Related derivations for electrochemical reactions can be found in refs 2b (pp 149–154) and 2c (Chapter 9) as well as Reiger, P. H. *Electrochemistry*; Prentice Hall: Englewood Cliffs, NJ, 1987; pp 289–291.

(19) Concepts akin to an "electrode reaction order" have occasionally appeared in the electrochemical literature (see, for example: Anson, F. C. *J. Electroanal. Chem.* **1973**, *47*, 279). Invariably, however, these have referred to a kinetic stoichiometry in surface coordination or adsorption sites, or to some closely related idea. The suggestion here is distinctly different: the relevant entity is the electron itself (or hole, if the reaction were an oxidation). It should be noted that the more conventional approach to reaction order assessment (i.e., variation of the reagent concentration and subsequent rate evaluation) would almost certainly be unsuccessful in the case of an electron from an electrode. The problem, of course, is that the supply of electrons having the ability to cross the electrode/solution interface (i.e., the current) cannot be controlled independently of the electrode potential (i.e., the free energy of the transferring electron). (On the other hand, a conventional concentration-based reaction-order analysis probably could be envisioned if electrons were to be delivered instead by a technique such as pulsed radiolysis. The cost, however, would be the complete loss of ability to modulate the electron's free energy—a key element in electrode kinetics. In other words, the externally variable supply of electrons would be deliverable only at a single, fixed, and predefined energy.)