

LETTERS

Solvational Barriers to Interfacial Electron Transfer: Minimization via Valence Delocalization

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Standard rate constants (k_s) for interfacial electron transfer (ET) have been obtained for several redox couples featuring very small internal activation barriers. To render these ordinarily fast rates more easily measurable, we have employed low-defect-density, highly ordered pyrolytic graphite (HOPG) as an electrode material (see: Allred and McCreery, *Anal. Chem.* **1992**, *64*, 444). At the HOPG/aqueous solution interface, we observe the systematic (exponential) increase of k_s with inverse reactant size predicted by Marcus for electrochemical reactions whose barriers are primarily defined by solvent reorganizational effects. We also observe that rates can be significantly accelerated by delocalizing electrons over multiple metal-centered trapping sites. The degree of rate acceleration is quantitatively consistent with the extent of solvent barrier lowering expected if electronic delocalization effectively increases the radius of the ET reaction site.

Activation barriers, and therefore rates, for electron transfer (ET) at electrochemical interfaces are believed to depend strongly on solvent repolarization and reorganizational energetics.¹ Furthermore, available continuum theory² suggests that interfacial solvent barriers (ΔG_s^*) should vary in a comparatively simple and predictable way with parameters such as molecular reactant/electrode separation distance (d), reactant radius (r), optical and static solvent dielectric constants (D_{op} and D_s), and amount of charge (e) actually transferred:

$$\Delta G_s^* = (e^2/8)(1/r - 1/d)(1/D_{op} - 1/D_s) \quad (1)$$

The expected behavior at interfaces, therefore, is quite similar to that in homogeneous solution.^{2,3} In contrast to ET in homogeneous solution, however, there has been remarkably little systematic documentation of solvent-related barrier effects for interfacial processes.⁴⁻⁶ Among the apparent experimental problems are (1) large and variable interfacial work terms (adsorption, diffuse double-layer effects, etc.) which tend to be both reactant and solvent specific and (2) inherently inefficient

one-dimensional diffusion to planar electrodes⁷—which tends to make all but the slowest reactions difficult to access by conventional methods.⁸ Slow reactions, in turn, often feature large internal reorganizational barriers, spin changes, bond breakage, coordination number changes, and/or other kinetic complexities which make the identification and isolation of purely solvent related effects difficult. Nevertheless, we wish to report here the experimental observation of interfacial rate behavior consistent with eq 1, where the experimental variable is the reactant size and where the reactants have been chosen so as to feature primarily solvent-based activation energetics. As detailed below, one of the keys in the investigation has been the use of highly ordered pyrolytic graphite (HOPG) as an electrode material. With HOPG, we have additionally observed that solvent barriers can be significantly reduced by employing electronically delocalized reactants.

Figure 1 shows a plot of the log of the standard electrochemical rate constant (k_s) for each of a series of mononuclear and dinuclear transition-metal complexes (primarily ruthenium) versus the inverse size of the complex. The reactants in all cases are low-spin d^6 species. They were chosen, in part,

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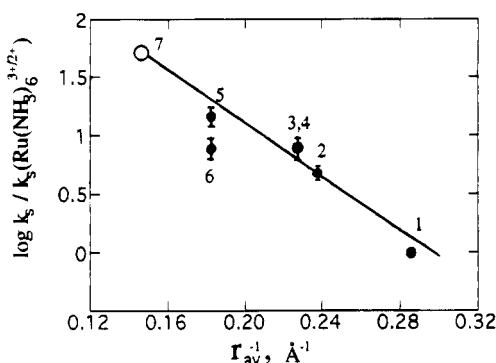
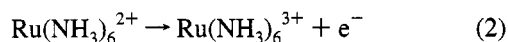


Figure 1. The log of k_s for the indicated ET reaction (normalized to k_s for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$) versus the inverse radius of the reactant (eq 3). The electrode material is low-defect-density HOPG;^{16,18} the electrolyte is 1 M aqueous KCl. Line drawn is a best-fit line for all points.^{25,31} Key to data points: (1) $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, (2) $\text{Ru}(\text{NH}_3)_5(\text{pyridine})^{3+/2+}$, (3) $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{5+/4+}$, (4) $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{6+/5+}$, (5) $t\text{-(pyridine)}(\text{NH}_3)_4\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_4(\text{pyridine})^{5+/4+}$, (6) $t\text{-(pyridine)}(\text{NH}_3)_4\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_4(\text{pyrazine})^{6+/5+}$, and (7) $\text{Fe}(\text{phenanthroline})_3^{3+/2+}$ (data for point 7 obtained from ref 16d).

because of known (or anticipated) minimal internal reorganizational requirements.^{9–11} The kinetics data plotted are actually ratios of k_s values in comparison to k_s for the slowest reaction:¹²



Rate parameters, in all cases, were determined by digital simulation¹³ and/or Nicholson analysis¹⁴ of experimental cyclic voltammograms obtained at conventional sweep rates (ca. 200 mV/s). Typical absolute rate constants for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ reaction at HOPG were ca. $1 \times 10^{-4} \text{ cm s}^{-1}$. In contrast, the same reaction proved immeasurably fast ($k_s > 3 \times 10^{-2} \text{ cm s}^{-1}$) at a conventional glassy carbon electrode/aqueous solution interface.¹⁵ The large rate difference is consistent with the more general observation by McCreery and co-workers of rate decreases of 4–5 orders of magnitude for a broad range of redox couples at low-defect-density HOPG.^{16d} While the origin of the attenuation effect is somewhat obscure (presumably it is electronic...), we (and others¹⁶) find that it is reproducible below a critical threshold surface defect density.¹⁸ In any case, rate attenuation is essential; without it, none of the targeted redox systems are kinetically accessible by the slow sweep-rate voltammetry method. A second key feature of the HOPG/aqueous interface is its extremely low capacitance^{15a,19}—which translates into the buildup of negligible amounts of surface charge, even at electrode potentials far removed from the potential of zero charge (ca. -0.2 V vs SCE¹⁹). This is tremendously advantageous because it effectively eliminates electrostatic work terms (diffuse double-layer effects²⁰) which might otherwise dominate the interfacial kinetics (especially with reactant and product charges varying from 2+ to 6+).^{21,22}

Returning to Figure 1, the size parameter chosen—in light of eq 1—was the inverse of the reactant radius. This parameter is reasonably well defined for roughly spherical, homoleptic complexes such as $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ but is obviously not so well defined for heteroleptic complexes—especially dinuclear complexes. For these complexes, we used an average radius defined as

$$r_{\text{av}} = (r_x r_y r_z)^{1/3} \quad (3)$$

where x , y , and z are metal–ligand bonding axes. While the averaging formula obviously is somewhat arbitrary, we note that it has been successfully used previously to correlate size-

dependent metal–complex diffusion coefficients,²³ redox reaction entropies,²⁴ and homogeneous electron self-exchange rate constants.^{3a} Furthermore, in our study the two complexes with the best defined radii bracket those that require size averaging. In any case, the observed correlation is compelling: k_s increases exponentially with increasing reactant radius. The slope of the $\log(k_s)$ vs r_{av}^{-1} plot is -10 Å or $14 \text{ kcal mol}^{-1} \text{ Å}$ for ΔG^* vs r_{av}^{-1} (correlation coefficient 0.93).^{25,26} If d is unchanging, the expected slope from eq 1 is $22 \text{ kcal mol}^{-1} \text{ Å}$. (On the other hand, if we assume (following Hush) that d varies as the sum of the reactant radius (eq 3) and the solvent inner-layer thickness (ca. 3.3 Å for water), the expected slope is $\sim 15 \text{ kcal mol}^{-1} \text{ Å}$.²⁸) Related studies^{3a} in homogeneous solution (work-corrected bimolecular self-exchange) yield a slope of $45 \text{ kcal mol}^{-1} \text{ Å}$, i.e., somewhat greater than the factor of 2 difference expected if d variations are again neglected.^{2,20}

On the basis of eq 1, we reasoned that redox reaction site sizes could be effectively increased and solvational barriers effectively lowered by delocalizing electrons over multiple trapping sites. The central data points in Figure 1, corresponding to the stepwise oxidation of the electronically delocalized Creutz–Taube ion ($(\text{NH}_3)_5\text{Ru}$ –pyrazine– $\text{Ru}(\text{NH}_3)_5^{4+}$) and a *trans*-pyridine-substituted analog,²¹ appear to confirm the hypothesis:²² Interfacial ET rates are significantly greater for these species than for the parent mononuclear complexes. From eqs 1 and 3, one would expect further solvent barrier diminution and further rate acceleration with larger oligomeric species. Extension and delocalization in only one dimension (i.e., linear oligomerization) are anticipated, however, to induce only modest additional barrier lowering. For example, extension of the Creutz–Taube ion to six metal centers total (i.e., the largest currently known Creutz–Taube oligomer;³² z -axis length of $\sim 42 \text{ Å}$) should further decrease ΔG_s^* by only about $0.9 \text{ kcal mol}^{-1}$ (based on extrapolation of the correlation in Figure 1).³³ A more effective strategy would appear to be to induce delocalization in a second (or even third) dimension. Selected ligand-bridged clusters would be attractive target systems.³⁴

We conclude that (1) solvent reorganization does play a major role in defining redox reactivity at surfaces, (2) the dependence of the barrier height on molecular reactant size is reasonably well predicted by conventional dielectric continuum theory, and (3) the barrier height is susceptible to manipulation and diminution by a valence delocalization strategy.

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References and Notes

- (1) See, for example: (a) Weaver, M. J. In *Comprehensive Chemical Kinetics*; Compton, R. G., Ed.; Elsevier: Amsterdam, 1988; Vol. 27. (b) Albery, W. J. *Electrode Kinetics*; Oxford University Press: Oxford, UK, 1975.
- (2) Marcus, R. A. *J. Chem. Phys.* **1965**, *45*, 679.
- (3) Representative studies: (a) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. (b) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635. (c) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289. (d) Hupp, J. T.; Dong, Y.; Blackburn, R. L.; Lu, H. *J. Phys. Chem.* **1993**, *97*, 3278.
- (4) In contrast to solvent energetics, a relatively large literature exists on interfacial solvent dynamics. See for example: (a) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463. (b) Fawcett, W. R.; Opallo, M. *J. Electroanal. Chem.* **1993**, *349*, 273. (c) Opallo, M. *J. Chem. Soc., Faraday Trans.* **1986**, *92*, 339.

(5) Nevertheless, a few reports exist for organic redox systems—most notably, studies by Peover and Powell (*J. Electroanal. Chem.* **1969**, 20, 427) and by Kojima and Bard (*J. Phys. Chem.* **1975**, 97, 6517). The former describes a correlation between experimental rate constants and two-component solvent reorganization energies estimated from localized charge distributions (where charge distributions were inferred from localized spin distributions (ESR measurements)). While perhaps correct, the correlation might be more reasonably ascribed to charge-density effects upon internal (i.e., vibrational) barrier contributions. The latter study describes an approximate correlation of ET barrier height with reciprocal radius (correlation coefficient = 0.37, for 20 reactions). In retrospect (see, for example: Weaver, M. J.; Gennett, T. *Anal. Chem.* **1984**, 56, 1444), the rate measurements seem to have been made at or near the upper limit of validity of the measurement technique (i.e., ac polarography with conventional-sized electrodes). On the other hand, persuasive homogeneous/heterogeneous (electrochemical) kinetic correlations are also reported. These lend substantial support to the view that the electrochemical kinetics results are valid. More closely related (chemically) to our work is an extensive study of common coordination complexes by Aoyagui and co-workers (*J. Electroanal. Chem.* **1977**, 86, 219). This study purports to show no dependence of electrochemical ET rate on anticipated parameters, once a critical reaction rate is reached. In light of more recent work,^{7,8,15} however, these findings are almost certainly in error. Evidently, limitations in instrument or cell response were mistaken for true kinetic responses.

(6) For additional representative reports see: (a) Fawcett, W. R.; Opallo, M. *J. Phys. Chem.* **1992**, 96, 408. (b) Saveant, J. M.; Tessier, *Faraday Discuss. Chem. Soc.* **1992**, 74, 57, 102. (c) Grampp, G.; Kapturkiewicz, A.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, 94, 439.

(7) Diffusion limitations can be overcome to some extent by using microelectrodes or nanoelectrodes. For a report on the latter, see: Penner, R.; Heben, M.; Longin, T.; Lewis, N. S. *Science* **1990**, 250, 1118.

(8) On the other hand, recent developments in fast-sweep voltammetry^{15b} and rapid potential step voltammetry (Forster, R.; Faulkner, L., unpublished), together with microelectrode technology, have appreciably extended the usual range of accessibility (i.e., the kinetics of reactions with effective half-lives of fractions of microseconds rather than fractions of milliseconds can be determined by these methods). (Selected fast reactions are also accessible by coulometric laser T-jump methods (Smalley et al. *J. Electroanal. Chem.* **1988**, 248, 255).)

(9) Pertinent homogeneous kinetics data: (a) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, 7, 2369. (b) Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, 99, 2468, and ref. 3a.

(10) Pertinent X-ray structural data: (a) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1981**, 20, 1522. (b) Fürholz, U.; Bürgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, 106, 121. (c) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, 20, 1522. (d) Bruntschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, 74, 113 and references therein.

(11) For example, calculated vibrational barriers¹⁰ for reactions 1, 2, and 7, respectively are 0.3, 0.5, and 0 kcal mol⁻¹.

(12) The actual reagent was Ru(NH₃)₆³⁺. Rate comparisons between this species and others were based on measurements made in solutions containing both reagents.

(13) Huang, Q.; Gosser, D. K. *Talanta* **1992**, 39, 1155.

(14) Nicholson, R. S. *Anal. Chem.* **1965**, 37, 1355.

(15) Published estimates of k_s for Ru(NH₃)₆^{3+/2+} (based on faster rate measurement methods at conventional interfaces) are ca. 0.35–0.45 cm s⁻¹ (Gennett, T. M.; Weaver, M. J. *Anal. Chem.* **1984**, 56, 1444. Wipf, D. O.; Kristensen, E. W.; Deakin, M. R.; Wightman, R. M. *Anal. Chem.* **1988**, 60, 306).

(16) (a) McDermott, M. T.; Kneton, K.; McCreery, R. L. *J. Phys. Chem.* **1992**, 96, 3124. (b) Rice, R. J.; McCreery, R. L. *Anal. Chem.* **1989**, 61, 1637. (c) Allred, C. D.; McCreery, R. L. *Anal. Chem.* **1992**, 64, 444. (d) Kneton, K. R.; McCreery, R. L. *Anal. Chem.* **1992**, 64, 2518.

(17) Electronic attenuation implies nonadiabaticity and raises the concern that nonadiabatic electron tunneling coefficients (or alternatively, initial-state/final-state electronic coupling energies) might be varying widely as the reactant identity is varied. Unfortunately, concerns of this kind are difficult to address in a rigorous fashion. Nevertheless, since all seven reactions are similar electronically (all involve nonbonding d⁵/d⁶ transformations), it is perhaps not unreasonable to expect them to require similar (electronic) kinetic prefactors. Conversely, if electronic prefactors are widely varying, it is difficult to see why they should vary in a way that

reproduces the apparent correlation in Figure 1. A reviewer has additionally raised the issue of solvent dynamical effects. If the reactions are nonadiabatic (i.e., if the dynamics are controlled by electronic factors), then solvent dynamics are not relevant. On the other hand, the reactions conceivably could be adiabatic (and subject, therefore, to solvent dynamical control) if, for example, the observed reactivity were governed primarily by residual defect sites. Nevertheless, since all of the reactions occur in the same solvent (water) and since all are dominated by solvent, rather than vibrational, reorganizational effects, wide variations in dynamical prefactors would not be expected.

(18) HOPG defect densities on well-characterized surfaces have been correlated with a number of interesting effects or parameters.^{15a} Such effects or parameters can subsequently be used as indirect probes of defect density on less well characterized surfaces.^{15c} An indirect probe which we found both convenient and relevant was the extent of kinetic reversibility of the Fe(CN)₆^{4-/3-} couple (poorer reversibility corresponding to lower defect density). Following Allred and McCreery,^{12c} we adopted the criterion that the CV peak separation (a measure of kinetic (ir)reversibility) exceed 700 mV before a surface could be accepted for further study.

(19) Randin, J. P.; Yeager, E. *J. Electroanal. Chem.* **1972**, 36, 257.

(20) For a basic discussion, see Chapter 2 of ref 1b.

(21) The capacitance of very low defect density HOPG/aqueous solution interfaces is ca. 0.6 μF/cm².^{16a} To estimate work-term corrections (Frumkin-type rate corrections),²⁰ we first integrated the capacitance from E_{pzc} to E_f to obtain the pertinent electrode surface charge for each redox reaction. We then assumed (a) that the reaction plane is coincident with the outer Helmholtz plane and (b) that a Gouy–Chapman–Stern double-layer description (without specific adsorption) is sufficient. These assumptions yielded diffuse layer potentials (ϕ_2^0 values) of 0, 0.9, 1.4, 2.8, 2, 3.2, and 4 mV respectively for reactions 1–7. If we assume transfer coefficients of 0.5 for all reactions, we obtain rate corrections (k_{corr}/k) of 1, 1.1, 1.3, 1.8, 1.4, 2.0, and 1.5, respectively. If the corrections are applied to the plot in Figure 1, the slope changes to -12 Å with a correlation coefficient of 0.94, i.e., only marginally different from the result obtained without work-term corrections. (If assumption (a) is relaxed, and the reaction distance is instead assumed (probably more realistically) to equal the sum of the solvent inner-layer thickness and the reactant radius (i.e., the reaction plane lies beyond the outer Helmholtz plane), then the work-term corrections are even smaller.)

(22) Fürholz, U.; Haim, A. *J. Phys. Chem.* **1986**, 90, 3686.

(23) Koval, C. A.; Ketterer, M. E.; Reidsma, C. M. *J. Phys. Chem.* **1986**, 90, 4201.

(24) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, 23, 3639.

(25) With point 6 excluded, the slope is -12 Å, or 16 kcal mol⁻¹ Å.

(26) Inclusion of residual work term corrections,²¹ if appropriate, would increase the experimental slope to 16 kcal mol⁻¹ Å.

(27) Hush, N. S. *Trans. Faraday Soc.* **1961**, 57, 557.

(28) Alternatively, if d is taken as twice this sum (Marcus assumption²), the expected slope is approximately 19 kcal mol⁻¹ Å.

(29) Kneton and McCreery^{16d} have also noted the existence of a homogeneous/heterogeneous (HOPG surface) reactivity correlation.

(30) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, 91, 3988; **1973**, 95, 1086.

(31) The origin of the deviation of the *t*-(pyridine)(NH₃)₄Ru(pyrazine)-Ru(NH₃)₄(pyridine)^{6+/5+} couple from the correlation in Figure 1 is unclear but might be related to the proximity of the 5+/6+ voltammetry wave to a much larger wave for electrolyte (Cl⁻) oxidation. Alternatively, it may be that the internal reorganizational requirements for this system significantly exceed those for the others examined.

(32) Von Kameke, A.; Tom, G. M.; Taube, H. *Inorg. Chem.* **1978**, 17, 1790.

(33) We recognize the somewhat hypothetical nature of the analysis, given the likely quantitative inapplicability of eq 3 in the context of ET reactions of linear oligomers. A more appropriate analysis would use ellipsoidal molecular reactant shapes. While the ellipsoidal analogue of Marcus' solvent reorganizational theory has been described for homogeneous redox reactions (Kharkats, Y. I. *Sov. Electrochem.* **1974**, 10, 1083; **1976**, 12, 1176), we are unaware of corresponding theoretical work for heterogeneous reactions.

(34) See, for example: Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Hood, P. L.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, 101, 2916.

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