Fast Interfacial Electron Transfer: Evidence for Inverted Region Kinetic Behavior

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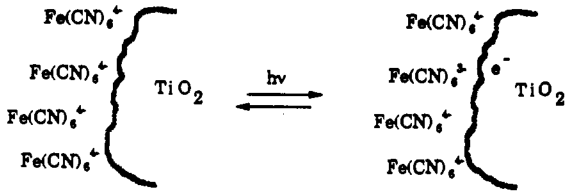
Both classical[1] and quantum mechanical[2,3] theories of electron transfer (ET) lead to the now familiar, but nevertheless remarkable, prediction that ET rates should ultimately decrease with increasing thermodynamic driving force ($-\Delta G°$). While these predictions of "inverted" rate behavior remained controversial and largely unsupported for a number of years,[4] more recent studies have convincingly demonstrated their veracity for a range of organic,[5] inorganic/organometallic,[6] and biological[7] redox processes in both liquid and frozen homogeneous solution environments. To the best of our knowledge, however, the phenomenon has never been demonstrated for interfacial or electrochemical processes; indeed there are solid theoretical reasons to suspect that interfacial rate inversion would, in many cases, be impossible.[1,8] Nevertheless, we now report the first experimental demonstration of fast, inverted, interfacial ET rate behavior and show that it is broadly consistent with the predictions of the most sophisticated contemporary theories.[2,3]

The prototypical reaction examined was ET from colloidal TiO_2 (a large-bandgap semiconductor) to ferricyanide.[9–11] The reaction was initiated photochemically by pumping the tail of a *direct* (i.e., not dye sensitized) molecule-to-surface charge–transfer transition (eq 1; $\lambda_{max} \approx 430$ nm)[10,11] with the amplified and doubled output of an Nd:YAG laser (532 nm, 2.5-ns pulses, 3–80 mJ/pulse). Kinetics were monitored by following (at 488 nm) the recovery of the charge–transfer absorbance. For reaction 1, the recovery kinetics are characterized by a short (τ = 270 ns) exponential decay and a much longer (microseconds → milliseconds) nonexponential decay.[12] While both processes are evidently ET related, we will further concern ourselves only with the better defined, shorter decay. This decay is responsible for roughly half of the total absorbance change.



(1)

Table I. Solution-Phase Formal Potentials and Interfacial Electron Transfer Reaction Times for $Fe^{III}(CN)_5L^{n-}$ Species

L	E_f (mV vs SCE)[a]	τ (ns)[b]
CN^-	118 ± 10	270 ± 30
3,5-dimethylpyridine	160 ± 20	280 ± 30
4-methylpyridine	183 ± 10	340 ± 40
pyridine	215 ± 10	430 ± 40
3-chloropyridine	268 ± 10	680 ± 60
pyrazine-ferrocyanide[c]	393 ± 10	1500 ± 100

[a] Measured in 1 M NaCl. [b] Obtained at ca. pH 2.5. [c] The reactant was $(NC)_5Fe^{III}$–pyrazine–$Fe^{II}(CN)_5^{5-}$.

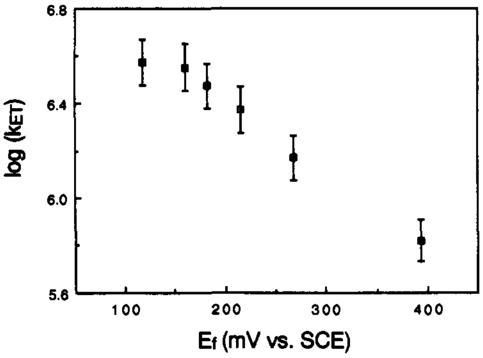


Figure 1. Plot of log k_{ET} at colloidal TiO_2 versus reduction potentials (solution phase) for $Fe^{III}(CN)_5L^{n-}$ species.

Interpretation of the short decay in terms of interfacial ET kinetics yields $k_{ET} = 3.7 \pm 0.4 \times 10^6$ s^{-1}.[13] Variations in pump power (25-fold) confirm that the decay is truly first order, i.e., effectively a geminate interfacial charge–transfer process. Temperature variations over an admittedly narrow range (25 deg) show no detectable change in lifetime, implying an activationless ET process. This result is fully consistent with our prior observation, by time-dependent Raman scattering methods, that the Franck–Condon barrier to ET is dominated by very high frequency (ca. 2000 cm^{-1}) cyanide stretching modes.[11]

Variations in driving force were introduced by replacing one CN^- ligand with any of several substituted pyridines.[14] Absolute driving forces have yet to be determined;[15] however, relative $\Delta G°$ values can be inferred from $Fe(CN)_5L^{3-/2-}$ potentials (Table I). Figure 1 clearly shows that log k_{ET} decreases as the relative driving force increases. Control experiments show (1) no change in k_{ET} with added (excess) pyridyl ligand and (2) no absorbance transient from either the TiO_2 colloid or the complexes separately.

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

(2) See, for example: (a) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183.

(3) For a brief and very clear explication of contemporary theories, see: Brunschwig, B. S.; Sutin, N. *Comments Inorg. Chem.* **1987**, *6*, 209.

(4) Representative experiments: (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 241.

(5) Representative reports: (a) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353. (b) Gould, I. R.; Moser, J. E.; Armitage, B.; Fairid, S.; Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1917. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewit, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (d) Mataga, N.; Asahi, T.; Kanda, Y.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 249.

(6) (a) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305. (b) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470. (c) Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069.

(7) See, for example: McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160.

(8) Most importantly, at metal surfaces the inverted rate effect would be circumvented by the ability to deliver electrons from a continuum of levels below the Fermi level.

(9) Colloidal TiO_2 samples were prepared as described previously[10,11] and were utilized in solutions of pH ≈ 2.5. Although this pH lies below the first pK_a of ferrocyanide, the complex appears to deprotonate upon binding to the semiconductor.[11]

(10) (a) Vrachnou, E.; Vlachopoulos, N.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1987**, 868. (b) Vrachnou, E.; Grätzel, M.; McEvoy, A. J. *J. Electroanal. Chem.* **1989**, *258*, 193.

(11) (a) Blackbourn, R. L.; Johnson, C. S.; Hupp, J. T. *J. Am. Chem. Soc.* **1991**, *113*, 1060. (b) Doorn, S. K.; Blackbourn, R. L.; Johnson, C. S.; Hupp, J. T. *Electrochim. Acta* **1991**, *36*, 1775.

(12) Grätzel et al.[10b] have reported single exponential decay kinetics with a half-life of ca. 3 μs. Almost certainly their preliminary observation corresponds to the long time scale, nonexponential decay we observe.

(13) Listed here and in Table I are uncertainties from multiple measurements on multiple samples prepared from a single colloid solution. Rate variations by as much as 50% were observed, however, for multiple samples from multiple colloid solutions.

(14) (a) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039. (b) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782.

(15) From interfacial charge transfer absorption maxima and line shapes, absolute $-\Delta G°$ values would appear to fall in the 14 000–20 000-cm^{-1} range. This is considerably greater than the energy differences between the conduction band edge (E_{CB}) for TiO_2 in contact with pH 2.5 solution and the formal potentials for the cyano iron complexes. Reconciliation would require either a large negative shift in E_{CB} or large positive shifts in E_f following binding of the anionic metal complexes to the positively charged colloid surface. We note that precedents exist for both: (a) Wang, C. M.; Mallouk, T. E. *J. Phys. Chem.* **1990**, *94*, 4276. (b) DeSilvestro, J.; Pons, S.; Vrachnou, E.; Grätzel, M. *J. Electroanal. Chem.* **1988**, *246*, 411.

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Expressed as an effective electrochemical transfer coefficient (or Brönsted slope),[16] the log k_{ET}/E plot in Figure 1 yields $\alpha \approx -0.2$. This result is quantitatively consistent with the predictions of a multimode quantum rate theory described by Jortner and co-workers,[2a,b] provided that (1) ET is regarded as highly exothermic;[15] (2) displacements in high-frequency intraligand modes and, to a lesser extent, intermediate-frequency metal–ligand and semiconductor lattice modes provide the necessary Franck–Condon overlaps;[11] (3) the displacements are more or less the same for each member of the redox series; and (4) all electrons are supplied at a single energy at or near the conduction band edge,[17] rather than over a range of energies corresponding to multiple mid-bandgap surface states.

We note that assumption 2 has already been experimentally validated[11] and that assumption 3 is at least qualitatively supported by existing studies of the $Fe(CN)_5L^{n-}$ series in homogeneous (bimolecular) redox processes.[20] If the absolute energetics of electron transfer (item 1) can be assessed, then more detailed confrontations with theory should be possible. Finally, we also hope to assess the effects of semiconductor electrode potential[11b,18] (by replacing colloidal TiO_2 with a single, high-area surface[19]). This should enable us to test assumption 4 and perhaps also gain significant physical insight into the longer time scale absorbance decay phenomenon.

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(16) See, for example: (a) Albery, W. J. *Electrode Kinetics*; Clarendon Press: Oxford, 1975; Chapter 4. (b) Weaver, M. J. In *Comprehensive Chemical Kinetics*; Compton, R. G., Ed.; Elsevier: Amsterdam, 1988; Vol. 27. (c) Ram, M. S.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 2378.

(17) "Near" in this context would mean near enough to make the overall reaction driving force substantially greater than the total ET reorganization energy.

(18) (a) Rothenberger, G.; Fitzmaurice, D.; Grätzel, M. *J. Phys. Chem.* **1992**, *96*, 5983. (b) O'Regan, B.; Grätzel, M.; Fitzmaurice, D. *Chem. Phys. Lett.* **1991**, *183*, 89. (c) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, *94*, 8720.

(19) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Liska, P.; Augustynski, J.; Grätzel, M. *J. J. Am. Chem. Soc.* **1988**, *110*, 1216.

(20) A linear free energy relationship (LFER) has been reported by Toma and Creutz (*Inorg. Chem.* **1977**, *16*, 545) for redox quenching of photoexcited $Ru(bpy)_3^{2+}$ by $Fe(CN)_5L^{n-}$ species. Although there are caveats (see Toma and Creutz), the LFER finding is broadly consistent with the idea of approximately fixed reorganizational energies (fixed vibrational displacements) for the $Fe(CN)_5L^{n-}$ redox series.