Interfacial Charge-Transfer Pathways: Evidence for Marcus-Type Inverted Electron Transfer in Metal Oxide Semiconductor/Inorganic Dye Systems

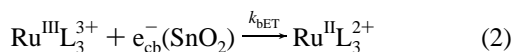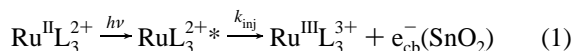Xiaojun Dang and Joseph T. Hupp*

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Under high driving force conditions, solution-phase charge-transfer processes are often characterized by Marcus-type inverted reactivity, i.e., a decrease in rate with an increase in thermodynamic driving force.[1] In contrast, *interfacial* charge-transfer reactions tend to exhibit either Marcus normal region behavior or asymptotically constant rate behavior.[2] The usual explanation for such behavior, at least at metal/solution interfaces, is the availability of a range of filled states below the Fermi level and a range of empty states above the Fermi level of the electrode, such that lower driving force reaction pathways are always available. If the lower driving force pathways are faster, then asymptotic rather than inverted kinetic behavior will be encountered. With semiconductor/solution interfaces, however, the existence of a finite band gap eliminates states immediately above the Fermi level (p-type semiconductors) or immediately below the Fermi level (n-type semiconductors) and opens up the possibility of inverted interfacial reactivity. Indeed, inverted behavior has often been invoked to explain the otherwise surprisingly slow back-electron-transfer reactivity typically encountered at inorganic-dye-sensitized metal oxide semiconductor/ solution interfaces.[3] Nevertheless, in the few cases where driving force effects at the semiconductor/dye interface have been systematically investigated, either by manipulating band edge energetics or by manipulating molecular dye redox potentials, either Marcus normal region behavior or driving-force-independent kinetic behavior has been observed.[2,4−7] We now report the direct observation of inverted interfacial electron-transfer reactivity at a molecular-dye-modified semiconductor/solution interface.

The systems examined were classic ruthenium tris(polypyridine) complexes (homoleptic complexes), electrostatically bound to tin dioxide nanoparticles.[8] Photoexcitation of the complexes leads to rapid electron injection into the semiconductor particle, followed—in the absence of an external electrical connection— by back electron transfer, as shown in eqs 1 and 2.

$$\text{Ru}^{II}\text{L}_3^{2+} \xrightarrow{h\nu} \text{RuL}_3^{2+}* \xrightarrow{k_{inj}} \text{Ru}^{III}\text{L}_3^{3+} + e_{cb}^-(\text{SnO}_2) \qquad (1)$$

$$\text{Ru}^{III}\text{L}_3^{3+} + e_{cb}^-(\text{SnO}_2) \xrightarrow{k_{bET}} \text{Ru}^{II}\text{L}_3^{2+} \qquad (2)$$

Curve b in Figure 1 illustrates the back reaction kinetics for tris-

Figure 1. Transient absorbance decay data obtained at 450 nm (following excitation at 532 nm) for aqueous SnO₂ colloid sensitized with Ru(5-Cl-phen)₃²⁺ (a), Ru(4,7-CH₃-phen)₃²⁺ (b) and Ru(3,4,7,8-CH₃-phen)₃²⁺ (c). Inset: curve c, expanded scale.

(4,7-dimethyl-1,10-phenanthroline)ruthenium/tin dioxide at pH = 9, based on visible region transient absorbance measurements. The absorbance decay was fit to both a biexponential plus constant recovery expression[4] and the Kohlrausch relaxation function[8] (see Supporting Information). The rate constants obtained (faster component) were 3.6×10^6 and 4.0×10^6 s⁻¹, respectively. Also illustrated in Figure 1, curves a and c, are absorbance bleach and recovery transients for the tris(5-chloro-1,10-phenanthroline)- and tris(3,4,7,8-tetramethyl-1,10-phenanthroline)ruthenium/tin dioxide systems. The decay time for the latter is clearly much shorter, while the former is apparently longer. The dependence of the apparent first-order electron-transfer rate constant (k_{app}) on the excitation intensity shows that the back reaction kinetics actually are second order; i.e., the rate depends not only on the concentration of oxidized dye attached to the semiconductor surface (Γ, mol cm⁻²) but also on the number of injected conduction band electrons (n_e, cm⁻³)[9,10] (see Supporting Information; second-order behavior was also observed in an ambient temperature, aqueous poly(vinyl alcohol) glass matrix). Following Royea et al., we can write:

$$\text{rate} = k_{app}\Gamma(\text{Ru}^{III}\text{L}_3^{3+}) = k_{et}\beta n_e \Gamma(\text{Ru}^{III}\text{L}_3^{3+}) \qquad (3)$$

where β is the electronic coupling attenuation factor (value unknown, but typically estimated as 0.4 < β < 1.5 Å⁻¹ for ET in molecular systems). Figure 2 shows, for a homologous series composed of seven such systems, that the composite quantity, $\log(k_{et}\beta)$,[11] can be correlated with the driving force for the back-electron-transfer reaction, where the driving force is approximated as the difference between the tin dioxide conduction band edge potential (−0.88 V vs SCE at pH = 9) and the ground-state Ru-(III/II) formal potential.[12]

In principle, the reaction driving force can also be altered by shifting the energy of the conduction band edge (E_{CB}). For metal oxide semiconductor/aqueous solution interfaces, a −60 mV shift

(1) Representative reports: (a) Turró, C.; Zaleski, J. M.; Karabatsos, Y. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 6060. (b) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353. (c) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305.

(2) (a) Yan, S. G.; Lyon, L. A.; Lemon, B. I.; Preiskorn, J. S.; Hupp, J. T. *J. Chem. Educ.* **1997**, *74*, 657. (b) Yan, S. G. Ph.D. Dissertation, Department of Chemistry, Northwestern University, 1996. (c) Yan, S. G.; Preiskorn, J. S.; Kim, Y.; Lemon, B. I.; Vance, F. W.; Hupp, J. T., manuscript in preparation.
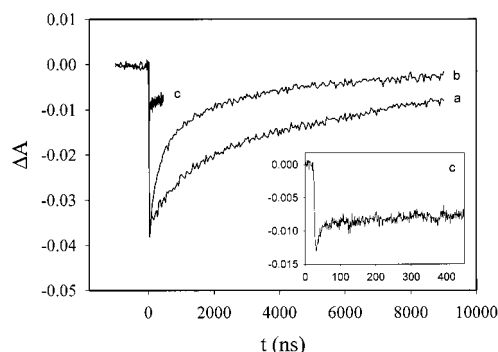
(3) See, for example: Moser, J. E.; Grätzel, M. *Chem. Phys.* **1993**, *176*, 493.

(4) Yan, S. G.; Hupp, J. T. *J. Phys. Chem.* **1996**, *100*, 6867.

(5) Meyer, G. J., private communication.

(6) Inverted behavior has been reported, however, for direct interfacial charge-transfer reactions: Lu, H.; Preiskorn, J. N.; Hupp, J. T. *J. Am. Chem. Soc.* **1993**, *115*, 4927.

(7) However, see: Martini, I.; Hodak, J. H.; Hartland, G. V. *J. Phys. Chem. B* **1998**, *102*, 9508. These authors report factor of 2 differences in back-ET rates for anthracenecarboxylic acid isomers on TiO₂, where the differences are ascribed to inverted reactivity and differences in ΔG°.

(8) See, for example: Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, *98*, 3822.

(9) (a) Royea, W. J.; Fajardo, A. M.; Lewis, N. S. *J. Phys. Chem. B* **1997**, *101*, 11152. (b) Lewis, N. S. *Annu. Rev. Phys. Chem.* **1991**, *42*, 543.

(10) For an alternative interpretation, see: Ford, W. E.; Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem. B* **1997**, *101*, 7435.

(11) $k_{et}\beta$ (units of cm³ s⁻¹) was calculated from the plot of apparent first-order rate constant (k_{app}) versus the number of injected conduction band electrons (n_e), where variations in k_{app} were obtained by varying the incident laser power. n_e was determined as $(\Delta A/A)N_{Ru}$, where ΔA is the time-dependent absorbance difference, A is the absorbance at the probe wavelength (450 nm), and N_{Ru} is the total number of adsorbed dye molecules. The volume used for the concentration calculation was the volume of the SnO₂ particles.

(12) The formal potentials of dye molecules were obtained from the following: Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
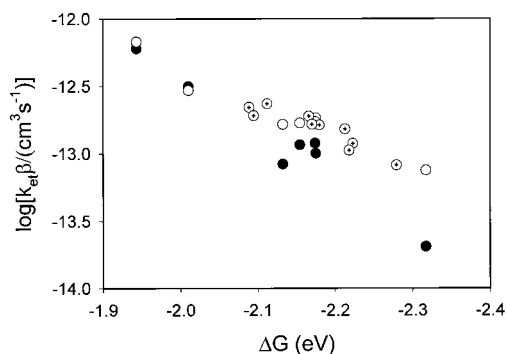
Figure 2. Plot of $\log(k_{et}\beta)$ versus driving force for back electron transfer to Ru(3,4,7,8-CH$_3$-phen)$_3^{3+}$, Ru(4,7-CH$_3$-phen)$_3^{3+}$, Ru(5,6-CH$_3$-phen)$_3^{3+}$, Ru(5-CH$_3$-phen)$_3^{3+}$, Ru(phen)$_3^{3+}$, Ru(bpy)$_3^{3+}$, and Ru(5-Cl-phen)$_3^{3+}$ at pH = 9, and Ru(phen)$_3^{3+}$ at several other pH values (points with cross inside). Open circles, best fit to biexponential plus constant; filled circles, best fit to Kohlrausch relaxation function.
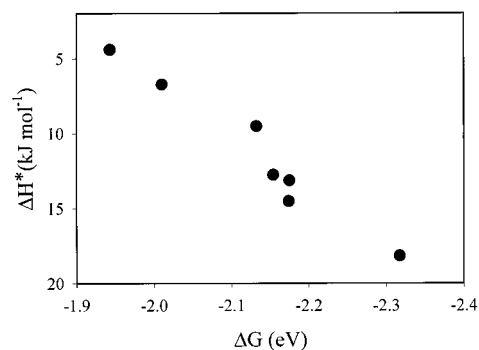

Figure 3. Plot of activation enthalpy for back electron transfer versus reaction driving force.

in E_{CB} accompanies each unit increase in pH.[13] The dual requirements of colloid stability and negative surface charge for cationic dye binding limit the range of pH that can be explored experimentally. Nevertheless, we observe a ca. 3-fold decrease in back-electron-transfer rate for the tris(phenanthroline)ruthenium/tin dioxide system upon elevation of the solution pH from ca. 7 to 11, consistent with a negative shift in E_{CB} and an increase in reaction driving force (see Figure 2). (Note that, in interpreting either driving force alteration experiment as Franck−Condon-based inverted kinetic behavior, we are assuming that electronic coupling is relatively constant.)[14]

Variable-temperature measurements show that the back-electron-transfer reactions are thermally activated (Supporting Information). Figure 3 illustrates that the activation enthalpies[15] systematically increase with increasing back reaction driving force, supporting the contention that systematic variations in Franck−Condon factors, rather than variations in electronic coupling, are responsible for the inverted kinetic behavior, at least in the chromophore variation experiments. In addition, the temperature dependence of the electron-transfer rate suggests only a minor role for nuclear tunneling. Because back electron transfer to Ru(III) is expected to involve only solvent reorganization and modest, low-frequency metal−ligand bond reorganization−i.e., high-frequency ligand-based vibrational modes should be Franck−Condon inactive[16]−

it is perhaps not unreasonable that thermally activated inverted behavior has been encountered.

The observation of Marcus-type inverted reactivity requires that the reaction exergonicity exceed the charge-transfer reorganization energy (λ).[17] For semiconductor-based back electron transfer to a nonbonding (t$_{2g}$) orbital of ruthenium(III) tris(bipyridine), λ has been estimated as 0.5−1 eV in polar solvents.[18] Given the ca. −1.9 to −2.3 eV driving force, the estimate is broadly consistent with the observation of inverted reactivity. On the other hand, inverted behavior is somewhat surprising in light of the known Marcus normal-type behavior for back electron transfer to carboxylate- and phosphonate-attached dyes at nanocrystalline titanium dioxide/water interfaces.[2] We speculate that the differences are due to semiconductor-binding induced surface state formation, resulting in localized Ti(III/IV) redox behavior and sequential electron-transfer/proton-transfer reaction sequences.[2] For the much less strongly interacting tin dioxide/dye systems, delocalized-conduction-band or near-conduction-band electrons apparently are available and are capable of motivating highly exoergic back-ET reactions that are fully decoupled from the putative localized interfacial proton-transfer process. In any case, the mechanistic differences for covalent vs electrostatically attached reactants suggest different strategies for optimization of solar cell efficiency-related factors such as light collection efficiency and recombination kinetics. We hope to extend the studies in order to test the generality of the idea that the mode of dye attachment can determine the mechanism of the back-electron-transfer process.

(13) See, for example: (a) Bolts, J. M.; Wrighton, M. S. *J. Phys. Chem.* **1976**, *80*, 2641. (b) Watanabe, T.; Fujishima, A.; Tatsuoki, O.; Honda, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 8. (c) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.

(14) A reviewer has raised the point that the slight increases in ET distance that are brought about by methyl substituent addition might be sufficient to account, on a purely electronic basis, for the observed variations in ET rate with dye composition: increases in Ru^{III}/semiconductor surface separation distance might lead to increases in electronic nonadiabaticity and decreases in ET rate constant. We find, however, that the ligands potentially most capable of configuring the metal center far from the tin oxide surface, i.e., tetramethyl-substituted ligands, yield the largest−rather than the smallest−interfacial k_{et} value. In addition, as noted below, k_{et} variations are driven primarily by variations in thermal activation terms, rather than preexponential terms; dominant preexponential effects would be expected if variations in electronic coupling were primarily responsible for the reactivity differences.

(15) The activation enthalpy (ΔH^*) was extracted from the slope of a modified Arrhenius plot of $\ln(k_{app}T^{1/2})$ versus T^{-1}; see: Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(16) We neglect possible high-frequency mode participation due to redox-induced changes in ruthenium-to-polypyridine back-bonding.

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

(18) See, for example: Clark, W. D. K.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 4676.