Nonadiabatic electron transfer at the nanoscale tin-oxide semiconductor/aqueous solution interface †

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Photo-excitation of chromophoric metal complexes electrostatically adsorbed to tin-oxide semiconductor nanoparticles is often accompanied by injection of electrons from the complexes into the semiconductor conduction band. The mechanism of back electron transfer (semiconductor particle to adsorbed molecule) for a family of tris-bipyridyl ruthenium and osmium complexes has been examined by evaluating the kinetics of transfer to derivatives featuring alkyl substituents of varying length, methyl to pentyl. The substituents serve to change the electron transfer (ET) distance under conditions of weak chemical interaction with the semiconductor surface. Accompanying increases in alkyl substituent length, and therefore transfer distance, are systematic decreases in back ET rate. The decreases are indicative of nonadiabatic ET, *i.e.* electronic rather than nuclear control of the reaction dynamics. Further analysis points to trap-mediated transfer, rather than direct transfer from the conduction band, as the most probable back-reaction pathway.

Introduction

The kinetics and dynamics of both forward and back electron transfer reactions involving molecular dyes and wide bandgap semiconductors are of considerable interest in the context of dye-sensitized liquid-junction cells for sunlight-to-electricalenergy conversion - for example, Grätzel cells.¹⁻³ We have examined the kinetics of back electron transfer (bET) under conditions where dye-attachment surface chemistry does not affect or only minimally affects the semiconductor surface states.⁴ For a variety of experimental reasons, we have focused on bET from negatively charged, nanoscale tin-oxide particles to electrostatically adsorbed transition-metal complexes (cationic dye molecules);⁵⁻⁷ see eqn. (1). These reactions, which were studied in water as solvent, are well described by semi-classical Marcus theory.^{8,9} At modest driving forces, bET rates increase with increasing thermodynamic driving force. Rates maximize at an apparent free energy driving force of about -1.4 eV, implying a reorganization energy, λ , of +1.4 eV, and then decrease at still higher driving forces, i.e. Marcus inverted behavior is encountered. Variable-temperature measurements show that the reactions are thermally activated, even in the inverted region implying that the reorganization energy is due largely to displacement of classically behaved low-frequency modes.9



Comparisons of maximum experimental rates with the maximum rates returned by standard ET theory suggested that the reactions are borderline nonadiabatic.⁶ In other words, electronic coupling rather than nuclear motion appears to govern the reaction dynamics. The reliability of this conclusion, however, clearly rests upon our ability to account for all factors that may

† Dedicated to Professor Fred Lewis on the occasion of his 60th birthday.

limit back ET rates under barrierless conditions. It also depends upon the validity of the assumed reaction mechanism. In our initial studies we concluded that bET occurs from the conduction band and therefore, involves delocalized charges.^{6,11} More recently, as discussed below, we as well as others have inferred 12-14 that bET may well be mediated by surface states (spatially localized mid-gap states). Regardless of mechanism, a good diagnostic for electronic rate control is a decrease in rate with increasing donor/acceptor separation distance.15,16

Here we report on this strategy to elucidate bET mechanisms at the nanoscale tin-oxide/aqueous solution interface. Separation distances were increased by introducing linear chain alkyl groups, R, of varying size to the dye periphery $(M^{II}(bpy-R)_3^{2+})$ where M^{Π} is either Ru^{Π} or Os^{Π} and bpy-R is 2,2'-bipyridine substituted in the 4 and 4' positions by alkyl chain R); see Fig. 1. Due to their flexibility and non-covalent binding to the semiconductor surface, the alkyl groups do not define unique separation distances; but, they do provide a means for progressively increasing separation distances under conditions of weak interaction. From thesse studies we find good evidence for nonadiabatic bET from tin oxide to electrostatically adsorbed ruthenium and osmium complexes. Finally, while a handful of recent reports describe the effects of distance-modulation upon forward or back ET kinetics for covalently attached dyes on semiconductors,^{11,17,18} to our knowledge no studies of weakly interacting systems have been reported.

Experimental

Materials

Tin(IV) oxide colloid (average diameter 0.015 µm) was purchased from Alfa Aesar. The 4,4'-dialkyl-2,2'-bipyridine ligands (bpy-R) were prepared according to either of two literature methods^{19,20} with the purity and identity of the products verified by ¹H NMR. The 4,4'-dimethyl-2,2'-bipyridine, 1-iodopropane, and 10% Pd/C were purchased from Aldrich and used as received. 4-ethyl-, 4-propyl-, and 4-pentylpyridine were purchased from City Chemical and vacuum distilled prior to use. The corresponding ruthenium(II) and osmium(II) complexes were also synthesized via literature methods^{21,22} with identity and purity confirmed by ¹H NMR, FAB-MS and electrochemical measurements.

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Fig. 1 Ligands used to form the tris-bipyridyl ruthenium and osmium compounds.

Characterization of M(bpy-R)₃Cl₂ complexes

[Ru(bpy-1)₃]Cl₂. FAB-MS (m/z) C₃₆H₃₆N₆Ru: calc.: 653.1967, found: 653.1967. ¹H NMR (D₂O): δ 2.48 (s, 18H), 7.14 (d, 6H), 7.56 (d, 6H), 8.30 (s, 6H).

[Ru(bpy-2)₃]Cl₂. FAB-MS (m/z) C₄₂H₄₈N₆Ru: calc.: 737.2906, found: 737.2906. ¹H NMR (d₆-acetone): δ 1.29 (t, 18H), 2.86 (q, 12H), 7.36 (d, 6H), 7.82 (d, 6H), 8.70 (s, 6H).

[Ru(bpy-3)₃]Cl₂. FAB-MS (m/z) C₄₈H₆₀N₆Ru: calc.: 821.3844, found: 821.3843. ¹H NMR (D₂O): δ 0.85 (t, 18H), 1.62 (m, 12H), 2.72 (t, 12H), 7.13 (d, 6H), 7.56 (d, 6H), 8.31 (s, 6H).

 $[Ru(bpy-4)_3]Cl_2$. FAB-MS (*m*/*z*) C₅₄H₇₂N₆Ru: calc: 906.4862, found: 906.4876.

 $[Ru(bpy-4)_3](PF_6)_2$. ¹H NMR (CDCl₃): δ 0.94 (t, 18H), 1.40 (m, 12H), 1.67 (m, 12 H), 2.81 (t, 12H), 7.26 (dd, 6H), 7.55 (dd, 6H), 8.11 (dd, 6H).

[Ru(bpy-5)₃]Cl₂. FAB-MS (m/z) C₆₀H₈₄N₆Ru: calc.: 989.5723, found: 989.5722. ¹H NMR (CD₃OD): δ 0.90 (m, 18H), 1.35 (m, 24H), 1.72 (m, 12H), 2.82 (m, 12H), 7.28 (d, 6H), 7.56 (d, 6H), 8.56 (s, 6H).

[Os(bpy-1)₃]Cl₂. FAB-MS (m/z) C₃₆H₃₆N₆Os: calc: 744.261, found: 744.262. ¹H NMR (D₂O): δ 2.55 (s, 18H), 7.07 (d, 6H), 7.48 (d, 6H), 8.29 (s, 6H).

[Os(bpy-2)₃]Cl₂. FAB-MS (m/z) C₄₂H₄₈N₆Os: calc.: 828.355, found: 828.357. ¹H NMR (D₂O): δ 1.23 (t, 18H), 2.84 (q, 12H), 7.08 (d, 6H), 7.49 (d, 6H), 8.32 (s, 6H).

[Os(bpy-3)₃]Cl₂. FAB-MS (m/z) C₄₈H₆₀N₆Os: calc.: 911.4494, found: 911.4498. ¹H NMR (CD₃OD): δ 1.0 (t, 18H), 1.75 (m, 12H), 2.87 (t, 12H), 7.25 (d, 6H), 7.52 (d, 6H), 8.55 (s, 6H).

 $[Os(bpy-4)_3]Cl_2$. FAB-MS (*m*/*z*) C₅₄H₇₂N₆Os: calc.: 996.5424, found: 996.5440.

 $[Os(bpy-4)_3](PF)_{6}$. ¹H NMR (CDCl₃): δ 0.94 (t, 18H), 1.39 (m, 12H), 1.66 (m, 12 H), 2.83 (t, 12H), 7.18 (dd, 6H), 7.44 (dd, 6H), 8.67 (dd, 6H).

[Os(bpy-5)₃]Cl₂. FAB-MS (m/z) C₆₀H₈₄N₆Os: calc.: 1080.6372, found: 1080.6373. ¹H NMR (CD₃OD): δ 0.90 (s, 18H), 1.35 (m, 24H), 1.70 (m, 12H), 2.86 (t, 12H) 7.20 (d, 6H), 7.50 (d, 6H), 8.55 (s, 6H).

Measurements

UV-visible, luminescence, and electrochemical were performed as previously described.⁶ Nanosecond transient absorption measurement were made using 532 nm radiation, the frequency-doubled output of a 10 Hz Q-switched Nd:YAG laser that has previously been described.⁶ Dye-loaded colloidal samples were prepared using [M(bpy-R)₃]Cl₂ in aqueous solution as previously described.⁶ With luminescence quenching yields of greater than 95% for the sensitizer/SnO₂ systems examined here, transient absorbance data were collected at the ML_3^{2+}/ML_3^{2+*} isosbestic point for each ruthenium (≈400 nm) and osmium (≈410 nm) system where the optical density was maintained between 0.3 and 0.6 for all samples.⁶ This protocol prevents bET kinetic traces from being contaminated with signals due to decay of the excited state. Variable-temperature transient absorption measurements were collected from 5 to 65 °C with a Flash 200 Quantum Northwest thermostated cuvette holder.

Results and discussion

Rate data

Fig. 2 shows representative absorbance transients for back ET from tin oxide to two of the ten dyes examined. The transients were fit to the following second-order rate expression: where ΔA_i is the amplitude of the *i*th component, c_i is the recombination constant in units of s⁻¹ and t is the time in seconds.^{23,24} The transients for the ruthenium complexes were fit utilizing one c (n = 1 in eqn. (2)) while the transients for osmium complexes required two c's (n = 2).

$$\Delta A_{i} = \sum_{i=1}^{n} \frac{\Delta A_{i}}{1 + \Delta A_{i}c_{i}t}$$
(2)



Fig. 2 Comparison of absorbance transients for bET from colloidal SnO_2 to: (a) $Ru(bpy-1)_3^{n+}$ and (b) $Ru(bpy-3)_3^{3+}$. The curves are offset for clarity.

Consistent with second-order kinetics, decay times decrease as the laser pump power increases. In order to fit the second-order rate behavior adequately, decays were collected for 18 μ s, which in all cases equates to longer than six half lives of the decay.

From Fig. 2, the rate of back ET from colloidal tin oxide to the oxidized dye is clearly dependent upon the identity of the alkyl spacer, R. Electrochemical measurements establish that the rate differences are *not* due to differences in bET driving force. For alkyl spacers methyl to pentyl the M(III/II) potentials are around 1.13 and 0.69 V *vs.* SCE for ruthenium and osmium, respectively. Elaboration of the alkyl groups has no appreciable affect upon the potential, and thus the driving force.

Extraction of rate constants from recombination parameters requires an assumption about the recombination mechanism. For the moment, we will assume that bET occurs from the SnO_2 conduction band rather than surface states. This permits us to use eqn. (3):²³

rate =
$$(c_1 C) \eta_e \Gamma (\mathbf{M}^{\text{III}} \mathbf{L}_3^{3+}) = k_{\text{ET}} \eta_e \Gamma (\mathbf{M}^{\text{III}} \mathbf{L}_3^{3+})$$
 (3)

In the equation, $k_{\rm ET}$ is the bET rate constant in units of cm³ s⁻¹, $\Gamma(M^{\rm III}L_3^{3+})$ is the concentration of oxidized dye on the semiconductor surface (mol cm⁻²), *C* is a constant defined below, and $\eta_{\rm e}$ is the concentration of electrons within the colloidal semiconductor particles (mol cm⁻³) determined in the following way:

$$\eta_{\rm e} = \left(\frac{\Delta A_{\rm o}}{A_{\lambda}}\right) \frac{\left[{\rm M}^{\rm II} {\rm L}_3^{2+}\right]}{\left[{\rm SnO}_2\right]} \left(\frac{1}{V_{{\rm SnO}_2}}\right) \tag{4}$$

The values of $k_{\rm ET}$ are determined from c_1 by:

$$k_{\rm ET} = c_1 C = c_1 \frac{A_{\lambda} [{\rm SnO}_2] V_{\rm SnO}}{[{\rm M}^{\rm I} {\rm L}_3^{2+}]}$$
(5)

where ΔA_o and A_{λ} are the initial bleaching intensity and absorbance, respectively, at the probe wavelength, $[M^{II}L_3^{2+}]$ is the concentration of the dye (mol dm⁻³), [SnO₂] is the concentration of SnO₂ particles (mol dm⁻³), and V_{SnO} is the average single-particle volume. We have estimated the volume to be 1.8×10^{-18} cm³ based on an average particle diameter of 15 nm for a spherical particle and a density of 6.95 g cm⁻³.

In Fig. 3 back ET rate constants for the ten alkyl-containing complexes are included on a larger plot of $k_{\rm ET}$ vs. apparent driving force (defined as the difference in potential of the conduction band edge $(E_{CB}(SnO_2) = -0.76 \text{ (pH 7)}, -0.88 \text{ V (pH 9)},$ and -0.94 (pH 10) vs. SCE and the M(III/II) couple).[‡] From Fig. 3 it is evident that both sets of alkyl reactions occur in the Marcus inverted region, with the ruthenium series more deeply inverted. It is also evident that reactivity is attenuated by the introduction of spacers. The behavior is illustrated more clearly in Fig. 4 where rate constants are plotted vs. the number of carbons comprising the alkyl chain. Notably, the effects are nearly the same for the ruthenium and the osmium series. Also included in Fig. 3 are data collected at pH 7 and 10. Our objective in making measurements at other pH values was to modulate the reaction driving force, since it is known that the conduction band edge shifts negatively by 60 mV for each unit increase in pH.25 Additional experiments clearly show that the observed distance/rate-attenuation effects are driving-force independent.

‡ Rate constants for the additional dye reactions included in Fig. 3 were obtained by fitting absorbance transients to eqn. (2). Because the fitting protocol used here differs slightly from the protocol used previously (ref. 6), $k_{\rm ET}$ values also differ slightly – a factor of 2 or less – from the previously reported $\beta k_{\rm ET}$ values. In the earlier report, apparent first-order rate constants were evaluated and the variation of these with laser power (*i.e.* concentration of injected electrons) was used to obtain approximate second-order rate parameters. Additionally the kinetics were treated with a model most appropriate to an electrode featuring a distribution of dyes (redox species) near the electrode. That treatment yields the composite quantity, $\beta k_{\rm ET}$, where β (cm⁻¹) is the electronic coupling attenuation factor and $k_{\rm ET}$ has units of cm⁴ s⁻¹ instead of cm³ s⁻¹. The method here, in contrast to ref. 6, does not require a knowledge (or assumption) of a value for β .



Fig. 3 Plot of back electron transfer rate constants (at 298 K) from SnO_2 to alkyl-spacer-containing Ru(III) (\bullet) and Os(III) (\blacksquare) complexes at pH 7, 9 and 10. They are overlaid with bET data at pH 9 from ref. 7 (\bigcirc)



Fig. 4 Plot of k_{ET} (at 298 K) for the Ru(III) (**II**) and Os(III) (**A**) species as a function of the number of carbon atoms comprising the spacer.

Although the decrease in rate with increasing length of alkyl chain (Fig. 4) points to a decrease in H_{ab} , systematic changes in the reorganization energy should also be considered. In principle, standard ET theory allows for this possibility. Specifically, the solvent component of the reorganization energy, λ_s , is expected to increase with increasing separation distance at short and intermediate distances, becoming constant at long distances.24,26 For a reaction in the inverted region, however, an increase in λ with increasing distance should translate into a decrease in activation barrier height and an increase in rate. We observe the opposite effect - a decrease in rate with increase in separation distance - thus indicating that distance-based modulation of λ_s is not responsible. Nevertheless, to test whether the activation barrier might be altered in some other way, we measured bET rates as a function of temperature and extracted activation enthalpies, ΔH^* , from modified Arrhenius plots (plots of $\ln(k_{\rm ET}T^{1/2})$ vs. 1/T; see eqn. (6), below).²⁷ Rather than increasing systematically with transfer distance, the extracted values of ΔH^* for both series vary modestly, in an apparently random fashion; see Table 1.

Quantifying nonadiabaticity: a conduction-band rate analysis

If we assume for simplicity (and in the absence of more detailed information) that activation entropies are small or zero and that activation enthalpies are temperature invariant, estimates for H_{ab} can be extracted from the following semiclassical interfacial rate expression, appropriate for bET from the conduction band:²⁴

$$k_{\rm ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda_{\rm s}kT}} |H_{\rm ab}|^2 \frac{l_{\rm sc}}{d_{\rm sc}^{2/3} (6/\pi)^{1/3}} \exp\left(-\frac{\Delta H^*}{kT}\right) a \qquad (6)$$

In eqn. (6), l_{sc} is the effective coupling length of the redox wave function into the semiconductor, d_{sc} is the atomic density

Compound	$10^{-13}k_{\rm ET}/{\rm cm^3~s^{-1}}$	$\Delta H^{*a}/\text{kJ} \text{ mol}^{-1}$
$\begin{array}{c} Ru(bpy-1)_{3}^{3+} \\ Ru(bpy-2)_{3}^{3+} \\ Ru(bpy-3)_{3}^{3+} \\ Ru(bpy-3)_{3}^{3+} \\ Ru(bpy-4)_{3}^{3+} \\ Os(bpy-1)_{3}^{3+} \\ Os(bpy-2)_{3}^{3+} \\ Os(bpy-2)_{3}^{3+} \\ Os(bpy-3)_{3}^{3+} \end{array}$	$\begin{array}{c} 1.5 \pm 0.08 \\ 1.2 \pm 0.06 \\ 0.7 \pm 0.04 \\ 0.6 \pm 0.03 \\ 0.5 \pm 0.03 \\ 15 \pm 0.7 \\ 13 \pm 0.7 \\ 10 \pm 0.5 \end{array}$	9.0 ± 0.7 10.3 ± 0.8 12.3 ± 1.3 11.2 ± 0.9 11.3 ± 1.6 7.5 ± 1.9 10.0 ± 1.6 9.1 ± 1.2
$Os(bpy-4)_{3}^{3+}$ $Os(bpy-5)_{3}^{3+}$	5.3 ± 0.3 5.2 ± 0.3	b b

^{*a*} ΔH^* values were determined from the slopes of plots of $\ln(k_{\rm ET}T^{1/3})$ vs. 1/T from 5 to 65 °C. ^{*b*} Linear plots were not obtained over the 5–65 °C temperature range.

of the semiconductor, h is Planck's constant, and k is Boltzmann's constant. Based on eqn. (6) using 1.4 eV for λ_{s} ,⁶ 3 Å for l_{sc} ,²⁴ 2.77 × 10²² atom cm⁻³ for d_{sc} ,²⁴ and choosing points at or near the top of the Marcus plot (dialkyl dyes excluded), H_{ab} is ca. 17 cm⁻¹.

Is the H_{ab} estimate indicative of nonadiabatic ET? This depends, of course, on the magnitude of the nuclear frequency with which the electronically defined barrier crossing frequency, v_{el} , is competing. From eqn. (6), v_{el} is 6×10^{11} s⁻¹. For comparison, the longitudinal relaxation frequency for water – a reasonable candidate for the nuclear frequency, v_n , is 10^{13} s⁻¹.²⁸ Expressed in terms of semiclassical ET theory (eqn. (7)),^{16,27} the estimated value of the electronic tunneling coefficient, κ_{el} , is 0.006. Thus, the reactions appear to be weakly nonadiabatic ($\kappa_{el} < 1$ but not $\kappa_{el} \ll 1$).

$$\kappa_{\rm el} v_{\rm n} = v_{\rm el} = \frac{4\pi^2}{h} \frac{H_{\rm ab}^2}{\sqrt{4\pi\lambda kT}}$$
(7)

Alternative reaction mechanisms

The observed second-order behavior, together with the dependence of the rate on ET driving force, has previously been interpreted as evidence for bET from the semiconductor's conduction band rather than from surface trap states.⁶ An electron that is delocalized in the conduction band is free to return to any oxidized dye molecule, not just the molecule from which it was initially injected; as a consequence, second-order interfacial rate behavior is expected.

The mechanistic assignment was further supported by the inconsistency of two alternative mechanisms with the available results.⁶ In the first mechanism, a locally trapped electron recombines with the oxidized dye from which it is injected, Scheme 1. This scenario displays first-order kinetics and appears to be operative in certain cases involving inorganic dyes



Scheme 1 Trap-based back ET *via* geminate recombination, a first-order kinetic process.

covalently bound to TiO_2 .^{4,29} For the second mechanism, the electron escapes from a local trap and samples many traps, with trap-to-trap hopping being rate determining; see Scheme 2. If this scenario is operative, approximate second-order kinetics can be recovered; but, the sensitivity to ET driving force is lost because the rate-determining step is not the bET to the oxidized dye. Similarly, sensitivity to variation in interfacial electronic coupling, the property altered by introducing spacer groups, is also lost.



Scheme 2 Trap-based back ET involving multiple traps and multiple candidate dyes for recombination with any specific injected electron. The kinetics can be controlled either by trap-to-trap hopping or by interfacial electron transfer, with either yielding approximate second-order rate behavior.

Arguing against a conduction-band mechanism is the large apparent reorganization energy (ca. 1.4 eV, see Fig. 2). Early work by Clark and Sutin, for example, pointed to a reorganization energy of just 0.3 eV for a closely related reaction: back ET from TiO₂ to Ru(bpy)₃³⁺.³⁰ A small value for λ would be expected, of course, based on the absence of significant internal reorganization for the dye¹⁶ and, at best, only a small amount (perhaps 0.1 eV) for the semiconductor.³¹ An alternative hypothesis which accounts for the apparent λ value of 1.4 eV does not involve electron transfer from the conduction band of tin oxide, but rather from surface trap states that are energetically far below the conduction band edge. In Scheme 2, trap-to-trap hopping occurs as a pre-equilibrium step with interfacial ET now being the rate-determining step. Under these conditions, the true driving force for back ET is the energy difference between the trap state and the dye redox couple. If the relevant trap states were located, say, 0.9 eV below the conduction band edge, the true maximum in the Marcus plot (Fig. 3) would be at ca. -0.5 eV and λ would equal +0.5 eV. In Fig. 5 a classical Marcus curve with $\lambda = 0.5$ eV but offset by 0.9 eV is shown for the data previously reported.^{6,7} (The poorer fit of the points in



Fig. 5 Plot of back electron transfer rate constants vs. apparent driving force together with classical Marcus curves for $\lambda = 1.4$ eV (—) and $\lambda = 0.5$ eV, translated by 0.9 eV (---) (see text). The data is taken from ref. 7.

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the inverted region to $\lambda = 0.5$ eV curve might signify that the smaller reorganization energy is incorrect. Alternatively, it could simply be due to neglected vibrational effects; if important, this would be manifested as positive deviations from the classical curve.)

Despite the fact that this alternative hypothesis also replicates the experimentally observed second-order rate behavior, we previously discounted this mechanism,^{6,7} the problem being that it appeared inconsistent with time-resolved photoacoustic measurements showing the reaction driving force to be close to the value expected based on electron return from the conduction band. We have subsequently discovered that the driving forces obtained from the photoacoustic analysis are unusually sensitive to initial conditions and to the assumed mathematical form of the observed signal decay; consequently, we are uncertain of the validity of our earlier conclusions regarding absolute reaction energetics.

Quantifying nonadiabaticity: a surface-state rate analysis

If trap states mediate bET as discussed above, the form of the rate analysis will differ from eqn. (3). The rates to be described are those from localized surface sites to adsorbed dye molecules. Spatial diffusion of electrons along the surface has been considered for dye-sensitized TiO2 previously,12,14 although these models do not consider bET itself to be rate determining. Thus, they describe reactions that differ in an important way from interfacially controlled reactions studied here. In the analysis that follows, we assume that trap-to-trap transport is fast compared to the interfacial electron transfer. We also assume that only traps located close to the oxidized dyes will be effective in transferring electrons back across the interface. Because of the peculiar geometry and reduced dimensionality of the system (a 2D population of traps on a curved, nanoscale surface and a 2D population of dye molecules adsorbed to that surface) the problem is analytically complicated. It becomes conceptually simpler and certainly more amenable to approximation in the limit where only one electron has been injected, and therefore only one oxidized dye molecule is available per colloidal SnO₂ particle.

Transient-absorbance derived reaction rates obtained at higher laser powers were extrapolated to the one-electron-perparticle injection limit. (As reported previously, data with good signal-to-noise can be obtained without too much difficulty down to five electrons per particle, making the extrapolation a short one.⁶) For simplicity, we then assumed that the half-life for the second-order electron/dye recombination reaction could be equated with the half-life of a first-order reaction – a reasonable assumption in the one-electron-per-particle limit where the distinction between second- and first-order rate processes becomes blurred or even artificial.

The extrapolated value is used as the apparent first-order rate constant, k_{app} (= (ln2)/ t_{ν_2}). Our model then assumes that k_{app} (eqn. (8)) is the product of a proximal (reactive) trap/ remote

$$k_{\rm app} = K_{\rm rz} k_{\rm ET, trap} \tag{8}$$

(unreactive) trap equilibrium constant (K_{rz} (unitless), eqn. (9)) and a first-order rate constant for an elementary step ($k_{ET,trap}$ (s⁻¹), eqn. (10)).

$$dye^{+}:SnO_{2}(trap) + SnO_{2}(trap e^{-}) \xleftarrow{K_{rz}} dye^{+}:SnO_{2}(trap e^{-}) + SnO_{2}(trap) dye^{+}:SnO_{2}(trap e^{-}) + SnO_{2}(trap) proximal pair remote trap (9)$$

 $\begin{array}{c} dye^{+}:SnO_{2}(trap e^{-}) \xrightarrow{k_{\text{ET,trap}}} dye:SnO_{2}(trap) \quad (10)\\ proximal pair \qquad bET product \end{array}$

To estimate K_{rz} we used Brunschwig and Sutin's "reaction zone" approach.³²⁻³⁴ Here the usual exponential fall-off in the electron tunneling probability with donor/acceptor separation distance is replaced with a step function. All potential reactants within a certain reaction zone (reactant/co-reactant approach zone) are treated as if they are equally likely to transfer an electron, while all found at greater distance are treated as having zero probability of reacting; see Scheme 3. It has been shown elsewhere that the effective *molecular* reaction zone thickness, *z*, is approximately $1/\beta$ where β is the distance/tunneling-efficiency attenuation factor (*i.e.* slope of a plot of ln(probability) *vs.* separation distance).³² For a spherical molecular reactant of radius, σ , then, the reaction zone is a spherical shell extending from σ to $\sigma + z$. A typical value for β in other contexts is 1 Å⁻¹, making *z* approximately 1 Å.



Scheme 3 Reaction-zone treatment of trapped-mediated nonadiabatic ET from a colloidal particle surface to an oxidized dye molecule. The top diagram illustrates how the exponential fall off of electron tunneling probability with molecule/trap separation distance can be replaced with an equivalent-area step function featuring regions of finite constant probability (over the separation distance σ to $\sigma + z$) and zero probability (distance greater than $\sigma + z$). The lower diagram depicts the dye/colloidal-particle interface. For a spherical molecular reactant (the dye) of radius, σ , the intersection of a molecular reaction zone, σ to $\sigma + z$, with the particle surface defines a reactive footprint. Electrons occupying trap sites within the footprint are treated as uniformly reactive (identical electron tunneling probabilities). Those outside the footprint are treated as unreactive.

To adapt the Brunschwig and Sutin approach to a dye/ colloidal-particle interface, we calculate the particle surface area encompassed by the molecular reaction zone when the molecule and particle are in contact; see Fig. 3. Using $\sigma = 8$ Å (approximately the radius for M(bpy-1)₃ⁿ⁺) and assuming z = 1 Å, the molecular reaction zone's footprint on the semiconductor particle surface is 37 Å². For a 15 nm diameter SnO₂ particle (sphere) the total surface area is 75000 Å². The equilibrium constant for formation of the reactive proximal pair in eqn. (9) is the ratio of the reactive area of the particle to the unreactive area or $K_{rz} = 37$ Å²/(75000 Å² – 37 Å²) \approx 1/2000. The extrapolated one-electron-per-particle rate constant at the top of the Marcus curve ($\Delta G^* = 0$), k_{app} , is 9×10^5 s⁻¹. From eqn. (8) the actual rate of back electron transfer for the proximal pair, $k_{ET,trap}$, is estimated to be 2×10^9 s⁻¹.

Under barrierless conditions, the electron transfer rate constant is identical to the barrier crossing frequency, *i.e.* $k_{\rm ET,trap}$ (maximum) = $v_{\rm el}$. Using 2×10^9 s⁻¹ for $v_{\rm el}$ and assuming for convenience (and in the absence of any specific information) that $\lambda_{\rm s} = 0.5$ eV, eqn. (7) returns an $H_{\rm ab}$ value of $2 \,{\rm cm^{-1}}$ and a $\kappa_{\rm el}$ value of 2×10^{-4} . Correspondingly smaller values can be assigned to the reactions of dialkyl dyes. While the estimates obtained are dependent on assumptions regarding the magnitudes of β and $K_{\rm rz}$, the trap-based analysis points to a greater degree of nonadiabaticity than does the conduction-band based analysis. Given the ability of the trap model to account for the large apparent λ values for bET, we favor it as the more probable mechanistic description.

Conclusions

Based on the sensitivity of rate constants to the presence of alkyl spacer groups, electronic coupling rather than nuclear motion controls the dynamics of bET from colloidal tin-oxide semiconductor particles to weakly bound (electrostatically bound) metal complexes. A conduction-band based analysis of absolute rate constants and activation parameters, for reactants lacking extended alkyl groups, yields estimates of a few tens of wavenumbers for H_{ab} . An alternative mechanism involving deep traps yields values that are roughly an order of magnitude smaller. The deep trap mechanism is able to account for experimentally observed large apparent reorganization energies, such that the true reorganization energy equals the difference between the apparent reorganization energy (derived from the maximum in a Marcus rate vs. driving force plot) and the trap depth with respect to the conduction band edge energy.

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