

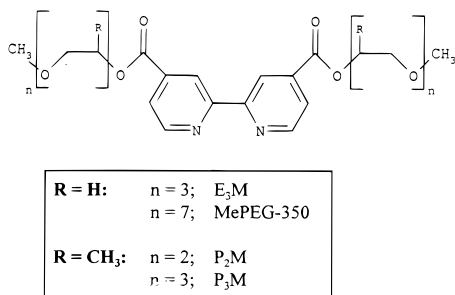
## A $10^{11}$ -Fold Range of Solvent Dynamics Control of Heterogeneous Electron Transfers of Cobalt(III/II)-tris(bipyridine)

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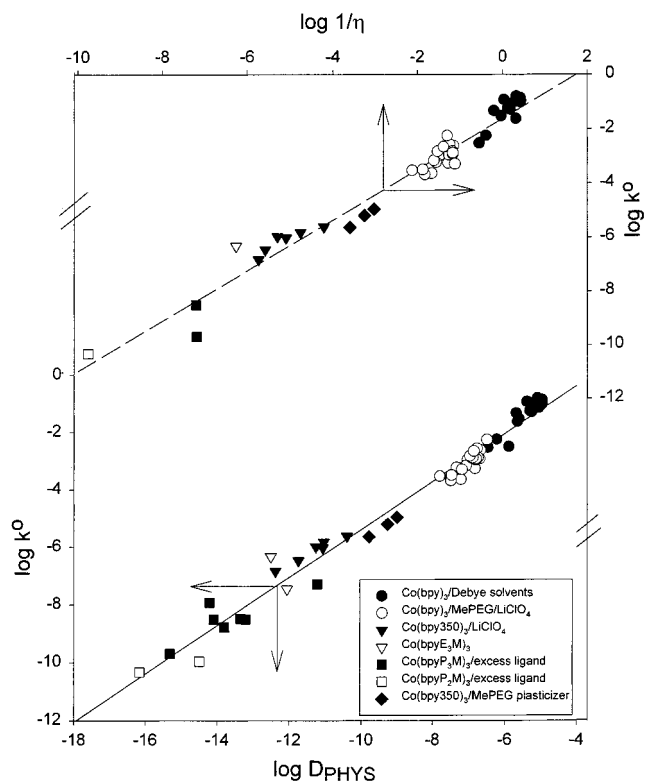
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This paper describes a remarkable proportionality, over a  $10^{11}$ -fold range of values, of the heterogeneous electron transfer rate constants ( $k^0$ ) of the Co(III/II) reaction of Co(II) tris(bipyridine) complexes to their physical self-diffusion coefficients ( $D_{\text{PHYS}}$ ). The  $k^0$ - $D_{\text{PHYS}}$  data shown at the middle right of Figure 1 (●, ○) are previously reported<sup>1</sup> results for dilute solutions of [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in a series of fluid solvents. The 21 new data points (◆, ▼, ■, ▽, □) for the Co(III/II) electrode reaction are encompass an even wider range of  $k^0$  and  $D_{\text{PHYS}}$  values and are obtained in undiluted Co(II) tris(bipyridine) room temperature molten salts, made<sup>2</sup> by attaching oligomeric polyethylene or polypropylene oxide chains to the bipyridine ligands, i.e.,



The  $D_{\text{PHYS}}$  self-diffusion coefficients of the polyether-tailed Co(II) complexes in their undiluted, ionically conductive, melts have been measured by microelectrode potential step chronoamperometry procedures described before.<sup>2</sup> The melt  $D_{\text{PHYS}}$  values are both very small and variable, by *ca.*  $10^8$ -fold, by choice of polyether chain, [LiClO<sub>4</sub>] (electrolyte depresses  $D_{\text{PHYS}}$ ), and adding small amounts of free tailed-ligand (plasticizes the melt, enhances  $D_{\text{PHYS}}$ ). The  $D_{\text{PHYS}}$  measurements are unaffected by ionic migration or homogeneous Co(III/II) self-exchange reactions, owing respectively to the relatively large value<sup>2a,b</sup> of  $D_{\text{ClO}_4^-}$  and to the small homogeneous Co(III/II) self-exchange rate constant ( $k_{\text{EX}}$ ).<sup>2a,b</sup> Also, the combinations of  $D_{\text{PHYS}}$  and potential step electrolysis times used avoid “molecule-scale diffusion,”<sup>3</sup> i.e., diffusion path-lengths are  $\gg$  molecular size.

The heterogeneous Co(III/II) electron transfer rate constants in the melts were obtained from cyclic voltammetric peak potential separations, confirming such measurement for a demanding example (at lower left in Figure 1) using small amplitude potential steps to the foot of the Co(III/II) wave. Comparisons also showed that results are independent of microelectrode geometry (disk, band, lithographically defined



**Figure 1.** Linear regression plot of  $k^0$  vs  $D_{\text{PHYS}}$  and  $\eta^{-1}$  at 25 °C for (●) [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in Debye solvents, from ref 1; (○) [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in MW 400 polyether solvent (MePEG-400) containing various [LiClO<sub>4</sub>], from ref 1; (▼) [Co(bpy)(CO<sub>2</sub>MePEG-350)<sub>2</sub>]<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> containing various [LiClO<sub>4</sub>]; (▽) [Co(bpy)(CO<sub>2</sub>E<sub>3</sub>M)<sub>2</sub>]<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>; (■) [Co(bpy)(CO<sub>2</sub>P<sub>3</sub>M)<sub>2</sub>]<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> containing various [free ligand]; (□) [Co(bpy)(CO<sub>2</sub>P<sub>2</sub>M)<sub>2</sub>]<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> containing various [free ligand]; (◆) [Co(bpy)(CO<sub>2</sub>MePEG-350)<sub>2</sub>]<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> containing various [MePEG-350]. Estimated uncertainties of individual experimental measurements are less than the symbol sizes. See structure for ligand notation and Supporting Information for other details.

line). The 21 melt data points (◆, ▼, ■, ▽, □) in Figure 1 include 17 different melt compositions studied by cyclic voltammetry plus four duplicate/comparison determinations. The  $k^0$  determinations, which are the first in such highly viscous media, and the melt compositions are outlined in Supporting Information and will be reported more fully in a future publication. The melt ionic conductivities decrease with  $D_{\text{PHYS}}$ , from right to left in Figure 1, but so do the experimentally measured currents, resulting in  $i_{\text{RUNC}}$  effects (uncompensated resistances can degrade  $k^0$  measurements) being minor or absent over the entire range of experiments.

The  $k^0$  measurements reveal an almost linear relation to  $D_{\text{PHYS}}$  over a *ca.*  $10^{11}$ -fold range; the isothermal log–log plot in Figure 1 has a slope of 0.82. The fluidity (*i.e.*, inverse viscosity,  $\eta^{-1}$ ) of the Co tris(bipyridine) complex solutions and melts measured at 25 °C in separate experiments by rheometry (Figure 1, top) also varies linearly (log–log slope 0.90) with  $k^0$  over a broad range of values; it follows that  $D_{\text{PHYS}}$  is nearly proportional to fluidity.

In homogeneous solutions, the rates of very fast electron transfer reactions can become controlled by the rates at which reaction partners diffuse together and collide. There is no possible parallel explanation for the heterogeneous rate results in Figure 1, since by the Einstein formulation,<sup>4</sup> interfacial

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collision rates ( $Z_{\text{HET}}$ ) depend on molecular mass but not on diffusion rates, and in any event  $Z_{\text{HET}}$  of the cobalt complex in its melt is much larger than any of the  $k^0$  results. Also, the Figure 1 results cannot be ascribed to long distance interfacial electron transfers<sup>5</sup> (a) being inconsistent with the overall span of  $k^0$ - $D_{\text{PHYS}}$  linearity and (b) from consideration of the values of characteristic<sup>5</sup>  $k^0/D_{\text{PHYS}}$  ratios.

We interpret Figure 1 as a remarkably broad example of solvent dynamics<sup>6</sup> control of electron transfer reaction rate. There have been previous observations<sup>6</sup> of proportionalities between heterogeneous electron transfer rates and diffusion constants, but none over such an extreme range. Our earlier evidence<sup>1</sup> for solvent dynamics control in dilute solutions of [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (Figure 1, ●, ○) in Debye (●) and ether (○) solvents of known longitudinal solvent relaxation time  $\tau_L$  was based on the proportionality of  $k^0$  to  $\tau_L^{-1}$ , along with  $k^0$ - $D_{\text{PHYS}}$  and fluidity proportionalities observed in these solvents and in small oligomeric polyethers, that could be understood through the relationship<sup>7-9</sup> for the rate of an adiabatic electron transfer

$$k^0 = \tau_L^{-1} \left[ \frac{\Delta G_{\text{OS}}^*}{4\pi k_{\text{B}} T} \right]^{1/2} K_{\text{A}} K_{\text{EL}} \exp \left[ \frac{-\Delta G^*}{RT} \right] \quad (1)$$

and that<sup>10</sup> between  $\tau_L^{-1}$ , viscosity ( $\eta$ ), and  $D_{\text{PHYS}}$

$$\tau_L^{-1} = \left( \frac{\epsilon_0}{\epsilon_\infty} \right) \frac{k_{\text{B}} T}{4\pi \alpha^3 \eta} = \left( \frac{\epsilon_0}{\epsilon_\infty} \right) \frac{3r_{\text{H}} D_{\text{PHYS}}}{2\alpha^3} \quad (2)$$

The central result of Figure 1 is that the cobalt complex melts follow the same, previously observed<sup>1</sup> pattern of  $k^0 - D_{\text{PHYS}} - \eta^{-1}$  proportionalities, over an even wider range of values. These proportionalities are expected from eqs 1 and 2 (although in eq 2 the numerical values of  $r_{\text{H}}$  and  $\alpha$  in extremely viscous oligomers may take on different meanings). The nature of the specific solvent relaxations that are mutually involved in control of electron transfer rate and physical transport for the Co

complexes are unknown. It is probably significant, however, that both processes occur with the metal complex in an alkyl ether environment, so that the same modes of solvent relaxation are available over the entire range of Figure 1. Although the connection between the repolarization rate  $\tau_L$  and  $D_{\text{PHYS}}$  is admittedly inferential, the combined observations of (a) Debye solvent-demonstrated<sup>1</sup> solvent dynamics control at large combinations of  $k^0$  and  $D_{\text{PHYS}}$  values and (b) contiguous, unbroken extension of linear  $k^0 - D_{\text{PHYS}}$  behavior to smaller values in ether-like media *form a compelling case for solvent dynamic control of electron transfer rate constants over the entire range. The results, indirectly, imply the absence of any lower limit of solvent dynamics control of electron transfers.*

While solvent dynamics control of electron transfers on time scales as slow as those suggested by Figure 1 is unprecedented, ample evidence for very slow solvent relaxation time scales exists from Stokes shift, ultrasonic, dielectric relaxation, photon correlation, and holographic photobleaching observations.<sup>11</sup> For example, Maroncelli et al.<sup>11a</sup> describe a 10<sup>10</sup>-fold frequency range of solvation dynamics in 2-methyl-THF (100 ps to 10<sup>2</sup> s); the observed parallel behavior of solvent fluidity showed that dipolar orientational motions governing the solvent relaxations were intimately linked to those responsible for viscous flow.

Finally, because the Co(II/I) couple's *homogeneous* electron transfer rate constants in these same polyether-tailed cobalt bipyridine complex melts<sup>2a,d</sup> are both faster and independent of polyether chain length, we can infer that the Co(III/II) rates in Figure 1 are unaffected by distance-related tunneling barriers imposed by the polyether shells around the complexes. At the same time, underscoring our incomplete understanding of electron transfer self-exchange rates in semisolid media, we should point out the somewhat surprising insensitivity<sup>2a,d</sup> of the Co(II/I) reaction rate constant to values of  $D_{\text{PHYS}}$ .

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**Supporting Information Available:** A brief description of  $k^0$  measurements and Figure S1 that identifies Co complex melts and microelectrodes used (9 pages). See any current masthead page for ordering and Internet access instructions.

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(9) (a)  $K_{\text{A}}$  is precursor formation constant,<sup>8b</sup>  $K_{\text{EL}}$  the electronic coupling term, and  $\Delta G^*$  and  $\Delta G_{\text{OS}}^*$  the total and outer-sphere reorganizational barrier energies, respectively.