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Experimental Observation of Excited-State Electron Transfer Quenching Involving Exchange-Coupled Dinuclear Fe^{III} Complexes

James P. Kirby, Brandon T. Weldon, and James K. McCusker*

Contribution from the Department of Chemistry University of California at Berkeley Berkeley, California 94720-1460

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Polynuclear metal complexes that exhibit intramolecular electron exchange interactions have been the subject of research in the inorganic community for several decades.[1] More recently, various groups have presented theoretical arguments for how electron exchange might manifest itself in the electron transfer properties of metal clusters.[2−5] Research in our group focuses on the effect of electron exchange on the photophysics and photochemistry of transition metal compounds. In this communication, we wish to report examples of photoinduced bimolecular electron transfer involving exchange-coupled metal complexes. The photosensitizer $[Ru(dmb)_3]^{2+}$ (where dmb is 4,4′-dimethyl-2,2′-bipyridine) was used to promote an excited-state electron transfer reaction with dinuclear Fe^{III} complexes (Fe^{III}-Fe^{III}) according to the following reaction:

$$[{}^*Ru(dmb)_3]^{2+} + (Fe^{III}Fe^{III}) \xrightarrow{k_{et}} [Ru(dmb)_3]^{3+} + (Fe^{II}Fe^{III})$$

On the basis of a comparative study of two closely related dinuclear Fe^{III} complexes, we suggest that differences noted in intermolecular electron transfer rates may be related to modulation of exchange interactions within the dinuclear Fe^{III} cores, thereby providing direct experimental evidence of a link between electron exchange and the kinetics of bimolecular electron transfer.

The present work is based on an oxo-bis-carboxylato dinuclear Fe^{III} system described in detail by Armstrong and Lippard.[6] The compound $Fe_2O(O_2CCH_3)_2(Tp)_2$, where Tp is hydrotris(1-pyrazolyl)borate, is an example of the well-studied oxo-bis-carboxylato-bridged class of dinuclear Fe^{III} complexes.[7] For our purposes, the attractiveness of this system lies in the fact that both the oxo- and hydroxo-bridged forms of this complex can be prepared and isolated.[6] Protonation of the oxo bridge to form the $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$ cation results in a reduction of the Heisenberg exchange integral[8] from $J = -122$ to -17 cm^{-1}. This system therefore provides us with two complexes that are quite similar in terms of chemical composition yet differ substantially in their intramolecular exchange interactions.

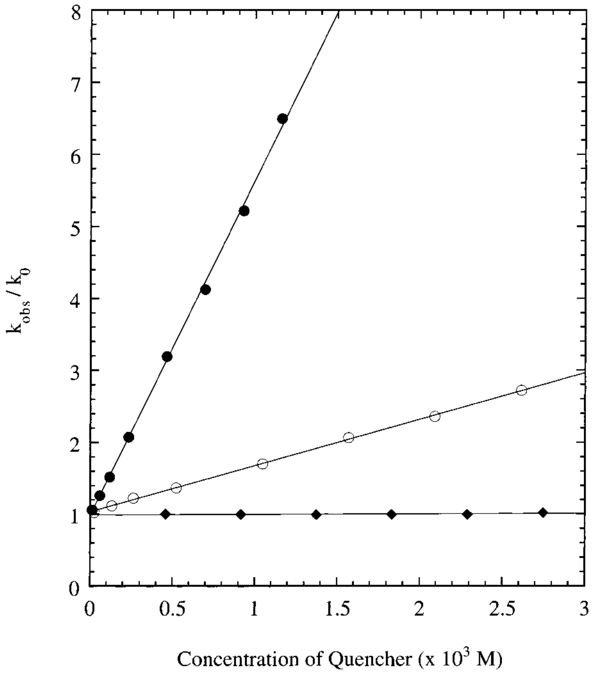

Figure 1. Stern−Volmer plots of the quenching of ^{3}MLCT emission from $[Ru(dmb)_3]^{2+}$. Data are shown for variable concentrations of $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$ (filled circles), $Fe_2O(O_2CCH_3)_2(Tp)_2$ (empty circles), and $Zn(Tp)_2$ (diamonds). The straight lines represent linear regression fits of the data from which values for k_q were determined. The slope of the regression for $Zn(Tp)_2$ is zero, indicating no quenching is observed for this control molecule.

All of the experiments were carried out on CH_3CN solutions of the compounds that were also 0.075 M in NBu_4PF_6.[9,10] Plots of the normalized rate of excited-state decay as a function of quencher concentration are illustrated in Figure 1. The difference in quenching rates between the oxo- and hydroxo-bridged complexes is substantial, with k_q increasing by almost an order of magnitude from $(7.1 \pm 0.3) \times 10^8$ M^{-1} s^{-1} in the case of $Fe_2O(O_2CCH_3)_2(Tp)_2$ to $(5.15 \pm 0.15) \times 10^9$ M^{-1} s^{-1} for $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$.[11] In general, the quenching of a sensitizer such as $^*[Ru(dmb)_3]^{2+}$ at any given concentration of quencher [Q] can be described by the expression $k_{obs} = k_0 + k_{en\ tr}[Q] + k_{el\ tr}[Q]$, where k_{obs} is the observed rate constant, k_0 is the rate constant for excited-state decay of the sensitizer in the absence of quencher, and $k_{en\ tr}$ and $k_{el\ tr}$ are the rate constants for bimolecular energy and electron transfer, respectively. It is well-

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(1) See, for example: (a) *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 1993. (b) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(2) Girerd, J.-J. *J. Chem. Phys.* **1983**, *79*, 1766.

(3) Bersuker, I. B.; Borshch, S. A. *Adv. Chem. Phys.* **1992**, *81*, 703.

(4) Blondin, G.; Girerd, J.-J. *Chem. Rev.* **1990**, *90*, 1359.

(5) Bominaar, E. I.; Achim, C.; Borshch, S. A.; Girerd, J.-J.; Münck, E. *Inorg. Chem.* **1997**, *36*, 3689.

(6) (a) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837. (b) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4632.

(7) (a) Que, L.; Dong, Y. H. *Acc. Chem. Res.* **1996**, *29*, 190 and references therein. For general references on the model chemistry of non-heme iron−oxo proteins, see: (b) Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759 and references therein. (c) Que, L.; Ho, R. Y. N. *Chem. Rev.* **1996**, *96*, 2607 and references therein.

(8) These *J* values are derived from a spin Hamiltonian of the form $\mathbf{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$.

(9) Solutions of the compounds were prepared in an inert atmosphere drybox using CH_3CN that had been distilled from CaH_2 under N_2. The spectrometer used for time-resolved emission and absorption measurements has been described previously (Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253). Samples were excited at 458 nm and monitored for emission at 620 nm. Static absorption spectra taken before and after all time-resolved measurements were indistinguishable.

(10) The need for added electrolyte when studying charged reactants has been reported by several other groups. See: Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagel, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815 and references therein.

(11) It should be noted that the data presented in Figure 1 have not been corrected for Coulombic and diffusional effects. However, qualitative considerations of these factors indicate that the corrected values of k_{obs} would increase the difference in k_q already noted.

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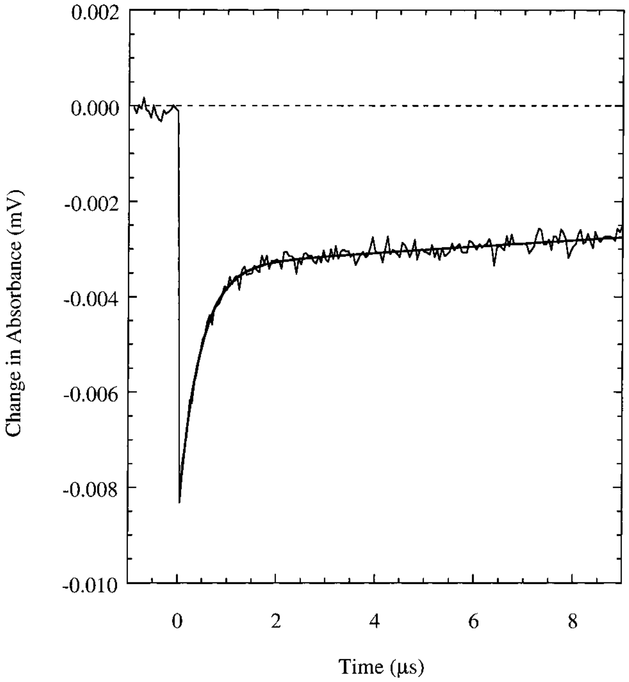

Figure 2. Plot of the excited-state absorption difference spectrum at $\lambda_{\text{probe}} = 440$ nm following excitation at 458 nm of a CH_3CN solution 3.1×10^{-5} M in $[Ru(dmb)_3]^{2+}$ and 4.6×10^{-4} M in $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$. The solid line is a fit to a biexponential function with $k_1 = (2.35 \pm 0.10) \times 10^6\ s^{-1}$ and $k_2 = (2.25 \pm 0.10) \times 10^4\ s^{-1}$. Although not shown in this figure, the kinetic trace returns fully to the baseline at longer time. The rate constant for the short-lived component matches what is obtained from time-resolved emission measurements, whereas the long-lived component is assigned to charge recombination of the $[Ru(dmb)_3]^{3+}$ and $Fe_2(OH)(O_2CCH_3)_2(Tp)_2$ photoproducts formed as the result of excited-state electron transfer.

known that mononuclear Fe^{III} complexes can oxidatively quench the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$;[12] we have established the occurrence of electron transfer in our dinuclear systems using excited-state absorption spectroscopy. Data for the hydroxo-bridged dimer are shown in Figure 2. The ca. 50 μs component of the biphasic transient in Figure 2 provides compelling evidence for the formation of electron transfer photoproducts that recover via bimolecular charge recombination.[13] An overlay of the emission spectrum of $[Ru(dmb)_3]^{2+}$ with the absorption spectra of the two dinuclear complexes indicates that energy transfer is favored in the case of the oxo-bridged dimer relative to the hydroxo-bridged dimer by virtue of the lack of absorbance of the latter in the 600−800 nm region. This fact, combined with larger value of k_q for $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$, effectively rules out changes in $k_{\text{en tr}}$ as being the origin of the difference in excited-state quenching rates between the oxo- and hydroxo-bridged species.[14]

Electrochemical measurements on both the oxo- and hydroxo-bridged complexes reveal a decrease in the reduction potential (i.e., a positive shift) for $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$ relative to $Fe_2O(O_2CCH_3)_2(Tp)_2$ of ca. 55 mV.[15] This implies an increase in the driving force of ca. 55 mV for quenching by the hydroxo-bridged species, qualitatively consistent with the observed trend in k_q. However, quenching measurements we have recently made on a series of similar complexes of the form $[Fe_2O(O_2CCH_3)_2(R_3\text{-}TACN)_2]^{2+}$, where R_3TACN is a hydrido- or methyl-substituted form of 1,4,7-triazacyclononane, indicate a change in k_q of only a factor of ca. 4.5 following a 200 mV change in driving force. These results suggest that consideration of ΔG_0 alone is not sufficient to account for the inferred change in electron transfer rate between the oxo- and hydroxo-bridged Tp complexes.

While the difference in electron transfer rates between these two compounds will arise due to changes in the magnitudes of terms in the Marcus equation, we suggest that the change in intramolecular electron exchange coupling that accompanies protonation of the oxo bridge in $Fe_2O(O_2CCH_3)_2(Tp)_2$ may be correlated with and/or influence these factors and, ultimately, electron transfer rates. Bertrand and Gayda,[16] using a simple effective spin Hamiltonian approach, suggested that the presence of exchange coupling in $[Fe_2S_2]^{2+}$ clusters of the type found in two-iron ferredoxins (Fd) could account for as much as 250 mV of the observed shift in reduction potential of Fd's as compared to single-ion rubredoxins. Noodleman and co-workers revisited this problem and reached qualitatively similar conclusions.[17] In terms of reorganization energies (λ), changes in electron exchange accompanying the formation of the mixed-valent $Fe^{II}Fe^{III}$ state may introduce Franck−Condon factors due to large zero-field splitting effects[18] or from the introduction of a resonance exchange term.[5,19] The larger ΔJ is as a result of electron transfer, the more significant these factors will become. Finally, in more general terms, the modification of electronic structure endemic to the presence of electron exchange could easily be imagined to have a global impact on both the thermodynamics and the kinetics of electron transfer due to the concomitant shift in the energies of various electronic states, which in turn could affect chemical reactivity. The implications of a link between electron exchange and the kinetics of electron transfer are profound, particularly with regard to biological systems. For example, given the sensitivity of electron exchange interactions to electronic and structural factors, tuning of the electron transfer properties of cluster-containing active sites could be coupled to, among other things, conformational changes of the protein.

Although the results described herein are compelling, it is difficult to say with certainty the extent to which Heisenberg exchange is affecting electron transfer rates in these compounds: some of the observed changes in ΔG_0 and λ may be trivial consequences of protonation of the oxo bridge, unrelated to the concomitant change in J. Thus, to establish the precise manner Heisenberg exchange influences bimolecular electron transfer processes, it will be necessary to study a more extensive series of compounds for which trends in ΔG_0 and λ can be accounted for in a systematic fashion independent of changes in electron exchange. Work along these lines is currently underway.

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(12) (a) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309. (b) Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468. (c) Boraselli, C. D.; Corti, H.; Goldfarb, D.; Braslavsky, S. E. *J. Phys. Chem. A* **1997**, *101*, 7718.

(13) Photoexcitation of solutions of the dinuclear complexes in the absence of $[Ru(dmb)_3]^{2+}$ revealed transient signals that were pulse width-limited on the nanosecond time scale.

(14) This assumes energy transfer proceeds by a Förster mechanism.

(15) Electrochemical measurements were carried out in an inert atmosphere drybox using a BAS 100A electrochemical analyzer with a Pt working electrode and a Ag/$AgNO_3$ reference. Compounds were dissolved in dry CH_3CN that was 0.1 M in NBu_4PF_6. The $\Delta\Delta G_0$ quoted here is based on Osteryoung square-wave potentiometric measurements carried out on both compounds under identical conditions.

(16) Bertrand, P.; Gayda, J.-P. *Biochim. Biophys. Acta* **1982**, *680*, 331.

(17) Mouesca, J. M.; Chen, J. L.; Noodleman, L.; Bashford, D.; Case, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 11898.

(18) McCormick, J. M.; Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 9066.

(19) Although resonance exchange does not likely play a role in the mixed-valent hyrdoxo-bridged dimer, it has been suggested that it may be an important factor in a mixed-valence oxo-bridged complexes (E. I. Solomon, personal communication).