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

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Received May 19, 1998

Polynuclear metal complexes that exhibit intramolecular electron exchange interactions have been the subject of research in the inorganic community for several decades.\textsuperscript{1} More recently, various groups have presented theoretical arguments for how electron exchange might manifest itself in the electron transfer properties of metal clusters.\textsuperscript{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)\textsubscript{3}]\textsuperscript{2+} (where dmb is 4,4′-dimethyl-2,2′-bipyridine) was used to promote an excited-state electron transfer reaction with dinuclear Fe\textsuperscript{III} complexes (Fe\textsuperscript{III}-Fe\textsuperscript{III}) according to the following reaction:

\[ \text{[Ru(dmb)\textsubscript{3}]}^{2+} + (\text{Fe\textsuperscript{III}-Fe\textsuperscript{III}}) \rightarrow \text{[Ru(dmb)\textsubscript{3}]}^{3+} + (\text{Fe\textsuperscript{III}-Fe\textsuperscript{II}}) \]

On the basis of a comparative study of two closely related dinuclear Fe\textsuperscript{III} complexes, we suggest that differences noted in intermolecular electron transfer rates may be related to modulation of exchange interactions within the dinuclear Fe\textsuperscript{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\textsuperscript{III} system described in detail by Armstrong and Lippard.\textsuperscript{6} The compound Fe\textsubscript{2}O(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp), where Tp is hydrotris(1-pyrrolato)borate, is an example of the well-studied oxo-bis-carboxylato-bridged class of dinuclear Fe\textsuperscript{III} complexes.\textsuperscript{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.\textsuperscript{6} Protonation of the oxo bridge to form the [Fe\textsubscript{2}(OH)(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp)]\textsuperscript{2+} cation results in a reduction of the Heisenberg exchange integral\textsuperscript{8} from \( J = -122 \) to \(-17 \) cm\textsuperscript{-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.

All of the experiments were carried out on CH\textsubscript{3}CN solutions of the compounds that were also 0.075 M in NBu\textsubscript{4}PF\textsubscript{6}.\textsuperscript{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\textsuperscript{-1} s\textsuperscript{-1} in the case of Fe\textsubscript{2}O(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp)\textsubscript{2} to \( (5.15 \pm 0.15) \times 10^9 \) M\textsuperscript{-1} s\textsuperscript{-1} for [Fe\textsubscript{2}(OH)(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp)]\textsuperscript{2+}.\textsuperscript{11} In general, the quenching of a sensitizer such as [Ru(dmb)\textsubscript{3}]\textsuperscript{2+} at any given concentration of quencher [Q] can be described by the expression \( k_{obs} = k_0 + k_{en t} [Q] + k_{dt} [Q] \), 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 \( k_{en t} \) and \( k_{dt} \) are the rate constants for bimolecular energy and electron transfer, respectively. It is well-known that the rate constant for energy transfer is highly dependent on the spectral overlap integral, but the rate constant for electron transfer depends on the exchange integral. This is a source of great difficulty when attempting to scale the difference in rates between the oxo- and hydroxo-bridged complexes.

For the present work, we have used a modified Stern-Volmer equation to describe the quenching process:

\[ k_{obs}/k_0 = 1 + \frac{k_q}{k_0} [Q] \]

The slopes of the regression fits of the data from which values for \( k_q \) were determined. The slopes of the regression for Zn(Tp)\textsubscript{2} is zero, indicating no quenching is observed for this control molecule.

Figure 1. Stern–Volmer plots of the quenching of \( ^3\)MLCT emission from [Ru(dmb)\textsubscript{3}]\textsuperscript{2+}. Data are shown for variable concentrations of Fe\textsubscript{2}O(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp)[\textsuperscript{2+} (filled circles), Fe\textsubscript{2}O(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(Tp)[\textsubscript{2} (empty circles), and Zn(Tp)[\textsubscript{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)[\textsubscript{2} is zero, indicating no quenching is observed for this control molecule.


(8) These \( J \) values are derived from a spin Hamiltonian of the form \( H = -2JS\textsubscript{N}S\textsubscript{S} \).

(9) Solutions of the compounds were prepared in an inert atmosphere drybox using CH\textsubscript{3}CN that had been distilled from CaH\textsubscript{2} under N\textsubscript{2}. The spectrometer used for time-resolved emission and absorption measurements has been described previously (Damrauer, N. H.; Bousie, 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 \( k_{en t} \) would increase the difference in \( k_q \) already noted.

S0020-1669(98)00561-8 CCC: $15.00 © 1998 American Chemical Society

Published on Web 07/03/1998
known that mononuclear Fe(III) complexes can oxidatively quench the 3MLCT 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 with the absorption spectra of the two dinuclear complexes, 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 changes 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.

Acknowledgment. This work was supported through a fellowship from the Alfred P. Sloan Foundation, the Hellman Family Faculty Fund, and the University of California.

Figure 2. Plot of the excited-state absorption difference spectrum at λ_robe = 440 nm following excitation at 458 nm of a CH_3 CN solution 3.1 x 10^{-4} M in [Ru(dmb)_3]^{2+} and 4.6 x 10^{-4} M in [Fe(OH)(O_2CCH_3)_2(Tp)]^{2+}. The solid line is a fit to a biexponential function with k_1 = (2.35 ± 0.10) x 10^4 s^{-1} and k_2 = (2.25 ± 0.10) x 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(OH)(O_2CCH_3)_2(Tp)] photoproducts formed as the result of excited-state electron transfer.

(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_3 CN that was 0.1 M in NBu_4 PF_6. The ΔG_0 quoted here is based on Osterquyug square-wave potentiometric measurements carried out on both compounds under identical conditions.


(19) Although resonance exchange does not likely play a role in the mixed-valent hydroxo-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).


(13) Photoexcitation of solutions of the dinuclear complexes in the absence of [Ru(dmb)_3]^{3+} revealed transient signals that were pulse width-limited on the nanosecond time scale.

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