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Long-Range Electron Transfer Across Peptide Bridges: The Transition from Electron Superexchange to Hopping

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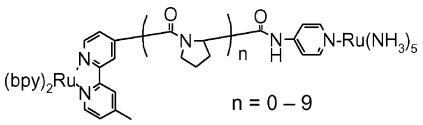
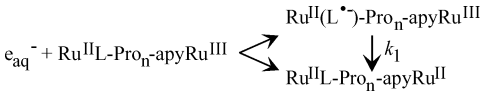
Long-range electron transfer (ET) where the separation of the donor (D) and acceptor (A) greatly exceeds their spatial extent is a subject of considerable interest for studies of ET mechanisms in biological systems and in nanoscale science.[1−3] A productive dialogue between experimentalists[3−9] and theoreticians[10−16] has arisen on the subject of variations in the distance dependence of ET reactions. Beyond the range of direct donor−acceptor electronic overlap, electron transfer may occur through bridge-mediated superexchange between donor and acceptor electronic states or through an incoherent hopping process between localized electronic states on the bridge. The relative contributions of these mechanisms depend in part on the energy gap between the donor- and bridge-localized electronic states. The overall rate constant at any intermediate distance can be a composite of both mechanisms. This communication describes a series of bridged donor−acceptor complexes in which the distance dependence of long-range electron-transfer rate constants shows a clear transition from a superexchange mechanism to a hopping mechanism. The complexes are of the type $[(bpy)_2Ru^{II}L-Pro_n-apyRu^{III}(NH_3)_5]^{5+}$ where the number of proline residues (n) varies from 0 to 9. We have studied the ET reactions from the picosecond to the millisecond time scales using different spectroscopic techniques in order to observe the change in electron-transfer mechanism over a distance range of 8.7−32 Å.[3,5,6]



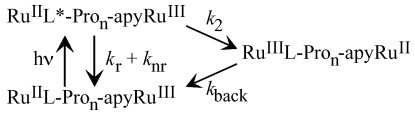
In prior studies, we and others have studied the distance dependence of ET rate constants in metal ion donor−acceptor complexes separated by proline oligomers.[3,5−9] However, in many of these studies the driving forces were not optimized with respect to the reorganization energies (according to Marcus−Hush Theory) in order to produce activationless, "maximum" ET rate constants (k_{max}) at a given distance. In the present work, the radiolysis experiments are near the activationless regime and corrected k_{max} values are obtained from all of the experimental rate constants.

Electron pulse radiolysis was used to determine the rate constants (k_1) for the reaction in Scheme 1 for $[(bpy)_2Ru^{II}(L^{\bullet})-Pro_n-apyRu^{III}(NH_3)_5]^{4+}$, where n = 3, 4, 5, and 8 prolines. Rate constants for n = 6, 7, and 9 were reported earlier.[5] The intermediate ligand-centered radical species $[(bpy)_2Ru^{II}(L^{\bullet})-Pro_n-apyRu^{III}(NH_3)_5]^{4+}$ were generated by the reaction of radiolytically produced e_{aq}^- with the peptide-bridged $Ru^{II}(L)-Ru^{III}$ complex. The kinetics of the ET process were followed by transient absorption at 510 nm for the decay of the $[(bpy)_2Ru^{II}(L^{\bullet})]$ species and at 410 nm for the growth of the reduced $[apyRu^{II}(NH_3)_5]$ species.[5,6]

Scheme 1



Scheme 2



For shorter bridges ($n \leq 3$), the pulse radiolysis approach is not practical, because intramolecular electron transfer occurs faster than precursor formation.[5] Instead, for $n = 0-4$, the rate constants for intramolecular electron transfer were measured from the MLCT excited state of the $(bpy)_2Ru^{II}(L)^*$ donor to the $apyRu^{III}(NH_3)_5$ acceptor (Scheme 2). Femtosecond transient absorption spectroscopy of $(bpy)_2Ru^{II}(L)^*$ excited-state decay was used to measure the ET rate constant k_2 for the $n = 0$ case.[17] For $n = 1-4$, the rate constants k_2 were determined from comparison of excited-state emission decay rates of the $[(bpy)_2Ru^{II}L^*-Pro_n-apyRu^{III}(NH_3)_5]^{5+}$ complexes ($k_{obs} = k_r + k_{nr} + k_2$) with those of mononuclear $[(bpy)_2Ru^{II}(L)^*-Pro_n-OH]^{2+}$ complexes ($k_{obs} = k_r + k_{nr}$). Steady-state fluorescence spectra for $[(bpy)_2Ru^{II}L^*-Pro_n-apyRu^{III}(NH_3)_5]^{5+}$, $n = 1-4$, were also determined, and the rate constants k_2 estimated from the corrected emission intensities were found to be in reasonable agreement with the time-resolved data for $n = 3$ and 4 (Table 1 footnote g). For the longer peptides, $n = 5-9$, the excited-state lifetime is too short ($k_r + k_{nr} \gg k_2$) to permit measurement of k_2 by photolysis.

The results of all the experiments are shown in Table 1 and plotted in Figure 1. For $n = 3$ and 4 prolines, it was possible to measure both k_1 and k_2 using the radiolysis and photolysis techniques, respectively. Because of the higher driving force, k_1 is larger than k_2 in both instances. Direct comparison of the k_{max} values obtained by both techniques is possible after correction of the observed rate constants k_1 and k_2 for driving force and distance-dependent reorganization energies. The calculations and the resulting k_{max} values are described in Table 1 and its footnotes and plotted in Figure 1.

For the shorter peptides, $n = 0-4$, the distance dependence is consistent with a superexchange electron-transfer mechanism between the donor excited state (or ligand-centered radical) and the metal ion acceptor. A fit to the $k_{2,max}$ values for $n = 0-3$ results in a rate attenuation constant $\beta = 1.4$ Å^{-1}, where $k = k_0 \exp(-\beta d)$, consistent with nonconjugated donor−bridge−acceptor systems. For the longer peptides, $n = 5-9$, the weak distance dependence of $k_{1,max}$ at long distances ($\beta = 0.18$ Å^{-1}, or 0.46 per

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Table 1. ET Rates from Pulse Radiolysis (k_1) and Photolysis (k_2) Experiments for the $[(bpy)_2Ru^{II}L-Pro_n-apyRu^{III}(NH_3)_5]^{5+}$ Complexes

n	distance[a] (Å)	λ[b] (eV)	10^{-6} k_1 (s^{-1})	10^{-6} $k_{1,max}$ [c] (s^{-1})	k_2 (s^{-1})	$k_{2,max}$ [c] (s^{-1})
0	8.7	1.30			7.0×10^{11} [d]	2.3×10^{12}
1	10.3	1.44			2.0×10^{10} [e]	1.4×10^{11}
2	12.8	1.59			2.6×10^{8} [e]	4.9×10^{9}
3	16.3	1.72	17[f]	21	0.8×10^{6} [g]	3.6×10^{7}
4	18.2	1.77	2.4[h]	3.3	0.2×10^{6} [g]	1.3×10^{7}
5	21.1	1.83	0.20[h]	0.32		
6	24.4	1.88	0.11[i]	0.21		
7	25.9	1.90	0.064[i]	0.13		
8	28.5	1.93	0.039[h]	0.087		
9	32.0	1.96	0.020[i]	0.050		

[a] Distance from the edge of the 4-carboxy-4′-methyl-2,2′-bipyridine donor to the center of the pentammineruthenium acceptor unit, calculated according to ref 14. [b] $\lambda = \lambda_{in} + \lambda_{out}$, where $\lambda_{in} = 0.085$ eV (2 kcal mol^{-1}), $\lambda_{out} = 7.91\ (1/2a_1 + 1/2a_2 - 1/d)$ eV, $a_1 = 4$ Å, $a_2 = 3.5$ Å, and d = edge to $Ru(NH_3)_5$ distance (Å).[15] [c] Maximum rate constants calculated by the formula $k_{max} = k_{obs}/\exp(-\Delta G^*_r/RT)$, where $\Delta G^*_r = (\lambda/4)(1 + \Delta G^\circ/\lambda)^2$, from ref 2. The driving force $\Delta G^\circ = -1.53$ eV[24] for k_1 and -0.90 eV[17] for k_2. [d] Measured by femtosecond transient absorption laser flash photolysis at Rutgers University Newark. [e] Emission measurements by streak camera or photodiode detection performed at the BNL Laser-Electron Accelerator Facility (LEAF). [f] Digitizer-based pulse radiolysis transient absorption kinetics measurements performed at the BNL LEAF facility. [g] Transient emission measurements performed at the Nanosecond Laser facility (Coherent)−Rutgers New Brunswick.[25] Rate constants determined from steady-state emission are 500 000 and 100 000 s^{-1} for $n = 3$ and 4, respectively. [h] Pulse radiolysis transient absorption measurements[24] using the BNL Chemistry Van de Graaff and methods described in refs 5 and 6. [i] Data from ref 5.

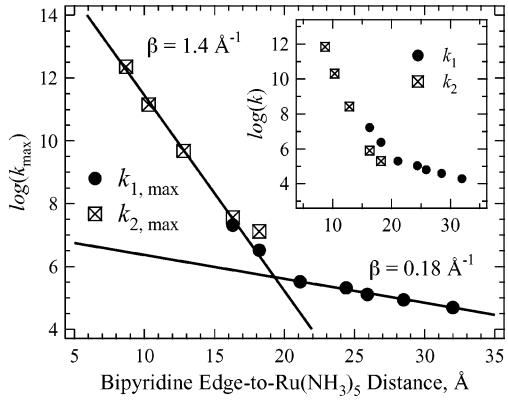

Figure 1. Plot of $\log(k_{max})$, ET corrected rate constants (see Table 1) for radiolysis ($k_{1,max}$, circles) and photolysis ($k_{2,max}$, squares), versus the distance from the edge of the 4-carboxy-4′-methyl-2,2′-bipyridine ligand to the $Ru^{III}(NH_3)_5$ acceptor for $n = 0-9$ prolines. The inset is a plot of $\log(k_{obs})$ versus the same distance parameter.

proline unit) is more consistent with an electron hopping mechanism. In the hopping model, an electron from the $(bpy)_2Ru^{II}(L^\bullet)$ donor transiently occupies localized sites on the peptide bridge as it transfers to the $apyRu^{III}(NH_3)_5$ acceptor.

For the $n = 0$ proline case ($d = 8.7$ Å), a "virtual hopping" rate can be extrapolated from the long distance regime in Figure 1. This extrapolation shows that the "virtual hopping" rate constant is approximately 1 x 10^6 times smaller than the observed electron-transfer rate operating through the superexchange mechanism. This is a direct reflection of the energetic penalty for promoting an electron onto the empty orbitals of the peptide bridge. The limiting step for the hopping reaction is surmounting this energy gap.

Charge transfer studies in the more rigid DNA constructs were also consistent with multiple mechanisms such as hole superexchange, hole hopping, and, more recently, electron hopping.[4,18−22] The report on superexchange-to-hopping transition in conjugated *p*-phenylenevinylene oligomers shows that conjugation of the bridge with the donor alters the donor−bridge energetics, leading to an abrupt change in rate constants with increasing distance.[23]

In conclusion, the oligoprolines described here present an example consistent with a smooth transition from a predominantly electron superexchange to a predominantly electron hopping mechanism as the peptide spacer distance increases from 8.7 to 32 Å. Furthermore, it is a verification for the change in ET mechanism with distance that has been repeatedly predicted in several theoretical papers over the past decade.[4,10−13]

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