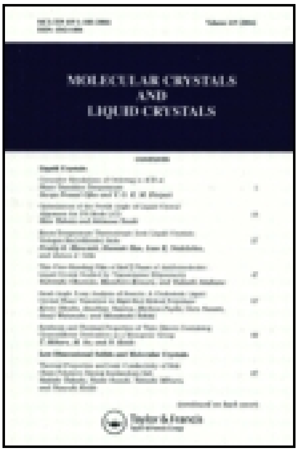

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Intramolecular Electron Transfer in Iridium Dimers

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INTRAMOLECULAR ELECTRON TRANSFER IN IRIDIUM DIMERS

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Abstract The kinetics of photoinduced electron transfer and thermal recombination have been measured in a series of covalently linked donor-acceptor complexes. The molecules are based on pyrazolate-bridged iridium(I) dimers with pyridinium groups covalently bound to terminal phosphinite ligands. The driving-force dependence of the electron-transfer kinetics in one series agrees well with the predictions of the classical theory of electron transfer. The donor-acceptor electronic coupling, however, exhibits a sensitive and unexpected dependence on the nature of the bridge between the redox partners.

Keywords: Intramolecular electron transfer, driving force dependence, photoinduced electron transfer, iridium dimers

Electron-transfer (ET) theories suggest that rates of intramolecular reactions can be described by the product of a frequency factor (ν_N), a nuclear factor (κ_N), and an electronic factor (κ_E).[1] κ_N reflects the degree of nuclear reorientation associated with the electron transfer and, in the classical theory, depends upon two quantities: the driving force for the reaction ($-\Delta G°$) and a reorganization parameter (λ). The classical theory predicts that κ_N should exhibit a Gaussian dependence on $-\Delta G°$, reaching a maximum value of 1 at $-\Delta G°=\lambda$. κ_E measures the electronic coupling strength for the reaction and is a function of the donor-acceptor separation and orientation, as well as the composition of the intervening medium. In the nonadiabatic (weak coupling) limit $\kappa_E \propto H_{AB}{}^2/\nu_N$, implying that at the optimum driving force the rate of the reaction is proportional to the square of the electronic coupling matrix element H_{AB}, and is independent of the frequency of motion along the reaction coordinate. The accuracy of these theories can be evaluated by examinations of the variation in ET rate with changes in reaction driving force, and with changes in the donor-acceptor linkage. We have been performing experiments of this type using pyrazolate-bridged iridium(I) dimers (Ir_2) as photoreductants covalently bound to alkyl pyridinium acceptors (Figure 1).

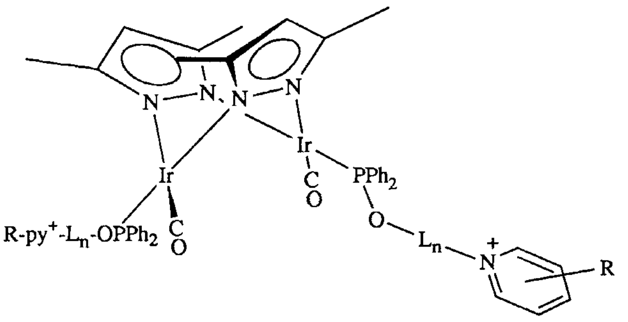

FIGURE 1 Molecular structure of Ir_2 donor-acceptor complexes.

Pyrazolate-bridged Ir(I) dimers possess two strongly reducing electronic excited states[2,3] that are sufficiently long lived to participate in intramolecular ET reactions with N-alkyl pyridinium groups. The two states, a singlet and a triplet, derive from a $d\sigma^* \rightarrow p\sigma$ excitation, and have decay times on the order of 100 ps and 1 μs, respectively. The lifetimes and potentials vary slightly with changes in bridging and terminal ligands. The pyridinium acceptors are coupled to the Ir_2 core via terminal phosphinite ligands. Complexes with the following linkers have been prepared: $-CH_2-CH_2-$ (L_1), $-CH_2-$ (L_2), and $-CH_2-CH_2-$ (L_3). The driving force for the ET reactions is modulated by changing substituents on the pyridinium acceptor. Three distinct reactions, each with a different driving force, can be studied with a single donor-acceptor pair: photoinduced ET from the singlet and triplet excited states (^{1}ET and ^{3}ET), and the corresponding thermal recombination process (ET^b).

A thorough driving-force study has been completed with the L_1-linked species.[3] ET kinetics were measured by picosecond time-resolved absorption and emission spectroscopies. The ET rates exhibit a near Gaussian free-energy dependence (Figure 2), in excellent agreement with classical ET theory. Fitting the data to this simple model yields a maximum rate of 1.5×10^{11} s^{-1} ($\nu_N \kappa_E$) at a driving force of 1.06 eV (λ). Using the nonadiabatic expression for $\nu_N \kappa_E$, this maximum rate corresponds to an electronic-coupling matrix element of 24 cm^{-1}. The strongly inverted character of the ET rates is especially noteworthy. In this system, the ET rate decreases by more than three orders of magnitude at a driving force 0.85 eV above the optimum. It is also interesting that a single set of nuclear and electronic parameters (λ and H_{AB}) adequately accounts for the rates of the ^{1}ET, ^{3}ET, and ET^b reactions. The reorganization energy and electronic coupling need not be identical for all three reactions, but in this particular case the variations seem to be small.

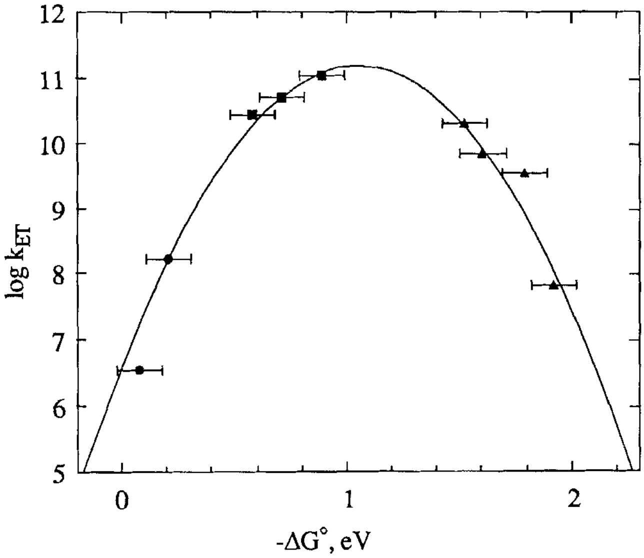

FIGURE 2 Plot of log k_{ET} versus driving force ($-\Delta G^\circ$) for electron transfer in L_1-linked complexes: ^{1}ET (■); ^{3}ET (●); and ET^b (▲).

Understanding the factors that determine the magnitude of H_{AB} is a current theme of much ET research. Especially important is elucidating the dependence of H_{AB} on the composition and structure of the intervening medium.[4] Ir_2 donor-acceptor complexes with L_2 and L_3 linkers were designed to address this point. The L_3 linker differs from L_1 by the insertion of a 1,4-phenylene group. The ^{1}ET rate for the L_3-linked complex with an unsubstituted pyridinium acceptor ($[Ir_2]$-L_3-py^+) is roughly six times slower than that found in the L_1-linked derivative (Table I). Assuming comparable values of λ for both systems, the ^{1}ET rate suggests H_{AB}~14 cm^{-1} for the L_3-linked species. The ^{3}ET rate measured with this L_3-linked complex is also consistent with a coupling element of this magnitude.

The ET kinetics of the $[Ir_2]$-L_2-py^+ complex are strikingly different (Table I). Both ^{1}ET and ^{3}ET rates in this molecule are slower than in the L_3-linked species, yet the linker is shorter by one methylene group. This observation runs counter to simple

TABLE I Driving forces and rates for ^{1}ET and ^{3}ET reactions in $[Ir_2]$-L_n-py^+ complexes.

Complex	^{1}ET		^{3}ET	
	$-\Delta G°$(eV)	k_{ET} (s^{-1})	$-\Delta G°$(eV)	k_{ET} (s^{-1})
$[Ir_2]$-$CH_2 \cdot CH_2 \cdot py^+$	0.89	1.1×10^{11}	0.39	a
$[Ir_2]$CH_2-py^+	0.78	1.0×10^{10}	0.29	$<6 \times 10^4$
$[Ir_2]$$CH_2 \cdot CH_2 \cdot py^+$	0.78	1.9×10^{10}	0.29	1.6×10^8

[a] Not measured owing to insufficient triplet population.

theoretical formulations in which H_{AB} is predicted to decay exponentially with increased donor-acceptor separation. Even more surprising is the disparity in H_{AB} for the ^{1}ET and ^{3}ET reactions in the L_2-linked complex. Again assuming insignificant changes in λ, values of H_{AB} are 10 and <0.2 cm^{-1} for the singlet and triplet reactions, respectively. The dramatic variation in H_{AB} produced by a relatively minor change in donor-acceptor linkage is indeed startling, and illustrates the subtle dependence of this parameter upon the structural characteristics of the donor-acceptor pair.

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