Photoinduced Charge Separation and Recombination Kinetics in a Dimeric Iridium(I) Complex with Covalently Bound Alkylpyridinium Acceptors

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In the ideal photochemical energy storage system a photoinduced charge separation must be generated rapidly with minimum energy loss and be maintained by virtue of inefficient electron-hole recombination. These rigorous requirements necessitate a thorough understanding of the diverse parameters that determine the barriers to electron-transfer reactions:[1] free energy changes; donor–acceptor separation, orientation, and electronic coupling; inner-sphere reorganization energy; and solvent reorganization energy and dynamics. Clearly, in order to elucidate the contributions of these parameters to electron-transfer barriers, model electron-transfer systems must be prepared which can be selectively modified to vary one or more of these parameters. An important requirement for such systems is the covalent coupling of donor and acceptor into one molecule to surpass diffusional limits and permit study of extremely fast intramolecular electron-transfer reactions.[2] We report here results from a prototypal synthetic donor–acceptor system which exhibits photoinduced electron-transfer rate constants in the vicinity of 10^{12} s^{-1} at driving forces of ca. 1 eV and charge-recombination rates slower than 2×10^{10} s^{-1}.

Our synthetic donor–acceptor complexes are based on [Ir(μ-pz$'$)(CO)(PPh$_2$\{O(CH$_2$)$_2$R\})]$_2$ (pz$'$ = 3,5-dimethylpyrazolyl; Ph = C$_6$H$_5$),[3] in which the Ir$_2$ core serves as the electron donor and the acceptors are incorporated into R on the terminal phosphines. When R is a poor electron acceptor such as –H or –$^+$N(C$_2$H$_5$)$_3$, these molecules luminesce from both singlet (^{1}B) and triplet (^{3}B) dσ*pσ excited states.[4] The excited singlet state lifetimes of ca. 100 ps (Table I) for these two model complexes were measured by transient absorption spectroscopy following 30-ps excitation at 355 nm.[5] The triplet lifetimes, measured both by transient

Table I. Lifetimes and Quantum Yields of Singlet and Triplet Excited States in [Ir(μ-pz$'$)(CO)(PPh$_2$\{O(CH$_2$)$_2$R\})]$_2$

R^a	$^1\Phi_{em}$^{b}	$^3\Phi_{em}$^{b}	$^1\tau$, ps	$^3\tau$, μs
–$^+$N(C$_2$H$_5$)$_3$^{c}	0.0015	0.034	90	1.25
–H^{c,d}	0.0023	0.025	100	1.11
–py	2.5×10^{-5}	$<10^{-5}$	1.5^e	
–4-Ph-py	$<10^{-5}$	$<10^{-5}$	$<1.0^e$	

^{a}All measurements performed in acetonitrile solution. $^b\lambda_{ex}$ = 436 nm. Referenced to Φ_{em} = 0.06 for *[Ru(bpy)$_3$]$^{2+}$ (Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590). $^c\lambda_{ex}$ = 355 nm for lifetime measurements. $^d\lambda_{ex}$ = 532 nm for lifetime measurements. ^{e}Estimated from $^1\Phi_{em}$.
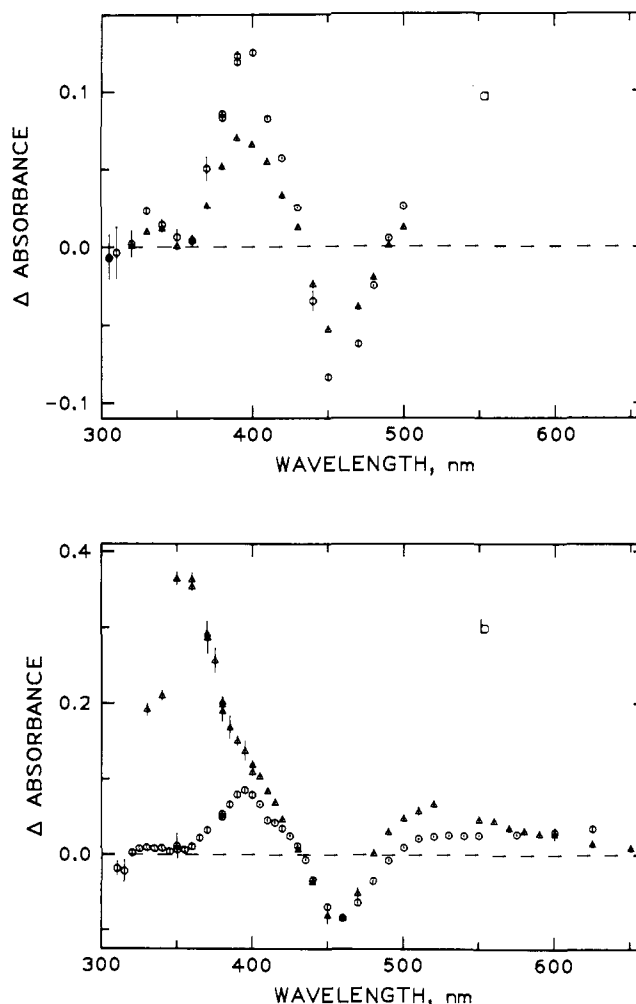
Figure 1. Transient difference spectra of 3×10^{-4} M acetonitrile solutions of [Ir(μ-pz$'$)(CO)(PPh$_2$\{O(CH$_2$)$_2$R\})]$_2$ complexes following 30-ps excitation in 2-mm pathlength cuvettes. (a) R = –H: (O) ^{1}B state, spectrum recorded during laser excitation; (Δ) ^{3}B state, spectrum recorded 5 ns after excitation (λ_{obsd} = 310–380 nm, λ_{ex} = 532 nm; λ_{obsd} = 380–500 nm, λ_{ex} = 355 nm). (b) (O) R = py (λ_{obsd} = 310–380 nm, λ_{ex} = 532 nm; λ_{obsd} = 380–500 nm, λ_{ex} = 355 nm); (Δ) R = 4-Ph-py (λ_{ex} = 532 nm); spectra recorded during excitation.

absorption and luminescence decay techniques, are about 1 μs (Table I). The transient difference spectra of the singlet and triplet excited states (Figure 1a) are quite similar, exhibiting only a strong absorption maximum near 390 nm and a bleach of the ground-state absorption maximum at 460 nm. Quasi-reversible, one-electron cyclic voltammetric oxidations of the model complexes appear at potentials of +0.32 V (R = –H) and +0.5 V (R = –$^+$N(C$_2$H$_5$)$_3$) vs. SSCE in CH$_2$Cl$_2$.[6] The electronically excited iridium dimers are therefore potent reductants ($E_{1/2}$, ca. –2 V vs.

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(2) Kinetics investigations of intramolecular electron transfer in closely coupled donor–acceptor complexes include the following: (a) Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442–5444. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080–1082. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562–5563. (d) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571–5573. (e) Gust, D.; Moore, T. A.; Makings, L. R.; Liddell, P. A.; Nemeth, G. A.; Moore, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 8028–8031.

(3) Compounds were recrystallized from acetonitrile solutions prior to quantum yield and kinetics measurements. A lone singlet for the aromatic protons on the bridging pyrazole ligands (δ = 5.6 ppm) indicates that the terminal phosphine ligands adopt a trans configuration with respect to the metal–metal axis. Preparative details will appear in a future publication.

(4) (a) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1593–1595. (b) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595–1596. (c) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571–4575. (d) Winkler, J. R.; Marshall, J. L.; Netzel, T. L.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2263–2266.

(5) For a description of the transient spectroscopy apparatus, see: (a) Winkler, J. R.; Nocera, D. G.; Netzel, T. L. *J. Am. Chem. Soc.* **1986**, *108*, 4451–4458. (b) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381–2392.

(6) Half-wave potentials were measured by cyclic voltammetry at a Pt disk electrode in a 0.1 M CH$_2$Cl$_2$ solution of (*n*-Bu)$_4$NPF$_6$ (Bu = C$_4$H$_9$) under an Ar atmosphere.

SSCE) which readily reduce alkylated pyridinium groups.[7] Accordingly, when R is changed to N-bound pyridine (py) or 4-phenylpyridine (4-Ph-py), luminescence from both excited singlet and triplet states is severely quenched. On the basis of an un-quenched singlet lifetime of 100 ps, the steady-state emission quantum yields of the two quenched complexes indicate singlet lifetimes of less than 2 ps. If electron transfer is the sole source of this nonradiative singlet decay, then the charge-separation rate constants are greater than 5×10^{11} s^{-1}.

Picosecond transient absorption spectroscopy provided additional insight into the excited-state decay kinetics. Excitation of the py and 4-Ph-py complexes with 532-nm,[8] 30-ps laser pulses generates transient species that decay exponentially with lifetimes of 130 and 54 ps, respectively. The difference spectrum of the py transient (circles, Figure 1b) is consistent with that of the electrochemically generated species $[Ir(\mu\text{-pz}')(CO)(PPh_3)]_2{}^+$ but also closely resembles the spectra of the singlet and triplet Ir$_2$ excited states (Figure 1a). The N-alkyl-py$^{\bullet}$ radical has no strong absorption bands in the 310–700-nm spectral region[9] which might confirm an assignment for the py transient. The difference spectrum of the 4-Ph-py transient (triangles, Figure 1b) exhibits, in addition to the bleach of the 460-nm ground-state absorption band, a strong feature maximizing near 350 nm and a weaker band at about 525 nm. This difference spectrum, which is quite distinct from the singlet and triplet difference spectra, is characteristic of the N-alkyl-4-Ph-py$^{\bullet}$ radical[10] and demonstrates that electron transfer occurs on a time scale comparable to or shorter than the duration of the laser pulse. By analogy with the 4-Ph-py complex, the py transient is most likely a charge-separated species. The measured 7.7×10^9 and 1.9×10^{10} s^{-1} rate constants, therefore, correspond to the electron-hole recombination rates in the py and 4-Ph-py complexes, respectively.

The rates of photoinduced electron transfer in the py and 4-Ph-py complexes approach 10^{12} s^{-1} which, depending upon the choice of preexponential factor, is within about a factor of ten of the fastest possible electron-transfer rates. The time scale of these virtually barrierless electron transfers ($E_a < 0.1$ eV[12]) is nearing that of intramolecular rotations[13] and solvent relaxation[14] such that the dynamics of these processes might be reflected in the charge-separation kinetics. The thermal back-reactions are about two orders of magnitude slower than the photoinduced electron transfers. These observations are especially noteworthy in view of the fact that the free energy changes for the back-re-actions exceed those of the photoinduced reactions by as much as 0.5 eV. The relative rates of the charge-separation and re-combination reactions in these systems reflect an important in-terplay among driving force, reorganization energy (λ), and do-nor–acceptor separation (r). The Marcus theory predicts that the reaction with a free-energy change $closer$ to the reorganization energy will be the faster process.[1a] Brunschwig et al.[15] have noted that while the donor–acceptor electronic coupling (κ) $decreases$ with r, the outer-sphere contribution to λ $increases$ with r. Hence,

the $ratio$ of forward to back-reaction rates will be a function of donor–acceptor separation because of the distance dependences of κ, λ, and $\Delta G°$.[16]

The results described above demonstrate that the Ir$_2$-based donor–acceptor system is well-adapted to detailed studies of in-tramolecular electron-transfer reactions. Driving forces can be adjusted over a wide range of potentials;[7] modifications of the donor–acceptor linkage can be used to examine the importance of distance and orientation on electron-transfer rates, and the effects of rate-limiting nuclear motions can be probed in studies of the extremely rapid charge-separation reactions.

(16) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984,** *106,* 6858–6859.

Factor S$_1$, a Natural Corphin from *Propionibacterium shermanii*

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Recent studies[1,2] on the methylation sequence of vitamin B$_{12}$ biosynthesis have revealed that eight methyl groups from S-adenosylmethionine (SAM) are inserted into uro'gen III (1) in the order $C_2 > C_7 > C_{20} > C_{17} > C_{12} > C_1 > C_5 \approx C_{15}$ on the way to cobyrinic acid (5) and that factors I (2), II (3), and III (4) constitute the known intermediates $post$ uro'gen III,[3] containing one, two, and three SAM-derived methyl groups, respectively (Scheme I).

On the basis of the sequential methylation data, our search for tetramethylated species by $^3H/^{14}C$ double labeling in cobalt-de-$ficient$ cell free extracts and whole cells of *Propionibacterium shermanii* in the presence of δ-aminolevulinic acid (ALA) and SAM has uncovered four new isomeric zinc complexes, factors S$_1$–S$_4$[4] ($C_{44}H_{51}O_{16}N_4ZnCl$), which were purified by extensive TLC

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(12) Estimate based on the observed rate constants and a frequency factor of 10^{13} s^{-1}. The rate constants will require a statistical correction factor to account for the presence of two electron acceptors.

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