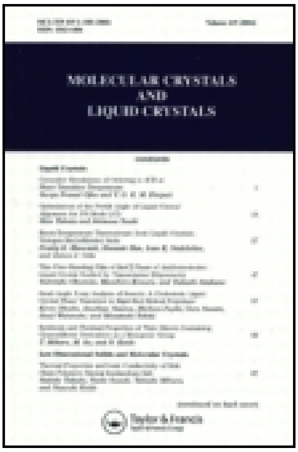


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Photoinduced Intramolecular Electron Transfer in RE(I) Chromophore-Quencher Complexes: Rate Dependence in the Inverted Region and the Use of a Rigid Organic Spacer

D. Brent Macqueen [a b c], Thomas A. Perkins [a b c], Russell H. Schmehl [a b d] & Kirk S. Schanze [a b c]

[a] Department of Chemistry, University of Florida, Gainesville, FL, 32611

[b] Department of Chemistry, Tulane University, New Orleans, LA, 70118

[c] University of Florida

[d] Tulane University

To cite this article: D. Brent Macqueen , Thomas A. Perkins , Russell H. Schmehl & Kirk S. Schanze (1991): Photoinduced Intramolecular Electron Transfer in RE(I) Chromophore-Quencher Complexes: Rate Dependence in the Inverted Region and the Use of a Rigid Organic Spacer, Molecular Crystals and Liquid Crystals, 194:1, 113-121

To link to this article: http://dx.doi.org/10.1080/00268949108041156

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 113–121
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER IN RE(I) CHROMOPHORE-QUENCHER COMPLEXES: RATE DEPENDENCE IN THE INVERTED REGION AND THE USE OF A RIGID ORGANIC SPACER

D. BRENT MACQUEEN,[†] THOMAS A. PERKINS,[†] RUSSELL H. SCHMEHL,[≠] AND KIRK S. SCHANZE,[†*] Department of Chemistry, University of Florida, Gainesville, FL 32611, and Department of Chemistry, Tulane University, New Orleans, LA 70118

Abstract Rates for intramolecular electron transfer (k_{ET}) were determined in two molecular systems in which an electron donor is covalently bonded to a transition metal chromophore of the type $[(\text{diimine})\text{Re}^{I}(\text{CO})_3\text{L}]^+$. In one system the dependence of k_{ET} on ΔG_{ET} was examined and in another the rates for charge separation and recombination across a rigid organic spacer were determined.

Keywords: Electron transfer, photochemistry, inverted region, metal complex

INTRODUCTION

Covalently linked "chromophore-quencher" compounds provide a powerful tool for the study of rates of intramolecular electron transfer (ET) reactions. Many investigations have examined intramolecular ET in compounds in which an organic chromophore is covalently linked to an electron donor (D) or acceptor (A).[1] Such studies have provided valuable information concerning factors that control ET rates.[2-4]

Our work concerns chromophore-quencher compounds in which the chromophore is a transition metal complex.[5,6] The present focus is on systems in which an organic electron donor is linked to a Re(I) chromophore that contains a low-lying metal-to-ligand charge transfer (MLCT) excited state. The Re(I) chromophore is suited to the study of intramolecular ET for several reasons: (1) the MLCT state is both a strong oxidant and reductant; (2) the MLCT state is long-lived and highly luminescent; (3) the redox potential of the MLCT state can be easily "tuned". In electron donor-substituted Re(I) complexes, photoexcitation leads to a sequence of intramolecular ET reactions:

$$(\text{b})\text{Re}^{I}\text{–D} \xrightarrow{h\nu} \underset{\text{MLCT}}{(\text{b}^-)\text{Re}^{II}\text{–D}} \underset{\Delta G_{FET}}{\xrightarrow{k_{FET}}} \underset{\text{CT}}{(\text{b}^-)\text{Re}^{I}\text{–D}^+} \underset{\Delta G_{BET}}{\xrightarrow{k_{BET}}} (\text{b})\text{Re}^{I}\text{–D} \qquad (1)$$

where b = a diimine type ligand (e.g. 2,2'-bipyridine)

[†] University of Florida
[≠] Tulane University

In the present communication the results of studies on two systems are presented. In the first, the dependence of k_{FET} and k_{BET} on ΔG was examined. Interestingly, back ET is highly exothermic, and an inverted dependence of rate on driving force is observed. In the second system, preliminary results are presented on studies aimed at utilizing the Re(I) chromophore in the study of long-range ET across rigid organic spacers.

THERMODYNAMICS AND KINETICS OF PHOTOINDUCED ET

The driving force for forward and back ET are determined from electrochemical and spectroscopic data by using the following expressions: [4-6]

$$\Delta G_{FET} = E_{1/2}(D/D^+) - E_{1/2}(b/b^-) - E_{MLCT} \quad (2)$$

$$\Delta G_{BET} = -\{E_{1/2}(D/D^+) - E_{1/2}(b/b^-)\} \quad (3)$$

In eqs 2 and 3, $E_{1/2}(D/D^+)$ and $E_{1/2}(b/b^-)$ are the half-wave potentials for oxidation of the donor and reduction of the acceptor diimine ligand, respectively, and E_{MLCT} is the energy of the MLCT excited state. The $E_{1/2}$ values are determined by cyclic voltammetry and the excited state energies are determined from the position of the MLCT emission bands.[6] Note that a coulombic term is not used because for the donor-substituted Re(I) cations ET involves charge shift.

The rate for forward ET is determined from the MLCT emission lifetime of the donor-substituted complex (τ) and the lifetime of a model complex (τ_{model}) that does not contain the donor by using the following expression: [4-6]

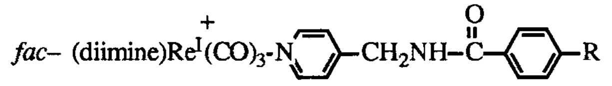
$$k_{FET} = 1/\tau - 1/\tau_{model} \quad (4)$$

The rate for back ET is determined by directly monitoring the decay of the transient absorption of the charge transfer (CT) state by using nanosecond laser flash photolysis.

ΔG DEPENDENCE OF FORWARD AND BACK ELECTRON TRANSFER

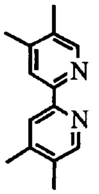
The two series of complexes (b)ReCH$_2$DMAB and (b)ReCH$_2$B were prepared and characterized by a variety of spectroscopic techniques. In the (b)ReCH$_2$DMAB series, the dimethylaminobenzoate (DMAB) group is a moderately good electron donor ($E_{1/2} \approx +1.0$ V) and, as a result, photoexcitation can lead to the sequence of intramolecular ET reactions shown in eq 1, where D = DMAB.

The thermodynamics for forward and back ET in the (b)ReCH$_2$DMAB series were calculated from electrochemical data and emission energies in two solvents (Table I). Several comments can be made concerning this data. First, ΔG_{FET} is moderately exothermic for all of the compounds; in addition, ΔG_{FET} is slightly more exothermic in CH_3CN than in CH_2Cl_2/TBAP. Second, ΔG_{FET} becomes more exothermic as $E_{1/2}(b/b^-)$ becomes less negative. The effect of ligand on ΔG_{FET} is comparatively slight because the change in $E_{1/2}(b/b^-)$ is partially compensated by a concomitant change in E_{MLCT}. Third, ΔG_{BET} becomes less exothermic as $E_{1/2}(b/b^-)$ becomes less negative. The effect of ligand on ΔG_{BET} is strong; a range of approximately 1.0 V is observed across the series.

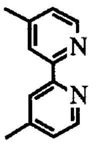


R = $N(CH_3)_2$: (b)ReCH$_2$DMAB   R = H : (b)ReCH$_2$B

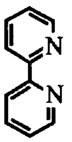
abbreviations for diimine ligands



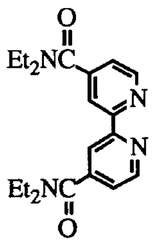
tmb



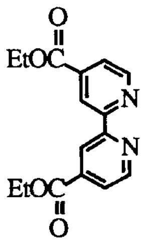
dmb



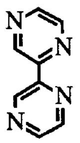
bpy



damb



desb



bpz

Photoexcitation of either the model complex series, (b)ReCH$_2$B, or the donor substituted series, (b)ReCH$_2$DMAB, initially produces the dπ (Re) → π* (diimine) MLCT excited state. Production of the MLCT state is confirmed by the observation of a broad emission band characteristic of this state between 500 and 800 nm. However, as predicted from the thermodynamic data, intramolecular ET (eq 1) is the predominant pathway for excited state decay in the (b)ReCH$_2$DMAB series. This is indicated by the fact that the lifetime of the MLCT emission is significantly less for each of the (b)ReCH$_2$DMAB complexes than for the corresponding models. The fact that ET occurs is confirmed by nanosecond transient absorption studies. For each (b)ReCH$_2$DMAB complex a strong transient absorption is observed in the mid-visible region (470 - 550 nm) that is not present in the corresponding model complex. This transient absorption feature is attributed to the DMAB radical cation that is produced by forward ET.

From the MLCT emission lifetimes of the two series of complexes, k_{FET} was determined in CH_3CN and CH_2Cl_2/TBAP by using eq 4 (Table I). Interestingly, k_{FET} increases strongly for moderate increases in ΔG_{FET}. The temperature dependence of k_{FET} was also determined for several of the complexes in CH_3CN. In this series,

$\Delta H^{\neq}_{FET}$ decreases from +3.8 kcal to +2.5 kcal (tmb ≈ dmb > bpy > damb) and $\Delta S^{\neq}_{FET}$ was approximately constant at −13 ± 1 eu.

By monitoring the decay of the transient absorption of the CT state, k_{BET} values were determined in CH_2Cl_2/TBAP solution (Table I). Remarkably, k_{BET} increases as ΔG_{BET} becomes less exothermic. This inverted dependence of k_{BET} on ΔG_{BET} is qualitatively consistent with theories of highly exothermic ET reactions.[7-10]

TABLE I. Thermodynamics and Kinetics for ET in (b)ReCH$_2$DMAB Complexes [a]

	CH_3CN		CH_2Cl_2/TBAP [b]			
Ligand [c]	ΔG_{FET}	k_{FET}	ΔG_{FET}	k_{FET}	ΔG_{BET}	k_{BET}
tmb	-0.19	2.1×10^7	-0.03	1.8×10^8	-2.57	2.2×10^6
dmb	-0.20	5.0×10^7	-0.07	5.2×10^8	-2.46	3.5×10^6
bpy	-0.25	9.0×10^7	-0.17	7.1×10^8	-2.28	5.2×10^6
damb	-0.35	2.0×10^8	-0.27	1.2×10^9	-2.05	9.0×10^6
desb	-0.49	d	-0.48	d	-1.75	2.4×10^7
bpz	-0.37	1.5×10^9	-0.53	d	-1.59	3.7×10^7

[a] ΔG and k values in units of eV and s^{-1}, respectively. Estimated error in ΔG is ± 25 mV and in k_{ET} is ± 10%. [b] TBAP = tetrabutylammonium perchlorate, 0.1 M. [c] See text for ligand abbreviations. [d] Emission from (b)ReCH$_2$DMAB too weak to determine lifetime.

A variety of theoretical expressions have been derived which allow the use of structural and thermodynamic data to predict ET rates.[7-10] An expression that is often used separates vibrational modes that are coupled to ET into two categories (eq 5): low-frequency modes (λ_s, outer-sphere) which are treated classically and high-frequency modes (λ_v, frequency = $\hbar\omega$, inner-sphere) which are quantized.[9,10]

$$k_{ET} = \{\pi/(\hbar^2\lambda_s k_B T)\}^{1/2} H_{AB}^2 \sum_{w=0}^{\infty} (e^{-S}S^w/w!) \exp -\{(\Delta G_{ET} + \lambda_s + w\hbar\omega)^2/4\lambda_s k_B T\} \quad (5)$$

In eq 5, λ_v and λ_s are the inner and outer sphere reorganization energies, respectively, H_{AB} is the donor-acceptor electronic coupling matrix element, $\hbar\omega$ is the average of the high-frequency vibrational modes coupled to ET, $S = \lambda_v/\hbar\omega$, the sum is taken over w, the number of quanta of the high-frequency mode, and h, k_B, and T have their usual meanings. In the limit in which both the high- and low-frequency modes are treated classically, eq 5 reduces to the semi-classical Marcus expression: [8]

$$k_{ET} = \{\pi/(h^2\lambda k_B T)\}^{1/2} H_{AB}^2 \exp -\{(\Delta G_{ET} + \lambda)^2/4\lambda k_B T\} \quad (6)$$

The variables in eq 6 have the same meaning as in eq 5 and $\lambda = \lambda_s + \lambda_v$.

These theoretical expressions were used to correlate the ET rate data for the (b)ReCH$_2$DMAB complexes. By assuming that $\Delta S^\circ = 0$ for the forward ET reaction, the activation parameters ($\Delta H^{\neq}_{FET}$ and $\Delta S^{\neq}_{FET}$) can be utilized to derive the total reorganization energy (λ), and the electronic coupling (H_{AB}) for the process.[11,12] The activation parameters for the (b)ReCH$_2$DMAB series in CH$_3$CN (see above) suggest that $\lambda \approx 1.0$ eV and $H_{AB} \approx 7.5$ cm^{-1}. Quite interestingly, by substituting these values into the classical Marcus expression (eq 6), the solid line in Fig 1a which passes through the CH$_3$CN data is obtained. By setting $\lambda = 0.8$ eV and $H_{AB} = 7.5$ cm^{-1}, eq 6 yields the solid line which passes through the CH$_2$Cl$_2$/TBAP. Clearly the semi-classical theory agrees reasonably well with the forward ET rate data.

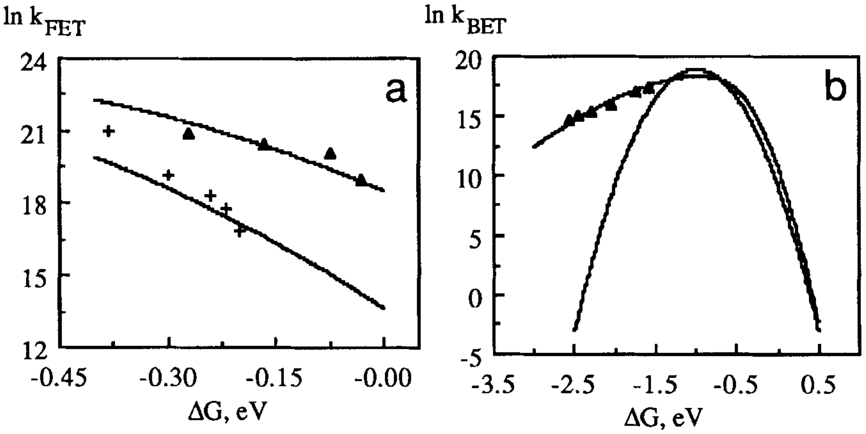


FIGURE 1 (a) Plot of ln k_{FET} vs ΔG for (b)ReCH$_2$DMAB series. (+) Data in CH$_3$CN; (▲) data in CH$_2$Cl$_2$/TBAP; solid lines calculated as described in text. (b) Plot of ln k_{BET} vs ΔG for (b)ReCH$_2$DMAB series. (▲) Data in CH$_2$Cl$_2$/TBAP; lines calculated as described in text.

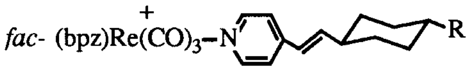
A striking feature is that for each complex, ΔG_{FET} is less exothermic in CH$_2$Cl$_2$ than in CH$_3$CN; however, k_{FET}(CH$_2$Cl$_2$) > k_{FET}(CH$_3$CN). The correlations with the Marcus expression suggest that the higher rates observed in CH$_2$Cl$_2$ result from the fact that λ is smaller in less polar CH$_2$Cl$_2$. Note that the difference in λ for CH$_2$Cl$_2$ and CH$_3$CN which is suggested by the fit to the experimental data in CH$_2$Cl$_2$ (λ is 20% smaller in CH$_2$Cl$_2$ compared to CH$_3$CN) is close to the difference in λ_o for the two solvents that is calculated by using the two-sphere Marcus-Hush expression.[4,7,8]

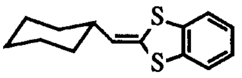
Figure 1b shows a plot of ln k_{BET} vs. ΔG_{BET} along with two calculated lines. The line which decreases sharply in the highly exothermic region was calculated by using the semi-classical expression (eq 6) with $\lambda = 1.0$ eV and $H_{AB} = 1.0$ cm^{-1}. Clearly the dependence of k_{BET} on ΔG_{BET} is less pronounced than is predicted based on the semi-classical expression. A possible reason for the attenuated dependence of rate on driving force is that nuclear tunnelling is important for this highly exothermic reaction.[8,10] Equation 5, which includes a high-frequency quantized vibrational mode coupled to ET, corrects for the probability of nuclear tunnelling. By using this expression with $\lambda_s = 0.75$ eV, $\lambda_v = 0.4$ eV, $\hbar\omega = 3000$ cm^{-1}, and $H_{AB} = 0.8$ cm^{-1} the solid line is generated which fits the data reasonably well. The parameters used for this fit are reasonable, with the possible exception of the vibrational frequency, which is larger than expected. This is because recombination essentially involves ET from an organic radical anion to an organic radical cation, and the dominant vibrational modes that are expected to be coupled to this process involve C-C stretching ($\hbar\omega \approx 1500$ cm^{-1}).

In organic-based systems in which an inverted dependence of k_{ET} on ΔG_{ET} has been observed the rate depends more strongly on the driving force.[2,3,9,13] Presently an explanation for the attenuated dependence of k_{BET} on ΔG_{BET} in the Re(I) system is unknown. However, it is important to note that a similar dependence of k_{BET} on ΔG_{BET} in the inverted region was observed by Meyer, et al. in a structurally similar phenothiazine substituted Re(I) complex.[14] Thus, in general it appears that the dependence of rate on driving force for highly exothermic ligand-to-ligand recombination reactions in metal complexes is unusual when compared to the dependences observed in organic-based systems.

ELECTRON TRANSFER ACROSS A RIGID ORGANIC SPACER

We have been involved in an effort directed toward the development of a synthetic methodology for construction of electron donor substituted ligands that will allow separation of a metal chromophore from a donor by rigid organic spacers. A methodology was tested by the preparation of a novel Re(I) complex that is covalently linked to a dithiafulvene (DTF) electron donor by a *trans*-1,4-cyclohexane spacer. The 1,4-cyclohexane spacer was selected for initial synthetic studies owing to the availability of 1,4-cyclohexanediol, the starting material for the synthesis.

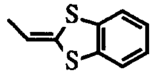




R = H : (bpz)ReCH

CH-DTF

R =



: (bpz)ReCH-DTF

In the complex (bpz)ReCH-DTF, photoexcitation of the dπ (Re) → π* (bpz) MLCT excited state can initiate the sequence of ET reactions in eq 1, where D = DTF. The driving force for the forward and back ET reactions in (bpz)ReCH-DTF were estimated from electrochemical and spectroscopic data in two solvents by using eqs 2 and 3 (Table II). Unfortunately, the DTF/DTF$^+$ redox couple is irreversible on the cyclic voltammetry timescale; as a result, E_p(DTF/DTF$^+$) was used to obtain the ΔG values listed in the table. Note that under most circumstances E_p is within 100 mV of $E_{1/2}$ and therefore the ΔG values are good approximations.[15]

TABLE II. Thermodynamics and Kinetics for ET in (bpz)ReCH-DTF [a]

Solvent [b]	ΔG_{FET}	k_{FET}	$\Delta H^{\neq}_{FET}$, kcal	$\Delta S^{\neq}_{FET}$, eu	ΔG_{BET}	k_{BET}
CH_3CN	-0.37	9.1×10^7	3.2	-11	-1.62	3.7×10^7
CH_2Cl_2/TBAP	-0.27	8.0×10^8	---	---	-1.84	3.1×10^7

[a] ΔG and k values in units of eV and s^{-1}, respectively. Estimated error in ΔG is ± 25 mV and in k_{ET} is ± 10%. [b] TBAP = tetrabutylammonium perchlorate, 0.1 M.

The occurrence of photoinduced ET in the (bpz)ReCH-DTF system was established by several experiments. First, the MLCT emission lifetime of (bpz)ReCH-DTF is considerably shorter than the emission lifetime of the corresponding model, (bpz)ReCH. Second, the CT state which is produced by forward ET was observed by nanosecond transient absorption spectroscopy. Figure 2 shows the transient absorption spectra of (bpz)ReCH and (bpz)ReCH-DTF after pulse excitation into the MLCT absorption band. The model complex shows a transient absorption spectrum which is typical of the MLCT excited state of (dimine)Re$(CO)_3$L complexes.[16] The lifetime of this transient is in good agreement with the emission lifetime, in accord with the MLCT assignment. By contrast, nanosecond photolysis of (bpz)ReCH-DTF produces a transient which absorbs more strongly than the model complex and has a broad visible absorption ($\lambda_{max} \approx 520$ nm) that is not in the spectrum of (bpz)ReCH. The transient observed following excitation of (bpz)ReCH-DTF is assigned to the CT state, (bpz$^-$)Re^{I}CH-DTF$^+$, which is produced by forward ET.

The fact that the mid-visible absorption band is due to the DTF radical cation was established by conventional flash photolysis. In this experiment, a solution of (bpz)ReCH and CH-DTF (concentrations 10^{-4} M and 10^{-2} M, respectively) was excited at 400 nm. A strong transient absorption with $\lambda_{max} = 520$ was observed that decayed with a half-life of ≈ 25 μs. This observation is consistent with the production of the radical cation CH-DTF$^+$ in a bimolecular reaction with photoexcited (bpz)ReCH. The long lifetime of the radical cation in the bimolecular system is due to the fact that the back reaction involves a comparatively slow diffusion controlled bimolecular reaction of the reduced metal complex and CH-DTF$^+$.

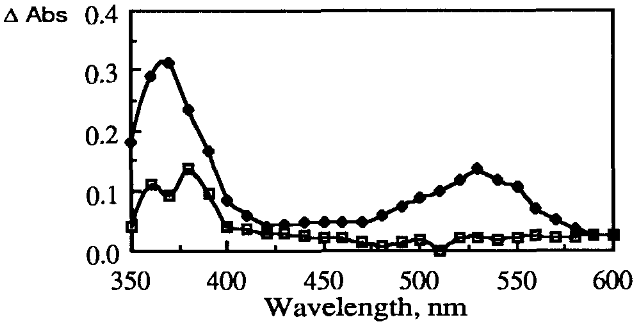


FIGURE 2 Transient absorption spectra of ReCH (open squares) and ReCHDTF (dark polygons) in CH_2Cl_2 solution 15 ns delay after 355 nm excitation.

Rate constants for forward ET in (bpz)ReCH-DTF in two solvents were determined from the emission lifetimes of the complex and (bpz)ReCH by using eq 4. The activation parameters for forward ET in CH_3CN were also determined from the temperature dependence of the lifetimes of the two complexes. Back ET rates were determined from the decay kinetics of the transient absorption due to the CT state. These kinetic data are summarized in Table II. In both solvents k_{FET} is comparatively fast, despite the fact that the center to center separation distance between DTF and Re is 16 Å. This suggests that the cyclohexane spacer is comparatively effective at transmitting electronic coupling between the DTF donor and the metal center. Note that the activation parameters for forward ET in (bpz)ReCH-DTF are similar to those observed in the (b)ReCH$_2$DMAB series. This suggests that the λ and H_{AB} are similar in the two systems, in spite of the fact that the separation distance between the donor and the Re(I) center is larger for the cyclohexane-bridged system. Another important point is that $k_{FET}(CH_2Cl_2) > k_{FET}(CH_3CN)$, even though the reaction is less exothermic in CH_2Cl_2. This effect is likely due to the fact that λ is smaller in less polar CH_2Cl_2. Finally, although back ET is much more exothermic than forward ET, $k_{BET} < k_{FET}$ in both solvents. The comparatively slow rate for back ET in the (bpz)ReCH-DTF system is very likely due to fact that this highly exothermic reaction is in the Marcus inverted region.

CONCLUSION

The studies of intramolecular ET in the (b)ReCH$_2$DMAB series clearly illustrate that by using the Re(I) chromophore the driving force for both forward and back ET are readily varied, without extensive synthetic manipulations, and more importantly, without significant perturbations in the molecular and electronic structure of the chromophore.

The synthetic studies which were tested by the preparation of (bpz)ReCH-DTF provide a pathway for the preparation of systems which utilize more complex bridging systems. Future experiments are directed toward the study of the effect of distance and driving force on intramolecular ET rates across rigid organic spacers. Toward this aim, work in progress is focused on the preparation of a series of spiroheptane based oligimers which are functionalized with a pyridyl ligand on one end and a DTF donor on the other.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The transient absorption experiments were performed at the Center for Fast Kinetics Research, which is supported jointly by the Biomedical Research Technology Program of the Division of Research Resources of the National Institutes of Health (RR00886) and by The University of Texas at Austin. We thank Dr. Elizabeth Galliard (CFKR) for assistance with the nanosecond transient absorption.

REFERENCES

1. Covalently Linked Donor-Acceptor Species for Mimickry of Photosynthetic Electron and Energy Transfer, D. Gust and T. A. Moore (Eds.) Tetrahedron, 45, 4669 (1989).
2. M. R. Wasielewski, in Photoinduced Electron Transfer. Part A, Conceptual Basis, M. A. Fox and M. Chanon (Eds.) Elsevier: Amsterdam, 1988; p. 161.
3. G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield and J. R. Miller, J. Phys. Chem., 90, 3673 (1986).
4. H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and N. S. Hush, J. Am. Chem. Soc., 109, 3258 (1987).
5. K. S. Schanze and K. Sauer, J. Am. Chem. Soc., 110, 1180 (1988).
6. K. S. Schanze and L. A. Cabana, J. Phys. Chem., 94, 2740 (1990).
7. R. A. Marcus and N. Sutin, Biochim. Biophys. Acta, 811, 265 (1985).
8. N. Sutin, Prog. Inorg. Chem., 30, 441 (1983).
9. J. R. Miller, J. V. Beitz and R. K. Huddleston, J. Am. Chem. Soc., 106, 5057 (1984).
10. J. Ulstrup and J. Jortner, J. Chem. Phys., 63, 4358 (1975).
11. The assumption that $\Delta S^\circ = 0$ was confirmed for (bpy)ReCH$_2$DMAB by non-isothermal electrochemistry (ref. 6).
12. S. S. Isied, A. Vassilian, J. F. Wishart, C. Creutz, H. A. Schwartz and N. Sutin, J. Am. Chem. Soc., 110, 635 (1988).
13. I. R. Gould, D. Ege, J. E. Moser and S. Farid, J. Am. Chem. Soc., 112, 4290 (1990).
14. P. Chen, R. Duesing, G. Tapolsky and T. J. Meyer, J. Am. Chem. Soc., 111, 8305 (1989).
15. R. Breslow, Pure Appl. Chem., 40, 493 (1974).
16. T. A. Perkins, W. Humer, T. L. Netzel and K. S. Schanze, J. Phys. Chem., 94, 2229 (1990).