

at both terminals at neutral pH; cf. Scheme I). As expected, the T_m values for PNA/DNA hybrids were little affected by changes in ionic strength (Table I).

The stoichiometry was determined by UV-titration curves to be 2:1 (2 PNA:1 DNA), as expected for a nonionic oligothymine derivative.²⁵⁻²⁷

By extending our findings to other nucleobases, a study that is currently under way, it may be possible to design reagents which recognize any sequence in single- or double-stranded DNA.²⁸

Acknowledgment. This work was supported by the Danish Natural Science Research Council and The Benzon Foundation. Ms. Vivi Hedeboe and Ms. Annette W. Jørgensen are thanked for skilled technical assistance.

Supplementary Material Available: Experimental procedures for compounds 4-6 (3 pages). Ordering information is given on any current masthead page.

(25) Miller, P. S.; Fang, K. N.; Kondo, N. S.; Ts'o, P. O. P. *J. Am. Chem. Soc.* **1971**, *93*, 6657-6665.

(26) Miller, P. S.; Yano, J.; Yano, E.; Carroll, C.; Jayaraman, K.; Ts'o, P. O. P. *Biochemistry* **1979**, *18*, 5134-5143.

(27) Letsinger, R. L.; Bach, S. A.; Eadie, J. S. *Nucleic Acids Res.* **1986**, *14*, 3487-3499.

(28) The affinity for (dA)₁₀ of H-PNA-T₁₀-LysNH₂ is so high that it displaces the (dT)₁₀ part of the opposite strand in a 248 base pair double-stranded DNA fragment with an inserted d(A)₁₀/d(T)₁₀. Nielsen, P. E.; Egholm, M.; Berg, R. H.; Buchardt, O. *Science* **1991**, *254*, 1497-1500.

(29) Heimer, E. P.; Gallo-Torres, H. E.; Felix, A. M.; Ahmad, M.; Lambros, T. J.; Scheidl, F.; Meienhofer, J. *Int. J. Pept. Res.* **1984**, *23*, 203-211.

Intramolecular Energy Transfer in the Inverted Region

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Received October 28, 1991

Quantum mechanical theories of nonradiative transitions such as electron transfer (ET), nonradiative excited-state decay, and triplet-triplet (exchange) electronic energy transfer (E_nT) predict that when the process is strongly exothermic, the rate will increase as the driving force decreases.¹⁻⁴ This "inverted" rate-driving force dependence has been well-established for nonradiative excited-state decay and for both inter- and intramolecular ET.⁵⁻¹⁴ By contrast, relatively few examples exist which provide clear

- (1) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187.
 (2) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358.
 (3) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1, p 153.
 (4) Orlandi, G.; Monte, S.; Barigelletti, F.; Balzani, V. *Chem. Phys.* **1980**, *52*, 313.
 (5) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389. (c) Worl, L. A.; Duesing, R.; Chen, P. Y.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.
 (6) Caspar, J. V. Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1983.
 (7) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3947.
 (8) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.
 (9) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305.
 (10) Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069.
 (11) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470.
 (12) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.
 (13) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
 (14) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4871.

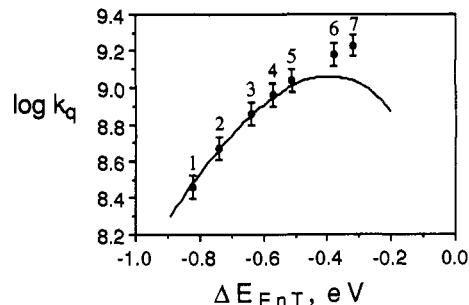
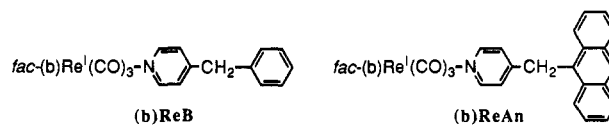


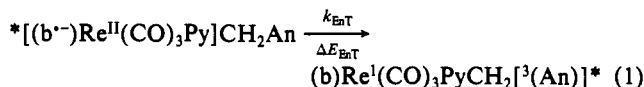
Figure 1. Plot of k_q vs ΔE_{E_nT} for the series of (b)ReAn complexes in 2-methyltetrahydrofuran solution at 298 K (1 = tmb, 2 = dmb, 3 = bpy, 4 = 4-dab, 5 = 5-dab, 6 = deb, 7 = bpz). ΔE_{E_nT} values were determined using the expression given in footnote 21. Error bars on k_q are estimated as $\pm 15\%$. The solid line was calculated using eq 2 with the parameters listed in the text.

evidence for the inverted effect for E_nT .^{15,16}

Series of d^6 transition-metal complexes with metal-to-ligand charge transfer (MLCT) excited states afford unique opportunities to study thermodynamic-kinetic relationships for ET and non-radiative excited-state decay.^{5,6,9,11,17} This is because the energy of the MLCT state (E_{MLCT}) can be readily tuned by varying ligands; and by using a series of structurally related ligands, electronic coupling terms are not strongly perturbed.^{5,6} We have recently applied this technique to study E_nT from the $d\pi$ (π) $\rightarrow \pi^*$ (diimine) MLCT chromophore to the anthracene (An) chromophore in the series of complexes (b)ReAn.¹⁸ In these "bichromophores", the MLCT excited state of the (b)Re^I(CO)₃ donor undergoes strongly exothermic E_nT to the lowest triplet state of the An acceptor via the Dexter exchange mechanism.¹⁹ The results of this study provide clear evidence for an inverted dependence of the rate of E_nT (k_{E_nT}) on ΔE_{E_nT} .



Photoexcitation of the (b)Re(CO)₃ chromophore in the near-UV region populates diimine-based $^1(\pi, \pi^*)$ and 1MLCT excited states which relax rapidly ($k > 10^{11} s^{-1}$) with unit quantum efficiency to the luminescent 3MLCT state.²⁰ Strong, relatively long-lived MLCT luminescence is observed from each of the (b)ReB model complexes which do not contain the An chromophore. By contrast, only very weak, short-lived MLCT emission is observed from the (b)ReAn complexes. The dominant mode for MLCT quenching is E_nT :



That MLCT quenching is due principally to intramolecular E_nT is supported by several lines of evidence. First, E_nT is strongly to moderately exothermic for each complex.²¹ Second, competitive

(15) Murtaza, Z.; Zipp, A. P.; Worl, L. A.; Graff, D.; Jones, W. E., Jr.; Bates, W. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 5113.

(16) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012.
 (17) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belsler, P.; Von Zelewski, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(18) Diimine ligand (b) abbreviations: tmb = 4,4',5,5'-tetramethyl-2,2'-bipyridine; dmb = 4,4'-dimethyl-2,2'-bipyridine; bpy = 2,2'-bipyridine; 5-dab = 5,5'-bis(*N,N*-diethylcarbamido)-2,2'-bipyridine; 4-dab = 4,4'-bis(*N,N*-diethylcarbamido)-2,2'-bipyridine; deb = 4,4'-bis(carboxy)-2,2'-bipyridine; bpz = 2,2'-bipyrazine.

(19) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 866.
 (20) Schanze, K. S.; Pourreau, D. B.; Netzel, T. L. Unpublished results.

(21) The ΔE_{E_nT} values were determined by $\Delta E_{E_nT} = E_T(An) - E_{MLCT}$, where $E_T(An)$ is the energy of ${}^3An^*$ and E_{MLCT} is defined in the text. $E_T(An)$ = 1.79 eV (ref 26), and the E_{MLCT} values were determined from emission spectra of the (b)ReB complexes as described in ref 6.

quenching by ET from An to the photoexcited (b^-)Re^{II} center is endothermic for b = tmb, dmb, bpy, and 4-dab and thermoneutral or only weakly exothermic for b = 5-dab, deb, and bpz.²² Third, nanosecond flash photolysis (ns-FP) provides unequivocal evidence for rapid formation of ³An* following excitation at wavelengths where light is absorbed almost exclusively (>90%) by the (b)-Re(CO)₃ chromophore. Excitation of each (b)ReAn complex (320 nm, 10 ns fwhm, 6 mJ/pulse) produces a strongly absorbing transient with a spectrum ($\lambda_{\max} = 425$ nm, $\lambda_{\text{shoulder}} = 405$ nm, $\Delta OD_{\max} = 0.8$) that is identical to the spectrum of ³An*.²³ No other transients were observed within the time resolution of the ns-FP apparatus, indicating that ³An* is formed with $k_{\text{EnT}} \geq 10^8$ s⁻¹.

Rates for MLCT quenching (k_q) in the (b)ReAn complexes in 2-methyltetrahydrofuran solution were calculated by using the expression $k_q = (1/\tau_{(b)\text{ReAn}}) - (1/\tau_{(b)\text{ReB}})$, where τ values are MLCT emission lifetimes of corresponding (b)ReAn and (b)ReB complexes. Figure 1 shows a plot of $\log k_q$ vs ΔE_{EnT} ; note that k_q clearly increases as ΔE_{EnT} becomes less exothermic.

In the limit of weak interchromophore electronic coupling, the rate for exchange E_nT from a donor to an acceptor is given by the following expression:^{2,4,15,16}

$$k_{\text{EnT}} = \frac{2H_{\text{DA}}^2}{h} \left(\frac{\pi^3}{\lambda_s k_B T} \right)^{1/2} \exp\left\{ -\frac{(S^D + S^A) \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \frac{(S^D)^{w_i}}{w_i!} \frac{(S^A)^{v_j}}{v_j!} \times \exp\left\{ \frac{-(\Delta E_{\text{EnT}} + \lambda_s + w_i \hbar \omega_D + v_j \hbar \omega_A)^2}{4\lambda_s k_B T} \right\}}{4\lambda_s k_B T} \right\} \quad (2)$$

In eq 2, H_{DA} is the exchange coupling matrix element,¹⁹ S^D (S^A) and $\hbar \omega_D$ ($\hbar \omega_A$) are, respectively, the unitless displacement and frequency of the dominant high-frequency mode which is displaced during E_nT in the donor (acceptor), λ_s is the sum of outer-sphere and low-frequency inner-sphere reorganization energies for de-excitation of the donor and excitation of the acceptor, the sums are taken over ground-state vibrational levels of the donor (w_i) and excited-state vibrational levels of the acceptor (v_j), and the other parameters have their usual meanings. This type of expression has been used extensively to model rate-driving force correlations for highly exothermic ET and nonradiative excited-state decay.^{1-7,9,11-13}

Equation 2 was used to fit the MLCT quenching rate data for the (b)ReAn complexes; the solid line in Figure 1 was calculated by using the following parameters: $S^D = 1.0$, $S^A = 0.9$, $\hbar \omega_D = \hbar \omega_A = 1300$ cm⁻¹, $\lambda_s = 0.15$ eV, $H_{\text{DA}} = 2.2$ cm⁻¹. Several key features emerge from this fit of the experimental data. First, although the line simply represents a six-parameter fit of the rates, the values of each parameter are reasonable given the structure of the two chromophores and the nonpolar solvent.²⁴ Second, it is clear that the calculated line reproduces k_q well for b = tmb, dmb, bpy, and 4-dab; however, k_q is larger than predicted for b = 5-dab, deb, and bpz. As noted above, ΔG for ET from An to the photoexcited Re center is thermoneutral or slightly exothermic for the latter complexes.²² We believe that the larger than expected k_q values for b = 5-dab, deb, and bpz arise because, in these complexes, ET is competitive with E_nT , and the k_q values represent a sum of the rates for the two processes. The relative quantum yield for ³An* formation (Φ_T^{rel}),²⁵ which was determined for each

(d)ReAn complex, provides evidence that a process competes with E_nT in some members of the series. For b = tmb, dmb, and bpy, Φ_T^{rel} is nearly constant ($\Phi_T^{\text{rel}} \approx 1.0, 0.9,$ and 1.0 , respectively); however, it decreases along the series b = 4-dab, 5-dab, deb, and bpz ($\Phi_T^{\text{rel}} \approx 0.8, 0.7, 0.5,$ and 0.6 , respectively). This result strongly implies that $k_q \approx k_{\text{EnT}}$ for b = tmb, dmb, and bpy, but $k_q > k_{\text{EnT}}$ for the other complexes. The Φ_T^{rel} data also suggest that the divergence between k_q and k_{EnT} is most significant for the latter two complexes, which is qualitatively consistent with the comparison between theory and experiment in Figure 1.

Finally, the results presented herein imply that the total reorganization energy for E_nT is markedly less than has been observed for ET in related complexes.^{9,11} Because of this difference, the optimal rate for E_nT occurs at considerably lower exothermicity than the optimal rate for ET.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Supplementary Material Available: Synthetic details and ¹H NMR data for all compounds (3 pages). Ordering information is given on any current masthead page.

- (25) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* 1986, 15, 1.
 (26) (a) Evans, D. F. *J. Chem. Soc.* 1957, 1351. (b) Padhye, M. R.; McGlynn, S. P.; Kasha, M. *J. Chem. Phys.* 1956, 24, 588.
 (27) Zhang, X.; Kozik, M.; Sutin, N.; Winkler, J. R. In *Electron Transfer in Inorganic, Organic, and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry 228; American Chemical Society: Washington, DC, 1991; p 247.

NMR Assignment of Leuococin A, a Bacteriocin from *Leuconostoc gelidum*, Supported by a Stable Isotope Labeling Technique for Peptides and Proteins

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Bacteriocins are peptides or proteins produced by bacteria that display antimicrobial activity against closely related species of microorganisms.¹ Their potential as nontoxic food preservation agents, especially for dairy products and meat, has stimulated interest in the production of bacteriocins by lactic acid bacteria.² However, with the exception of nisin A, which is well-characterized³ and approved for commercial use in over 45 countries,⁴ only a few bacteriocins have been purified to homogeneity and had their primary sequence fully elucidated.⁵ This lack of in-

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[§] Department of Food Science.

(1) Tagg, J. R.; Dajani, A. S.; Wannamaker, L. W. *Bacteriol. Rev.* 1976, 40, 722–756.

(2) Klaenhammer, T. R. *Biochimie* 1988, 70, 337–345.

(3) (a) Gross, E.; Morell, J. L. *J. Am. Chem. Soc.* 1971, 93, 4634–4635. (b) Roepstorff, P.; Nielsen, P. F.; Kamensky, I.; Craig, A. G.; Seif, R. *Biomed. Environ. Mass Spectrom.* 1988, 15, 305–310. (c) Chan, W. C.; Lian, L.-Y.; Bycroft, B. W.; Roberts, G. C. K. *J. Chem. Soc., Perkin Trans. 1* 1989, 2359–2367. (d) Liu, W.; Hansen, J. N. *Appl. Environ. Microbiol.* 1990, 56, 2551–2558. (e) Fukase, K.; Kitazawa, M.; Wakamiya, T. *Bull. Chem. Soc. Jpn.* 1990, 63, 1838–1840. (f) Gao, F. H.; Abee, T.; Koenings, W. N. *Appl. Environ. Microbiol.* 1991, 57, 2164–2170.

(4) (a) Hurst, A. *Adv. Appl. Microbiol.* 1981, 27, 85–123. (b) Delves-Broughton, J. *Food Technol.* 1990, 44, 100–117.

(5) (a) Joerger, M. C.; Klaenhammer, T. R. *J. Bacteriol.* 1986, 167, 439–446. (b) Muriana, P. M.; Klaenhammer, T. R. *Appl. Environ. Microbiol.* 1991, 57, 114–121. (c) Piard, J.-C.; Muriana, P. M.; Desmazeaud, M.; Klaenhammer, T. R. *FEMS Microbiol. Rev.* 1990, 87, 90 (abstract). (d) Mørtvendt, C. I.; Nissen-Meyer, J.; Sletten, K.; Nes, I. F. *Appl. Environ. Microbiol.* 1991, 57, 1829–1834. (e) Rammelsberg, M.; Müller, E.; Radler, F. *Arch. Microbiol.* 1990, 154, 249–252. (f) Lyon, W. J.; Glatz, B. A. *Appl. Environ. Microbiol.* 1991, 57, 701–706.

(22) ΔG values for excited-state ET (ΔG_{ET}) were estimated from $\Delta G_{\text{ET}} = E_p(\text{An}/\text{An}^+) - E_{1/2}(\text{b}/\text{b}^-) - E_{\text{MLCT}}$, where $E_p(\text{An}/\text{An}^+)$ and $E_{1/2}(\text{b}/\text{b}^-)$ are, respectively, peak and half-wave potentials for oxidation of An and reduction of b in the (b)ReAn complexes in CH₃CN, and E_{MLCT} was determined as described in ref 6. The estimated ΔG_{ET} values are as follows (eV): +0.19 (tmb), +0.13 (dmb), +0.07 (bpy), +0.02 (4-dab), 0.0 (5-dab), -0.12 (deb), -0.08 (bpz).

(23) Kligler, D. S.; Albrecht, A. C. *J. Chem. Phys.* 1970, 53, 4059.

(24) The values of $\hbar \omega_D$ and $\hbar \omega_A$ represent diimine- and An-based C–C ring stretching modes. S^A and S^D are comparable to values obtained from emission spectral fitting studies (refs 5c and 15). λ_s is associated mainly with the MLCT chromophore; the value used in the fit is in accord with experimentally determined λ_s values for decay of the MLCT excited state in Ru-diimine complexes (ref 27).