pentadiene can be semihydrogenated selectively. 1-Hexyne is transformed to 1-hexene with 98% yield.

All hydrogenation processes are definitely heterogeneously catalyzed, as no case has been observed where the filtered products showed catalytic activities. The activities of repeatedly used catalyst samples turned out to be absolutely constant.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie for their financial support. The HREM work (J.-O.M. and J.-O.B.) was supported with grants from the Swedish Energy Administration.

Modulation of Photoinduced Electron-Transfer Reactivity by Intramolecular Folding

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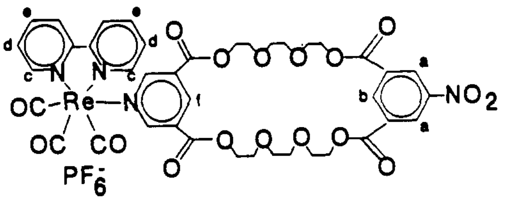
Rates of electron transfer (ET) between molecule-based donors (D) and acceptors (A) are known to depend strongly on DA separation distance, for both Franck–Condon (solvent reorganization) and electronic (orbital overlap) reasons.[1] Distances are often fixed, therefore, by linking D and A (covalently) with molecular bridges.[2] If the bridge structure is flexible, however, a range of distances can still result.[3] Recently we reported on ET from a photoexcited donor ($\mathrm{(Re(CO)_3(bpy)(py)^+}$ (bpy is 2,2′-bipyridine, py is pyridine)) to an electron acceptor (nitrobenzene, NB), where the two are connected by a flexible crown ether-based link (see assembly **1**).[4] The initial experiments were performed in nitromethane as solvent, and the results were consistent with reactivity from a single conformational form. We now report experiments in methylene chloride as solvent which clearly demonstrate the existence of two structural forms. The two are interrelated by intramolecular folding and can be reversibly interconverted via changes in temperature. Importantly, the two forms exhibit marked differences in ET reactivity.



1

The likely existence of two structural forms was initially indicated by variable temperature kinetics measurements. Figure 1 shows an ln rate/inverse temperature plot for intramolecular redox quenching of the $\mathrm{Re^{II}}\dot{\mathrm{p}}\mathrm{y}$ fragment of **1** by pendant NB.[5] Notably, the plot is biphasic with a transition temperature of ~280 K. From the high-temperature slope, $\Delta H_{\mathrm{ET}}^{*}$ is 1.4 kcal mol^{-1}; from the high-T intercept, the preexponential factor A_{ET} is 3×10^6 s^{-1}. In contrast, from the low-T measurements, $\Delta H_{\mathrm{ET}}^{*}$ and A_{ET} are 9 kcal mol^{-1} and 2×10^{12} s^{-1}, respectively. Despite the kinetic differences, however, no shift in steady-state emission energy (or bandwidth) with temperature was seen.[6]

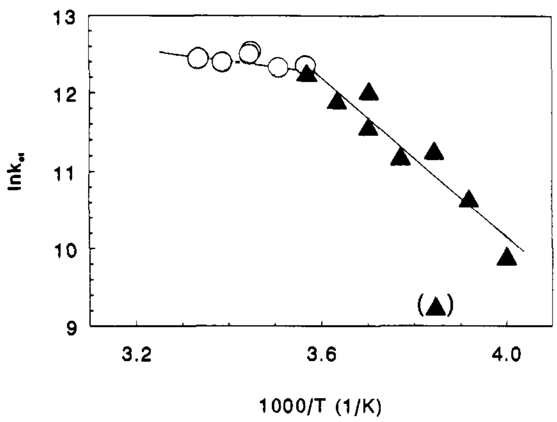


Figure 1. Logarithm of rate constant for intramolecular electron transfer ($\dot{\mathrm{p}}$y → NB; see Scheme I) vs inverse temperature in deoxygenated $\mathrm{CH_2Cl_2}$ as solvent. (Data point in parentheses was omitted from the low-T fit.)

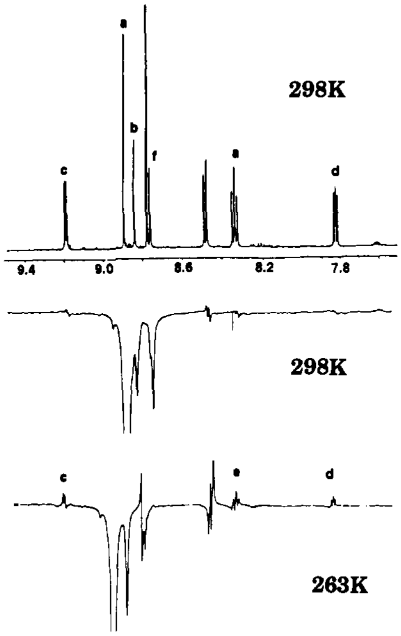


Figure 2. Proton NMR (top) and 1-D NOE (middle and bottom) spectra for **1** (aromatic region) and $\mathrm{CD_2Cl_2}$ at 298 and 263 K (600-MHz Bruker spectrometer).

Confirmation that the biphasic kinetics are related to a temperature-dependent, secondary structural change was obtained by 1-D NOE in $\mathrm{CD_2Cl_2}$ (Figure 2).[7] At 263 K, irradiation of

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(1) See, for example: (a) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635. (b) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 6858. (c) Sutin, N. *ACS Adv. Chem. Ser.* **1991**, *228*, 25.

(2) Representative work: (a) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958. (b) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061. (c) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227. (d) Finckh, P.; Heitele, H.; Michel-Beyerle, M. *J. Phys. Chem.* **1988**, *92*, 6584. (e) Osuka, A.; Maruyama, H.; Mataga, N.; Asaki, T.; Yamazaki, I.; Tamdi, H. *J. Am. Chem. Soc.* **1990**, *12*, 4958. (f) Schanze, K. S.; Cabana, L. A. *J. Phys. Chem.* **1990**, *94*, 2740.

(3) See, for example: Cooley, L. F.; Larson, S. L.; Elliott, C. M.; Kelley, D. F. *J. Phys. Chem.* **1991**, *95*, 10694.

(4) Yoon, D. I.; Berg-Brennan, C, A.; Lu, H.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3192.

(5) Rate constants were obtained[4] by comparing luminescence lifetimes for **1** with those for an equivalent assembly featuring a redox-inactive pyridine moiety in place of nitrobenzene (assembly **3** in ref 4) and by ascribing the differences to an intramolecular ET decay pathway. Representative data: T = 299.5 K, $\tau(1)$ = 680 ns, $\tau(3)$ = 820 ns, $k_{\mathrm{ET}} = 2.5 \times 10^5$ s^{-1}; T = 298 K, $\tau(1)$ = 750 ns, $\tau(3)$ = 900 ns, $k_{\mathrm{ET}} = 2.2 \times 10^5$ s^{-1}; T = 260 K, $\tau(1)$ = 860 ns, $\tau(3)$ = 920 ns, $k_{\mathrm{ET}} = 7.6 \times 10^4$ s^{-1}.

(6) UV absorption spectra were also unchanged in energy, although a very slight increase in extinction accompanied cooling. No unusual changes were seen in the vicinity of the transition temperature.

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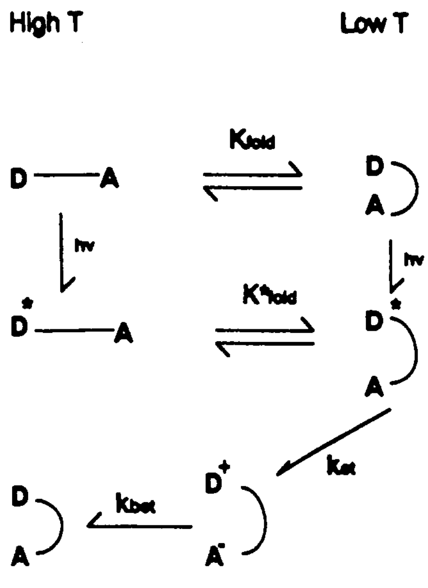
Scheme I



nitrobenzene protons *a* and *b* reveals significant coupling to bipyridyl protons *c*, *d*, and *e*. At 298 K, the cross polarizations are absent. Evidently, ground-state **1** exists in a folded form at the lower temperature and unfolded forms at higher temperatures. Additional NMR experiments reveal a deshielding of pyridyl proton *f* with decreasing *T*, implying that the macrocyclic spacer is substantially flexed near the py functionality upon folding. X-ray crystallography with a related assembly featuring crown attachment to *bi*pyridine shows that a stable folded structure with an offset rather than a cofacial bpy/nitrobenzene configuration can be formed.[8] The exact nature of the analogous folded py/nitrobenzene configuration obtained here is unclear;[9] however, on the basis of the observed insensitivity of the $\mathrm{Re^{II}}\overset{\cdot -}{\mathrm{p}}\mathrm{y}$ emission energy to conformational form, a cofacial configuration can probably again be ruled out.

Returning to Figure 1, we propose (Scheme I) that the actual ET step occurs, in both temperature regimes, from a folded geometry. At high temperatures ($T > 280$ K) this would require an "uphill" conformational change as a preceding step.[10] If the conformational change occurs in a preequilibrium fashion, then the differences in activation parameters between the two temperature regimes would describe the thermodynamics of the excited-state folding step.[11] On this basis, we obtain $\Delta H^\circ_{\text{folding}} = -7.5$ kcal mol^{-1} and $\Delta S^\circ_{\text{folding}} = -27$ eu.[12] Alternatively, the folding step might be kinetically slow; the overall kinetics could then be viewed as conformationally gated, in much the same sense as was recently proposed for certain metalloprotein redox systems.[13,14] In any case, the overall kinetic incentive for ET via an uphill (at high *T*) folding sequence almost certainly must be avoidance of the extreme nonadiabaticity (and therefore, extreme inefficiency) likely connected with an open conformation pathway.

Our current efforts are focused on: (1) evaluating the solvent dependence of folding (in part as a means for understanding the nature of the forces driving the folding) and (2) controlling folding by cation encapsulation. Evidently because of its net positive charge, **1** is ineffective for cation binding. Related neutral assemblies based ion bispyridyl, chloro (rather than bipyridyl, pyridyl) coordination *are* effective,[16] however, and should be capable (like **1**) of engaging in photoinduced electron transfer.

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(7) A reviewer has suggested that the observed conformational change might be driven by temperature-dependent ion-pairing effects. While ion pairing in methylene chloride cannot be ruled out at the concentration levels used in the kinetics experiments (ca. 10 μM), it can be disregarded in higher dielectric solvents. On the basis of similar biphasic activation parameter plots recently obtained (unpublished) in acetonitrile and other high polarity solvents, therefore, we regard the ion-pairing explanation as insufficient to account for our findings.

(8) Absi, M. P.; Yoon, D. I., unpublished work.

(9) Nevertheless, a speculative assignment, consistent with both the preliminary NOE and electronic absorption[6]/emission data, would be an edge-(bpy)-to-face(NB) configuration.

(10) For an example of folding *after* photoinduced ET, see: Brouwer, A. M.; Mout, R. D.; Maasen van den Brink, P. H.; van Ramesdonk, H. J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *Chem. Phys. Lett.* **1991**, *186*, 481.

(11) For Scheme I it can easily be shown that: ΔH_{ET}^{*} (high *T*) = ΔH_{ET}^{*} (low *T*) + $\Delta H^\circ_{\text{folding}}$, and $R \ln A_{\text{ET}}(\text{high } T) = R \ln A_{\text{ET}}(\text{low } T) + \Delta S^\circ_{\text{folding}}$. (Note that the low-temperature ET kinetics are effectively *de*coupled from the folding process.)

(12) In a previous report,[4] observation of a small preexponential factor for electron transfer within **1** was taken as evidence for strongly nonadiabatic behavior. While ET for **1** in unfolded form (i.e., the probable form in ref 4) is almost certainly nonadiabatic, A_{ET} (in view of Scheme I) does not provide a direct, quantitative measure of the degree of nonadiabaticity. Instead, the parameter reflects the entropic demands (either kinetic or thermodynamic) associated with folding to an electronically more favorable form.

(13) (a) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249. (b) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237. (c) Hoffman, B. M.; Ratner, M. A.; Wallin, S. A. *ACS Adv. Chem. Ser.* **1990**, *226*, 125. (d) Hoffman, B. M.; Natan, M. J.; Nocek, J. M.; Wallin, S. A. *Struct. Bonding* **1991**, *75*, 86. (e) McLendon, G.; Pardue, K.; Bak, P. *J. Am. Chem. Soc.* **1987**, *109*, 7540. (f) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454. (g) Isied, S. S. *ACS Adv. Chem. Ser.* **1991**, *228*, 229. (h) Bechtold, R.; Kuehn, C.; Isied, S. S. *Nature* **1986**, *322*, 286.

(14) In principle, the two possibilities could be distinguished by examining the dependence of the kinetics on either the viscosity of the medium or the ET driving force. Comparisons to directly measured ground-state folding thermodynamic parameters (if they can be obtained) would also be illuminating.

(15) An additional incentive conceivably could be diminution of the separation-distance-dependent solvent reorganization energy (see, for example, ref 1a).

(16) Yoon, D. I.; unpublished work.

Specific Molecular Recognition via Multipoint Hydrogen Bonding Ubiquinone Analogues—Porphyrin Having Four Convergent Hydroxyl Groups Pairing

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Interaction between quinone and porphyrin is of current interest in the study of electron transfer in photosynthesis and the respiratory chain.[1,2] The noncovalent interaction of ubiquinone at the both redox sites of enzymes seems to be especially important in respiratory electron transfer via molecular recognition.[3,4]

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(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385.

(2) Gennis, R. B. *Biomembranes*; Springer-Verlag: New York, 1989.

(3) (a) Crane, F. L. *Annu. Rev. Biochem.* **1977**, *46*, 439. (b) Hackenbrock, C. R.; Chazotte, B.; Gupte, S. S. *J. Bioenerg. Biomembr.* **1986**, *18*, 331. (c) Lenaz, G.; Fato, R. *J. Bioenerg. Biomembr.* **1986**, *18*, 369.

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