nucleophiles together with the potential use of this functionalized Ni–Ni dimer in synthesis is under active investigation.

Acknowledgment. We thank the Ministre des Affaires Etrangères (France) and the DAAD (Germany) for their support through the PROCOPE program and a DAAD fellowship to H.K.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (2 pages); listing of observed and calculated structure factors for **2** (8 pages). Ordering information is given on any current masthead page.

---

(9) Kreissl, F. R.; Friedrich, P.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 314. Jeffery, J. C.; Navarro, R.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2471–2478.

Temperature-Independent Long-Range Electron Transfer Reactions in the Marcus Inverted Region

Nong Liang,[†] John R. Miller,[*,†] and Gerhard L. Closs[*,†,‡]

Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

Received February 26, 1990

The Marcus theory made the remarkable prediction that rates of highly exoergic electron transfer (ET) reactions would slow down with increasing thermodynamic driving force ($-\Delta G^\circ$) and give rise to a so-called inverted region.[1] Although that prediction was controversial for two decades,[2] a number of groups have now confirmed the bell-shaped free-energy dependence of rates on ΔG°.[3] According to the Marcus theory in its original, classical form, the inverted region is caused by the reappearance of an activation energy when the negative free energy is larger than λ, the reorganization energy. We report here the measurements of the temperature dependence of two highly exoergic intramolecular ET reactions providing a direct critical test of this theory. Although these reactions have previously been shown to fall deep into the inverted region, they show almost no activation energies in accord with theories that include quantum-mechanical treatments of high-frequency molecular vibrations of the donor and acceptor groups.[4]

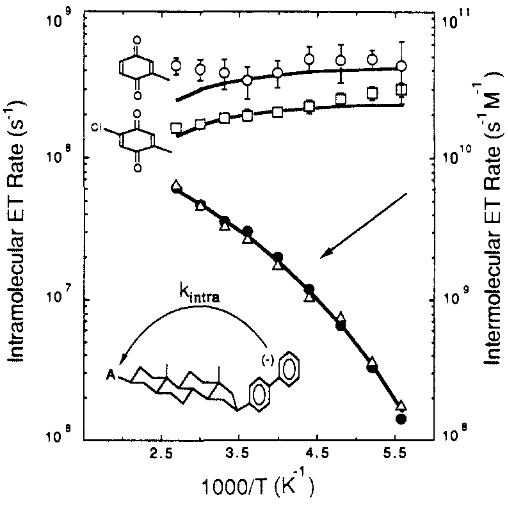

Figure 1. Temperature dependence of intramolecular (upper) and intermolecular (lower) electron transfer rate constants. The solid line at the lower portion represents the best fit to the VTF equation (see text for detail; open triangle, ClQSB; solid circle, QSB). The solid lines at the upper portion were calculated by eq 1 with the experimentally determined parameters from refs 3d and 6. For clarity, the theoretical $k_{intra}(T)$ of ClQSB has been multiplied by a factor of 1.69. At this stage, we tend to attribute the minor discrepancies between the theory and the experiment to the oversimplification of our model. Three independent experiments at concentrations of 30, 9.6, and 7.3 mM, respectively, were performed for QSB, while for ClQSB, two experiments (23 and 11 mM) were performed.

The reactions studied were the intramolecular charge shift ETs from the negative ion of a 4-biphenylyl group (B^-), attached to the 16-position of 5α-androstane (S), to a 2-benzoquinonyl (Q, $\Delta G^\circ = -2.10$ eV), QSB, or 5-chloro-2-benzoquinonyl (ClQ, $\Delta G^\circ = -2.29$ eV), ClQSB, at the 3-position of the steroid (inset, Figure 1). The ions were generated in 2-methyltetrahydrofuran (MTHF) by pulse radiolysis, reaction rates were measured by fast transient absorption spectroscopy, and the data were analyzed as described previously.[3d,h] The temperature range of the measurements reached from −94 to 100 °C. In another set of experiments, intermolecular rates were measured between the monofunctional steroids B^-S and QS or ClQS. By subtraction of the intermolecular rates from the total ET rates obtained on the bifunctional compounds, the intramolecular rate constants were obtained.[3h]

In Figure 1, k_{intra} and k_{inter} are plotted against $1/T$. Clearly k_{intra} for both QSB and ClQSB is almost temperature independent, with slower rates for the more exoergic ClQSB. This observation cannot be explained by the classical Marcus theory, which predicts a change of k_{intra} of more than 3 orders of magnitude over the temperature range studied.[5] On the other hand, eq 1 provides an excellent description (solid lines in upper Figure 1) using parameters that were determined independently and were published earlier.[3d]

[†] Argonne National Laboratory.

[‡] The University of Chicago.

(1) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(2) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909. (c) Frank, A.; Gratzel, M.; Henglein, A.; Janata, E. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 547. (d) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 241. (e) Jonah, C. D.; Metheson, M. S.; Meisel, D. *J. Am. Chem. Soc.* **1978**, *100*, 449. (f) Nagle, J. K.; Dresick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993. (g) Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350.

(3) (a) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579. (b) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670. (c) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (d) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (e) McLendon, G.; Miller, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 7811. (f) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (g) Irvine, M. B.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315. (h) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (i) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429. (j) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794. (k) Ohno, T.; Yoshimura, A.; Shioyama, H.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 4365. (l) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (m) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242. (n) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7883. (o) Mataga, N.; Kanda, Y.; Asahi, T.; Miyasaka, H.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 239. (p) Mataga, N.; Asahi, T.; Kanda, Y.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 249. (q) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 6575. (r) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 3993. (s) Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S.; Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1917. (t) Meade, T. J.; Gray, H. B.; Winkler, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 4353.

(4) (a) Levich, V. G.; Dogonadze, R. R. *Dokl. Akad. Nauk SSSR* **1960**, *133*, 158. (b) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148. (c) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (d) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (e) Efrima, S.; Bixon, M. *Chem. Phys.* **1976**, *13*, 447. (f) Fischer, S. F.; Van Duyne, R. P. *Chem. Phys.* **1977**, *26*, 9. (g) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741. (h) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748. (i) Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 4494. Excellent reviews: (j) Ulstrup, J. *Charge Transfer Processes in Condensed Media*; Springer-Verlag: Berlin, 1979. (k) Devault, D. *Quantum Mechanical Tunnelling in Biological Systems*, 2nd ed.; Cambridge Univ. Press: Cambridge, 1984. (l) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437. (m) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(5) The estimate was made in the contemporary classical formulation (Sutin, N.; Brunschwig, B. S.; Creutz, C.; Winkler, J. R. *Pure Appl. Chem.* **1988**, *60*, 1817): $k = 2|V^2|(\pi^3/\lambda h^2 k_B T)^{1/2} \exp[-(\lambda + \Delta G^\circ)^2/4\lambda k_B T]$; $\lambda = \lambda_s + \lambda_v$. From 100 to −94 °C, k_{intra} would decrease by factors of 200 for QSB and 3000 for ClQSB.

0002-7863/90/1512-5353$02.50/0

$$k = (2\pi/\hbar)|V^2|(\mathrm{FCWD}) \quad (1a)$$

$$\mathrm{FCWD} = (4\pi\lambda_s k_B T)^{-1/2}\sum_{w=0}^{\infty}(e^{-S}S^w/w!)\exp\{-[(\lambda_s + \Delta G° + whv)^2/4\lambda_s k_B T]\} \quad (1b)$$

$$S = \lambda_v/h\nu \quad (1c)$$

Equation 1 is based on the golden rule (eq 1a) and incorporates the quantum-mechanical treatment of high-frequency modes of the donor and acceptor groups, together with the classical treatment of the solvent modes.[4,3c] The parameters were derived from room-temperature measurements on QSB, ClQSB, and six others with different acceptor groups providing a range from −0.06 to −2.5 eV. Fitting these data to eq 1 provided the solvent reorganization energy (λ_s = 0.75 eV for MTHF), the reorganization energy (λ_v = 0.45 eV) of the high-frequency vibrational modes, here represented by a single average skeletal vibration of 1500 cm^{-1}, and the coupling matrix element V (6.2 cm^{-1}).[3d] The parameters were further confirmed by measuring the temperature dependence of k_{intra} of NSB (N = 2-naphthyl) and λ_s of MTHF.[6] However, because of the weak exoergicity ($\Delta G°$ = −0.06 eV), the high-frequency mode is restricted to $w = 0$, making the part of eq 1 that depends on temperature equal to the classical Marcus expression.

According to eq 1, the rates are very weakly dependent on temperature because of the quantum-mechanical nature of the high-frequency modes. These modes are "frozen" in our temperature range. Their Franck–Condon factors are not improved by increasing temperature in our range because of nuclear tunneling in these modes. The nuclear tunneling makes the high-frequency modes efficient at disposing the excess energy in these highly exoergic reactions. In addition, λ_s of MTHF increases by 20% from 100 to −94 °C,[6] which is responsible for the slightly negative activation energies (≈−0.18 kcal/mol for ClQSB). If λ_s were independent of temperature, the rates would still have been predicted to be almost independent of temperature, but with a very weakly positive activation energy (0.5 kcal/mol).

For the same donor–acceptor pairs, the intermolecular rate constants (lower Figure 1) are quite sensitive to temperature but insensitive to $\Delta G°$. This is because k_{inter} is primarily determined by diffusion as demonstrated by the excellent fit of the data to the phenomenological VTF equation:[7] $k = k_0 \exp[-E_0/(T - T_0)]$ with E_0 = 0.40 K^{-1} and T_0 = 100 ± 20 K. This is another demonstration of how the unique features of the inverted region are buried in rate-limiting transport processes in bimolecular reactions.

In conclusion, while the Marcus theory in its classical form describes the temperature dependence of ET at least qualitatively in the normal region, the present study finds it to be inadequate in the inverted region. Here, it is essential to include a quantum-mechanical treatment of high-frequency modes. In kinetic terms, the classical theory attributes the inverted region to an increasing activation energy in the exponential term of the rate equation, while because of nuclear tunneling it is the decreasing preexponential factor that is primarily responsible for the diminishing rate. Other evidence for the necessity of quantum modes in ET processes is abundant.[8a,9,10] The observations reported here resemble the temperature-independent ET processes in photosynthetic reaction centers[8] and may shed some light on the understanding of this important problem.

Acknowledgment. We are indebted to Radhika Bal for resynthesizing some of the compounds and to Professor R. A. Marcus for helpful comments on the role of tunneling in the inverted region. Work at Argonne was supported by the Office of Basic Energy Sciences, Division of Chemical Science, U.S. Department of Energy, under Contract No. W-31-109-ENG-38. Work at the University of Chicago was supported by NSF Grant CHE-8520326.

---

(6) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 8740.

(7) (a) Vogel, H. *Phys. Z.* **1921**, *22*, 645. (b) Fulcher, G. S. *J. Am. Chem. Soc.* **1925**, *8*, 339. (c) Tammann, G.; Hesse, G. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245. (d) Recent review: Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1988**, *39*, 149.

(8) (a) Gunner, M. R.; Dutton, P. L. *J. Am. Chem. Soc.* **1989**, *111*, 3400. (b) Kirmaier, C.; Holten, D.; Parson, W. W. *Biochim. Biophys. Acta* **1985**, *810*, 33. (c) Schenck, C. C.; Parson, W. W.; Holten, D.; Windsor, W. W.; Sarai, A. *Biophys. J.* **1981**, *36*, 479.

(9) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.

(10) 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.

Feasibility of a "Building-Block" Approach to Higher Nuclearity Mn/O/RCO$_2^-$ Aggregates: Directed Conversion of an [Mn$_4$O$_2$] to an [Mn$_8$O$_4$] Complex

Eduardo Libby, Kirsten Folting, John C. Huffman, and George Christou*[,1]

Department of Chemistry
and the Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

Received January 19, 1990

In recent years we have been reporting our progress toward developing oxide-bridged Mn carboxylate chemistry.[2] Efforts have been directed primarily toward di- and tetranuclear species to obtain potential models of the Mn units within certain Mn biomolecules.[2] We, and others, have occassionally encountered higher nuclearity products, and structurally characterized species include Mn$_6$,[3] Mn$_9$,[4] Mn$_{10}$,[5] and Mn$_{12}$.[6] In parallel, other groups have reported high nuclearity Fe carboxylates, Fe$_6$,[7] Fe$_8$,[8] Fe$_{11}$,[9] and Fe$_{16}$M (M = Co, Mn).[10] In all cases, it is probably fair to say that serendipity has provided a helping hand, in that reactions were under thermodynamic control and the precise nuclearity could not have been predicted from the reagents employed. Higher nuclearity species are important for a variety of reasons, including providing insights into the assembly of the polynuclear core of the ferritin protein[11] and understanding the variation of magnetic exchange interactions as a function of nuclearity and metal oxidation state.[2] The latter has been particularly interesting for Mn where ferromagnetic interactions have occasionally led to high spin ground states. For example, Mn$_{12}$O$_{12}$(O$_2$CPh)$_{16}$(H$_2$O)$_4$ has an S = 14 ground state, and we have commented on the potential of such species as precursors to molecular ferromagnets.[6a] Given this importance of high-nuclearity species and the serendipitous nature of their discovery to date, we felt it important to overcome this lack of control and develop methodology for their rational synthesis. One attractive approach is to link together, in a controlled manner, smaller nuclearity "building blocks" derived from available smaller nuclearity species. Preliminary efforts have

---

(1) Alfred P. Sloan Research Fellow, 1987–1991. Camille and Henry Dreyfus Teacher-Scholar, 1987–1992.

(2) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328 and references therein.

(3) (a) Schake, A. R.; Vincent, J. B.; Li, Q.; Boyd, P. D. W.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1989**, *28*, 1915. (b) Baikie, A. R. E.; Howes, A. J.; Hursthouse, M. B.; Quick, A. B.; Thornton, P. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1587. (c) Gerbeleu, N. V.; Batsanov, A. S.; Timko, G. A.; Struchkov, Y. T.; Inrichan, K. M.; Popovich, G. A. *Dokl. Akad. Nauk SSSR* **1987**, *294*, 256.

(4) Christmas, C.; Vincent, J. B.; Chang, H.-R.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 823.

(5) Hagen, K. S.; Armstrong, W. H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 774.

(6) (a) Boyd, P. D. W.; Li, Q.; Vincent, J. B.; Folting, K.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8537. (b) Lis, T. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2042. (c) Luneau, D.; Savariault, J.-M.; Tuchagues, J.-P. *Inorg. Chem.* **1988**, *27*, 3912.

(7) (a) Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372. (b) Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067. (c) Batsanov, A. S.; Struchkov, Y. T.; Timko, G. A. *Koord. Khim.* **1988**, *14*, 266.

(8) Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77.

(9) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337.

(10) Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6856.

(11) (a) Theil, E. C. *Annu. Rev. Biochem.* **1987**, *56*, 289. (b) Crichton, R. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 57.

0002-7863/90/1512-5354$02.50/0