Explanation of the Driving-Force Dependence of Return Electron Transfer in Contact Radical-Ion Pairs

Ian R. Gould,*[†] Dimitri Noukakis,[‡] Luis Gomez-Jahn,[‡]
Joshua L. Goodman,[‡] and Samir Farid*[†]

Center for Photoinduced Charge Transfer, Hutchison Hall
University of Rochester, Rochester, New York 14627
Corporate Research Laboratories, Eastman Kodak Company
Rochester, New York 14650-2109
Department of Chemistry, University of Rochester
Rochester, New York 14627

Received January 25, 1993

The widely used nonadiabatic theory of electron transfer, which gives the reaction rate k_{et} as the product of an electronic coupling matrix element (V) and a Franck–Condon weighted density of states (FCWD) (eq 1a),[1] has been particularly successful in explaining many aspects of electron-transfer kinetics.[2] The FCWD term commonly includes the driving force for electron transfer (ΔG_{et}), a reorganization energy associated with rearranged low frequency modes (λ_s), and a reorganization energy (λ_v) associated with a single, averaged, high-frequency mode (ν_v) (eq 1b,c).[1]

$$k_{\mathrm{et}} = \frac{4\pi^2}{h} V^2 \mathrm{FCWD} \tag{1a}$$

FCWD =

$$\sum_{j=0}^{\infty} \frac{e^{-S} S^j}{j!} (4\pi\lambda_s k_B T)^{-1/2} \exp\left[-\frac{(jh\nu_v + \Delta G_{\mathrm{et}} + \lambda_s)^2}{4\lambda_s k_B T}\right] \tag{1b}$$

$$S = \frac{\lambda_v}{h\nu_v} \tag{1c}$$

Despite the success of eq 1, it has been suggested that the driving force dependence, $-\Delta G_{-\mathrm{et}}$, of the rates of return electron transfer in contact radical-ion pairs (CRIP), $k_{-\mathrm{et}}$, cannot be explained using such nonadiabatic theories and that these processes should be described using an alternate mechanism.[3] In the present work, however, we show that the $k_{-\mathrm{et}}$ for these reactions can be explained using eq 1, when *properly* applied, from a complete analysis of both the nonradiative and radiative return electron-transfer processes in the CRIP.

Table I. Emission Maxima, Electron-Transfer Parameters, and Calculated and Measured Rate Constants for Nonradiative Return Electron Transfer in Tetracyanobenzene Acceptor/Methylbenzene Donor Contact Radical-Ion Pairs in Chloroform

donor[a]	ν_{max}[b] (10^3 cm^{-1})	V[c] (cm^{-1})	λ_s[d] (eV)	$-\Delta G_{-\mathrm{et}}$[d] (eV)	$(k_{-\mathrm{et}})_{\mathrm{calcd}}$[e] ($10^8$ s^{-1})	$(k_{-\mathrm{et}})_{\mathrm{measd}}$[f] ($10^8$ s^{-1})
p-XY (2.06)	16.6	660	0.70	3.01	0.96	1.2
TMB (1.92)	15.7	730	0.65	2.86	2.8	2.7
DUR (1.78)	15.0	740	0.59	2.70	6.7	5.9
PMB (1.71)	14.6	760	0.53	2.60	9.3	10.0
HMB (1.59)	14.0	800	0.45	2.44	19.5	20.4

[a] *p*-XY, TMB, DUR, PMB, and HMB refer to *p*-xylene, 1,2,4-trimethylbenzene, durene, pentamethylbenzene, and hexamethylbenzene, respectively. The numbers in parentheses are the oxidation potentials of the donors, E_{ox} (V vs SCE).[2k] [b] Frequency of the maximum of the reduced emission spectrum.[8] [c] Obtained from CRIP radiative rate measurements.[8] [d] Obtained from fitting the emission spectra.[8,9] [e] Calculated using eq 1, using values for V and λ_s given in the table and 0.31 eV and 1400 cm^{-1} for λ_v and ν_v, respectively. [f] Measured values from time-resolved emission experiments.

The electron acceptor used here is 1,2,4,5-tetracyanobenzene (TCB), and the donors are the methyl-substituted benzenes indicated in Table I. Excitation of TCB/methylbenzene ground-state charge-transfer (CT) complexes results in the formation of TCB radical anion/methylbenzene radical cation CRIP.[4] Although nonradiative return electron transfer dominates the decay processes of these CRIP, emissions can also be observed[5] which correspond to radiative return electron-transfer processes.[6,7] The spectral distributions of such emissions are controlled by the same FCWD that determine the dependence of $k_{-\mathrm{et}}$ on $\Delta G_{-\mathrm{et}}$.[6,7] Thus, the reorganization parameters λ_s, λ_v, and ν_v and also $\Delta G_{-\mathrm{et}}$ for the nonradiative return electron-transfer process can be estimated from analyses of the corresponding emission spectra.[7,8]

Emission spectra were measured for the TCB/methylbenzene CRIP in chloroform. With increasing donor oxidation potential, $E^{\mathrm{ox}}{}_{\mathrm{D}}$, the energy of the CRIP increases ($-\Delta G_{-\mathrm{et}}$ increases), and a corresponding increase is observed in the emission energy ν_{max} (Table I). However, a plot of ν_{max} versus $E^{\mathrm{ox}}{}_{\mathrm{D}}$ (not shown) has a slope that is substantially less than 1.00 (0.59). In addition, with increasing $E^{\mathrm{ox}}{}_{\mathrm{D}}$, an increase is observed in the Stokes shift between the reduced CT absorption and emission spectra. These observations indicate that the reorganization energy for electron transfer increases with increasing $E^{\mathrm{ox}}{}_{\mathrm{D}}$. Furthermore, the blue edges of the reduced emission spectra of the CRIP become less steep with increasing $E^{\mathrm{ox}}{}_{\mathrm{D}}$, suggesting an increase in λ_s.[6,7] This was confirmed by spectral fitting of the CRIP emissions, using the procedure described previously.[8,9] The electron-transfer parameters used to fit the spectra are summarized in Table I. Values for the electronic coupling matrix elements V were obtained from measurements of the CRIP radiative rates.[8] A small dependence on the structure of the donor is observed (Table I) for reasons which are not clear. Using the data of Table I together with eq 1, values for the nonradiative return electron-transfer

---

[†] Corporate Research Laboratories, Eastman Kodak Company.

[‡] Department of Chemistry, University of Rochester.

(1) (a) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975,** *63,* 4358. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984,** *106,* 5057. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta.* **1985,** *811,* 265.

(2) See, for example: (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984,** *106,* 5057. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984,** *106,* 3047. (c) Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986,** *104,* 315. (d) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* ***1987,*** *109,* 3794. (e) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991,** *95,* 2068. (f) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986,** *90,* 3673. (g) Finckh, P.; Heitele, H.; Volk, M.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1988,** *92,* 6584. (h) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989,** *111,* 3751. (i) Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S.; Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1989,** *111,* 1917. (j) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990,** *112,* 5353. (k) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990,** *112,* 4290. (l) Chung, W.-S.; Turro, N. J.; Gould, I. R.; Farid, S. *J. Phys. Chem.* **1991,** *95,* 7752.

(3) (a) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989,** *93,* 6575. (b) Asahi, T.; Mataga, N.; Takahashi, Y.; Miyashi, T. *Chem. Phys. Lett.* **1990,** *171,* 309. (c) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990,** *94,* 7534. (d) Mataga, N. In *Electron Transfer in Inorganic, Organic and Biological Systems.* Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series 228; American Chemical Society: Washington DC, 1991. (e) Mataga, N. In *Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena*; Mataga, N., Okada, T., Masuhara, H., Eds.; Elsevier: Amsterdam, 1992. (f) Segawa, H.; Takehara, C.; Honda, K.; Shimidzu, T.; Asahi, T.; Mataga, N. *J. Phys. Chem.* **1992,** *96,* 503.

(4) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990,** *94,* 5834. (b) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990,** *94,* 4147.

(5) (a) Iwata, S.; Tanaka, J.; Nagakura, S. *J. Chem. Phys.* **1967,** *47,* 2203. (b) Mataga, N.; Murata, Y. *J. Am. Chem. Soc.* **1969,** *91,* 3144. (c) Kobayashi, T.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1971,** *44,* 2603. (d) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1972,** *45,* 987. (e) Masuhara, H.; Saito, T.; Maeda, Y.; Mataga, N. *J. Mol. Struct.* **1978,** *47,* 243. (f) Kozankiewicz, B.; Prochorow, J. *Chem. Phys.* **1989,** *135,* 307.

(6) Marcus, R. A. *J. Phys. Chem.* **1989,** *93,* 3078 and references therein.

(7) Gould, I. R.; Farid, S.; Young, R. H. *J. Photochem. Photobiol. A: Chem.* **1992,** *65,* 133.

(8) (a) Gould, I. R.; Noukakis, D.; Goodman, J. L.; Young, R. H.; Farid, S. *J. Am. Chem. Soc.*, in press. (b) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.*, submitted for publication.

(9) In the fitting procedure, λ_v and ν_v were fixed at 0.31 eV and 1400 cm–1, respectively, and $\Delta G_{-\mathrm{et}}$ and λ_s were varied.

0002-7863/93/1515-4405$04.00/0

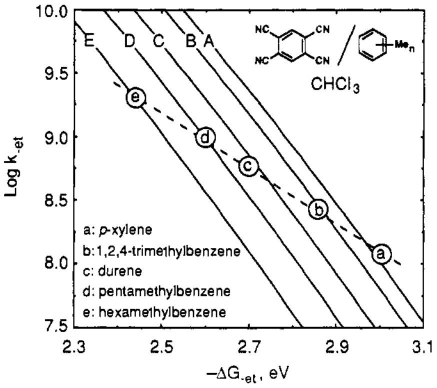

Figure 1. Plot of log measured return electron-transfer rate constant ($k_{-\mathrm{et}}$, ○ s) versus driving force, $-\Delta G_{-\mathrm{et}}$, for contact radical–ion pairs of 1,2,4,5-tetracyanobenzene and methylbenzenes. The solid lines represent the calculated driving force dependencies for the reorganization parameters characteristic of each radical–ion pair (the slopes of the approximate straight lines are −4.6 eV^{-1}). The dashed line represents the apparent driving force dependence of the data (slope of the approximate straight line −2.2 eV^{-1}) if the variation of the reorganization parameters with the structure of the radical–ion pair is not taken into account.

rate constants for the CRIP could then be calculated, $(k_{-\mathrm{et}})_{\mathrm{calcd}}$ (Table I).

Experimental values for the nonradiative return electron-transfer rate constants $(k_{-\mathrm{et}})_{\mathrm{measd}}$, were obtained from emission lifetime measurements.[8,10] When the $\log((k_{-\mathrm{et}})_{\mathrm{measd}})$ data are plotted against $-\Delta G_{-\mathrm{et}}$, the apparent driving force dependence is shallow (the slope of the approximately linear plot is -2.2 eV^{-1}, Figure 1), in a similar manner to that reported previously for related CRIP.[3] This weak and approximately linear dependence was previously taken as evidence against the applicability of eq 1.[3] However, the agreement between $(k_{-\mathrm{et}})_{\mathrm{measd}}$ and $(k_{-\mathrm{et}})_{\mathrm{calcd}}$ is remarkably good (Table I). Why, then, is the driving force dependence so shallow? Analysis of the driving force dependence for a series of acceptor/donor pairs is valid only *if the reorganization parameters for the different pairs are constant*. This, however, is clearly not the case for the TCB/alkylbenzene CRIP (Table I). The predicted driving force dependencies for constant reorganization parameters are, in fact, steep, as indicated in Figure 1 (the plots of the approximately linear plots are ca. −4.6 eV^{-1}). The apparent driving force dependence is weak because the reorganization energies increase with increasing $-\Delta G_{-\mathrm{et}}$.

The increase in solvent reorganization energy with decreasing number of methyl substituents on the donor is consistent with the report that a plot of $E^{\mathrm{ox}}{}_{\mathrm{D}}$ versus gas-phase ionization potential has a slope which is less than 1.00 (ca. 0.7).[11] This suggests that the solvent stabilization energy for the alkylbenzene radical cations, and presumably the λ_s for the appropriate CRIP, increases with decreasing methyl substitution, i.e., increasing $E^{\mathrm{ox}}{}_{\mathrm{D}}$. The solvent reorganization energies for all of the CRIP studied here are large in comparison to those estimated for related systems.[2e] This presumably reflects the fact that the molecular dimensions of both the radical anion and the radical cation are small compared to those of most acceptor/donor pairs.

The nonadiabatic theory appears to be valid for the present systems, despite the large values of V, which might suggest that an adiabatic approach is more appropriate.[1c] In previous work on CRIP electron-transfer reactions, however, we showed that nonadiabatic and adiabatic theories were in quantitative agreement when $-\Delta G_{-\mathrm{et}} \gg \lambda_s + \lambda_v$,[2e] which is the case here. We note, however, that when $-\Delta G_{-\mathrm{et}}$ approaches $\lambda_s + \lambda_v$, the nonadiabatic theory should not apply.

The results clearly demonstrate that the CRIP systems are not unusual in their electron-transfer behavior. It is anticipated that further studies of the quantitative relationship between radiative and nonradiative electron transfer will provide even more detailed insight into the factors controlling the rates of these important processes.[8,12]

Acknowledgment. The authors are grateful to the National Science Foundation for a Science and Technology Center grant (CHE-8810024) and to R. H. Young (Eastman Kodak Company) for many helpful discussions.

Supplementary Material Available: Measured and calculated CRIP emission spectra, the method for obtaining the corrected spectra and the electronic coupling matrix elements, and the equations used to calculate the spectra (7 pages). Ordering information is given on any current masthead page.

---

(10) $(k_{-\mathrm{et}})_{\mathrm{measd}}$ were obtained as $(1/\tau)$, where τ is the lifetime measured in time-resolved emission experiments.[8] Intersystem crossing and emission were ignored since the contributions of these processes to the CRIP decays were less than 10% and 1%, respectively. Separation of the ions should not occur in the relatively nonpolar chloroform. The emission lifetimes were extrapolated to zero donor concentration where necessary.

(11) Howell, J. O.; Gonclaves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(12) See, for example: (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (c) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (d) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751. (e) Khundkar, L. R.; Stiegman, A. E.; Perry, J. W. *J. Phys. Chem.* **1990**, *94*, 1224. (f) Barqawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47. (g) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712. (h) Barbara, P. F.; Walker, G. C.; Smith, T. P. *Science* **1992**, *256*, 975. (i) Walker, G. C.; Åkesson, E.; Johnson, A. E.; Levinger, N. E.; Barbara, P. F. *J. Phys. Chem.* **1992**, *96*, 3728. (j) Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1992**, *191*, 371. (k) Zeng, Y.; Zimmt, M. B. *J. Phys. Chem.* **1992**, *96*, 8395.