

Dynamics of Bimolecular Photoinduced Electron-Transfer Reactions

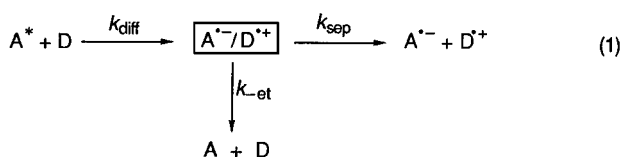
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Received March 13, 1996

Introduction

From the accumulated results of several research groups over the last 25 years, it is clear that photoinduced electron-transfer reactions have significantly broadened the scope of organic photochemistry.¹ The fundamental mechanistic principle is that when quenching of an excited state via electron transfer is sufficiently exothermic, the reaction occurs at or close to the diffusion-controlled limit (k_{diff}).² In polar solvents, where most reactions are carried out, the primary intermediate is a geminate radical-ion pair, $A^{\cdot-}/D^{\cdot+}$ (eq 1).³ Return electron transfer within the



geminate radical-ion pair ($k_{\text{-et}}$) is a universal feature of the overall process, which decreases the efficiency of product formation by competing with separation (k_{sep}) to form separated radical ions, where most of the chemical reactions take place.⁴ Even when reactions are fast enough to occur in the geminate pair, their efficiencies are usually low due to competition with return electron transfer.

Efficiencies of Electron-Transfer Reactions: The "Inverted Region" Problem

In work carried out in these laboratories in the 1970s and early 1980s, a variety of chemical reactions initiated by photoinduced electron transfer were identified.⁵ In the course of these investigations, it was observed that the quantum yields for product formation varied over a wide range. From steady-state kinetic studies, estimates for $k_{\text{-et}}$ could be obtained, and by 1982, data from enough reactions had accumulated that it became obvious that there was a correlation between $k_{\text{-et}}$ and the exothermicity of the reaction, $-\Delta G_{\text{-et}}$ (Figure 1).⁶ Remarkably, $k_{\text{-et}}$ decreased with increasing reaction exothermicity,⁷ which

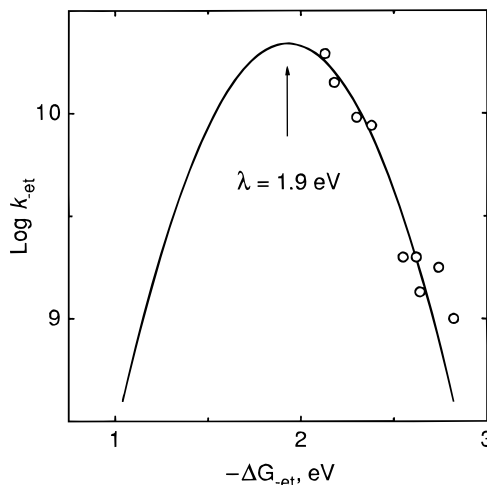


Figure 1. Rate constants for return electron transfer in acetonitrile, $k_{\text{-et}}$, plotted versus exothermicity, $-\Delta G_{\text{-et}}$. The $k_{\text{-et}}$ values are estimated from steady state kinetic studies of the following acceptor/donor systems, listed in order of decreasing exothermicity: DCA/biphenyl,^{6a} DCA/diphenylacetylene,^{6b} DCA/phenyl vinyl ether,^{6c} DCA/1,2-diphenylethylene,^{6a} DCA/benzyl-trimethylsilane,^{6d} TCA/biphenyl,^{6a} TCA/diphenylacetylene,^{6e} TCA/1,2-diphenylethylene,^{6a} and TCA/1,1-dimethylindene.^{6b} The curve represents a fit using the classical Marcus theory.⁸ The reorganization energy, λ , is equal to the exothermicity at which the maximum rate is attained.

seemed to correspond to the "inverted region" effect predicted by the theory of Marcus nearly 30 years earlier.⁸ Although Miller had provided evidence in support of the inverted region for reactions involving radical ions in low-temperature rigid glasses in 1979,⁹ in 1982 it was doubtful whether this particular prediction of the theory would ever be experimentally verified for reactions in fluid media. The findings

(1) (a) *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; Jai Press: Greenwich, CT, 1991–1994; Vols. 1–4. (b) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (c) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(2) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(3) (a) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129. (b) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255.

(4) Being a second-order process, return electron transfer in the separated radical ions is much slower than in the geminate pair.

(5) For a review see: Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

(6) The data points in Figure 1 are from the following: (a) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386. (b) Mattes, S. L.; Farid, S. Unpublished results. (c) Farid, S.; Hartman, S. E.; Evans T. R. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 327. (d) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (e) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 457.

(7) This effect was described in ref 5, p 305, ref 6a, and Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917.

(8) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(9) (a) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

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were presented at the International Conference on Photochemistry and Photobiology in Alexandria, Egypt, in January 1983. During a bus ride to the famous WWII cemetery at El-Alamein, the data shown in Figure 1 were further discussed with Rudy Marcus. The excitement was dashed, however, when Marcus correctly pointed out that the data implied a reorganization energy of nearly 2 eV (Figure 1). At that time, the best estimates for reorganization energies came from studies of self-exchange reactions, for which values of ca. 0.5–0.7 eV were typical in acetonitrile.¹⁰ The fact that the return-electron-transfer data suggested a value 3–4 times larger shed doubt on the interpretation. Nevertheless, the observations were intriguing, especially in light of the famous 1984 work of Miller and Closs on rigidly linked systems, in which relatively large reorganization energies were also observed.¹¹ The data also underscored the key role of return electron transfer in determining the efficiencies of photoinduced electron-transfer reactions. If the efficiencies were to be optimized, the factors controlling these electron-transfer reactions had to be understood. For these reasons we initiated a comprehensive investigation of the primary processes in bimolecular electron-transfer reactions, with a particular emphasis on the predictive power of current electron-transfer theories¹² (see Figure 2).

We started by measuring quantum yields for formation of separated radical ions in acetonitrile ($A^- + D^+$), Φ_{ions} , for reactions of the excited states of the electron acceptors 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA).¹⁴ Simple alkyl-substituted aromatic hydrocarbons were used as the electron donors. The acceptor/donor pairs were selected so that the exothermicities for return electron transfer varied by ca. 1 eV. A rather wide range of values for Φ_{ions} was measured, as shown in Figure 3. According to eq 1, $k_{\text{-et}}$ is directly proportional to $\Phi_{\text{ions}}^{-1} - 1$, eq 2, and when this quantity was plotted versus

$$\Phi_{\text{ions}} = k_{\text{sep}} / (k_{\text{-et}} + k_{\text{sep}}) \quad (2a)$$

$$k_{\text{-et}} / k_{\text{sep}} = \Phi_{\text{ions}}^{-1} - 1 \quad (2b)$$

exothermicity (Figure 3), an obvious trend of decreasing $k_{\text{-et}}/k_{\text{sep}}$ with increasing exothermicity was apparent, although the data showed significant scatter. Nearly scatter-free relations could be obtained, however, when the quantum yields were extrapolated to zero donor concentration,¹⁵ and when the “one-ring”

(10) See for example: Ebersol, L. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1982; Vol. 18, p 79.

(11) (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

(12) (a) Van Duynne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(13) (a) Resonance Raman experiments can give the frequencies and individual reorganization energies of the actual vibrational modes involved.^{13b–e} (b) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712. (c) Markel, F.; Ferris, N. S.; Gould, I. R.; Myers, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 6208. (d) Doorn, S. K.; Dyer, R. B.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 6398. (e) Kulinowski, K.; Gould, I. R.; Myers, A. B. *J. Phys. Chem.* **1995**, *99*, 9017.

(14) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

(15) (a) There are at least two mechanisms for the concentration dependence, one involving interception of the geminate pair by a second donor molecule,^{15b} and one due to formation of ground state CT complexes.¹⁶ (b) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

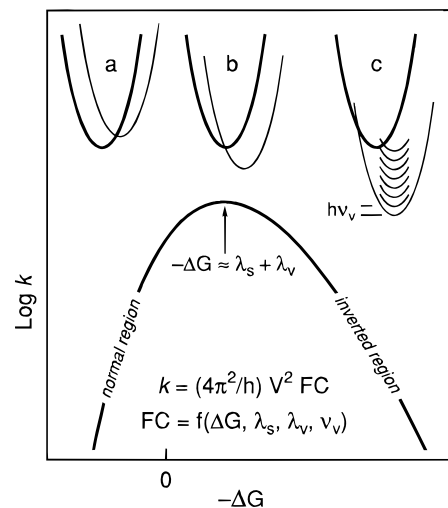


Figure 2. Dependence of the electron-transfer rate constant, k , on the driving force, $-\Delta G$, according to semiclassical theory.¹² When endothermic (a), the reaction proceeds from reactants (heavy potential energy curve) to products (light curve) via thermal activation. With decreasing endothermicity the activation energy decreases, and k increases, until a maximum is reached when the reaction becomes essentially activationless. The exothermicity at this point (b) is the energy (λ) required to reorganize the system to an optimum configuration for electron transfer. λ consists of a solvent component, λ_s , and a component associated with the donor and acceptor molecules, λ_v . Further increases in exothermicity populate vibrationally excited states of the product, and k decreases due to increasingly poor vibrational overlap of the product and reactant wave functions. The vibrational energy levels associated with λ_v are usually approximated by a single averaged energy, $h\nu_v$, and are indicated by the multiple levels in (c).¹³ The electronic coupling matrix element, V , is related to the extent of overlap of the appropriate donor and acceptor orbitals, and scales the dependence on ΔG in the vertical axis. The term FC contains the reorganization parameters and ΔG , and determines the shape of the plot of k versus ΔG and its displacement on the horizontal axis.

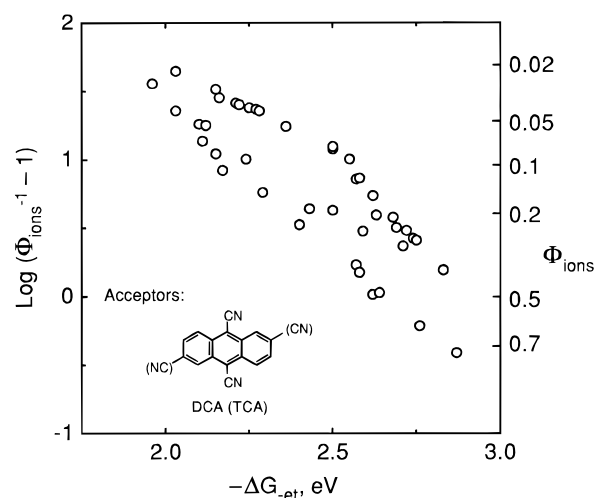


Figure 3. (right axis) Quantum yields for formation of separated radical ions, Φ_{ions} , for quenching of DCA and TCA excited states by simple aromatic hydrocarbons in acetonitrile, and (left axis) a function that is directly proportional to the rate constant of return electron transfer ($k_{\text{-et}}$, eq 2b), plotted versus reaction exothermicity, $-\Delta G_{\text{-et}}$.

(alkyl-substituted benzenes), “two-ring” (naphthalenes and biphenyls), and “three-ring” (phenanthrenes) data were plotted separately.¹⁶ Values for $k_{\text{-et}}$ were obtained by assuming a constant value for k_{sep} , which was estimated to be $5 \times 10^8 \text{ s}^{-1}$ (Figure 4). Good fits

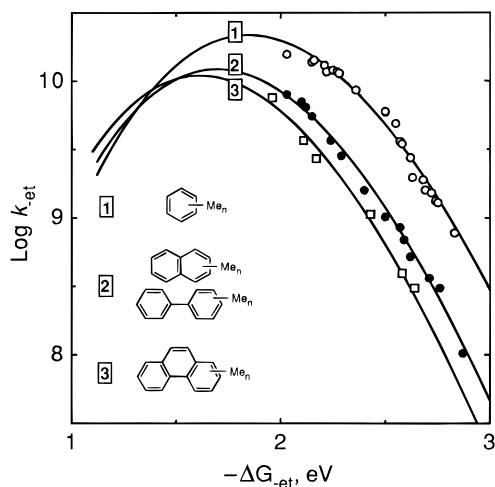


Figure 4. Rate constants for return electron transfer in radical-ion pairs, k_{-et} , plotted as a function of exothermicity, $-\Delta G_{-et}$, for cyanoanthracenes as acceptors with (1) alkyl-substituted benzenes, (2) naphthalenes and biphenyls, and (3) phenanthrenes as donors, in acetonitrile. The curves through the data points are fits to the data as described in ref 16.

to these data were obtained according to conventional electron-transfer theories.¹⁶ The data confirmed the existence of the inverted region, and illustrated the sensitivity of the reactions to subtle changes in molecular structure.¹⁷ The large reorganization energies were still an issue, however, and to solve this problem, a more detailed mechanism than that shown in eq 1 had to be considered.

Intermediates and General Mechanism

There had been evidence for some time that two kinds of radical-ion pairs could be considered,^{3,18} a contact radical-ion pair (CRIP, $A^{\cdot-}D^{\cdot+}$) and a solvent-separated radical-ion pair (SSRIP, $A^{\cdot-}(S)D^{\cdot+}$), as shown in Figure 5.^{19,20} The CRIP is a specific case of the more general exciplex or excited charge-transfer complex.²¹ These latter species can have variable charge-transfer (CT) character as a consequence of mixing of the pure radical-ion pair state with locally excited states (indicated by the double-headed arrow in Figure 5), whereas charge transfer in the CRIP is essentially complete (i.e., mixing is negligible). The radical ions are assumed to have a face-to-face configuration with a center-to-center $A^{\cdot-}D^{\cdot+}$ separation distance of ca. 3.5 Å in the CRIP, and to be separated by ca. one layer of solvent molecules in the SSRIP, so

(16) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(17) (a) In related work, the return-electron-transfer reactions of *cis*- and *trans*-stilbenes could be differentiated on the basis of molecular size.^{17b} (b) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055.

(18) (a) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, Chapter 4. (b) Mataga, N. In *Photochemical Processes in Organized Molecular Systems*; Honda, K., Ed.; Elsevier: New York, 1991; p 3.

(19) Gould, I. R.; Young, R. H.; Farid, S. In *Photochemical Processes in Organized Molecular Systems*; Honda, K., Ed.; Elsevier: New York, 1991; p 19.

(20) (a) Penetrated ion pairs represent another more specialized species.^{20b} (b) Murphy, S.; Yang, X.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2411.

(21) (a) Weller, A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975, p 23. (b) Mataga, N.; Ottolenghi, M. In *Molecular Association*; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 1. (c) Jones, G., III. In *Photoinduced Electron Transfer. Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 245.

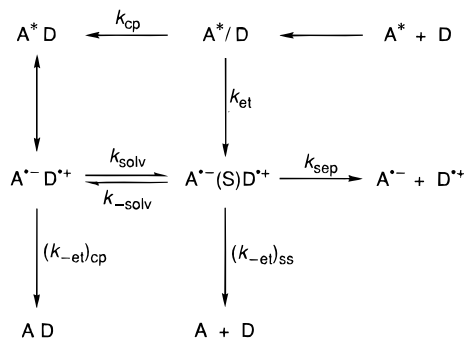


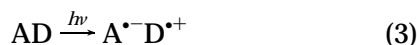
Figure 5. Intermediates in bimolecular photoinduced electron-transfer reactions in fluid solution, for an acceptor (A) as the excited state and a donor (D) as the quencher. A^*/D represents an encounter pair, in which electron transfer (k_{et}) leading to the formation of a solvent-separated radical-ion pair (SSRIP, $A^{\cdot-}(S)D^{\cdot+}$) occurs in competition with diffusive motion to form a contact pair (k_{cp}). When the A^* and D are in contact, electron transfer presumably occurs very rapidly to form a contact radical-ion pair (CRIP, $A^{\cdot-}D^{\cdot+}$). In the general case, mixing of the pure ion pair and locally excited states is possible in the contact configuration, represented by a double-headed arrow ($A^*D \leftrightarrow A^{\cdot-}D^{\cdot+}$), resulting in species with variable charge-transfer character (exciplexes). For the systems studied here, charge transfer is essentially complete and the exciplexes are thus equivalent to CRIP. Depending upon the medium, solvation of the CRIP can occur (k_{solv}) to form a SSRIP; desolvation (k_{-solv}) is the reverse process. Return electron transfers in CRIP and SSRIP, $(k_{-et})_{cp}$ and $(k_{-et})_{ss}$, respectively, are deactivation paths leading to a neutral acceptor and donor. Further separation of the SSRIP (k_{sep}) leads to the formation of fully separated or free radical ions ($A^{\cdot-} + D^{\cdot+}$).

that the average separation distance is probably ca. 7 ± 1 Å. The SSRIPs are more dynamic than the CRIPs, and thus have a less well-defined structure. Importantly, the CRIPs can be identified by characteristic CT emissions, whereas the SSRIPs do not emit.

At the time of the initial quantum yield experiments in 1986, the roles of the two radical-ion pairs in bimolecular reactions were not clear, although it was generally assumed that, in polar solvents, only the SSRIP played an important role.^{18a} We therefore ignored the CRIP, and thus $(k_{-et})_{cp}$, and assigned the geminate pair dynamics to those of the SSRIP.^{14,16} We were lucky that this assumption turned out to be valid, because of a coincidence that was unknown to us at the time. As indicated in Figure 5, either a CRIP or a SSRIP can be formed from the encounter pair A^*/D . For the systems studied, CRIPs were, in fact, formed in several of the reactions. However, in these cases $(k_{-et})_{cp}$ was so small that it did not measurably influence Φ_{ions} , and all of the return electron-transfer reactions occurred in the SSRIP. The lucky part was that in the few systems where $(k_{-et})_{cp}$ was large enough to influence Φ_{ions} , the CRIPs were not formed in the diffusive quenching process because of direct formation of SSRIPs in the encounter pair, as discussed below.

Information about $(k_{-et})_{cp}$ could be obtained, however, by taking advantage of the fact that TCA forms ground state CT complexes with the donors, AD.²² The product of excitation of such a CT complex is a CRIP, eq 3. For those systems where the CRIP is bypassed in the encounter pair, excitation of the CT complex gave smaller Φ_{ions} values compared to excitation of A

(22) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

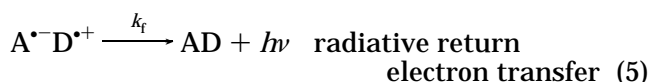


followed by bimolecular quenching of A^* , because return electron transfer occurred in *both* the CRIP, $(k_{-et})_{cp}$, and the SSRIP, $(k_{-et})_{ss}$. By comparing ion yields for the different excitation conditions, values for $(k_{-et})_{cp}$ could be obtained for several of the same systems for which $(k_{-et})_{ss}$ had been measured.²²

The data for $(k_{-et})_{cp}$ are compared to those for $(k_{-et})_{ss}$ in Figure 6. Because of the limited range of driving force for the CRIP reactions, curve fitting analogous to that for the SSRIP is obviously very dangerous, although this did not deter us from trying when we first obtained the data!²³ The stronger dependence of $(k_{-et})_{cp}$ on exothermicity, however, clearly indicated that the CRIP reactions were characterized by a higher electronic coupling matrix element and a smaller solvent reorganization energy than those of the SSRIP. A more quantitative analysis of the CRIP data was obtained, however, when the electron-transfer reactions were considered from another perspective.

Radiative and Nonradiative Return Electron Transfer: Clues from Emission Spectra

The CRIPs are characterized by CT emissions that have proven to be the key to accurately determining the parameters controlling their return-electron-transfer reactions.²⁴ In the return-electron-transfer reaction, eq 4, the neutral acceptor and donor are regenerated. As indicated in eq 5, the product of CRIP emission is also the neutral acceptor and donor; i.e., the emission is also a return-electron-transfer reaction.²⁵



Varying the energy of the emitted photon in eq 5 is analogous to varying ΔG_{-et} in eq 4. In fact, *the shape of the CT emission spectrum is determined by the same reorganization parameters that control the shape of a plot of electron-transfer rate constant versus driving force.*^{24,25} This is illustrated in Figure 7, where CRIP emission spectra for the 1,2,4,5-tetracyanobenzene (TCB)/hexamethylbenzene (HMB) pair are fitted in a manner analogous to that for electron-transfer reactions (e.g., Figure 4).²⁶⁻²⁸ The reorganization parameters for the CT emission, *and* the free energy of formation of the CRIP (equivalent to $-\Delta G_{-et}$), are accurately determined because, unlike the k_{-et} plot in

(23) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.

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

(25) Marcus, R. A. *J. Phys. Chem.* **1984**, *81*, 4494.

(26) (a) Gould, I. R.; Noukakis, D.; Goodman, J. L.; Young, R. H.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 3830. (b) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Goodman, J. L.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4405.

(27) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(28) (a) A similar approach has been taken in studies of rigidly linked donor/acceptor systems.^{28b} (b) Zeng, Y.; Zimmt, M. B. *J. Phys. Chem.* **1992**, *96*, 8395.

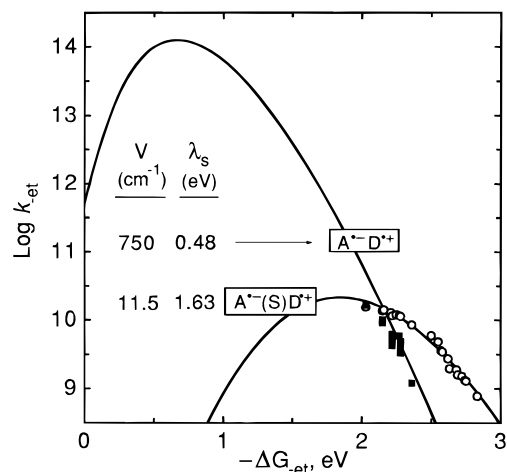


Figure 6. Rate constants for return electron transfer, k_{-et} , for contact ($A^{\bullet-}D^{\bullet+}$) and solvent-separated ($A^{\bullet-}(S)D^{\bullet+}$) radical-ion pairs with cyanoanthracenes as acceptors and alkylbenzenes as donors in acetonitrile, plotted as a function of exothermicity, $-\Delta G_{-et}$. The curves through the data points are calculated as described in the text, using a semiclassical electron-transfer theory,¹² with the parameters shown, and 0.25 eV for λ_v and 1500 cm^{-1} for ν_v .

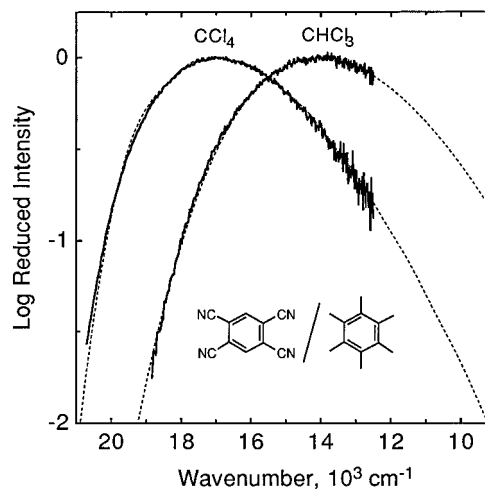


Figure 7. Charge-transfer emission spectra for the CRIP of 1,2,4,5-tetracyanobenzene/hexamethylbenzene in carbon tetrachloride and chloroform, plotted logarithmically and in "reduced" form,^{24,25} to illustrate the similarity between CT emission spectra and a plot of the electron-transfer rate constant versus the driving force, Figure 2. The dashed curves are fits using a semiclassical electron-transfer theory.²⁷ The high- and low-energy sides of the spectrum are analogous to the Marcus normal and inverted regions, respectively.^{24,25}

Figure 6, the critical turnover region is well defined. Furthermore, the absolute intensities of the CT spectra are related to the electronic coupling matrix elements for the corresponding nonradiative process.^{24,29} Thus, from analyses of the shape and intensity of a CRIP emission spectrum, *all* of the adjustable parameters required to predict the rate constant of the nonradiative electron-transfer reaction, $(k_{-et})_{cp}$, are obtained. For example, we found that the measured values for $(k_{-et})_{cp}$ could be *predicted* within a factor of 3, for rate constants that varied by almost 3 orders of magnitude when the polarity of the solvent was changed from cyclohexane to dichloroethane.²⁷ This

(29) Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1992**, *191*, 371.

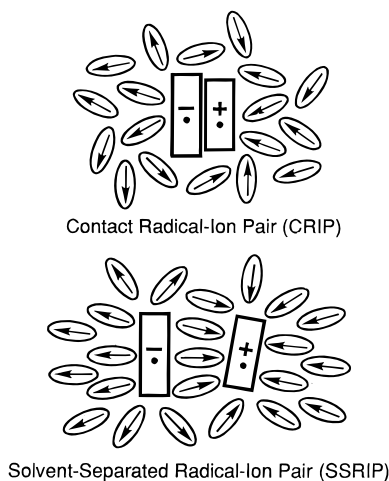


Figure 8. Simple schematic representation of contact (CRIP) and solvent-separated (SSRIP) radical-ion pairs in a polar solvent. The arrows represent the direction of the solvent dipoles.

remarkably good agreement confirms the strong quantitative relationship between the radiative and non-radiative electron-transfer reactions.³⁰

Contact and Solvent-Separated Radical-Ion Pairs: Solution to the Problem

Having demonstrated that $(k_{-et})_{cp}$ can be predicted from analysis of CRIP emissions, the CRIP data shown in Figure 6 were revisited. Weak emission from several of these CRIPs was detected in acetonitrile, and analyzed as indicated above.^{22,31} The curve through the CRIP data shown in Figure 6 is actually a prediction of the driving force dependence, based purely on the reorganization parameters and the matrix element derived from the emission spectra. The fit to the measured $(k_{-et})_{cp}$ is clearly very good, which indicates that the electron-transfer parameters for the CRIP are well defined (Figure 6).

The electronic coupling matrix element for the CRIP reactions (750 cm^{-1}) is almost 2 orders of magnitude larger than that for the SSRIP reactions ($\sim 12 \text{ cm}^{-1}$). This is not surprising because the degree of orbital overlap should be significantly larger when the radical ions are in contact than when separated by a layer of solvent molecules. On the other hand, the solvent reorganization energy for return electron transfer in the CRIP reactions ($\sim 0.5 \text{ eV}$) is much smaller than that for the SSRIP reactions ($\sim 1.6 \text{ eV}$). This can be rationalized in terms of the highly schematic representation of the radical-ion pairs shown in Figure 8. The reorganization energy for the SSRIP is larger than that for the CRIP not only because of the extra solvent molecules between the radical ions, but more importantly, because interpenetration of outer shell solvent molecules around the radical ions is greatly diminished due to the larger separation distance, resulting in higher overall solvation.^{12c,22}

The original problem with the much larger reorganization energies observed in the radical-ion pair reac-

tions compared with those encountered in self-exchange reactions was finally resolved. From Figure 6 it is obvious that an electron-transfer reaction with a free energy change of zero, which is the case for a self-exchange reaction, will occur much faster in a contact than in a solvent-separated configuration. Thus, the reorganization energies for the self-exchange reactions ($0.5\text{--}0.7 \text{ eV}$) should be similar to those for the CRIP electron-transfer reactions, as is observed. The large reorganization energy observed in the original work (Figure 1) was simply because the reactions were of the highly solvated SSRIP.

The inverted region is now well established, both in rigidly linked molecules^{11,32} and in several radical-ion pair systems.³³ Because different donor/acceptor systems could be studied easily in the radical-ion pairs, we were able to use these systems to test other molecular factors that control electron-transfer rate constants. In addition to the effect of molecular size (Figure 4),^{16,34a} we were able to demonstrate isotope^{34b} and steric effects,^{34c} and to investigate the influence of external pressure^{34d} and molecular charge.^{34e}

Reactions in the Encounter Pair: "Normal Region" Behavior

At the start of our work it was not clear whether the bimolecular quenching reaction always resulted in CRIP formation, or whether direct formation of a SSRIP could occur, bypassing the CRIP. In fact, this issue was somewhat controversial.³⁵ It was known that the yield of exciplex emissions decreased rapidly with increasing solvent polarity, but it was not known whether this was because the exciplexes were formed less efficiently,^{35a} or simply emitted less efficiently.^{35b} The product of the bimolecular quenching reaction is determined in the encounter pair A^*/D , Figure 5. No particular structure is envisioned for this species. Two competing reactions are considered to occur in the A^*/D , electron transfer to form a SSRIP, k_{et} , and diffusive motion leading to a contact configuration, k_{cp} . A reasonable assumption is that electron transfer is very fast in the contact configuration, and that the rate-determining step for CRIP formation is the diffusive process k_{cp} . If k_{et} is sufficiently large to compete with k_{cp} , then a SSRIP is formed and the contact pair is bypassed.

To determine the efficiency of CRIP formation from the encounter pair, α , we once again made use of the CRIP emissions.³⁶ The intensity of the emission for

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(35) (a) Knibbe, H.; Röllig, K.; Schäfer, F. P.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1184. (b) Mataga, N.; Murata, Y. *J. Am. Chem. Soc.* **1969**, *91*, 3144.

(36) (a) Gould, I. R.; Mueller, J. L.; Farid, S. *Z. Phys. Chem. (Munich)* **1991**, *170*, 143. (b) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176.

(30) (a) Meyer *et al.* have also used fitting of the CT emission spectra of organometallic complexes in calculating rate constants for the corresponding nonradiative decay.^{30b,c} (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (c) Barqawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47.

(31) (a) Examples of spectra and some preliminary analyses are described in ref 31b. (b) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635.

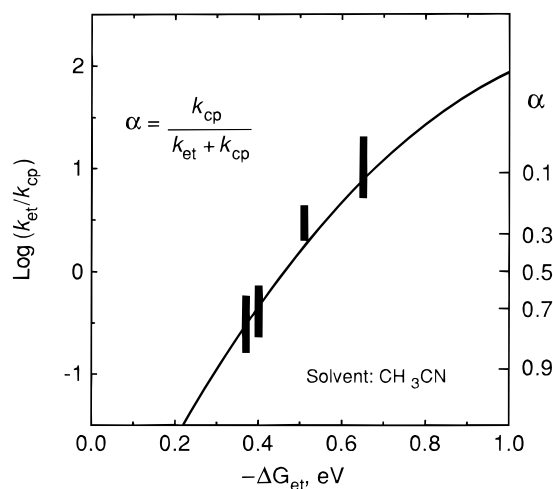


Figure 9. (left axis) Ratio of the rate constants for formation of a SSRIP (k_{et}) and a CRIP (k_{cp}) in the encounter pair A^*/D , and (right axis) CRIP formation efficiencies (α), plotted versus the driving force of the SSRIP-forming reaction, $-\Delta G_{et}$.

the bimolecular quenching reaction was compared with that via excitation into the absorption band of the corresponding CT complex, where CRIP formation is necessarily 100% efficient. Using this method, it could be shown that α was indeed less than unity for some of the reactions of the cyanoanthracenes in acetonitrile (and also in butyronitrile).³⁶ It was also shown that α is determined by the competition between k_{et} and k_{cp} (Figure 5), and depends inversely upon k_{et} , eq 6.^{22,36b} In fact, the rate constant ratio $k_{et}/$

$$\alpha = k_{cp}/(k_{et} + k_{cp}) \quad (6a)$$

$$k_{et}/k_{cp} = \alpha^{-1} - 1 \quad (6b)$$

k_{cp} was found to increase with increasing driving force, i.e., consistent with Marcus "normal region" behavior (Figure 9). Approximate values were obtained for the electron-transfer parameters for k_{et} by assuming a constant value of 10^{10} s^{-1} for k_{cp} , and curve fitting as shown in Figure 9.^{36b} The solvent reorganization energy, ca. 1.2 eV, and electronic coupling matrix element, ca. 150 cm^{-1} , lie between those of the CRIP and the SSRIP reactions (Figure 6). This suggests that formation of the SSRIP is occurring, perhaps not surprisingly, at smaller A^*/D separation distances than those typical for thermalized SSRIPs.³⁷

The SSRIP-forming reaction (k_{et}) seems to depend very strongly upon the driving force. For the cyanoanthracene/alkylbenzene systems in acetonitrile, hardly any SSRIPs are formed when the exothermicity is less than 0.4 eV, but SSRIP formation occurs with essentially unit efficiency when the exothermicity is greater than 0.6 eV. These values are, of course, a function of the reorganization parameters and electronic coupling matrix element, and could be different for other A/D systems.

Emission studies were also carried out in less polar solvents, all the way to cyclohexane. As observed

(37) (a) A change from CRIP to SSRIP formation in the bimolecular quenching reaction has been proposed to explain the absence of an inverted region in these processes.^{37b-d} (b) Rau, H.; Frank, R.; Greiner, G. *J. Phys. Chem.* **1986**, *90*, 2476. (c) Stevens, B.; Biver, C. J.; McKeithan, D. N. *Chem. Phys. Lett.* **1991**, *187*, 590. (d) Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403.

previously in other systems,³⁵ the emission yield increased rapidly with decreasing solvent polarity. However, by comparing the emission yields for bimolecular quenching and for excitation of the corresponding CT complexes, as above, it could be shown that formation of contact pairs³⁸ occurred with essentially unit efficiency in almost all of the systems studied.³⁶ The only exceptions were the reactions in the polar solvents mentioned above, and in one instance where the solvent "mediated" the electron transfer.³⁶ Thus, the increase in emission yield with decreasing solvent polarity is due to changes in the emission efficiency, rather than changes in the formation efficiency; i.e., with only a few exceptions, the CRIP is *always* an intermediate in the bimolecular quenching reaction.³⁹

Diffusional Processes and Radical-Ion Pair Energetics

A complete understanding of the radical-ion pair dynamics requires the study of the diffusive processes, indicated by the horizontal arrows in Figure 5. In a suitably polar solvent the CRIP may solvate to form a SSRIP (k_{solv}). The SSRIP may separate to form free radical ions (k_{sep}), or desolvate to reform the CRIP (k_{-solv}). As mentioned above, k_{sep} has been estimated for the reactions of DCA and TCA with alkylbenzenes as donors in acetonitrile to be ca. 5×10^8 to $1 \times 10^9 \text{ s}^{-1}$.^{6a,e,31b} For some of these systems we were also able to obtain estimates for k_{solv} . A wider range of values (ca. 2×10^8 to $1 \times 10^{10} \text{ s}^{-1}$) was determined for this process, depending upon the particular acceptor/donor pair.^{15b,22} A fairly wide range of solvation/separation rate constants have also been reported by other research groups.⁴⁰ One of the factors that is likely to control the rates of interconversion of the radical-ion pairs is their relative energies.²² In order to define this and any other factors that control the rate constants of the diffusive processes, we began a systematic study of the solvent effect on the complete dynamics of the interconverting radical-ion pairs.

The TCB/*p*-xylene pair was chosen as a model system. Rate constants were determined using a combination of time-resolved absorption and emission studies.⁴¹ As qualitatively expected, when the dielectric constant of the solvent is increased (from 7 to 24), k_{solv} and k_{sep} increase (by a factor of ca. 20), and k_{-solv} decreases (by a factor of 3).⁴² Importantly, the ratios of k_{solv}/k_{-solv} , which are equal to the equilibrium constant for the CRIP/SSRIP interconversion, K_{RIP} , were obtained.^{42,43}

By combining the K_{RIP} with free energies of formation of the CRIP obtained from emission spectra, as

(38) (a) The term contact pair is used here because, in the less polar solvents, the emitting species are not pure CRIPs, due to mixing with the locally excited states of the cyanoanthracenes.^{38b} (b) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.

(39) When the CRIP is formed with unit efficiency, it is difficult to determine whether it is formed directly from the encounter pair (k_{cp}) or whether some may come from partial SSRIP formation (via k_{et}) followed by "desolvation" to the CRIP (k_{-solv}). See ref 36b for further discussion.

(40) For a review, see: Peters, K. S. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; Jai Press: Greenwich, CT, 1994; Vol. 4, p 27.

(41) Arnold, B. R.; Noukakis, D.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1995**, *117*, 4399.

(42) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.

(43) (a) Analogous experiments have been performed for ion pairs.^{43b} (b) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401.

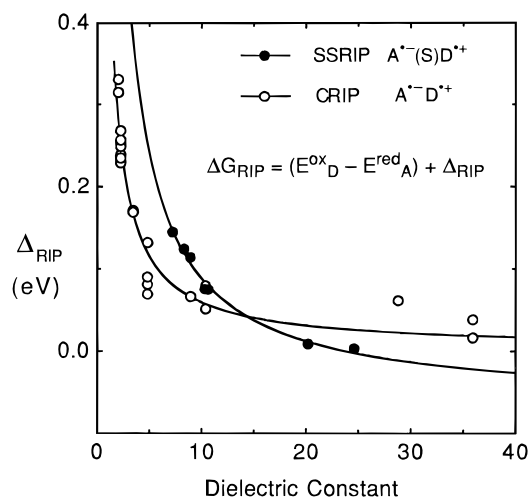


Figure 10. Plots illustrating the dependence of the free energy of formation of contact ($A^{\cdot-}D^{\cdot+}$) and solvent-separated ($A^{\cdot-}(S)D^{\cdot+}$) radical-ion pairs from the neutral acceptor and donor, as a function of solvent polarity. Δ_{RIP} is the difference between the formation free energy, ΔG_{RIP} , and the electrochemical redox energy, where E^{ox}_D and E^{red}_A are the oxidation and reduction potentials of the donor and acceptor, respectively, measured in acetonitrile. Plotting Δ_{RIP} allows A/D pairs with different electrochemical redox energies to be compared. The SSRIP data are for the TCA/*p*-xylene pair (see text). The CRIP data are for various acceptors and donors, as described in ref 42. The formation free energies are equal to the exothermicities for return electron transfer; i.e., $\Delta G_{RIP} = -\Delta G_{-et}$.

described above, the free energy of formation of *both* radical-ion pairs could be determined. The variation in these energies as a function of solvent polarity is illustrated in Figure 10. Qualitatively, the data agree with predictions of Weller for the relative energies of the radical-ion pairs,⁴⁴ although there are some quantitative differences.⁴² When the solvent dielectric constant is less than 7, the SSRIP is more than 0.1 eV higher in energy than the CRIP, and is unlikely to play any significant role in the bimolecular electron-transfer reactions. The SSRIP and CRIP energies become equal when the solvent dielectric constant is approximately 13, and maintain a fairly small energy difference to higher polarities. Extrapolation to a dielectric constant of 36, i.e., that of acetonitrile, indicates that the SSRIP is only ca. 0.04 eV lower in energy than the CRIP. This gap is sufficiently small that CRIP/SSRIP interconversion is possible even in this polar solvent, although for the systems we have studied, $(k_{-et})_{ss}$ and k_{sep} are so large in acetonitrile that re-formation of the CRIP from the SSRIP does not occur to any significant extent. Further work is

(44) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, 133, 93.

required to determine whether the relative energies of the CRIP and SSRIP vary with the structure of the A/D pair, which would provide an explanation for the relatively large variations in k_{solv} mentioned above.

Concluding Remarks

Building on pioneering concepts advanced largely by Weller and Mataga, a clear picture of the roles of the various intermediates in bimolecular electron transfer has emerged. One interesting outcome has been the demonstration of the crucial role of the Marcus inverted region in controlling the reactions of the radical-ion pairs. Remarkably, return electron transfer in the SSRIP can actually be *faster* than in the CRIP, depending upon the reaction exothermicity (Figure 6), because of the marked differences in their solvent reorganization energies. The return-electron-transfer rate constants, and hence the overall reaction efficiencies, can be manipulated using a number of different molecular properties,⁴⁵ although the reaction driving force exerts the largest influence.^{45a} This is taken advantage of in the "cosensitization" scheme, where relatively slow return electron transfer in the radical-ion pair of a high oxidation potential donor (the cosensitizer) results in efficient formation of separated radical cations that can subsequently oxidize a wide range of other donors with high overall quantum yield.¹⁶

So far, this work has been limited mainly to cyanoaromatic acceptors and simple aromatic hydrocarbon donors. The extent to which their quantitative behavior can be generalized to other systems is not clear, although the broad mechanistic trends are surely universal. A final important issue is that although the electron-transfer theories describe the reactions of the CRIP very well, they will have to be extended for the more general case of exciplexes, where the extent of charge transfer is variable (see Figure 5). Work along these lines is currently in progress.

We are very grateful for the efforts of all our collaborators, whose names appear in the references. We particularly acknowledge the invaluable contributions of Ralph H. Young, Eastman Kodak Co., to the theoretical understanding of many of the processes discussed here, and a very fruitful collaboration with Joshua L. Goodman, University of Rochester, on the dynamics of radical-ion pairs. This part of the work was performed at the Center for Photoinduced Charge Transfer at the University of Rochester (NSF Grant CHE-8810024).

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