Bimolecular Electron Transfers That Follow a Sandros−Boltzmann Dependence on Free Energy

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Ⓢ *Supporting Information*

ABSTRACT: Rate constants (k) for exergonic and endergonic electron-transfer reactions of equilibrating radical cations ($A^{\bullet+} + B \rightleftharpoons A + B^{\bullet+}$) in acetonitrile could be fit well by a simple Sandros−Boltzmann (SB) function of the reaction free energy (ΔG) having a plateau with a limiting rate constant k_{lim} in the exergonic region, followed, near the thermoneutral point, by a steep drop in log k vs ΔG with a slope of $1/RT$. Similar behavior was observed for another charge shift reaction, the electron-transfer quenching of excited pyrylium cations (P^{+*}) by neutral donors ($P^{+*} + D \rightarrow P^{\bullet} + D^{\bullet+}$). In this case, SB dependence was observed when the logarithm of the quenching constant (log k_q) was plotted vs $\Delta G + s$, where the shift term, s, equals +0.08 eV and ΔG is the free energy change for the net reaction ($E_{redox} - E_{excit}$). The shift term is attributed to partial desolvation of the radical cation in the product encounter pair ($P^{\bullet}/D^{\bullet+}$), which raises its free energy relative to the free species. Remarkably, electron-transfer quenching of neutral reactants ($A^* + D \rightarrow A^{\bullet-} + D^{\bullet+}$) using excited cyanoaromatic acceptors and aromatic hydrocarbon donors was also found to follow an SB dependence of log k_q on ΔG, with a positive s, +0.06 eV. This positive shift contrasts with the long-accepted prediction of a negative value, −0.06 eV, for the free energy of an $A^{\bullet-}/D^{\bullet+}$ encounter pair relative to the free radical ions. That prediction incorporated only a Coulombic stabilization of the $A^{\bullet-}/D^{\bullet+}$ encounter pair relative to the free radical ions. In contrast, the results presented here show that the positive value of s indicates a decrease in solvent stabilization of the $A^{\bullet-}/D^{\bullet+}$ encounter pair, which outweighs Coulombic stabilization in acetonitrile. These quenching reactions are proposed to proceed via rapidly interconverting encounter pairs with an exciplex as intermediate, $A^*/D \rightleftharpoons$ exciplex $\rightleftharpoons A^{\bullet-}/D^{\bullet+}$. Weak exciplex fluorescence was observed in each case. For several reactions in the endergonic region, rate constants for the reversible formation and decay of the exciplexes were determined using time-correlated single-photon counting. The quenching constants derived from the transient kinetics agreed well with those from the conventional Stern−Volmer plots. For excited-state electron-transfer processes, caution is required in correlating quenching constants vs reaction free energies when ΔG exceeds ∼+0.1 eV. Beyond this point, additional exciplex deactivation pathways—fluorescence, intersystem crossing, and nonradiative decay—are likely to dominate, resulting in a change in mechanism.
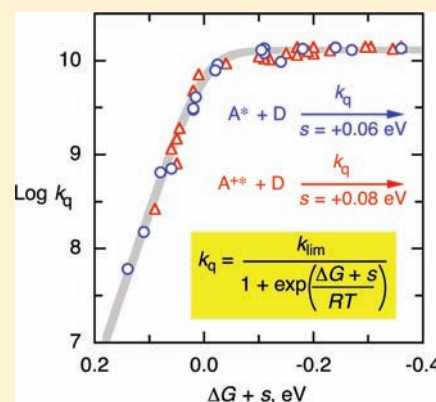
■ INTRODUCTION

Electron-transfer processes are ubiquitous in chemistry. A subset of these reactions—photoinduced electron transfers—plays an important role in nature and in several technological applications.[1] As a result, considerable effort has been devoted to exploring photoinduced electron-transfer processes from both experimental and theoretical perspectives.[2] In a landmark paper, Rehm and Weller demonstrated 40 years ago how the energetics of bimolecular photoinduced electron transfer are a function of the excitation energies and redox potentials of the reactants.[3] They also described the functional dependence of the excited-state quenching constants on the free energies of electron transfer. Importantly, their kinetic model introduced a *negative* free-energy shift term to accommodate Coulombic stabilization of the radical ion pair that is initially formed by electron-transfer

quenching. This term has been nearly universally used in subsequent studies.[4]

Since the pioneering work of Rehm and Weller, other models have been proposed to explain the kinetics of photoinduced electron-transfer reactions, especially those in polar solvents.[5] To critically evaluate any of these models, it is essential to have thermodynamically meaningful redox potentials for the substrates undergoing electron transfer. Unfortunately, oxidation and reduction potentials commonly obtained from electrochemical measurements for many of the reactants studied to date are unreliable because the electrochemical processes are not reversible. The irreversible nature of these processes can be traced to rapid decomposition of the radical ions produced by electron

transfer and/or slow heterogeneous electron transfer at electrode surfaces. Clearly, solutions to this problem are needed to make progress in the development and refinement of models for electron-transfer reactions in general, and photoinduced electron-transfer reactions in particular.

We recently described flash photolysis methods for accurately determining oxidation potentials for a number of benzene and biphenyl derivatives in acetonitrile.[6] This work additionally provided an opportunity to determine the rate constants for electron exchange between the neutral electron donors and their corresponding radical cations, i.e., a charge-shift reaction.[6a] Herein, we present data showing that these electron-transfer rate constants depend on the reaction free energy in a surprising manner: they follow a simple Boltzmann-type dependence. In addition, similar Boltzmann-type dependences were found for photoinduced electron transfers from these neutral electron donors to cationic and neutral excited-state electron acceptors. Interestingly, both sets of photoinduced electron-transfer reactions required introduction of a *positive* free-energy shift term to best fit the dependence of the electron-transfer quenching constants on the free energies for electron transfer. Rationalization of this revised free-energy shift term will be provided, as well as general implications for the interpretation of photoinduced electron-transfer rate data.

■ RESULTS AND DISCUSSION

1. Ground-State Electron Transfer between a Radical Cation and a Neutral Donor. Using techniques described in detail elsewhere,[6a] laser flash photolysis methods were used to generate the radical cations of neutral electron donors (A and B) in acetonitrile and to measure the kinetics and equilibrium constants for the charge-exchange reaction shown in eq 1. When the difference between the oxidation potentials (E_{ox}) of molecules A and B was small (≤ 0.2 V), the respective forward and reverse electron-transfer rate constants, k and k', could both be determined. The equilibrium constant K was also determined and used to evaluate the associated free-energy difference, ΔG, eq 2, which is identical to the difference in oxidation potentials, eq 3. Thus, in these cases for each A,B pair, two rate constants at corresponding negative and positive ΔG were obtained. When the difference between the oxidation potentials was larger than 0.2 V, the endergonic electron-transfer rate constant became too small to determine accurately. In these cases the exergonic electron-transfer rate constants could nonetheless be determined from the pseudo-first-order decay of the radical cation signal as a function of the electron donor concentration, e.g., k for disappearance of $[A^{\bullet+}]$ as a function of $[B]$; the difference between the oxidation potentials[6] of A and B was used to determine ΔG, eq 3.

$$A^{\bullet+} + B \underset{k'}{\overset{k}{\rightleftharpoons}} A + B^{\bullet+} \tag{1}$$
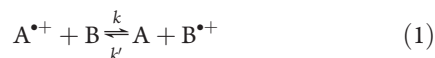
$$K = e^{-\Delta G/RT} = k/k' \tag{2}$$

$$\Delta G = E_{ox}(B) - E_{ox}(A) \tag{3}$$

A plot of the logarithm of the electron-transfer rate constants vs ΔG for various A,B pairs consisting of benzene and biphenyl derivatives (Table 1) is shown in Figure 1. Surprisingly, the data can be fit by a simple Boltzmann-type relationship (eq 4), where k represents the electron-transfer rate constant in either direction

Table 1. Rate Constants for Equilibration between Radical Cations of Benzene and Biphenyl Derivatives[a] in Acetonitrile at Room Temperature and the Corresponding Reaction Free Energy Change[b]

A	B	ΔG (eV)	k (M^{-1} s^{-1})	k' (M^{-1} s^{-1})
BP1	durene	−0.043	7.63×10^9	1.39×10^9
BP5	toluene	−0.087	7.65×10^9	2.55×10^8
BP3	*p*-xylene	−0.094	9.98×10^9	2.56×10^8
HMB	fluorene	−0.12	7.1×10^9	6.0×10^7
benzene	BP5	−0.13	5.8×10^9	3.1×10^7
toluene	BP3	−0.15	9.8×10^9	3.0×10^7
benzene	BP4	−0.20	7.5×10^9	3.4×10^6
toluene	BP2	−0.31	1.3×10^{10}	
BP2	HMB	−0.37	9.7×10^9	
o-xylene	HMB	−0.51	9.0×10^9	

[a] BP1−5 are biphenyl derivatives (BP1, 4-methyl; BP2, unsubstituted; BP3, methyl 4-carboxylate; BP4, di-*n*-butyl 4,4′-dicarboxylate; BP5, *n*-butyl 4-carboxylate 4′-trifluoromethyl); HMB is hexamethylbenzene. [b] Compounds arranged so that $E_{ox}(A) > E_{ox}(B)$ and in order of increasing exergonicity. For the last three entries only the exergonic rate constant could be measured; see text.
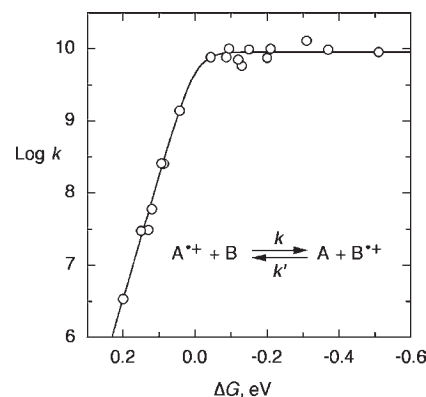

Figure 1. Plot of electron-transfer rate constants, eq 1, vs free energy change for reactions of radical cations with neutral donors in acetonitrile (Table 1). The curve is a fit to eq 4, with $k_{lim} = 9 \times 10^9$ M^{-1} s^{-1}.

and k_{lim} is the limiting or plateau value at relatively high exergonicity. Rate constants in the plateau region are largely controlled by the second-order rate constant for diffusion. Equation 4 is similar to the expression first proposed by Sandros[7] that has often been applied to classical triplet energy transfer, i.e. to triplet energy transfer without an apparent activation barrier. We will refer to this type of behavior as a Sandros−Boltzmann (SB) dependence on free energy.

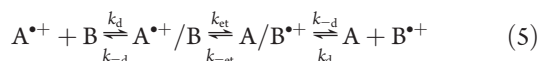$$k = \frac{k_{lim}}{1 + \exp\left(\dfrac{\Delta G}{RT}\right)} \tag{4}$$

To understand the implications of eq 4, the reaction intermediates for electron transfer should be considered. Endergonic or mildly exergonic electron transfer is expected to occur at contact according to the expanded reaction scheme in eq 5. There, $A^{\bullet+}/B$ and $A/B^{\bullet+}$ represent encounter (contact) pairs, k_d and k_{-d} are the rate constants for their formation and dissociation, and k_{et} and k_{-et} are rate constants for electron exchange

Table 2. Symmetrically Substituted Pyrylium Acceptors and Their Excitation Energies (E_{excit}), Reduction Potentials (E_{red}), Excited-State Oxidizing Power ($E_{excit} + E_{red}$), and Singlet Excited-State Lifetimes (τ), All Measured in Acetonitrile[a]

pyrylium acceptor	R	R′	E_{excit}[b] (eV)	E_{red}[c] (V vs SCE)	$E_{excit} + E_{red}$ (V vs SCE)	τ[d] (ns)
P1$^+$	OEt	H	2.40	−0.46	1.94	5.7
P2$^+$	Me	Me	2.70	−0.42	2.28	4.7
P3$^+$	Et	H	2.67	−0.38	2.29	5.0
P4$^+$	Et	CN	2.58	−0.25	2.33	5.9
P5$^+$	H	H	2.83	−0.32	2.51	4.4
P6$^+$	H	CN	2.73	−0.19	2.54	5.4
P7$^+$	CN	H	2.90	−0.11	2.79	4.5

[a] Compounds listed in increasing order of their excited-state oxidizing power. [b] See Supporting Information for spectral data. [c] The reduction potentials are from ref 8; new measurements confirmed their accuracy to be within 2 mV. [d] The lifetimes were measured under air. Because of the short lifetime and relatively high (less negative) reduction potential, these compounds are fairly insensitive to oxygen quenching. For example, the lifetime of P5^{+*} under argon is only 2% longer than under air. The lifetimes of P1^{+*}–P7^{+*} have been reported previously;[8] those for P2$^+$–P6$^+$ agree within 1% with the new measurements (listed in the table); remeasured values for P1$^+$ and P7$^+$ were found to be greater than those reported earlier.

within an encounter pair. Here the reasonable approximation is made that k_d and k_{-d} for reactant and product pairs are the same because of their structural similarity. Further, while there is a difference in free energy between an encounter pair and the corresponding free ions (see below), that difference is assumed to be the same for the reactants and the products. Therefore, the free energy of reaction between the encounter pairs is the same as that for the overall reaction, ΔG. Applying the steady-state approximation to the encounter pairs results in eq 6.

$$A^{\bullet+} + B \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} A^{\bullet+}/B \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} A/B^{\bullet+} \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} A + B^{\bullet+} \quad (5)$$

$$k = \frac{k_d}{1 + \dfrac{k_{-d}}{k_{et}} + \exp\left(\dfrac{\Delta G}{RT}\right)} \quad (6)$$

Equation 6 reduces to the SB form, eq 4, with $k_{lim} = k_d$, provided that the term k_{-d}/k_{et} is always small compared to 1 plus the exponential term. That the data fit well to eq 4 provides strong support for this conclusion. It follows, further, that k_{-d} is small compared to k_{et} in the weakly endergonic through exergonic region and that k_{-d} is small compared to k_{-et} in the endergonic through the weakly exergonic region. Hence, in the latter region, equilibrium is maintained between the encounter pairs, and eq 4 is a direct consequence of this equilibrium. (For details see the Supporting Information.)

The observation of an SB dependence instead of a more gradual transition between the endergonic and exergonic regimes in Figure 1—the usual expectation for a Rehm–Weller-type plot[3]—prompted us to explore other types of bimolecular electron-transfer reactions to test the generality of this behavior.

2. Quenching of an Excited-State Cation by a Neutral Donor. We chose next to investigate charge-shift excited-state electron-transfer reactions because of their similarity to the ground-state reactions described above. In these excited-state reactions, pyrylium cationic electron acceptors (P^{+*}) and neutral electron donors (D) were used, eq 7.

$$P^{+*} + D \overset{k_q}{\longrightarrow} P^{\bullet} + D^{\bullet+} \quad (7)$$

Symmetrically substituted pyrylium salts (P$^+$) are ideally suited as excited-state electron acceptors. Their reduced absorption and emission spectra are superimposable mirror images, allowing the accurate determination of the excited-state energies

(see Supporting Information). The one-electron reductions of P$^+$ in acetonitrile by cyclic voltammetry are reversible, thus providing accurate reduction potentials. In addition, the oxidizing power of the pyrylium cations can be varied over a large range by appropriate substitution (cf. Table 2).

P$^+$
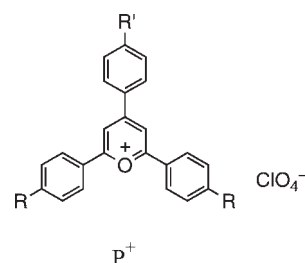
Benzene and biphenyl derivatives were chosen as electron donors to determine quenching constants (k_q) of the pyrylium acceptors because accurate oxidation potentials for these donors have been recently measured.[6] The quenching constants of seven P$^+$ derivatives were determined in acetonitrile from Stern–Volmer plots of the fluorescence quenching and/or from lifetime measurements as a function of quencher concentration (Table 3). The two techniques yielded the same results within experimental error (<10%). Comparison between the two sets of data is shown in the Supporting Information for the quenching of P3$^+$ with o-, m-, and p-xylenes.

As shown in Figure 2, the quenching constants, k_q, can be fit well with an SB free-energy dependence if ΔG, the net reaction free energy, eq 8, is replaced by $\Delta G + s$, eq 9. In eq 8, E_{redox} is the difference between the oxidation potential of D and reduction potential of P$^+$, and E_{excit} is the excitation energy of P$^+$. Best fit was obtained for a shift value of $s = 0.08$ eV and $k_{lim} = 1.3 \times 10^{10}$ M^{-1} s^{-1}.

$$\Delta G = E_{redox} - E_{excit} \quad (8)$$

$$k_q = \frac{k_{lim}}{1 + \exp\left(\dfrac{\Delta G + s}{RT}\right)} \quad (9)$$

Equation 9 can be understood in terms of the mechanistic scheme in eq 10, where P^{+*}/D and P$^{\bullet}$/D$^{\bullet+}$ are encounter pairs for the forward and reverse reactions; k_d, k_{-d} and k'_d, k'_{-d} are

Table 3. Reactions of Pyrylium Acceptors with Aromatic Hydrocarbon Donors, Oxidation Potentials of the Donors,[6a] Free Energy Change for Electron Transfer (ΔG), Given by $E_{ox}(D) - E_{red}(A) - E_{excit}$, from Table 2, and Quenching Constants for Singlet Excited Pyryliums in Acetonitrile at Room Temperature (k_q)[a]

acceptor	donor[b]	$E_{ox}(D)$ (V v SCE)	ΔG + 0.08 (eV)	k_q (10^9 M^{-1} s^{-1})
P6$^+$	m-xylene	2.10	−0.36	14.1
P4$^+$	124-TMB	1.905	−0.345	13.4
P3$^+$	124-TMB	1.905	−0.305	14.0
P2$^+$	124-TMB	1.905	−0.295	14.0
P7$^+$	benzene	2.48	−0.23	12.8
P3$^+$	p-xylene	2.01	−0.20	11.8
P6$^+$	toluene	2.26	−0.20	13.9
P2$^+$	p-xylene	2.01	−0.19	12.6
P5$^+$	toluene	2.26	−0.17	13.9
P1$^+$	PMB	1.69	−0.17	11.5
P2$^+$	mesitylene	2.05	−0.15	12.0
P3$^+$	o-xylene	2.09	−0.12	10.3
P1$^+$	durene	1.75	−0.11	11.0
P3$^+$	m-xylene	2.10	−0.11	10.8
P2$^+$	o-xylene	2.09	−0.11	11.1
P2$^+$	m-xylene	2.10	−0.10	11.1
P1$^+$	1235-TMB	1.82	−0.04	9.3
P4$^+$	toluene	2.26	+0.01	7.1
P6$^+$	benzene	2.48	+0.02	4.8
P1$^+$	124-TMB	1.905	+0.045	1.91
P3$^+$	toluene	2.26	+0.05	1.48
P5$^+$	benzene	2.48	+0.05	0.81
P2$^+$	toluene	2.26	+0.06	1.15
P1$^+$	biphenyl	1.95	+0.09	0.26

[a] Data listed in order of decreasing exergonicity. [b] 124-TMB is 1,2,4-trimethylbenzene, and 1235-TMB is 1,2,3,5-tetramethylbenzene.
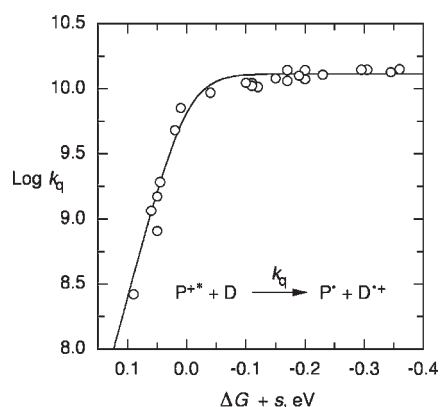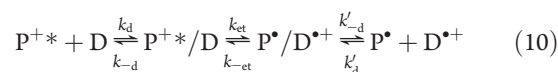

Figure 2. Plot of log k_q vs $\Delta G + s$ for electron-transfer quenching of excited pyrylium cations in acetonitrile (circles). The curve is according to eq 9 with s = +0.08 eV and k_{lim} = 1.3 × 10^{10} M^{-1} s^{-1}. Contributions to the shift term s are discussed in the text.

rate constants for diffusional encounter and separation. The reverse reaction, k'_d, has been included formally, but it is insignificant because the free D$^{\bullet+}$ are relatively short-lived in acetonitrile and generated in low concentration. The intrinsic

deactivation of P^{+*} in eq 10 is omitted for clarity.

$$P^{+*} + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} P^{+*}/D \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} P^{\bullet}/D^{\bullet+} \underset{k'_d}{\overset{k'_{-d}}{\rightleftharpoons}} P^{\bullet} + D^{\bullet+} \quad (10)$$

No exciplex fluorescence was detected (quantum yield <10^{-4}) for any of the pyrylium quenching reactions. Furthermore, all of the decays of P^{+*} measured by single-photon counting (SPC) were cleanly monoexponential. Therefore, the quenching constant, k_q, is also the effective rate constant for the net reaction in eq 7. These data require that if any exciplexes are formed, they must be short-lived and/or have low radiative rate constants. As described in section 3, another potential intermediate between P$^{\bullet}$/D$^{\bullet+}$ and the free species is a solvent-separated pair, P$^{\bullet}$(S)D$^{\bullet+}$. While some return electron is possible from such an intermediate, it does not contribute detectably to the steady-state or transient emissions.

An expression for k_q, eq 11, is readily derived by use of the steady-state approximation for the two intermediates (see Supporting Information). In eq 11, $\Delta G + \delta$ is the free energy of reaction within the encounter pairs. It may differ from the overall free energy of reaction, ΔG, because formation of the encounter pairs entails desolvation of ions, and the associated free energy change may be different for P^{+*}/D and P$^{\bullet}$/D$^{\bullet+}$. A positive value of δ means that the free energy of P$^{\bullet}$/D$^{\bullet+}$ relative to P$^{\bullet}$ + D$^{\bullet+}$ is greater than the free energy of P^{+*}/D relative to P^{+*} + D.

Similar to the discussion in section 1, eq 11 reduces to the SB form, eq 9, if k_{-d}/k_{et} is small compared to the rest of the denominator. As in the previous reaction, equilibrium is maintained between the encounter pairs throughout the endergonic and weakly exergonic regions, and the SB dependence is a consequence. Then k_{lim} corresponds to k_d and s to $\delta + RT\ln(k_d/k'_{-d})$.

$$k_q = \frac{k_d}{1 + \dfrac{k_{-d}}{k_{et}} + \dfrac{k_d}{k'_{-d}} \exp\left(\dfrac{\Delta G + \delta}{RT}\right)} \quad (11)$$

Although formation of P^{+*}/D from P^{+*} + D entails a partial desolvation of an ion, this factor apparently does not appreciably reduce the limiting value of k_q,[9] because k_{lim} observed for the quenching of P^{+*} is the same as for the quenching of excited neutral acceptors with similar neutral donors, as described below in section 3. The reason may be that the large, delocalized P^{+*} is relatively poorly solvated and, from it, the small D displaces only a small fraction of the surrounding solvent molecules. On the product side, however, P$^{\bullet}$/D$^{\bullet+}$ likely requires a greater desolvation energy relative to P$^{\bullet}$ + D$^{\bullet+}$ because D$^{\bullet+}$ is a smaller ion than P^{+*} and because D$^{\bullet+}$ is shielded to a greater extent by the much larger, neutral partner P$^{\bullet}$. Assuming a face-to-face geometry for P$^{\bullet}$/D$^{\bullet+}$, the adjacent P$^{\bullet}$ would prevent solvent access to one entire face and part of the edge of D$^{\bullet+}$. This effect will raise the free energy of P$^{\bullet}$/D$^{\bullet+}$ relative to that of P$^{\bullet}$ + D$^{\bullet+}$; i.e., the free energy of reaction will be higher for the encounter pairs than for the net reaction, implying that $\delta > 0$. Because of the exergonicity of the dissociation reaction (k'_{-d}), the term $RT\ln(k_d/k'_{-d})$ is likely to be small or negative, and δ is likely to be the main contribution to the observed shift (s) of +0.08 eV.

For the present reactions and those discussed below in section 3, k_{lim} (1.3 × 10^{10} M^{-1} s^{-1}) is larger than the value found for reactions of small radical ions, A$^{\bullet+}$ + B (9 × 10^9 M^{-1} s^{-1}) in section 1. This difference is consistent with a greater desolvation to form a reactant encounter pair, A$^{\bullet+}$/B, in the latter case.

Table 4. Cyanoaromatic Acceptors, with Their Excitation Energies and Reversible Reduction Potentials (V vs SCE),[8] Donor Quenchers, with Their Oxidation Potentials (V vs SCE),[6a] Free Energy Change for the Quenching Reaction (ΔG), Given by $E_{ox}(D) - E_{red}(A) - E_{excit}$, and Quenching Constants (k_q) for Singlet Excited State in Acetonitrile at Room Temperature

acceptor[a]	donor[b]	E_{excit} (eV)	$E_{red}(A)$	$E_{ox}(D)$	$\Delta G + 0.06$ (eV)	k_q (10^9 M^{-1} s^{-1})
TCA	p-xylene	2.87	−0.44	2.01	−0.36	13.5
TCA	m-xylene	2.87	−0.44	2.10	−0.27	13.0
DCA	PMB	2.90	−0.91	1.69	−0.24	13.8
DCA	durene	2.90	−0.91	1.75	−0.18	13.4
DCN	m-xylene	3.57	−1.27	2.10	−0.14	9.7
TCA	toluene	2.87	−0.44	2.26	−0.11	12.0
TriCA	p-xylene	2.85	−0.67	2.01	−0.11	13.5
DCA	1234-TMB	2.90	−0.91	1.825	−0.105	13.0
DCA	124-TMB	2.90	−0.91	1.905	−0.025	9.1
TriCA	m-xylene	2.85	−0.67	2.10	−0.02	7.9
1CN	124-TMB	3.83	−1.88	1.905	+0.015	4.1
DCA	biphenyl	2.90	−0.91	1.95	+0.02	3.1
DCN	toluene	3.57	−1.27	2.26	+0.02	3.0
1CN	biphenyl	3.83	−1.88	1.95	+0.06	0.71
DCA	p-xylene	2.90	−0.91	2.01	+0.08	0.65
TCA	benzene	2.87	−0.44	2.48	+0.11	0.15
TriCA	toluene	2.85	−0.67	2.26	+0.14	0.061

[a] Acceptors: 1-cyanonaphthalene (1CN), 1,4-dicyanonaphthalene (DCN), 9,10-dicyanoanthracene (DCA), 2,9,10-tricyanoanthracene (TriCA), 2,6,9,10-tetracyanoanthracene (TCA). [b] Donors: 1,2,4-trimethylbenzene (124-TMB), 1,2,3,4-tetramethylbenzene (1234-TMB), pentamethylbenzene (PMB).

3. Quenching of a Neutral Excited State by a Neutral Donor. Having established that both ground- and excited-state electron transfers to cationic acceptors described above follow an SB dependence on the reaction free energy, we next turned to the most commonly studied photoinduced electron-transfer reactions—those involving neutral donors and acceptors. In this section we sequentially discuss the following aspects of one set of such quenching reactions: (1) the observed dependence of k_q on the reaction energetics, (2) a reaction scheme that incorporates all intermediates, (3) the ranges of ΔG where a single quenching mechanism applies, (4) the kinetic parameters, (5) a detailed analysis of the transient and steady-state kinetics, and (6) the relative energies of the intermediates.

3.1. Dependence of k_q on Reaction Energetics. We chose to study several cyanoanthracenes and cyanonaphthalenes as neutral, excited-state electron acceptors (A*) because they have well-characterized excitation energies and show reversible reduction potentials.[8] The quenching of these excited-state acceptors by the substituted benzene and biphenyl electron donors (D) used above was studied in acetonitrile. These acceptor/donor systems have been extensively investigated, the reaction intermediates characterized, and their deactivation paths quantified.[10]

The quenching constants (k_q), Table 4, were determined from Stern−Volmer plots and/or from single-photon counting (SPC) kinetics; details are discussed in section 3.3. We first present the final results, however, to help guide the discussion about the nature of the reactive intermediates in the following section. As shown in Figure 3, the quenching constants for the cyanoaromatics exhibit an SB dependence (eq 9) when plotted vs the free energy of the net reaction ΔG (eq 8), with a shift $s = +0.06$ eV and $k_{lim} = 1.3 \times 10^{10}$ M^{-1} s^{-1}. The origin of the shift parameter, s, is similar to that for the pyrylium quenching reactions although, as described below, different in its details.

3.2. Intermediates in Electron-Transfer Fluorescence Quenching. Equation 12 incorporates the key intermediates
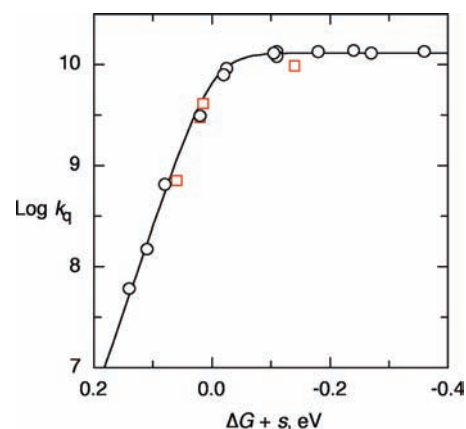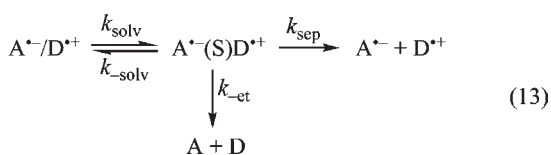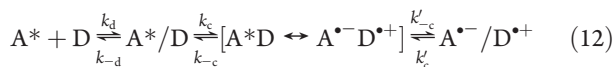

Figure 3. Plot of log k_q, the quenching constants of excited cyanoaromatics by benzene and biphenyl derivatives in acetonitrile, vs $\Delta G + s$, where $\Delta G = E_{redox} - E_{excit}$, the free energy change for the net electron-transfer reaction, and s is a free-energy shift term (see text for details). The black circles are for cyanoanthracenes, and the red squares are for cyanonaphthalenes as acceptors, Table 4. The fitting curve is according to eq 9, with $k_{lim} = 1.3 \times 10^{10}$ M^{-1} s^{-1} and $s = 0.06$ eV.

necessary to discuss the quenching reactions of neutral acceptors and donors. Species A*/D is an encounter pair where A* and D are in contact, but with various possible orientations and no specific binding. Analogously, A$^{•−}$/D$^{•+}$ represents an encounter pair on the product side, a radical ion pair in contact with various possible orientations and no specific binding. Intermediate between these encounter pairs is an exciplex, represented by [A*D ↔ A$^{•−}$D$^{•+}$]. This is a bound species where the two components are in contact, with the proper orientation for strong orbital overlap. Mixing between locally excited (A*D) and ion-pair (A$^{•−}$D$^{•+}$) components contributes to the binding energy of the exciplex; the free energy of the exciplex, relative to

the pure A^*D and $A^{\bullet-}D^{\bullet+}$ components, varies with the energy gap between them. The rate constants k_c and k_{-c} refer to conformational alignment of the components to form the exciplex and reversion to the A^*/D encounter pair, respectively. Analogously, k'_c and k'_{-c} refer to the interchange between the exciplex and an $A^{\bullet-}/D^{\bullet+}$ encounter pair.

It has long been recognized that, besides the radical ion pair at contact, a solvent-separated radical ion pair (SSRIP), $A^{\bullet-}(S)D^{\bullet+}$, plays an important role in electron-transfer reactions.[11] Thus, the ionic encounter pair, $A^{\bullet-}/D^{\bullet+}$, can undergo solvation to form a SSRIP, eq 13, which decays by return electron transfer (k_{-et}) or dissociation to the free ions, k_{sep}.[12]

$$A^* + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} A^*/D \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} [A^*D \leftrightarrow A^{\bullet-}D^{\bullet+}] \underset{k'_c}{\overset{k'_{-c}}{\rightleftharpoons}} A^{\bullet-}/D^{\bullet+} \quad (12)$$

$$A^{\bullet-}/D^{\bullet+} \underset{k_{-solv}}{\overset{k_{solv}}{\rightleftharpoons}} A^{\bullet-}(S)D^{\bullet+} \overset{k_{sep}}{\longrightarrow} A^{\bullet-} + D^{\bullet+}$$
$$\downarrow k_{-et}$$
$$A + D \quad (13)$$

At the low excitation intensities used here, the concentrations of free $A^{\bullet-}$ and $D^{\bullet+}$ are very low.[13] Consequently, the diffusional reencounter of $A^{\bullet-}$ and $D^{\bullet+}$ cannot compete with their first-order decay processes (reaction with solvent, water, or trace impurities), and the terminal dissociation step (k_{sep}) is effectively irreversible.

In principle, additional deactivation pathways of the exciplex are possible but play a minor role *for the reactions studied here* and have not been included in eqs 12 and 13.[10a] For example, exciplexes can undergo a number of decay processes: fluorescence (k_f), intersystem crossing (k_{isc}), and internal conversion (nonradiative decay to the ground state, k_{nr}). For the cyanoanthracene/alkylbenzene exciplexes shown above, all of these deactivation paths have been previously characterized quantitatively.[10] For the exciplexes associated with reactions in the endergonic and mildly exergonic range, down to ($\Delta G + s$) = -0.05 eV of Figure 3, the sum of $k_f + k_{isc} + k_{nr}$ is not expected to exceed 2×10^7 s^{-1},[10a] whereas the measured rate constants for disappearance of the exciplex (k_E) are about an order of magnitude higher (see below). Clearly, the k_f, k_{isc}, and k_{nr} deactivation processes are minor contributors *in this range of free energies*. As for the $A^{\bullet-}/D^{\bullet+}$ encounter pair in the same range, the analogous deactivation rate constants should be no larger, and insignificant compared with a $k_{solv} \approx 7 \times 10^9$ s^{-1} (see below). Therefore, in the endergonic and mildly exergonic range, separation of the radical ion pair should be the only important deactivation process. At high exergonicities, the quenching is diffusion-limited, and it does not matter if additional decay channels become possible.

3.3. Quenching Mechanism in Different Ranges of ΔG.
For electron-transfer quenching, it is useful to consider four approximately defined regions of reaction free energy (ΔG) with regard to the intervention of exciplexes. Two of these regions are relevant to the current work. In the moderately endergonic to moderately exergonic region ($\Delta G \approx -0.1$ to $+0.1$ eV), exciplexes of varying charge-transfer character are likely to be formed and to interconvert with A^*. Evidence for this situation will be presented below. In the moderately exergonic region

($\Delta G \approx -0.1$ to -0.4 eV), any exciplex that forms will not dissociate to regenerate A^*, and k_q will level off at a limiting value, k_{lim}.

Beyond these ranges, in the highly exergonic region (ΔG more negative than -0.4 eV), formation of an exciplex is likely to be bypassed[10f] by long-distance electron transfer, leading directly to SSRIP with a rate constant that can exceed that in the moderately exergonic region.[14] Additional evidence for such an increase in the quenching constant has been reported recently.[5e] However, the flat plateau in our experiments as well as numerous other analyses[5e,14d,14h−14k,14m] in polar solvents of low viscosity supports the adequacy of a simple encounter complex or contact electron transfer model for ΔG less negative than -0.4 eV.

Finally, in the more highly endergonic region ($\Delta G > +0.1$ eV; here, $\Delta G + s > 0.16$ eV; see below), the free energy of $A^{\bullet-}/D^{\bullet+}$ relative to that of the exciplex becomes so large and dissociation of the exciplex to produce SSRIP becomes so slow that other decay processes of the exciplex (fluorescence, intersystem crossing, and nonradiative decay to the ground state) can become the major contributors to the net quenching, and the reaction mechanism can deviate from simple electron transfer. There is another problem with quenching data in this endergonic range. High donor concentrations are required to measure the inefficient quenching in this range, which can alter the polarity and other properties of the medium, potentially altering the lifetime or the ratio of the deactivation paths of free A^* and the redox energies of A and D. The range of ΔG selected in Figure 3 was chosen with these considerations in mind to represent a uniform quenching mechanism.

3.4. Kinetic Parameters.
The SB dependency of k_q in Figure 3 can readily be explained if the two encounter pairs in eq 12, A^*/D and $A^{\bullet-}/D^{\bullet+}$, interconvert rapidly; i.e., k_c and k'_c are appreciably larger than k_{-d} and k_{solv}, respectively. In this case, k_q is given by the SB eq 9, with k_{lim} approximately equal to k_d and with the shift term s given by eq 14.[15] Eq 14 can again be regarded as a consequence of a rapid equilibrium between the reactant and product encounter pairs. (See Supporting Information for derivations.)
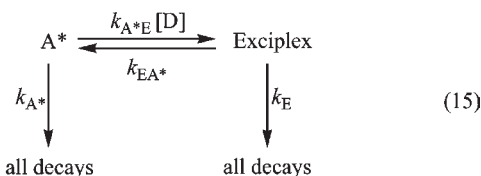
$$s = \delta + RT \ln\left\{\frac{k_d}{k_{solv}/(1+r)}\right\} \quad (14)$$

where $r = (k_{-solv})/(k_{-et}+k_{sep})$. Here the term δ is again the free energy of the product encounter pair, $A^{\bullet-}/D^{\bullet+}$, relative to the free ions $A^{\bullet-} + D^{\bullet+}$. The quantity $k_{solv}/(1 + r)$ is the effective deactivation rate constant of $A^{\bullet-}/D^{\bullet+}$ and is analogous to k'_{-d} for the pyrylium quenching reaction (eq 11 and the resulting expression for s in that case).

The logarithmic term in eq 14 is estimated to be between 0.01 and 0.02 eV.[16] Accordingly, from this estimate and the value of s of 0.06 eV, the difference in free energies between the encounter pair $A^{\bullet-}/D^{\bullet+}$ and the free species $A^{\bullet-} + D^{\bullet+}$, δ, is a *positive* term of ~0.04 eV or slightly larger. As detailed in the Supporting Information, this conclusion is still valid even if k_d is larger than k_{lim}. Furthermore, additional support for the conclusion that the main contribution to s is the free-energy difference, δ, is obtained from independent experiments; see section 3.6, below.

3.5. Transient and Steady-State Kinetic Analyses.
As reported previously[10e,f] and in this work, exciplex emission is detected in acetonitrile in all of the reactions listed in Table 4. The fluorescence quantum yields of these exciplexes vary from ~0.01 to 0.1 for the most endergonic reactions to ~10^{-3} in the exergonic region. When the reaction kinetics were examined

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by SPC, the fluorescence decay of A* and the growth and decay of the exciplex could be monitored. If the exciplex is formed reversibly, i.e., if there is significant feedback though k_{-c} and k_{-d} in eq 12, the decay of A* should not be monoexponential. If the exciplex and the encounter pairs are approximately in equilibrium, consistent with eq 9, the kinetics should be biexponential, as was found to be the case. Assuming that the exciplex is the dominant intermediate, the data were analyzed as a biexponential system with the four effective rate constants shown in eq 15.[17] Of these rate constants, k_{A*} is simply the reciprocal of the lifetime of A* in the absence of D. The remaining three rate constants are determined from the decay parameters (λ_1 and λ_2) as functions of [D].

$$A* \underset{k_{EA*}}{\overset{k_{A*E}[D]}{\rightleftarrows}} \text{Exciplex}$$

$$k_{A*} \downarrow \qquad\qquad\qquad \downarrow k_E \qquad\qquad (15)$$

$$\text{all decays} \qquad\quad \text{all decays}$$

The decay parameters of the biexponential kinetics λ_1 and λ_2 are given by the well-known eqs 15a and 15b.[17]

$$\lambda_1 = 0.5(X + Y) - 0.5\{(X - Y)^2 + 4k_{A*E}[D]k_{EA*}\}^{1/2} \tag{15a}$$

$$\lambda_2 = 0.5(X + Y) + 0.5\{(X - Y)^2 + 4k_{A*E}[D]k_{EA*}\}^{1/2} \tag{15b}$$

where

$$X = k_{A*} + k_{A*E}[D] \tag{15c}$$

$$Y = k_E + k_{EA*} \tag{15d}$$

The three rate constants obtained from the fitting of the transient kinetic data, k_{A*E}, k_{EA*}, and k_E, can be used to evaluate the quenching constant k_q, eq 16, along with the free energy of the exciplex relative to that of (A* + D) (Δ_E, eq 17), and the shift term (s, eq 18) (derivation given in the Supporting Information).

$$k_q = k_{A*E}k_E/(k_E + k_{EA*}) \tag{16}$$

$$\Delta_E = RT \ln(k_{EA*}/k_{A*E}) \tag{17}$$

$$s = \Delta_E - \Delta G + RT \ln(k_{lim}/k_E) \tag{18}$$

Three reactions of singlet-excited 9,10-dicyanoanthracene (DCA*), in which the exciplex is formed reversibly, were studied by transient kinetics; the data are summarized in Table 5. These reactions—with the aromatic donors 1,2,4-trimethylbenzene (124-TMB), biphenyl, and p-xylene—were chosen to cover the critical endergonic to nearly isoergic region. The reaction of DCA* with 124-TMB is described in detail to illustrate the kinetic analysis. The decay parameters (λ_1, λ_2) from SPC measurements were collectively fit by adjustment of k_{A*E}, k_{EA*}, and k_E (Figure 4a). This procedure leads to a predicted value of k_q from eq 16 that is in excellent agreement with that obtained by a steady-state Stern–Volmer quenching experiment (Figure 4b). The small difference (<10%) probably represents the initially

Table 5. Reaction of Excited DCA with Different Donors in Acetonitrile: ΔG, the Net Free Energy Difference for Electron Transfer (eq 8); Δ_E, the Difference between the Free Energies of the Exciplex and (A* + D) (eq 17); s, the Free-Energy Shift Term (eqs 9 and 18); and k_E, the Effective Exciplex Decay Rate Constant[a]

donor	ΔG, eV	Δ_E, eV	k_E, s^{-1}	s, eV
124-TMB[b]	−0.085	−0.11	4.0×10^8	0.064
biphenyl	−0.04	−0.084	1.7×10^8	0.066
p-xylene	+0.02	−0.032	2.2×10^8	0.052

[a] The exciplex emission maxima for 124-TMB, biphenyl, and p-xylene are 517, 513, and 458 nm, respectively; the corresponding quantum yields are 0.014, 0.038, and 0.086. [b] 124-TMB is 1,2,4-trimethylbenzene.
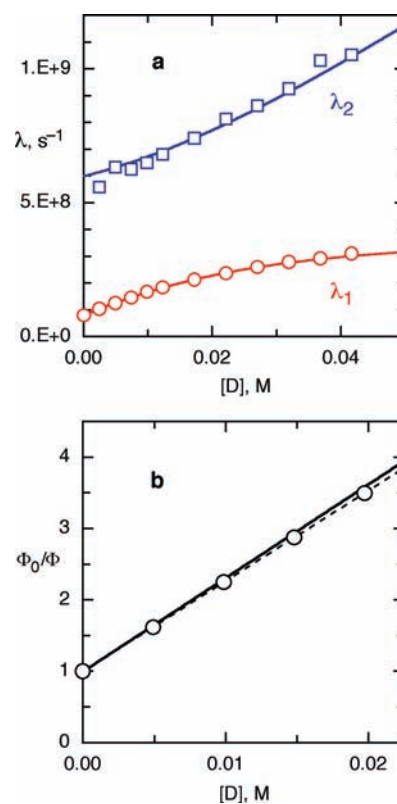

Figure 4. Transient and steady-state kinetic data for the quenching of 9,10-dicyanoanthracene (DCA) by the donor 1,2,4-trimethylbenzene (D) in acetonitrile. (a) Decay parameters λ_1 and λ_2 as functions of [D]. (b) Ratio of the fluorescence quantum yield of DCA in the absence and presence of D. In both figures the solid curves are the calculated quantities based on $k_{A*E} = 1.6 \times 10^{10}$ M^{-1} s^{-1}, $k_{EA*} = 2 \times 10^8$ s^{-1}, and $k_E = 4 \times 10^8$ s^{-1}. The dashed line in (b) is the least-squares fit to the steady state Φ_0/Φ data points.

time-dependent nature of the rate constants for rapid bimolecular reactions in solution (see Supporting Information).

The determination of k_{EA*} and k_{A*E} allows one to calculate the free energy of the exciplex, Δ_E, relative to that of A* + D using eq 17. In addition, the shift term for the individual reaction, s, can be calculated using eq 18 (Table 5), where k_{lim} is taken from the limiting quenching constant for reactions in the exergonic region (Figure 3). Also given in Table 5 are the results from the kinetic analyses with the other two donors (see Supporting Information for the corresponding experimental data). Importantly, the magnitude of s derived from the SPC measurements agrees well
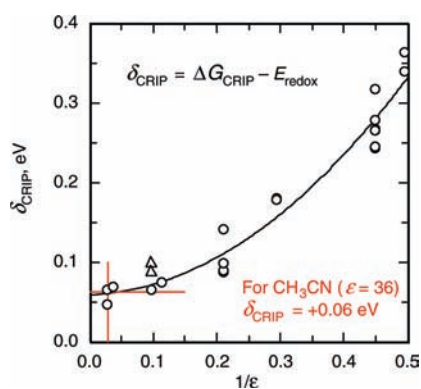
Figure 5. Plot of the free-energy difference between contact radical ion pairs (CRIP) and the corresponding free, fully solvated radical ions in acetonitrile (δ_{CRIP}) vs the reciprocal of the dielectric constant of the solvent (see text for explanation). The circles are from ref 18a and the triangles from ref 18c; the lower triangle represents two overlapping data points. The solid curve is used to smooth the data. In acetonitrile, the free energy of a CRIP is estimated to be ~0.06 eV *higher* than that of the free radical ions.
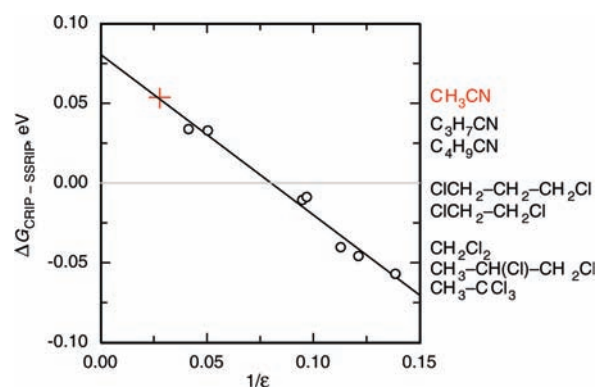

Figure 6. Difference between the free energies of formation for the contact radical ion pairs (CRIP) and the corresponding solvent-separated radical ion pairs (SSRIP) as a function of the reciprocal dielectric constant of the solvent. The data are for 1,2,4,5-tetracyanobenzene/p-xylene, taken from ref 18a. The free-energy difference in acetonitrile, extrapolated from the fitting straight line (red marking), is 0.053 eV.

with the value determined for the entire set of reactions from steady-state quenching experiments.

From the biexponential kinetics and from the observation of exciplex fluorescence, it is clear that the exciplex is an important intermediate. It is lower in free energy than both A*/D and A•−/D•+, and it must be the *dominant* intermediate. It may seem surprising, therefore, that the quenching constant, k_q, is governed by only the difference in free energy between the two encounter pairs. Unlike the transient kinetics, the efficiency of quenching depends only on the rate of product formation relative to the rate of regeneration of A* + D. Those rates are proportional to [A•−/D•+] and [A*/D], respectively, and the efficiency of quenching depends exclusively on the their ratio. Direct deactivation of the exciplex is negligible for these reactions. As mentioned above, the observed SB dependence is consistent with a rapid interconversion among the intermediates, such that equilibrium is maintained among them. The concentration ratio that determines k_q, namely [A•−/D•+]/[A*/D], then is determined solely by the difference in free energies of the two encounter pairs, regardless of the binding energy and greater concentration of the exciplex.

3.6. Relative Energies of the Intermediates. We discuss here two opposing factors that affect the free energy of A•−/D•+ relative to that of the free radical ions. First, Coulombic stabilization is expected to lower the free energy of A•−/D•+ vs the free ions.[3] In opposition to this effect, partial desolvation of the free ions to form the encounter pair is expected to raise the relative free energy of A•−/D•+. In addition, the close proximity of the ions at contact will lead to cancellation of the favorable orienting of solvent molecules, especially those in the outer shells.[10f] The relative magnitudes of these opposing effects will largely determine the sign and magnitude of δ, the free energy difference between A•−/D•+ and the free radical ions. Two independent experiments are consistent with the conclusions that δ is positive and that decreased solvent stabilization of the A•−/D•+ pairs outweighs the Coulombic stabilization relative to the free ions. The first experiment is based on spectroscopic measurements of the free energies of excited charge-transfer complexes of several electron acceptors with alkylbenzene donors in different solvents.[18] These excited complexes are essentially pure contact radical ion pairs (CRIP), and thus similar to

highly ionic exciplexes. Using the newly determined oxidation potentials of the donors,[6a] the free energies of the free radical ions in acetonitrile relative to the corresponding neutrals are equal to the difference in redox potentials in acetonitrile, $E_{ox}(D) - E_{red}(A)$, i.e., E_{redox}. The free energy of the CRIP relative to the free neutrals is denoted ΔG_{CRIP}. The difference between the free energies of the CRIP and the free radical ions in acetonitrile, δ_{CRIP}, is equal to $\Delta G_{CRIP} - E_{redox}$. Shown in Figure 5 is a plot of δ_{CRIP} as a function of the reciprocal of the dielectric constant of the solvent (ε). As expected, the free energy of the CRIP decreases with increasing dielectric constant, but it remains higher than that of the free ions in all solvents. The value of δ_{CRIP} for acetonitrile ($\varepsilon = 36$) is 0.06 ± 0.01 eV.

In the second experiment, the free-energy difference between the radical ions of 1,2,4,5-tetracyanobenzene (TCB) and p-xylene, in CRIP and in the SSRIP, was determined as a function of solvent polarity from the kinetics of their interconversion.[18a,d] In low-polarity solvents, the free energy of the CRIP is much lower than that of the SSRIP, because the gain in Coulombic stabilization at the shorter separation distance is only partially countered by the modest loss in solvent stabilization. In medium-polarity solvents, this free-energy gap narrows. The two species become isoergic at a dielectric constant (ε) of ~13, and the CRIP lies above the SSRIP at higher ε (see Figure 6). In acetonitrile, the free energy of the CRIP is above that of the SSRIP by ~0.05 eV. It is clear that desolvation makes a significant positive contribution to the free energy of the CRIP in acetonitrile.

The independent results described above support two major conclusions from the quenching experiments: (1) in acetonitrile, the free energy of an encounter radical ion pair is higher than that of the free ions and (2) the higher free energy of that encounter pair is due to a loss of solvent stabilization that exceeds the energetic gain of Coulombic stabilization. The similarity between the free-energy differences derived from Figures 5 and 6 and the value of δ, ~+0.04, required to fit the quenching data of the cyanoaromatics (Figure 3) is striking and is likely not a coincidence. The reason that the pyryliums exhibit a larger value of s than the cyanoaromatics (0.08 vs 0.06 eV) may be that the pyrylium case has negligible Coulombic stabilization to counter the loss of solvation in P•/D•+.

4. Deviation from the Sandros—Boltzmann (SB) Dependency in Other Electron-Transfer Reactions. For the reactions

presented in sections 1–3, any potential information about the reorganization energies associated with the electron-transfer steps is necessarily obscured by the adherence of the rate or quenching constants (k or k_q) to an SB dependency on the reaction free energy. As described above, the SB dependency in these cases indicates that electron transfer within the encounter pair must be significantly faster than dissociation of an encounter pair and, therefore, does not determine the value of k or k_q. It should be noted that this will not always be true. In other acceptor/donor systems, several factors can slow electron transfer and lead to deviation from the SB dependencies exhibited here. For pure electron-transfer processes such as k_{et} and k_{-et} here, it is well established that the rates depend on the electronic coupling between the reactants and on the reorganization energies associated with the electron transfer.[19] In the Marcus normal region, the reaction range under consideration here, a decrease in the electronic coupling or an increase in the reorganization energy can lead to a decrease in the electron-transfer rate constants. Limiting the discussion to reactions in polar solvents such as acetonitrile, a number of factors can decrease the electronic coupling, e.g., electrostatic repulsion if both reactants have the same (positive or negative) charges or steric crowding if it hinders effective orbital overlap. Increase in reorganization energies (inner and/or outer sphere) can also result from significant changes in the structures of the reactants upon electron transfer.

For reactions similar to those described in sections 1 and 2, the deviation from the SB dependency would begin to be noticeable if the ratio k_{-d}/k_{et} at the isoergic point (where the deviation is most evident) started to exceed ~0.3. As the reaction endergonicity increases, k_{et} would decrease and the k_{-d}/k_{et} ratio would increase, but more slowly than the exponential term (see Supporting Information). Thus, SB dependency would still eventually be observed. The endergonicity for onset of SB behavior depends on the magnitude of k_{et}, which is a function of the electronic coupling and the reorganization energy.

There are cases reported in the literature where deviation from the SB behavior is quite clear and is beyond any reasonable uncertainty in the thermodynamic parameters or the quenching data. Although reviewing these cases is beyond the scope of this work, the quenching of excited Ru(bpy)$_3^{2+}$ by various electron donors and acceptors offers good examples to illustrate the point (bpy = 2,2′-bipyridine).[20] The rate constants for reductive quenching by amines[20,21] and for oxidative quenching by bipyridinium cations[20] are clearly so slow that, throughout the experimentally achievable rate constant range, the reactions do not approach an SB dependency. On the other hand, in the case of oxidative quenching of excited Ru(bpy)$_3^{2+}$ by nitroaromatics,[20] the electron-transfer rate constants are in the range where the data deviate appreciably from the SB curve near the isoergic point but approach the SB curve at higher endergonicity.[22]

There are numerous publications describing quenching reactions similar to those discussed in section 3 where, in general, it is not possible to conclude whether the reactions actually follow an SB dependency. A primary reason is that the thermodynamic parameters governing electron transfer (redox potentials and excitation energies) are rarely determined with sufficient accuracy to critically test an SB dependency. In addition, the occasional use of reactants with heavy-atom substituents or carbonyl moieties that induce intersystem crossing can lead to additional deactivation paths for electron-transfer intermediates (e.g., exciplexes) that, if not taken into account, compromise a rigorous

kinetic analysis. There are also cases where measurements probably extend too far into the endergonic regime, where other quenching mechanisms besides electron transfer are likely to intervene.

5. Concluding Remarks. Using electron donors for which accurate oxidation potentials have been measured, the dependence of the electron-transfer rate constants and/or quenching constants on the reaction driving force has been determined for three types of electron-transfer reactions. For electron exchange between neutral electron donors and radical cations, a plot of the logarithm of the electron-transfer rate constants vs the free energies for electron transfer was found to follow a simple SB dependence. A similar dependence was observed for electron transfer from neutral donors in two types of photoinduced electron-transfer reactions: one involving cationic excited-state acceptors and the other involving neutral excited-state acceptors. To explain these results, interconversion among the exciplex and/or electron-transfer intermediates must be fast compared to diffusional separation of the encounter pairs, even in the critical region near the isoergic point. Whenever this is the case, the experimental data offer no information on the microscopic rate constants for electron transfer or exciplex formation and their dependence on free energy, except that they must be considerably faster than diffusional separation.

Both of the excited-state reactions required introduction of a positive free-energy shift term to fit the experimental data. The shift terms are primarily ascribed to free-energy differences between electron transfer within encounter pairs vs those for the free reactants and products. For the reactions with pyrylium excited-state acceptors, the shift term is attributed mostly to desolvation of the radical ion within the product radical/radical ion encounter pair relative to the corresponding free species. For the reactions with neutral excited-state acceptors, the shift term is proposed to be largely determined by two opposing effects. A decrease in solvent stabilization raises the free energy of the encounter pair A$^{•-}$/D$^{•+}$ relative to that of the free radical ions, whereas Coulombic stabilization lowers it. The observed, positive shift term is consistent with the desolvation contribution being larger than the Coulombic contribution. This conclusion has general implications for rate constant vs driving force correlations of both ground- and excited-state electron-transfer reactions, where only a Coulombic correction term is commonly used to calculate the free-energy change for electron transfer within encounter pairs.[23] For example, the Coulombic effect in acetonitrile has been estimated[3] to be −0.06 eV, whereas the data presented here show that the net shift term is actually +0.06 eV. In the endergonic region, the difference between these values (0.12 eV) corresponds to a factor of ~100 in rate constant! The fact that the original assumption about the shift was unjustified may, therefore, require reinterpretation of many prior electron-transfer studies, particularly those that were taken to yield information about the reorganization energies.

For the photoinduced electron-transfer reactions involving a neutral acceptor and donor, an understanding of the differing nature of excited-state quenching within different driving force regimes is essential to a proper interpretation of experimental data. For reactions in the moderately exergonic region, the initial product of electron transfer will be a highly ionic exciplex whose free energy should closely parallel that of the corresponding free radical ions. In the isoergic and moderately (<~0.1 eV) endergonic region, however, considerable mixing[10c,d,11] between the pure locally excited and ion pair states can lead to a partially ionic exciplex. The exciplex is thus stabilized, and its free energy falls

well below what would be expected in the absence of the mixing. In both regions, the nonexponential kinetics and the emission spectra clearly show the importance of the exciplex. Even so, for the reactions described above, the overall quenching constant depends only on the free-energy difference between the encounter pairs A*/D and A$^{\bullet-}$/D$^{\bullet+}$ over both regions of ΔG. Importantly, when the reaction becomes endergonic by more than ~0.1 eV, the activation barrier from the exciplex to A$^{\bullet-}$/D$^{\bullet+}$ increases to the point that other exciplex deactivation processes (fluorescence, intersystem crossing, and internal conversion) start to become competitive and ultimately dominate. At this point the reactions no longer represent only electron-transfer quenching, in contrast to the reactions in the other free-energy regions. Furthermore, in the strongly endergonic region, high quencher concentrations, which are required to produce observable quenching, can alter the properties of the medium and affect the intrinsic photophysics of the excited states. These medium-induced perturbations can easily be misinterpreted as quenching, even when none exists.

Our work has obvious implications for the experimental results reported in the classic study by Rehm and Weller.[3] As described above, a rigorous analysis of the free-energy dependence of excited-state quenching by electron transfer requires the use of accurate redox potentials and the exclusion of reactions in the suspect, highly endergonic region. For these reasons, a complete reanalysis of the original Rehm–Weller systems appears warranted. This work is currently underway and will be reported separately.

■ EXPERIMENTAL SECTION

Materials. Acetonitrile (99.93+% Baker, HPLC grade, <10 ppm H_2O) was used as received. Solid benzene and biphenyl derivatives were purified by recrystallization, and liquids were fractionally distilled as previously described.[6a] The pyrylium salts and cyanoaromatics were from a previous study.[8]

Laser Flash Photolysis Measurements. Transient kinetic measurements on radical cations were performed using a nanosecond laser flash photolysis apparatus, and data were analyzed as detailed previously.[6a]

Steady-State Luminescence Measurements. Emission spectra and intensities were measured using a Fluorolog-3 spectrofluorometer (Jobin Yvon, Horiba). Spectra were corrected for the efficiency of the monochromator and the spectral response of the photomultiplier tube. For exergonic and mildly endergonic quenching processes in which static quenching can become important, quencher concentrations were reduced to levels that provided linear Stern–Volmer plots.

Single-Photon Counting Measurements. Excited-state lifetimes and quenching kinetics were measured using time-correlated single-photon counting with a FluoTime200 spectrofluorometer equipped with a TimeHarp200 TCSPC board (Pico-Quant). A diode laser (LDH-P-C-400 driven by PDL800-B driver, PicoQuant) emitting at 410 nm was used as the excitation source for the pyrylium salts and the cyanoanthracenes. The instrument response functions extended over ~280–290 ps. The emission decays were monitored at wavelengths near the fluorescence maxima. The data were analyzed using the FluoFit, version 4.1 (Picoquant) software package. The emission decays of the pyrylium salts at all quencher concentrations were strictly first order. Errors in the measured lifetimes, typically ≤0.02 ns, were calculated using the error surface analysis included in the software.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Reduced absorption and emission spectra of pyrylium salts; transient and steady-state

quenching of singlet excited pyrylium cations with aromatic donors; transient kinetics of the reaction of DCA with biphenyl and p-xylene; transient and steady-state quenching of singlet excited cyanoanthracenes with aromatic donors; derivation of eqs 6, 11, 14, and 18; general trend toward SB dependency with increasing endergonicity; discussion of the magnitudes of k_{-d}/k_{et} and k'_{-d}/k_{-et}; and the equilibrium approximation. This material is available free of charge via the Internet at http://pubs.acs.org.

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