JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
ARTICLE
pubs.acs.org/JACS

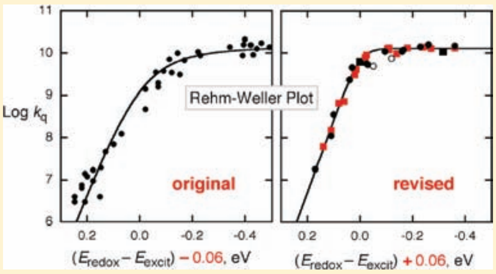
Reexamination of the Rehm−Weller Data Set Reveals Electron Transfer Quenching That Follows a Sandros−Boltzmann Dependence on Free Energy

Samir Farid,*,† Joseph P. Dinnocenzo,*,† Paul B. Merkel,*,† Ralph H. Young,*,† Deepak Shukla,*,‡ and Gonzalo Guirado*,§

†Department of Chemistry, University of Rochester, Rochester, New York 14627, United States
‡Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, United States
§Departament de Química (Quimica-Fisica), Universitat Autònoma de Barcelona, Edifi C, 08193-Bellaterra, Barcelona, Spain

Supporting Information

ABSTRACT: In a landmark publication over 40 years ago, Rehm and Weller (RW) showed that the electron transfer quenching constants for excited-state molecules in acetonitrile could be correlated with the excited-state energies and the redox potentials of the electron donors and acceptors. The correlation was interpreted in terms of electron transfer between the molecules in the encounter pair ($A^*/D \rightleftharpoons A^{\bullet-}/D^{\bullet+}$ for acceptor A and donor D) and expressed by a semiempirical formula relating the quenching constant, k_q, to the free energy of reaction, ΔG. We have reinvestigated the mechanism for many Rehm and Weller reactions in the endergonic or weakly exergonic regions. We find they are not simple electron transfer processes. Rather, they involve exciplexes as the dominant, kinetically and spectroscopically observable intermediate. Thus, the Rehm−Weller formula rests on an incorrect mechanism. We have remeasured k_q for many of these reactions and also reevaluated the ΔG values using accurately determined redox potentials and revised excitation energies. We found significant discrepancies in both ΔG and k_q, including A^*/D pairs at high endergonicity that did not exhibit any quenching. The revised data were found to obey the Sandros−Boltzmann (SB) equation $k_q = k_{\lim}/[1 + \exp[(\Delta G + s)/RT]]$. This behavior is attributed to rapid interconversion among the encounter pairs and the exciplex ($A^*/D \rightleftharpoons \text{exciplex} \rightleftharpoons A^{\bullet-}/D^{\bullet+}$). The quantity $k_{\lim}$ represents approximately the diffusion-limited rate constant, and s the free energy difference between the radical ion encounter pair and the free radical ions ($A^{\bullet-}/D^{\bullet+}$ vs $A^{\bullet-} + D^{\bullet+}$). The shift relative to ΔG for the overall reaction is positive, $s = 0.06$ eV, rather than the negative value of −0.06 eV assumed by RW. The positive value of s involves the poorer solvation of $A^{\bullet-}/D^{\bullet+}$ relative to the free $A^{\bullet-} + D^{\bullet+}$, which opposes the Coulombic stabilization of $A^{\bullet-}/D^{\bullet+}$. The SB equation does not involve the microscopic rate constants for interconversion among the encounter pairs and the exciplex. Data that fit this equation contain no information about such rate constants except that they are faster than dissociation of the encounter pairs to (re-)form the corresponding free species ($A^* + D$ or $A^{\bullet-} + D^{\bullet+}$). All of the present conclusions agree with our recent results for quenching of excited cyanoaromatic acceptors by aromatic donors, with the two data sets showing indistinguishable dependencies of k_q on ΔG.



INTRODUCTION

The pioneering work of Albert Weller on photoinduced electron transfer has significantly expanded the scope of organic photochemistry over the past four decades. In a landmark publication, Rehm and Weller showed that electron transfer quenching of excited states can be correlated with the excitation energy and the redox potentials of the reactants.[1] Rehm and Weller's effective reaction free energy ($\Delta G'$) is related to the free energy of the net reaction (ΔG) by eq 1.[2]

$$\Delta G' = \Delta G - \frac{e^2}{\varepsilon a} \tag{1a}$$

$$\Delta G = E_{redox} - E_{excit} = (E_{ox} - E_{red}) - E_{excit} \tag{1b}$$

E_{excit} is the free energy of excitation for the excited reactant, which can be either the electron acceptor or the electron donor. The free energy of the *free* radical ions (E_{redox}) relative to the corresponding neutrals is given by the difference between the oxidation potential of the donor (E_{ox}) and the reduction potential of the acceptor (E_{red}). The free energy of the primary electron transfer product, the radical ion encounter pair ($A^{\bullet-}/D^{\bullet+}$), was assumed to equal that of the free radical ions *minus* a Coulombic term to account for the electrostatic attraction at an encounter distance a in a solvent having a dielectric constant ε.[1] The plot of the logarithm of the quenching constant k_q vs $\Delta G'$ became known as the Rehm−Weller (RW) plot and has been widely used in electron transfer studies.[3]

As originally formulated, the correlation between k_q and $\Delta G'$ (Figure 1) was expressed by an empirical formula

Received: March 17, 2011
Published: July 07, 2011

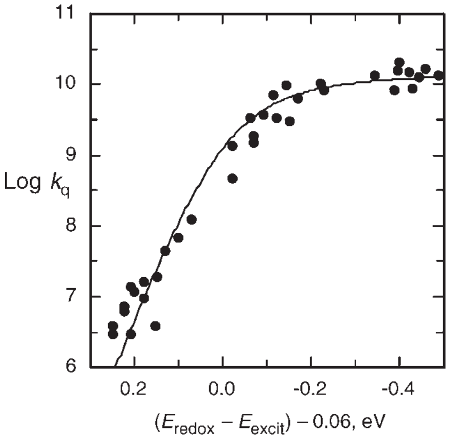


Figure 1. Fluorescence quenching data reported by Rehm and Weller[1a] from +0.25 to −0.5 eV, the range currently under consideration. The fitting curve, according to eq 2, is based also on the parameters from ref 1a, $\Delta G^{\ddagger}(0) = 0.104$ eV, $k_d = 2 \times 10^{10}$ M^{-1} s^{-1}, and $k_{-d}/k^0 = 0.25$.

(eq 2)

$$k_q = k_d/\{1 + (k_{-d}/k^0)(e^{\Delta G^{\ddagger}/RT} + e^{\Delta G'/RT})\} \qquad (2a)$$

$$\Delta G^{\ddagger} = \{(\Delta G'/2)^2 + [\Delta G^{\ddagger}(0)]^2\}^{1/2} + \Delta G'/2 \qquad (2b)$$

where $\Delta G^{\ddagger}$ represents the free energy of activation for electron transfer, $\Delta G^{\ddagger}(0)$ is the "intrinsic" value for $\Delta G' = 0$, k_d and k_{-d} are the rate constants for diffusional encounter and separation, and k^0 is the frequency factor in an Arrhenius expression for the electron transfer rate constants.[1] In the Rehm–Weller formulation, when the starting reactants are neutral, the Coulombic stabilization in the encounter pair ($A^{\bullet -}/D^{\bullet +}$) in acetonitrile is estimated as $e^2/\varepsilon a \approx 0.06$ eV. Thus, in the RW original treatment, $\Delta G'$ is given by

$$\Delta G' = (E_{redox} - E_{excit}) - 0.06 \text{ eV} \qquad (3)$$

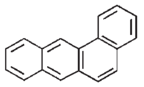
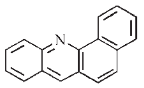
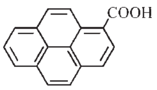
We recently showed that excited-state electron transfer quenching of cyanoaromatic acceptors by aromatic donors deviates from the RW formulation in two significant ways.[4] First, while RW assumed a direct electron transfer mechanism, our reactions involve an exciplex as the major intermediate. Thus, eq 2 is deprived of its mechanistic basis for these reactions. In fact, our k_q follows a Sandros–Boltzmann (SB) dependence on ΔG, eq 4, where k_{lim} is approximately equal to a diffusion-limited rate constant. Second, an effective free energy of reaction defined by $\Delta G' = \Delta G + s$ involves a *positive* free energy shift (s) of 0.06 eV, eq 5,

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

$$\Delta G' = \Delta G + 0.06 \text{ eV} \qquad (5)$$

rather than the negative shift postulated by RW. The positive shift was ascribed[4] to the decreased solvation of the radical ion pair when in contact relative to that of the free, fully solvated species. This conclusion is supported by independent experimental data, which showed that the free energy of radical ion pairs in contact exceeds that of the separated radical ions. This fact was not recognized at the time of the original RW work.

Table 1. Comparison between the Original (RW)[1] and Revised Excitation Energies and Reduction Potentials of the Acceptors in Acetonitrile

Acceptor		E_{excit}, eV		E_{red}, V vs SCE	
		RW	Revised	RW	Revised
A		3.23	3.23	−2.03	−2.06
B		3.20	3.20	−1.75	−1.70
C		3.17	3.21	−1.67	−1.64

In principle, the differences between our recent results[4] and those of RW[1] could be due to the different reactants used in the two studies. To test this hypothesis, it was necessary to perform a critical reexamination of the original RW data, which is the subject of this paper.

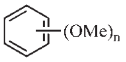
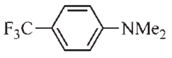
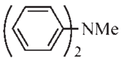
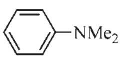
RESULTS AND DISCUSSION

The RW plot and the fitting procedure were based on data collected over 40 years ago using redox potentials of questionable accuracy. In addition, quenching constants used to evaluate $\Delta G^{\ddagger}(0)$ included data points in the highly endergonic region, which, as we have discussed elsewhere,[4] are subject to large experimental errors. No exciplex emission was observed in the RW study, so it was assumed that exciplexes do not play a role as intermediates in electron transfer quenching in *polar solvents* such as acetonitrile.[1] It has been subsequently shown that exciplexes can be formed in acetonitrile.[4,5] As we will show here, exciplexes are also formed in the RW systems; thus, a complete kinetic scheme should include their role in the quenching reactions. The aim of the present paper is to reexamine the quenching data in the endergonic to mildly exergonic regions—the regions in which factors such as reorganization energies are most commonly investigated. The reactions in the highly exergonic region are mechanistically distinct, have been discussed elsewhere,[6] and will not be addressed here.

Thermodynamic Parameters. Two sets of photoinduced electron transfer reactions were reported by RW: (1) the quenching of excited aromatic and heteroaromatic acceptors by several alkoxybenzenes and aromatic amines and (2) the quenching of excited aromatic donors by benzonitrile, 1,4-dicyanobenzene, and tetracyanoethylene. Most of the RW data are from the first set and are reinvestigated here. Of the second set, the reactions with benzonitrile are in the free energy range relevant to this work and are also addressed below. The reactions with 1,4-dicyanobenzene and tetracyanoethylene are mostly in the strongly exergonic region and, as mentioned above, are discussed elsewhere.[6]

The quenching reactions of three structurally diverse excited-state acceptors reported by RW were reinvestigated: 1,2-benzanthracene (**A**), 3,4-benzacridine (**B**), and 1-pyrenecarboxylic acid (**C**) (Table 1).[7] Their excitation energies were determined from

Table 2. Comparison between the Original (RW)[1] and Revised[9] Oxidation Potentials of Alkoxybenzene and Aromatic Amine Donors in Acetonitrile[a]

Donor		E_{ox}, V vs SCE	
		RW	Revised
1	1-	1.76	1.77
2	1,3-	1.49	1.55
3	1,3,5-	1.49	1.54
4	1,2-	1.45	1.41_5
5	1,2,3-	1.42	1.39
6	1,4-	1.34	1.28
7	1,2,4-	1.12	1.08
8	1,2,4,5-	--	0.79_5
9		--	1.11
10		0.84	0.94_5
11		0.78	0.85

[a] Donors **8** and **9** were not part of the original RW study.

Table 3. Comparison between the Original (RW)[1a] and Revised Quenching Constants of Excited Acceptors (Table 1) by Alkoxybenzene and Aromatic Amine Donors (Table 2) in Acetonitrile[a]

			k_q (M^{-1} s^{-1})	
acceptor	donor	$\Delta G + 0.06$ (eV)	RW	revised
A	2	+0.44	7.5×10^6	NQ
A	3	+0.43	7.6×10^6	NQ
A	4	+0.305	9.6×10^6	NQ
A	5	+0.28	1.95×10^7	NQ
A	6	+0.17	1.23×10^8	1.8×10^7
A	9	0.0		6.2×10^9
A	7	−0.03	3.08×10^9	5.3×10^9
A	10	−0.165	9.1×10^9	1.2×10^{10}
A	11	−0.26	1.38×10^{10}	1.6×10^{10}
A	8	−0.315		1.1×10^{10}
B	2	+0.11	1.37×10^9	1.1×10^8
B	3	+0.10	4.7×10^8	3.5×10^8
B	4	−0.025	3.46×10^9	5.6×10^9
B	5	−0.05	3.75×10^9	5.1×10^9
B	6	−0.16	6.68×10^9	1.1×10^{10}
B	7	−0.36	8.7×10^9	1.5×10^{10}
C	1	+0.26	1.2×10^7	NQ
C	2	+0.04	1.92×10^9	2.3×10^9
C	3	+0.03	1.57×10^9	4.4×10^9
C	4	−0.095	7.1×10^9	1.1×10^{10}
C	5	−0.12	9.9×10^9	7.4×10^9
C	6	−0.23	1.07×10^{10}	1.4×10^{10}

[a] ΔG is the net reaction free energy given by $E_{ox} - E_{red} - E_{excit}$. NQ indicates cases where no fluorescence quenching was observed.

the midpoint of the reduced[8] absorption and emission spectra in acetonitrile, which showed significant overlap of the respective first vibrational bands and very small Stokes shifts (see the Supporting Information). Their reduction potentials were determined by cyclic voltammetry and found to exhibit one-electron reversible waves at sufficiently high scan rates. The differences between the revised oxidizing powers of the excited acceptors ($E_{excit} + E_{red}$) and those reported in RW are −0.03, +0.05, and +0.07 eV for **A**, **B**, and **C**, respectively. These deviations mean that in a revised RW plot the data points for the acceptors will be displaced relative to one another by as much as 0.1 eV.

The electron donors listed in Table 2 are those from the RW work that provided quenching data in the endergonic to mildly exergonic regions, along with two additional donors from the same classes of compounds. Newly revised oxidation potentials[9] were determined in acetonitrile by using a nanosecond redox equilibration method previously shown[10] to give accurate oxidation potentials with <10 mV precision. As shown in Table 2, the revised oxidation potentials deviate in some cases significantly from those used by RW. For example, the revised E_{ox} for **2** is *higher* by 0.06 V, whereas that for **6** is *lower* by 0.06 V.

Quenching Constants. The quenching constants (k_q) were remeasured using steady-state (Stern−Volmer) and transient kinetics, as described in ref 4. Details of the transient experiments are described in the section "Role of an Exciplex in the Kinetic Scheme". Importantly, the two methods yielded very similar values (within ∼5%) for k_q. The revised quenching constants are listed in Table 3; those from RW[1a] are also listed for comparison.

The most dramatic differences between the revised and the originally reported values for k_q are those in the more strongly endergonic region. These cases tend to be problematic because high quencher concentrations are required to observe measurable quenching. High quencher concentrations can complicate the quenching measurements because trace impurities of low-E_{ox} compounds will lead to artificially high k_q values. In addition, high quencher concentrations alter the properties of the medium, which can affect the rate constants for unimolecular deactivation processes of an excited molecule. Changes in the ratios of the rate constant for radiative decay (k_f) to those for internal conversion (k_{ic}) and intersystem crossing (k_{isc}) can give the appearance of quenching where none exists. As described below (in the section "Limits to Detection of Quenching"), careful reexamination of RW data in the strongly endergonic region revealed an absence of detectable quenching.

A plot of log k_q vs $\Delta G + s$ according to eq 4 using revised redox potentials, excited-state energies, and k_q values shows a good fit for $s = +0.06$ eV (Figure 2), similar to that observed previously for analogous reactions involving the quenching of excited cyanoaromatic acceptors by alkylbenzene donors.[4] Two exceptional points, with 1,2,3-trimethoxybenzene (**5**) as quencher (unfilled circles, Figure 2), fall noticeably below the fitting curve. These deviations are likely to be due to conformational differences between the neutral donor and the radical cation caused by the steric crowding of three adjacent methoxy groups. Consistent with this explanation, thermal equilibration experiments between the neutral donor and radical cations have

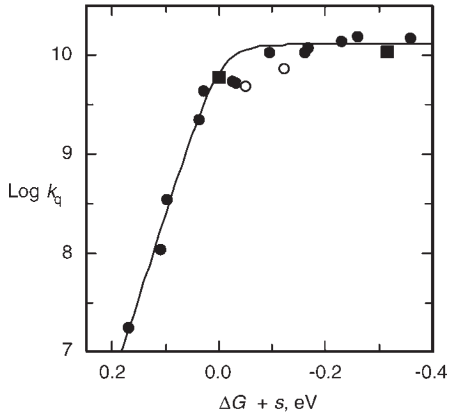


Figure 2. log k_q vs $\Delta G + s$ (eq 4) for electron transfer quenching of excited acceptors by alkoxybenzenes and aromatic amine derivatives in acetonitrile (Table 3). Here $\Delta G = E_{redox} - E_{excit}$ (eq 1b) and $s = 0.06$ eV. Key: circles, reevaluated RW data (unfilled circles, reactions with sterically crowded 1,2,3-trimethoxybenzene (**5**) as quencher; filled circles, the rest of the reevaluated data); squares, additional quenching data for 1,2-benzanthracene (**A**) with 4-(trifluoromethyl)-*N*,*N*-dimethylaniline (**9**) and 1,2,4,5-tetramethoxybenzene (**8**). The curve is according to eq 4 with $s = +0.06$ eV and $k_{lim} = 1.3 \times 10^{10}$ M^{-1} s^{-1}.

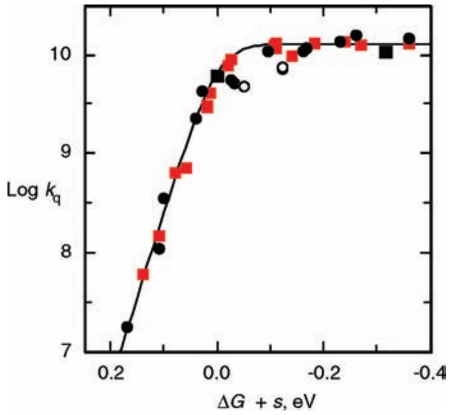


Figure 3. Data and fitting curve shown in Figure 2, together with data for the quenching of excited cyanoaromatics with alkylbenzene derivatives, also in acetonitrile, from ref 4 (red squares).

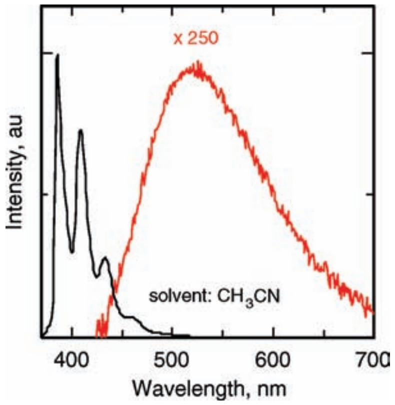


Figure 4. Emission spectra in argon-purged acetonitrile of 1,2-benzanthracene (**A**), black, structured curve, and its exciplex with 1,2,4-trimethoxybenzene (**7**), red, structureless curve. The exciplex fluorescence quantum yield is ~0.02 times that of **A**, and its emission maximum is at 18.7×10^3 cm^{-1}.

shown a similar decrease in electron transfer rate constants for this donor.[11]

Figure 3 shows the previous data points for the quenching of cyanoaromatics by alkylbenzenes[4] superimposed on those from Figure 2. That both sets of data fit so well to the same SB dependence curve (eq 4) strongly suggests that the kinetic scheme discussed in ref 4 also applies to the reactions discussed in the current work. Additional support for this conclusion is discussed in the section "Role of an Exciplex in the Kinetic Scheme".

Role of an Exciplex in the Kinetic Scheme. The quenching reactions of excited cyanoaromatics with alkylbenzenes in acetonitrile were shown to proceed via an exciplex intermediate between two encounter pair species, A*/D on the reactant side and $A^{\bullet-}/D^{\bullet+}$ on the product side, eq 6.[4]

$$A^* + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} A^*/D \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} [A^*D \leftrightarrow A^{\bullet-}D^{\bullet+}] \underset{k'_c}{\overset{k'_{-c}}{\rightleftharpoons}} A^{\bullet-}/D^{\bullet+} \xrightarrow{k_{term}} \begin{matrix} A^{\bullet-} + D^{\bullet+} \\ (\text{or } A + D) \end{matrix} \qquad (6)$$

In the encounter pairs, the reactants are in contact, but with various possible orientations and no specific binding. The exciplex, $[A^*D \leftrightarrow A^{\bullet-}D^{\bullet+}]$, is a long-lived 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 ($A^{\bullet-}D^{\bullet+}$) character 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. In eq 6, k_d and k_{-d} are the rate constants for the formation and dissociation of A*/D. 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. An effective termination rate constant of $A^{\bullet-}/D^{\bullet+}$, k_{term}, leads (via a solvent-separated radical ion pair)[4] to free radical ions or neutral reactants. At the low light intensities used here, the bulk recombination of free $A^{\bullet-}$ and $D^{\bullet+}$ to regenerate $A^{\bullet-}/D^{\bullet+}$ is negligible. Equation 4 for k_q can be derived[4] for the scheme in eq 6 if k_c and k'_c are large compared to k_{-d} and k_{term}, and/or if the three intermediates interconvert rapidly enough to maintain equilibrium (see the Supporting Information).

Careful fluorometric examination showed that exciplex emissions could be detected in the reactions listed in Table 3 over the entire range of ΔG, similar to those in ref 4. Transient (time-correlated single-photon counting, SPC) experiments confirmed that when the reactions are near the isoergic point or in the endergonic region, the exciplex formation from A* + D is a reversible process. We use the reaction of **A**/**7**, Table 3, as an example to illustrate these points. Shown in Figure 4 are the fluorescence spectrum of **A** and that of its exciplex with **7**.

When the reaction kinetics were examined by SPC, the fluorescence decay of A* and the growth and decay of the exciplex could be monitored. If the exciplex and the encounter pairs are approximately in equilibrium and are formed reversibly from A* + D, the kinetics should be biexponential, as was found to be the case. Assuming that the exciplex is the dominant

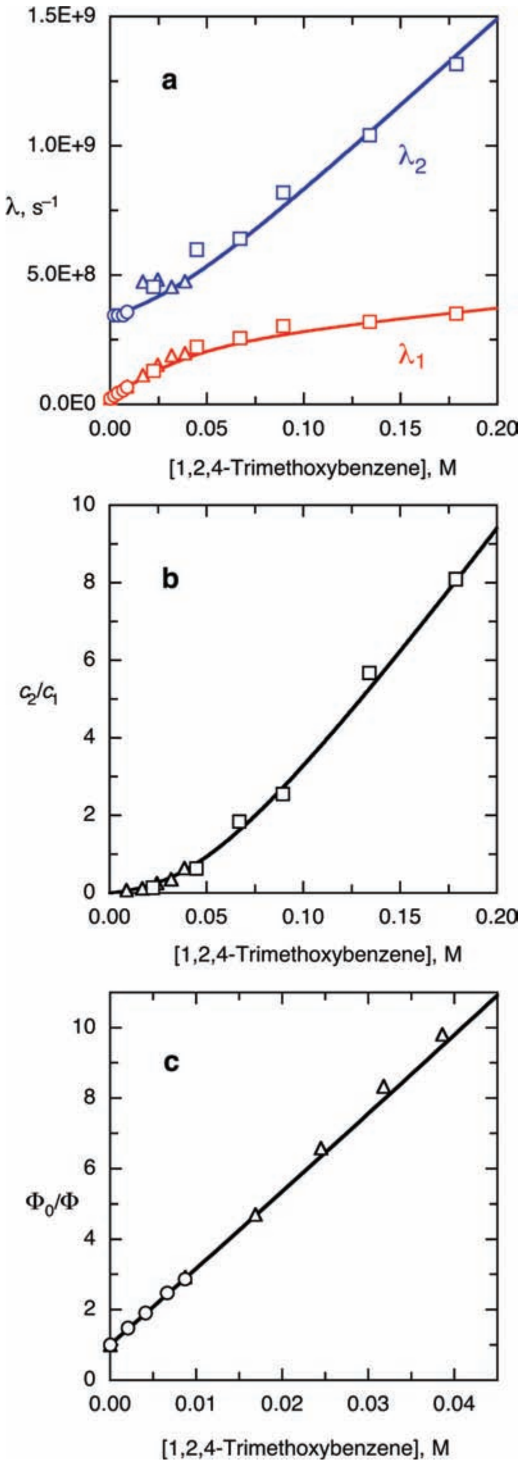


Figure 5. Transient and steady-state kinetic data for the quenching of 1,2-benzanthracene (**A**) by 1,2,4-trimethoxybenzene (**7**) in argon-purged acetonitrile. Different symbols refer to data from different sets of experiments. (a) Decay parameters λ_1 and λ_2 as functions of [**7**]. (b) Ratio of the corresponding pre-exponentials c_2/c_1, monitored at 390 nm, where no exciplex emission is detectable. (c) Ratio of the fluorescence quantum yield of **A** in the absence and presence of **7**. In all three figures the curves are the calculated parameters based on the scheme outlined in eq 7, where $k_{A^*} = 2.4 \times 10^7$ s^{-1}, $k_{A^*E} = 6.8 \times 10^9$ M^{-1} s^{-1}, $k_{EA^*} = 7.0 \times 10^7$ s^{-1}, $k_E = 2.6 \times 10^8$ s^{-1}, and $k_q{}^E = 7.0 \times 10^8$ M^{-1} s^{-1}. Note that the steady-state measured Φ_0/Φ and that calculated from the parameters of the transient experiment are in very good agreement.

Table 4. Free Energy Difference (Δ_E) between the Exciplex and A* + D and Shift Term *s* for Reactions Having Similar ΔG ($E_{redox} - E_{excit}$)[a]

acceptor	donor	ΔG, eV	Δ_E, eV	*s*, eV
1,2-benzanthracene	1,2,4-trimethoxybenzene	−0.09	−0.117	+0.073
9,10-dicyanoanthracene	1,2,4-trimethylbenzene	−0.085	−0.110	+0.064

[a] The first entry is from Table 3 (**A**/**7**) and the second from a previous data set.[4]

intermediate, the data were analyzed as a biexponential system with the five effective rate constants shown in eq 7.[12]

$$\begin{tikzcd}
A^* \arrow[r, shift left, "k_{A^*E}\,[D]"] \arrow[d, "k_{A^*}"'] & \text{Exciplex} \arrow[l, shift left, "k_{EA^*}"] \arrow[d, "k_E"'] \arrow[d, bend left, "k_q{}^E\,[D]"] \\
\text{all decays} & \text{all decays}
\end{tikzcd} \qquad (7)$$

Of these rate constants, k_{A^*} is the reciprocal of the lifetime of A* in the absence of D. The remaining four rate constants are determined from the two kinetic decay parameters (λ_1 and λ_2) and the prefactor ratios (c_2/c_1) as functions of [D] (see the Supporting Information for the derivation).

In the case of the reaction of **A**/**7**, there was a minor additional deactivation path ($k_q{}^E$) of the exciplex that was dependent on the concentration of the donor. This additional decay may be due to a 2:1 complex formation, which has been observed in other reactions,[13] or due to trace impurities of low E_{ox} in the donor. The data and the rate constants derived from the fitting are shown in Figure 5.

The stability of the exciplex relative to A* + D, denoted Δ_E, is given by $RT \ln(k_{EA^*}/k_{A^*E})$.[4] The shift term *s* can then be calculated for individual reactions in the series from the SPC analysis according to eq 8.[4]

$$s = \Delta_E - \Delta G + RT \ln(k_{lim}/k_E) \qquad (8)$$

Table 4 compares values of Δ_E and *s* for the pair **A**/**7** (Table 3) with those for a pair from the previous study that has nearly the same net driving force (ΔG). The close similarity between the Δ_E and *s* values for these two reactions further supports the conclusion that the two data sets (Figure 3) share a common kinetic scheme as well as very similar controlling parameters.

Limits to Detection of Quenching. As noted above, the RW work includes many data points for quenching where the net reaction free energy ΔG exceeds ~0.14 eV (i.e., $\Delta G + s > \sim 0.2$ eV). In this section we demonstrate that there is actually *no* detectable quenching in this free energy range. We begin with the steady-state fluorescence spectra for the **A**/**4** pair, for which $\Delta G = 0.24_5$ eV. As shown in Figure 6, the spectrum with 1 M **4** is slightly shifted relative to that of **A** but, importantly, shows an *increase* in the fluorescence quantum yield—not a decrease as would be expected for excited-state quenching. Similar behavior was observed for other donors with **A** when $\Delta G > 0.2$ eV (see the Supporting Information). A logical conclusion from these experiments is that the high donor concentrations required to test for quenching in this free energy regime result in perturbation of the medium, which alters the ratios of fluorescence to other unimolecular deactivation processes (intersystem crossing and internal conversion), leading to small increases in the fluorescence intensities. In retrospect, the

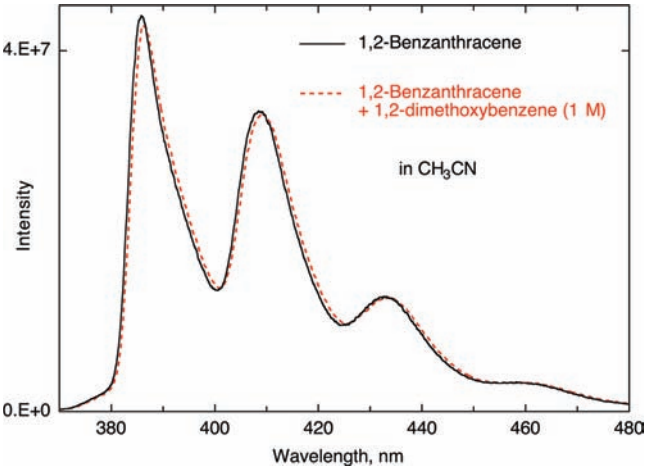


Figure 6. Emission spectra of 1,2-benzanthracene (**A**) in acetonitrile in the absence (solid, black curve) and presence (red, dashed curve) of 1 M 1,2-dimethoxybenzene (**4**). The samples had identical optical densities at the excitation wavelength (358 nm). The integrated area in the presence of **4** is 1.01 times *larger* than in the absence of **4**. Correction for differences in refractive indices[14] (a factor of 1.039) shows that the presence of **4** (at 1 M concentration) leads to an *increase* in the fluorescence quantum yield of **A** by a factor of 1.05. The spectrum in the presence of **4** is shifted to lower energies by 35 cm^{-1}. A similar shift to lower energies is observed in the corresponding absorption spectra (25 cm^{-1} for the lowest energy transition, 384 nm, and 50 cm^{-1} for the higher transitions, <370 nm).

quenching previously reported by RW for these experiments could be ascribed to use of a fluorometer with fixed-wavelength excitation and emission capabilities, which did not easily allow for corrections of medium-induced changes to both the emission *and* absorption spectra (see the Supporting Information) and/or to trace impurities with low E_{ox} in the donors.

We have additionally reexamined the reaction of excited 1-pyrenecarboxylic acid (**C**) with anisole (**1**), for which ΔG = 0.22 eV. The lifetime of excited **C** in argon-purged acetonitrile was 10.33 ± 0.06 ns, whereas in the presence of 1 M anisole it was 9.83 ± 0.08 ns. This small difference in lifetimes could be attributed to quenching or to a medium perturbation at the high concentration of anisole. To test the latter hypothesis, the lifetime of **C** in the presence of 1 M benzyl methyl ether (BME) was measured. BME is structurally similar to anisole but has a much higher oxidation potential. The oxidation potential of BME is expected to be higher than that of toluene (E_{ox} = 2.26 V vs SCE)[10a] and, therefore, at least 0.5 V higher than that of anisole (E_{ox} = 1.77 V vs SCE). With such a high E_{ox}, electron transfer quenching of excited **C** by BME can be safely ruled out. The lifetime of excited **C** in the presence of 1 M BME was 9.86 ± 0.08 ns, which is indistinguishable from that in the presence of anisole. Thus, the slight decrease in the lifetime of excited **C** in the presence of anisole or BME can clearly be ascribed to a medium-induced perturbation which, in this case, happens to slightly increase the rate constant of one or more of the intrinsic decay processes (fluorescence, intersystem crossing, or internal conversion) of singlet excited **C**. Importantly, there is no evidence of electron transfer quenching for the **C**/**1** pair.

As noted above, the original RW plot also included data for quenching of excited aromatic donors by benzonitrile. In this subset of reactions, the largest reported quenching constant (4.6×10^{7} $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) is that for excited 9,10-dimethylanthracene (DMA).[15] The reported values for the other donors are much lower, $(3-4) \times 10^{6}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Reexamination showed that benzonitrile does *not* quench excited DMA. The lifetime of excited DMA in argon-purged acetonitrile was 16.55 ± 0.10 ns. The lifetime in the presence of 1 M benzonitrile is indistinguishable, 16.54 ± 0.11 ns; thus, no quenching is observed (see the Supporting Information). Having ruled out quenching in the case of DMA, for which the reported quenching constant was an order of magnitude greater than for the other donors, quenching in these other cases is clearly unlikely.

Implications of the Fit to the Sandros−Boltzmann Equation (4). As discussed previously,[4] the SB dependency of k_{q} in Figures 2 and 3 can readily be explained if the two encounter pairs in eq 6, A*/D and $\mathrm{A}^{\bullet-}/\mathrm{D}^{\bullet+}$, interconvert rapidly, i.e., k_{c} and k'_{c} are appreciably larger than $k_{-\mathrm{d}}$ and k_{term}, respectively. In this case, k_{q} is given by the SB equation (4), with k_{lim} approximately equal to k_{d} and with the shift term s given by eq 9.

$$s = \delta + RT \ln\left(\frac{k_{\mathrm{d}}}{k_{\mathrm{term}}}\right) \qquad (9)$$

Derivation of eq 9 is analogous to that given earlier[4] (see the Supporting Information). The term δ in eq 9 is the free energy of the product encounter pair, $\mathrm{A}^{\bullet-}/\mathrm{D}^{\bullet+}$, relative to the free ions $\mathrm{A}^{\bullet-} + \mathrm{D}^{\bullet+}$, and is estimated to be the main contribution to the shift term s of 0.06 eV.[4]

Deviation from the SB dependence, eq 4 with $k_{\mathrm{lim}} \approx k_{\mathrm{d}}$ and s given by eq 9, is expected only if the conformational alignment (exciplex formation) rate constants, k_{c} and k'_{c}, are not large enough relative to the competing dissociation rate constants, $k_{-\mathrm{d}}$ and k_{term}. In such cases the intermediates would not maintain equilibrium during the reaction. As pointed out in the section "Quenching Constants", the data points for the quenching by the sterically crowded donor 1,2,3-trimethoxybenzene (**5**), which deviate from the rest of the data (see Figures 2 and 3), are plausibly due to slower conformational alignment. Smaller values of k_{c} and k'_{c} are expected if the geometry of the donor in the exciplex is sufficiently different from that in the neutral reactant and/or its radical cation, which is likely the case here.[16] For the rest of the data points in Figures 2 and 3, there is clearly no information regarding any of the conformational alignment (exciplex formation) rate constants. More broadly, for any reaction that displays Sandros−Boltzmann behavior, no information can be obtained about the microscopic rate constants for interconversion of the contact species, except that they are greater than the separation rate constants of the encounter pairs. Such behavior has long been recognized in triplet energy transfer.[18] While it is surely not universal, it may be more common than previously thought.

Concluding Remarks. In this paper we reexamined the original RW reactions. Using remeasured quenching constants and excitation energies, together with accurate redox potentials, led to the observation that the quenching constant (k_{q}) follows a simple SB dependency on the reaction free energy. We also showed that this dependency is indistinguishable from what we reported recently for a different set of acceptors and donors. In most of the RW data set, (hetero)aromatics were used as the excited-state acceptors and alkoxybenzenes and anilines were used as donors, whereas in our previous reactions,[4] the excited acceptors were cyanoaromatics and the donors were alkylbenzenes and biphenyls. That both sets of data show the same dependency suggests that the SB equation may apply more broadly, at least for reactants of similar structures. In general, quenching data that fit a Sandros−Boltzmann dependence indicate that the encounter pairs interconvert so rapidly that *no detailed information* can be extracted from an RW plot regarding the individual steps in the quenching process.

There are four main reasons why Rehm and Weller reached conclusions that differ so greatly from those presented here. First was the inclusion of erroneous points in the strongly endergonic region, where in reality no quenching occurs. As a result, the dependence of k_q on free energy in the endergonic region appeared considerably less steep than it actually is. Second was inclusion of data points in the strongly exergonic region. The lack of a decrease in k_q with increasing exergonicity (inverted region effect) is now attributed to a changed mechanism, namely, long-range (noncontact) electron transfer.[6,19] Third was the assumption that the free energy of the primary electron transfer intermediate, the encounter radical ion pair ($A^{\bullet-}/D^{\bullet+}$), is lower than that of the free, fully solvated species by 0.06 eV, where in reality it is the other way around. This factor caused the values of k_q to fall below the diffusion limit for reactions that were believed to be significantly exergonic. Fourth was the inability at the time to detect weak exciplex emissions,[20] which led to the assumption that the mechanism was simply electron transfer within the encounter pairs. Exciplexes are now shown to play a pivotal role as intermediates in these reactions.

The assumption of a simple electron transfer mechanism with a negative free energy shift (eq 1a) led Rehm and Weller to eq 2. To fit the quenching data, it was proposed that the reorganization energy for the putative electron transfer process, $\Delta G^{\ddagger}$, could be described by a simple (but ad hoc) functional form, eq 2b, with $\Delta G^{\ddagger}(0)$ as an adjustable parameter.[1]

Rehm and Weller[1] and several subsequent authors have also attempted to fit the same RW data using theories of electron transfer to evaluate the rate constants for electron transfer within the encounter pair.[21] For the mildly endergonic to mildly exergonic reactions that are of interest here, such treatments miss the mark for three fundamental reasons. (1) Some rely on the originally postulated −0.06 eV shift to evaluate the free energy of reaction within the encounter pair. Others, equivalently, assume that the Coulomb potential applies even at contact—an assumption that is no longer justified. (2) The fundamental theories by Marcus and others apply to one-step *complete* transfer of an electron from a donor to an acceptor in contact. This is *not* the mechanism of the quenching reactions discussed here, which involve *partial* electron transfers from A*/D to the exciplex and from the exciplex to $A^{\bullet-}/D^{\bullet+}$. (3) If a microscopic theory of the interconversion rates among the exciplex and the encounter pairs were available, and if one attempted to apply it to the RW reactions, little could be learned except that the interconversion is too fast to evaluate from the data.

The data presented here and the examples in ref 4 all show a Sandros−Boltzmann dependence of the quenching constants on the reaction free energy. It will be interesting to see how widespread this SB dependence is and under what conditions deviations will occur. Work along these lines is under way. As should be clear from the present work, to draw definitive conclusions, it is critical to use reliable redox potentials, excited-state energies, and quenching constants. Also, particular caution is needed when attempting to evaluate very weak quenching that requires a high quencher concentration to detect, as this can affect the competing intrinsic unimolecular rate constants of the fluorophore.

Although the kinetics of electron transfer quenching are now shown to be quite different from those envisioned by Rehm and Weller, their seminal concept to correlate electron transfer quenching with the excitation energy and redox potentials was extraordinarily important and will undoubtedly continue to be. The revised kinetic scheme involving exciplexes, the rapid and reversible interconversion of the intermediates, and the role of incomplete solvation in determining the energy of the ionic encounter pair are, however, significant modifications to the original RW formulation. They represent a paradigm shift in how to understand the Rehm−Weller reactions and, potentially, many others in the literature.

■ EXPERIMENTAL SECTION

Materials. Acetonitrile (99.93+% Baker, HPLC grade, <10 ppm H_2O) was purified by passing the solvent over a bed of activated alumina.[22] The acceptors and donors were purified by fractional distillation (liquids) or recrystallization (solids).

Steady-State Luminescence Measurements. Emission spectra and intensities were measured using a Fluorolog-3 spectrofluorometer (Jobin Yvon, Horiba) at 20 °C. 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 (Figures S3−S5 in the Supporting Information).

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-C-H 375 driven by a PDL800-B driver, PicoQuant) emitting at 370 nm was used. The instrument response functions extended over ca. 285−290 ps. The emission decays were monitored at wavelengths near the fluorescence maxima of the excited monomers. The data were analyzed using the FluoFit, version 4.1 (Picoquant), software package. Errors in the measured lifetimes, typically ≤0.02 ns, were calculated using the error surface analysis included in the software.

Electrochemical Measurements. Cyclic voltammetry experiments were performed at scan rates ranging from 0.1 to 20 V/s (for 1,2-benzanthracene, benzonitrile, and 9,10-dimethylanthrancene) and at 1000 V/s (for 3,4-benzacridine and 1-pyrenecarboxylic acid) in argon-purged acetonitrile containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate and ∼1 mM substrate (see the Supporting Information for voltammograms). The derived standard potentials were electronically corrected (positive feedback) for ohmic drop. A computer-controlled Versatile Modular potentiostat was used for scan rates up to 20 V/s. A homemade, solid-state amplifier potentiostat with positive feedback *iR* drop compensation and a Tacussel GSTP 4 function generator were used for the high scan rate measurements. Voltammograms were recorded on a digital oscilloscope. All experiments were conducted with a standard three-electrode setup in a conical electrochemical cell encased in a jacket that allowed the temperature to be controlled at 20 °C by means of a thermostated circulating bath. The working electrode was a glassy carbon disk (0.5 mm diameter) that was polished using a 1 μm diamond paste. The counter electrode was a glassy carbon disk (0.3 cm diameter). All potentials are recorded vs an SCE electrode that was isolated from the working electrode compartment by a salt bridge with a ceramic frit that allowed ionic conduction between the two solutions while avoiding appreciable contamination. Numerical simulations of the voltammograms were performed (BAS Digisim Simulator 3.03) to precisely determine the values of the standard potentials.[23]

ASSOCIATED CONTENT

Supporting Information. Excitation energies, cyclic voltammograms, Stern−Volmer plots, spectra of 1,2-benzanthracene in the absence and presence of high-E_{ox} alkoxybenzenes, lifetime of 9,10-dimethylanthracene in the presence of benzonitrile, detection of weak exciplex fluorescence, computed structure of 1,2,3-trimethoxybenzene radical cation, derivation of eqs 4 and 9, derivation of k_q based on the scheme in eq 7, and equilibrium approximation. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

farid@chem.rochester.edu; jpd@chem.rochester.edu; pmerkel@rochester.rr.com; young@chem.rochester.edu; deepak.shukla@kodak.com; gonzalo.guirado@uab.es

ACKNOWLEDGMENT

Research support was provided by a grant from the National Science Foundation (CHE-0749919). G.G. is grateful to the Spanish Ministerio de Ciencia e Innovacion for financial support (Grant CTQ2009-07469).

REFERENCES

(1) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.

(2) $\Delta G'$ is denoted ΔG_{23} in ref 1.

(3) As of March 2011, a Science Citation Index search (ISI Web of Knowledge; Thomson Reuters, 2009, http://isiknowledge.com/wos) shows that ref 1 has been cited ∼2900 times.

(4) Farid, S.; Dinnocenzo, J. P.; Merkel, P. M.; Young, R. H.; Shukla, D. *J. Am. Chem. Soc.* **2011**, *133*, 4791.

(5) See, for example: (a) Gould, I. R.; Young, R. H.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068. (b) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176. (c) Wang, Y.; Haze, O.; Dinnocenzo, J. P.; Farid, S.; Farid, R. S.; Gould, I. R. *J. Org. Chem.* **2007**, *72*, 6970.

(6) (a) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622. (b) Keizer, J. *J. Phys. Chem.* **1982**, *86*, 5052. *Chem. Rev.* **1987**, *87*, 167. (c) Tachiya, M. *Radiat. Phys. Chem.* **1983**, *21*, 167. (d) Murata, S.; Tachiya, M. *J. Phys. Chem.* **1996**, *100*, 4064. (e) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 6858. (f) Domingue, R. P.; Fayer, M. D. *J. Chem. Phys.* **1985**, *83*, 2242. (g) Weidemaier, K.; Tavernier, H. L.; Swallen, S. F.; Fayer, M. D. *J. Phys. Chem. A* **1997**, *101*, 1887. (h) Eads, D. D.; Dismer, B. G.; Fleming, G. R. *J. Chem. Phys.* **1990**, *93*, 1136. (i) Nishikawa, S.; Asahi., T.; Okada, T.; Mataga, N.; Kakitani, T. *Chem. Phys. Lett.* **1991**, *185*, 237. (j) Matsuda, N.; Kakitani, T.; Denda, T.; Mataga, N. *Chem. Phys.* **1995**, *190*, 83. (k) Kakitani, T.; Matsuda, N.; Yoshimori, A.; Mataga, N. *Prog. React. Kinet.* **1995**, *20*, 347. (l) Burshtein, A. I. *Chem. Phys. Lett.* **1992**, *194*, 247. (m) Burshtein, A. I.; Frantsuzov, P. A. *J. Chem. Phys.* **1997**, *106*, 3948. (n) Burshtein, A. I.; Neufeld, A. A.; Ivanov, K. L. *J. Chem. Phys.* **2001**, *115*, 2652. (o) Rosspeintner, A.; Kattnig, D. R.; Angulo, G.; Landgraf, S.; Grampp, G. *Chem.—Eur. J.* **2008**, *14*, 6213.

(7) (a) The IUPAC numbering scheme for pyrene differs from that used in ref 1 such that the compound listed there as 3-pyrenecarboxylic acid is now named 1-pyrenecarboxylic acid. (b) RW also reported data with 2-pyrenecarboxylic acid (referred to as the 4-isomer in ref 1) as an excited-state electron acceptor. This compound was not reinvestigated here because of its structural similarity to 1-pyrenecarboxylic acid and because the driving force range of its quenching experiments overlaps that of the other acceptors and is, therefore, not distinctive.

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

(9) Pu, L.; Guirado, G.; Farid, S.; Dinnocenzo, J. P. Manuscript in preparation.

(10) (a) Merkel, P. B.; Luo, P.; Dinnocenzo, J. P.; Farid, S. *J. Org. Chem.* **2009**, *74*, 5163. (b) Guirado, G.; Fleming, C. N.; Lingenfelter, T. G.; Williams, M. L.; Zuilhof, H.; Dinnocenzo, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 14086.

(11) Pu, L.; Farid, S.; Dinnocenzo, J. P. Manuscript in preparation.

(12) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. (b) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, A* **1963**, *275*, 575.

(13) (a) In some cases, interception of an exciplex by a second donor molecule may lead to emission from the 2:1 exciplex and, in others, to exciplex quenching via faster return electron transfer. For an example of the latter, see ref 13b and references therein. (b) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

(14) (a) To compare the fluorescence intensity of a solution with a refractive index n to that of a reference sample with a refractive index n_R, the former is to be multiplied by n^2/n_R^2.[14b,c] (b) Knoblauch, O. *Ann. Phys. (Weinheim, Ger.)* **1895**, *54*, 193.(c) Lakowicz, J. P. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York; 1999; p 52.

(15) The excitation energy (E_{excit}) of 9,10-dimethylanthracene (DMA), derived from the midpoint of the reduced absorption and emission spectra in acetonitrile, is 3.09 eV, and its oxidation potential is 1.09 V vs SCE (see the Supporting Information). The reduction potential of benzonitrile (BN) is −2.34 eV (see the Supporting Information). These three values yield a ΔG ($E_{redox} - E_{excit}$) for electron transfer quenching of excited DMA with BN of +0.34 eV.

(16) A number of experiments in both the solid state and solution demonstrate that at least one of the methoxy groups in neutral 1,2,3-trimethoxybenzene is twisted out of conjugation with the aromatic ring.[17] In contrast, MO calculations (B3LYP/6-311+G**) show that all three methoxy groups in the radical cation are aligned for conjugation (see the Supporting Information).

(17) (a) Carter, C. M.; Facelli, J. C.; Alderman, D. W.; Grant, D. M.; Dalley, N. K.; Wilson, B. E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3673. (b) Makriyannis, A.; Fesik, S. *J. Am. Chem. Soc.* **1982**, *104*, 6462. (c) Emsley, J. W.; Hadenfeldt, S.; Horne, T. J.; Celebre, G.; Longeri, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 419. (d) Emsley, J. W.; Foord, E. K.; Lindon, J. C. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1211.

(18) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.

(19) In the closely related reactions of cyanoaromatics/alkylbenzenes, as ΔG becomes more negative than ca. −0.4 eV, long-range electron transfer leads directly to the formation of a solvent-separated radical ion pair (SSRIP).[5a] This alternate quenching process is rapid, precluding a decrease in k_q at high exergonicity, because of the large reorganization energy involved. In this case λ_s associated with the SSRIP is ∼1 eV larger than for an ion pair at contact.[5a] In contrast, for ΔG values less negative than −0.4 eV, numerous analyses[6d,h,j,k,m,o] in polar solvents of low viscosity support the adequacy of a simple encounter complex or contact electron transfer model.

(20) Detecting weak exciplex emissions at the time of the original RW work would not have been easy, if at all possible. Digital recording of fluorometry data was not available 40 years ago, and instruments were far less sensitive. Since then, the much lower dark count of photomultiplier tubes and the ease of manipulating the data digitally, e.g., by curve subtraction and logarithmic plots, have made it practical to detect such weak exciplex emissions at the tail of the much stronger residual monomer fluorescence (see Figure 4 and the Supporting Information).

(21) (a) Legros, B.; Vandereecken, P.; Soumillion, J. Ph. *J. Phys. Chem.* **1991**, *95*, 4752. (b) Tachiya, M.; Murata, S. *J. Am. Chem. Soc.* **1992**, *96*, 8441. (c) Matsuda, N.; Kakitani, T.; Denda, T.; Mataga, N. *Chem. Phys.* **1995**, *190*, 83. (d) Burshtein, A. I.; Ivanov, K. L. *J. Phys. Chem. A* **2001**, *105*, 3158.

(22) (a) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518. (b) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.

(23) Andrieux, C. P.; Savéant, J.-M. In *Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: NewYork, 1986; Vol. 6, 4/E, Part 2, p 305.