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Electron Transfer by Excited Benzoquinone Anions: Slow Rates for Two-Electron Transitions

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Ⓢ *Supporting Information*

ABSTRACT: Electron transfer (ET) rate constants from the lowest excited state of the radical anion of benzoquinone, $BQ^{-\bullet*}$, were measured in THF solution. Rate constants for bimolecular electron transfer reactions typically reach the diffusion-controlled limit when the free-energy change, $\Delta G°$, reaches -0.3 eV. The rate constants for ET from $BQ^{-\bullet*}$ are one-to-two decades smaller at this energy and do not reach the diffusion-controlled limit until $-\Delta G°$ is 1.5−2.0 eV. The rates are so slow probably because a second electron must also undergo a transition to make use of the energy of the excited state. Similarly, ET, from solvated electrons to neutral BQ to form the lowest excited state, is slow, while fast ET is observed at a higher excited state, which can be populated in a transition involving only one electron. A simple picture based on perturbation theory can roughly account for the control of electron transfer by the need for transition of a second electron. The picture also explains how extra driving force ($-\Delta G°$) can restore fast rates of electron transfer.
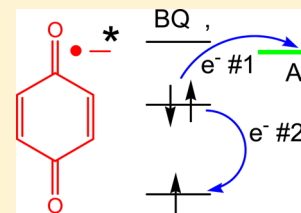
INTRODUCTION

Electron transfer (ET) by excited states is ubiquitous in chemistry, physics, and biology, including its fundamental role in photosynthesis. Usually excited states of molecules transfer a single electron, while other electrons change little; they are spectators whose spatial distributions change only moderately. Here, we investigate electron transfer from the lowest excited state of the radical anion of benzoquinone, $BQ^{-\bullet*}$. Previous work[1,2] pointed to excited state formation upon electron attachment to BQ. $BQ^{-\bullet*}$ in THF was found to have 60 ns of lifetime,[2] which is much longer than lifetimes typical of excited radical ions.[3−10] The long lifetime could make $BQ^{-\bullet*}$ a good candidate for participation in ET reactions. Observations of fluorescence and computations led to the conclusion that $BQ^{-\bullet*}$ has an electronic configuration differing from the ground state, $BQ^{-\bullet}$, in the occupancies of two electrons, as depicted in the orbital diagram in Figure 1.

The electronic configuration of $BQ^{-\bullet*}$ implies that to make use of its excitation energy, transfer of an electron from $BQ^{-\bullet*}$ would require that a second electron undergo a transition within $BQ^{-\bullet}$: electron transfer by that $BQ^{-\bullet*}$ is a two-electron process. A second possibility, thermal repopulation of $BQ^{-\bullet**}$ followed by transfer, is unlikely due to the 0.5 eV higher energy of $BQ^{-\bullet**}$. How does the need for two electron changes effect rates of electron transfer? This paper describes experiments aimed to test this question. Two types of experimental results appear below. One type creates $BQ^{-\bullet}$ by chemical reduction in THF and photoexcites it to form $BQ^{-\bullet*}$ in the presence of neutral acceptor molecules. The second uses pulse radiolysis to create solvated electrons (e^-_s) in THF, which then react with BQ or substituted BQs. Substituted BQs were used to vary the free-energy change, $\Delta G°$. The effect of $\Delta G°$ on the reaction rate constants yields evidence that despite sufficient energetics,
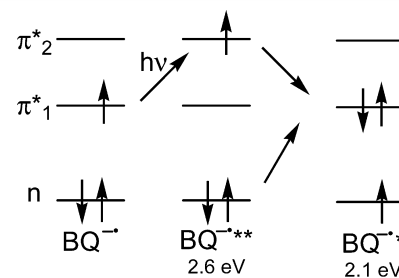

Figure 1. Occupancies of frontier spin−orbitals in the radical ion in its ground state ($BQ^{-\bullet}$). Photoexcitation of the strongly allowed transition at 450 nm promotes an electron to a higher π^* orbital, yielding $BQ^{-\bullet**}$. Relaxation of two electrons gives the lowest excited state $BQ^{-\bullet*}$.

electron attachment to BQ does not appear to appreciably populate the lowest excited state $BQ^{-\bullet*}$ or the ground state, $BQ^{-\bullet}$. Instead, the rates are best understood in terms of ET to exclusively populate $BQ^{-\bullet**}$, rather than involving two electron internal rearrangements to form $BQ^{-\bullet*}$.

Transitions of two electrons are known in the Dexter exchange mechanism of triplet energy transfer[11] and may be involved in singlet fission, a process with great potential for enhancement of photovoltaics.[12] It is well-known from X-ray spectroscopies[13] that excited states can relax by transitions of more than one electron but still occur rapidly. In that field, transitions of two electrons seem facile and commonplace. Transfers of two or more electrons, usually with protons, are

needed for water splitting or CO_2 reduction.[14−16] The need for proton transfers is clearly a kinetic limitation, but it is not clear whether there is any difficulty due to transfer of two electrons. Here, we will report rates of electron transfer from $BQ^{−\bullet}*$ or to BQ to populate $BQ^{−\bullet}*$ and draw comparisons. Transition of two electrons does appear to have substantial effects on the rates, which are often slow, probably due to the configuration shown in Figure 1.

■ EXPERIMENTAL SECTION

Chemicals. 1,4-Benzoquinone (BQ) and 1,4-dicyanobenzene from Aldrich were sublimed and stored under nitrogen in the dark. Fluorobenzene, phenanthrene, biphenylene, 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (the 2.2.2 cryptand, abbreviated C_{222}), o-terphenyl, pyrene, and sodium potassium alloy from Aldrich, diethyl terephthalate (TCI), and 9-fluorenone (Fluka) were used as received. Biphenyl was 3× recrystallized from ethanol. Tetrahydrofuran (Aldrich, anhydrous, inhibitor free) was purified under argon by a Vacuum Atmospheres purification system. Water was purified by Milli-Q water purification system (18 MΩ $cm^{−1}$).

Preparation of BQ Anion in THF Solution. Upon addition of NaK to THF with C_{222} present, the solution color changed immediately to blue, with an absorption peaking near 700 nm, known to be $Na^−$.[17−19] C_{222} is the 2.2.2 cryptand, which encapsulates alkali metal ions such as K^+ or Na^+,[20,21] substantially insulating them from their surroundings (see Figure S1 of the Supporting Information for depictions). Addition of ~5 mM BQ yielded a yellowish BQ anion solution. The absorption spectra were recorded to monitor production of ~0.1 mM of BQ anion. Photoexcitation gave bleach of BQ anion having a lifetime of ~10 ns, which is, shorter than the lifetime of $BQ^{−\bullet}*$ free ions formed in THF.[2] The short lifetime of $BQ^{−\bullet}*$ appears to be related to the presence of the counterion and, in part, to the reaction with unreduced BQ remaining in the solution. Reduction with sodium metal in THF or cobaltocene in acetonitrile did not lengthen the lifetime. Nearly half of the laser-produced bleach of BQ anions did not recover. The reason is not clear but probably involves photochemistry of $BQ^{−\bullet}*$, possibly by slow proton transfer to create semiquinone $BQH^\bullet$ radicals. Addition of electron acceptors shortens the lifetime of the bleach, as described below, and restores recovery of the bleach.

Nanosecond UV−visible Transient Absorption Spectroscopy of BQ Anion. UV−vis transient absorption experiments were conducted with a home-built apparatus reported previously.[22] Briefly, excitation was provided by an Opotek Vibrant LD 355 II OPO laser (420 nm, ~2 mJ/pulse) at 5 Hz. The laser pulse was measured to be 3.2 ns fwhm. The sample was probed by a pulsed Xe arc lamp in a 90° beam geometry arrangement, and a Tektronix DPO4032 digital phosphor oscilloscope (350 MHz, 2.5 GS/s) was used to digitize the transient signals from a Hamamatsu R928 PMT detector. The sample was held in a thermostatted cell holder, which was maintained at 25.0 ± 0.1 °C. The useful range of wavelengths for probing the sample with this apparatus is 300−820 nm. For the experiment, the BQ anion was excited at 420 nm and probed at 450 nm.
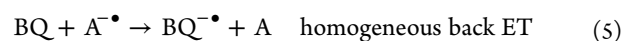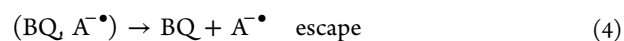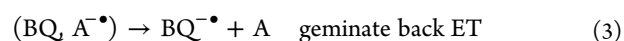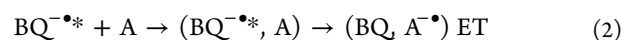
Pulse Radiolysis measurements were carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF). The LEAF facility and the methods used are described in detail elsewhere.[23,24] Briefly, the electron pulse (<50 ps duration) was focused into a sample cell and probed

collinearly with light from a xenon arc lamp pulsed to ~200 times its normal intensity. Probe wavelengths were selected with 10 nm bandpass interference filters. Electron pulses used typically produce 3−5 μM solvated electrons in water at 2 ns, corresponding to a dose/pulse of 7−12 Gy.

■ RESULTS AND ANALYSIS

Production of Benzoquionone Anions. The absorption of $BQ^{−\bullet}$ showed peaks at 454, 424, and 405 nm (Figure S2 of the Supporting Information), probably due to $(BQ^{−\bullet},\{K^+\})$, where $\{K^+\}$ represents the metal ion, probably potassium, encapsulated by C_{222}. Ion pairs are likely to be the dominant species because the dissociation constant, K_d, for the small $BQ^{−\bullet}$ is almost certainly less than $K_d = 1.5 × 10^{−7}$ M for naphthalene[25] based on the correlation of dissociation constant to anion size.[25] From the extinction coefficient of $BQ^{−\bullet}$ at 420 nm ($\varepsilon_{420} = 6 × 10^3$ $M^{−1}$ $cm^{−1}$),[26] the concentration of BQ anion produced was 0.14 ± 0.02 mM for the laser transient absorption experiments.

Electron Transfer From $BQ^{−\bullet}*$. $BQ^{−\bullet}$ produced by chemical reduction was photoexcited. The $BQ^{−\bullet}*$ was allowed to react with a series of acceptor molecules having redox potentials more positive than that of $BQ^{−\bullet}*$. The concentration of electron acceptors was adjusted to obtain rates of electron transfer to the acceptors in the range from $3 × 10^7$ to $1 × 10^8$ $s^{−1}$, according to the following scheme:

$$BQ^{−\bullet} + hv \rightarrow BQ^{−\bullet}** \rightarrow BQ^{−\bullet}* \quad \text{excitation} \qquad (1)$$

$$BQ^{−\bullet}* + A \rightarrow (BQ^{−\bullet}*, A) \rightarrow (BQ, A^{−\bullet}) \quad \text{ET} \qquad (2)$$

$$(BQ, A^{−\bullet}) \rightarrow BQ^{−\bullet} + A \quad \text{geminate back ET} \qquad (3)$$

$$(BQ, A^{−\bullet}) \rightarrow BQ + A^{−\bullet} \quad \text{escape} \qquad (4)$$

$$BQ + A^{−\bullet} \rightarrow BQ^{−\bullet} + A \quad \text{homogeneous back ET} \qquad (5)$$

Here $BQ^{−\bullet}$ signifies the $(BQ^{−\bullet},\{K^+\})$ ion pair. Excitation produces $BQ^{−\bullet}**$. $BQ^{−\bullet}**$ relaxes promptly to $BQ^{−\bullet}*$ and is not observed. During the excited state lifetime of $BQ^{−\bullet}*$ electron transfer, reaction 2 can occur when the acceptor, A, collides with the excited complex. The product $(BQ, \{K^+\},A^{−\bullet})$ might back transfer an electron to the nearby geminate BQ to recreate $(BQ^{−\bullet},\{K^+\})$ in its ground state, reaction 3, or $A^{−\bullet}$ may escape from the encounter complex to form BQ, reaction 4. Reaction 4, escape of neutral BQ from the $(A^{−\bullet},\{K^+\})$ occurs by diffusion with D~$2 × 10^{−5}$ cm^2 $s^{−1}$ against little or no binding, so it occurs in the ps time region. It would ultimately be followed by homogeneous back electron transfer from $A^{−\bullet}$ to reform $BQ^{−\bullet}$, reaction 5.

The reactions were monitored by a bleach of $BQ^{−\bullet}$ absorption at its 450 nm peak and ground state recovery of $BQ^{−\bullet}$ (see Figure 2). $BQ^{−\bullet}*$ was not observed directly because its absorption bands are weak and obscured by those of $BQ^{−\bullet}$.[2] Efforts to measure the electron transfer by quenching of the fluorescence of $BQ^{−\bullet}*$ were not successful due to the weakness of the fluorescence, which has a quantum yield of 0.3%.[2] The recovery of the bleach occurs as $BQ^{−\bullet}*$ returns to the ground state. With the exceptions of pyrene and methyl-terphenyl (see below) for all the reactions, including those in Figure 2, geminate back ET (reaction 3) is so much faster than escape (reaction 4) that the $A^{−\bullet}$ ions were too few to detect. The absence of observable $A^{−\bullet}$ ions in most cases indicates that when ET (reaction 2) occurs, it is promptly followed by much
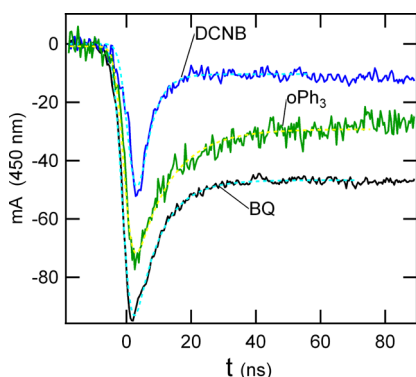
Figure 2. Transient absorption at 450 nm following excitation at 420 nm of solutions containing BQ⁻• alone and with 50 mM of 1,4-dicyanobenzene (DCNB) or o-terphenyl (oPh₃). Fit curves shown are single exponential decays [$A_0 \exp(-k_1 t) + A_{inf}$] convoluted with a Gaussian function (3.2 ns FWHM) to account for laser pulse width and response of the detection system.

faster back ET. As a result the bleach upon photoexcitation is followed by an increased rate of recovery of ground state BQ⁻• absorption when A molecules are present. ET from BQ⁻•*, which is the slow step, determines the rate of the recovery.

Recoveries of the bleaches like those shown in Figure 2 were fit to single exponential functions to extract rate constants. Convolution with a Gaussian response function allowed fitting of the growth as well as the decay of the bleach. Adjustment of the width gave 3.2 ns fwhm. The same decay rate was found without convolution when the fit was started ~0.5 ns past the peak. Convolution was found to be necessary and was used when the (pseudo first order) decay rate constant was >2×10^8 s⁻¹. For data in Figure 2, a rate constant was determined for reaction with DCNB, but for reaction with o-terphenyl, the recovery rate was not sufficiently different from that observed without o-terphenyl to determine a definite rate constant. For o-terphenyl and most other weakly exoergic reactions, the rates were found to be slow; only upper limits were determined for the slow rate constants. It should be possible, in principle, to push the determination of the rate constants to lower values, but in practice, we found this difficult. The limit of the measurement would be imposed by the 50 ns lifetime of BQ⁻•* free ions, but as noted above, we did not achieve the long lifetime using BQ⁻• produced by chemical reduction.

Attempts to Observe Formation of Products A⁻•. Attempts to observe absorption bands of electron acceptor anions p-terphenyl⁻• at 480 nm, biphenylene⁻• at 615 nm, or diethylterephthalate⁻• at 650 nm produced by reactions 2−4, were not successful. Although these anions have extinction coefficients 2−4 times larger[26] than that of BQ⁻• at 450 nm, their absorptions were not observed. The only signals possibly attributable to them were instead 2−10 times smaller than the bleach of BQ⁻• at 450 nm and showed no decay on the timescale of 8 μs. Curiously, while no absorption due to p-terphenyl⁻• was observed, an absorption from 4-methyl-p-terphenyl⁻• was detected. Two thirds of this absorption decayed with τ = 50 ns; a lifetime possibly consistent with homogeneous back-electron transfer (reaction 5) from 4-methyl-p-terphenyl⁻• to BQ with a rate constant of 2×10^{10} M⁻¹ s⁻¹. The 4-methyl-p-terphenyl⁻• absorption was formed within the laser pulse. A similar absorption due to pyrene⁻• was observed at 490 nm where the extinction coefficient ($\varepsilon = 4.3 \times 10^4$ M⁻¹ cm⁻¹)[27,28] is about six times larger than that of BQ⁻•

at 450 nm (Figures S3 and S4 of the Supporting Information). As with 4-methyl-p-terphenyl, this absorption was rapidly formed in the pulse, but it decayed with an apparent time constant of 3.6 ns, which is partly limited by the detection system. This rapidly produced component almost certainly was not produced from BQ⁻•* but instead may be formed if pyrene is reduced by the higher-lying BQ⁻•** initially formed by photoexcitation. An alternative is photoejection to form solvated electrons, which requires 2.98 eV based on redox potentials in Table 1, although the energetics appear marginal for the 420 nm, 2.95 eV excitation photons.

Table 1. Bimolecular Rate Constants for Reaction of BQ⁻•* with Electron Acceptors with Redox Potentials

acceptor[a]	abbreviation	k (M⁻¹ s⁻¹)[b]	E^0 (V)[c]	ΔG°
FBz fluorobenzene	FBz	1×10^8	−2.69[d]	0.06
biphenyl	Ph₂	<2.3×10^7	−2.65[e]	0.02
phenanthrene	phen	<7.0×10^7	−2.52[e]	−0.11
biphenylene	bpln	1.9×10^9	−2.33[e]	−0.3
pyrene	pyr	<1.4×10^8	−2.12[e]	−0.5
nitrobenzene	PhNO₂	2.5×10^9	−1.31[f]	−1.32
DCNB	DCNB	2.6×10^9	−1.74[f]	−0.89
Et₂terp	Et₂terp	4.6×10^8	−1.68[g]	−0.95
oxygen[m]	O₂	1.0×10^{10}	−0.8[g]	−1.83
p-terphenyl	Ph₃	7.0×10^8	−2.38[h]	−0.25
benzonitrile	PhCN	8.6×10^8	−2.48[i]	−0.14
NapCN	NapCN	8.1×10^8	−2.14[j]	−0.48
1,4-benzoquinone	BQ	2.5×10^{10}	−0.526[k]	−2.1
o-terphenyl	oPh₃	$9.4 \times \times 10^7$	−2.58[h]	−0.05

[a]DCNB = 1,4-dicyanobenzene, Et₂terp = diethylterphthalate, NapCN = 1-cyanonaphthalene. [b]Uncertainties ±30%, but ±15% for O₂. [c]Reduction potentials in V vs SCE and ΔG° in eV. Refs for potentials include the following: [d]Ref 35. [e]Ref 29. [f]Ref 32. [g]Ref 34. [h]Ref 33. [i]Ref 30. [j]Ref 31. [k]Ref 36. [l]Ref 37. [m]The rate constant with O₂ was measured with pulse radiolysis of O₂ and BQ in THF, taking advantage of the slow electron attachment to O₂.

Prompt Back ET Versus Escape. With the scheme of reactions 1−5, these results signal that geminate back ET, reaction 3, is very fast $k_3 \sim 2.8 \times 10^8$ s⁻¹ for pyrene and probably much faster for others. The exception of methyl-p-terphenyl is apparently the only example of escape. For others, the rate of escape, k_4, is apparently much slower; the back ET reaction 3 seems to dominate in the competition of these two reactions. The observation that k_3 is fast is consistent with A⁻• ions being formed at or near contact with BQ. Indeed this interpretation is in agreement with the slow rates of reaction of BQ⁻•* with the acceptors; slow rates are consistent with reaction only at short encounter distances. Back ET from A⁻• to BQ, reaction 3, is a simple one-electron transfer.

In the competition between reactions 3 and 4, if some observable fraction (>10%) went by reaction 4, the resulting escaped ({K⁺},A⁻•) pairs would then transfer electrons to BQ in bimolecular reaction 5 to give an additional recovery of BQ⁻• absorption with an expected rate of ~6×10^7 s⁻¹. This estimate assumes that reaction 5 is diffusion-controlled (~10^{10} M⁻¹ s⁻¹) at the ~5 mM concentration of BQ used in the experiments. No such recovery component of BQ⁻• was observable.

Rate Versus ΔG°. Table 1 reports bimolecular electron transfer rate constants from BQ⁻•* to acceptors and estimates energetics. Figure 3 plots the rate constants as a function of free energy change, ΔG°. Free energy changes were calculated using
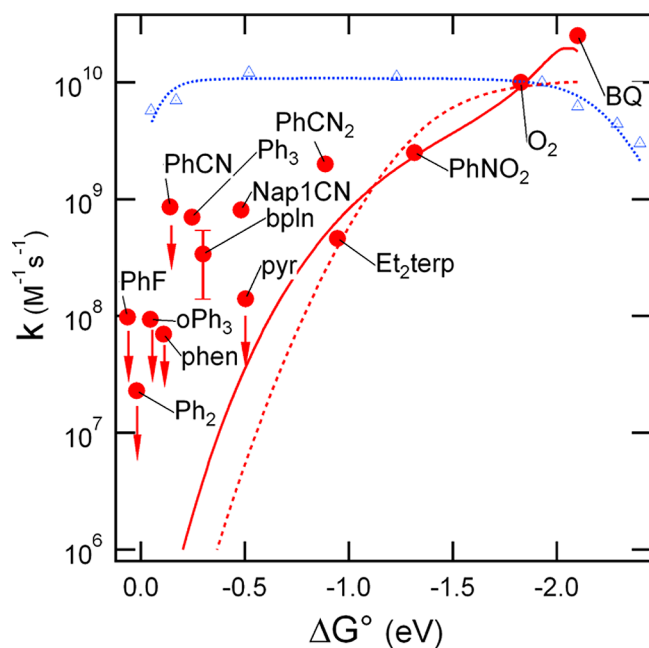
Figure 3. Bimolecular rate constants for electron transfer from $BQ^{-\bullet}*$ to electron acceptors in THF at 296 K. The rate constants were measured by observing $BQ^{-\bullet}$ ground state recovery at 450 nm after excitation at 420 nm in solutions of 5 mM BQ partially reduced by NaK in the presence of C_{222}. The observed rate constants are compared with earlier data. A fit (red dashed line) to a single-step electron transfer mechanism (eq 6) having a constant electronic coupling, V = 223 cm^{-1}, does not describe the data well, even with large reorganization energies, λ_s = 0.6 and λ_v = 2.9 eV (see Discussion). Equation 7 includes transition of a second electron in simple description, predicting that V varies with $\Delta G°$, yields a slightly improved fit (solid line). This description, described in Discussion, requires a much smaller λ_v = 0.85 eV. For comparison rates of bimolecular electron transfer from anions of biphenyl are shown (blue △).[38]

redox potentials of arenes,[29] Ph_n's[30] and others.[31−34] The redox potential of $BQ^{-\bullet}*$ was estimated as 2.1 V more negative than the reduction potential of benzoquinone, where 2.1 eV is the excited state energy of $BQ^{-\bullet}*$ determined by fluorescence.[2]

The rate constants reported in Figure 3 are compared with bimolecular rate constants for electron transfer from biphenyl anion in its ground state to acceptors in 2-methyltetrahydrofuran.[38] This comparison is apt because, like the present results, these are electron transfers from anions to neutrals, and the redox potential of biphenyl is close to that of $BQ^{-\bullet}*$ and some of the acceptors in that study are the same as those used here. Because both biphenyl and the acceptors were attached to separate steroids, the diffusion limit for those bimolecular rate constants was lower than in the present experiments, probably by a factor near 2. The well-known data for electron transfer by excited neutral molecules by Rehm and Weller[39] and more recent data[40,41] would provide similar comparisons.

The free energy dependence of electron transfer rates in the four studies cited for comparison[38−41] are similar to each other. In those past results the rates rise with increasing driving force and reach a plateau at the diffusion-controlled limit for $-\Delta G°>$ ~ 0.3 eV. In each of those comparison studies,[38−41] the rates all depend on $\Delta G°$ in a very regular way. The present results by contrast have much smaller rates at low driving forces, reach the diffusion-controlled limit only at $\Delta G°$ = ~-2.0 eV, and show

considerably less regularity (more scatter). After presenting additional data on electron attachment to form $BQ^{-\bullet}*$, we will consider two possible explanations.

Quantum Yield for $BQ^{-\bullet}*$ Formation. Photoexcitation of 9-fluorenone neutral in THF at 420 nm produced triplet fluorenone having an absorption at 450 nm, 1.6× larger than the bleach at 450 nm when $BQ^{-\bullet}$ was photoexcited under the same conditions. On the basis of the extinction coefficient at 450 nm of triplet fluorenone (ε = 6 × 10^3 M^{-1} cm^{-1})[42] and triplet quantum yield (0.48−1.0)[42−46] for fluorenone, the quantum yield for bleaching of $BQ^{-\bullet}$ upon photoexcitation was found to be 0.45 ± 0.2. Formation of $BQ^{-\bullet}*$ is therefore reasonably efficient. The very low fluorescence quantum yield (φ = 0.003)[2] following photoexcitation of $BQ^{-\bullet}$ arises mainly from poor fluorescence quantum efficiency once $BQ^{-\bullet}*$ has been formed, presumably favoring nonradiative excited state decay channels, rather than due to rapid or prompt loss of $BQ^{-\bullet}**$ and $BQ^{-\bullet}*$.

Transfer of Electrons to Quinones to Create Excited States. The requirement for transition of a second electron might also slow electron transfer to BQ to create $BQ^{-\bullet}$. Solvated electrons in THF or isooctane are known to react with BQ (k_{THF} = 2.5 × 10^{10} M^{-1} s^{-1}; k_{iso} = 2 × 10^{13} M^{-1} s^{-1}).[2,47] Cook found electron attachment to form excited states, $BQ^{-\bullet}*$, almost exclusively.[2] Very few $BQ^{-\bullet}$ ground states are formed, but they grow in as $BQ^{-\bullet}*$ decays. The free energy of the reaction of e^-_s with BQ was changed by adding substituents to BQ, which changed its ground and, thus, excited state redox potential. It is apparent that the reaction rate constant decreases with addition of methyl groups, known to make reduction potentials more negative,[37] while addition of chlorine groups makes the rate faster (see Figure 4). The changes in rate appear to be well-correlated with the changes in reaction free energies (Figure 4 and Discussion below).
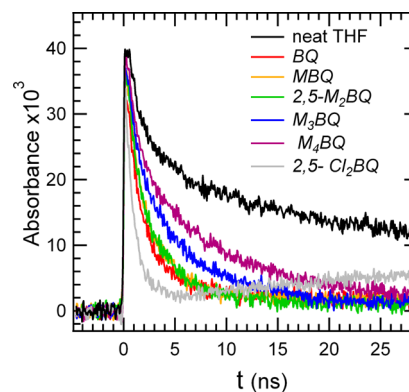

Figure 4. Disappearance of solvated electrons measured by their absorbance at 650 nm (top curve) in THF and in THF with ~10 mM BQ or substituted BQ's, where M denotes a methyl group.

Transfer of Electrons From Anions BQ. Anions of biphenyl, dibenzofuran, fluorene, fluorobenzene, and para-cyclophane were created by pulse radiolysis of solutions of ~100 mM of these solutes in THF. Reactions of these anions with 1 mM benzoquinone yielded rate constants of 1.38, 1.23, 1.23, 0.99, and 0.80 × 10^{10} M^{-1}s^{-1}. These rate constants are all at or near the diffusion-controlled limit, which helps to explain why the geminate back ET reactions tend to be very fast.

■ DISCUSSION

Results reported herein from photoexcitation experiments show that BQ$^{-\bullet}$* reacts slowly with electron acceptors at small driving forces, approaching the diffusion-controlled limit, where $\Delta G°$ no longer controls rates, only at $\Delta G°$ is approximately −2.0 eV. These results are in striking contrast to earlier electron transfer investigations that find a sharp rise near $\Delta G° = 0$. Results from pulse radiolysis show that rates of highly exoergic reactions of solvated electrons in THF with BQ and its derivatives are well below the diffusion-controlled limit and depend on $\Delta G°$ in a manner that will be found below to be consistent with creation of an excited state at ~2.6 eV. That pattern of rates strongly militates against the reaction to form ground states. Those results also indicate that electron attachment directly forms the 2.6 eV BQ$^{-\bullet}$**, not the lowest excited state BQ$^{-\bullet}$*. That BQ$^{-\bullet}$* uniquely formed indirectly by relaxation from BQ$^{-\bullet}$** is probable but not established with high certainty. These two types of results are consistent with the conclusion that BQ$^{-\bullet}$* is an unusual excited state: electron transfer to form it or electron transfer from it is slow, except perhaps at large driving forces. Two explanations will be considered to account for these observations.

Large Reorganization Energy. A possible reason for slow electron transfer from BQ$^{-\bullet}$* to acceptors at moderate driving forces ($-\Delta G°$) is an unusually large reorganization energy. For electron transfer from BQ$^{-\bullet}$*, the solvent reorganization energy, λ_s, would not be expected to be very different from λ_s for other electron transfer reactions, such as the reactions of ground state radical anions pictured in Figure 3 for comparison with the present data or the several studies of ET by excited states. The structure of BQ$^{-\bullet}$* could be very different from that of BQ. If so then the internal reorganization energy, λ_v, might be unusually large. Figure 3 shows a best fit to the data using electron transfer theory, eq 6,[48−52] (red dashed line). Equation 6 includes solvent and internal reorganization energy, represented by a single vibrational mode. To describe these bimolecular rate constants, integration[48,53,54] over all space with electronic coupling $V(r)^2 = |V(R_0)|^2 \exp(-\beta r)$ for the distant-dependent ET rate gives the electron transfer rate without diffusion, k_{act}, which is close to the rate constant at contact distance, R_0. Waite's expression,[55] $k_{Bi}^{-1} = k_{act}^{-1} + k_d^{-1}$, gives the overall bimolecular rate constant including diffusion control, k_{Bi}.

$$k_{ET} = \frac{2\pi}{\hbar} |V(r)|^2 \text{ FCWD} \qquad (6)$$

$$\text{FCWD} = (4\pi\lambda_s k_B T)^{-1/2} \sum_{w=0}^{\infty} \left(e^{-S} \frac{S^w}{w!} \right)$$

$$\exp\left\{ - [(\lambda_s + \Delta G° + w\hbar\omega)^2 / 4\lambda_s k_B T] \right\}$$

$$S = \lambda_V / h\omega$$

The earlier data for a simple ET reaction from the biphenyl anion shown for comparison in Figure 3 is described with $\lambda_s = 0.6$ and $\lambda_v = 0.35$ eV. With the same λ_s, the best fit of eq 6 to the rates for ET from BQ$^{-\bullet}$* (dashed line) gives $\lambda_v = 2.9$ eV. This large λ_v, which is required so the ET theory curve continues to rise for $-\Delta G° > 1.5$ eV, causes the theory curve to fall below the data at small driving forces. Other values make the poor fit worse: A large reorganization energy does not

provide a good explanation for the dependence of rate on free energy change. Further evidence that such a large reorganization energy is not realistic comes from the emission spectrum of BQ$^{-\bullet}$* (Figure S5 of the Supporting Information). This spectrum indicates that a total reorganization of only ~0.32 eV accompanies the transition from BQ$^{-\bullet}$* to the ground state BQ$^{-\bullet}$, pointing to quite normal reorganization energies for BQ$^{-\bullet}$*. With comparable reorganization energies from the acceptors and solvent reorganization energy for movement of the charge, the total reorganization energy is likely to be <1.0 eV, in disagreement with the 0.6 + 2.9 = 3.5 eV total that fits the data based on the assumption of simple, one electron transfer. Another explanation is needed.

Inhibition of Electron Transfer by the Requirement for Transition of a Second Electron. As noted in Figure 1, electron transfer by BQ$^{-\bullet}$* requires a transition of another electron. This requirement might be responsible for the slow ET rates and the unusual dependence on $\Delta G°$. While the two electrons could change in a completely concerted manner, another possible mechanism is indicated in Figure 5. It depicts
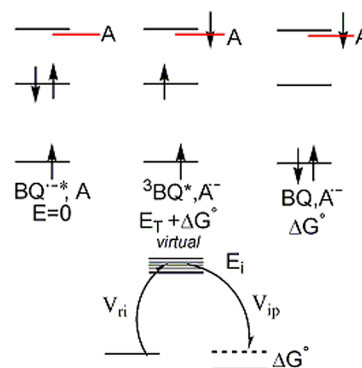

Figure 5. Schematic orbital diagram (upper) and state diagram (lower) for electron transfer from BQ$^{-\bullet}$* to an acceptor, A. The two-electron change is depicted to be accomplished first by transfer of an electron to the acceptor to create a high-energy (virtual) intermediate (the configuration in the middle of the three shown). This is followed by a second virtual step that moves the now unpaired electron to the lowest orbital shown. The state diagram shows ET to occur from the reactants to the products, lower by ΔG, via interaction with a high-energy virtual intermediate having an energy well above that of the reactants. The energy of the intermediate, relative to that of the reactants, E_i, is approximately the triplet energy (E_T) of BQ + $\Delta G°$ (note that $\Delta G°$ is usually negative).

endothermic transfer of a single electron to create an intermediate excited state followed by relaxation of a second electron to form products. The electronic configuration of the intermediate state includes excited BQ. The triplet, with an energy of 2.3 eV[27,56,57] is in the lowest energy excited state, so the lowest energy for such an intermediate is 2.3 eV − $\Delta G°$ above the reactants. For moderate values of $\Delta G°$, this intermediate is far too high in energy to be reached thermally at appreciable rates and may participate only as a virtual state, a superexchange[58−63] intermediate. Figure 5 depicts a super-exchange sequence via the high-energy, virtual intermediate in which an electron is transferred to the acceptor without deexcitation of the second electron.

Perturbation theory gives the effective electronic coupling from reactants to products via the superexchange intermediate at E_i as

$$V(r)_{eff} = V_{ri}V_{ip}/E_i = V_i^2/E_i \qquad (7)$$

where V_i is the geometric mean of matrix elements V_{ri} from reactants to the intermediate and V_{ip} from the intermediate to products. The overall electronic coupling for the reaction, V_{eff}, therefore becomes dependent on ΔG°: V_{eff} is small at $\Delta G^\circ = 0$ and increases for larger driving forces, a behavior that can potentially better explain the results in Figure 3. Substitution of V_{eff} into eq 6 yields only a slightly improved fit, as shown in Figure 3, with $V_i = 222$ cm^{-1} and $E_i = 2.06$ eV. The dependence of V_{eff} on ΔG° for these values is shown in Figure S6 of the Supporting Information, which shows that while V_{eff} increases with increasing $-\Delta G^\circ$, it changes the rate by only a factor of 9 from $\Delta G^\circ = 0$ to $\Delta G^\circ = -1.5$ eV. With a smaller V_i, the fit could produce a larger change in V_{eff} but at the expense of decreased rates that would make the fit worse. It is possible to obtain a somewhat improved description of the data by addition of a multiplication factor in eq 7 that makes V_{eff} larger without increasing V_i, but we have not examined it further because no apparent basis for this in a model is apparent.

Other factors are not included in eq 7. An important one might be the role of counterions, which despite mitigation by enclosure of Na$^+$ in C$_{222}$, may play an important role. Another is that the structure of BQ$^{-\bullet *}$ might be closer to the structure of the intermediate (tentatively ^{3}BQ*,A$^{-\bullet}$) so that the energy denominator, E_i, is smaller than the estimate given above. Still another is that vibrations might bring those structures closer to similarity. These and others might play roles in the unusual dependence on ΔG° seen in Figure 3 not accounted for in the descriptions of equations 6 and 7.

Reactions of Solvated Electrons, e^-_s, with Substituted Benzoquinones. Transfer of an electron to BQ could reverse the scheme in Figure 5, or if the donor is strong enough, it could directly populate BQ$^{-\bullet **}$ in a simple one-electron transfer. This would require that E° (D)$^{0/-}$ < E° (BQ)$^{0/-}$ = -0.4 V $- 2.6$ eV (the excitation energy of BQ$^{-\bullet **}$), so -3.0 V versus SCE. The solvated electron, e^-_s, in THF with a redox potential estimated as -3.38 V versus SCE^{64} is a sufficiently strong electron donor. Rate constants from data in Figure 4 are listed in Table 2 and plotted as a function of free energy change, ΔG°, in Figure 6. In Figure 6, they are also compared with the rate constant for reaction of e^-_s with fluorobenzene,

Table 2. Rate Constants for Reaction of Solvated Electrons with Substituted Bezoquinones in THF, with Reduction Potentials and Free Energy Changes for Formation of Radical Anions of the Quinones in Their Ground State (e.g., BQ$^{-\bullet}$), Lowest, nπ* Excited State (BQ$^{-\bullet *}$), or the Higher, π*π* Excited State (BQ$^{-\bullet **}$)^a

quinone[b]	k (M^{-1}s^{-1})	E° vs SCE[c]	ΔG°_{gnd}	$\Delta G^\circ_{n\pi}$	ΔG°_{π}
Cl$_2$BQ	8.9×10^{10}	-0.065	-3.27	-1.2	-0.67
BQ	3.9×10^{10}	-0.4	-2.94	-0.84	-0.34
MeBQ	2.8×10^{10}	-0.48	-2.86	-0.76	-0.26
Me$_2$BQ	2.6×10^{10}	-0.56	-2.78	-0.68	-0.18
Me$_3$BQ	1.4×10^{10}	-0.64	-2.7	-0.6	-0.1
Me$_4$BQ	7.9×10^{9}	-0.74	-2.6	-0.5	-0.002

^{a}The free energy changes were estimated using a reduction potential for formation of solvated electrons of -3.38 V versus SCE.^{64} ^{b}Cl$_2$BQ = 2,5-dichlorobenzoquinone, BQ = benzoquinone, MeBQ = methylbenzoquinone, Me$_2$BQ = 2,5-dimethylbenzoquinone, Me$_3$BQ = trimethylbenzoquinone, and Me$_4$BQ = tetramethylbenzoquinone. All are 1,4-benzoquinones. ^{c}Reduction potentials.^{37}
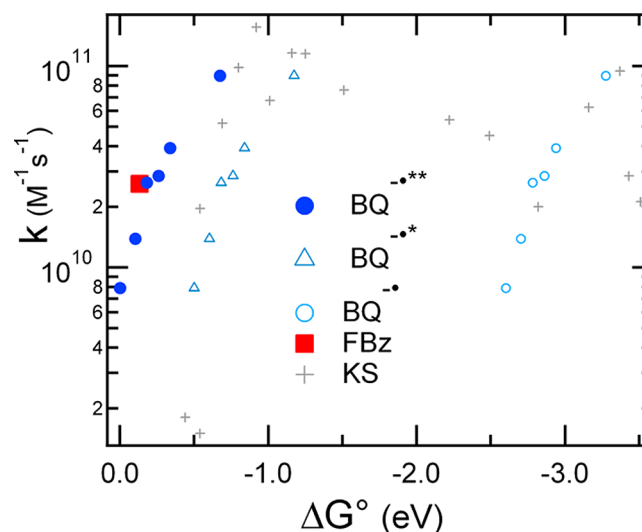

Figure 6. Rate constants for reaction of solvated electrons e^-_s in THF with substituted benzoquinones (RBQ) as a function of free energy change, ΔG°, for attachment to form ground state radical anions, RBQ$^{-\bullet}$(blue $\bigcirc$). These rates are replotted vs $\Delta G^\circ + 2.6$ eV to estimate energetics for reaction to form the π* excited states RBQ$^{-\bullet **}$ (blue $\bullet$), and vs $\Delta G^\circ + 2.1$ eV for the nπ* RBQ$^{-\bullet *}$ (light blue $\triangle$) (excited states). The measurements are compared with rate constants for e^-_s with fluorobenzene (red $\blacksquare$),^{35} and a series of molecules by Kadhum and Salmon (KS, +).^{47} Free energy changes for the substituted benzoquinones (denoted BQ) and the KS data were estimated from redox potentials and Kukharenko's determination for the solvated electron.^{64}

where ΔG° is known accurately from the observed equilibrium constant, and with rate constants in THF measured by Kadhum and Salmon,^{47} who also measured reduction potentials electrochemically. Their reduction potentials were used to estimate ΔG°, using $E^\circ = -3.38$ V versus SCE.^{64}

The rate constants in Figure 6 increase with increasing driving force, $-\Delta G^\circ$, signaling that the principle reaction channel is not highly exoergic, inverted region ET to form ground state BQ$^{-\bullet}$. In inverted region ET reactions, the rates decrease with increasing driving force. Instead, they are clearly weakly exoergic reactions forming excited states, with rates increasing as driving force increases above the excited state energy. Indeed the rates versus ΔG° curve appear to rise in a logical way near zero when the 2.6 eV energy of the π* excited state is added to ΔG°. With this 2.6 eV shift, the data compares well with the point for fluorobenzene,^{35} a weakly exoergic reaction with an accurately known ΔG°. This agreement supports the conclusion that these reactions form BQ$^{-\bullet **}$, with negligible contributions from reactions to form ground state or the nπ* state, BQ$^{-\bullet *}$.

■ CONCLUSIONS

Photoexcitation of BQ$^{-\bullet}$ produces BQ$^{-\bullet *}$ with a quantum yield of 0.45 $\pm$ 0.2. BQ$^{-\bullet *}$ paired with Na$^+$ in C$_{222}$ ({K$^+$}) has a lifetime of $\tau \sim 10$ ns, where τ is shorter without C$_{222}$ or if Cocp$_2^+$ is the counterion. BQ$^{-\bullet *}$ reacts slowly with acceptors near its redox potential and displays an unusual dependence on ΔG° with rates rising to the diffusion-controlled limit only when ΔG° is approximately -2.0 eV. The unusual dependence on ΔG° is best understood as a consequence of the requirement for transition of a second electron. A simple expression for the electronic coupling from first order

perturbation theory yields a description based on more reasonable reorganization energies. This description is improved but is only partly successful in providing a quantitative account of the rates. Other factors not explained are considerable variability of the rates, which do not follow a smooth dependence on $\Delta G°$ or the occasional exceptions to a low yield of escape of acceptor anions from BQ.

While the photoexcitation data point to substantial reduction of electron transfer rates from $BQ^{-•}*$, due to the need for transition of a second electron, a rate constant for attachment of solvated electrons to BQ complement this picture. Variation of these rates with $\Delta G°$ are most consistent with formation of the higher $\pi*$ excited state, $BQ^{-•}*$, with little contribution from reactions to form $BQ^{-•}*$, despite their more favorable energetics. Rates of electron transfer from $BQ^{-•}*$ and rates to form $BQ^{-•}*$ both point to a large reduction due to the need for transition of a second electron.

The requirement for transition of a second electron during electron transfer to or from $BQ^{-•}*$ may provide insight into multielectron processes. It differs from triplet energy transfer in which both electrons transfer between molecules, which may also be true for singlet fission. In ET by $BQ^{-•}*$, one electron transfers to or from another molecule, while the second undergoes a transition within the BQ. The process differs from two-electron processes in water splitting and CO_2 reduction in that simultaneous proton transfers are not required. In this way it may shed light on the two-electron processes themselves. ET by $BQ^{-•}*$ may bear the most similarity to cascades following X-ray excitation, but these are usually high-energy excitations, which may account for them typically occurring in very short times. Indeed, it appears that when $-\Delta G° > 2$ eV, ET by $BQ^{-•}*$ seems no longer to be slowed by the transition of the second electron. We suggest that the slow rates of weakly exoergic ET reactions of $BQ^{-•}*$ may be of modest importance in themselves, but they provide a nice example of the control of ET rate by the need for involvement of a second electron.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Depictions of the K^+, C_{222} complex, graphs showing spectra of BQ anion, transient absorption of pyrene anion and corresponding spectra, fluorescence spectrum of BQ anion, and V_{eff} as a function of free energy change. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Holroyd, R. A. Electron-Attachment to *p*-Benzoquinone and Photodetachment from Benzoquinone Anion in Non-Polar Solvents. *J. Phys. Chem.* **1982**, *86*, 3541−3547.

(2) Cook, A. R.; Curtiss, L. A.; Miller, J. R. Fluorescence of the 1,4-Benzoquinone Radical Anion. *J. Am. Chem. Soc.* **1997**, *119*, 5729−5734.

(3) Fujita, M.; Ishida, A.; Majima, T.; Takamuku, S. Lifetimes of Radical Anions of Dicyanoanthracene, Phenazine, and Anthraquinone in the Excited State from the Selective Electron-Transfer Quenching. *J. Phys. Chem.* **1996**, *100*, 5382−5387.

(4) Majima, T.; Fukui, M.; Ishida, A.; Takamuku, S. Stilbene Radical Anions in the Excited Doublet State. *J. Phys. Chem.* **1996**, *100*, 8913−8919.

(5) Gumy, J. C.; Vauthey, E. Investigation of the Excited-State Dynamics of Radical Ions in the Condensed Phase Using the Picosecond Transient Grating Technique. *J. Phys. Chem. A* **1997**, *101*, 8575−8580.

(6) Ichinose, N.; Tanaka, T.; Kawanishi, S.; Majima, T. Energy Transfer Quenching of A Fluorescent Excited Radical Cation by Counter Radical Anion: Dissipation of Radical Ions Generated by Photoinduced Electron Transfer. *Chem. Phys. Lett.* **2000**, *326*, 293−298.

(7) Brodard, P.; Sarbach, A.; Gumy, J. C.; Bally, T.; Vauthey, E. Excited-State Dynamics of Organic Radical Ions in Liquids And in Low-Temperature Matrices. *J. Phys. Chem. A* **2001**, *105*, 6594−6601.

(8) Cai, X. C.; Sakamoto, M.; Fujitsuka, M.; Majima, T. Direct Fluorescence Lifetime Measurement of Excited Radical Cation of 1,3,5-Trimethoxybenzene by Ns-Ps Two-Color Two-Laser Flash Photolysis. *Chem. Phys. Lett.* **2006**, *432*, 436−440.

(9) Samori, S.; Fujitsuka, M.; Majima, T. Properties of Excited Radical Cations of Substituted Oligothiophenes. *J. Phys. Chem. A* **2008**, *112*, 11312−11318.

(10) Grilj, J.; Buchgraber, P.; Vauthey, E. Excited-State Dynamics of Wurster's Salts. *J. Phys. Chem. A* **2012**, *116*, 7516−7522.

(11) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. A Connection Between Intramolecular Long-Range Electron, Hole, And Triplet Energy Transfers. *J. Am. Chem. Soc.* **1989**, *111*, 3751−3753.

(12) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891−6936.

(13) Gomilsek, J. P.; Kodre, A.; Arcon, I.; Hribar, M. K-Edge X-Ray Absorption Spectra of Cs and Xe. *Phys. Rev. A* **2003**, *68*, 042505-1−042505-7.

(14) Muckerman, J. T.; Fujita, E. In *Chemical Evolution II: From the Origins of Life to Modern Society*; Zaikowski, L., Friedrich, J., Seidel, R., Eds.; American Chemical Society: Washington, D.C., 2009; Vol. *1025*, pp 283−312.

(15) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q. X.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, *110*, 6446−6473.

(16) Morris, A. J.; Meyer, G. J.; Fujita, E. Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels. *Acc. Chem. Res.* **2009**, *42*, 1983−1994.

(17) Tehan, F. J.; Barnett, B. L.; Dye, J. L. Alkali Anions: Preparation and Crystal-Structure of A Compound Which Contains Cryptated Sodium Cation and Sodium Anion. *J. Am. Chem. Soc.* **1974**, *96*, 7203−7208.

(18) Dye, J. L.; Ceraso, J. M.; Lok, M. T.; Barnett, B. L.; Tehan, F. J. Crystalline Salt of Sodium Anion (Na^-). *J. Am. Chem. Soc.* **1974**, *96*, 608−609.

(19) Dye, J. L.; Andrews, C. W.; Mathews, S. E. Strategies for Preparation of Compounds of Alkali-Metal Anions. *J. Phys. Chem.* **1975**, *79*, 3065−3070.

(20) Steed, J. W.; Gale, P. A. *Supramolecular Chemistry: From Molecules to Nanomaterials*; Wiley: West Sussex, U.K., 2009.

(21) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinhiem, Germany, 1995.

(22) Polyansky, D. E.; Cabelli, D.; Muckerman, J. T.; Fukushima, T.; Tanaka, K.; Fujita, E. Mechanism of Hydride Donor Generation Using a Ru(II) Complex Containing and a Model Ligand: Pulse And Steady-State Radiolysis Studies. *Inorg. Chem.* **2008**, *47*, 3958−3968.

(23) Miller, J. R.; Penfield, K.; Johnson, M.; Closs, G.; Green, N. In *Photochemistry and Radiation Chemistry. Complementary Methods for the Study of Electron Transfer*; Wishart, J. F., Nocera, D. G., Eds.; Americal Chemical Scoiety: Washington D.C., 1998; Vol. 254, pp 161−176.

(24) Wishart, J. F.; Cook, A. R.; Miller, J. R. The LEAF Picosecond Pulse Radiolysis Facility at Brookhaven National Laboratory. *Rev. Sci. Instrum.* **2004**, *75*, 4359−4366.

(25) Slates, R. V.; Szwarc, M. Dissociative Equilibria in the Systems Aromatic Hydrocarbon−,Na$^+$ ⇌ Radical Anion[UNK] + Na$^+$. *J. Phys. Chem.* **1965**, *69*, 4124−4131.

(26) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier Science Publishers B.V.: Amsterdam, 1988.

(27) Gill, D.; Szwarc, M.; Jagurgro, J. Chemistry of Radical-Ions: Electron-Transfer Reactions: $^-DD^-$ + Dimethyl Anthracene And $^-DD^-$ + Pyrene. *Trans. Faraday Soc.* **1964**, *60*, 1424−31.

(28) Funston, A. M.; Lymar, S. V.; Saunders-Price, B.; Czapski, G.; Miller, J. R. Rate And Driving Force for Protonation of Aryl Radical Anions in Ethanol. *J. Phys. Chem. B* **2007**, *111*, 6895−6902.

(29) Streitweiser, A. J., Jr.; Schwager, I. A Molecular Orbital Study of the Polarographic Reduction in Dimiethylformamide of Unsubstituted and Methyl Substituted Aromatic Hydrocarbons. *J. Phys. Chem.* **1962**, *66*, 2316−20.

(30) Meerholz, K.; Heinze, J. Electrochemical Solution And Solid-State Investigations on Conjugated Oligomers And Polymers of the Alpha-Thiophene And the P-Phenylene Series. *Electrochim. Acta* **1996**, *41*, 1839−1854.

(31) Pedersen, S. U.; Christensen, T. B.; Thomasen, T.; Daasbjerg, K. New Methods for the Accurate Determination of Extinction And Diffusion Coefficients of Aromatic And Heteroaromatic Radical Anions in N,N-Dimethylformamide. *J. Electroanal. Chem.* **1998**, *454*, 123−143.

(32) Shalev, H.; Evans, D. H. Solvation of Anion Radicals: Gas-Phase vs Solution. *J. Am. Chem. Soc.* **1989**, *111*, 2667−2674.

(33) Vasudevan, D.; Wendt, H. Electroreduction of Oxygen in Aprotic Media. *J. Electroanal. Chem.* **1995**, *392*, 69−74.

(34) Bard, A. J.; Lund, H. *Encyclopedia of Electrochemistry of the Elements. Organic Section*; Marcel Dekker, Inc.: New York, 1978; Vol. 11.

(35) Marasas, R. A.; Iyoda, T.; Miller, J. R. Benzene Radical Ion in Equilibrium With Solvated Electrons. *J. Phys. Chem. A* **2003**, *107*, 2033−2038.

(36) Davidson, R. S.; Lewis, A.; Whelan, T. D. Excited Complex-Formation Between Heterocyclic-Compounds And Aromatic-Hydrocarbons And Amines. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1280−1284.

(37) Prince, R. C.; Gunner, M. R.; Dutton, P. L. In *Function of Quinones in Energy Conserving Systems*; Trumpower, B. L., Ed.; Academic Press: New York, 1982; pp 29−33.

(38) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. Intramolecular Long-Distance Electron-Transfer in Radical-Anions: The Effects of Free-Energy And Solvent on the Reaction-Rates. *J. Am. Chem. Soc.* **1984**, *106*, 3047−3049.

(39) Rehm, D.; Weller, A. Kinetics of Fluorescence Quenching by Electron And H-Atom Transfer. *Isr. J. Chem* **1970**, *8*, 259−71.

(40) Niwa, T.; Kikuchi, K.; Matsusita, N.; Hayashi, M.; Katagiri, T.; Takahashi, Y.; Miyashi, T. Solvent Effects on Photoinduced Electron-Transfer Reactions. *J. Phys. Chem.* **1993**, *97*, 11960−11964.

(41) Rosspeintner, A.; Kattnig, D. R.; Angulo, G.; Landgraf, S.; Grampp, G. The Rehm-Weller Experiment in View of Distant Electron Transfer. *Chem.—Eur. J.* **2008**, *14*, 6213−6221.

(42) Andrews, L. J.; Deroulede, A.; Linschitz, H. Photophysical Processes in Fluorenone. *J. Phys. Chem.* **1978**, *82*, 2304−2309.

(43) Kobayashi, T.; Nagakura, S. Picosecond Time-Resolved Spectroscopy And Intersystem Crossing Rates of Anthrone And Fluorenone. *Chem. Phys. Lett.* **1976**, *43*, 429−434.

(44) Lower, S. K.; El-Sayed, M. A. Triplet State And Molecular Electronic Processes in Organic Molecules. *Chem. Rev.* **1966**, *66*, 199−241.

(45) Amand, B.; Bensasson, R. Determination of Triplet Quantum Yields by Laser Flash Absorption Spectroscopy. *Chem. Phys. Lett.* **1975**, *34*, 44−48.

(46) Biczok, L.; Berces, T.; Marta, F. Substituent, Solvent, and Temperature Effects on Radiative and Nonradiative Processes of Singlet Excited Fluorenone Derivatives. *J. Phys. Chem.* **1993**, *97*, 8895−8899.

(47) Kadhum, A. A. H.; Salmon, G. A. Reactivity of Solvated Electrons in Tetrahydrofuran. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2521−2530.

(48) Marcus, R. A.; Siders, P. Theory of Highly Exothermic Electron-Transfer Reactions. *J. Phys. Chem.* **1982**, *86*, 622−630.

(49) Jortner, J. Temperature-Dependent Activation-Energy for Electron-Transfer Between Biological Molecules. *J. Chem. Phys.* **1976**, *64*, 4860−4867.

(50) Ulstrup, J.; Jortner, J. The Effect of Intramolecular Quantum Modes on Free Energy Relationships for Electron Transfer Reactions. *J. Chem. Phys.* **1975**, *63*, 4358−4368.

(51) Fischer, S. F.; Van Duyne, R. P. On the Theory of Electron Transfer Reactions. The Naphthalene$^-$/TCNQ System. *Chem. Phys.* **1977**, *26*, 9−16.

(52) Levich, V. G. In *Advances in Electrochemistry & Electrochemical Engineering*; Delahay, Tobias, Ed.; Wiley: New York, 1966; Vol. 4, p 249.

(53) Marcus, R. A. On the Frequency Factor in Electron Transfer Reactions and its Role in the Highly Exothermic Regime. *Int. J. Chem. Kinet.* **1981**, *13*, 865−872.

(54) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. Effect of Free Energy on Rates of Electron Transfer Between Molecules. *J. Am. Chem. Soc.* **1984**, *106*, 5057−68.

(55) Waite, T. R. Theoretical Treatment of the Kinetics of Diffusion-Limited Reactions. *Phys. Rev.* **1957**, *107*, 463−470.

(56) NIST, S. G. L. 2013.

(57) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(58) Sumi, H.; Kakitani, T. Unified Theory on Rates for Electron Transfer Mediated by a Midway Molecule, Bridging Between Superexchange and Sequential Processes. *J. Phys. Chem. B* **2001**, *105*, 9603−9622.

(59) Petrov, E. G.; Zelinskyy, Y. R.; May, V. Bridge Mediated Electron Transfer: A Unified Description of the Thermally Activated And Superexchange Mechanisms. *J. Phys. Chem. B* **2002**, *106*, 3092−3102.

(60) Sutin, N.; Brunschwig, B. S.; Creutz, C.; Feldberg, S. W. Implications of An Electron-Hopping Model for Charge Transport Through Donor-Bridge-Acceptor Assemblies Connected to Metal Electrodes. *J. Phys. Chem. B* **2004**, *108*, 12092−12102.

(61) Paulson, B. P.; Miller, J. R.; Gan, W. X.; Closs, G. Superexchange And Sequential Mechanisms in Charge Transfer With A Mediating State Between the Donor And Acceptor. *J. Am. Chem. Soc.* **2005**, *127*, 4860−4868.

(62) Saito, K.; Mukai, K.; Sumi, H. The Importance of a Hot-Sequential Mechanism in Triplet-State Formation by Charge Recombination in Reaction Centers of Bacterial Photosynthesis. *Chem. Phys.* **2006**, *326*, 221−229.

(63) Goldsmith, R. H.; DeLeon, O.; Wilson, T. M.; Finkelstein-Shapiro, D.; Ratner, M. A.; Wasielewski, M. R. Challenges in Distinguishing Superexchange and Hopping Mechanisms of Intramolecular Charge Transfer Through Fluorene Ligomers. *J. Phys. Chem. A* **2008**, *112*, 4410−4414.

(64) Kukharenko, S. V.; Strelets, V. V. Cryoelectrochemical One-Electron Reduction of Benzene. *Elektrokhimiya* **1988**, *24*, 1379.