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Electron Transfer

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Increasing Electron-Transfer Rates with Increasing Donor–Acceptor Distance

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Abstract: Electron transfer can readily occur over long (\geq 15 Å) distances. Usually reaction rates decrease with increasing distance between donors and acceptors, but theory predicts a regime in which electron-transfer rates increase with increasing donor–acceptor separation. This counter-intuitive behavior can result from the interplay of reorganization energy and electronic coupling, but until now experimental studies have failed to provide unambiguous evidence for this effect. We report here on a homologous series of rigid rodlike donor-bridge-acceptor compounds in which the electron-transfer rate increases by a factor of 8 when the donor–acceptor distance is extended from 22.0 to 30.6 Å, and then it decreases by a factor of 188 when the distance is increased further to 39.2 Å. This effect has important implications for solar energy conversion.

Lectron transfer plays an important role in chemistry, biology, and physics. Many processes indispensable to life, for example photosynthesis and respiration, rely on electron transfer between distant redox partners.^[1] Collisional encounters between reactants are not needed, because the electron can be transfered rapidly over long (≥ 15 Å) distances due to its low mass.^[2] Usually the rates for electron transfer decrease with increasing distance between reactants.^[3] More than 30 years ago it was predicted that under certain conditions, electron-transfer rates could actually increase with increasing distance.^[4] We report here direct experimental evidence for a maximum electron-transfer rate at large reactant separations, compatible with the long-sought effect predicted by theory.

Electron-transfer rates $(k_{\rm ET})$ exhibit a Gaussian dependence (Figure 1) on reaction free energy $(\Delta G_{\rm ET}^{0})$.^[5] The maximal rate is reached when $-\Delta G_{\rm ET}^{0}$ is equal to the reorganization energy (λ), which is the energy expenditure associated with the reorganization of the solvent and reactant in the course of electron transfer. When $-\Delta G_{\rm ET}^{0} > \lambda$, then $k_{\rm ET}$ decreases with increasing driving force, and this is known as the "inverted" regime.^[6]

$$k_{\rm ET} = \sqrt{\frac{\pi}{\hbar^2 \cdot \lambda \cdot k_{\rm B} \cdot T}} \cdot H_{\rm DA}^2 \cdot \exp\left(-\frac{\left(\lambda + \varDelta G_{\rm ET}^0\right)^2}{4 \cdot \lambda \cdot k_{\rm B} \cdot T}\right)$$
(1)

When the distance between the donor and the acceptor (r_{DA}) increases, their electronic coupling $[H_{\text{DA}},$ middle term in



Figure 1. Schematic drawing of $\ln(k_{\text{ET}})$ vs. $-\Delta G_{\text{ET}}^{0}$ showing so-called Marcus parabolas. The effect of increasing donor-acceptor distance (r_{DA}) on these parabolas is illustrated. The maxima of these parabolas occur at $-\Delta G_{\text{ET}}^{0} = \lambda$. The dotted vertical line marks a driving force for which k_{FT} exhibits a maximum at intermediate distances.

Eq. (1)] usually decreases exponentially, and this leads to an exponential decrease of $k_{\rm ET}$ with increasing $r_{\rm DA}$ in the tunneling regime.^[3,7] The outer-sphere (solvent) contribution to λ increases with increasing r_{DA} , because more isolated point charges result when the electron-hole separation distance is larger.^[8] The combination of a decrease of $H_{\rm DA}$ and an increase of λ results in a shift of the driving-force parabola in Figure 1 towards the bottom right corner:^[9] As H_{DA} decreases, $k_{\rm ET}$ must decrease because $k_{\rm ET} \propto H_{\rm DA}^2$ [Eq. (1)], shifting the parabolas down. As λ increases, the maximum of the parabola shifts to the right because maximal $k_{\rm ET}$ is reached when $-\Delta G_{\rm ET}^{0}$ is equal to λ . Figure 1 illustrates this effect by showing three generic parabolas, one each for short, intermediate, and long donor-acceptor distances. We note that when $-\Delta G_{\rm ET}^{0}$ becomes sufficiently large relative to λ , there can be situations in which $k_{\rm ET}$ is largest for intermediate $r_{\rm DA}$ at constant driving force (dotted vertical line). In other words, as the donor-acceptor distance increases in this regime, the reaction rate should first increase, reach a maximum at a given distance, and then decrease.^[4]

In the three compounds shown in Figure 2a (see the Supporting Information for syntheses) selective excitation of the $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) photosensitizer induces a rapid sequence of intramolecular electron transfers leading to an oxidized triarylamine (TAA) and a reduced

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Figure 2. a) Molecular structures of the three key compounds investigated in this work. b) Transient absorption spectra recorded by time integration over 200 ns directly following excitation at 532 nm with laser pulses of ca. 10 ns duration (I, II) or with a delay time of 3 μ s (III), respectively. Red: I, blue: II, green: III (multiplied by a factor of 3.5), sample concentrations were 20 μ M. Spectro-electrochemical UV/ Vis difference data obtained for II after different time intervals following application of potentials of c) -0.9 V and d) +0.8 V vs. SCE leading to formation of AQ⁻ (c) and TAA⁺ (d), respectively. The UV/ Vis spectrum prior to application of any potential served as a baseline, sample concentrations were 0.1 mM. The solvent was deaerated 1:1 (v:v) CH₃CN/H₂O at 20°C in all cases.

anthraquinone (AQ). Electron transfer is mediated by *p*-xylene spacers of different lengths (n = 1-3) which impose a rigid rodlike molecular structure. The transient

absorption data in Figure 2b were obtained after excitation at 532 nm with laser pulses of ca. 10 ns duration. The spectra were recorded by time integration over 200 ns, either directly after excitation (compounds **I**, **II**) or with a time delay of 3 µs (compound **III**). All three spectra exhibit absorption maxima at 370, 510, and 770 nm, compatible with the formation of TAA⁺ and AQ⁻, as the comparison with spectro-electrochemical data (Figure 2 c/d) shows (Supporting Information (SI) page S15). All data were recorded in deaerated mixtures of 1:1 (v:v) CH₃CN/H₂O. In compounds **I** and **II**, the TAA⁺ and

 AQ^- products form within the duration of the laser excitation pulse, whereas in compound III the time constant for complete formation of the fully charge-separated state is 210 ns (SI pages S16–S19) hence the use of the 3 µs time delay noted above. Of key interest in this paper is the kinetics for thermal electron transfer from AQ^- to TAA^+ . This intramolecular charge-recombination event has to occur across 2–6 *p*-xylene spacers and a bpy ligand. According to molecular modeling, the (center-to-center) donor–acceptor distances are 22.0 (I), 30.6 (II), and 39.2 Å (III).

The rates for thermal electron transfer from AQ⁻ to TAA⁺ ($k_{\rm ET}$) can be extracted from the decays of the transient absorption signals at 370, 510, and 770 nm (Figure 3). For a given compound, at all three wavelengths identical decays are measured, confirming that TAA⁺ (which absorbs at 370 and 770 nm) and hydrogen-bonded AQ⁻ (which absorbs at 370 and 510 nm) disappear simultaneously. $k_{\rm ET}$ values extracted from fits to the experimental decay curves are reported in Table 1.



Figure 3. Decays of the transient absorption signals at a) 370, b) 510, and c) 770 nm for I (red), II (blue), III (green) in deaerated 1:1 (v:v) CH_3CN/H_2O at 20 °C following excitation at 532 nm with laser pulses of ca. 10 ns duration. See text and SI pages S16, S17 for explanation of the fast decay component detected for III.

Table 1: Center-to-center donor-acceptor distance (r_{DA}), rate constant (k_{ET}), (negative) reaction free energy ($-\Delta G_{ET}^{0}$), activation free energy (ΔG_{ET}^{+}), reorganization energy (λ), and electronic coupling (H_{DA}) associated with thermal electron transfer between AQ⁻ and TAA⁺ in compounds I–III in 1:1 (v:v) CH₃CN/H₂O.

Cmpd	r _{da} [Å]	κ _{ετ} [s ⁻¹]	$-\Delta G_{ m ET}^{0}$ [eV]	$\Delta G_{ m ET}^{\ \ \pm}$ [meV]	λ [eV]	<i>H</i> _{DA} [cm ⁻¹]
I	22.0	$(3.58\pm 0.36) \times 10^5$	1.33 ± 0.05	43 ± 2	0.93 ± 0.35	0.09 ± 0.02
11	30.6	$(2.87 \pm 0.29) imes 10^{6}$	1.29 ± 0.05	-2 ± 1	1.29 ± 0.05	0.10 ± 0.02
	39.2	$(1.53\pm0.15)\times10^4$	1.23 ± 0.05	108 ± 9	2.21 ± 0.28	0.08 ± 0.02

For compound II $k_{\rm ET}$ is a factor of 8 larger than that for compound I, despite the fact that the donor-acceptor distance $(r_{\rm DA})$ is 8.6 Å longer. While compounds I and II yield singleexponential decays, the transient absorption decay of compound III is triple-exponential at all three detection wavelengths (but only the shorter two out of the three decay components are visible in Figure 3). The shortest of the three time components is 210 ns and can be attributed unambiguously to the photoinduced charge-separation reaction in which TAA^+ and AQ^- are formed (SI pages S16, S17; the ³MLCT excited state of **III** has higher extinction coefficients at the relevant detection wavelengths than the final chargeseparated state). The intermediate time component is 65.4 µs and is attributable to intramolecular thermal electron transfer from AQ^- to TAA^+ , i.e., to the process of main interest. The third time component ($\geq 400 \,\mu s$; not seen in Figure 3) is caused by intermolecular electron-transfer reactions (SI pages S20-S23). Thus, the kinetics for intramolecular electron transfer is clear-cut: $k_{\rm ET}$ increases by a factor of 8 between compounds I and II, and then decreases by a factor of 188 between **II** and **III**. The reaction free energy $(\Delta G_{\rm ET}^{0})$ for intramolecular thermal electron transfer from AQ⁻ to TAA⁺ is very similar in I, II, and III (Table 1, SI page S11).

The temperature dependence of $k_{\rm ET}$ was analyzed to determine activation free energies ($\Delta G_{\rm ET}^{*}$). From Arrhenius plots the $\Delta G_{\rm ET}^{+}$ values reported in Table 1 were extracted (SI page S24). In compound II electron transfer proceeds in essentially activationless manner, whereas in compounds I and III $\Delta G_{\rm ET}^{\dagger}$ is $43 \pm 2 \text{ meV}$ and $108 \pm 9 \text{ meV}$, respectively. Since $\Delta G_{\text{ET}}^{\dagger} = (\lambda + \Delta G_{\text{ET}}^{0})^2 / 4 \cdot \lambda$ [last term in Eq. (1)],^[6b] reorganization energies (λ) can be determined from these values. In the case of II, λ must be equal to $-\Delta G_{\rm ET}^{0}$ (1.29 ± 0.05 eV) because the reaction is barrierless. For compounds I and III, the quadratic relationship between $\Delta G_{\rm ET}^{+}$ and λ yields two mathematical solutions, but in each case only one solution is physically meaningful because λ is expected to increase with increasing r_{DA} (SI pages S26, S34).^[4a, 8, 10] Thus we obtain $\lambda = 0.93 \pm 0.35$ eV for I, 1.29 ± 0.05 eV for II, and 2.21 ± 0.28 eV for III in 1:1 (v:v) CH₃CN/H₂O (Table 1).

The dominant contribution to λ usually comes from the outer-sphere reorganization energy (λ_0), while the innersphere contribution is small and largely independent of r_{DA} .^[10] Simple two-sphere electrostatic models fail to quantitatively reproduce the experimentally observed increase in λ for compounds I-III in 1:1 (v:v) CH₃CN/H₂O,^[8,11] because they do not take hydrogen bonding into account. Direct evidence for the importance of hydrogen bonding in our systems comes from the AQ--related transient absorption band at 510 nm (Figure 2b,c). In neat CH₃CN, this band appears at 565 nm for compounds I-III, (SI page S27) and the shift to shorter wavelength in 1:1 (v:v) CH₃CN/H₂O is in line with hydrogenbond donation from water.^[12] Based on prior electrochemical studies and on calculations for benzoquinone radical anion, we expect that 4-5 H₂O molecules are involved in hydrogen bonding to AQ⁻,^[13] and this raises λ significantly with respect to what is predicted by a simple dielectric continuum model.^[8,11] The further AQ⁻ is spatially separated from cationic charges $(Ru(bpy)_3^{2+}, TAA^+)$, the more important the effect of hydrogen-bonding becomes. For comparison, a study of phototriggered phenol oxidation found $\lambda = 2.0 \text{ eV}$ because the phenolic O-H bond was broken in the course of electron transfer.^[14]

In neat CH₃CN the reorganization energy (λ) for compound III is only 1.62 ± 0.05 eV because no hydrogen bonding

to AQ⁻ can occur (SI page S33). We note that the change from 1:1 (v:v) CH₃CN/H₂O to neat CH₃CN does also increase the driving force for thermal charge recombination in a significant manner (by ca. 0.3 eV) because non-hydrogenbonded AQ⁻ is easier to oxidize than its hydrogen-bonded analogue, and TAA⁺ reduction is more facile in neat CH₃CN (SI page S13). Thus, solvent changes do not only affect λ , but they also lead to significant changes of $\Delta G_{\rm ET}^{0}$ in our compounds (SI page S36). As $\Delta G_{\rm ET}^{0}$ for charge recombination increases, the driving force for photoinduced charge separation decreases, because the energy of the initially populated ³MLCT excited state remains relatively constant. In CH₂Cl₂ and more apolar solvents one reaches a point at which efficient charge separation is no longer possible in compounds II and III. This precludes further solvent-dependence studies.

With the λ , $\Delta G_{\rm ET}^{0}$, and $k_{\rm ET}$ values from Table 1 for 1:1 (v:v) CH₃CN/H₂O mixtures at hand, Equation (1) can be used to obtain estimates of $H_{\rm DA}$. We find that the electronic coupling is only very weakly distance dependent with H_{DA} values of 0.09 ± 0.02 cm⁻¹ (I), 0.10 ± 0.02 cm⁻¹ (II), and $0.08 \pm$ 0.02 cm^{-1} (III). At first glance this is a somewhat unexpected result, particularly in view of prior studies of donor-acceptor compounds with oligo-p-xylene bridges which have produced distance decay constants (so-called β -values) between 0.52-0.77 Å⁻¹ for $k_{\rm ET}$.^[15] However, the earlier studies have exclusively focused on photoinduced (forward) electron transfer in the so-called normal regime. It has been noted earlier that the kinetics of photoinduced (forward) electron transfer and thermal (reverse) electron transfer can exhibit significantly different distance dependences, because the superexchange coupling pathways (determining the magnitude of H_{DA}) can be fundamentally different.^[9,16] We suspect that the weak distance dependence of $H_{\rm DA}$ in compounds I– III is due to increasing π -conjugation between the central bpy and adjacent p-xylene units with increasing length. This interpretation is supported by the observation that the spectroscopic signature of the ³MLCT state of a reference complex lacking the AQ and TAA components but bearing pxylene bridging units is substantially different from the ³MLCT spectrum of $[Ru(bpy)_3]^{2+}$ (SI page S19).

Because of the initial population of a ³MLCT excited state, a radical ion pair (AQ⁻/TAA⁺) with triplet spin multiplicity forms initially. Charge recombination must occur directly to the singlet ground state, but spin effects are not expected to play a decisive role as far as the distance dependence of $k_{\rm ET}$ is concerned. Possible spin and electron-vibration coupling effects are discussed in the Supporting Information (pages S38–S41).^[6b,16b,17]

In conclusion, the highly unusual observation of an electron-transfer-rate maximum at large (30.6 Å) reactant separation can be explained by a weak distance dependence of electronic donor–acceptor coupling (H_{DA}) combined with a strong distance dependence of the reorganization energy (λ), as predicted by theory more than three decades ago.^[4a] As λ increases with increasing donor–acceptor distance, our reaction systems pass through the inverted (**I**), barrierless (**II**), and normal (**III**) regimes of electron transfer, and all the while the reaction free energy (ΔG_{ET}^{0}) stays essentially constant





Figure 4. Reactant (black) and product (red) potential energy wells illustrating the changeover from inverted (left) to activationless (middle) to normal (right) electron transfer as a function of increasing distance (r_{DA}) between AQ⁻ and TAA⁺ in compounds I, II, and III. The driving force ($-\Delta G_{ET}^{0}$) stays nearly constant (Table 1), the changeover is essentially due to increasing reorganization energy (λ) with increasing r_{DA} . The lower half of the figure shows enlargements of the regions marked by dotted rectangles in the upper half.

(Figure 4), in marked contrast to prior driving-force dependence studies. $^{\left[6\right] }$

The simple model illustrated in Figure 4 is fully compatible with the experimentally observed rate constants, reaction free energies, and activation free energies. We are unaware of prior studies that have reported a rate maximum at large distances caused by a changeover from inverted to barrierless to normal electron transfer as a function of r_{DA} .

The effect observed herein is not merely an oddity of purely academic interest, but it has important practical implications. Photoinduced electron transfer between a donor (D) and an acceptor (A) leads to electron-hole pairs (D⁺, A⁻), a form of chemically stored energy.^[18] These light-induced reactions commonly occur in the normal regime where $-\Delta G_{\rm ET}^{0} < \lambda$, hence in bimolecular processes they take place preferentially when reactants are in close contact ($r_{\rm DA} \leq$ 10 Å), because in the normal regime $k_{\rm ET}$ simply decreases with increasing r_{DA} .^[4] When aiming to convert solar light into chemical energy, it is then desirable that oxidation (D^+) and reduction products (A⁻) diffuse away from each other without undergoing direct charge recombination. However, such energy-wasting processes often occur in the inverted driving-force regime at close contact. Consequently, as the distance between the D⁺ and A⁻ photoproducts increases in the course of diffusion, the rate for charge recombination increases until a critical separation distance is reached (i. e., the r_{DA} for which $-\Delta G_{\text{ET}}^{0} = \lambda$). Only past that point does the charge-recombination rate decrease with increasing r_{DA} . This can severely limit the quantum efficiency of light-to-chemical energy conversion.

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