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Reversible Charge Migration in the Excited State of an Electron Donor–Donor–Acceptor System Detected via Delayed Charge Transfer Fluorescence

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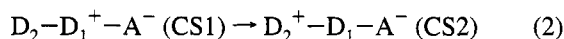
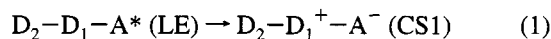
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Trichromophoric electron donor–donor–acceptor compounds are described which emit fluorescence exclusively from a charge-separated state best described as $D_2D_1^+A^-$. This state, which has a dipole moment $\mu_e \approx 24$ D, is formed quantitatively upon excitation of the electron acceptor chromophore. In solvents of moderate polarity subsequent electron transfer from D_2 to D_1 , leading to the formation of the $D_2^+D_1A^-$ state ($\mu_e \approx 42$ D), can occur in a reversible fashion. This reversibility gives us the unique opportunity to experimentally investigate the energetics of the charge migration $D_2D_1^+A^- \rightleftharpoons D_2^+D_1A^-$.

Introduction

Supramolecular systems in which photoinduced charge separation is accomplished by a sequence of electron transfer steps can be highly efficient in terms of quantum yield and lifetime of the long-range charge separated state.^{1–3} Optimal design of such systems requires precise knowledge of the factors determining the kinetics and thermodynamics of the individual steps. Our studies are aimed at obtaining such precise data from experiments using simple organic molecules in which two electron donors and a photoexcitable electron acceptor are linked together in a linear arrangement. The excited state charge separation occurs in two steps:

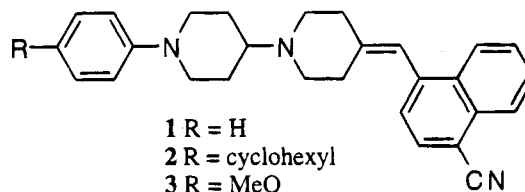


In this Letter we describe a compound **2** (Scheme 1) which has the novel feature that the second step is *reversible* in a range of low-polarity solvents (alkyl ethers), which allows us to obtain thermodynamic information on the driving force for this important process.

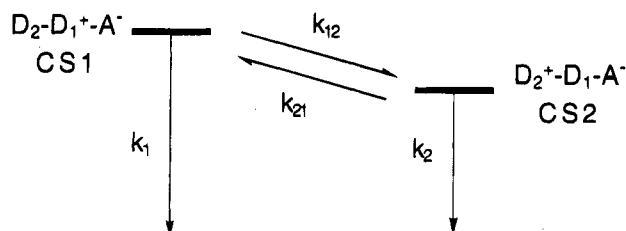
Accurate measurements of the kinetics (Scheme 2) over a large dynamic range are possible by virtue of the fact that the CS1 state can be easily detected via its charge recombination fluorescence.^{4–8} The reversibility of the charge migration $\text{CS1} \rightleftharpoons \text{CS2}$ leads to delayed fluorescence,⁹ of a kind not reported before.

In multistep charge separation schemes the first step (1) is relatively easy to accomplish because a large amount of excitation energy is invested. The charge migration step (2) is crucial in determining the efficiency of the overall charge separation in a multicomponent system. It is a thermal electron transfer process, which has to be rapid enough to compete with the usually rapid deactivation ((sub)nanosecond time scale) of the CS1 excited state. Especially in media of low polarity this “charge escape” step is energetically costly because the Coulomb attraction between D_1^+ and A^- is large owing to the small distance between the charges. Subsequent steps in multicomponent D/A systems are more facile because the Coulomb potential gets smaller as the charges are further apart. Note that the same phenomena also play a role in doped conducting

SCHEME 1: Compounds Investigated



SCHEME 2: Definition of Rate Constants



polymers, where charge migration is hampered by the Coulomb fields of counterions.¹⁰

Results

Excitation of compounds **1**, **2**, and **3** at wavelengths between 308 and 320 nm initially produces a locally excited state of the acceptor moiety. The fluorescence of this chromophore is completely absent, and a characteristic charge transfer emission is observed instead. For **1** and **3** we have demonstrated⁷ that the emission can be unequivocally attributed to the product of the first step of electron transfer, i.e., the $D_2-D_1^+-A^-$ state, which has a dipole moment of ca. 24 D. The solvatochromic shift of the emission of **2** is virtually identical to that of **1** and **3**, showing that also in this case the observed species in fluorescence measurements is the CS1 state. As in our previous study, no indication for fluorescence from the long-range charge-separated state (CS2) was found. This is not surprising because the electronic coupling between D_2 and A is much smaller than that between D_1 and A . In this paper we shall focus on the photophysical dynamics of compound **2** in comparison to **1** in a range of low-polarity solvents, viz. alkyl ethers. The relevant fluorescence parameters are given in Table 1.

As shown previously,⁷ in compound **1** the second step $D_2-D_1^+-A^- \rightarrow D_2^+-D_1-A^-$ does not occur. In the case of compound **2**, however, the lower quantum yield of fluorescence

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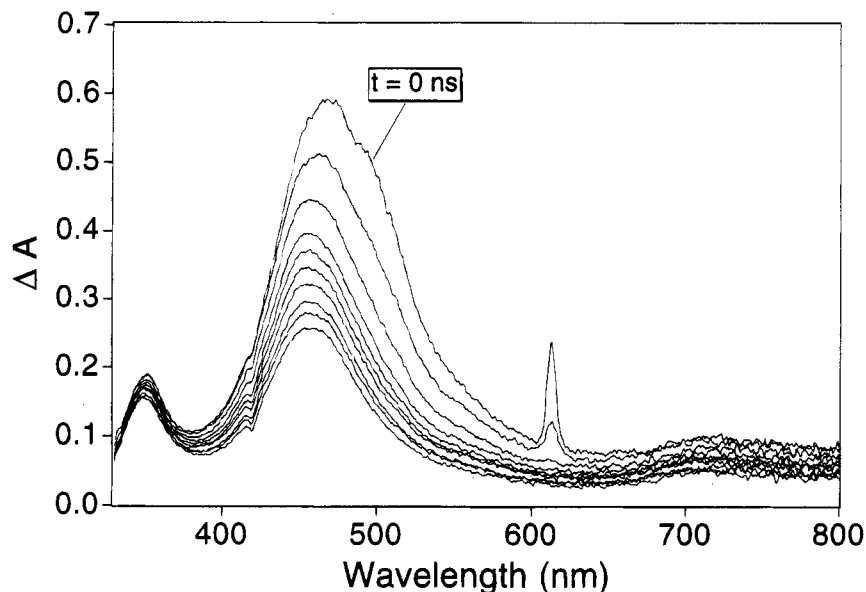


Figure 1. Transient absorption spectrum of **2** in diethyl ether. The first spectrum was taken at the maximum of the exciting laser pulse (7 ns fwhm), and the subsequent ones were taken with time increments of 4 ns.

TABLE 1: Emission Maxima λ_{\max} (nm), Quantum Yields ϕ_f (Excitation at 308 nm; Reference 9,10-Diphenylanthracene, $\phi_f = 0.9^a$), Decay Times τ_f (ns) of the CT Fluorescence of **1, and Observed Decay Times $\gamma_{f,2}$ (ns) of the CT-Fluorescence of **2** with Amplitudes $g_{1,2}$ (Excitation at 315 or 320 nm)**

solvent	1		2		
	λ_{\max} [ϕ_f]	τ_f	λ_{\max} [ϕ_f]	γ_{f_1} [g_1]	γ_{f_2} [g_2]
di- <i>n</i> -butyl ether	458 [0.11]	1.92	460 [0.11]	1.20 [0.42]	3.13 [0.16]
di- <i>n</i> -propyl ether	466 [0.14]	3.13	466 [0.12]	1.57 [0.32]	4.71 [0.11]
diisopropyl ether	472 [0.16]	3.79	472 [0.13]	1.59 [0.29]	13.0 [0.04]
diethyl ether	483 [0.20]	5.10	486 [0.13]	1.68 [0.26]	20.9 [0.03]

^a Eaton, D. F. *J. Photochem. Photobiol. B* **1988**, *2*, 523.

from the $D_2-D_1^+-A^-$ state indicates the partial conversion to $D_2^+-D_1-A^-$. The formation of this state (CS2) is clearly demonstrated by the transient absorption spectra (Figure 1). At short times after the exciting pulse (7 ns fwhm) a strong band at ca. 480 nm and a weak band at ca. 730 nm are observed. The former can be attributed to a superposition of bands of the D_2 radical cation and the acceptor radical anion; the long-wavelength band is characteristic of the acceptor radical anion.¹¹ At longer times the CS species have decayed, and two bands (350 and 460 nm) of the local triplet state of the acceptor chromophore remain. Thus, the charge-separated states decay to a local triplet as well as to the ground state. Elucidation of the decay pathways of the individual CS states requires higher time resolution than is presently available to us.

Time resolved fluorescence measurements¹² indicate simple exponential decay for **1** but distinctly biexponential decay in the case of **2** (Figure 2). This can be interpreted as a result of reversible formation of CS2 from CS1 (Scheme 2), leading to the well-known phenomenon of delayed fluorescence.⁹ Biphasic fluorescence decay as a result of reversible charge separation has been observed before in the field of photoinduced electron transfer, but in those cases the observed state was the locally excited state.¹³⁻¹⁶ In our case the fluorescent state as well as the nonfluorescent "reservoir" state is a charge-separated state. The decay parameters are given in Table 1. A further argument for this interpretation is that the transient absorption bands of **2** in the four solvents decay with approximately the same rates as the slowest fluorescence decay component.

The fluorescence decay parameters of **2** can be analyzed to yield rate constants,¹⁷ using **1** as a reference compound to

provide the value of k_1 (Table 2). Clearly, there is a pronounced solvent effect on k_{12} and k_{21} and thus on the equilibrium constant K_{eq} . An increase of the forward electron transfer rate and a decrease of the back electron transfer rate are caused by the increased stabilization of the CS2 state relative to CS1 upon increasing the solvent polarity. Moreover, the charge recombination in the CS1 state becomes slower upon increasing the dielectric constant, which further contributes to the increased efficiency of the second charge transfer step. The polarity dependence of the recombination rates (also observed for the CS2 state) is opposite to the Marcus inverted region behavior which would be expected in view of the large energy gap separating the CS states from the ground state. This unusual phenomenon definitely calls for further investigation.

Discussion

In the charge migration process $CS1 \rightarrow CS2$ loss of electrostatic stabilization energy (ΔE^{Coul}) must be compensated by a gain in redox energy ΔE^{ox} . Using a simple charged spheres/dielectric continuum model in the spirit of the classical electron transfer theories,^{18,19} the driving force (in electronvolts) for step 2 is given by eq 3.

$$\Delta G_2 = \Delta E^{ox} + \Delta E^{Coul} = \Delta E_{polar}^{ox} + 14.4 \left(\frac{q_1^2}{2r_{ion1}} - \frac{q_2^2}{2r_{ion2}} \right) \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{polar}} \right) + \frac{14.4}{\epsilon} \left(\frac{q_1^2}{R_{D_1A}} - \frac{q_2^2}{R_{D_2A}} \right) \quad (3)$$

The first two terms in eq 3 account for the fact that oxidation potentials are measured in polar solvents. The q indicate the charge on the donor (D_1 or D_2) and acceptor, the r_{ion} are the Born ion radii (angstroms) of D_1 and D_2 , and the R_{DA} (angstroms) represent the distances of charge separation in the two CS states.

Regardless of further assumptions concerning the values of parameters, eq 3 predicts a linear dependence of ΔG_2 on $1/\epsilon$, the intercept at $1/\epsilon = 0$ being equal to the difference in oxidation potentials of D_2 and D_1 at high solvent polarity. A fit of the as yet small collection of data points to eq 3 (Figure 3) yields a slope of 0.59 ± 0.08 eV and an intercept of -0.18 ± 0.02 eV. The meaning of this result is best appreciated by comparing with the results of some assumptions regarding the parameters

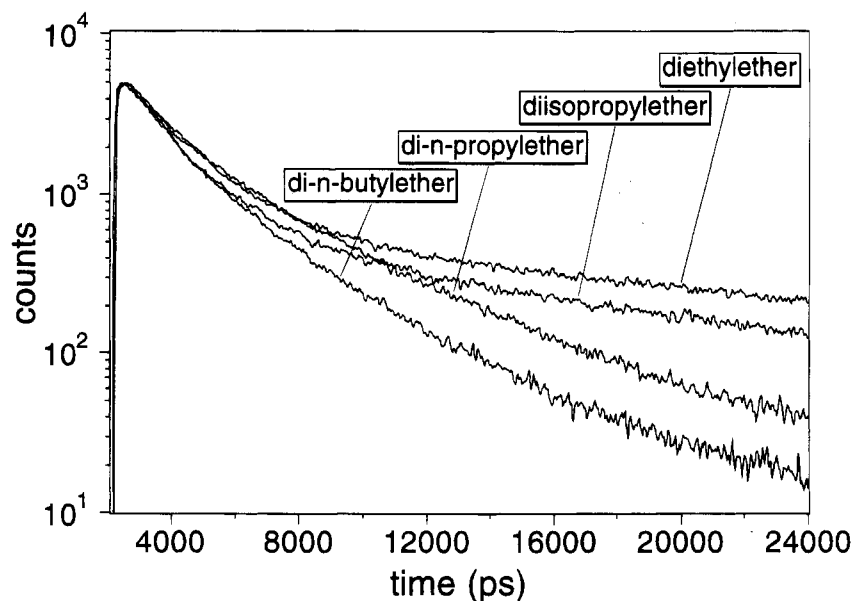


Figure 2. Decay curves of the charge transfer fluorescence of **2** in di-*n*-butyl ether, di-*n*-propyl ether, diisopropyl ether, and diethyl ether. Excitation was at 315 or 320 nm.

TABLE 2: Rate Constants (10^8 s^{-1}) Characterizing the Decay Processes in **2 (Cf. Scheme 2)**

solvent (ϵ_s) ^a	k_1	k_2	k_{12}	k_{21}	ΔG_2 (eV)
di- <i>n</i> -butyl ether (3.06)	5.2	1.6	1.7	3.1	0.015 ± 0.005
di- <i>n</i> -propyl ether (3.39)	3.2	1.6	2.1	1.6	-0.008 ± 0.004
diisopropyl ether (3.88)	2.6	0.4	3.0	1.1	-0.026 ± 0.003
diethyl ether (4.24)	2.0	0.3	3.5	0.8	-0.039 ± 0.002

^a *Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993.

in eq 3. First of all, it is reasonable to neglect the second term in eq 3 because the differences in q and r_{ion} are likely to be small. If we furthermore assume complete charge separation, i.e. $q = 1$, we can derive the distances R_{D_1A} and R_{D_2A} from the experimentally known dipole moments of CS1 (24 D; $R_{D_1A} \approx 5.0 \text{ \AA}$) and CS2 (42 D; $R_{D_2A} \approx 8.7 \text{ \AA}$).⁷ This yields an expected slope of 1.23 eV, clearly a much stronger dependence on solvent polarity than what is experimentally found.

One possible explanation for this discrepancy is that the assumption of full charge separation for the CS1 state is not correct. Mixing of the CS1 charge separated configuration with a locally excited state of the acceptor chromophore is facilitated by the large electronic coupling ($V > 1000 \text{ cm}^{-1}$ in closely related systems)^{20, 21} and the relatively small energy gap. It is in fact this mixing which leads to the high radiative rate constants ($k_f \geq 10^7 \text{ s}^{-1}$)^{20, 21} in these systems. Recently, it was also shown for intermolecular exciplexes that charge separation is often considerably less than complete.²² For the CS2 state complete charge separation is more likely because of the smaller electronic coupling. So, the ion-pair model may be appropriate for the CS2 state but is less likely to be so for the CS1 state. A description in terms of a dipole solvation model may be more appropriate for this state. The application of the Weller equation (3) is thus limited, and there is an obvious need for a more accurate model to describe the driving force for the second step of electron transfer. At the present stage eq 3 at least has allowed us to deduce a useful empirical relationship.

The intercept of our experimental plot indicates that ΔE^{ox} in polar solvent is ca. -0.18 V . Complete experimental data for the oxidation potentials of the amine donors in our compounds are unfortunately not available. Cyclic voltammetry measurements yielded the oxidation potentials of D_2 (using the corresponding substituted phenylpiperidines as models) as 0.75 V

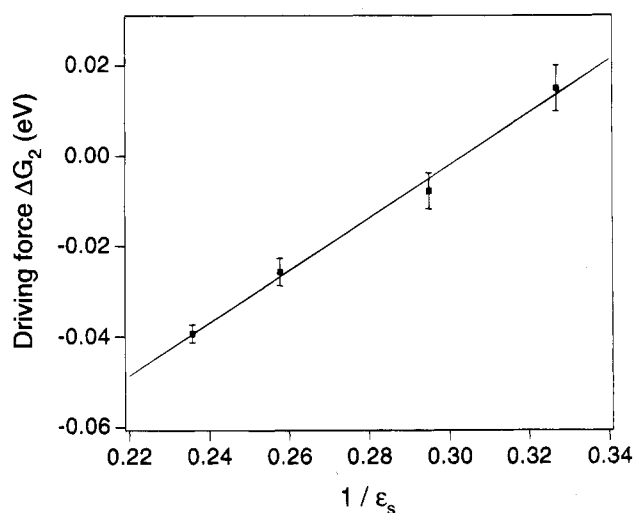


Figure 3. Solvent polarity dependence of the driving force ΔG_2 of the process CS1 \rightarrow CS2 in **2**.

for **2**¹¹ and 0.61 V for **3** (vs SCE, in CH_3CN).²³ Saturated amines such as D_1 and anilines that are not substituted at the para position (D_2 in **1**) cannot be oxidized reversibly, and conflicting values of oxidation potentials can be found in the literature.^{23–27} For *N*-phenylpiperidine the oxidation potential was estimated as 0.81 V .²³ The oxidation potential of D_1 can be estimated as 0.93 V using the experimentally determined difference $\Delta E^{\text{ox}}(\mathbf{2}) = -0.18 \text{ V}$ and the oxidation potential of $D_2(\mathbf{2})$ of 0.75 V . From comparison of exciplex emission energies and from ionization potentials relative oxidation potentials can be estimated (provided that the reorganization energies are the same). Such comparisons indicate that a 4-alkyl group lowers the oxidation potential of an aniline by 0.05 – 0.1 V . Taking the value of 0.75 V for 1-(4-cyclohexylphenyl)piperidine, this implies that the oxidation potential of the aniline donor D_2 in **1** is between 0.8 and 0.85 V , in agreement with the estimated value²³ of 0.81 V .

It is reasonable to assume that the empirically found solvent dependence of the CS2/CS1 energy difference in **2** also applies to the related systems **1** and **3**, because the charge distributions in the CS states will not be dramatically influenced by the 4-substituent on the aniline moiety of D_2 . Thus, applying the

relation $\Delta G_2 = \Delta E^{\text{ox}} + 0.59/\epsilon$, we infer that a net driving force for the second charge transfer step in **1** ($\Delta E^{\text{ox}} \approx -0.12$ V) should exist in solvents with $\epsilon \geq 4.9$. Nevertheless, no indication is found for this process even in more polar solvents such as tetrahydrofuran ($\epsilon = 7.6$). The reason is probably twofold: the nonradiative charge recombination in the CS1 state is faster than at lower polarity, while the electron transfer step suffers from an increased activation energy as a result of a larger solvent reorganization energy in more polar solvents. When **D**₂ is a methoxyaniline as in **3**, the driving force for the second charge separation is enhanced by 0.14 V relative to **2** ($\Delta E^{\text{ox}} \approx -0.32$ V). This shifts the polarity region where $\Delta G \approx 0$ to $\epsilon \approx 1.8$, and as a result efficient two-step charge separation can occur⁷ already in benzene and dioxane ($\epsilon \approx 2.3$). The dramatic differences in the photophysical behavior of **1**, **2**, and **3** underscore the importance of accurate fine-tuning in multistep electron transfer systems.

In conclusion, the dependence of the estimated driving force on the parameters describing the Coulomb energy change in low-polarity media is so large that an a priori estimate of useful accuracy is not possible. Therefore, the demonstrated possibility to derive this driving force directly from experimental data, making use of the reversibility of the "charge escape" process, is a major step forward in our investigations of intramolecular multistep charge separation. Further studies of the role of the solvent and the temperature dependence of the charge migration are in progress. Small changes of the oxidation potential of **D**₂ should furthermore allow the observation of delayed charge transfer fluorescence in solvents of different polarity ranges.

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