

Diffusionless Intermolecular Electron Transfer in Solution: Photoexcited Cyanine Borate Ion Pairs[#]

Alexander Tatikolov,^{a,*} Xiqiang Yang,^b Björn Sauerwein^b and Gary B. Schuster^{b,*}

^aInstitute of Chemical Physics, Kosygin Street 4, Moscow, USSR 117334 and ^bDepartment of Chemistry, University of Illinois, Urbana, Illinois USA 61801

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Irradiation of the 1-ethyl-2-(1-ethyl-1,2-dihydroquinolin-2-ylidenemethyl)quinolinium butyl(tris-*p*-tert-butylphenyl)borate (*N,N'*-diethyl-2,2'-cyanine borate, **1**) ion pair in non-polar solution gives rise to a locally excited state of the dye. Intra-ion-pair electron transfer from the borate to the cyanine generates a radical pair. The self-association of the electron donor and the electron acceptor prior to excitation, and the very short excited-state lifetime of the cyanine permits measurement of electron transfer rates far above the diffusion limit: the special features of this reaction make it a suitable probe for theories of electron transfer reactions.

Recently there has been expanding interest in the development of the theory of electron transfer reactions and in designing experiments to probe the predictions of these theories.¹ Among the most active areas in this field have been the examination of how the rate of reaction is affected by its free energy change and by changes in solvent properties.²

Theories of electron transfer reactions are highly developed, but experimental approaches to the examination of intermolecular electron transfer in solution are severely limited. Since a diffusive encounter must normally precede the electron transfer reaction, observable rates in isotropic solutions are commonly restricted to ranges below the encounter limit. Normally, all but endothermic electron transfer reactions are predicted to occur with rates many times the limit imposed by diffusion. Recognition of this restriction has led to the development of experimental tactics to circumvent the diffusion speed restriction.

In one successful approach, Farid and Gould employed a technique where transient reagents for an intermolecular electron transfer reaction are created in a bimolecular process.³ The fraction of the reagent that escapes into solution before being consumed in the electron transfer reaction is then related to the rate of electron transfer. Since the escape yield is 50% when the electron transfer and diffusion rates are equal, this technique permits measurement of electron transfer rates that are somewhat faster than diffusion.

Angel and Peters recently described a second approach for the measurement of intermolecular electron transfer

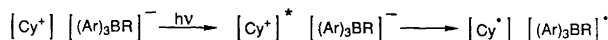
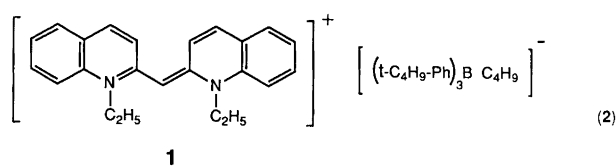
rate constants above the diffusion limit.⁴ The lifetime of an electronically excited donor was monitored as the concentration of an electron acceptor in solution was increased. Analysis of the electron transfer rate constants showed that both time-dependent near-neighbor and time-independent diffusional quenching processes are operative. By modeling the behavior of acceptor molecules in the neighborhood of the excited donor, they are able to obtain estimates of rate constants for electron transfer reactions that are well above the limit set by diffusion.

Similarly, Kemnitz reported the measurement of rate constants for intermolecular electron transfer reactions far above the diffusion limit.⁵ In this approach, the fluorescence efficiency of a dye molecule dissolved in a solution of a melted (ca. 500 K) aromatic electron donor was determined. Since the electron donor is the solvent, no diffusion is required before electron transfer occurs. By assuming that all non-radiative processes except electron transfer are independent of the donor ionization potential, the measured fluorescence efficiencies were related to the electron transfer rates.

Herein we describe an investigation of the photochemistry and photophysics of 1-ethyl-2-(1-ethyl-1,2-dihydroquinolin-2-ylidenemethyl)quinolinium butyl(tris-*p*-tert-butylphenyl)borate (*N,N'*-diethyl-2,2'-cyanine borate, **1** see Scheme 1).⁶ This compound allows the measurement of intermolecular electron transfer rates far above the diffusion limit. Our approach takes advantage of the self-organization of the cationic dye with the anionic electron donor into an ion pair when it is dissolved in a non-polar solvent.⁷ Thus, electron transfer from the donor to the excited acceptor does not require a diffusive encounter. Since this experiment must be performed in non-polar solvents, where the reorganization energy is small, very high intrinsic rate constants may be obtained. This combination of assets

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* To whom correspondence should be addressed.



Scheme 1.

should allow the application of this system to critical tests of electron transfer theories.

Experimental

Cyanine borate **1** was prepared by metathesis of the chloride salt of the dye with the tetrabutylammonium salt of the borate in acetonitrile/water solution. Slow evaporation of the solvent gave solid **1** that was pure and homogeneous. Analysis: $\text{C}_{57}\text{H}_{71}\text{BN}_2$; C,H,N.

Fluorescence spectra were recorded on a Farrand Mark I spectrofluorimeter with Rhodamine B as the standard. Absorption spectra were recorded on a Perkin-Elmer 552 spectrometer. Laser flash photolysis was performed with a Quantel mode-locked Nd-YAG laser; this spectrometer has been described elsewhere.⁸ The conductivity of cyanine-containing solutions was measured under flow conditions with a Dionex Conductivity detector.

Results

Cyanine borate (1): structure, absorption, and lifetime in solution. The structures of cyanine dyes in solution and in the solid phase have been extensively studied. Crystalline *N,N'*-diethylcyanine, as its iodide salt, has been shown by X-ray studies⁹ to be non-planar with a dihedral angle between the two quinolinyl rings of 44°. The distortion from planarity, the conformation having the maximum value for conjugative stabilization, is ascribed to unavoidable steric interactions in the planar forms. It is generally agreed that this dye also adopts a non-planar structure in solution. This conclusion is consistent with the exceedingly short fluorescent lifetime of the dye.¹⁰ Several attempts to measure its lifetime have been reported, but only an upper limit of 5 ps in ethanol solution has been obtained.¹¹ The exceedingly short singlet lifetime is said to indicate that only a very small change in the already large dihedral angle is required for non-radiative relaxation of the dye to its ground state.

We obtained an estimate of the singlet lifetime of *N,N'*-diethylcyanine chloride in ethanol solution by measuring the fluorescence efficiency of the dye and calculation of its radiative rate constant from the Strickler-Berg relationship.¹² A solution of the cyanine in ethanol (1.2×10^{-5} M) fluoresces very weakly with an emission maximum at 561 nm. The fluorescence excitation spectrum matches the absorption spectrum of the dye. Comparison of the intensity

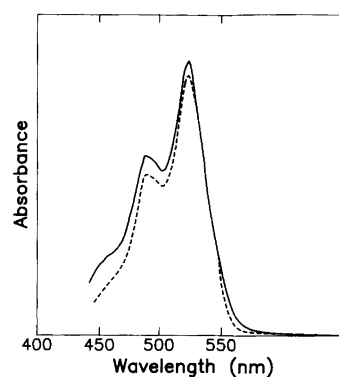


Fig. 1. Absorption spectrum of cyanine borate **1** in ethyl acetate solution. Solid line, 4.1×10^{-4} M, dashed line 2.7×10^{-7} M. The spectra are normalized to the same absorption intensity maximum for presentation purposes; they were recorded in cells of different pathlength.

of the fluorescence with that of Rhodamine B under identical conditions shows a maximum value for the cyanine fluorescence quantum yield of 9×10^{-5} .

The absorption spectrum of the cyanine dye is shown in Fig. 1; it displays features common to most of the cyanine dyes. There are two peaks in the spectrum, assigned to the $0 \rightarrow 0$ and $0 \rightarrow 1$ vibronic transitions, at 522 nm ($\epsilon = 6.6 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) and 490 nm, ($\epsilon = 4.4 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$), respectively. Calculation of the oscillator strength by integration of the intensity of these absorption bands gives an estimate for the natural radiative lifetime (τ_0) for the cyanine of 3.8 ns. Some confirmation of this estimate may be obtained by comparison of the calculated radiative lifetime with that obtained experimentally from examination of related cyanines in rigid media. Jaraudias studied the viscosity dependence of fluorescence from *N,N'*-diethyloxycarbocyanine (absorption $\lambda_{\text{max}} = 578$ nm) in a series of alcohols. These experiments reveal a medium- and temperature-independent value of τ_0 for this dye of 2.8 ns.¹³

The lifetime of an emitting excited state in solution (τ_s) may be obtained from τ_0 and Φ_f according to eqn. (1). For the *N,N'*-diethylcyanine in ethanol (or acetonitrile) solution this calculation yields a value for τ_s of ca. 330 fs. It is important to note that this estimate represents an upper limit to the lifetime of the cyanine. If the weak fluorescence we observe is due in part to emission from a trace impurity, the lifetime of the dye would be less than the calculated value. The short lifetime of the cyanine dye provides a very rapid 'clock' for measuring the rates of reactions that compete with decay of its excited singlet state.

$$\tau_s = \Phi_f \tau_0 \quad (1)$$

The absorption and emission studies of *N,N'*-diethylcyanine permit the estimation of the energy of its excited singlet state to be 2.31 eV. This value is of importance in calculation of the free energy change reactions involving this state.

Cyanine borate 1: ion pairing in solution. Salts dissolved in organic solvents exist as a mixture of freely solvated ions and ion pairs. We have examined the state of association of some cyanine dyes in different solvents by conductometric means. In ethyl acetate solution (dielectric constant = 6.02) measurement of the concentration dependence of the equivalent conductivity (Λ_0) gives a value for the dissociation constant (K_D) for the cyanine borate of 2.9×10^{-6} M.¹⁴ In benzene solution (dielectric constant = 2.28), K_D was estimated by extrapolation according to the Fuoss equation¹⁵ to be ca. 10^{-17} M. Thus in ethyl acetate solution, the cyanine borates exist primarily as ion pairs when its concentration is above ca. 10^{-5} M, and primarily as freely solvated ions when its concentration is ca. 10^{-7} M. In benzene solution, the cyanine borate exists primarily as ion pairs at all concentrations practical for spectroscopic measurements.

We examined the concentration dependence of the absorption spectrum of the cyanine borate **1** to probe the effect of ion pairing on the electronic properties of the dye. Fig. 1 shows the absorption spectra of **1** in ethyl acetate solution at 2.5×10^{-7} M and at 4.1×10^{-4} M. Over this range, in this solvent, the cyanine borate salt changes from predominantly ion pairs to predominantly free ions. However, there is no change apparent in the shape or the intensity of the cyanine absorption spectrum over this concentration range. This finding shows that there is little or no interaction in the ground state between the dye and the borate.¹⁶ Therefore, it appears that irradiation of the cyanine in an ion pair with the borate at 532 nm generates a 'locally' excited state of the dye, not the excited state of a charge transfer complex.

Cyanine borate 1: time resolved absorption spectroscopy. Studies of the laser flash photolysis of *N,N'*-diethylcyanine have been reported previously.^{10,11} Consistent with this earlier work, we find that irradiation of the *N,N'*-diethylcyanine chloride in ethanol solution with the output of a mode-locked Nd-YAG laser (532 nm, 15 ps, 240 μ J) leads to immediate bleaching of the dye and formation of a photoproduct having an apparent absorption maximum at 550 nm (Fig. 2, upper spectrum). The absorption of the photoproduct decays as the cyanine dye absorption returns according to a first-order rate law with a lifetime 330 ps. The metastable photoproduct formed in this reaction is usually identified as a photoisomer of the cyanine formed by rotation about the central carbon-carbon double bond.

Laser flash photolysis of the cyanine borate in benzene solution leads to a different outcome. Fig. 2 shows an absorption spectrum recorded 18 ps after the start of the reaction. The bleaching of the characteristic absorptions of the cyanine dye is apparent, but less of the photoisomer is detectable in the spectrum. There is also a feature in this spectrum with an apparent maximum at 430 nm that is not formed from irradiation of the cyanine chloride. This new species appears instantaneously on the timescale of this experiment and does not decay measurably within 10 ns.

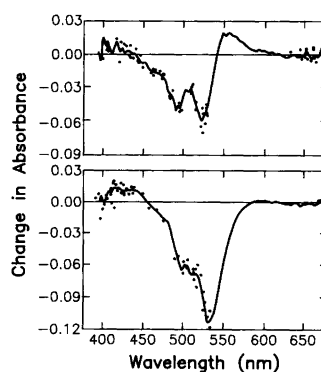
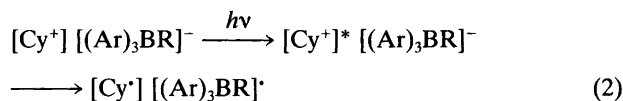


Fig. 2. Absorption spectrum (upper) recorded 18 ps after excitation of cyanine chloride with a 15 ps pulse. Absorption spectrum (lower) of cyanine borate recorded 18 ps after excitation with a 15 ps pulse.

The 430 nm absorbing intermediate formed from irradiation of the cyanine borate in benzene solution is assigned to the *N,N'*-diethylcyanine radical by comparison with the absorption spectra of similar cyanine radicals formed electrochemically.^{6,17} Evidently, intra-ion-pair electron transfer from the borate to the excited singlet state of the cyanine generates the cyanine-boranyl radical pair as shown in eqn. (2).



The quantum yield of electron transfer from the borate to the excited singlet state of *N,N'*-diethylcyanine was estimated by comparison with *N,N'*-dibutyltetramethylindocarbocyanine. The efficiency of radical formation from steady-state photolysis of the indocarbocyanine *n*-butyltriphenylborate has been measured previously by chemical methods.⁶ Irradiation of equally absorbing, optically dilute benzene solutions of the diethylcyanine and the indocarbocyanine borates leads to irreversible bleaching of the dye absorptions in both cases. Comparison of the change in absorption of the two dyes at their respective absorption maxima ($\Delta_{\text{OD}} = -0.05$, and -0.22 , respectively) 5 ns after the laser pulse, shows that the quantum yield for electron transfer from the borate to the excited singlet state of *N,N'*-diethylcyanine borate is 0.62. Similarly, the relative rate of irreversible reaction of **1** by irradiation under steady-state conditions was compared with that of the indocarbocyanine *n*-butyltriphenylborate. This method gives a quantum efficiency for electron transfer to the *N,N'*-diethylcyanine of 0.59. These experiments show that intra-ion-pair electron transfer to the excited state of *N,N'*-diethyl-2,2'-cyanine from butyl(tris-*p*-tert-butylphenyl)borate is a monophotonic process that is sufficiently fast to compete with relaxation of the excited dye. Calculation from the computed singlet lifetime of the *N,N'*-diethylcyanine and the measured quantum efficiency for the electron transfer (θ_{et}) according to eqn. (3) reveals that the rate

constant (k_{et}) for this reaction is $2 (\pm 1) \times 10^{12} \text{ s}^{-1}$. This value is ca. 100 times greater than the diffusion-limited rate for a bimolecular reaction in benzene solution.

$$k_{et} = \theta_{et} \cdot 1 / [\tau_s (1 - \theta_{et})] \quad (3)$$

Discussion

These experiments establish that visible light irradiation of the cyanine borate **1** in benzene solution generates the locally excited singlet state of the dye and that electron transfer from the borate to its cyanine counter-ion occurs in competition with decay of the excited state. The self-organization of the donor and the acceptor into an ion pair prior to excitation allows the electron transfer reaction to occur despite the exceedingly short lifetime of the excited cyanine. Moreover, the short singlet lifetime of *N,N'*-diethylcyanine provides the means of measuring an intermolecular electron transfer rate constant many times greater than the limit imposed by diffusion.

It is of some interest to examine the electron transfer reaction revealed by these experiments in the light of current theories. The semiclassical Marcus equation [eqn. (4)] provides a model for consideration of the factors that affect electron transfer rates. In this equation $V(r)^2$ is the electron exchange matrix element for through-space interaction of the donor and acceptor wave functions at distance r , and the summation term incorporates the Franck–Condon state densities.

$$k_{et} = (\pi / \hbar^2 \lambda_s k_B T)^{1/2} |V(r)|^2 \times \sum_{w=0}^{\infty} (e^{-S} S^w / w!) \exp - [(\Delta G^\circ + \lambda_s + wh\omega) / 4 \lambda_s k_B] \quad (4)$$

$$S = \frac{\lambda \nu}{h\nu}$$

In the usual analysis of eqn. (4), it is considered that the magnitude of $V(r)$ falls off exponentially with distance (r) according to eqn. (5). An obvious advantage to the use of the cyanine borate ion pairs in the study of electron transfer is that r can be determined experimentally from X-ray crystallography. Also, since coulombic attraction forces are strong in non-polar solvents, r should be nearly equal to R_0 (the distance of maximum rate) for these compounds. This reasoning suggests that the exponential term of eqn. (5) should be nearly invariant and close to its asymptotic value of 1 for cyanine borate ion pairs, essentially independent of structural details.

$$V(r) = V(R_0) \exp [-\beta(r - R_0)/2] \quad (5)$$

The Franck–Condon term in eqn. (4) is so complex as to require simplifying assumptions to permit its experimental investigation. Miller and Closs suggested that all skeletal vibrations (ν) be represented by an averaged frequency at

1500 cm^{-1} .¹⁹ It is also usually assumed that the reorganizational energy λ is the sum of low-frequency solvent components (λ_s) and high-frequency internal vibrations of the donor and acceptor (λ_v). For the intra-ion-pair electron transfer of the cyanine borate in benzene solution, we set $\lambda_s = 0$ since the high frequency and static dielectric constants of this solvent are nearly identical.²⁰ Thus the maximum rate constant for this electron transfer reaction is predicted to occur when the free energy change for the reaction (ΔG°) is equal to $-\lambda_v$.

The free energy change for a photoinitiated electron transfer may be calculated according to eqn. (6) where E_{ox} and E_{red} represent the oxidation potential of the donor (borate) and the reduction potential of the acceptor (cyanine), ΔE^* is the singlet energy of the cyanine, and W_p and W_r are work terms associated with bringing the products and reactants to within encounter distance from infinity.

$$\Delta G^\circ = E_{ox} - E_{red} - \Delta E^* - (W_p - W_r) \quad (6)$$

The singlet energy of *N,N'*-diethylcyanine is known as is its reduction potential in acetonitrile solution.²¹ The oxidation of the borate shows an irreversible wave by cyclic voltammetry, so we obtained this value by kinetic means using the approach of Rehm and Weller.²² In acetonitrile solution butyl(tris-*p*-tert-butylphenyl)borate has an oxidation potential of 1.11 V vs. SCE. The photochemical experiments were carried out in benzene solution, so the redox potentials must be modified to accommodate the solvent change. The usual procedure for this modification is to calculate the change in solvation energy by means of the Born equation. However, in the case of the cyanine borates there is a fortunate cancellation in the solvent effects on the redox potentials and the work change associated with charge recombination during the electron transfer. These two solvent-dependent quantities enter eqn. (6) with opposite signs and magnitude that differ by $(1/\epsilon_{MeCN})$.²⁰ Since the dielectric constant of acetonitrile is large, this difference may safely be ignored. These considerations give ΔG° for electron transfer from the borate to the excited cyanine in benzene solution equal to -0.03 eV .

The maximum possible rate for an intermolecular electron transfer reaction is defined by the internal vibrational frequencies of the reactants. For the assumed average of 1500 cm^{-1} , this leads to a limiting rate constant of $4 \times 10^{13} \text{ s}^{-1}$. The rate constant for photoinitiated electron transfer in cyanine borate **1** is below this limit. From the data available it is not possible to decide if this is due to $V(r)$ having less than its maximum value or because $\lambda_v \neq -\Delta G^\circ$. This point will be addressed in additional experiments. We note however that in the electron transfer reaction to photoexcited cationic dyes in the melt system, Kemnitz obtains $\lambda_v = 0.1 \text{ eV}$. On this basis, and because k_{et} for **1** is as high as any ever measured for an intermolecular electron transfer, we speculate that $\lambda_v \approx -\Delta G^\circ$; if so $V(r)$ for **1** is ca. 60 cm^{-1} . Confirmation of this estimate through further experimentation is underway in our laboratories.

Conclusions

Irradiation of a cyanine borate ion pair in non-polar solution gives a locally excited state of the dye. Intra-ion-pair electron transfer from the borate to the cyanine generates a radical pair. The self association of the electron donor and the electron acceptor prior to excitation, and the very short excited-state lifetime of the cyanine permit measurement of electron transfer rates far above the diffusion limit. The special features of this reaction may make it a suitable probe for theories of electron transfer reactions.

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