

Influence of Diffusion on Photoinduced Electron Transfer

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Electron transfer from an optically excited donor (rubrene) to randomly distributed acceptors (duroquinone) has been investigated experimentally. The forward electron-transfer process under the influence of diffusion in liquid solution (diethyl sebacate) is compared with that in solid solution (sucrose octaacetate). Steady-state fluorescence yield and time-resolved fluorescence measurements were used to measure the excited-state population of the donor (rubrene). The parameters were used to analyze the electron-transfer dynamics under a variety of acceptor concentrations. The agreement between theoretical predictions and experiments is very good. The forward transfer parameters (a_f and R_0) in liquid solution are almost identical with those obtained in solid solution.

I. Introduction

Photoinduced electron transfer from a donor molecule to an acceptor molecule is responsible for an important class of chemical reactions. Following the transfer of an electron from an excited neutral donor to a neutral acceptor or neutral donor to an excited acceptor, the highly reactive radical ions can go on to do useful chemistry.¹⁻⁴

In this paper, we present a study of the influence of molecular diffusion on photoinduced electron transfer. Steady-state fluorescence yield and time-resolved fluorescence measurements are used to measure the population of the donor's excited state. Since electron transfer quenches the fluorescence from the initially excited state, fluorescence provides a direct observable for the yield and time dependence of the electron-transfer process. The excited-state population was analyzed by using a method that included donor-acceptor and acceptor-acceptor excluded volume and the appropriate donor-acceptor reflecting boundary condition.

Photoinduced electron transfer between randomly distributed donors and acceptors embedded in solid solution has been studied theoretically^{1,5-7} and experimentally.^{1,8} Recently, diffusion-influenced electron transfer has also been treated theoretically⁹⁻¹³ and experimentally.^{9,14} Here we compare the results obtained in solid solution⁸ to the results in liquid solution for the same donor and acceptor molecules. The comparison to solid solution provides an important control for judging the applicability of the theoretical model to the problem with diffusion. For a wide range of acceptor concentrations, theory and experiment are in very good agreement. The parameters used to characterize the electron-transfer dynamics in liquid solutions are virtually identical with those used in solid solutions.

II. Experimental Procedures

The donor was rubrene (RU) and the acceptor was duroquinone (DQ). The rubrene was dissolved in solvent, either acetone for the solid solution or diethyl sebacate (DS) for the liquid solution, and then filtered to remove dust. No other purification steps were used. The DQ was twice sublimated and also dissolved in solvent and run through a filter. For the samples in solid solution the method of preparation has been described previously.⁸ The liquid

samples were made by using serial dilution to obtain the desired concentrations for RU and DQ. Typically, the RU concentration was 10^{-4} M (an optical density of ≈ 0.2 at 532 nm) and the DQ concentration ranged from 0 to 0.33 M. The solvent diethyl sebacate was filtered. Each sample was placed into a 1-mm optical cuvette. The cuvette had an adaptor for a vacuum line so the sample could be freeze-pump-thawed (3-5 cycles) to remove oxygen⁸ to prevent RU decomposition in the presence of oxygen and light.

The viscosities of the pure diethyl sebacate (DS) and DQ/DS solutions were measured with an Ubbelohde viscometer. At the highest concentrations of DQ, the viscosities of the solutions differed from pure solvent. The measured viscosities were used.

The time-resolved fluorescence decays were measured by time-correlated single photon counting. The laser system and the single photon counting instrument have been described in detail previously.¹⁵ Briefly, the frequency-doubled (532 nm) output from an acoustooptically mode-locked YAG laser is used to synchronously pump a cavity dumped dye laser. The excitation wavelength is 555 nm. The fluorescence is detected in a 60-nm window centered at 590 nm. Scattered light is blocked from entering the detector (a multichannel plate) by a 1-mm antislit placed in the position normally occupied by the center slit of a subtractive double monochromator. The broad spectral bandwidth of this arrangement essentially eliminated solvent relaxation effects on the time dependence of the emission. The instrument response of the system is ≈ 70 ps. The output of the instrument is transferred to computer for data analysis. The detection polarization was set to the magic angle from the excitation polarization to remove the influence of rotational relaxation of the donor molecules on the time dependence of the fluorescence.

The fluorescence yield data were taken, using the frequency-doubled (532 nm) single pulses from a CW pumped acoustooptically mode-locked and Q-switched Nd:YAG laser. The fluorescence was collected by a lens, and the output went through a set of three 532-nm cutoff filters. The broad-band fluorescence was detected by a phototube, and the signal was sent to a lock-in amplifier. To obtain the relative yield accurately, all the samples were positioned the same way relative to the excitation-detection setup. For each sample a corresponding yield was measured for a sample that just contained RU/DS. Dividing the fluorescence intensities of the DQ/RU/DS samples by the plain RU/DS sample after correcting for their optical density differences in RU gave the relative fluorescence yield.

III. Theory

Here we present a brief description of the theory. Although this theory for the forward transfer is not in itself new,⁹⁻¹³ it does contain the appropriate boundary conditions (reflecting) and does have for the first time not just donor-acceptor excluded volume but also acceptor-acceptor excluded volume. In the model, the

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donors and acceptors are randomly distributed at $t = 0$ when the sample is excited. It is assumed that the donor has only one accessible electronic excited state and the acceptor has only one acceptor state. The transfer rates are exponentially decaying functions of distance.^{1,7,8} After pulsed excitation, two processes can occur from the excited state: decay to the ground state by fluorescence and nonradiative relaxation and electron transfer. Rubrene, studied here, is reported to have essentially unit quantum yield for fluorescence.¹⁶ The rate constants are

$$K = \frac{1}{\tau} \quad (1a)$$

$$K_f(R) = \frac{1}{\tau} \exp\left(-\frac{R_0 - R}{a_f}\right) \quad (1b)$$

where R is the donor-acceptor separation. R_0 and a_f are molecular parameters that characterize the distance scale of the forward transfer rate.^{1,8} τ is the donor excited-state lifetime in the absence of acceptors.

There are two steps involved in calculating the excited-state population. The first is deriving the survival probability for a single donor-acceptor pair as a function of initial separation,⁹⁻¹³ and the second is using the survival probability to perform the ensemble average over all initial distances for all of the acceptors to obtain the state populations in the thermodynamic limit.⁹⁻¹³

In solid solution, the survival probability is given by⁵⁻⁸

$$P_{\text{ex}}(R^0, t) = \exp(-t/\tau) \exp(-K_f(R^0)t) \quad (2)$$

where R^0 is the donor-acceptor separation. In solid solution the donor-acceptor separation does not change with time. In liquid solution, the Fick diffusion equation is used and we obtain the following result⁹⁻¹³

$$\frac{\partial}{\partial t} P_{\text{ex}}(R^0, t) = D \nabla^2 P_{\text{ex}}(R^0, t) - K_f(R^0) P_{\text{ex}}(R^0, t) \quad (3)$$

where D is the sum of the donor (D_d) and the acceptor (D_a) diffusion constants and ∇^2 for the spherically symmetric case is

$$\nabla^2 = \frac{2}{R^0} \frac{\partial}{\partial R^0} + \frac{\partial^2}{\partial R^0{}^2} \quad (4)$$

Equation 3 must be solved numerically.

The ensemble-averaged excited-state population in the thermodynamic limit for point particles is given by¹⁰⁻¹³

$$\langle P_{\text{ex}}(t) \rangle = \exp(-t/\tau) \exp\left(-4\pi C \int_0^\infty [1 - P_{\text{ex}}(R^0, t)] R^0{}^2 dR^0\right) \quad (5)$$

where C is the concentration of the acceptors. For solid solution, $P_{\text{ex}}(R^0, t)$ is given by eq 2 and for liquid solution is obtained from eq 3. For donors and acceptors of finite size the excited-state probability is^{5,17,18}

$$\langle P_{\text{ex}}(t) \rangle = \exp(-t/\tau) \exp\left(-\frac{4\pi}{d^3} \sum_{k=1}^{\infty} \frac{p^k}{k} \int_{R_m}^{\infty} [1 - P_{\text{ex}}(R^0, t)]^k R^0{}^2 dR^0\right) \quad (6)$$

where R_m is the sum of the donor and the acceptor radii, d is the diameter of the acceptor, and $p = Cd^3$.

The relative fluorescence yield is obtained by integrating the excited-state population over time⁸

$$\frac{\eta}{\eta_0} = \frac{1}{\tau} \int_0^\infty \langle P_{\text{ex}}(t) \rangle dt \quad (7)$$

There are seven parameters in the problem: R_0 , a_f , τ , R_m , d , D , and C . The concentration, C , is measured spectroscopically. The molecular sizes, R_m and d , are obtained from X-ray crystallographic data.¹⁹ The diffusion constants, D_d and D_a , are

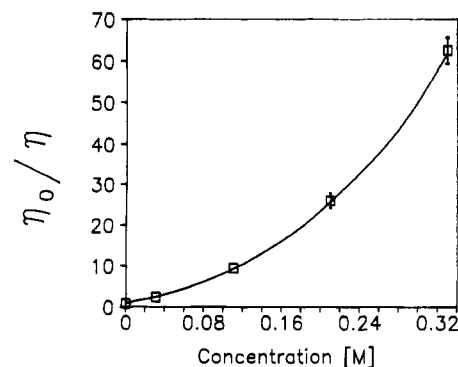


Figure 1. A Stern-Volmer plot of the fluorescence yield data. Error bars are shown for two points. The others are smaller than the data square. The best fit (solid line) gave $a_f = 0.22 \text{ \AA}$ and $R_0 = 12.8 \text{ \AA}$. The other parameters are given in the text.

obtained by combining the measured viscosity (Ubbelohde viscometer) of the solvent with the molecular sizes in the Stokes-Einstein equation. The lifetime, τ , of the donor's excited state is measured by time-resolved fluorescence. The remaining two parameters are obtained by analyzing the time-resolved fluorescence quenching and the relative yield data with eqs 6 and 7.

IV. Results and Discussion

The molecular sizes used for the analysis are $R_m = 9.0 \text{ \AA}$ and $d = 7.2 \text{ \AA}$.¹⁹ The viscosity of the solvent varied slightly as a function of DQ concentration. For the concentrations used here the diffusion constants are as follows: $C = 0.031 \text{ M}$, $D = 18.3 \text{ \AA}^2/\text{ns}$; $C = 0.11 \text{ M}$, $D = 18.4 \text{ \AA}^2/\text{ns}$; $C = 0.21 \text{ M}$, $D = 18.6 \text{ \AA}^2/\text{ns}$; and $C = 0.33 \text{ M}$, $D = 18.8 \text{ \AA}^2/\text{ns}$. The fluorescence lifetime of RU in diethyl sebacate is $\tau = 14.4 \text{ ns}$ and in sucrose octaacetate is $\tau = 15.0 \text{ ns}$.

Equation 3, the differential equation for the survival probability of the excitation with an acceptor at a distance R^0 at $t = 0$, was solved numerically by using the Crank-Nicholson method²⁰ and also using a master equation method.²¹ Both methods gave the same results. Care was taken to make sure the results were stable, accurate, and converged. These depend on the spatial and temporal step sizes used in the calculations. Typically, the spatial step was less than 0.5 \AA but was made much smaller to test for convergence. The temporal step was typically less than 10^{-4} ns . The integrations in eqs 5-7 were performed using Gaussian quadrature.²⁰ All programs were written in the C language and run on a DECstation 3100.

At $t = 0$ RU is excited. As time progresses, there is decay to the ground state with a rate constant of $1/\tau$, and there is forward electron transfer to the radical ion state with the rate constant $K_f(R)$. In liquid solution the pair separation, R , is a function of time. All states are singlets.

Figure 1 shows the experimental and theoretical inverse of the steady-state relative fluorescence yield (a Stern-Volmer plot) in diethyl sebacate (liquid solution). The theoretical curve was calculated by using the inverse of eq 7. The error bars are as indicated. The symbols are the data. For the first three concentrations the error bars were smaller than the symbol for the data points. The curve is the best fit. As can be seen, the curve goes essentially through the middle of the error bars. This fit is obtained when $a_f = 0.22 \text{ \AA}$ and $R_0 = 12.8 \text{ \AA}$. The other parameters are stated above. The yield data taken in sucrose octaacetate (solid solution) has been previously reported⁸ and rechecked during these experiments. In contrast to the data taken in liquid solution, it is known that the fit to the solid solution data is only sensitive to the R_0 value.⁷ In solid solution $R_0 = 13.1 \text{ \AA}$.⁸

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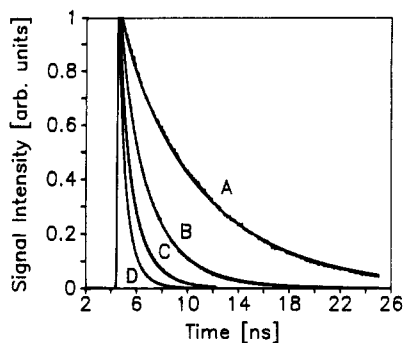


Figure 2. Time-resolved fluorescence decay (data and fits) in diethyl sebacate (liquid solution). The best fit through all the concentrations gave the same parameters as the Stern–Volmer plot; see Figure 1. Curve A is 0.031 M, B is 0.11 M, C is 0.21 M, and D is 0.33 M duroquinone, respectively.

The time-resolved fluorescence quenching data in diethyl sebacate are presented in Figure 2. The calculated excited-state population ($P_{ex}(t)$) given in eq 6 is convolved with the instrument response function and then compared to the data. The appropriate equation is

$$I(t) = \int_0^{\infty} IR(t-t')(P_{ex}(t')) dt' \quad (8)$$

where $IR(t)$ is the measured instrument response. The parameters a_f and R_0 were adjusted to fit the experimental data. The initial values of a_f and R_0 were taken from the values determined previously⁸ in solid solution. Either a_f or R_0 can be adjusted or both can be adjusted to fit the data. All of these procedures were used to analyze the data. It is found that the best fit is obtained for both the time-resolved fluorescence quenching and the fluorescence yield when a_f is the same as in the rigid glass while R_0 differs slightly. The slight difference from the rigid result is most likely due to differences in the nature of the solvent, for example, dielectric properties. The best fit gives $a_f = 0.22 \text{ \AA}$ and $R_0 = 12.8 \text{ \AA}$. This is identical with that obtained from the fluorescence yield data. The calculated fits are shown in Figure 2 along with the data. In some of the curves it is difficult to distinguish the data and the fit.

Time-resolved fluorescence data were taken, using single photon counting on rubrene and duroquinone in sucrose octaacetate in solid solution, confirming previous results. A detailed study of the solid solution results have been presented.⁸ The results yield $a_f = 0.22 \text{ \AA}$ and $R_0 = 13.1 \text{ \AA}$. The agreement between theory and experiment is also very good. In the case of rigid solution, only a_f is adjusted to fit the time-resolved data. The R_0 parameter is found by a Perrin plot (natural log of the relative yield vs concentration) of the yield data. These two parameters are thus found independently in solid solution.⁸ Comparing the solid (no diffusion) and liquid (diffusion) results shows that the a_f values are identical and the R_0 values differ by $\approx 2\%$.

a_f and R_0 are molecular parameters describing the forward transfer dynamics.^{1,8} Therefore, a_f and R_0 are expected to be the same for the same donor–acceptor pair under different diffusion environments (ignoring solvent relaxation effects). However, since the electron-transfer dynamics are effected by the solvent reorganization energy,¹ it is not surprising that these parameters are slightly different from one solvent to another due to differences in the solvent's dielectric properties. The fact that very similar electron-transfer parameters are obtained for liquid diethyl sebacate ($a_f = 0.22 \text{ \AA}$ and $R_0 = 12.8 \text{ \AA}$) and rigid sucrose octaacetate ($a_f = 0.22 \text{ \AA}$ and $R_0 = 13.1 \text{ \AA}$) solutions indicates that a_f and R_0 are good molecular parameters to characterize the forward transfer process.

In a recent related work, Eads et al.¹⁴ measured the relative yields and time-resolved fluorescence decays of the rhodimine B/ferrocyanide/water system. The concentration of their anionic donor (ferrocyanide) ranged from 0.1 to 0.4 M. The relative diffusion constant for their system was $125 \text{ \AA}^2/\text{ns}$. They analyzed their results using a variety of methods. They analyzed the early

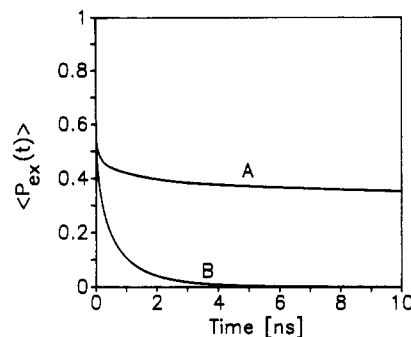


Figure 3. Calculation of the time dependence of donor quenching by electron transfer for the solid (curve A) and the liquid (curve B) solutions (equivalent to those studied experimentally). The excited-state lifetime decay is not included so that the electron transfer can more directly be compared. $C = 0.27 \text{ M}$, $R_0 = 13 \text{ \AA}$, and the other parameters are the same as those used in Figure 2. For curve B, $D = 18.6 \text{ \AA}^2/\text{ns}$. Diffusion results in a large increase in electron transfer.

part of their data (0–25 ps) using a single electron-transfer rate and no diffusion (transfer only at contact). At later times (0–200 ps) they used the Collins and Kimball model,^{9,14} which uses a single electron-transfer rate, and electron transfer can occur in a spherical shell around the acceptor called the reaction zone. They found that this fit their data well only up to 0.2 M. The time regime from 0 to 4 ns they attempted to fit with the Smoluchowski diffusion-controlled reaction model^{9,14} (where there is an infinite electron-transfer rate only at contact) and were not able to fit their data with physically realistic parameters (the contact distance and diffusion constant). They also tried fitting their data with a model similar to the one we used here (the diffusion equation with a sink function proportional to the position-dependent electron-transfer rate). They took into account donor–acceptor excluded volume but did not include acceptor–acceptor excluded volume. They did use the appropriate donor–acceptor reflecting boundary condition. They were not able to get consistent fits throughout their concentrations or between the two experiments (yield and time-resolved fluorescence). They also included a bare Coulomb potential and determined that was inappropriate for their system even though they had diffusing ions. They concluded that a screened potential was necessary. In this paper, transfer between initially neutral molecules was studied, and it was not necessary to include a Coulomb potential. Eads et al.¹⁴ found in their work that $a_f \approx 0.2\text{--}0.5 \text{ \AA}$, which is on the same order as the value obtained here.

It can be seen by comparing Figure 2 with the data reported previously⁸ that the excited-state population decays (electron transfer) much faster in the liquid solution than in the solid solution. Figure 3 shows a calculation of the time-dependent donor quenching by electron transfer (excited-state lifetime decay not included) for the solid and liquid solutions. (The concentration $C = 0.27 \text{ M}$ is one used in the solid solution study and falls between the concentrations used in curves C and D in Figure 2 of this report.) The difference is dramatic. At short times ($< 5 \text{ ps}$) when the displacement of the molecules is negligible, the curves are identical. At longer times, diffusion leads to faster and more electron transfer. Diffusion of the molecules has a profound influence on the transfer process in spite of the fact that the transfer parameters, a_f and R_0 , are virtually identical in the two systems. This can be understood qualitatively. In a solid, acceptors that are too far away from the excited donor to receive an electron within the donor lifetime do not participate in the transfer dynamics. In a liquid, an acceptor too far from a donor at $t = 0$ can move in at later times and receive an electron. Because of the motion, more acceptors pass through the transfer range (in the lifetime of the excited state) than would normally be there in solid solution. The net result is that, all other things being equal, an increased rate of diffusion will increase the rate of depletion of the excited state.

The agreement between theory and experiment that is displayed in this study is very good. Comparing the solid and liquid solutions

provides an excellent control on the study. The theory for the solid solution is straightforward. Since the solid and liquid solvents have similar properties, it is expected and found that the transfer parameters are virtually the same in the two types of systems. The parameters obtained from the liquid data are, therefore, not arbitrary fitting parameters. The results demonstrate that, at least for this system, we have a clear description of the influence of spatial diffusion on photoinduced electron transfer.

In a subsequent study,²² results like those presented above will be combined with experimental measurements of the dynamics

of electron back-transfer (geminate recombination) and theory. This will provide a description of the competition between back-transfer and radical ion separation by diffusion.

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