Influence of Diffusion on the Kinetics of Donor−Acceptor Electron Transfer Monitored by the Quenching of Donor Fluorescence

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The problem of photoinduced donor−acceptor electron transfer in liquid solution is analyzed to obtain an understanding of the relationship between approximate treatments of the role of diffusion in electron transfer, that is, the Collins−Kimball approach, and a detailed analysis of the problem. It is shown why previous analyses of experimental data have yielded distance dependences of electron transfer that are much too long range. From an appropriate fitting of the nonstationary kinetics of donor fluorescence quenching by diffusion-assisted electron transfer, the effective radii and the steady-state constants associated with electron transfer are found for a donor−acceptor system studied experimentally in seven solvents with different viscosities. The dependence of diffusion agrees with the one predicted theoretically for electron transfer having a distance-dependent transfer rate initially taken to be exponential with distance. In the fast-diffusion limit, the dependence on the rate of diffusion is well approximated by the Collins−Kimball relationship, which permits the kinetic rate constant and the effective radius associated with diffusion-induced quenching to be extracted from the experimental data. The effective radius is then related to the electron transfer rate with arbitrary distance dependence. From this relationship, the tunnelling length for both exponential and Marcus-type rates is obtained from the data analysis, and it is demonstrated that the latter is almost twice as long as the former. For the Marcus transfer rate, it is found that the Marcus parameter $\beta = 1.2$ Å^{-1} ($\beta = 2$/tunnelling length), which is in accord with previous measurements on a variety of systems. The theoretical analysis presented here resolves the apparent discrepancies between early measurements of very long tunnelling lengths in liquid systems and physically reasonable values of $\beta \approx 1$ Å^{-1}.

I. Introduction

One of the simplest bimolecular reactions in liquid solutions is the impurity quenching of an excited donor D* by charge transfer to electron acceptors A. The competition of the excitation decay with the diffusion-assisted electron transfer is represented by the following reaction scheme

$$\begin{array}{l} D^* + A \rightarrow D^+ + A^- \\ \downarrow\tau \end{array} \tag{1.1}$$

where τ is the donor excited-state lifetime in the absence of acceptors. The energy dissipation is often described by conventional (Markovian) chemical kinetics, represented by a single equation for the excitation density $N = [D^*]$

$$\dot{N} = -k_i c N \tag{1.2}$$

where $c = [A]$ remains constant if acceptors are present in great excess. Under this condition, the quenching proceeds exponentially with the time-independent rate ck_i and the rate constant

$$k_i = 4\pi R_Q D \tag{1.3}$$

where $D = D_D + D_A$ is the coefficient of encounter diffusion and R_Q is the effective radius of the reaction.

In the classical theory of bimolecular reactions,[1,2] the transfer proceeds with a kinetic rate constant k_0 in a thin layer adjacent to the contact sphere of radius σ. In this case, the effective radius is related to the external radius of the reaction layer, R, according to the Collins−Kimball (CK) relationship:

$$R_Q = R\frac{k_0}{k_0 + 4\pi R D} \tag{1.4}$$

R_Q increases with viscosity but cannot exceed R. In the original CK theory, the reaction layer was assumed to be infinitely thin; therefore, $R \equiv \sigma$. This is actually a contact model of transfer reactions. Later, R came to be regarded as a fitting parameter, partially accounting for the remote nature of transfer, but only for $R - \sigma \ll \sigma$.

Evidently, both the contact and generalized CK models of electron tunnelling are simplifications that are too rough to describe real transfer that is governed by the distance-dependent tunnelling rate, $W_I(r)$. Much better, though not perfect, is an exponential model of this dependence:

$$W_I(r) = W_c e^{-2(r-\sigma)/l} \tag{1.5}$$

It is often assumed that the rate decreases exponentially with a characteristic tunnelling length, l. It is possible to obtain l in some circumstances from experimental studies of intramolecular electron transfer.[3,4] In the case of intermolecular transfer assisted by diffusion, l can be obtained only indirectly from experiments

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through the rate constants related to $W_I(r)$ by the theory of distance-dependent electron transfer in liquid solution.

Early theoretical treatments, presented almost simultaneously, were developed intuitively[5] but were justified in terms of a binary approximation in ref 6. Not only the rate processes but also the dynamic transfer governed by the Hamiltonian were studied using the approach called encounter theory (ET).[7] At present, the method is better known as differential encounter theory (DET), which can be deduced, in some limits, from the more general integral encounter theory.[8] DET permitted calculation of the $R_Q(D)$ dependence for the exponential rate[5] and proved that the CK model, with $R \approx \sigma$, is valid in the fast-diffusion limit.[7] However, for slower diffusion (higher viscosity), the steady-state constant $k_i = 4\pi R_s D$, where $R_s > R$. The dependence on diffusion for R_Q was given in a number of papers:[7,9,10]

$$R_Q = R_s \approx \sigma + \frac{l}{2}\ln\left(\frac{\gamma^2 W_c l^2}{4D}\right) \qquad \text{at } R_s \gg R \tag{1.6}$$

where $\gamma = \exp(C)$ and C is the Euler constant.

The effective quenching radius, R_Q, is a liquid analogue of the reaction cross section in gas-phase kinetics. The specification of the dependence on the diffusion of $R_Q(D)$ is the main achievement of DET. This dependence plays an important role in chemical kinetics of liquid-state reactions, which is the same role as the energy (velocity) dependence of the gas-phase reaction cross section. The gas-phase reaction cross section is the subject of numerous theoretical studies and related cross-beam experiments. However, the variation of molecular velocities in the beams is more readily accomplished than is changing the mobility (diffusion) of particles in liquid solutions. Changing the diffusion can be done in a very limited range by varying the solvents or their compositions or by using external pressure, which changes the viscosity of the solution. However, any of these methods can affect not only diffusion but also other properties of the media (solvation, polarity, refractive index, etc.).[11] Whenever the experimental difficulties were overcome, new and very important results were obtained.[12−14]

As far as we know, the first experimental inspection of the $R_Q(D)$ dependence[6] launched by a joint team of experimentalists and theoreticians was presented in ref 13. The fluorescence quenching of pheophytin a by toluquinone was studied in a number of different pure solvents having viscosities that were either known or measured. The diffusion coefficients obtained from the Stokes−Einstein relationship vary in the series of solvents studied by 2 orders of magnitude. The effective quenching radius, $R_Q = k_i/4\pi D$, was found by assuming that only steady-state quenching could be detected experimentally. However, the best fit of the theoretical dependence of $R_Q(D)$ to the data gave the following unsatisfying results:[13] $W_c = 1.8 \times 10^{10}$ s^{-1},$\sigma = 4$ Å, and $l = 5.4$ Å. The last number is much larger than any reasonable value for the tunnelling length, which should be 1 to 2 Å. Two other attempts were undertaken to correct this result by changing the form of the transfer rate's spatial dependence.[15,16] Only in the last attempt[16] was a reasonable reduction of l obtained by assuming that $W_I(r)$ has a bell shape with its maximum shifted far from contact. This reduction is possible, but only in the inverted Marcus region. In the normal region, where the exponential approximation[5] works well, the problem of unreasonably large physical tunnelling lengths remained unsolved.

Unfortunately, until now no other attempts to resolve this problem theoretically or experimentally were made. Only recently, electron transfer in the normal Marcus region was studied again in another system and in seven different solvents.[17] However, the quenching kinetics that were measured much more accurately were found to be nonstationary, that is, the evolution of $N(t)$ is not exponential; the rate depends on the time when it is measured. The preliminary analysis of these results showed that l is overestimated if the experiments are analyzed in the same way as in ref 13. This overestimation stimulated the critical analysis of the way in which R_Q should be extracted from the experimentally studied kinetics. Here, we prove that a systematic mistake is made when the quenching kinetics are considered to be exponential, even at the very end of the available time interval.

In our present study, we fit the non-Markovian quenching theory to nonstationary experimental kinetics to find a single quenching radius R_Q for each of the solvents. For fast diffusion, the viscosity dependence of R_Q obeys the Collins−Kimball equation (3.3), permitting the determination of the CK parameters: the kinetic rate constant k_0 and the phenomenological reaction radius R. However, the CK model does not describe the $R_Q(D)$ dependence over the full range of viscosities studied. The more general dependence obtained by means of DET[7] for exponential $W_I(r)$ covers a much larger range of viscosity variation. From the fitting of this dependence to the experimental one, more reasonable parameters of the exponential rate (1.5) and the tunnelling length $l = 0.85$ Å are obtained. The latter can be easily related to the true tunnelling length L of the Marcus formula for $W_I(r)$, which is not exactly exponential. The true tunnelling length is found to be only twice as large as l and gives the Marcus parameter $\beta = 1.2$ Å^{-1}. This result is reliable and compatible with others obtained earlier for intramolecular electron transfer.[3] Thus, the theoretical results presented below resolve the problem of unphysical long-range tunnelling that came from the analysis of an earlier experimental study of electron transfer in liquids.

II. Nonstationary Energy Quenching

It is remarkable that in the theory of contact reactions first developed by Smoluchowski,[1] the limitations of the Markovian approach were removed from the very beginning. The "time-dependent" rate constant, $k_I(t)$, was substituted for k_i in the kinetic equation (1.2). In the Collins−Kimball theory, $k_I(t)$ is defined as follows:[2]

$$k_I(t) = k_i\left(1 + \frac{k_0}{k_D}\, e^x \operatorname{erfc}\sqrt{x}\right) \tag{2.1}$$

where $k_D = 4\pi RD$ is the diffusional rate constant and $x = (1 + k_0/k_D)^2 Dt/R^2$. As a result, the survival probability of excitation vanishes nonexponentially:

$$N(t) = \exp(-c \int_0^t k_I(t')\, dt' - t/\tau) \tag{2.2}$$

This effect is especially pronounced when $k_0 \gg k_D$ so that the reaction is under diffusion control. The quenching always starts with the maximal reaction rate constant k_0 and then slows down gradually, approaching a much smaller diffusional value, k_D:

$$k_I(t) = \begin{cases} k_0 & \text{at } t = 0 \\ k_D\left(1 + \dfrac{R}{\sqrt{\pi D t}}\right) & \text{at } t \to \infty \end{cases} \tag{2.3}$$

From Figure 1, which demonstrates the evolution of the

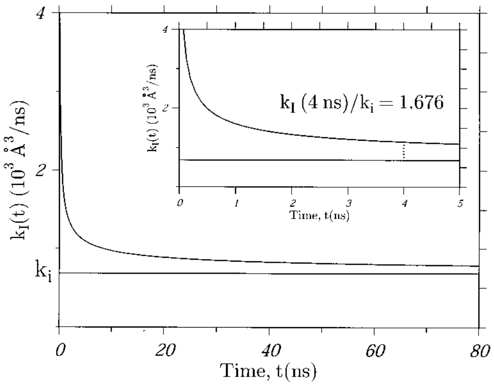

Figure 1. Time dependence of the instantaneous rate constant $k_I(t)$ compared to its asymptotic (steady-state) value k_i in the contact theory of diffusion-assisted electron transfer. Two parameters of the theory, k_0 and σ, are taken to be the same as in Figure 3. The vertical dotted line in the inset indicates the upper bound of the time interval, which was available experimentally, where the instantaneous rate constant is still almost 70% larger than the steady state value.

Collins−Kimball rate constant (2.1) in the full time domain, it is easy to see that the CK rate constant is larger than the steady state constant, k_i, at any finite time, and the difference is more pronounced the earlier they are compared.

From work done in the last decade, there is growing evidence that fluorescence quenching by electron transfer is actually nonexponential.[18] In this and other studies[19], the non-Markovian Collins−Kimball theory[2] was used to fit the experimental kinetics from very short times to long times. However, this manner of extracting quenching parameters from nonstationary kinetics was deservedly criticized in ref 20 because there are too many parameters to obtain reliable results. It should be added that the electron transfer in the inverted region studied in ref 19 does not occur at contact at all, which makes the Collins−Kimball theory inapplicable, at least at short times. Instead of fitting all of the kinetics, the authors of ref 20 analyzed only the long-time asymptotic behavior of the survival probability, which is given by the well-known two term expression[23]

$$\ln P = \ln[N \exp(t/\tau)] = -c[4\pi RDt + 8R^2\sqrt{\pi Dt}] \qquad (2.4)$$

This expression accounts for the nonstationary diffusional transfer for any free energy of reaction. Varying the solvent viscosity by changing the external pressure, the authors provided an example of how to obtain the kinetic constant k_0 from the Collins−Kimball model of the $R_Q(D)$ dependence. This constant was found to be an order of magnitude smaller than that reported in ref 19.

The kinetics at the shortest times can be somewhat smoothed by excitation with a light pulse of finite duration.[24,25] However, the subsequent nonstationary quenching is not actually perturbed by excitation and is worthy of quantitative investigation. The first term in eq 2.4 represents the steady-state quenching with a diffusional rate constant of $4\pi RD$, whereas the second term accounts for the initial nonstationary quenching, which is faster. Because of the second term, the long-time asymptote of this process never becomes exponential in a strict sense. There is the pseudo-Markovian asymptotic expression

$$P(t) \rightarrow A\mathrm{e}^{-ck_it}$$

but the pre-exponent permanently decreases with time: $A = \exp(-8R^2c\sqrt{\pi Dt})$. For this reason, one cannot obtain an accurate estimate of k_i by setting it equal to d ln P/dt at the latest available time. If this derivative $ck_I(t)$ is identified with the steady-state rate of quenching, ck_i, the rate constant $k_i = 4\pi R_QD$ and the effective quenching radius R_Q are overestimated. This naive method of specifying R_Q was a source of systematic error that led to abnormally large values of the tunnelling parameter that was obtained in ref 13.

At even higher viscosities, when the electron transfer is already under diffusional control, a noticeable difference appears between encounter theory and the primitive contact model of Collins−Kimball. This difference is usually attributed to the remote nature of electron transfer described by either the rectangular model of $W(r)$ proposed by Szabo[26] or the exponential approximation of $W(r)$ (eq 1.5).[27,28] However, the best alternative to any model is the true Marcus-type rate of transfer, which is a product of both the tunnelling and Arrhenius factors:[29]

$$W_I(r) = V_0^{\,2} \exp\left(-\frac{2(r-\sigma)}{L}\right)\frac{\sqrt{\pi}}{\sqrt{\lambda T}} \exp\left(-\frac{(\Delta G_i + \lambda)^2}{4\lambda T}\right) \qquad (2.5)$$

Here, V_0 is the tunnelling matrix element, L is the true tunnelling distance, and ΔG_i is the free-energy change associated with electron transfer. The advantage of employing the true transfer rate compared to using the CK model has been recognized in ref 24, but an attempt to fit the nonstationary quenching kinetics using eq 2.5 was launched by this group later.[25] Unfortunately, their choice of ethylene glycol as a more viscous solvent was inappropriate for the reasons that were presented in ref 30 and are confirmed here (see below). Other authors also appealed to the Marcus $W_I(r)$,[28,31,32] though in the vast majority of earlier works, the exponential approximation of this dependence was used.[7,29,33,34]

In the next section, we show how the effective radius R_Q can be properly found from the nonstationary kinetics of electron transfer causing fluorescence quenching. Then the diffusional dependence of this radius, $R_Q(D)$, will be used to specify the main parameters of the CK model: the external radius of the reaction zone, R, and the kinetic rate constant, k_0. The method for the extraction of R_Q is similar to the one proposed in ref 20, but its utilization here is different, and it is used to investigate not only the CK model but also the results obtained for the exponential transfer rate.

III. Extraction and Fitting of $R_Q(D)$

The long-time diffusional asymptote of quenching (eq 2.4) is actually a universal kinetic law, provided that the effective radius R_Q is substituted for R:

$$\ln P = -c[4\pi R_QDt + 8R_Q^{\,2}\sqrt{\pi Dt}] \qquad \text{at } t \gg R_Q^{\,2}/D \qquad (3.1)$$

When the concentration of quenchers in solution and the viscosity are known (as well as D, which is given by the Stokes−Einstein relationship $D = k_BT/6\pi\sigma\eta$), R_Q is the only fitting parameter in eq 3.1. It is expected that for fast diffusion R_Q coincides with the Collins−Kimball radius (eq 1.4) but that for slow diffusion R_Q becomes identical to R_s from eq 1.6.

In Figure 2, we demonstrate how R_Q can be obtained from the best fit of the two-term expression (eq 3.1) to the experimentally measured ln $P(t)$. $P(t) = N(t) \exp(t/\tau) = N/N|_{c=0}$ is obtained from the measured kinetics of energy dissipation, $N(t)$, which is related to the same kinetics in the absence of acceptors, $N(t)|_{c=0}$. The initial discrepancy between these kinetic parameters is natural and should be ignored.[24,25] The convolution of the excitation pulse with system response makes the top of a signal smoother whereas the long-time asymptote (eq 3.1)

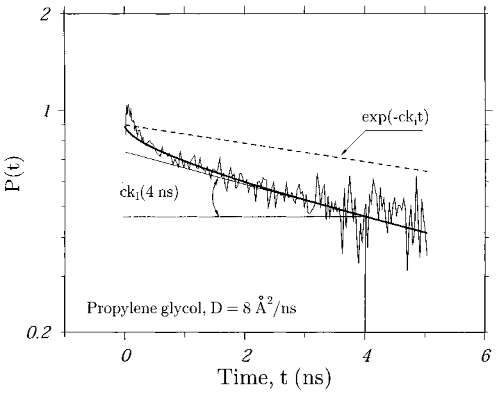

Figure 2. Fit of nonstationary electron-transfer kinetics (thick curve) to the experimental data obtained in propylene glycol, the most viscous solution studied in ref 17. The thin line represents the tangent to the kinetic curve at the longest time within the available interval. The dashed, straight line is the purely exponential decay, with the steady-state rate constant $k_i = 4\pi R_Q D$ obtained from the best R_Q value.

TABLE 1

	solvent	c (M)	τ (ns)	D (Å^2/ns)	R_Q (Å)	k_i (Å^3/ns)
		0.033			4.000	21 991
1	acetonitrile	0.067	1.45	438	4.110	22 622
		0.100			4.110	22 622
		0.025			4.545	13 823
2	ethanol	0.050	2.07	242	4.545	13 823
		0.075			4.545	13 823
		0.050			7.000	3985
3	eth gly/ethanol	0.100	2.21	45.3	7.000	3985
		0.150			7.000	3985
		0.050			7.470	3078
4	glycerol/butanol	0.100	2.60	32.8	6.402	2638
		0.150			6.646	2739
		0.050			6.597	2388
5	pr gly/butanol	0.100	2.66	28.8	6.597	2388
		0.150			6.597	2388
		0.050			7.624	2702
6	glycerol/ethanol	0.100	2.34	28.2	7.624	2702
		0.150			7.624	2702
		0.050			8.125	819
7	propylene glycol	0.100	2.80	8.0	7.500	754
		0.150			7.375	741
		0.050			10.067	1885
	ethylene glycol	0.100	2.38	14.9	10.067	1885
		0.150			10.067	1885

extrapolated into this region is sharper than the true $P(t)$. The time interval of fitting is also restricted from above by noise, whose relative value increases with time. However, even in a limited time interval, the fitting, which accounts for the nonstationary quenching, is much better than the estimate of the steady-state rate from the tangent to the kinetic curve. Even at the end of the available interval, the data are steeper than the line $\ln P = -c4\pi R_Q Dt$, the slope of which is the true stationary rate ck_i.

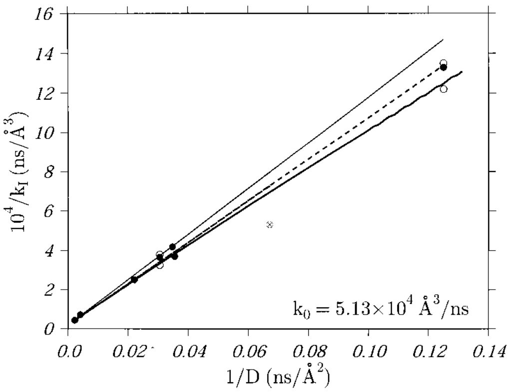

Figure 3. Dependence of the steady-state rate constant on diffusion. The points taken from Table 1 are interpolated by a thick line representing the theoretical dependence for the exponential transfer rate with $l = 0.85$ Å. The thin, straight line plots a contact approximation with $k_0 = 5.13 \times 10^4$ Å^3/ns and $\sigma = 6.87$ Å, whereas the dashed line represents the Collins−Kimball result with $\mu = 0.91$. The higher and lower values of the rate constants related to the same system but with different concentrations are depicted here and in successive Figures by empty circles.

In ref 20, reliable values of both R_Q and D were obtained using an iterative nonlinear least-squares method with sophisticated optimization of the fitted function. The time-zero shift parameter was also adjusted in the analysis. Knowing D from the separate measurements, we can do the same thing in a much simpler manner by varying only R_Q and using the vertical shift of the whole curve as an adjustable parameter. An example of such a fit is shown by the thick line in Figure 2. This procedure was used to find reaction radii as well as the corresponding steady-state rate constants

$$k_i = 4\pi R_Q D \tag{3.2}$$

Some authors[21,22] prefer to deal with k_i instead of R_Q. For a fixed value of D, it does not matter which of these is taken as the primary fitting parameter. However, R_Q is a more fundamental property of the transfer. The relationship of the value of R_Q to the contact distance σ and the tunneling length l contains a good deal of information about the transfer mechanism. In addition, there are analytical estimates of R_Q for high viscosities, for example, the one given in eq 1.6. For all of the systems studied here experimentally, the results for both R_Q and k_i are summarized in Table 1.

It is common and convenient to represent the CK equation (eq 1.4) as a linear relationship between inverse k_i and viscosity:

$$\frac{1}{k_i} = \frac{1}{k_0} + \frac{1}{4\pi RD} \tag{3.3}$$

This relationship is expected to hold, at least in the low-viscosity region where the contact approximation ($R \approx \sigma$) is the most reasonable. There is no contradiction in the fact that at small D some of our tabulated data deviate from the straight line (eq 3.3). The data need only approach the line as $D \rightarrow \infty$. There, $1/k_i \rightarrow 1/k_0$, so the kinetic rate constant can be unambiguously found from the intersection of the extrapolated straight line with the ordinate (Figure 3). For the system under study, k_0 was found in this way:

$$k_0 = 5.13 \times 10^4 \text{ Å}^3/\text{ns} \tag{3.4}$$

With this value for k_0 and $R = \sigma = 6.87$ Å taken from ref 17, we plotted the corresponding CK straight line, but its slope is somewhat too large to fit the experimental data well.

To improve agreement, the CK radius is often taken to be an adjustable parameter:[19,20,24]

$$R = \sigma/\mu \tag{3.5}$$

By changing μ, one changes the slope of the line representing the Collins−Kimball relationship. Selecting the proper value of μ permits the experimental data at low viscosities (in the fast-diffusion limit) to be fit very well because the electron transfer in this limit is really a quasi-contact, provided the thin reaction layer is included in the reaction sphere of radius $R \gtrsim \sigma$.[28] The CK approximation works better the smaller the width of the actual reaction layer, $R - \sigma$.

In the case of the exponential transfer rate (eq 1.5), this width is approximately $^{l}/_{2}$. More accurately, it can be determined if the predictions of the CK model are compared with the exact solution obtained by means of encounter theory. In fact, the exponential transfer rate has the privilege of being one of the few models of $W_I(r)$ that enables a rigorous solution of the DET equations to be obtained. The solution results in the following dependence on diffusion of the effective radius:[7,29]

$$R_Q = \sigma + \frac{l}{2}\left[\ln(\gamma^2\beta_m) + 2\theta\left(\beta_m, \frac{2\sigma}{l}\right)\right] \qquad (3.6)$$

Here

$$\theta(x, y) = \frac{K_0(2\sqrt{x}) - y\sqrt{x}K_1(2\sqrt{x})}{I_0(2\sqrt{x}) + y\sqrt{x}I_1(2\sqrt{x})} \qquad \beta_m = \frac{W_c l^2}{4D}$$

$$\gamma = e^C \approx 1.781$$

where C is the Euler constant and $K(x)$ and $I(x)$ are modified Bessel functions. By substituting eq 3.6 into eq 1.3, one can easily deduce that

$$k_i = 4\pi\sigma D + 2\pi l D\left[\ln(\gamma^2\beta_m) + 2\theta\left(\beta_m, \frac{2\sigma}{l}\right)\right] \qquad (3.7)$$

where

$$\beta_m = \frac{k_0\rho}{8\pi\sigma D(1 + \rho + \rho^2/2)} \qquad \rho = l/\sigma$$

and

$$k_0 = \int_\sigma^\infty W_I(r) 4\pi r^2\, dr = 2\pi W_c \sigma^2 l(1 + l/\sigma + l^2/2\sigma^2) \qquad (3.8)$$

Because k_0 and σ are fixed, there is only a single free parameter, l, that can be used for fitting.

In the data presented in Figure 3 (as well as in Figures 6 and 7), there are a few points in which somewhat different rate constants were obtained for the three concentrations studied. In such cases, we have plotted all of them with the higher and lower values depicted by empty circles. Almost all points fall on the theoretical curve (thick line) representing the exact solution (eq 3.7) with W_c fixed by the known kinetic constant and the tunnelling length found from the best fit,

$$l = 0.85 \text{Å} \qquad (3.9)$$

Only a single point for ethylene glycol marked by the crossed circle is too low, but this system was recognized as exceptional by experimentalists themselves. The reasons that it is so different were discussed in a separate article.[30] For the same reasons, we excluded it from our fitting as well.

The exact result for exponential $W_I(r)$ was reduced in ref 7 to the standard CK relationship with $R = \sigma$ ($\mu = 1$), which appears in the zero-order approximation with respect to ρ. If the higher-order corrections were included, then $\mu < 1$ would be obtained. With the true value of μ, the CK straight line fits the data in the fast-diffusion region almost as well as the exact curve (see Figure 3) does. To specify the slope of this line theoretically, we have to find the general $\mu(\rho)$ dependence by means of DET. Therefore, in the next section, the CK relationship will be rederived for an arbitrary functional form of the transfer rate. Then $\mu(\rho)$ will be found not only for the exponential rate but also for the Marcus rate of electron transfer. From the analysis with the Marcus rate, the true tunnelling distance in liquids emerges.

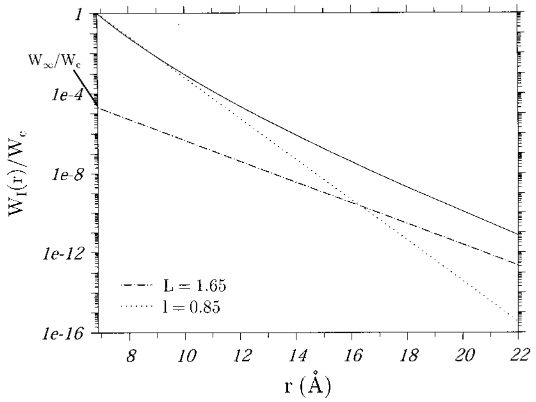

Figure 4. Distance dependence of the Marcus transfer rate (eq 2.5) in the normal region ($\Delta G_i = -0.59$ eV) with $L = 1.65$ Å and $\lambda_c = 1.3$ eV (thick line) in comparison to its exponential approximations for short (dotted line) and long (dashed−dotted line) distances.

IV. CK Approximation for Remote Electron Transfer

Although we obtained rather good agreement between the experiment and theory on the basis of the exponential transfer rate model (eq 1.5), this is not firm evidence that the distance dependence is actually exponential. In the Marcus theory of outer-sphere (solvent-assisted) electron transfer, the rate (eq 2.5) contains the Arrhenius factor that depends on the distance. In highly polar solvents, the free energy of transfer $\Delta G_i \approx$ a constant, but the reorganization energy $\lambda(r)$ slowly increases with distance, approaching twice the contact value, $2\lambda_c$:[29]

$$\lambda(r) = \lambda_c(2 - \sigma/r) \qquad (4.1)$$

In the normal Marcus region ($\Delta G_i < \lambda_c$), this effect significantly reduces the Arrhenius factor near the contact, though at large distances this factor approaches a constant. As a result, $W_I(r)$ can be approximated by exponential functions, but near contact and far from it, they have different decrements. The former ($2/l$) is larger then the latter ($2/L$), which is expressed through the true tunnelling length L:

$$W = \begin{cases} W_c e^{-2(r-\sigma)/l} & \text{at } r \approx \sigma \\ W_\infty e^{-2(r-\sigma)/L} & \text{at } r \gg \sigma \end{cases} \qquad (4.2)$$

Here, we have

$$W_c = \frac{V_0^{\,2}\sqrt{\pi}}{\sqrt{\lambda_c T}} \exp\left(-\frac{(\Delta G_i + \lambda_c)^2}{4\lambda_c T}\right)$$

$$W_\infty = \frac{V_0^{\,2}\sqrt{\pi}}{\sqrt{2\lambda_c T}} \exp\left(-\frac{(\Delta G_i + 2\lambda_c)^2}{8\lambda_c T}\right)$$

In Figure 4, the functions given in (eq 4.2) are compared with the true nonexponential Marcus rate in the normal region ($\Delta G_i = -0.59$ eV, $\lambda_c = 1.3$ eV). As was expected, the Marcus rate near the contact decreases much faster than does its exponential asymptote at large distance. The long-distance asymptote contains the true tunnelling parameter L, which is almost twice as large as the l value used above to obtain the best fit to the experimental results. A more accurate relationship between l and L will be established below.

Moreover, the effective width of the reaction layer can be attributed to a nonexponential transfer rate provided that the CK reaction constant's dependence on diffusion (eq 3.3) can be approximately identified with that derived by DET for arbitrary $W_I(r)$. The derivation starts with the general definition of the steady-state constant in DET:

$$k_i = \int W_I(r) n_s(r)\, d^3r = 4\pi R_Q D \tag{4.3}$$

This expression relates k_i to the arbitrary rate of transfer and the steady-state pair distribution of reactants

$$n_s(r) = \lim_{t\to\infty} n(r, t) = \lim_{s\to 0} s\tilde{n}(r, s) \tag{4.4}$$

where $\tilde{n}(r, s) = \int e^{-st} n(r, t)\, dt$. The nonstationary distribution $n(r, t)$ is the solution of the diffusion equation:

$$\dot{n} = -W_I(r)n + \hat{L}n \qquad \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} = 0 \qquad n(r, 0) = g(r) \tag{4.5}$$

Here, $\hat{L}$ is the diffusion operator for nonreacting particles, and $g(r) = e^{-U(r)}$ is the initial equilibrium distribution for a pair of reactants. The distribution is not homogeneous if there are electrostatic or other interactions, which are represented by the interparticle potential $U(r)$, but for $U = 0$, we have $\hat{L} = \frac{D}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$ and $g = 1$.

The general solution of eq 4.5 can be expressed through its Green function

$$n(r, t) = \int G(r, r_0, t)\, g(r_0)\, d^3r_0 \tag{4.6}$$

that has a Laplace transform that obeys the known integral equation[35]

$$\tilde{G}(r, r_0, s) = \tilde{G}_0(r, r_0, s) - \int \tilde{G}_0(r, r'\, s)\, W_I(r')\, \tilde{G}(r', r_0, s)\, d^3r' \tag{4.7}$$

Here, $G_0(r, r_0, t)$ is the Green function for diffusive motion without reaction, which obeys the much simpler differential equation

$$\dot{G}_0 = \hat{L}G_0 \qquad \left.\frac{\partial G_0}{\partial r}\right|_{r=\sigma} = 0 \qquad G_0(r, 0) = \frac{\delta(r - r_0)}{4\pi r^2} \tag{4.8}$$

It has the following general property following from the stationary nature of $g(r) = \int G(r, r_0, t)\, g(r_0)\, d^3r_0$:

$$\int \tilde{G}_0(r, r_0, s)\, g(r_0)\, d^3r_0 = \frac{g(r)}{s} \tag{4.9}$$

Using this property after the integration of eq 4.7 over r_0 with the weight $g(r_0)$, we obtain

$$\tilde{n}(r, s) = \frac{g(r)}{s} - \int \tilde{G}_0(r, r', s)\, W_I(r')\, \tilde{n}(r', s)\, d^3r' \tag{4.10}$$

After inserting this result into eq 4.4, we get the final integral equation for the desired stationary distribution:

$$n_s(r) = g(r) - \int W_I(r')\, \tilde{G}_0(r, r', 0)\, n_s(r')\, d^3r' \tag{4.11}$$

Equation 4.11 can be further simplified using the well-known Green function for free diffusion of charged reactants:[35]

$$\tilde{G}_0(r, r', 0) = \begin{cases} \dfrac{\exp(r_c/r)[1 - \exp(-r_c/r')]}{4\pi r_c D} & \text{at } r < r' \\[2ex] \dfrac{\exp(r_c/r) - 1}{4\pi r_c D} & \text{at } r > r' \end{cases} \tag{4.12}$$

$r_c = q^2/\epsilon k_B T$ is the Onsager radius.

For neutral reactants ($q = 0$) or highly polar solvents ($\epsilon \gg 1$), one can take $r_c = 0$ and $g(r) = 1$. Inserting the simplified Green function into the general equation (4.11) reduces eq 4.11 to

$$n_s(r) = 1 - \frac{1}{rD}\int_\sigma^r W_I(r_0)\, n_s(r_0)\, {r_0}^2\, dr_0 - \frac{1}{D}\int_r^\infty W_I(r_0)\, n_s(r_0)\, r_0\, dr_0 \tag{4.13}$$

The first integral in this expression describes the large distance asymptote, whereas the second integral determines the contact reduction of the particle density:

$$n_s(r) = \begin{cases} 1 - \dfrac{k_i}{4\pi D r} = 1 - \dfrac{R_Q}{r} & \text{at } r \to \infty \\[2ex] 1 - \alpha/D & \text{at } r = \sigma \end{cases}$$

$\alpha = \int_0^\infty W_I(r_0)\, n_s(r_0)\, r_0\, dr_0$. The asymptote at large r is very general and is well-established[7], whereas the contact reduction depends on the model of the transfer rate $W_I(r)$ and is more pronounced the slower the diffusion.

However, we need to use the whole distribution $n(r)$ in the calculation of the steady-state rate constant (eq 4.3). Near the kinetic limit, $n(r)$ can be readily obtained from eq 4.13. For fast diffusion, both corrections to 1 (the first term) in eq 4.13 are small and can be estimated by iteration. The first one gives us the following:

$$n_s(x) = 1 - \frac{1}{\sigma D}\left[\frac{1}{x}\int_1^x W_I(y)\, y^2\, dy + \int_x^\infty W_I(y)\, y\, dy\right] \quad \text{for } k_0 \ll 4\pi\sigma D \tag{4.14}$$

$x = {}^r\!/_\sigma$ and $W_I(x) = W_I(r)\sigma^3$. Substituting this approximate result into the general definition of the rate constant, eq 4.3, we obtain

$$k_i = k_0\left[1 - \frac{k_0}{4\pi\sigma D}\mu(\rho)\right] \tag{4.15}$$

This is, in fact, the CK eq 3.3 expanded in terms of $k_0/4\pi RD \ll 1$, where $R = {}^\sigma\!/_\mu$ according to the definition in eq 3.5. However, μ is no longer a phenomenological parameter. Rather, it acquires the proper definition in terms of the arbitrary transfer rate:

$$\mu = \frac{\int_1^\infty \frac{W_I(x)}{x}\, d^3x \int_1^x W_I(y)\, d^3y + \int_1^\infty W_I(x)\, d^3x \int_x^\infty \frac{W_I(y)}{y}\, d^3y}{(\int_1^\infty W_I(x)\, d^3x)^2} \tag{4.16}$$

After substituting $W_I(x) = \frac{k_0}{4\pi}\delta(x - 1)$ into this equation, we obtain $\mu = 1$, which reduces eq 4.15 to the original Collins–Kimball expression for the contact reaction. However, for the exponential rate (eq 1.5), which accounts for the finite size of the reaction zone l, it follows that after integration (4.16)

$$\mu(\rho) = \frac{1 + 5\rho/4 + 5\rho^2/8 + 5\rho^3/32}{1 + 2\rho + 2\rho^2 + \rho^3 + \rho^4/4} \leq 1 \qquad (4.17)$$

This expression is identical to one that can be obtained from eq 54 of ref 21. That work used a different method (EDA), which implies the complete solution of the kinetic equation for electron transfer. In contrast, our general result, eq 4.16, does not depend on reactant dynamics and is applicable to an arbitrary $W_I(r)$. In particular, we will use it below to find $\mu(\rho)$ for a Marcus rate $W_I(r)$, eq 2.5.

As seen from Figure 3, the difference between the dashed line representing the CK result and the solid curve that is considered to be exact is rather small within the available range of viscosity variation. However, the difference increases at higher viscosity, indicating that the electron transfer when diffusion is slow is neither contact ($R = \sigma$) nor quasi-contact ($R \approx \sigma$) as in the Collins−Kimball approximation.

To illustrate the nature of this approximation, let us insert eq 4.11 into the definition (eq 4.3) and use only the zero iteration under the integral ($n_s = 1$). The result can be presented as

$$k_i = k_0 - \frac{k_0^2}{k_D} \qquad (4.18)$$

where

$$1/k_D = \frac{\int\int W_I(r)\, \tilde{G}_0(r, r', 0)\, W_I(r')\, d^3r\, d^3r'}{[\int W_I(r)\, d^3r]^2} \qquad (4.19)$$

By substituting this k_D for $4\pi RD$ in a more general Collins−Kimball expression (eq 3.3), one obtains the result derived with a "closure approximation"[36] that is given in ref 37. Evidently, $\mu = 4\pi\sigma D/k_D$, which is obtained from eq 4.19, accounts for the difference between remote and contact transfer.

The slope of the CK line obtained using the exponential transfer rate is given by the factor μ from eq 4.17, which decreases with $\rho = l/\sigma$ as shown in Figure 5. But the same parameter can be calculated numerically from eq 4.16 for the Marcus-type rate as well. From the numerical calculations, we found how the corresponding μ depends on $\rho = L/\sigma$, that is, on the true tunnelling parameter L. By comparing these curves in Figure 5, we see that L is larger than l if μ is the same for both curves. In particular, the exponent with $l = 0.85$ Å is equivalent in the CK approximation to the Marcus rate with $L = 1.65$ Å. The latter value is very close to the L value found in ref 17. There, $\beta = 2/L = 1$ Å^{-1} was obtained from fitting the DET theory with the Marcus rate to the experimental kinetic curves reflecting the fluorescence quenching by electron transfer. The small difference between the value obtained here and that reported previously[17] may be attributable to the fact that we included neither the solvent radial distribution function $g(r)$ nor the distance dependence of the diffusion constant $D(r)$.

V. High-Viscosity Asymptote of the Quenching Radius

The analysis of the dependence of the rate constant on diffusion, which is shown in the curves in Figure 3, was proven to be very useful. A similar analysis of the quenching radii variation with the diffusion constant, which is displayed in Figure 6, is even more instructive. The curve that represents the transition from kinetic to diffusion control in the simplest contact approximation levels off at the value of the true contact radius σ, whereas the generalized Collins−Kimball approximation, which includes the reaction layer in the reaction sphere, magnifies this value to the size of R. However, the effective quenching radii R_Q in more viscous solvents exceed even this value and tend to increase as $R_s(D)$ does with further increases of the viscosity.

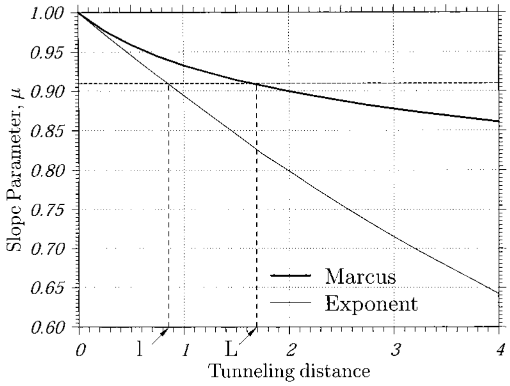

Figure 5. Slope parameter μ of the Collins−Kimball relationship for the Marcus transfer rate in the normal region (thick line) and for its exponential transfer rate equivalent (thin line). The difference between L and l related to the same μ is indicated by the vertical dashed lines.

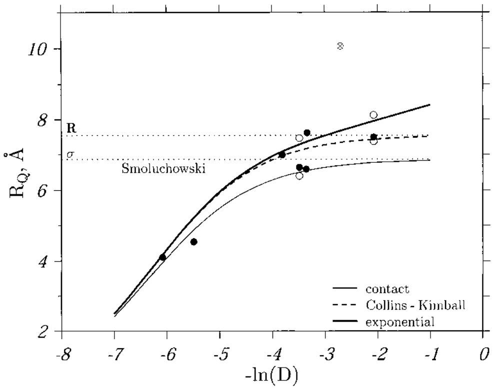

Figure 6. Dependence of the effective electron-transfer radius R_Q on diffusion. Experimental data, indicated by circles, are approximated by thin and dashed lines representing the contact and the Collins−Kimball relationships, respectively. The thick line depicts the same dependence, but for the exponential transfer rate with $l = 0.85$ Å and $W_c = 180$ ns^{-1} that is depicted by a dotted line in Figure 4.

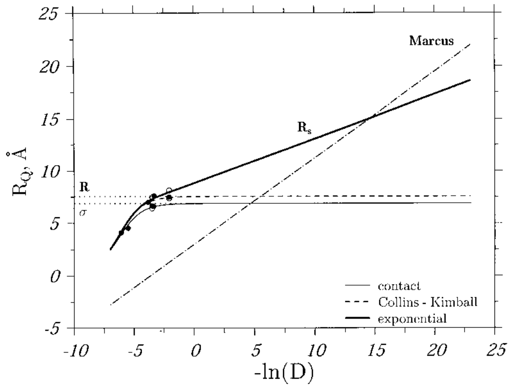

Figure 7. Same data as in Figure 6, but for a much larger range of viscosity variation. The dashed−dotted line represents the linear asymptote for the true Marcus rate, which is steeper than the asymptote for the exponential approximation of the transfer rate (the end of the thick line).

The model dependencies of the radii on diffusion can be seen better in Figure 7, where they are represented over a much larger range of viscosity variation than the range that was available experimentally. In the region of deep diffusion control of electron transfer, both the contact and the generalized Collins−

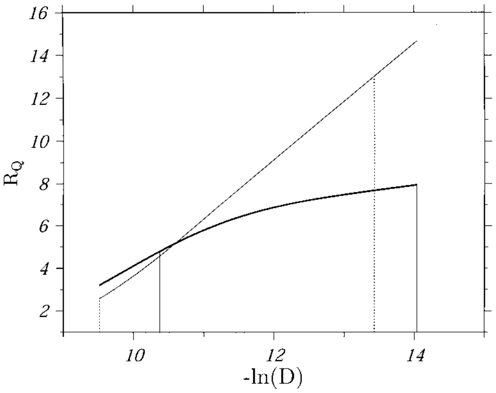

Figure 8. $R_Q(D)$ dependence for the exponential transfer rate for two different values of the tunnelling parameter. The thick line represents the short tunnelling length obtained in the present work ($l = 0.85$Å), whereas the thin line represents the overestimated $l = 5.4$ Å value found in ref 13. The vertical solid lines indicate the viscosity range used in the present study, whereas the dotted lines indicate the range studied in ref 13 in which the effective electron-transfer radii were substantially overestimated.

Kimball approximations are represented by horizontal lines. The heights of these plateaus indicate the sizes of the external radii of the reaction spheres. In contrast, the radius for remote quenching with the exponential transfer rate lies far above the plateaus and increases as the logarithm of inverse viscosity following eq 1.6. In fact, this relationship for $R_s(D)$ is the straight line with slope $^1/_2$ in the coordinates of Figure 7. This linear asymptote is common for reflecting[7] and absorbing[9,10] boundary conditions because under diffusional control it does not matter whether there is quenching at contact. The excitations never reach contact because, for slow diffusion, they are quenched by electron transfer farther apart, at $R_s \gg \sigma$.

However, it is important to remember that the largest R_Q results from the most remote electron transfer represented by the larger exponent of the Marcus transfer rate (eq 4.2) (see Figure 4). There, the asymptotic equation (eq 1.6) gives way to a similar equation but one with the true tunnelling length L:

$$R_Q = \sigma + \frac{L}{2}\ln\left(\frac{\gamma^2 W_\infty L^2}{4D}\right) \tag{5.1}$$

Because in our case L is almost twice as large as l, the dashed−dotted line representing the final asymptotic behavior of $R_Q(\ln D)$ in Figure 7 is twice as steep as the heavy line calculated with the pure exponential rate. However, experiments at such a high viscosity seem unattainable. Even the initial change in the slope of the data is not definitive, which means that not only the kinetic but also the diffusional electron transfer remains near-contact in the available range of viscosities.

The opposite situation was expected in early work.[13] Owing to a strong overestimation of the effective radii, which were incorrectly extracted from the nonstationary quenching, the maximal values (about 15 Å) exceeded the contact radius (4 Å) by a factor of almost 4. The transfer reaction at such a large distance was attributed to diffusion control where $R_Q(D)$ has to obey the asymptotic relationship (eq 1.6), which is represented by the linear increase of $R_Q(\ln D)$ in Figure 8. Because the slope of this line can be greatly overestimated by the incorrect extraction of R_Q from the kinetic data, there is nothing surprising about the fact that the value of l found in ref 13 is also too large: $l = 5.4$ Å. When R_Q was found in the same way from the present data and was fit by the same linear asymptotic relation (eq 1.6), the result obtained was also incorrect: $l \approx 4$ Å. The real values of R_Q that we have obtained from the proper analysis of the same data are much smaller then their rough estimates that ignore nonstationary quenching. Therefore, fitting the data with the remote quenching equation (eq 1.6) is inappropriate, whereas the Collins−Kimball approximation of quasi-contact quenching holds in almost all situations.

VI. Conclusions

By fitting the differential encounter theory to the most accurate experimental data on electron-transfer kinetics observed by fluorescence quenching, we obtained excellent agreement between data and theory over the entire viscosity range used in the seven experimental systems. Reasonable values of the important parameters of electron transfer were obtained from the best fit of the predicted diffusion dependence of the transfer rate constant to the experimental value. A few important conclusions can be deduced from this work:

(1) The effective quenching radii should be extracted from the real quenching kinetics, taking into account its nonstationary nature.

(2) The linear relationship between the inverse rate constant and the inverse diffusion constant should be used to specify the kinetic rate constant, k_0, and the effective Collins−Kimball radius of the quenching sphere, R.

(3) For electron transfer in the Marcus normal region, the exponential approximation of the Marcus model is reasonable. Allowing an analytical solution of the problem, the exponential approximation gives a better fit to the experimental data than do contact or generalized Collins−Kimball models. The effective tunnelling length l is obtained from the appropriate fitting procedure.

(4) This length can be related to an actual length by equalizing the slopes of the Collins−Kimball lines corresponding to the Marcus transfer rate and its exponential approximation. The data can also be fit using the Marcus transfer rate with numerical methods.

The work presented here solves an important, long-standing problem—the overestimation of the tunnelling length L in liquid solutions.[13] Now it is clear that proper analysis will yield values similar to those obtained here, such as $L = 1.65$ Å, which corresponds to the Marcus value of $\beta = 2/L = 1.2$ Å^{-1} and does not exceed earlier reports.[3] In rigid structures, tunnelling over long distances was sometimes attributed to the super exchange through molecular intermediates (as occurs in molecular wires).[4] However, in liquid solutions, intermolecular electron transfer is expected to be shorter than intramolecular electron transfer. When the intermediates are mobile solvent molecules, the coherence of transfer is broken, and super exchange becomes ineffective.[38]

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