Qualitative Features of Electron Transfer Reaction for High Viscosity of Solvent and Low Activation Barrier

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We investigated qualitative features of an electron-transfer reaction in the case where the viscosity of a solvent is high and the activation barrier for the reaction is low so that decay of the reactant population is nonexponential. Using the reaction-diffusion equation for the Sumi−Marcus model and dividing a slow nuclear coordinate into diffusion-dominated and reaction-dominated regions, we derived expressions for the powers of dependence of the generalized mean lifetimes on the viscosity. We also derived an expression for the survival probability at short times. These expressions show fractional (not integer) powers and an algebraic decay at short times under certain conditions, which were found previously by numerical calculations. Moreover, from these expressions we found that the time dependence of the survival probability at short times is intimately related to the viscosity dependence of the mean lifetime. The expressions are in reasonable agreement with exact numerical calculations for large viscosity.

I. Introduction

Recently, extensive studies have been carried out on the dynamic effects of a solvent (environment) on an electron transfer (ET) reaction,[1] and the fractional (not integer) power dependence of the mean lifetime $\tau^{(0)}$ on viscosity η of the solvent was predicted[2] and observed experimentally in many ET systems.[3] In the present work, our main interest is in an analytical expression of this fractional power dependence.

Let us give a brief survey of theoretical and experimental results on the dynamic effects. After static theories for the ET rate were developed,[4] Zusman calculated the ET rate with the dynamic effects incorporated using a one-dimensional reaction-diffusion equation.[5] As a result, the ET rate is inversely proportional to the relaxation time scale of the solvent when this time scale is large. This work triggered extensive theoretical activities.[2,6−14] Kosower and Huppert found that the ET rate is inversely proportional to the longitudinal relaxation time of the solvent in the excited-state intramolecular ET of arylaminonaphthalene sulfonates in alcohol solutions.[15] The longitudinal relaxation time is equal to the relaxation time scale of the solvent for a Debye-type solvent with a single dielectric relaxation time.[16] The correlation between the solvent relaxation times and the intramolecular ET rates has been investigated experimentally by various authors.[17−22] It has been shown that nuclear dynamics coupled to ET is characterized by a broad range of time scales. However, Zusman's model includes only one time scale of solvent relaxation. Thus, Sumi and Marcus developed the model which includes the broad range of time scales.[2] They divided nuclear modes into fast ones (the intramolecular or atomic vibrations) and slow ones (the conformational fluctuation of solvent molecules) and eliminated the former. As a result, they obtained the one-dimensional reaction-diffusion equation in the slow nuclear coordinate. In the Sumi−Marcus model the slow nuclear coordinate fluctuates about its equilibrium value and the ET reaction occurs at a rate depending on its value. The fractional power dependence of $\tau^{(0)}$ on η was found by solving numerically the reaction-diffusion for the Sumi−Marcus model with the assumption that η is proportional to the relaxation time scale τ_s of the slow nuclear mode.[2,6] Moreover, it was found that the survival probability decays algebraically at short times.[6] The Sumi−Marcus model was applied to several ET systems to explain a nonexponential feature of the dynamics and a reaction rate faster than solvation,[17−19] and the fractional power dependence was observed in many ET systems.[3] Walker et al. extended this model to include the effect of high-frequency quantum modes,[23] and this extended model was used to analyze experimental results.[19,23,24]

Let us now review theories using one-dimensional reaction-diffusion equations that have been used not only in electron transfer reactions but also in different areas of chemical physics, for example, diffusion-controlled bimolecular reactions,[25] polymer reactions,[26] protein reactions,[27−29] and electronic transition reactions.[30] Because exact solutions can be obtained in only a few cases,[5,29,31] perturbation theories (or their equivalent) were developed in the case where the reaction effect is small compared to the diffusion effect,[25−27,31] and in the opposite case.[27,32] Theoretical development beyond perturbation theory is as follows. Agmon and Rabinovich developed analytic approximations for the survival probability by assuming a delta-function or a Gaussian-function form of the population distribution.[28] Basilevsky and Davidovitch obtained a semianalytical expression for the survival probability for slow diffusion using quasiclassical theory.[33] Pechukas and Ankerhold simplified the reaction-diffusion equation by applying an asymptotic approximation analogous to the WKB approximation.[34] Berezhkovskii and Zitserman calculated the reaction rate by dividing

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the space into two domains, separated at the point where the escape time equals the solvent relaxation time depending on the environment state, in the case where τ_s is not too large so that the decay kinetics is single-exponential.[35] Okada calculated the power of the dependence of $\tau^{(0)}$ on τ_s for a large τ_s by dividing space into reaction-dominated and diffusion-dominated regions.[36]

In the present work, we consider the case where the viscosity of the solvent is large and the activation barrier for the reaction is low. In this case, the time evolution of the reactant survival probability is nonexponential, and so no single number can characterize the kinetics completely. Thus, we calculate not only $\tau^{(0)}$ but also the generalized mean lifetimes $\tau^{(n)}$ ($n = 0,1,2,...$) and derive expressions for the powers of the dependence of $\tau^{(n)}$ on τ_s by extending the theory developed in ref 36. Here we define $\tau^{(n)}$ ($n = 0,1,2,...$) so that a set of all of their values can characterize the time evolution of the reactant survival probability completely. Moreover, we derive the expression for the decay of the survival probability at short times, which shows clearly the algebraic dependence on time. We find that this algebraic dependence is intimately related to the fractional power dependence of $\tau^{(0)}$ on τ_s. We confirm that for a large η (or τ_s) the expressions are in reasonable agreement with exact numerical calculations under a nonequilibrium initial condition as well as under an equilibrium initial condition.

This article is organized as follows. In Section II, we review the reaction-diffusion equation for ET and introduce the division of the slow nuclear coordinate into the reaction-dominated region and the diffusion-dominated region. In Section III, we investigate the powers of the dependence of the generalized mean lifetimes on the viscosity of the solvent. In Section IV, we consider the survival probability at short times. Finally, the discussion and summary appear in Section V.

II. Theory

In this section, we review the reaction-diffusion equation for ET and define values characterizing the kinetics (Section II.A.). To calculate these values, we divide the slow nuclear coordinate into the reaction-dominated and diffusion-dominated regions[36] (Section II.B.). Using this division, we show how the kinetics at short times is related to that at long times (Section II.C.). Moreover, we prove that the value of the power of the dependence of $\tau^{(0)}$ on τ_s decreases (or does not change) with increasing width of the reaction window.

A. Reaction-Diffusion Equation. Let us now describe the reaction-diffusion equation for ET. We consider that ET is affected by nuclear motions of solvents and solutes. For simplicity, we neglect a backward reaction from a product state to a reactant state by assuming a highly exothermic reaction. Eliminating the fast nuclear modes, we obtain the reaction-diffusion equation in the slow nuclear coordinate q as[2]

$$\frac{\partial \rho'(q,t')}{\partial t'} = \left[S'\left(q, \frac{\partial}{\partial q}\right) - k'(q)\right]\rho'(q,t') \tag{1}$$

where $\rho'(q,t')$ is the population distribution in the reactant state at the time t', normalized as $\int \mathrm{d}q\rho'(q,0) = 1$. The operators S' and k' represent the diffusion and the local reaction rate, respectively,

$$S'\left(q, \frac{\partial}{\partial q}\right) \equiv \frac{1}{2\tau_s}\frac{\partial}{\partial q}\left[k_B T \frac{\partial}{\partial q} + \frac{\mathrm{d}U(q)}{\mathrm{d}q}\right] \tag{2}$$

$$k'(q) \equiv \tau_t^{-1}\left(\frac{\lambda_f}{\lambda}\right)^{-1/2} \exp\left[-\frac{(-2\sqrt{\lambda_s}q + \Delta G + \lambda)^2}{4\lambda_f k_B T}\right] \tag{3}$$

where τ_s and τ_t are the time scale of the relaxation of the slow nuclear mode and that of the local reaction, respectively, k_B, T, $U(q)$, and ΔG are the Boltzmann constant, the temperature, the free energy as a function of q, and the free energy of the product minus that of the reactant, respectively, and λ_s, λ_f, and λ are the reorganization energy of the slow nuclear mode, that of the fast nuclear modes, and the sum of these two, respectively. Here we assume that $U(q) = q^2$.[2] The time scale τ_t is given by $\tau_t^{-1} = (J^2/\hbar)\sqrt{\pi/(\lambda k_B T)}$ when the local ET reaction is nonadiabatic, and by $\tau_t^{-1} = \nu(\lambda_f/\lambda)^{1/2}$ when it is adiabatic. Here J is the electronic coupling between the reactant and the product states, $\hbar$ is Plank's constant, and ν is the average frequency of the fast nuclear modes.[2,7] From now on, for convenience, we will use dimensionless parameters and variables, κ, r, a, γ, t, and x, and the population distribution $\rho(x,t)$ normalized as $\int \mathrm{d}x\rho(x, 0) = 1$, where

$$\kappa \equiv \frac{\tau_s}{\tau_t},\ r \equiv \frac{\lambda_f}{\lambda_s},\ a \equiv \frac{\Delta G + \lambda}{\sqrt{4\lambda_s k_B T}},\ \gamma \equiv \frac{\lambda_f}{\lambda},\ t \equiv t'/\tau_s,$$
$$x \equiv q/\sqrt{k_B T} - a \tag{4}$$

We refer to r as the width of the reaction window. The wide reaction window and the narrow reaction window correspond to $r > 1$ and $r < 1$, respectively. Throughout the present work, we consider the case where a thermal activation process is not a rate-determining step and assume that $|a| < 1$ or $|a| \approx 1$. Using the dimensionless variables and parameters, we recast eq 1 as

$$\frac{\partial \rho(x,t)}{\partial t} = L\left(x, \frac{\partial}{\partial x}\right)\rho(x,t) \tag{5}$$

where L denotes $S - k$, and

$$S\left(x, \frac{\partial}{\partial x}\right) \equiv \frac{1}{2}\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x} + \frac{\mathrm{d}u(x)}{\mathrm{d}x}\right] \tag{6}$$

$$k(x) \equiv \kappa f(x) \tag{7}$$

with

$$f(x) \equiv \gamma^{-1/2} e^{-r^{-1}x^2} \tag{8}$$

$$u(x) \equiv (x + a)^2 \tag{9}$$

Note that a large η corresponds to a large κ under the assumption that $\eta \propto \tau_s$. A schematic representation of $k(x)$ and $u(x)$ is shown in Figure 1.

Let us describe the initial condition for $\rho(x,t)$. For a large κ, generally we should not assume that the initial population distribution is equilibrated. In the present work, we consider mainly a photoinduced ET and assume that the free energy curves for the ground and excited states of the reactant are quadratic in q with the same curvature and different centers. That is, the former and the latter free energy curves are expressed as $U_g(q) = (q - \Delta q)^2 + \Delta G_g$ and $U(q) = q^2$, respectively, where ΔG_g is the free energy of the ground-state minus that of the excited state. The initial distribution in the excited states is the same as the equilibrium distribution in the

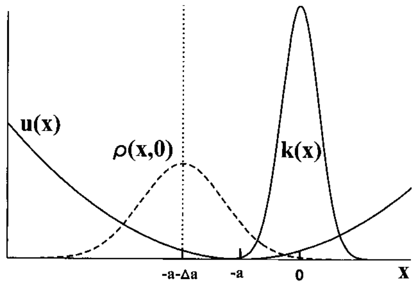

Figure 1. Figure 1. A schematic representation of the sink $k(x)$, the potential $u(x)$, and the initial population distribution $\rho(x,0)$.

ground state, therefore we have the initial condition

$$\rho(x,0) = \pi^{-1/2}\exp[-(x + a + \Delta a)^2] \qquad (10)$$

with $\Delta a \equiv -\Delta q/\sqrt{k_B T}$. We refer to eq 10 with $\Delta a \neq 0$ as the nonequilibrium initial condition and that with $\Delta a = 0$ as the equilibrium initial condition. A schematic representation of the initial condition is shown in Figure 1.

Let us now define the values characterizing the kinetics. Using $\rho(x,t)$ governed by eq 5, we define the reactant survival probability $P(t)$ as

$$P(t) \equiv \int_{-\infty}^{\infty} dx \rho(x,t) \qquad (11)$$

The survival probability $P(t)$ decays exponentially at long times, $P(t) = P_A \exp(-\epsilon t)$ because the eigenvalues of $-L$ are positive and discrete, where P_A is the amplitude of the exponential tail, and ϵ is the lowest eigenvalue of $-L$. In the small κ limit ($\kappa \rightarrow 0$) and in the wide reaction window limit ($r \rightarrow \infty$), it is well-known that the decay is exponential, $P(t) = \exp(-\tau_{eq}^{-1}\tau_s t)$, with the rate τ_{eq}^{-1} calculated by transition state theory, $\tau_{eq}^{-1} \equiv \tau_t^{-1} \int dx k(x)\rho^{(eq)}(x)$. Here τ_s appears because of the normalization of t and $\rho^{(eq)}(x)$ is the equilibrium distribution. The rate is given by $\tau_{eq}^{-1} = \tau_t^{-1}\exp[-\Delta G^*/(k_B T)]$, where the thermal activation energy ΔG^* is $(\Delta G + \lambda)^2/(4\lambda)$ $(=(k_B T\lambda_s/\lambda)a^2)$.[4] Using $P(t)$, we define the nth moment $P^{(n)}$ as

$$P^{(n)}(\kappa) \equiv \frac{1}{n!}\int_0^{\infty} dt\, t^n P(t) \qquad (12)$$

Using $P^{(n)}$, we define the nth mean lifetime $\tau^{(n)}$ (>0) as

$$\tau^{(0)}(\kappa) \equiv \tau_t \kappa P^{(0)},\ \tau^{(n)}(\kappa) \equiv \tau_t \kappa \left[\frac{P^{(n)}}{P^{(0)}}\right]^{1/n} \text{ for } n \geq 1 \qquad (13)$$

Using $\tau^{(n)}$, we define the nth power $\alpha^{(n)}(\kappa)$ as

$$\alpha^{(n)}(\kappa) \equiv \frac{d \log \tau^{(n)}(\kappa)}{d \log \kappa} = \frac{d \log \tau^{(n)}(\tau_s/\tau_t)}{d \log \tau_s} \qquad (14)$$

Finally, we define the power $\alpha_A(\kappa)$ for the amplitude P_A as

$$\alpha_A(\kappa) \equiv \frac{d \log P_A(\kappa)}{d \log \kappa} = \frac{d \log P_A(\tau_s/\tau_t)}{d \log \tau_s} \qquad (15)$$

Note that $\tau^{(0)}$ is the mean lifetime, and that a set of all the values of $P^{(n)}$ (or $\tau^{(n)}$) is sufficient to reproduce the time evolution of $P(t)$ for the following reason. Let $\tilde{P}(s)$ be the Laplace transformation of $P(t)$ ($\tilde{P}(s) \equiv \int_0^{\infty} dt e^{-st} P(t)$). Using $\lim_{t\rightarrow\infty} P(t) = 0$, we then obtain $\tilde{P}(s) = \sum_{n=0}^{\infty} (-s)^n P^{(n)}$. Therefore, using this equation, we can calculate $P(t)$ from a set of all of the values of $P^{(n)}$ (or $\tau^{(n)}$). The power $\alpha^{(0)}(\kappa)$ was proved to satisfy two inequalities,[36]

$$\alpha^{(0)}(\kappa) \leq 1 \text{ under an arbitrary initial condition} \qquad (16)$$

$$\alpha^{(0)}(\kappa) \geq 0 \text{ under the equilibrium initial condition } \rho(x, 0) = \rho^{(eq)}(x) \qquad (17)$$

Note that $\alpha^{(0)}(\kappa)$ can be negative for a certain initial condition.

B. Reaction-Dominated Region and Diffusion-Dominated Region. In this subsection, we divide the x-coordinate into the reaction-dominated and diffusion-dominated regions. Using this division, we develop an approximation for $P(t)$, which is expected to be only qualitatively correct. In the case of the Gaussian sink (eq 8), the reaction predominates over the diffusion around the origin $x = 0$ for a large κ, and the latter predominates over the former in the region far from the origin. We assume that if the local reaction rate is larger than the relaxation rate of the slow nuclear mode, then the reaction predominates over the diffusion, and if it is not, then the latter predominates over the former. Accordingly, we divide the x-coordinate into the reaction-dominated region Ω_r and the diffusion-dominated region Ω_d as

$$\begin{cases} \Omega_r \equiv \{x | k(x) > 1\} \\ \Omega_d \equiv \{x | k(x) \leq 1\} \end{cases} \qquad (18)$$

Using this division, we express $P(t)$ as a sum of the contribution $P_r(t)$ from Ω_r and that $P_d(t)$ from Ω_d,

$$P(t) = P_r(t) + P_d(t) \qquad (19)$$

Because the reaction is considered to predominate over the diffusion in Ω_r, neglecting the effect of the diffusion, we obtain

$$P_r(t) = \int_{x\epsilon\Omega_r} dx e^{-k(x)t}\rho(x,0) \qquad (20)$$

If the particle representing the ET system is initially in Ω_d, it needs to migrate to Ω_r for the reaction to occur. This migration is considered to be a rate-determining process in this case. It takes roughly the relaxation time of the slow nuclear mode, because we are considering the case of a low activation barrier. Thus, we approximate $P_d(t)$ by roughly

$$P_d(t) = e^{-t}\int_{x\epsilon\Omega_d} dx \rho(x,0) \qquad (21)$$

Note eq 21 is not about the population distribution as a function of x but about the amount of population. That is, we cannot discuss the time evolution of the population distribution using eq 21. In the limit of large κ, eq 20 leads to the exact result for $P(t)$ at short times. On the other hand, eq 21 leads to at least qualitatively correct behavior of the tail of $P(t)$ at long times as follows. As mentioned in Section II.A. $P(t)$ decays exponentially, $P(t) \propto \exp(-\epsilon t)$, for long times, where ϵ is the lowest eigenvalue of $-L$. Equations 19−21 also lead to the exponential tail, but somewhat differently, $P(t) \propto \exp(-t)$. However, the effect of this difference on the values of the powers defined in Section II.A. are expected to be small for a large κ. We will describe the reason and discuss this effect in Section V. Let us now approximate $P^{(n)}$ and τ in a similar way as for $P(t)$,

$$P^{(n)}(\kappa) = P_r^{(n)}(\kappa) + P_d^{(n)}(\kappa) \qquad (22)$$

$$\tau^{(0)}(\kappa) = \tau_r^{(0)}(\kappa) + \tau_d^{(0)}(\kappa) \qquad (23)$$

where

$$P_{\mathrm{r}}^{(n)}(\kappa) = \frac{1}{n!}\int_0^{\infty} \mathrm{d}t t^n P_{\mathrm{r}}(t) \tag{24}$$

$$P_{\mathrm{d}}^{(n)}(\kappa) = P_{\mathrm{d}}(t = 0) \tag{25}$$

$$\tau_i^{(0)}(\kappa) \equiv \tau_s P_i^{(0)} \qquad \text{for } i = \text{r or d} \tag{26}$$

Using $\tau_i^{(0)}(\kappa)$ (i = r or d) that is the contribution from Ω_i to $\tau^{(0)}(\kappa)$, we define the power $\alpha_i^{(0)}(\kappa)$ as

$$\alpha_i^{(0)}(\kappa) \equiv \frac{\mathrm{d}\log \tau_i^{(0)}(\kappa)}{\mathrm{d}\log \kappa} = \frac{\mathrm{d}\log \tau_i^{(0)}(\tau_s/\tau_t)}{\mathrm{d}\log \tau_s} \text{ for } i = \text{r or d} \tag{27}$$

Note that using eqs 18−21, we obtain

$$P_A = P_{\mathrm{d}}(t = 0) \tag{28}$$

C. The Relationship between the Kinetics at Short Times and at Long Times. In this subsection, we derive an equation describing the relationship between $P(t)$ at short times and the amplitude $P_A(\kappa)$ as a function of κ. Suppose that there are two systems (system 1 and system 2) and the only difference between them is in the values of κ, $\kappa < \kappa_2$. Here the subscript 2 indicates values, variables, functions, or operators of system 2. We do not use such subscripts for system 1 in this subsection. First, we consider the amplitude $P_A(\kappa)$ of system 1. Using eqs 21 and 28, we obtain

$$P_A(\kappa) = \int_{x\epsilon\Omega_{\mathrm{d}}} \mathrm{d}x \rho(x,0) \tag{29}$$

where $\Omega_{\mathrm{d}} \equiv \{x|k(x) \leq 1\}$. Next, we consider the survival probability $P_2(t)$ of system 2 at short times. At short times (before the diffusion starts: $t \ll 1$), we can approximate $P_2(t)$ as $P_2(t) = \int \mathrm{d}x \exp[-k_2(x)t]\ \rho(x, 0)$. To proceed further, we consider the case where the slope of $k_2(x)t$ is large, that is $\langle \mathrm{d}k_2(x)t/\mathrm{d}x\rangle \gg 1$. Here $\langle F_2(x)\rangle$ is the average $\int \mathrm{d}x F_2(x)\rho_2(x,t)/\int \mathrm{d}x\rho_2(x,t)$. We approximate $k_2(x)t$ by roughly $\kappa_2 t$, thus this inequality is recast as $k_2^{-1} \ll 1$. Under this condition, we can approximate $P_2(t)$ by roughly

$$P_2(t) = \int_{x\epsilon\Omega_t} \mathrm{d}x \rho(x,0) \tag{30}$$

where $\Omega_t \equiv \{x|k_2(x)t \leq 1\}$. Finally, because $\Omega_{t^*} = \Omega_{\mathrm{d}}$ for $t^* = \kappa/\kappa_2$, we obtain

$$P_A(\kappa) = P_2(t^*) \tag{31}$$

under the condition $\kappa_2^{-1} \ll t^* \ll 1$. We expect that eq 31 is at least qualitatively correct for a large κ.

D. The Smaller Power $\alpha^{(0)}(\infty)$ for the Larger Width r of the Reaction Window. In this subsection, we prove

Statement 1: Under an arbitrary initial condition, if $\alpha^{(0)}(\kappa)$ converges to a finite value $\alpha^{(0)}(\infty)$ in the large κ limit, $\alpha^{(0)}(\infty)$ decreases (or does not change) with increasing r.

Statement 1 means that the less strongly the slow nuclear mode couples to ET, the smaller the power $\alpha^{(0)}(\infty)$ becomes (or it does not change). This agrees with the intuitive idea that the larger value of $\alpha^{(0)}(\infty)$ indicates the greater importance of the slow nuclear mode in the reaction. To prove Statement 1, we use

Statement 2: If the only difference between system 1 and system 2 is in the sink operators and $k_2(x) \geq k_1(x)$, then we obtain $\rho_2(x,t) \leq \rho_1(x,t)$ for $t \geq 0$.

The subscript i indicates values, variables, functions, or operators of system i in this subsection. Statement 2 simply means that the larger the sink, the smaller the population distribution. Note that from $\rho_2(x,t) \leq \rho_1(x,t)$ we can immediately obtain $P_2^{(n)} \leq P_1^{(n)}$. Let us prove statement 1 using statement 2. Suppose that the only difference between system 1 and system 2 is in the sink operators. Let us assume that $r_1 \leq r_2$ and fix these two values. We vary κ_1 and κ_2 by keeping the ratio κ_2/κ_1 fixed to $(\gamma_2/\gamma_1)^{1/2}$ so that $k_2(0) = k_1(0)$. We then obtain $k_2(x) \geq k_1(x)$. Thus, from statement 2 we obtain $P_2^{(0)}(\kappa_2) \leq P_1^{(0)}(\kappa_1)$. If $\alpha^{(0)}(\kappa)$ converges to a finite value $\alpha^{(0)}(\infty)$, we obtain $P_i^{(0)}(\kappa_i) \approx \kappa_i^{\alpha_i^{(0)}(\infty)-1}$ for $i = 1$ and 2, and so we obtain $P_2^{(0)}(\kappa_2) \approx \kappa_1^{\alpha_2^{(0)}(\infty)-1}$. Here we have used the relationship between κ_1 and κ_2. Thus, if $\alpha_1^{(0)}(\infty) < \alpha_2^{(0)}(\infty)$, then we obtain $P_2^{(0)}(\kappa_2) > P_1^{(0)}(\kappa_1)$ at some value of κ_1. This contradicts statement 2. Therefore, we obtain $\alpha_1^{(0)}(\infty) \geq \alpha_2^{(0)}(\infty)$.

III. Power Laws for Large Viscosity

In this section, we derive expressions for the powers, $\alpha_{\mathrm{r}}^{(0)}(\kappa)$, $\alpha_{\mathrm{d}}^{(0)}(\kappa)$, and $\alpha_A(\kappa)$ under the initial condition eq 10. We show that the present results are in reasonable agreement with those found by the numerical calculations for a large κ.

Let us first calculate $P_{\mathrm{r}}^{(n)}(\kappa)$ and $P_{\mathrm{d}}^{(n)}(\kappa)$ for a large κ. Using eq 18, we obtain the dividing points $x = \pm x_{\mathrm{rd}}$ between Ω_{r} and Ω_{d} as

$$x_{\mathrm{rd}}(\kappa) = \sqrt{r \log(\kappa\gamma^{-1/2})} \tag{32}$$

Substituting eq 32 into eqs 20 and 21, we obtain

$$P_{\mathrm{d}}^{(n)}(\kappa) = \int_{-x_{\mathrm{rd}}(\kappa)}^{x_{\mathrm{rd}}(\kappa)} \mathrm{d}x k^{-(n+1)}(x)\rho(x,0) \tag{33}$$

$$P_{\mathrm{r}}^{(n)}(\kappa) = \int_{-\infty}^{-x_{\mathrm{rd}}(\kappa)} \mathrm{d}x\rho(x,0) + \int_{x_{\mathrm{rd}}(\kappa)}^{\infty} \mathrm{d}x\rho(x,0) \tag{34}$$

Note that $P_{\mathrm{d}}^{(n)}(\kappa)$, and $P_{\mathrm{r}}^{(n)}(\kappa)$ depend on the initial distribution but not on the potential in the present approximation. That is, they are functions of the sum of a and Δa. We can now calculate the values of the powers using eqs 33 and 34. If κ is so large that we can use the asymptotic forms[37] of the error function and the complex error function appearing in eqs 33 and 34, we obtain the expressions

$$P_{\mathrm{d}}^{(n)}(\kappa) \approx \frac{1}{2\sqrt{\pi}} \exp\{-[x_{\mathrm{rd}}(\kappa) - |a + \Delta a|]^2\}\ f_{\mathrm{d}}(\kappa) \text{ when } \kappa \gg \mu, \tag{35}$$

$$P_{\mathrm{r}}^{(n)}(\kappa) \approx \begin{cases} \dfrac{1}{2\sqrt{\pi}} \exp\{-[x_{\mathrm{rd}}(\kappa) - |a + \Delta a|]^2\} f_{\mathrm{r}}^{(n)}(\kappa) & \text{for } r < n + 1 \\ \left(\dfrac{\sqrt{\gamma}}{\kappa}\right)^{n+1} F_{\mathrm{r}}^{(n)}(\kappa) & \text{for } r > n + 1 \end{cases} \quad \text{when } \kappa \gg \mu_n, \tag{36}$$

where we define the parameters, μ and μ_n, and the auxiliary functions, $f_d(\kappa)$, $f_{\mathrm{r}}^{(n)}(\kappa)$, and $F_{\mathrm{r}}^{(n)}(\kappa)$ as

$$\mu \equiv \gamma^{1/2} \exp[(1 + |a + \Delta a|)^2/\mathrm{r}] \tag{37}$$

$$\mu_n \equiv \gamma^{1/2} \exp\{[|\zeta_n|^{-1/2} + |\zeta_n^{-1}(a + \Delta a)|]^2/r\} \tag{38}$$

$$f_{\mathrm{d}}(\kappa) \equiv \frac{1}{x_{\mathrm{rd}}(\kappa) - |a + \Delta a|} + \frac{\exp[-4|a + \Delta a|x_{\mathrm{rd}}(\kappa)]}{x_{\mathrm{rd}}(\kappa) + |a + \Delta a|} \tag{39}$$

$$f_{\mathrm{r}}^{(n)}(\kappa) \equiv \frac{1}{\zeta_n x_{\mathrm{rd}}(\kappa) + |a + \Delta a|} + \frac{\exp[-4|a + \Delta a|x_{\mathrm{rd}}(\kappa)]}{\zeta_n x_{\mathrm{rd}}(\kappa) - |a + \Delta a|}, \tag{40}$$

$$F_{\mathrm{r}}^{(n)}(\kappa) \equiv \frac{\exp\left[-\frac{(\zeta_n+1)(a+\Delta a)^2}{\zeta_n}\right]}{\sqrt{\pi|\zeta_n|}}\left\{1 - \left(\frac{\sqrt{\gamma}}{\kappa}\right)^{r-(n+1)} \frac{\exp[\zeta_n^{-1}(a + \Delta a)^2]}{2\sqrt{|\zeta_n|}} \times \left[\frac{\exp[-2|a + \Delta a|x_{\mathrm{rd}}(\kappa)]}{x_{\mathrm{rd}}(\kappa) - \zeta_n^{-1}|a + \Delta a|} + \frac{\exp[2|a + \Delta a|x_{\mathrm{rd}}(\kappa)]}{x_{\mathrm{rd}}(\kappa) + \zeta_n^{-1}|a + \Delta a|}\right]\right\} \tag{41}$$

with $\zeta_n \equiv (n + 1)r^{-1} - 1$. Note that the strongest dependence of $P_{\mathrm{d}}^{(n)}(\kappa)$ and $P_{\mathrm{r}}^{(n)}(\kappa)$ on κ is algebraic, namely $\exp[-x_{\mathrm{rd}}^2(\kappa)] \approx \kappa^{-r}$ or $\kappa^{-(n+1)}$. The second strongest dependence comes from the factor $\exp[2|a + \Delta a|x_{\mathrm{rd}}(\kappa)]$. The auxiliary functions, $f_{\mathrm{d}}(\kappa)$ and $f_{\mathrm{r}}^{(n)}(\kappa)$ are less dependent on κ, compared with these factors. However, the auxiliary function $F_{\mathrm{r}}^{(n)}(\kappa)$ contains the factor $\exp[2|a + \Delta a|x_{\mathrm{rd}}(\kappa)]$, and so its dependence is comparable to the second strongest one. Equations 35 and 36 show that $P_{\mathrm{d}}^{(n)}(\kappa)$ and $P_{\mathrm{r}}^{(n)}(\kappa)$ depend on κ in a similar way for $r < n + 1$ and the large κ. Let us now calculate the values of the powers using eqs 35 and 36,

$$\alpha_{\mathrm{d}}^{(0)}(\kappa) = 1 - r\left[1 - \frac{|a + \Delta a|}{x_{\mathrm{rd}}(\kappa)}\right] \text{ for } \kappa \gg \mu \text{ and } \kappa \gg \mu_0 \tag{42}$$

$$\alpha_{\mathrm{r}}^{(0)}(\kappa) = \alpha^{(0)}(\kappa) = 1 - r\left[1 - \frac{|a + \Delta a|}{x_{\mathrm{rd}}(\kappa)}\right] \text{ for } r < 1,\ \kappa \gg \mu, \text{ and } \kappa \gg \mu_0 \tag{43}$$

$$\alpha_A(\kappa) = -r\left[1 - \frac{|a + \Delta a|}{x_{\mathrm{rd}}(\kappa)}\right] \text{ for } \kappa \gg \mu \tag{44}$$

Here we have neglected the dependence of $f_d(\kappa)$ and $f_{\mathrm{r}}^{(n)}(\kappa)$ on κ. The second term in the square bracket of the rhs of eqs 42–44 converges very slowly to 0 in the limit of large κ. Physically, this slow convergence is attributed to the fact that the reaction-dominated and diffusion-dominated regions vary only very slowly with increasing viscosity. This slow convergence explains the limiting behavior of $\alpha^{(0)}(\kappa)$ observed by the numerical calculations,[6] namely that $\alpha^{(0)}(\kappa)$ varies very slowly with increasing κ. Let us calculate the values of the powers in the large κ limit. Using eqs 35 and 36 and taking the large κ limit, we obtain

$$\alpha_{\mathrm{d}}^{(0)}(\infty) = 1 - r \tag{45}$$

$$\alpha_{\mathrm{r}}^{(0)}(\infty) = \alpha^{(0)}(\infty) = \begin{cases} 1 - r \text{ for } r < 1 \\ 0 \text{ for r} \geq 1 \end{cases} \tag{46}$$

$$\alpha^{(n)}(\infty) = \begin{cases} 1 & \text{for } r < 1 \\ \dfrac{n+1-r}{n} & \text{for } 1 \leq r < n + 1 \quad \text{when } n \geq 1 \\ 0 & \text{for } n + 1 \leq r \end{cases} \tag{47}$$

$$\alpha_A(\kappa) = -r \tag{48}$$

The expression for $\alpha^{(0)}(\infty)$ in eq 46 was obtained in the previous work.[36] Note that this expression for $\alpha^{(0)}(\infty)$ contradict neither statement 1 in Section II.D. nor the exact results, $\alpha^{(0)}(\infty) = 1$ for $r = 0$ and $\alpha^{(0)}(\infty) = 0$ for $r = \infty$. Let us compare the present results to those found by the exact numerical calculations. We comment on these numerical calculations briefly. If κ is not extremely large, there is no difficulty in these calculations. However, if it is, a difficulty lies with the previously used methods.[38] In the present work, we use time splitting[39] in order to avoid a very small time step required for a numerical time integration when κ is very large. Computer time and memory required then increase only very slowly as κ increases. We plot $\alpha^{(0)}(\kappa)$ and $\alpha^{(1)}(\kappa)$ as functions of r with $\kappa = 10^5$ under the initial condition that $a = 0$ and $\Delta a = 0$ in Figure 2, and under the two initial conditions that $a = -1$ and $\Delta a = 0$ and that $a = 0$ and $\Delta a = -1$ in Figure 3. These figures show that the present results are in reasonable agreement with those found by the exact numerical calculations for a large κ. The differences between the cases when $a = -1$ and $\Delta a = 0$ and when $a = 0$ and $\Delta a = -1$ are small for a large κ. This shows that the values of the powers are similar for a large κ as long as the initial distributions are the same, even if the potentials are different. The powers $\alpha_A(\kappa)$, $\alpha_{\mathrm{r}}^{(0)}(\kappa)$ and $\alpha_{\mathrm{d}}^{(0)}(\kappa)$ were also calculated (not shown), and the results support the same conclusions. Here the powers $\alpha_{\mathrm{r}}^{(0)}(\kappa)$ and $\alpha_{\mathrm{d}}^{(0)}(\kappa)$ are calculated as follows. We obtain $P_{\mathrm{d}}(t)$ and $P_{\mathrm{r}}(t)$ from $P(t)$ found by the numerical calculations as $P_{\mathrm{d}}(t) = P(1/\epsilon)$ for $t \leq 1/\epsilon$ and $P_{\mathrm{d}}(t) = P(t)$ for $t > 1/\epsilon$, and $P_{\mathrm{r}}(t) = P(t) - P(1/\epsilon)$ for $t \leq 1/\epsilon$ and

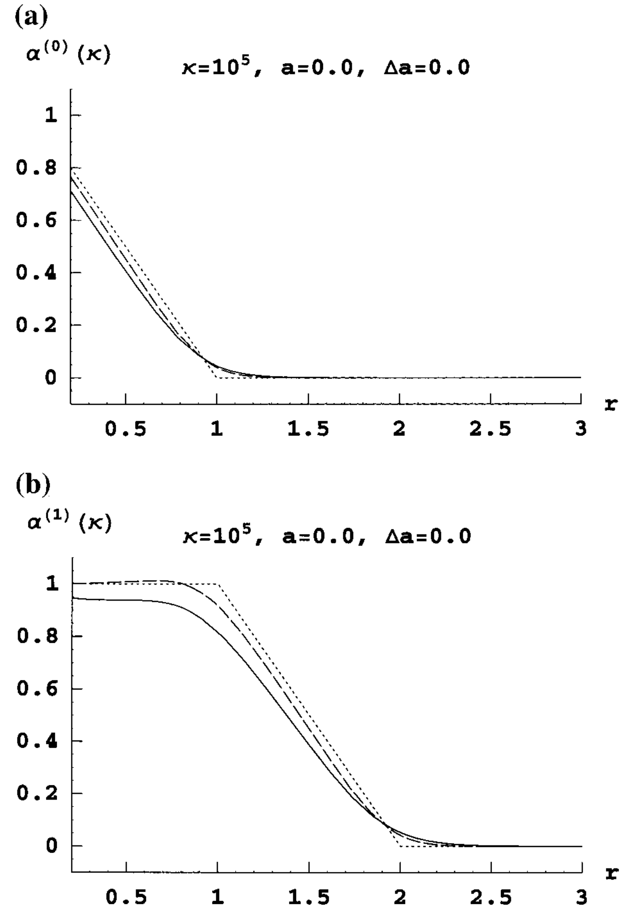

Figure 2. The powers $\alpha^{(0)}(\kappa)$ and $\alpha^{(1)}(\kappa)$ as functions of r with $\kappa = 10^5$, $a = 0$, and $\Delta a = 0$. The definitions of the parameters are given by eqs 4 and 10. (a) $\alpha^{(0)}(\kappa)$ is plotted. Solid line: exact numerical solution. Dashed line: present approximation, eqs 33 and 34. Dotted line: the large viscosity limit ($\kappa \to \infty$) of the present approximation, eqs 45–48. (b) Same as (a) but for $\alpha^{(1)}(\kappa)$.

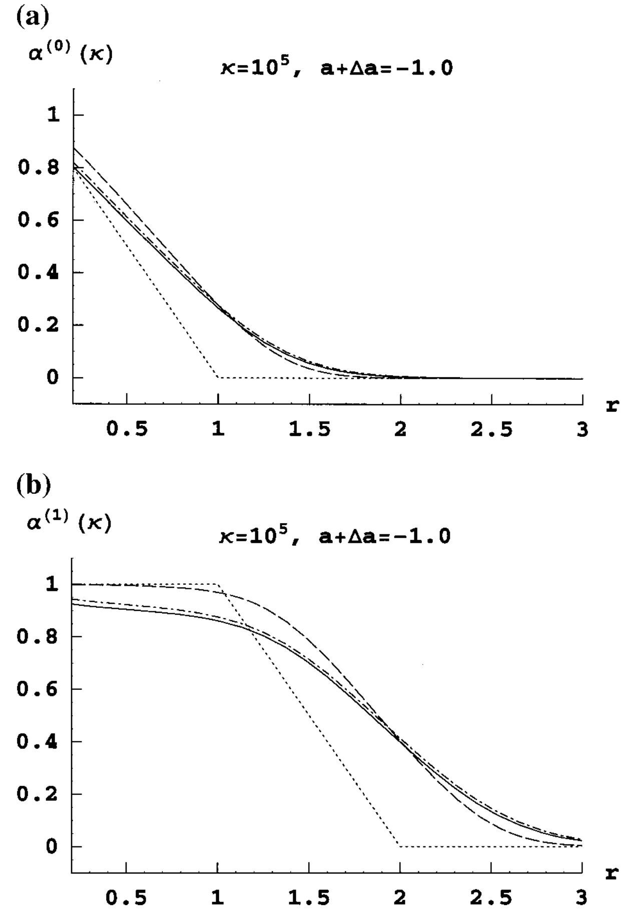

Figure 3. Same as Figure 2, but with $a = -1$ and $\Delta a = 0$, and $a = 0$ and $\Delta a = -1$. Solid line: exact numerical solutions for $a = -1$ and $\Delta a = 0$. Dash-dotted line: exact numerical solutions for $a = 0$ and $\Delta a = -1$. The present approximations, eqs 33, 34, and 42–44, are the same for the two cases when $a = -1$ and $\Delta a = 0$ and when $a = 0$ and $\Delta a = -1$. The powers in the large viscosity limit ($\kappa \to \infty$) do not depend on a and Δa (eqs 45–48).

$P_r(t) = 0$ for $t > 1/\epsilon$. From $P_d(t)$ and $P_r(t)$ obtained in this way, we calculate $\alpha_d^{(0)}(\kappa)$ and $\alpha_r^{(0)}(\kappa)$.

IV. The Decay of the Reactant Population at Short Times.

In this section, we derive an expression for $P(t)$ at short times and find that the time dependence of $P(t)$ at short times is intimately related to the viscosity dependence of the mean lifetime $\tau^{(0)}(\kappa)$. We confirm this relationship by the exact numerical calculations. Let us derive the expression for $P(t)$ at short times. Using eq 30, we obtain

$$P(t) \approx \frac{1}{2\sqrt{\pi}}\exp\{-[x_{\mathrm{rd}}(\kappa t) - |a + \Delta a|]^2\} f_{\mathrm{d}}(\kappa t) \text{ for } \kappa^{-1}\mu \ll t \ll 1 \qquad (49)$$

Note that we do not use eqs 18–21 when we derive eq 49. Equation 49 shows that when $\mu \ll \kappa$ the algebraic decay, $\exp[-x_{\mathrm{rd}}^2(\kappa t)] \approx (\kappa t)^{-r}$, occurs during $\kappa^{-1}\mu \ll t \ll 1$. Note that there is a weaker, compared with this algebraic dependence, but nonnegligible time dependence of $P(t)$, namely the factor $\exp[2|a + \Delta a| x_{\mathrm{rd}}(\kappa t)]$. Because this algebraic decay is limited to a certain range of time, the moments $P^{(n)}$ do not diverge.

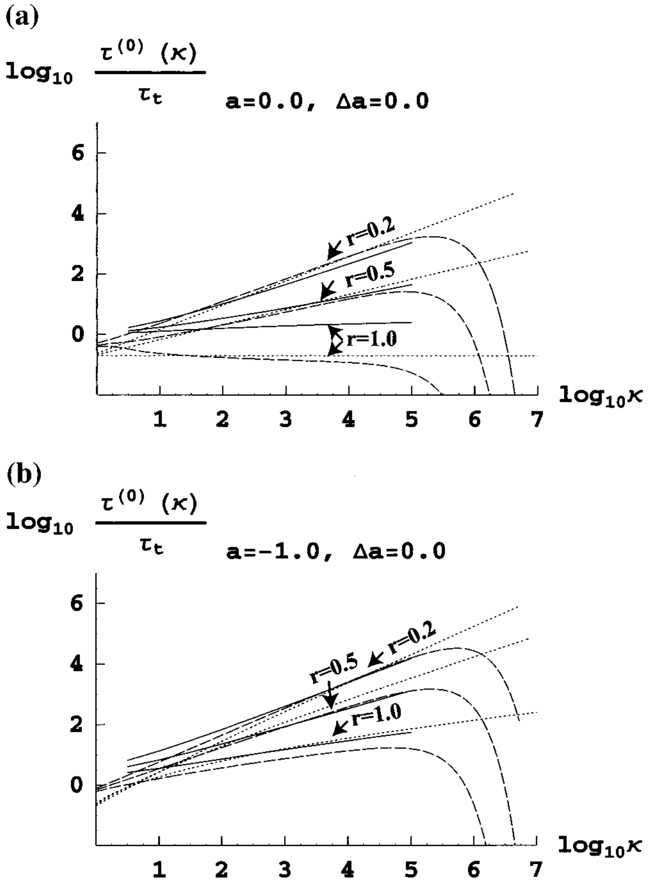

Figure 4. Functions $\log_{10}(\tau^{(0)}(\kappa)/\tau_t)$ and $\log_{10}(\kappa_2 t^* P_2(t^*))$ as functions of $\log_{10}\kappa$ under the condition that $t^* = \kappa/\kappa_2$ with different values of r. Solid line and long dashed line: exact numerical solutions for $\log_{10}(\tau^{(0)}(\kappa)/\tau_t)$ and $\log_{10}(\kappa_2 t^* P_2(t^*))$, respectively. Short dashed line: present approximation, eq 49 with $f_{\mathrm{d}}(\kappa t) \approx 1$. The values of $\log_{10}(\tau^{(0)}(\kappa)/\tau_t)$ and $\log_{10}(\kappa_2 t^* P_2(t^*))$ depend on κ in a similar way, but their absolute values can be different. Parameters are as follows: $\tau_t = 1.0$, $\Delta a = 0.0$, $\kappa_2 = 10^6$, and (a) $a = 0.0$ and (b) $a = -1.0$.

Let us consider the relationship between $\tau^{(0)}(\kappa)$ of system 1 and $P_2(t)$ of system 2, where the only difference between system 1 and system 2 is in the values of κ, $\kappa < \kappa_2$. Here the subscript 2 indicates operators, functions, variables, or values for system 2 introduced in Section II.C. We do not use such subscripts for system 1 in this subsection. Using eqs 35, 36, and 49 and neglecting the dependence of $f_{\mathrm{d}}(\kappa)$ and $f_{\mathrm{r}}^{(n)}(\kappa)$ on κ, we obtain

$$\frac{\tau^{(0)}(\kappa)}{\tau_t} \approx \kappa_2 t^* P_2(t^*) \text{ for } r < 1 \text{ and } \kappa_2^{-1}\mu,\ \kappa_2^{-1}\mu_0 \ll t^* \ll 1 \qquad (50)$$

with $t^* = \kappa/\kappa_2$. We plot $\log_{10}(\tau^{(0)}(\kappa)/\tau_t)$ and $\log_{10}[\kappa_2 t^* P_2(t^*)]$ as a function of $\log_{10}\kappa$ ($=\log_{10}\kappa_2 t^*$) in Figure 4. This figure shows that the leading dependence of $\tau^{(0)}(\kappa)$ on κ is similar to the leading dependence of $tP_2(t)$ on t at short times. Note that the absolute values of both sides in eq 50 can be different, although they depend on κ in a similar way.

V. Discussion and Summary

In the previous sections, we have seen that the values of the powers calculated from eqs 18–21 are in reasonable agreement with those found by the numerical calculations for a large κ, although eq 21 leads to the tail of the survival probability, $P(t) \propto \exp(-t)$, which is slightly different from the exact tail, $P(t) \propto \exp(-\epsilon t)$. We can reduce this discrepancy by modifying eqs 18 and 21 as

$$\begin{cases} \Omega_{\mathrm{r}} \equiv \{x | k(x) > \epsilon\} \\ \Omega_{\mathrm{d}} \equiv \{x | k(x) \leq \epsilon\} \end{cases} \tag{51}$$

$$P_{\mathrm{d}}(t) = e^{-\epsilon t} \int_{x \epsilon \Omega_{\mathrm{d}}} \mathrm{d}x \rho(x,0) \tag{52}$$

As a result of numerical calculations (not shown), the values of the powers by eqs 51 and 52 are much closer to the exact ones compared to those calculated from eqs 18 and 21. Thus, it is probable that the errors included in the present approximation are mainly due to this discrepancy. However, the effect of the tail difference on the values of the powers is small for a large κ for the following reason. If we use eqs 51 and 52 in calculating the values of the powers, ϵ always appears in the form $\kappa^{c}\epsilon$, where c is a constant. Because ϵ depends on κ very weakly as $\epsilon \approx$ (r/2) log κ,[33] compared with the algebraic factor κ^{c}, we can neglect the dependence of ϵ on κ for a large κ.

In summary, we investigate the qualitative features of ET in the case where the viscosity is large and the activation energy for the reaction is smaller than or similar to the thermal energy such that the decay of the reactant population is nonexponential. We proved that the power of the dependence of the mean lifetime on the viscosity decreases (or does not change) with increasing width of the reaction window. We derived the expressions for the powers of the dependence of the generalized mean lifetimes $\tau^{(n)}$ on the viscosity η by dividing the slow nuclear coordinate into the diffusion-dominated and reaction-dominated regions. These expressions show the fractional power dependence $\tau^{(n)} \propto \eta^{\alpha^{(n)}}$ under the condition on the ratio of the reorganization energy of the fast nuclear modes to that of the slow one (See eq 47). When there is a barrier for the reaction, the convergence of the values of the powers in the large viscosity limit is very slow. This slow convergence is attributed to the fact that the reaction-dominated and diffusion-dominated regions vary only very slowly with increasing viscosity. We also derived the expression for $P(t)$ at short times. This expression shows the algebraic decay $P(t) \propto t^{\beta}$. From these expressions we find that $\alpha^{(0)} = \beta + 1$ under the condition that the reorganization energy of the fast nuclear modes is smaller than that of the slow one. The present results are in reasonable agreement with those found by the numerical calculations for a large κ under the nonequilibrium initial condition as well as under the equilibrium initial condition.

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