Proton Transfer from Photoacid to Solvent

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We calculated the proton-transfer rate constant from a super photoacid, 5,8-dicyano-2-naphthol (DCN2), to a protic solvent as a function of temperature. Previously, we found that the temperature dependence of the proton-transfer rate constant is explained as a continuous transition from nonadiabatic to solvent-controlled limits. The model we used to calculate the proton-transfer rate constant is based on a diffusive propagation of the solvent configuration along a generalized solvent coordinate from the reactant potential surface toward the crossing point with the product potential surface. The proton transfer occurs at the crossing point, and the rate is calculated by a sink term placed at the crossing point. The sink term includes the solvent velocity and the Landau−Zener transmission coefficient. Both the diffusion constant and the Landau−Zener transmission coefficient depend on the dielectric relaxation of the solvent. The calculations are compared with the experimental data and an interpolation expression that bridges the nonadiabatic limit and the solvent-controlled limit.

Introduction

In their excited state, photoacids and photobases are stronger acids or bases, respectively. Excitation of these compounds in a solution of protic solvents enables the study of the dynamics of the proton-transfer reaction of acids and bases in solution.[1−6]

In recent papers,[7−10] we described our experimental results on an unusual temperature dependence of excited state proton transfer from a super photoacid (5,8-dicyano-2-naphthol, DCN2) to several monols, diols, and a glycerol. At relatively high temperatures, the rate of proton transfer is almost temperature-independent, while at relatively low temperatures, the rate exhibits large temperature dependence and the rate constant value is similar to the inverse of the dielectric relaxation time. We proposed a simple stepwise model to describe and calculate the temperature dependence of the proton transfer to the solvent. The model accounts for the large difference in the temperature dependence of the proton-transfer rate at high and low temperatures.

The temperature dependence of the rate constant for proton transfer to the protic solvent is explained as a continuous transition from nonadiabatic (high temperature) to solvent-controlled (low temperature) proton transfer. This phenomenon can be described by the Landau−Zener curve-crossing formula[11,12] for the proton-transfer rate constant.

The theoretical analysis for the solution-phase proton-transfer reaction was undertaken by Dogonadze, Kuznetzov, Ulstrup, and co-workers[13−17] and then extended by Borgis and Hynes,[18] Cukier,[19] and Voth.[20] These theories suggest that when a potential energy barrier is present in the proton-reaction coordinate, the reaction pathway involves tunneling through the barrier, as opposed to passage over the barrier. The proton transfer can be described as a quantum tunneling between two wells formed by two interacting electronic states. The transfer of the proton, from one well to the other, is associated with a change of electronic state of the system. The crossover between the electronic states can only occur when the proton tunnels through the barrier.

Conventional Landau−Zener (LZ) theory[11,12] provides an accurate description of the process in the absence of interaction with the environment. It is applicable if the motion in the vicinity of the crossing point is nearly uniform (ballistic).[21,22] The interaction of the particle with the environment causes complications.

The curve-crossing problem in the presence of dissipation has been studied extensively.[23−31] Expressions for the transition rate of various physical limits have been derived. When the coupling, V, between the diabatic terms is the smallest parameter of the system, the dynamics in the crossing region in this nonadiabatic limit is fast, the tunneling rate is the rate-limiting step, and the reaction rate is given by the Fermi Golden Rule expression.

When the coupling between the diabatic states is larger than k_BT, the adiabatic representation of the coupled potential energy surfaces is adequate, the upper adiabatic potential surface plays a negligible role, and the rate expression is given by the standard transition state theory (TST) formula.

Another physical limit is realized when $V \leq k_BT$ and the interaction with the environment is strong enough. In this solvent-controlled limit, the rate is inversely proportional to the solvent relaxation time (friction) and is independent of the coupling V.

A number of attempts have been made to bridge these physical limits. Zusman[23] derived an expression for the rate, bridging the nonadiabatic limit and the solvent-controlled limit. Rips and Jortner have used a simple physical argument to obtain a rate expression that bridges all three limits.[27] They assumed that the crossover could be described in terms of a single dimensionless parameter, the ratio of the mean-free path and the root-mean-square displacement of the reaction coordinate.

In this study, we use a simple model to calculate the temperature dependence of the proton-transfer rate constant and

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compare the results with experimental measurements described in our previous papers.[7−10] The model is based on a diffusive propagation of solvent configuration along a generalized solvent coordinate potential surface. The potential surface is constructed by a cusped double well potential. The proton transfer is modeled by introducing a sink term that includes both the LZ transmission coefficient and the average solvent configuration velocity.

Modeling of the Proton Transfer to the Solvent. The reaction of proton transfer to the solvent can be described schematically:

$$\mathrm{A^{*}H\cdots S_B} \rightarrow \mathrm{A^{-}{}^{*}\cdots HS_B^{+}}$$

The reactant is an intermolecular hydrogen-bonded complex between an excited photoacid, AH*, and a solvent molecule, S_B. S_B serves as a base, characterized by a hydrogen bond to the photoacid and also to other solvent molecules. In water, this specific water molecule, S_B, has three hydrogen bonds to three water molecules. To form the product, $\mathrm{A\cdots HS_B^{+}}$, in water, one hydrogen bond of S_B to a water molecule must be broken. Thus, relatively long-range reorganization of the hydrogen bond network takes place upon proton transfer to the solvent. This complex rearrangement, to accommodate the product, is probably the reason for a slow solvent generalized configuration motion which corresponds to a low-frequency component in the solvent dielectric spectrum. Its time constant is close to the slow component of the dielectric relaxation time. According to Kuznetsov and co-workers,[13−17] Borgis and Hynes,[18] Bernstein and co-workers,[32] and Syage,[33] a second important coordinate should be taken into account. This second coordinate is the distance between the two heavy atoms, O−H···O in our case. This distance is modulated by a low-frequency vibrational mode, Q.[18,32] The proton tunnels through the barrier from the reactant well to the product well via the assistance of the low frequency, Q, mode whenever the solvent configuration equalizes the energies of the reactant and the product.

Borgis and Hynes[18] derived an expression for the proton-transfer rate constant, k. They wrote an expression for k in a transition state theory form. k is expressed as the average one-way flux along the solvent coordinate, through the crossing point $S^{\ddagger}$ of the two free energy surfaces, with the inclusion of a transmission coefficient, κ, giving the probability of a successful curve crossing:

$$k = \langle \dot{S}\Theta(\dot{S})\delta(S - S^{\ddagger})\kappa(\dot{S},S^{\ddagger})\rangle_R \tag{1}$$

where S is the generalized solvent coordinate, $\dot{S}$ is the solvent velocity, and $\Theta(\dot{S})$ is the step function. The brackets denote averaging over the classical solvent distribution normalized by the partition function of the solvent.

To find the appropriate nonadiabatic transmission coefficient, κ, for use in this equation, Borgis and Hynes[18] used the general Landau−Zener (LZ) transmission coefficient, κ, adapted for the present problem. The LZ factor, appropriate for a positive velocity approach to the crossing point, is

$$\kappa = [1 - {}^{1}/_{2}\exp(-\gamma)]^{-1}[1 - \exp(-\gamma)] \tag{2}$$

where

$$\gamma = \frac{2\pi|V|^2}{\hbar\Delta F\dot{S}} = \frac{2\pi|V|^2}{\hbar k_S\dot{S}} \tag{3}$$

is the adiabaticity parameter. The expression for the transmission coefficient κ includes multiple passage effects on the transition probability. V is the coupling matrix element between the reactant and the product, and ΔF is the slope difference of the diabatic potentials of mean force at the crossing point, $\Delta F = k_S$, where k_S is the parabolic potential surface force constant. When $\gamma \ll 1$, one obtains the nonadiabatic limit result

$$\kappa \cong 2\gamma \tag{4}$$

leading to

$$k_{NA} = \frac{2\pi}{\hbar}|V|^2\left(\frac{\beta}{4\pi E_S}\right)^{1/2}\exp(-\beta\Delta G^{\ddagger}_{NA}) \tag{5}$$

in which $\Delta G^{\ddagger}$ is the Marcus activation free energy

$$\Delta G^{\ddagger}_{NA} = \frac{1}{4E_S}(E_S + \Delta G)^2 \tag{6}$$

The adiabaticity parameter, γ (see eq 3), depends on the potential surfaces curvature, ΔF, the coupling, $|V|^2$, and the velocity in the vicinity of crossing, $\dot{S}$. $|V|^2$ is independent of temperature. The solvent velocity, $\dot{S}$, on the other hand, strongly depends on the temperature. In our previous papers, we suggested that $\dot{S}$ is related to the slow components of the solvent relaxation. On the basis of the experimental data, we infer that $\dot{S} = b/\tau_D$, where τ_D is the solvent dielectric relaxation time[34] and b is an empirical factor, dependent on the specific protic solvent, and its value is between 1 and 4. In all the solvents used, τ_D depends, nearly exponentially, on the temperature. The activation energy of τ_D for these solvents ranges from 12 (methanol) to 48 kJ/mol (glycerol). Thus, for glycerol and long chain diols, τ_D changes by about 3 orders of magnitude within the temperature range studied, $\Delta T \cong 120$ K

$$\gamma \propto \tau_D(T); \qquad \tau_D = \tau_D^0 e^{E_a/RT} \tag{7}$$

The adiabaticity parameter, γ, is small at high temperatures and large at low temperatures. For the solvents used in the experiments, the value of γ as a function of the temperature increases smoothly from a value close to 0, i.e., $\gamma \ll 1$ (the nonadiabatic limit) to a value $\gamma \gg 1$ (the adiabatic limit).

In the adiabatic limit, $V \gg k_BT$, $\kappa \approx 1$, the adiabatic rate expression is

$$k_{AD} = (\omega_s/2\pi)\exp(-\beta\Delta G^{\ddagger}_{AD}) \tag{8}$$

where ω_S is the solvent high-frequency response, which can be expressed via the average thermal rotational frequency of the polar solvent[27,35] or can be determined experimentally[36] from the ultrafast inertial part of the solvation time-correlation function. $\Delta G^{\ddagger}_{AD} \cong \Delta G^{\ddagger}_{NA} - V$ is the free energy of activation.

Another physical limit is realized when $V \le k_BT$ and the interaction with the environment is strong enough. In this solvent-controlled limit, the rate is inversely proportional to the solvent relaxation time (friction) and independent of the coupling V. Rips and Jortner[29] derived an expression for the resonant (symmetric, $\Delta G = 0$) electron-transfer rate in the solvent-controlled limit

$$k_{SC} = \frac{1}{\tau_L}\left(\frac{E_S}{16\pi k_BT}\right)^{1/2}\exp(-\beta\Delta G^{\ddagger}_{NA}) \tag{9}$$

For the nonresonance cases, the prefactor in the rate expression (eq 9) only changes by about 20%. τ_L is the longitudinal

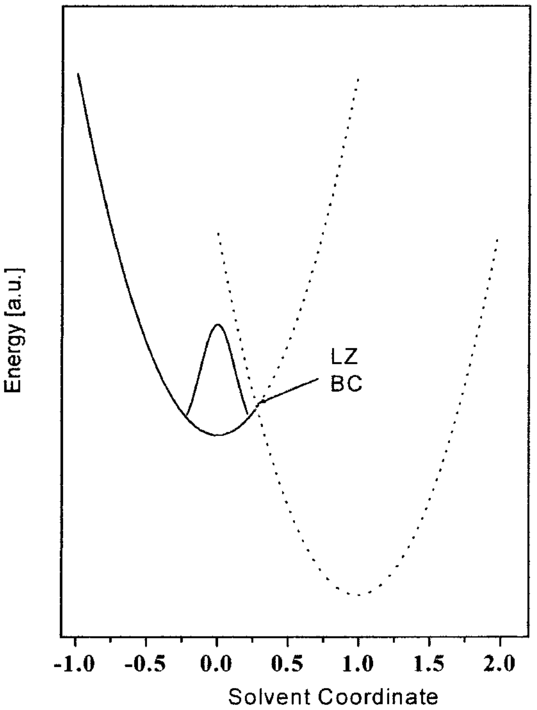

Figure 1. Schematic representation of the potential surfaces of both the reactant and product along the generalized solvent coordinate.

dielectric relaxation time, $\tau_L = (\epsilon_\infty/\epsilon_S)\tau_D$, where ϵ_∞ and ϵ_S are the high-frequency and static dielectric constant, respectively.

The preexponent depends on the solvent's dynamical properties. At low temperatures, we found that the preexponential factor in the solvent-controlled limit is related to the slowest component of the dielectric relaxation time. We also found that the temperature dependence of the proton transfer can be explained as a continuous transition from the nonadiabatic limit at high temperature to the solvent-controlled limit at low temperature.

In our previous papers, we used the mean-first-passage expression to bridge between the nonadiabatic limit and the solvent-controlled limit to obtain the rate expression:

$$k_{PT}(T) = \frac{k_{NA}(T)k_{SC}(T)}{k_{NA}(T) + k_{SC}(T)} \qquad (10)$$

where k_{PT} is the overall rate and k_{NA} and k_{SC} are given by eqs 5 and 9.

In this paper, we take a different course to obtain a temperature-dependent proton transfer rate constant that continuously changes from the nonadiabatic limit to the solvent-controlled limit as the temperature decreases.

Figure 1 schematically shows the model for the calculation of the proton-transfer rate. The model includes the following building blocks and assumptions. We use two crossing parabolic potential surfaces representing the free energy of the reactant and product along the solvent coordinate. For numerical calculation purposes, we focus our attention on the reactant single-well parabolic potential surface in the generalized solvent coordinate. The numerical calculation is based on the diffusive propagation of the solvent generalized coordinate from the equilibrium position of the reactant well to the crossing point. We solve the Debye−Smoluchowski equation (DSE) for the specific problem. The probability density function, $p(S,t)$, to find a solvent configuration, S, along the generalized solvent coordinate at time t obeys the DSE[23,37,38]

$$\frac{\partial p}{\partial t} = D\frac{\partial}{\partial S}e^{-\beta U(S)}\frac{\partial}{\partial S}e^{\beta U(S)} \qquad (11)$$

where D is a diffusion constant and $U(S)$ is the potential surface.

In the numerical calculation, we used

$$U_r(S) = \frac{1}{2}k_S S^2$$
$$U_p(S) = \frac{1}{2}k_S(S - S_p)^2 \qquad (12)$$

where $k_S = 2E_S$ and S is the generalized and normalized solvent coordinate. In this solvent coordinate, the reactant and product equilibrium positions are at $S_r = 0$ and $S_p = 1$, respectively. E_S is the solvent reorganization energy. For methanol, we used $E_S = 0.3$ eV. The calculation's initial condition is a thermal equilibrium of the probability density function, $p(S)$, of the solvent coordinate of the reactant and is given by a Gaussian distribution centered at the minimum of the reactant well

$$p_{eq}(S) = \frac{1}{(2\pi\langle S^2\rangle)^{1/2}}\exp\left(-\frac{S^2}{2\langle S^2\rangle}\right) \qquad (13)$$

where $\langle S^2\rangle$ is the mean square displacement, with a Gaussian width $U(\langle S^2\rangle) = \sqrt{2E_S k_B T}$.

The diffusion constant, D, is related to the dielectric relaxation time, τ_D, and the widths of the Gaussian initial distribution,[37] $D = (\langle S^2\rangle/2\tau_D)$. For $E_S = 0.3$ eV, $\langle S^2\rangle \cong 0.16$ at room temperature.

The activation energy, $\Delta G^\ddagger$, to cross between the reactant well and the product well is determined from the experimental activation energy, measured at high temperatures (the nonadiabatic limit). For methanol and glycerol, $\Delta G^\ddagger \approx 2.5$ kJ/mol. The position of the activation barrier is determined by $\Delta G^\ddagger = U(S)^\ddagger$ and $S^\ddagger = 0.22$.

The next step in the calculation is based upon solving the DSE of a single parabolic potential surface with the relevant initial and boundary conditions. To solve it, we used a modification of a user-friendly graphic program, SSDP (Ver. 2.61), of Krissinel and Agmon.[39] The modification is based on using the Landau−Zener transmission coefficient, κ(eq 2), in the sink term at the crossing point between the reactant well and the product well. The boundary condition at the crossing point is given by

$$\frac{\partial p}{\partial S}\Big|_{S=S^\ddagger} = -k_0\kappa D p(S^\ddagger,t) \qquad (14)$$

The boundary condition eq 14 we chose has ingredients similar to those of the expression for the rate constant, expressed in a transition state theory form eq 1. The average solvent velocity is proportional to $1/\tau_D$, κ appears in both expressions, and k_0 is a numerical factor, independent of temperature and determined by fitting the numerical solution to the experimental proton-transfer rate constant at high temperatures.

Finally, the proton-transfer rate constant is obtained from the slope of the plot of ln(p) versus time. Figure 2 shows the experimental results along with the calculated results using the DSE for the proton-transfer reaction from DCN2 to a methanol (2a) and glycerol (2b) solutions as a function of T^{-1}. Full circles are the computed rates; open circles are the experimental rates. The solid line is a calculation on the basis of the mean-first-

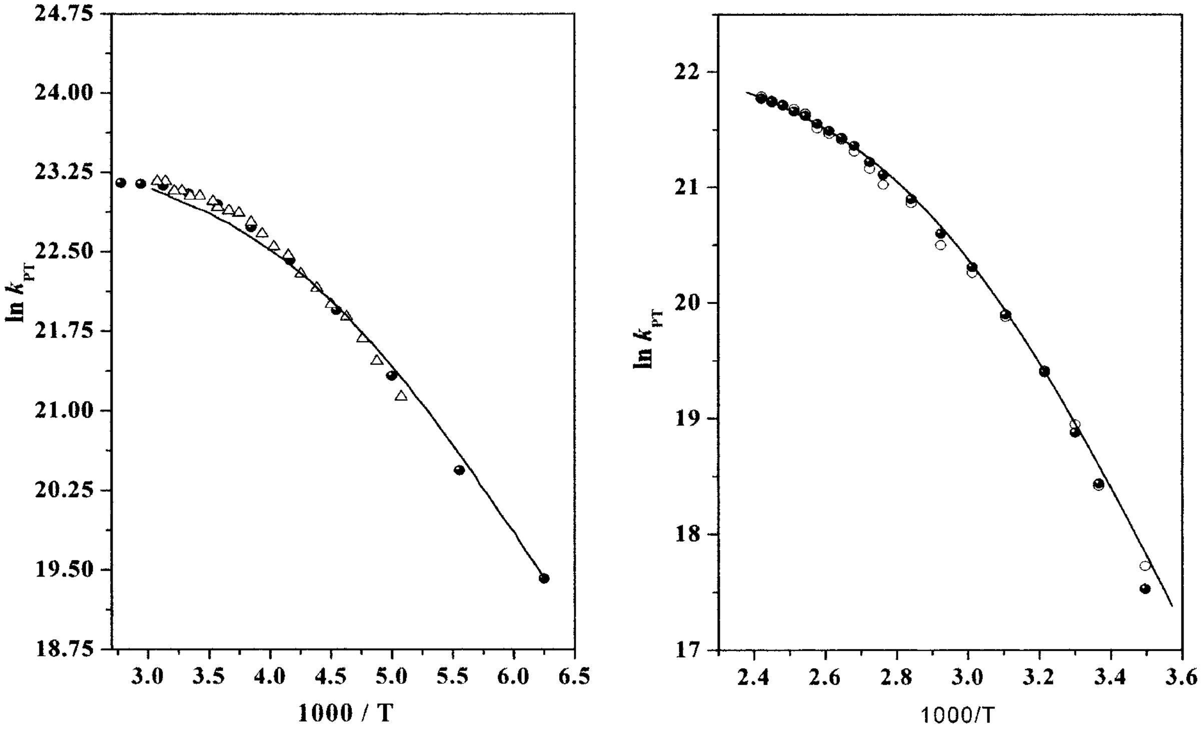

Figure 2. Semilogarithmic plot of the proton-transfer rate constant from DCN2 to solvent vs T^{-1}: (a) methanol and (b) glycerol. Open circles, experimental data; close circles,calculation according to our diffusive model and LZ boundary condition; solid line, the interpolation formula using eq 10.

TABLE 1: Relevant Parameters for Model Calculations[a]

	τ_D (298 K) [ps]	k_0 [Å/ns]	γ'	D(298 K) [cm^2/s]
MeOH	50	1.35×10^3	4.5×10^8	3.2×10^{-7}
glycerol	6.5×10^3	0.60×10^3	3.0×10^8	2.4×10^{-9}

[a] For calculation with the SSDP program,[39] we used the solvent coordinate in length dimension of Angstroms. Solvent reorganization energy, $E_S = 0.3$ eV. Activation energy, $\Delta G^{\ddagger} = 0.024$ eV. Crossing point position between the two diabatic potential surfaces, $S_r = 0$ and $S_p = 1$ Å. We placed the minima of the reactant and product potential surfaces at 0 and 1 Å respectively. Dielectric relaxation time at 298 K. k_0 is a numerical factor, independent of temperature and determined by fitting the numerical solution to the experimental proton-transfer rate constant at high temperatures. γ' is a free adjustable parameter, $\gamma = \gamma'\tau_D(T)$ (eq 15). The calculated value of γ' is larger by ~2 than the actual value used in the fit in Figure 2. The diffusion coefficient is calculated by[37] $D = (\langle S^2\rangle/\tau_D)$, $\langle S^2\rangle = 0.16$ is the mean square displacement, $U\langle S^2\rangle = \sqrt{2E_S k_B T}$ and $U\langle S\rangle = (1/2)k_S S^2$, where $k_S = 2E_S$.

passage expression eq 10. The relevant parameters for the calculation using the diffusion model are given in Table 1.

The rate constant calculated using the interpolation equation eq 10 the solid line in Figure 2 also gives a good fit to the experimental data.

The free adjustable parameter in the calculation is γ'

$$\gamma = \gamma'\tau_D(T) \tag{15}$$

We find that $\gamma' = 4.5 \times 10^8$ s^{-1} from the best fit to the experimental data for the rate of proton transfer of DCN2 to a methanol solution and $\gamma' = 3 \times 10^8$ s^{-1} for the glycerol solution. Figure 3 shows $\kappa(T)$ as a function of $1/T$ for the proton-transfer reaction in methanol (3a) and for glycerol (3b). For a methanol solution, we find $\kappa = 0.5$ at 200 K and $\tau_D \approx 1000$ ps.

Discussion

Conventional Landau−Zener (LZ) theory[11,12] provides an accurate description of the process in the absence of interaction with the environment. It is applicable if the motion in the vicinity of the crossing point is nearly uniform (ballistic).[21,22] The interaction of the particle with the environment causes complications.

Rips and Pollak[30] showed that variational transition state theory (VTST) allows for the identification of a collective coordinate along which the dynamics in the curve-crossing region is maximally separated from the remaining solvent induced dynamics (quasiballistic). The problem of calculation of the transition rate can then be handled using conventional LZ theory. The resulting theory reduces to the respective three above-mentioned physical limits.

In this paper, we calculate the proton transfer rate constant, as a function of temperature, using the DSE and proper boundary condition. Previously[7,8,9,10] we used an interpolation equation (eq 10) that bridges between the nonadiabatic limit and the solvent-controlled limit to calculate the temperature dependence of the proton-transfer rate constant. Both ways of calculating the rate of proton transfer in the transition region between the nonadiabatic limit and the solvent-control limit are based on the behavior of the rate constant in both limiting cases. Both calculations give a good fit to the experimental results.

At high temperatures, (the nonadiabatic limit in our experiments) the solvent motion is fast, the activation energy is sufficiently low, and the proton-tunneling rate is the rate-determining step. The LZ transmission coefficient is small and hence limits the rate of population transfer to the product (crossing to the product diabatic potential surface). From the rate constant at high temperatures (the nonadiabatic limit, eq 5), we determine the preexponential factor and the activation energy of the process. According to the Marcus theory, the activation energy is determined by ΔG and E_S (eq 6).

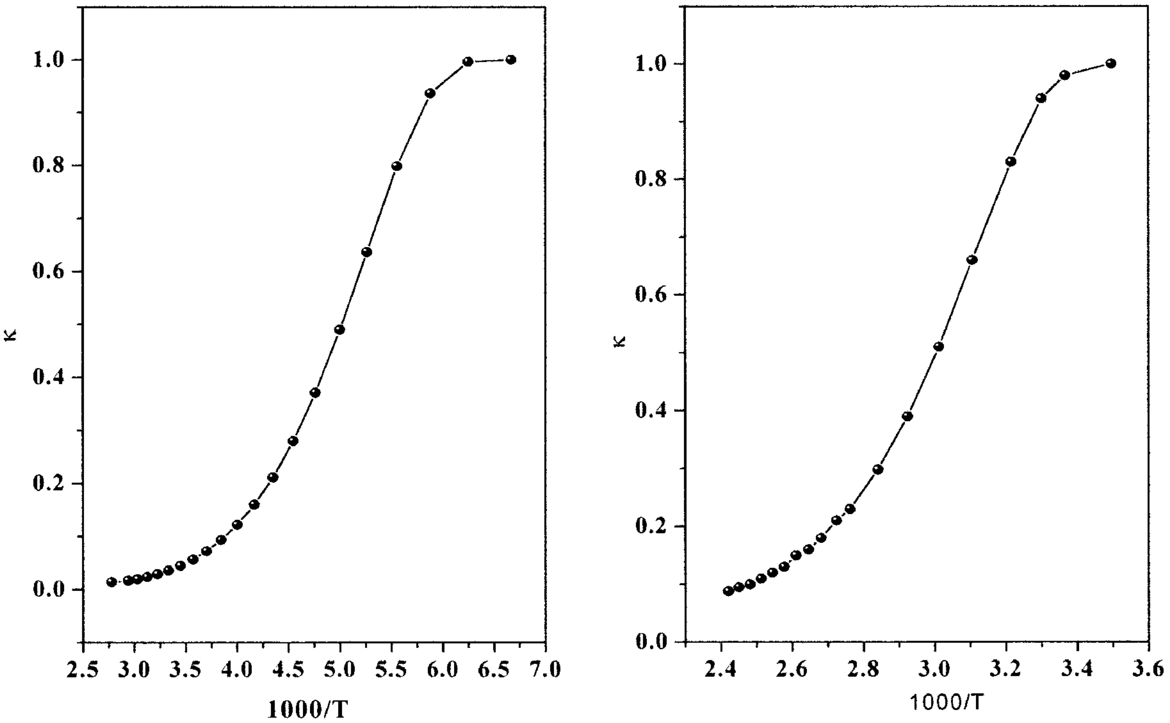

Figure 3. Calculated Landau–Zener transmission coefficient as a function of T^{-1} for the proton-transfer reaction from DCN2 to (a) methanol and (b) glycerol.

The preexponential factor is mainly determined by the value of the coupling matrix element. The transmission coefficient from the reactant well to the product well at the crossing point (at the top of the barrier) is given by the Landau–Zener transmission coefficient (eq 2). The adiabaticity parameter, γ (eq 3), is determined by three parameters, $|V|^2$, ΔF, and $\dot{S}$. $|V|^2$ can be evaluated from the experimental high-temperature rate constant. We find that the preexponential factor is 3×10^{10} s^{-1}. From the preexponential expression, we evaluate V to be 2 cm^{-1} and $(2\pi/\hbar)|V|^2 \cong 10^{-10}$ Js^{-1}. $\Delta F = k_S$, where k_S is the mean force constant, which is related to the solvent reorganization energy, $k_S = 2E_S$. For methanol, we used reorganization energy, $E_S = 0.3$ eV. To quantitatively evaluate the adiabaticity parameter, $\gamma = \gamma'\tau_D$, we used $\gamma' = (2\pi/\hbar)|V^2|1/\Delta F \cong 10^9$ s^{-1}. The calculated value of γ' is only larger by about a factor of 2 than the value we used as a fitting parameter in the actual calculation of the temperature dependence of the experimental proton-transfer rate constant shown in Figure 2.

At a low enough temperature, (the solvent-controlled limit), the diffusive propagation of the solvent configuration toward the crossing region is slow compared to the tunneling rate. The LZ transmission coefficient is close to one since the average solvent velocity is slow (eq 3) and the rate-determining step is the transport motion of the probability density function of the solvent configuration itself, which appears also in the sink term (eq 14). The activation energy of the solvent coordinate remains small but the diffusion constant exhibits large temperature dependence. In the solvent-controlled limit rate expression (eq 9), the preexponential factor of the proton-transfer rate constant is determined by the average solvent velocity at the crossing point, $\dot{S} = b/\tau_D$, where b is an empirical factor. For a methanol solution it is about 2.2, and for glycerol it is about 1.

As previously mentioned, the longest dielectric relaxation time, $\tau_D(T)$, is approximately exponential with the temperature.[34] The activation energy of $\tau_D(T)$ for methanol and glycerol is 12 and 48 kJ/mol respectively. At 295 K, the dielectric relaxation for glycerol is about 100 times slower, $\tau_D \approx 6.5$ ns, than that of methanol, ~50 ps. For both solvents, the proton transfer from DCN2 to the solvent shows the same general behavior of temperature dependence. At high temperatures, the rate constant is almost temperature independent (low activation energy), while at low temperatures, the temperature dependence is large and follows the dielectric relaxation time. Since the two solvents differ drastically in their dielectric relaxation characteristic time and temperature dependence, the proton transfer rate also differs drastically between the two solvents. In glycerol, the transition from the nonadiabatic proton-transfer limit to the solvent-controlled limit occurs at much higher temperatures. From the calculation of the proton-transfer rate constant of DCN2 in glycerol, we find that $\kappa = 0.5$ at $T = 330$ K and $\tau_D = 800$ ps. For methanol, the midpoint ($\kappa = 0.5$) occurs at much lower temperature, 200 K and $\tau_D = 1000$ ps. The temperature dependence of the proton transfer rate in the solvent-controlled limit for glycerol has an Arrhenius dependence with a slope of 48 kJ/mol, while for methanol, it is only 12 kJ/mol, exactly the same as that of the dielectric relaxation time of these solvents.

Our experimental findings show that the activation energy of the proton-transfer process from DCN2 to protic solvents, like alcohols, is rather small, $\Delta G_{NA}^{\ddagger} \approx 2.5$ kJ/mol. Rips and Jortner[40] discussed the applicability of electron transfer theory to small activation barriers ($\Delta G^{\ddagger} \approx k_BT$) or even the activationless case. They found that the theory is applicable even to these extreme cases. When the activation energy is low, the crossing rate depends on the initial preparation of the solvent configuration and the reactant potential surface (see Figure 1). In proton transfer, from photoacids to the solvent, the excitation of the molecule from its ground state (equilibrium solvent configuration distribution) to the excited state usually prepares a nonequilibrium solvent configuration distribution in the excited state. The position of the initial distribution depends on the photon energy. In such a case, the proton-transfer rate might be altered with respect to the case of an initial distribution located at the equilibrium position (the minimum of the potential surface of the generalized solvent coordinate). In our experimental study,[7−10] we used several excitation wavelengths to look at the effect of preparation of the excited state on the proton transfer rate. We found only minor effects on the proton-transfer rate constant and the fluorescence signal in general.

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