J. Phys. Chem. A **2000,** *104,* 2663−2667 **2663**

Unusual Temperature Dependence of Excited State Proton Transfer Rates in Alcohols

Boiko Cohen and Dan Huppert*

Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

Received: September 13, 1999; In Final Form: December 23, 1999

The reversible proton dissociation and geminate recombination of photoacids is studied as a function of temperature in alcohols. For this purpose we used a strong photoacid 5,8-dicyano-2-naphthol (DCN2) (pK_a^* ∼ −4.5 in water) that is capable to transfer a proton to alcohols. The experimental data are analyzed by the Debye−Smoluchowski equation solved numerically with boundary conditions to account for the reversibility of the reaction. We propose a qualitative model to describe the unusual temperature dependence of the proton-transfer rate constant in alcohols in the liquid phase.

Introduction

The study of excited-state proton transfer (ESPT) reactions in solutions is fundamental to the understanding of the nature of the reactions of acids and bases in solution. These studies were conducted on a photoacid molecule that dissociates upon excitation to produce an excited anion and a proton.[1−4] Even though this subject has been studied for more than thirty years [5,6] the exact nature of ESPT reactions is still not completely clear, and neither is the dual role played by the solvent molecules: (1) as proton acceptors and (2) solvation of the parent molecules.[7−9]

Experimental and theoretical studies of ESPT processes in solution have led to the development of a two step model[10,11] (Scheme 1).

SCHEME 1

$$\mathrm{ROH}^* \underset{k_r}{\overset{k_d}{\rightleftharpoons}} [\mathrm{RO}^{-}{*}\cdots\mathrm{H}^{+}]_{(r=a)} \overset{\mathrm{DSE}}{\rightleftharpoons} \mathrm{RO}^{-}{*} + \mathrm{H}^{+}$$

The first step is described by back-reaction boundary conditions with intrinsic rate constants k_d and k_r. This is followed by a diffusional second step, in which the hydrated proton is removed from the parent molecule. This latter step is described by the Debye−Smoluchowski equation (DSE). In the continuous diffusion approach, one describes the photoacid dissociation reaction by a spherically symmetric diffusion equation (DSE)[12] in three dimensions.[10,11] The boundary conditions at $r = a$ are those of back reaction (Scheme 1). k_d and k_r are the “intrinsic” dissociation and recombination rate constants at the contact sphere radius a. Quantitative agreement was obtained between theory and experiment,[10,11] and as a result, it was possible to make a closer study of the ESPT process itself, and also the dynamic and static properties of the solvent.

Lee et al.[3] studied the temperature dependence of the excited-state proton-transfer reaction in aqueous solutions of 1- and 2-naphthols. They were unable to find a temperature dependence for the stronger photoacid, 1-naphthol (pK_a^* ∼ 0.5) in the temperature range 0−80 °C. The proton-transfer rate for 2-naphthol (K_a^* ∼ 2.7) was found to be temperature dependent with an activation energy of 2.6 kcal/mol. The proton-transfer rate constant for 1-naphthol is more than 2 orders of magnitude larger than for 2-naphthol. They conclude that the difference in the activation energy between 1-naphthol and 2-naphthol fits a free energy relationship.

Recently[13] we have studied the proton-transfer rate of DCN2 in methanol as function of T. We have noticed that the activation energy of the process is temperature dependent. The aim of this study is to extend the previous one and to characterize the temperature dependence of photoacid dissociation in several alcohols in the liquid phase. We propose a qualitative model to describe the unusual temperature dependence. As a photoacid, for this study, we have chosen 5,8-dicyano-2-naphthol (DCN2). The solvents for the proton transfer study are linear monols, at the temperature range of 60 °C (333 K) to −110 °C (163 K).

Using the above-mentioned model, see Scheme 1, the temperature dependencies of proton dissociation and recombination rates were determined by fitting the time-resolved fluorescence curve of ROH* and RO$^-$* with the DSE computer model simulation.[10−12] The temperature dependence of the proton-transfer rate is discussed and compared with the proposed proton-transfer model and solvent properties.

Experimental Section

Time-resolved fluorescence was measured using time-correlated single-photon counting (TCSPC) technique. As an excitation source, we used a cw mode-locked Nd:YAG-pumped dye laser (Coherent Nd:YAG Antares and a 702 dye laser) providing high repetition rate (>1 MHz) of short pulses (2 ps at full width half-maximum, fwhm). The (TCSPC) detection system is based on a Hamamatsu 3809U, photomultiplier, Tennelec 864 TAC, Tennelec 454 discriminator, and a personal computer-based multichannel analyzer (nucleus PCA-II). The overall instrumental response was about 50 ps (fwhm). Measurements were taken at 10 nm spectral width. Steady-state fluorescence spectra were taken using SLM AMINCO-Bowman-2 spectrofluoremeter.

DCN2 was synthesized by Tolbert and co-workers.[14] The samples concentrations were between 2 × 10^{-4} and 2 × 10^{-5} M. Solvents were reagent grade and were used without further purification. The solution’s pH was about 6.

---

* Corresponding author: Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel. E-mail: huppert@chemosf1.tau.ac.il. Fax: 972-3-6407012.

10.1021/jp9932416 CCC: $19.00

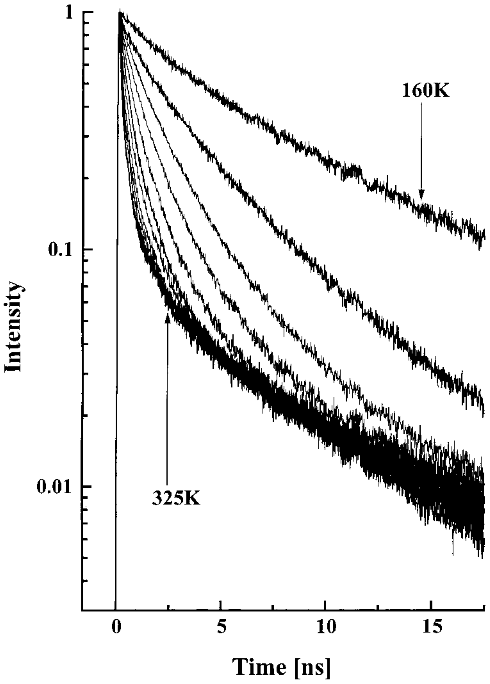


Figure 1. Time-resolved emission of DCN2 in ethanol solution of the protonated form (ROH*) measured at several temperatures in the range 160−325 K (top to bottom: 160, 173, 185, 197, 210, 222, and 325 K).

The DCN2 fluorescence spectrum consists of two structureless broad bands (~40 nm fwhm). The emission band maximum of the acidic form (ROH*) emits at 450 nm in water and in alcohols. The emission band maximum of the alkaline form $RO^{-}*$ is at 600 nm in water and in alcohols. At 450 nm the overlap of the two luminescence bands is rather small and the contribution of the $RO^{-}*$ band to the total intensity at 450 nm is less than 0.5%. To avoid overlap between contributions of two species, we have mostly monitored the ROH* fluorescence at 450 nm.

The temperature of the irradiated sample was controlled by placing the sample in a liquid N_2 cryostat with thermal stability of approximately ±1 K.

Results and Discussion

Proton Dissociation and Geminate Recombination in the Liquid Phase. 1. General Considerations. An important parameter in our model is the mutual diffusion coefficient $D = D_{H^+} + D_{RO^-}$. The temperature dependence of the proton diffusion constant D_{H^+} for various alcohols was deduced from the proton conductance measurements as a function of T.[15,16] The anion diffusion constant D_{RO^-}, as a function of T was estimated from the solvent viscosity data.[17] The temperature dependence of the dielectric constant and the dielectric relaxation of neat alcohols data were taken from refs 18−20. Figure 1 shows, on a semilog scale, the time-resolved emission intensity of DCN2 in ethanol solutions measured at 450 nm at various temperatures in the range of 160−325 K. Using Scheme 1 and the numerical solution of the DSE,[10] we fit the experimental data and extract both the intrinsic proton dissociation and recombination (k_d and k_r) rate constants. Typical chi-squares of the fit range from 1.2 to 2. We determine the proton-transfer rate constant k_d from the fit to the initial fast decay of the ROH* fluorescence (~150 ps for DCN2 in ethanol at room temperature). The initial fast component of the fluorescence decay is mainly determined by the deprotonation process and is almost insensitive to the geminate recombination process. We estimate that the error in determination of k_d is 5%. The long time behavior (the fluorescence tail) seen in the ROH* time-resolved emission is a consequence of the repopulation of the ROH* species by reversible recombination of $RO^{-}*$ with the geminate proton. The reprotonation is an adiabatic process and therefore the excited ROH* can undergo a second cycle of deprotonation. The overall effect is a nonexponential fluorescence tail.[10]

The comparison of the numerical solution with the experiment involves several parameters. Some are adjustable parameters such as k_d and k_r, others, like the contact radius, a, have acceptable literature values.[10,11] The static dielectric constant ε is known as a function of the temperature for the solvents used. There may be uncertainties concerning the values of the mutual diffusion constant D at low temperatures. Thus, we are facing a multi parameter problem in adjusting a solution of a partial differential equation to fit experimental data. As mentioned above, the estimated uncertainty in the determination of k_d is 5%, while the uncertainty in the determination of k_r is much larger, ~20%. The relative large uncertainty in the values of k_r arises from the complex relation between the above-mentioned parameters which determine the ROH* fluorescence tail.

The asymptotic expression (the long time behavior) for the fluorescence of ROH*(t) is given by[21]

$$[\mathrm{ROH}^*] \cong \frac{\pi}{2}a^2 \exp(R_D/a)\frac{k_r}{k_d(\pi D)^{3/2}}t^{-3/2} \qquad (1)$$

In the above equation R_D is the Debye radius, given by

$$R_D = \frac{|z_1 z_2| e^2}{\varepsilon k_B T} \qquad (2)$$

where z_1 and z_2 are the charges of the proton and anion; ε, the static dielectric constant of the solvent, and the absolute temperature T. e is the electronic charge and k_B is Boltzmann's constant.

2. The Temperature Dependence of the Proton-Transfer Rate. A semilog plot of the dissociation rate constant, k_d of DCN2 in methanol, ethanol, and propanol solutions versus $1/T$ is shown in Figure 2a. k_d in methanol and ethanol is almost independent of the liquid temperature in the range +60 °C to +20 °C. The temperature dependence of k_d in propanol at the high-temperature range is larger than that in methanol and ethanol. At lower temperatures, k_d in all the alcohols used in this study decreases rapidly as the temperature decreases.

The temperature dependence of k_d is quite unusual for chemical reactions. In general, chemical reactions obey a constant exponential (Arrhenius) decrease of the reaction rate constant as a function of $1/T$ in a large temperature range. As described before, the value of k_d is almost insensitive to the solvent temperature at $T > 10$ °C, while below −20 °C, k_d decreases with the decrease in the sample temperature with a relatively large activation energy.

The activation energies of k_d of DCN2 in liquid methanol, ethanol and propanol solutions as a function of $1/T$ are shown in Figure 2b. The activation energies are obtained by differentiating a polynomial fit to the data of Figure 2a. At the low-temperature range <10 °C the activation energy of k_d in all the three alcohols increases monotonically as T decreases and approach a constant value similar to the one of the dielectric relaxation time. The literature values[18] of the activation energies of τ_D are 12, 16, and 21 kJ/mol for methanol, ethanol, and propanol, respectively. For the proton-transfer activation energies

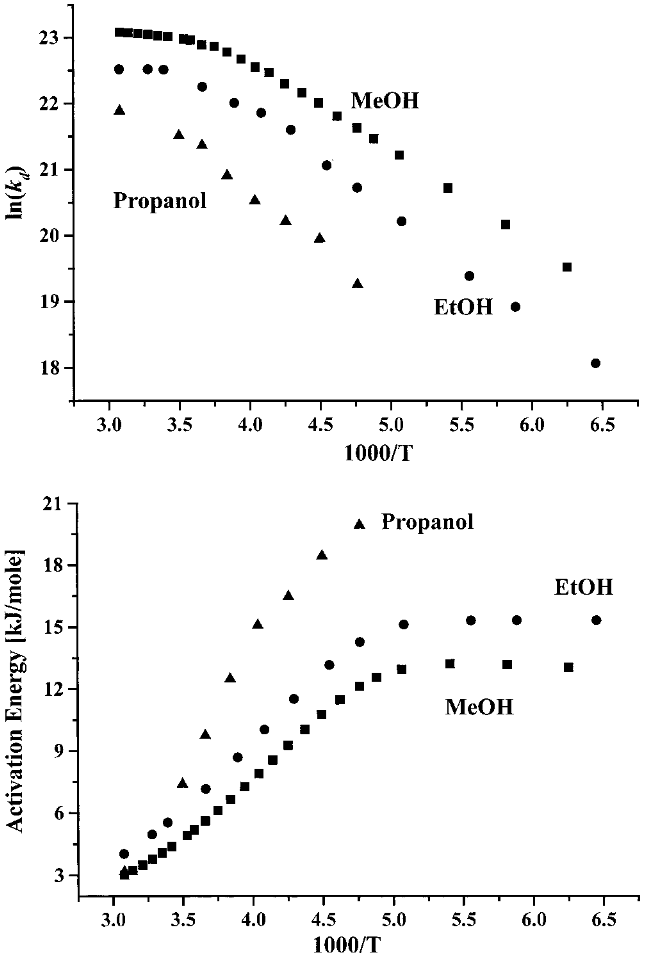


Figure 2. (a) Arrhenius plot of the proton-transfer rate constant of DCN2 in methanol (■), ethanol (●), and propanol (▲) as a function of *1/T*. (b) The activation energies of the proton-transfer rate in methanol (■), ethanol (●), and propanol (▲) as a function of *1/T*.

at low temperatures we obtained 13, 15.5, and 20 kJ/mol for methanol, ethanol, and propanol, respectively.

3. The Temperature Dependence and the Free Energy Relationship. Pines and co-workers[22,23] correlated the value of the proton dissociation rate k_d of many photoacids with their K_a^* value. They used a procedure published by Agmon and Levine.[24] Recently Solntsev et al.[25] used the free energy correlation for 5-cyano-2-naphthol in several solvents. The basic assumption in such a correlation is that within a family of similar reactions the intrinsic free-energy barrier for the reaction is modified by the total free energy change following the reaction. In our case we have

$$\Delta G = -RT \ln K_a^* \qquad (3)$$

for the total free-energy change.

The free-energy barrier for the reaction G_a is assumed to depend on some intrinsic barrier G_a^0, defined for a symmetric ($\Delta G = 0$) proton transfer and on ΔG. The measured rates may be correlated according to an Arrhenius plot

$$k_d = k_d^0 \exp\left[-\frac{G_a}{RT}\right] \qquad (4)$$

where,

$$G_a = \Delta G - G_a^0 \ln(n^\ddagger)/\ln(2) \qquad (5)$$

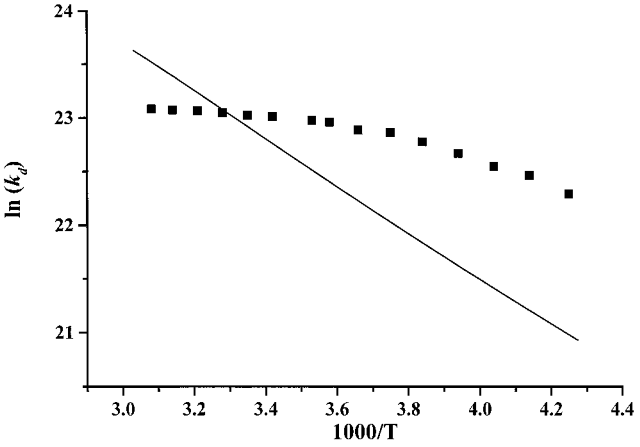


Figure 3. Temperature dependence of the proton-transfer rate of DCN2 in methanol; free energy model with $1/\tau_D$ as preexponential (solid line), experimental results (full circles).

and $n^\ddagger$ is the location of the reaction barrier along the proton coordinate, $n^\ddagger = 0$ (reactant like) for the endothermic limit, and $n^\ddagger = 1$ (product like) for the exothermic one. $n^\ddagger$ is given by

$$n^\ddagger = \left[1 + \exp\left(\frac{-\Delta G \ln(2)}{G_a^0}\right)\right]^{-1} \qquad (6)$$

From the data analysis correlating the rate in water with pK_a^* of many acids Pines et al.[22] found $k_d^0 = 3 \times 10^{11}$ s^{-1} and $G_a^0 = 2.9$ kcal/mol. This places the activationless limit of proton-transfer reactions between Debye relaxation time ($\tau_D \approx 7$ ps for water at 25 °C) and the longitudinal relaxation time $\tau_L = (\varepsilon_\infty/\varepsilon_0)\tau_D \approx (2 \pm 1)$ ps, where ε_∞ and ε_0 are the dielectric constants of the solvent at "infinite" and zero frequencies, respectively.

Robinson et al.[26] have suggested that moderately strong photoacids dissociate with an Arrhenius behavior given by

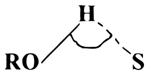
$$k_d = \tau_d^{-1} \exp(-\Delta G^\ddagger/k_B T) \qquad (7)$$

where τ_d is the collective dipole correlation time $\tau_d \cong \tau_D$ and $\Delta G^\ddagger$ is the activation free energy of the dissociation that is mainly determined by the change in the solvent entropy following the proton solvation by water.[26]

The solid line in Figure 3 shows a computer fit to the temperature dependence at the temperature range of 250−330 K of the proton-transfer rate of DCN2 in ethanol, predicted by equations 4−6 using $k_d^0 = 1/\tau_D$ as the preexponential factor, p$K_a^* = -0.33$ and $G_a^0 = 3.0$ kJ/mol.

The calculated activation energy G_a for DCN2 in ethanol is ~2 kJ/mol. The relative large temperature dependence of the computed signal of k_d arises mainly from the large temperature dependence of τ_D and only partially from the activation energy of the reaction. Using $1/\tau_D$ as the preexponential in the free energy relationship model increases the temperature dependence by a factor of 20 over the temperature range. The actual change in the experimental proton transfer rate of DCN2 to ethanol is only a factor of 2. Thus the use of τ_D as a preexponential factor at the high-temperature range is not a good choice for the proton-transfer reactions.

4. A Qualitative Model for the Temperature Dependence of Excited-State Proton-Transfer Reactions. We present a qualitative model that accounts for the unusual temperature dependence of the excited-state proton transfer.The proton-transfer reaction depends on two coordinates; the first one depends on the solvent configuration. A plausible coordinate can be the relative orientation of the hydrogen bonded solvent molecule with respect to the OH bond of the photoacid molecule. For simplicity we assume that the relevant solvent coordinate is the angle of the hydrogen bond



coordinate, where S denotes a solvent molecule. When the proton lies on the straight line connecting the two oxygen atoms the energy is minimal. This assumption is not critical for the model and is used for its description only. For the alcohols used in this study the solvent coordinate characteristic time is within the range of the dielectric relaxation time τ_D and the longitudinal relaxation τ_L. The second coordinate is the actual proton translational motion along the reaction path.

$$\mathrm{RO{-}H{\cdots}S} \rightarrow \mathrm{RO^{-}{\cdots}H{-}S^{+}}$$

The solvent coordinate dictates the barrier height for the actual proton transfer movement. We used an oversimplified model calculation for the qualitative description of the temperature dependence of the experimental proton transfer rate constant DCN2 in monols. The model restricts the proton transfer process to be stepwise. The proton moves to the adjacent hydrogen bonded solvent molecule only when the solvent configuration brings the system to the lowest energy barrier of the proton coordinate. This simple model excludes parallel routes for the ESPT in which many solvent configurations permit the reaction to take place with a distribution of reaction rates, while in a two-dimensional model these parallel routes are permitted and contribute to the overall effective rate. In the stepwise model the overall proton-transfer time is a sum of two times, $\tau = \tau_1 + \tau_2$, where τ_1 is the characteristic time for the solvent reorganization and τ_2 is the time for the proton to pass over the barrier. The overall rate constant $k_d(T)$ at a given T is

$$k_d(T) = \frac{k_H(T)k_s(T)}{k_H(T) + k_s(T)} \tag{8}$$

where k_s is the solvent coordinate rate constant and k_H is the proton coordinate rate constant.

Similar expressions for an overall rate constant are used for several important phenomena, like the overall rate constant for electron-transfer rate[27] and a diffusion assisted chemical reaction.[28,29]

Equation 8 provides the overall excited-state proton-transfer rate constant along the lines of a stepwise process similar to the processes mentioned above. As a solvent coordinate rate constant we use $k_s = b(1/\tau_D)$, where b is an adjustable empirical factor determined from the computer fit of the experimental data. We find that the empirical factor lies between 2 and 5. For the alcohols τ_L is usually smaller than τ_D by a factor of 2−6. Thus the solvent characteristic time $\tau_S = 1/k_s$ for monols lies between the dielectric relaxation and the longitudinal time $\tau_L < \tau_S < \tau_D$. It is worth to note that in a Debye solvent the orientational diffusion constant is related to the dielectric relaxation time[30] $D_R = 2/\tau_D(T)$. The reaction rate constant k_H along the proton coordinate is expressed by the usual activated chemical reaction description given by eq 4. At high temperature the solvent relaxation is fast and the rate determing step is the actual proton-transfer coordinate.

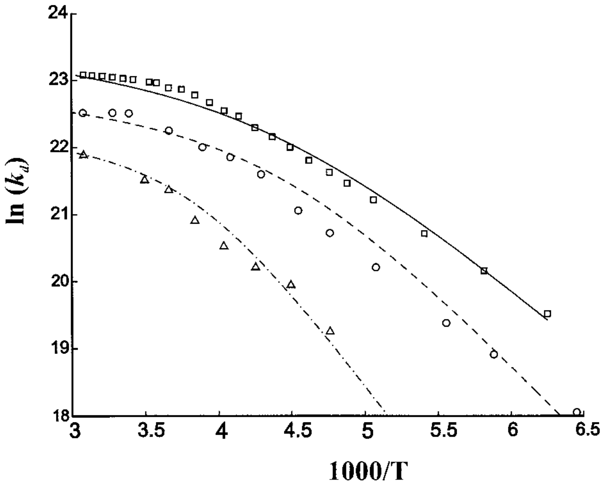


Figure 4. Two step model calculations (see text) of the temperature dependence of the proton-transfer rate in methanol (solid line), ethanol (broken line), and propanol (dotted line), along with the experimental results: methanol (squares), ethanol (circles), and propanol (triangles).

$$k_H = k_H^0 \exp\left(-\frac{G_a^H}{RT}\right) \tag{9}$$

where k_H^0 is the preexponential factor determined by the fit to the experimental results and G_a^H is the activation energy.

The activation energy G_a^H is determined from the excited-state acid equilibrium constant K_a^*. It is calculated from the rate parameters derived from the time-resolved emission at ~320 K, assuming that $k_H \approx k_d$, according to

$$K_a^* = 10^{27} k_d \exp(-R_D/a)/(N_A k_a) \tag{10}$$

where N_A is Avogadro's number and $k_a = 4\pi a^2 k_r$. The electrostatic contribution to pK_a^* is eliminated from eq 10.

$$K_a^*(ROH) = \mathrm{p}K_{a,\mathrm{chem}}^* + pK_{a,\mathrm{el}}^* \tag{11}$$

where p$K_{a,\mathrm{chem}}^*$ is the chemical part of the equilibrium and p$K_{a,\mathrm{el}}^*$ is the electrostatic part given by

$$pK_{a,\mathrm{el}}^* = R_D/2.303a \tag{12}$$

where a is the initial separation between the ion-pair following the complete dissociation of the bound state. Finally the activation energy is calculated from eqs 5 and 6 and using $K_{a,\mathrm{chem}}^* = 10^{27} k_d/(N_A k_d)$

Figure 4 shows the experimental rate constant of DCN2 in methanol, ethanol, and propanol as a function of *1/T* along with the computer simulation using our simplified qualitative model. As seen from the figure, our model calculation is in agreement with the DCN2 measurements. The model accounts for both the low and the high-temperature regime as well as the intermediate regime between them. The parameters for the fit of Figure 4 using eqs 3−8 are given in Table 1. There are three adjustable free parameters in the computer fits shown in Figure 4. These parameters are b, k_H^0, and G_a^0, where b is an empirical factor, k_H^0 is the preexponential in eq 9, and G_a^0 is the intrinsic activation energy. For methanol the parameters are as follows: $k_H^0 = 3 \times 10^{10}$ s^{-1} and $k_s = 2.1/\tau_D$. From Table 1, we find that the preexponential k_H^0 is solvent dependent and its value is similar to $1/\tau_D$ at room temperature and b ranges from 2 to 4.

TABLE 1: Relevant Parameters for Model Calculations

	$K^*_{a,chem}$	$pK^*_{a,chem}$	G_a^H [kJ/mol]	G_a^0 [kJ/mol]	k_H^0 at 298 K [s^{-1}] 10^{-10}	k_H at 298 K [s^{-1}] 10^{-10}	k_s at 298 K [s^{-1}] 10^{-10}	τ_D[ps] at 298 K	b[b]
MeOH	2.3	−0.37	2.0	3.0	2.9	1.25	4.3	48	2.1
EtOH	2.1	−0.33	2.1	3.0	1.5	0.63	1.7	132	2.3
propanol	2.1	−0.33	2.2	3.0	0.80	0.33	1.4	341	4.0

[a] pK* is calculated by eq 11. The estimated error in the determination of pK* is 8%. [b] b is an empirical factor used in the determination of the proton-transfer rate at the low-temperature range ($k_s = b/\tau_D$, see text).

We used $G_a^0 = 3$ kJ/mol for all three solvents. This value is slightly smaller than the one used by Pines et al.[23] The activation energies are only slightly dependent on the solvent and were calculated according to eq 5 and eq 6. For methanol the activation energy is $G_a^H = 2.0$ kJ/mol and $pK_a^* = -0.37$.

From the model it appears that at low temperatures, a solvent motion with a characteristic time approximately that of the dielectric relaxation time controls the reaction rate of the proton transfer. This is clearly seen in the case of proton transfer to the solvent from excited DCN2 to neat methanol, ethanol, and propanol at $T < 250$ K. At the high-temperature limit the solvent relaxation time is faster than the passage of the proton over the barrier and the overall rate constant is determined by the proton motion.

An extension of this stepwise model can be described by a two-dimensional Markovian reaction−diffusion model.[31,32] Using such a model will increase the effective proton transfer rate, especially in the intermediate temperature range, where $k_s \approx k_H$. From Figure 4 it can be seen that for methanol at this range the computer fit underestimates the experimental proton-transfer rate.

Summary

We have studied by time-resolved emission techniques the proton dissociation and the reversible geminate recombination processes in alcohols. DCN2 is used as the excited-state proton emitter (photoacid). The experimental data are analyzed by the exact numerical solution of the transient Debye−Smoluchowski equation (DSE).

We have found that the proton dissociation rate constant, k_d of excited DCN2 in neat alcohols at temperatures above 10 °C is almost temperature independent, while at $T < 250$ K the proton-transfer rate is similar to the inverse of the dielectric relaxation time. We propose a simple stepwise model to describe and calculate the temperature dependence of proton transfer to the solvent reaction. The calculated temperature dependence is in a good agreement with the experimental results.

Acknowledgment. We thank Prof. L. Tolbert for providing the 5,8-dicyano-2-naphthol. We also thank Prof. N. Agmon and Dr. E. Pines for the helpful discussions. This work was supported by grants from the Israel Science Foundation and the James-Franck German-Israel Program in Laser-Matter Interaction.

References and Notes

(1) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

(2) Huppert, D.; Gutman, M.; Kaufmann, K. J. in *Advances in Chemical Physics*; Jortner, J., Levine, R. D., Rice, S. A., Eds.; Wiley: New York, 1981; Vol. 47, 681. Koswer, E.; Huppert, D. In *Annual Reviews of Physical Chemistry*; Strauss, H. L., Babcok, G. T.; Moore, C. B., Eds.; Annual Reviews, Inc.: New York, 1986; Vol. 37, p 122.

(3) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.

(4) Gutman, M.; Nachliel, E. *Biochim. Biophys. Acta* **1990**, *391*, 1015.

(5) Förster, Th. *Z. Naturwiss.* **1949**, *36*, 186.

(6) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 189.

(7) Kolodny, E.; Huppert, D. *J. Chem. Phys.* **1981**, *63*, 401.

(8) Ando, K.; Hynes, J. T. In *Structure, Energetics, and Reactivity in Aqueous Solution*; Cramer, C. J., Truhlar, D. G., Eds.; ACS Books: Washington, DC, 1994.

(9) Agmon, N.; Huppert, D.; Masad, A.; Pines, E. *J. Phys. Chem.* **1991**, *96*, 952.

(10) Pines, E.; Huppert, D.; Agmon, N. *J. Chem. Phys.* **1988**, *88*, 5620.

(11) Agmon, N.; Pines, E.; Huppert, D. *J. Chem. Phys.* **1988**, *88*, 5631.

(12) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(13) Carmeli, I.; Huppert, D.; Tolbert, L. M.; Haubrich, J. E. *Chem. Phys. Lett.* **1996**, *260*, 109.

(14) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 8163. Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593.

(15) Erdey-Gruz, T.; Lengyel, S. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., Eds.; Plenum: New York, 1964; pp 1−40.

(16) Dolgin, B. MSc Thesis, Ben-Gurion University, Beer Sheva, 1997.

(17) Andrussow, L., Schramm, B., Schaffer, K., Eds. *Landolt-Bornstein*; Springer: Berlin, 1969; Vol. 2, Part 5a.

(18) Richert, R. Unpublished results. Bötcher, C. J. F.; Bordevik, P. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1978; Vol. II, p 254.

(19) Bertolini, D.; Cassettari, M.; Salvetti, G. *J. Chem. Phys.* **1983**, *78*, 365.

(20) Garg, S. K.; Smyth, C. P. *J. Phys. Chem.* **1965**, *69*, 1294.

(21) Agmon, N.; Goldberg, S. Y.; Huppert, D. *J. Mol. Liq.* **1995**, *64*, 161.

(22) Pines, E.; Fleming, G. R. *Chem. Phys. Lett.* **1994**, *183*, 393.

(23) Pines, E.; Magnes, B.; Lang, M. J.; Fleming, G. R. *Chem. Phys. Lett.* **1997**, *281*, 413.

(24) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197. Agmon, N.; Levine, R. D. *Is. J. Chem.* **1980**, *19*, 330.

(25) Solntsev, K.; Huppert, D.; Agmon, N. *J. Chem. Phys.* In press.

(26) Robinson, G. W.; Thistlethwaite, P. J.; Lee, J. *J. Phys. Chem.* **1986**, *90*, 4224.

(27) Rips, I.; Jortner, J. *J. Chem. Phys.* **1987**, *87*, 2090.

(28) Szabo, A. *J. Phys. Chem.* **1989**, *93*, 6929.

(29) Collins, F. C.; Kimball, G. E. *J. Colloid Sci.* **1949**, *4*, 425.

(30) Agmon, N. *J. Phys. Chem.* **1996**, *100*, 1072.

(31) Agmon, N.; Rabinovich, S. *J. Phys. Chem.* **1992**, *97*, 7270.

(32) Bicout, D. J.; Szabo, A. *J. Chem. Phys.* **1998**, *109*, 2325.