J. Phys. Chem. A **2001,** *105,* 4177−4181

Solvent Effects for Nonadiabatic Proton Transfer in the Benzophenone/*N*,*N*-Dimethylaniline Contact Radical Ion Pair

Kevin S. Peters* and Ganghyeok Kim

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

Received: October 20, 2000; In Final Form: February 14, 2001

Picosecond absorption spectroscopy is employed in determining the dynamics of proton transfer within a variety of substituted benzophenones/*N*,*N*-dimethylaniline in a series of alkanenitrile solvents. A correlation of the rate constants for proton transfer with driving force reveals a normal region and an inverted region for proton transfer. The kinetics are analyzed within two theoretical frameworks for nonadiabatic proton transfer. The Borgis−Hynes model, which is based upon a low-frequency promoting mode that modulates the tunneling frequency, is found to be only in qualitative accord with the experiment. The Lee−Hynes model, which not only includes a low-frequency promoting mode but also allows for contributions from vibrational excitation of the proton reaction coordinate in the reactant and product states, is found to give an excellent fit to the experimental data.

Introduction

The nature of the reaction path for proton-transfer processes continues to be the subject of extensive discussion since the first theoretical formulation some 50 years ago.[1] The models developed for describing the dynamics of proton transfer fall within three general categories. The classical model, formulated within the context of transition-state theory, was advanced by Bigeleisen[1] and then extended by Westheimer.[2] The assumed reaction path for the classical model postulates passage of the proton through a transition state defined by a free energy maximum along the proton reaction coordinate. The semiclassical model, developed principally by Bell,[3] modifies the classical model by proposing that, in the vicinity of the transition state, the quantum nature of the proton is manifested through a tunneling contribution to the reaction rate; this formalism has found wide application for numerous kinetic studies, both experimental and theoretical, in chemistry and biochemistry.[4−11] The quantum model for proton-transfer reactions, when there exists an electronic barrier in the proton-transfer coordinate, invokes the transfer as occurring exclusively through tunneling, even at ambient temperatures.[12−21] The thermal activation component for the transfer process is associated with solvent and vibrational reorganization for the system.

From an experimental perspective, distinguishing between the three models is rather problematic given the limited number of variables accessible to the experimentalist. Kinetic deuterium isotope effects have been employed extensively in the study of proton-transfer reactions. However, the magnitude of the kinetic deuterium isotope effect in itself does not allow for the unambiguous distinction in mechanism since isotope effects in the range of 2−7 can be rationalized in each of the three models.[2,3,16] Another parameter often varied in proton-transfer experiments is that of temperature. Examining the kinetics over a wide range in temperature often leads to a high-temperature regime where the reaction is thermally activated and a low-temperature regime where the rate of reaction is independent of temperature. In the semiclassical model, this behavior is attributed to thermal activation for passage of the proton over the reaction barrier in the high-temperature limit and tunneling through the barrier in the low-temperature limit.[4,8] However the quantum model can be used to rationalize this temperature dependence for the thermally activated component is associated with solvent and vibrational reorganizations, and the low-temperature component reflects the quantum nature of the proton and solvent modes.[22]

One experimental approach for distinguishing the semiclassical and quantum models is to examine the functional relationship between the rate of proton transfer and the driving force.[23,24] For the quantum models of nonadiabatic proton transfer, there is the prediction of a parabolic relationship between the rate of proton transfer and the driving force. As with nonadiabatic electron transfer, when the driving force for proton transfer initially increases the rate of reaction increases, but then a further increase in the driving force leads to a decrease in the rate of proton-transfer giving rise to an “inverted region”. The existence of an inverted region in a proton-transfer process serves to distinguish the quantum and semiclassical models.[24] This kinetic behavior was recently observed, for the first time, in the proton-transfer reactions found in the contact radical ion pairs of benzophenones and *N*,*N*-dialkylanilines.[23,24] Varying the overall driving force for proton-transfer reactions by employing varying substituents at the 4,4′ positions of benzophenones, both a normal region and an inverted region were found for the solvents cyclohexane and benzene, supporting the quantum model for proton transfer in this particular system.

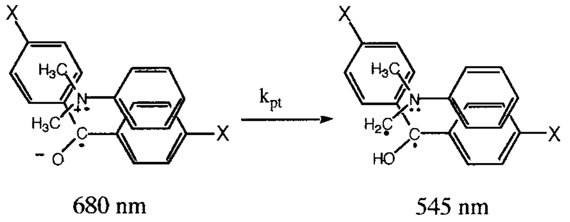
In the present paper we extend our initial studies by examining the dynamics of proton transfer within the contact radical ion pair of benzophenones/*N*,*N*-dimethylaniline in four polar solvents. The goal of the paper is to address the question as to whether a single mode model, developed by Borgis and Hynes for nonadiabatic proton transfer,[15] can account for the functional form of the observed kinetic behavior or whether it is important for the kinetic model to take into account additional vibrational excitations in the reactant and product states associated with the transferring proton, as suggested by Lee and Hynes.[22]

Experimental Section

The solvents acetonitrile, propanenitrile, butanenitrile, and pentanenitrile were obtained from Aldrich; the solvents were

10.1021/jp003889e CCC: $20.00

SCHEME 1



used as received. Benzophenone, 4-chlorobenzophenone, 4-fluorobenzophenone, 4-methylbenzophenone, 4-methoxybenzophenone, 4,4′-dimethoxybenzophenone were obtained from Aldrich, and 4,4′-dimethylbenzophenone was obtained from Kodak. Each was recrystallized from ethanol. *N*,*N*-Dimethylaniline (Aldrich) was distilled from calcium hydride under reduced pressure and stored under argon.

The laser system, based upon a Continuum (PY61C-10) Nd:YAG with a 19 ps pulse width, as been described.[25] The experiments were undertaken at 23 °C, and the sample continuously flowed through a 1 cm quartz cuvette. The samples were irradiated at 355 nm, and the ensuing reaction dynamics of the radical anions of the various benzopheones were monitored at 680 nm.

Results

The photochemistry leading to the formation of benzophenone/*N*,*N*-dimethylaniline triplet contact radical ion pair and subsequent proton transfer to produce the triplet radical pair has been described in detail in a preceding publication;[23] thus the nature of the reaction paths will be only briefly summarized. The 355 nm irradiation of the benzophenones employed in the present experiments, in the presence of 0.4 M *N*,*N*-dimethylaniline, leads to the formation of the first excited singlet state, S_1, of the benzophenones which subsequently intersystem crosses to the triplet state, T_1, on a time scale of 10 ps. The *N*,*N*-dimethylaniline then transfers an electron on the 50 ps time scale to the T_1 state to produce a triplet contact radical ion pair, absorbing at 680 nm. The geometry of the contact triplet radical ion pair is assumed to be that of a π-stack, Scheme 1, which serves to maximize the Coulombic attraction. Proton transfer within the π-stack to produce a triplet radical ion pair, absorbing at 545 nm, occurs on the 100 ps to 1 ns time scale depending on the nature of the solvent.

In polar solvents, competitive with proton transfer is the diffusional separation of the contact radical ion pair to form the solvent separated radical ion pair which does not undergo proton transfer.[23] Thus, the kinetic modeling of the experimental data must account not only for the proton-transfer process, k_{pt}, but also the diffusional separation of the contact radical ion pair, k_{dif}.

$$\mathrm{RP} \xleftarrow{k_{pt}} \mathrm{CRIP} \xrightarrow{k_{dif}} \mathrm{SSRIP}$$

An example of a fit of this model to the experimental data is shown in Figure 1 for 4-methylbenzophenone/*N*,*N*-dimethylaniline in butanenitrile.

The rates of proton transfer, k_{pt}, for each of the substituted benzophenones in the presence of *N*,*N*-dimethylaniline as a function of solvent are presented in Table 1. In addition, the energetics associated with the proton-transfer process k_{pt} for decay of the triplet contact radical ion pair giving rise to the triplet radical pair are also given in Table 1. The methodology for deriving the enthalpy changes associated with each of the transformations has been discussed in a preceding publication and will not be reiterated.[23]

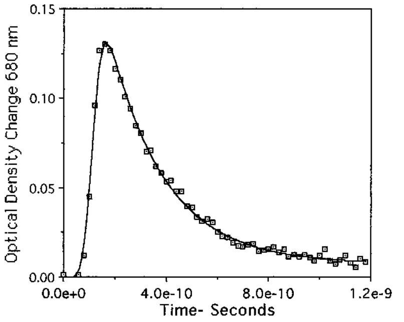


Figure 1. Transient absorption at 680 nm following the 355 nm excitation of 0.02 M/0.4 M 4-methylbenzophenone/*N*,*N*-dimethylaniline in butanenitrile (where the notation "4.0e-10", for example, means 4.0 $\times$ 10^{-10}): $k_{pt} = 4.3 \times 10^9$ s^{-1}; $k_{dif} = 2 \times 10^8$ s^{-1}; pulse width, 25 ps; $t_0 = 95$ ps. Key: (squares) experimental points; (solid line) fit to data.

Discussion

In the following discussion, we begin by briefly presenting the theory developed by Borgis and Hynes for nonadiabatic proton transfer; a more extensive presentation of the theory for nonadiabatic proton transfer can be found in the first paper of this series.[23] We will examine how accurately the Borgis–Hynes model accounts for the kinetic behavior of proton transfer within benzophenone/dimethylaniline contact radical ion pairs, focusing particularly on the rates of proton transfer as a function of driving force for the solvent butanenitrile; we find that the predictions of this model is only in qualitative accord with the experimental data. This discussion is then followed by an analysis of the kinetic data within the context of the Lee–Hynes model for nonadiabatic proton transfer, which extends the Borgis–Hynes model by allowing for vibrational excitation in the reactant state and product state for the transferring proton.

Borgis–Hynes Model. The kinetics of proton-transfer reactions are governed by the degree of coupling between the reactant state and the product state.[15] When the coupling is weak, due to a large separation between the two heavy atoms involved in the proton transfer, the reaction falls within the nonadiabatic regime. In this regime the vibrational mode associated with the transferring proton lies below the maximum of the electronic energy barrier associated with the proton-transfer coordinate. The reaction path for proton-transfer entails tunneling through the reaction barrier associated with the proton-transfer coordinate. When the distance between the two heavy atoms decreases leading to an enhanced coupling between the reactant state and product state so that the barrier for reaction is below the zero point energy of the proton stretch, then the reaction falls within the adiabatic regime. In this regime, the proton does not encounter an electronic barrier in the proton-transfer coordinate, and thus the rate-limiting motion involves the reorganization of the solvent structure. Thus, the choice of the theoretical model to be employed in the analysis of proton-transfer dynamics will depend on whether the reaction falls within the adiabatic or nonadiabatic regimes.

In our original study of the dynamics of proton transfer within the benzophenone/dimethylaniline contact radical ion pairs, we argued that the reaction occurs within the nonadiabatic regime.[23] This is attributed to the constraints imposed by the structure of the contact radical ion pair, Scheme 1. It is estimated that the separation between the π-stack system is of the order of 3.3 Å, which places the reaction in the nonadiabatic regime; from model calculations, the adiabatic regime becomes important for

TABLE 1: Observed Rate Constants, k_{pt}, and the Negative Enthalpy Change, *E*, for Proton Transfer in Substituted Benzophenone/Dimethylaniline Triplet Contact Radical Ion Pairs

compnd		pentanitrile		butanenitrileile		propanenitrilerile		acetonitrile	
4	4′	E^a	$k_{pt}{}^b$ ($\times 10^9$ s^{-1})	E	k_{pt} ($\times 10^9$ s^{-1})	E	k_{pt} ($\times 10$ ^{9} s^{-1})	E	k_{pt} ($\times 10^9$ s^{-1})
CH_3O	CH_3O	8.4	2.7	8.2	3.2	8.0	4.3	7.4	3.9
CH_3	CH_3	5.9	3.8	5.7	4.3	5.5	4.1	5.0	2.9
CH_3O	H	5.9	3.6	5.7	4.0	5.5	4.0	5.0	2.9
CH_3	H	4.6	4.2	4.4	4.3	4.2	3.8	3.7	2.3
H	H	3.6	4.2	3.4	3.9	3.2	2.9	2.7	1.3
F	F	3.0	4.1	2.8	3.9	2.6	2.6	2.1	1.0
Cl	H	1.8	3.1	1.6	2.9	1.4	1.8	0.9	0.7

[a] Kilocalories per mole. [b]Estimated uncertainties in rate constants ±10% (1σ).

distances less than 2.5 Å.[15] Furthermore, the dependence of the rate constants for proton transfer upon the driving force for reaction is in accord with the theoretical predictions of nonadiabatic proton transfer for the existence of an inverted region. An inverted region does not exist for adiabatic proton transfer.[15]

Borgis' and Hynes' theoretical model for nonadiabatic proton transfer is based upon a Landau−Zener curve crossing formalism.[15] The nonadiabatic rate constant is given by

$$k = \sum_n \sum_m P_n\, k_{nm} \qquad (1)$$

where

$$k_{nm} = 2\pi (C_{nm}/2)^2 (\pi/h^2 k_B T E_s)^{1/2} \exp(-\Delta G^{\ddagger}{}_{nm}/k_b T) \qquad (2)$$

$$\Delta G^{\ddagger}{}_{nm} = (\Delta E + E_s + \Delta E_{nm})^2/4E_s \qquad (3)$$

The free energy of activation, $\Delta G^{\ddagger}{}_{nm}$, depends parametrically upon the energetics of the reaction asymmetry ΔE, normally defined as the enthalpy change for the reaction, the solvent reorganization energy, E_s, and the vibrational asymmetry on going from the n vibrational level in the reactant state to the m vibrational level in the product state, ΔE_{nm}. The parameter P_n is the Boltzmann term for the thermal population over the states n in the reactant. The tunneling term C_{nm} is given by

$$C_{nm}{}^2 = C_0{}^2 \exp(-\alpha \Delta Q_e) \exp((E_\alpha - E_Q)/h\omega_Q)\, F[L(E_Q, E_\alpha, \omega_Q)] \qquad (4)$$

The tunneling term depends critically upon a low-frequency vibrational mode Q which serves to decrease the distance between the two heavy atoms between which the proton tunnels and thus exponentially enhances the rate of proton transfer. The vibrational frequency associated with Q is ω_Q, and the reorganization energy for Q is E_Q. In the Borgis−Hynes model, the nth vibration in the reactant and the mth vibration in the product are associated with the low-frequency promoting mode Q. The term α is a parameter that governs the exponential decay of the tunneling matrix element with distance; values for α range from 25 to 35 Å^{-1}.[15] The energy entity E_α is a quantum term associated with the proton reaction coordinate coupling to the Q vibration, $E_\alpha = h^2\alpha^2/2m$, where m is the reduced mass associated with vibration Q. C_0 is the tunneling matrix element for the proton transfer from the 0 vibrational level in the reactant state to the 0 vibrational level in the product state for the low frequency promoting modes. The term ΔQ_e is the shift in the oscillator equilibrium position. $F[L(E_Q,E_\alpha,\omega_Q)]$ is a function of a Laguerre polynomial.[15] In terms of the all important promoting mode Q, the present manifestation of the Borgis−Hynes theory is inherently a single mode model.[15)] However, for the contact radical ion pair of benzophenone/dimethylaniline, potentially several low-frequency vibrations would serve to reduce the distance between the two heavy atoms and thus contribute to enhancing the rate of proton transfer. The question then arises as to whether a single mode picture can account for the observed correlation between the rate of proton transfer and the driving force. To this end, we have examined how accurately Borgis−Hynes theory can account for the observed correlation between rate constants and the driving force. Given the great number of parameters contained within the theory of nonadiabatic proton transfer, it is not possible to achieve a unique fit of the theory to the kinetic data for proton transfer within the substituted benzophenone/dimethylaniline contact radical ion pairs in the solvents employed in the present study. Since it is not possible to determine the tunneling matrix element C_0 nor the magnitude of the change in the displacement in the promoting mode Q, ΔQ_e, in our fit of the theoretical model to the experimental data, we calculate only a reduced rate of proton transfer defined by $k/C_0{}^2 \exp(-\alpha\Delta Q_e)$. Furthermore, for this one-dimensional model, we assume that the frequency of the promoting mode Q is 400 cm^{-1} and the associated reorganization energy E_Q = 1.0 kcal/mol. Finally, an estimation of E_α is based upon the Borgis and Hynes determination of a E_α = 5.0 kcal/mol for the O−H···O system, where the reduced mass is 8 amu and α = 30 Å^{-1}.[15] For the benzophenone/dimethylaniline contact radical ion pair, the reduced mass of the complex is of the order of 84 amu, assuming that Q is associated with the vibration that changes the internuclear separation of the contact radical ion pair. Since E_α is inversely related to the reduced mass, the value of E_α for the contact radical ion pair should be of the order of 1.0 kcal/mol. Therefore, the only remaining parameter to be varied in modeling the kinetic data is the solvent reorganization energy, E_s. The optimum fit of the theoretical model to the experimental data for the solvent butanenitrile occurs where E_s = 1.5 kcal/mol when E_α and E_Q are set to 1.0 kcal/mol, as shown in Figure 2.

Although the prediction of the Borgis−Hynes model, Figure 2, is in qualitative accord with the experimental data, it does fail in a quantitative sense because the model underestimates the rate constant for proton transfer in the regimes of both low and high driving force. As previously suggested, the discrepancy between the fit of theory to experiment may lie in the single mode nature of Borgis−Hynes model.[12] Within the contact radical ion pair, several vibrational modes may serve to reduce the distance associated with proton transfer and thus several vibrational modes may serve to enhance the rate of proton tunneling. Thus, a more realistic model would provide for the summation over numerous promoting vibrational modes. In addition, for reactions that are exothermic, the possibility exists for producing product states where the O−H oscillator is vibrationally excited; this is not taken into account in the present formulation of the Borgis−Hynes theory for nonadiabatic proton transfer.

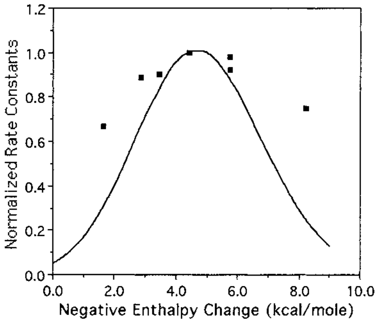


Figure 2. Plot of the normalized rate constants for proton transfer versus negative enthalply change ($-\Delta E$, kcal/mol) for the solvent butanenitrile. Key: (squares) experimental data. The solid curve is calculated rate constants for proton transfer based on eq 1, where $E_s = 1.5$ kcal/mol, $E_\alpha = 1.0$, $E_Q = 1.0$, $\omega_Q = 400$ cm^{-1}, and $T = 298$ K.

Although the correlation between the Borgis−Hynes theory for nonadiabatic proton transfer is only in qualitative accord with the present experiments, the theory does make the important prediction, which is born out by experiment, that an inverted region should exist in the correlation of the rate constant for proton transfer with driving force. This kinetic behavior cannot be found for models that are derived from transition-state theory.

Lee−Hynes Model. In 1996, Lee and Hynes developed a theory for nonadiabatic proton transfer that not only incorporates the features of the Borgis−Hynes model but also allows for the contributions to the rate constant from the excited vibrations associated with the transferring proton in both the reactant and product states.[22] Thus, the model includes the features of a proton reaction coordinate coupled to the solvent, a low-frequency vibration Q which modulates the distance associated with proton tunneling, and contributions from vibrational excitation for the reacting proton in both the reactant state and product state.

The reaction rate for the tunneling of the proton from the *n*th vibrational level in the reactant state to the *m*th vibrational level in the product state which is associated with the vibration along the proton-transfer coordinate, is given by[22]

$$k(n_r \rightarrow m_p) = k_{m_p,n_r}(0)(\pi/2A_2)^{1/2}\exp(-A_1{}^2/2A_2) \qquad (5)$$

where $k_{m_p,n_r}(0)$, A_1, and A_2 are defined as

$$k_{m_p,\, n_r}(0) = 2(2\pi/h)^2[C_{m_p,n_r}(Q)]^2 \exp\{2\coth(\beta E/2)\} \qquad (6)$$

$$A_1 = (2\pi/h)\{\Delta E + E_s + E_Q + E_\alpha + (2\pi/h)[m_P\omega_P - n_R\omega_R]\} \qquad (7)$$

$$A_2 = 2(2\pi/h)^2 k_B T\{E_s + (E_\alpha + E_Q)(\beta h\omega_Q/4\pi \coth\{\beta h\omega_Q/4\pi\}) \qquad (8)$$

In the above expression, ω_R and ω_P are the frequencies associated with the *n*th level of the reacting proton in the reactant state and the *m*th level in the product state, and ω_Q is the frequency associated with the low-frequency mode developed in the Borgis−Hynes model. $C_{m_p,n_r}(Q)$ is the tunneling matrix element from the *n*th level in the reactant state to the *m*th level in the product state. The definition of the remaining terms can be found in the preceding discussion of the Borgis−Hynes model. In this formulation, both the anharmonicity of the vibrational mode, σ, and the net displacement in the promoting mode Q, ΔQ, have not been taken into account; a more complete treatment of the Lee−Hynes model incorporating these terms can be found in reference 22.

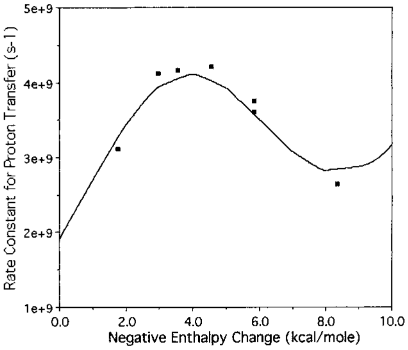


Figure 3. Plot of the rate constants for proton transfer versus negative enthalphy change ($-\Delta E$, kcal/mol) for the solvent pentanenitrile (where the notation "5e+9", for example, means 5×10^9). Key: (squares) experimental data. The solid curve is the calculated rate constants for proton transfer based on eq 5, where $E_s = 7.0$ kcal/mol, $E_\alpha = 1.0$, $E_Q = 0.0$, $\omega_Q = 200$ cm^{-1}, $\omega_R = 3000$ cm^{-1}, $\omega_P = 3500$ cm^{-1}, $\omega^\ddagger = 2500$ cm^{-1}, $V^\ddagger = 17.5$ kcal/mol, and $T = 298$ K.

An explicit evaluation of the tunneling matrix element $C_{m_p,n_r}(Q)$ is obtained within the WKB semiclassical framework[22] and is given by

$$C_{m_p,n_r}(Q) = (h/4\pi^2)(\omega_R\omega_P)^{1/2}\exp\{-2\pi^2/h\omega^\ddagger[V^\ddagger - (1/2)(V_{n_r} + V_{m_p})]\} \qquad (9)$$

where $\omega^\ddagger$ is the frequency associated with the inverted parabola of the transition state for the proton-transfer coordinate, $V^\ddagger$ is the energy of the transition state, and V_{n_r} and V_{m_p} are the energies of the reactant state and the product state, which depends on the level of vibrational excitation in the two states. For the present analysis, we assume that the vibrational frequency in the reactant state, associated with the C−H stretch, is 3000 cm^{-1} while the vibrational frequency in the product state, associated with the O−H stretch, is 3500 cm^{-1}. The frequency of the transition state, $\omega^\ddagger$, is set to 2500 cm^{-1}.[12] Thus, the only variable contained within the expression for the tunneling matrix element that will serve as a fitting parameter in the data analysis for the four solvents is the barrier height, $V^\ddagger$.

The fitting of the Lee−Hynes model begins with the consideration of the kinetic data in the solvent pentanenitrile. Given that the vibrational frequency, ω_Q, for the internuclear separation of the contact radical ion pair which serves as the promoting mode Q is unknown, a value of 200 cm^{-1} is assumed.[15] Also, the modified formulation of the Lee−Hynes model given in eqs 5−9 does not take into account a shift in the equilibrium position for the mode Q upon proton transfer; therefore, the vibrational reorganization energy for Q, E_Q, is set to 0. Thus, the only parameters remaining to be specified are the solvent reorganization energy E_s and the barrier height, $V^\ddagger$. The optimum fit of the model to the experimental data occurs when $E_s = 7.0$ kcal/mol and $V^\ddagger = 17.5$ kcal/mol, as shown in Figure 3. It is evident that the Lee−Hynes model yields are far more satisfactory fits to the kinetic data relative to the Borgis−Hynes model.

Applying the Lee−Hynes model to the remaining set of experimental data, it is assumed that the effect of a change in the solvent polarity will be manifested only in the solvent reorganization energy, E_s, as well as vibrational frequency of the promoting Q, ω_Q, given Coulombic nature of the molecular interaction within the contact radical ion pair. For simplicity, the barrier height $V^\ddagger$ is assumed to be only minimally effected

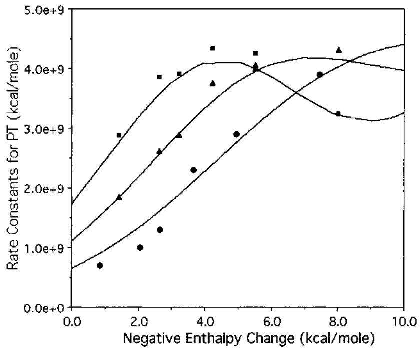


Figure 4. Plot of the rate constants for proton transfer versus negative enthalpy change (-ΔE, kcal/mol; the notation "5.0e+9", for example, means 5.0×10^9). Key: (squares) butanenitrile data; (triangles) propanenitrile data; (circles) acetonitrile data. The solid curve is the calculated rate constants for proton transfer based on eq 5. Butanenitrile: $E_s = 8.0$ kcal/mol; $E_\alpha = 1.0$; $E_Q = 0.0$; $\omega_Q = 195$ cm^{-1}; $\omega_R = 3000$ cm^{-1}; $\omega_P = 3500$ cm^{-1}; $\omega^\ddagger = 2500$ cm^{-1}; $V^\ddagger = 17.5$ kcal/mol; $T = 298$ K. Propanenitrile: $E_s = 12.0$ kcal/mol; $E_\alpha = 1.0$; $E_Q = 0.0$; $\omega_Q = 179$ cm^{-1}, $\omega_R = 3000$ cm^{-1}; $\omega_P = 3500$ cm^{-1}; $\omega^\ddagger = 2500$ cm^{-1}; $V^\ddagger = 17.5$ kcal/mol; $T = 298$ K. Acetonitrile: $E_s = 17.0$ kcal/mol; $E_\alpha = 1.0$; $E_Q = 0.0$; $\omega_Q = 164$ cm^{-1}; $\omega_R = 3000$ cm^{-1}; $\omega_P = 3500$ cm^{-1}; $\omega^\ddagger = 2500$ cm^{-1}; $V^\ddagger = 17.5$ kcal/mol; $T = 298$ K.

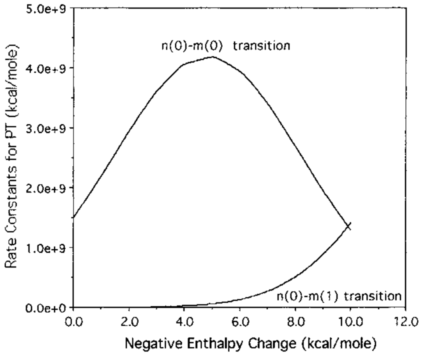


Figure 5. Calculated rate constants for proton transfer based upon eq 5 for the $n(0) \rightarrow m(0)$ transition and $n(0) \rightarrow m(1)$ transition (the notation "5.0e+9", for example, means 5.0×10^9), where $E_s = 7.0$ kcal/mol, $E_\alpha = 1.0$, $E_Q = 0.0$, $\omega_Q = 200$ cm^{-1}, $\omega_R = 3000$ cm^{-1}, $\omega_P = 3500$ cm^{-1}, $\omega^\ddagger = 2500$ cm^{-1}, $V^\ddagger = 17.5$ kcal/mol, and $T = 298$ K.

by a change in dielectric upon replacing the solvent pentanitrile ($\epsilon = 19.5$) by the more polar solvents. With $V^\ddagger$ set to 17.5 kcal/mol, the fit of the Lee−Hynes model to the remaining sets of kinetic data is shown in Figure 4. The derived values for the parameters E_S and ω_Q are as follows: butanenitrile ($E_s = 8.0$ kcal/mol and $\omega_Q = 195$ cm^{-1}), propanenitrile ($E_s = 12.0$ kcal/mol and $\omega_Q = 179$ cm^{-1}), and acetonitrile ($E_s = 17.0$ kcal/mol and $\omega_Q = 164$ cm^{-1}). Clearly the Lee−Hynes model gives an excellent account for the solvent dependence of the rate of proton transfer as a function of the enthalpy change for proton transfer.

It must be emphasized at this point in the discussion that in fitting the Lee−Hynes model to the experimental data, the various parameters contained within the theory are highly correlated so that given the limited amount of experimental data, no unique fit of the model to the experiment can be achieved. Thus, caution must be exercised in the interpretation of the derived parameters.

In the application of the Lee−Hynes model for the analysis of the pentanenitrile kinetic data shown in Figure 3, the question arises as to what contribution does the formation of vibrationally excited product states make to the overall rate constant for proton transfer. The individual rate constants, given by eq 5, as a function of driving force are shown in Figure 5. The $n(0) \rightarrow m(0)$ transition has a maximum rate when the enthalpy change for the reaction is −5 kcal/mol. The $n(0) \rightarrow m(1)$ transition begins to contribute to the overall rate constant for enthalpy changes greater than −6 kcal/mol; at −10 kcal/mol, the $n(0) \rightarrow m(1)$ transition begins to dominate the $n(0) \rightarrow m(0)$ transition. In our modeling, we examined the contribution from vibrationally excited reactant, the $n(1) \rightarrow m(0)$ and $n(1) \rightarrow m(1)$ transitions and found that they do not significantly contribute to the overall rate constant. Although the tunneling frequencies are greater for these transitions, the Boltzmann population at 298 K of the $n(1)$ level, corresponding to 3000 cm^{-1} above the zero point energy, is exceedingly low, leading to a negligible contribution to the overall rate constant for proton transfer.

Conclusions

In the preceding discussion, we have analyzed the kinetic data for proton transfer in the benzophenone/*N*,*N*-dimethylaniline contact radical ion pair within the context of both the Borgis−Hynes model and the Lee−Hynes model for proton transfer. Although the Borgis−Hynes model predicts an inverted region for the kinetics of proton transfer in the nonadiabatic regime, the model cannot quantitatively reproduce the experimental data. This would suggest that the single mode nature of the theory is incomplete. By incorporating the vibrational contributions associated with the reacting proton in the reactant and product states into the Borgis−Hynes model, the Lee−Hynes model appears to account for the important parameters governing the dynamics of proton transfer. A more rigorous test of the Lee−Hynes model will come when the rates of proton transfer in the contact radical ion pair are examined as a function of temperature and when the proton is replaced by a deuteron. Such experiments are in progress.

Acknowledgment. This work is supported by grants from the National Science Foundation, CHE-9816540.

References and Notes

(1) Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675.
(2) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.
(3) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.
(4) Kohen, A.; Klinman, J. P. *Acc. Chem. Res.* **1998**, *31*, 397.
(5) Silverman, D. N. *Biochim. Biophys. Acta* **2000**, *1458*, 88.
(6) Scheiner, S. *Acc. Chem. Res.* **1985**, *18*, 174.
(7) O'Ferrall, R. A. M. *J. Chem. Soc. B* **1970**.
(8) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.
(9) Kim, Y.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 7116.
(10) Truhlar, D. G.; Gordon, M. S. *Science* **1990**, *249*, 491.
(11) Saunders, W. H. J. *J. Am. Chem. Soc.* **1985**, *107*, 164.
(12) Borgis, D. C.; Lee, S.; Hynes, J. T. *Chem. Phys. Lett.* **1989**, *162*, 19.
(13) Borgis, D.; Hynes, J. T. *The Enzyme Catalysis Process*; Plenum: New York, 1989.
(14) Borgis, D.; Hynes, J. T. *J. Chem. Phys.* **1991**, *94*, 3619.
(15) Borgis, D.; Hynes, J. T. *J. Phys. Chem.* **1996**, *100*, 1118.
(16) Kuznetsov, A. M. *Charge Transfer in Physics, Chemistry and Biology*; Gordon and Breach: Luxembourg, 1995.
(17) Cukier, R. I.; Morillo, M. *J. Chem. Phys.* **1989**, *91*, 857.
(18) Morillo, M.; Cukier, R. I. *J. Chem. Phys.* **1990**, *92*, 4833.
(19) Li, D.; Voth, G. A. *J. Phys. Chem.* **1991**, *95*, 10425.
(20) Lobaugh, J.; Voth, G. A. *J. Chem. Phys.* **1994**, *100*, 3039.
(21) Barbara, P. F.; Walsh, P. K.; Brus, L. E. *J. Phys. Chem.* **1989**, *93*, 29.
(22) Lee, S.; Hynes, J. T. *J. Chim. Phys.* **1996**, *93*, 1783.
(23) Peters, K. S.; Cashin, A.; Timbers, P. *J. Am. Chem. Soc.* **2000**, *122*, 107.
(24) Peters, K. S.; Cashin, A. *J. Phys. Chem. A* **2000**.
(25) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1993**, *97*, 3761.
(26) Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 10337.
(27) Vath, P.; Zimmt, M. B. *J. Phys. Chem. A* **2000**, *104*, 2626.