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A Theory–Experiment Conundrum for Proton Transfer

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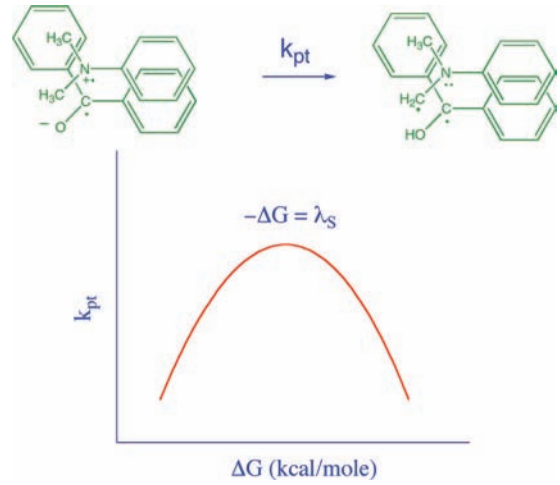
CONSPECTUS

For the past 60 years, the framework for understanding the kinetic behavior of proton transfer has been transition state theory. Found throughout textbooks, this theory, along with the Bell tunneling correction, serves as the standard model for the analysis of proton/hydrogen atom/hydride transfer. In comparison, a different theoretical model has recently emerged, one which proposes that the transition state occurs within the solvent coordinate, not the proton transfer coordinate, and proton transfer proceeds either adiabatically or nonadiabatically toward product formation. This Account discusses the central tenets of the new theoretical model of proton transfer, contrasts these with the standard transition state model, and presents a discrepancy that has arisen between our experimental studies on a nonadiabatic system and the current understanding of proton transfer.



Transition state theory posits that in the proton transfer coordinate, the proton must surmount an electronic barrier prior to the formation of the product. This process is thermally activated, and the energy of activation is associated with the degree of bond making and bond breaking in the transition state. In the new model, the reaction path involves the initial fluctuation of the solvent, serving to bring the reactant state and the product state into resonance, at which time the proton is transferred either adiabatically or nonadiabatically to form the product. If this theory is correct, then all of the deductions derived from the standard model regarding the nature of the proton transfer process are called into question.

For weakly hydrogen-bonded complexes, two sets of experiments are presented supporting the proposal that proton transfer occurs as a nonadiabatic process. In these studies, the correlation of rate constants to driving force reveals both a normal region and an inverted region for proton transfer. Yet, the experimentally observed kinetic behavior does not align with the recent theoretical formulation for nonadiabatic proton transfer, underscoring the gap in the collective understanding of proton transfer phenomena.

Introduction

Proton transfer processes are ubiquitous in chemistry and biochemistry.[1] As such, proton transfer reactions have been the subject of investigation by both theory and experiment for well over 60 years. Today, the standard theoretical framework for the interpretation of proton transfer experiments is based upon Eyring transition state theory the development of which began in 1935.[2] In 1949, Biegeleisen extended transition state theory to account for the kinetic deuterium isotope effect.[3] By 1960, Westheimer formulated a model for the kinetic deuterium isotope effect that found wide-ranging application in organic and biochemical reactions and was used to gain insight into the properties of the transition states associated with

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proton transfer.[4] The essence of model is that there is an activated complex located along the proton-transfer coordinate through which the system traverses. The origin of the kinetic-isotope effect is traced to the difference in the energies of the zero-point vibrations in the reactant and transition states. This standard model is found throughout the textbooks today.[5−8]

In the above treatments, the quantum nature of the proton is expressed only in the vibrational frequencies of the reactive modes found in the reactant state and the transition state. Acknowledging the quantum characteristics of the proton, Bell modified the transition state model for proton transfer to allow for proton tunneling in the region of the transition state; the tunneling correction to transition state theory serves to enhance the predicted rate of proton transfer relative to the standard model.[9] Transition state theory with the Bell tunneling correction is extensively employed in molecular dynamic simulations of proton, hydrogen atom, and hydride transfers in enzymatic systems.[10−12]

While transition state theory gained acceptance as the standard theoretical framework for the discussion of proton transfer reactions, a very different theoretical perspective for proton transfer was developed in the 1960s that received little attention from the chemistry community. German, Kuznetsov, and Dogonadze proposed that the transition state is to be found in the solvent coordinate, much like nonadiabatic electron transfer, and not in the proton transfer coordinate.[13−15] The reaction path involves an initial solvent fluctuation to bring the reactant and product states into resonance subsequent to which the proton tunnels through the adiabatic electronic barrier found in the proton transfer coordinate; proton transfer does not require thermal activation to surmount the electronic barrier in the proton transfer coordinate. This reaction pathway is referenced as nonadiabatic proton transfer. If the solvent fluctuation brings the reactant state and product state into resonance where there is no electronic barrier in the proton transfer coordinate, then the proton will move across the surface in a vibrational motion not requiring the penetration of an electronic barrier; this reaction pathway is adiabatic proton transfer. This nonconventional view of proton transfer has since received further theoretical elucidation and amplification by Hynes and co-workers.[16−18] The Hynes model for nonadiabatic proton transfer has been incorporated into Hammes-Schiffer's theory of proton-coupled electron transfer.[19]

In 2000, our research group initiated an experimental program whose focus is to examine the nature of the reaction pathways for proton transfer in light of the contrasting views presented by the Bell tunneling corrected transition state theory and nonadiabatic proton theories of Kuznetsov and Hynes.[20,21] In particular, we seek to ascertain how the rate constant of proton transfers depends upon driving force.[22−25] The inspiration for these studies comes from Closs and Miller's pioneering investigations into nonadiabatic electron transfer where they found both a normal region and an inverted region in the correlation of the rate constants of electron transfer with driving force, kinetic behavior that is consistent with Marcus nonadiabatic electron transfer theory.[26,27] Prior to our studies, an inverted region for proton transfer had not been observed. However in 2000, we reported a study of driving force dependence of the rate constants for proton transfer within variously substituted benzophenones/*N*,*N*-dimethylaniline triplet contact radical ion pairs and found both a normal region and an inverted region for proton transfer.[21] As will be shown in the following discussion, an inverted region can only arise for nonadiabatic proton transfer. A few years later in 2003, Savéant and co-workers presented evidence for an inverted region in the proton transfer reactions of diphenylmethyl carbanion with a variety of acids.[28] Both our studies and the Savéant study suggest that the reaction pathway for proton transfer for our two systems falls within the nonadiabatic regime. The experimentally observed correlation of rate constants for proton transfer with driving force cannot be accommodated within the Bell tunneling corrected transition state model.

In 2004, Kiefer and Hynes further expanded their theoretical analysis of nonadiabatic proton transfer reactions in a polar environment to include kinetic isotope effects.[18,29] Furthermore, they examined the contributions of excited vibrational modes in the product state to the overall reaction path for nonadiabatic proton transfer. To our surprise, they found that the correlation of the rate constants for proton transfer with driving force for nonadiabatic proton transfer should not display an inverted region if excited vibrations in the product state are active. This predicted dynamical behavior is not consistent with our studies as well as those of Savéant. To date, this inconsistency between theory and experiment is not resolved.

This Account seeks to clarify the nature of the inconsistency between theory and experiment. To this end, the underlying principles for nonadiabatic proton transfer, as formulated by Hynes, will first be presented. Then the two sets of experimental studies that suggest the nonadiabatic nature of the proton transfer are discussed. Finally, the origin of the source of the discrepancy between theory and experiment is examined.

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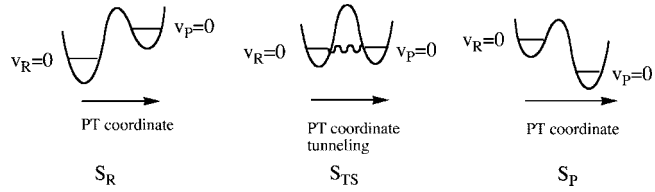

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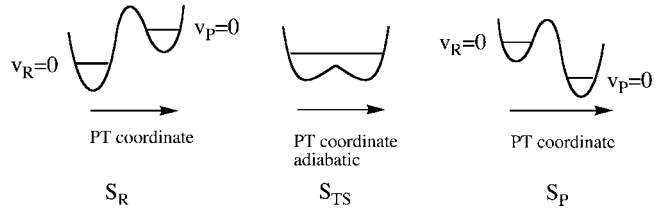


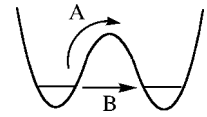
Nonadiabatic and Adiabatic Proton Transfer

The theory for nonadiabatic proton transfer, as developed by both Kuznetsov and Hynes, envisions a reaction coordinate comprised of a solvent fluctuation bringing the reactant and product states into resonance, followed by proton tunneling through an adiabatic electronic barrier in the proton transfer coordinate to form the product state, which is subsequently stabilized by solvent relaxation.[13,18,30] These processes are depicted in Scheme 1.

The initial state for the system has the solvent equilibrated with the reactants, S_R. At this solvent configuration, the reactants are lower in energy than the products. However, due to thermal fluctuations of the solvent, the solvent structure about the reactants can change leading to a destabilization of the reactant state and a stabilization of the product state. There will be a solvent structure, S_{TS}, where the reactant state and product state are isoenergetic. At this solvent configuration, the proton tunnels from the ground vibrational state of the reactant, $v_R = 0$, to the ground vibrational state of the product, $v_P = 0$. Following proton transfer, the solvent undergoes a further fluctuation that serves to stabilize the product state relative to the reactant state, S_p, completing the reaction.

While nonadiabatic proton transfer is assumed to be the dominant reaction pathway for weakly hydrogen-bonded complexes, adiabatic proton transfer is assumed to be the dominant reaction pathway for strongly hydrogen-bonded complexes, Scheme 2.[17] Again, the reactant state has a solvent structure S_R. A thermal fluctuation of the solvent structure leads to the destabilization of the reactant state and stabilization of the product state resulting in an equilibration of the two states at S_{TS}. If the electronic coupling between the reactant state and product state is very large, the electronic barrier in the proton transfer coordinate will lie below the zero-point vibration of the transferring mode; the transferring proton does not encounter an electronic barrier in the proton transfer coordinate and thus moves adiabatically across the reaction surface. The reaction is completed upon the evolution of the solvent structure from S_{TS} to S_P. The free energy for activation for adiabatic proton transfer, $\Delta G^{\ddagger}$ is given by

SCHEME 3



$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \alpha_0 \Delta G_{RXN} + \alpha_0' \frac{(\Delta G_{RXN})^2}{2} \qquad (1)$$

where $\Delta G_0^{\ddagger}$ is the intrinsic reaction barrier at $\Delta G_{RXN} = 0$, α_0, the Brønsted coefficient, is the derivative of the reaction barrier with respect to ΔG_{RXN} evaluated at $\Delta G_{RXN} = 0$, and α_0' is the Brønsted coefficient slope evaluated at $\Delta G_{RXN} = 0$.[17] The correlation of the rate constant for proton transfer with ΔG_{RXN} cannot give rise to an inverted region under the conditions of adiabatic proton transfer.

Returning to nonadiabatic proton transfer, support for the tunneling path as the dominant reaction pathway when the reactant state and product states are at equal energies, S_{TS} in Scheme 1, is found in the theoretical modeling of Assouz and Borgis.[31] They examined the reaction dynamics for proton transfer in the model system OH−N where the molecular parameters are those associated with a weak hydrogen-bonded complex so that there is an electronic barrier in the proton reaction coordinate, Scheme 3; the barrier height is 12 kcal/mol when the O−N separation is 2.7 Å.

The question becomes, does the transfer process occur by thermal activation in the proton transfer coordinate, k_{TS} (pathway A), or by tunneling through the adiabatic electronic barrier, k_{LZ} (pathway B). The tunneling reaction path is modeled as a quantum hopping process within the context of Landau−Zener theory. The classical reaction pathway is described by transition state theory with the Bell tunneling correction at the transition state. They found that the nonadiabatic pathway k_{LZ} dominates the conventional Bell corrected transition state pathway k_{TS} by $k_{LZ}/k_{TS} = 200$. Azzouz and Borgis conclude that solvent fluctuations modulating the tunneling process is the fundamental reaction pathway. The importance of solvent fluctuations as a governing factor in proton transfer is not captured by transition state theory with the Bell tunneling correction. The limits of the generalization

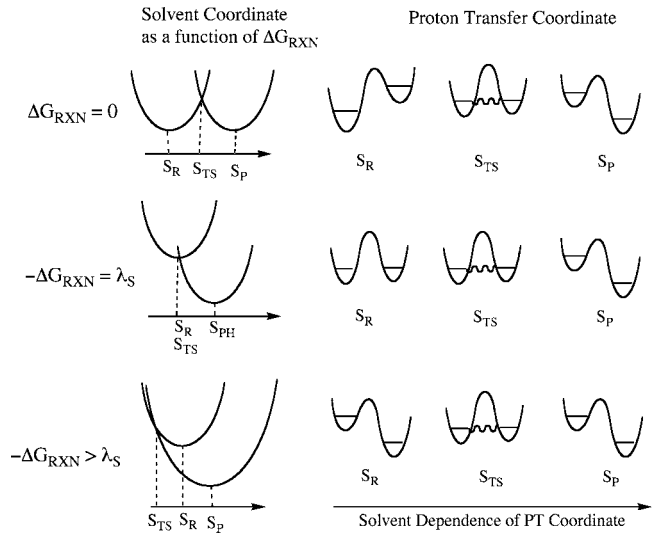
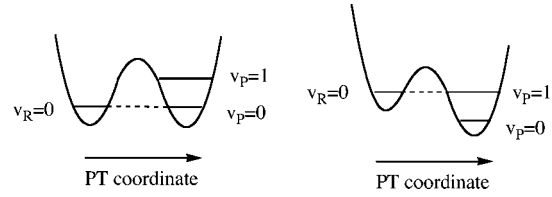


FIGURE 1. Potential energy surfaces for solvent fluctuations and proton transfer as a function of driving force, ΔG_{RXN}: λ_S is the solvent reorganization energy; S_R is the solvent structure around the reactants; S_{TS} is the solvent structure at the transition state in the solvent coordinate; S_P is the solvent structure around the products. Proton tunneling occurs at solvent configuration S_{TS}.

that $k_{LZ} \gg k_{TS}$ have not been fully explored theoretically and await further elucidation.

If the dominant tunneling reaction path involves tunneling between the lowest vibrational energy levels of the reactant and product states, then there should be a normal and inverted region in the correlation of the rate constants for proton transfer with driving force. This can be understood with the aid of Figure 1. When $\Delta G_{RXN} = 0$ for reaction, there is a barrier in the solvent coordinate located at S_{TS} whose amplitude is $\lambda_s/4$, where λ_s is the solvent reorganization energy; this is the energy required to transform the reactants into the products holding the solvent structure unchanged. A similar term is found in nonadiabatic electron transfer.[26] For reaction to occur, there must be a thermal activation in the solvent coordinate to bring the reactant state and product states into resonance at which point the tunneling occurs. For proton transfer reactions where the overall energy change matches the solvent reorganization energy, $-\Delta G_{RXN} = \lambda_s$ in Figure 1, there is no barrier in the solvent coordinate and the rate for overall proton transfer will be at a maximum. Finally, if the overall driving force for proton transfer is greater than the solvent reorganization energy, $-\Delta G_{RXN} > \lambda_s$ in Figure 1, a barrier reappears in the solvent coordinate so that there must again be a solvent fluctuation prior to proton tunneling serving to reduce the rate constant for proton transfer. Thus, as the driving force for reaction increases from 0 to λ_s, the rate constant for proton transfer will increase reaching a maximum at $-\Delta G_{RXN} = \lambda_s$. A further increase in driving force will then lead

SCHEME 4



to a decrease in the rate constant of proton transfer, producing an inverted region for proton transfer. As stated earlier, based on eq 1, an inverted region for adiabatic proton transfer does not exist.[17]

The basic form of the theoretical formulation for nonadiabatic proton transfer that captures the normal–inverted behavior is[18]

$$k = \frac{C^2}{h/(2\pi)}\sqrt{\frac{\pi}{\lambda_s RT}}\exp\left[-\frac{\Delta G^{\ddagger}}{RT}\right] \qquad (2)$$

where the free energy of activation $\Delta G^{\ddagger}$ is given by

$$\Delta G^{\ddagger} = \frac{(\Delta G_{RXN} + \lambda_s)^2}{4\lambda_s} \qquad (3)$$

The tunneling probability is related to the proton coupling between reactant and product states, C. As a result, the transition state is to be found in the solvent coordinate, and the transition from reactant to product is governed by the preexponential factor containing the proton tunneling term.[18]

If the tunneling occurs only between $v_R = 0$ in the reactant state and $v_P = 0$ in the product state, then the correlation of the rate constant k_{pt} with driving force, ΔG_{RXN}, displays both a normal region and an inverted region, given the quadratic nature of eq 2. However, in 2004, Kiefer and Hynes proposed that at large driving force, the tunneling between $v_R = 0$ in the reactant state and $v_P = 1$ in the product will make a contribution to the overall rate of proton transfer.[18] Indeed, the tunneling term is larger for $v_R = 0 \rightarrow v_P = 1$ compared with $v_R = 0 \rightarrow v_P = 0$ due to the shorter distance associated with the $v_R = 0 \rightarrow v_P = 1$ transition, Scheme 4.

Incorporating the contributions of excited vibrational states of the product state into the formalism based on eq 2 eliminates the inverted region for proton transfer. As ΔG_{RXN} becomes more exergonic, the rate constant for proton transfer continues to increase. This kinetic characteristic differs from nonadiabatic electron transfer as the $v_R = 0 \rightarrow v_P = 0$ transition dominates the $v_R = 0 \rightarrow v_P = 1$ transition due to the nature of the Franck–Condon factors.[26]

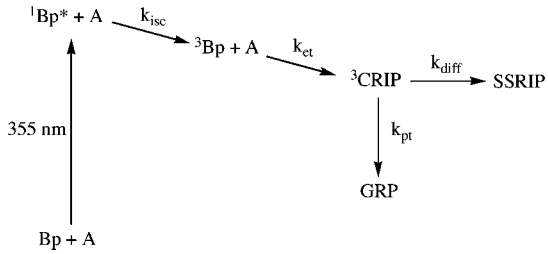


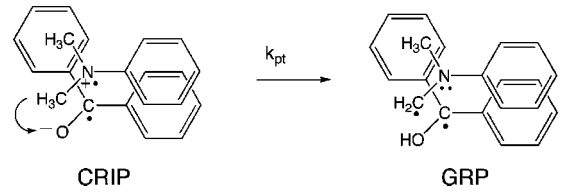
FIGURE 2. Reaction pathway for the photochemical reduction of benzophenone by *N*,*N*-dimethylaniline: Bp = benzophenone; ^{1}Bp* = first excited singlet state of benzophenone; A = *N*,*N*-dimethylaniline; ^{3}Bp = triplet state of benzophenone; ^{3}CRIP = triplet contact radical ion pair; SSRIP = solvent separated radical ion pair; GRP = triplet geminate radical pair.

Proton Transfer within Benzophenone/Aniline Contact Radical Ion Pairs

One component of our research program for the past 30 years has focused upon the mechanism by which photoactivated ketones are reduced by amines through the net transfer of a hydrogen atom.[32] The experiments employ femtosecond−picosecond absorption spectroscopy and time-resolved photoacoustic calorimetry.[33−35] The systems most often studied utilized derivatives of benzophenone and aniline. The reaction mechanisms for these molecular transformations are now understood in great detail. For example, the 355 nm excitation of benzophenone in the presence of *N*,*N*-dimethylaniline in acetonitrile at 298 K creates the first excited singlet of benzophenone, ^{1}Bp*, which decays on the 10 ps time scale through intersystem crossing, k_{isc}, to form the triplet state of benzophenone, ^{3}Bp, Figure 2.[22] In the presence of 0.4 M *N*,*N*-dimethylaniline (DMA), an electron is transferred from DMA to ^{3}Bp to produce the triplet contact radical ion pair (^{3}CRIP) with a rate constant $k_{et} = 8.3 \times 10^9$ s^{-1}. The absorption spectrum of the ^{3}CRIP is characterized by the superposition of absorption spectra for the radical anion of benzophenone, $\lambda_{max} = 710$ nm, and the radical cation of DMA, $\lambda_{max} = 460$ nm.[22] The ^{3}CRIP decays by either diffusional separation to the solvent separated ion pair, $k_{diff} = 5.0 \times 10^8$ s^{-1}, or proton transfer to form the triplet geminate radical pair (GRP) with $k_{pt} = 1.3 \times 10^9$ s^{-1}, Figure 2. This latter proton transfer is depicted in more detail in Scheme 5 where the ^{3}CRIP is assumed to be π-stacked.

The ^{3}CRIP of substituted benzophenones/*N*,*N*-dialkylanilines are ideal molecular systems for the study of the dynamics of proton transfer. Given the π-stacked structure of the ^{3}CRIP, the reacting entities do not require translation diffusion for reaction, and thus there is no work term associated proton transfer; the kinetics for proton transfer are unimolecular. The energetics for proton transfer can be varied over a wide range in energy through *p*,*p*′ substitution on the benzophenone aromatic rings or changes in the *N*,*N* substitution of the amine; the method for the determination of the free energy associated with proton transfer is described in ref 22. Also, the ^{3}CRIP is readily formed in solvents of wide ranging polarity, from acetonitrile ($\varepsilon = 37.5$) to tetrahydrofuran ($\varepsilon = 7.6$). Finally, the kinetics of proton transfer are readily monitored at 710 nm where only ^{3}CRIP absorbs, avoiding the complications from the buildup of reaction products.

SCHEME 5



By employing a variety of substituents (CH_3O, CH_3, F, Cl) at the *p*,*p*′ positions of benzophenone, the energetics for proton transfer are varied by 8 kcal/mol.[22] A further extension in the range of energies probed is achieved by the utilization of a variety of substituted anilines that includes *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, *N*,*N*-dimethyl-*p*-toluinide, and *N*,*N*-diallyaniline. Overall driving forces ranging from $\Delta G_{RXN} = -4$ to -23 kcal/mol are accessible.[24] An example of the correlation of the rate constant with driving force in tetrahydrofuran is shown in Figure 3. For each of the substituted anilines with the eight substituted benzophenones, both a normal region and an inverted region are observed in the correlation.[24] The fit of the experimental data to Hynes theory for nonadiabatic

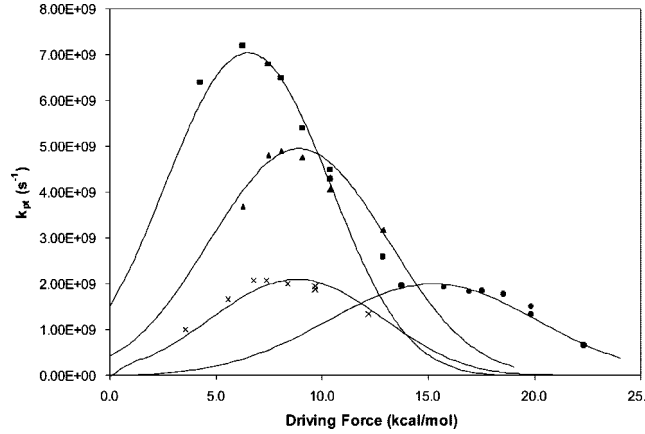


FIGURE 3. Plot of the experimental rate constants for proton transfer vs driving force (kcal/mol) defined as $-\Delta G_{RXN}$ for the solvent tetrahydrofuran. Experimental data: (■) benzophenones/*N*,*N*-dimethylaniline; (▲) benzophenones/*N*,*N*-dimethyl-*p*-toluinide; (×) benzophenones/*N*,*N*-diethylaniline; (●) benzophenones/*N*,*N*-diallylaniline; (—) fits to Lee−Hynes theory for nonadiabatic proton transfer, ref 30. Reprinted with permission from ref24.Copyright 2006 American Chemical Society.

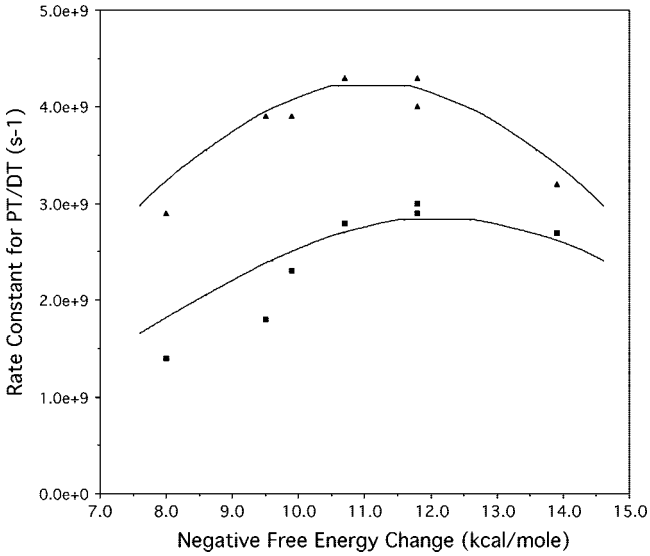


FIGURE 4. Plot of the experimental rate constants for proton (deuteron) transfer vs negative free energy change, $-\Delta G_{RXN}$ (kcal/mol), for reaction: (▲) benzophenones/*N*,*N*-dimethylaniline; (■) benzophenones/*N*,*N*-dimethyl-d_6-aniline; solvent = butanenitrile. Solid curve is the fit of Lee−Hynes theory, ref 30, to the experimental data. Reprinted with permission from ref 22. Copyright 2004 American Chemical Society.

proton transfer assuming only a $v_R = 0$ to $v_P = 0$ transition is also shown; the fit of the theory to the experiment is excellent.[24] The various shifts in four correlations of k_{pt} with ΔG_{RXN}, Figure 3, points toward the importance of vibrational reorganization as well as solvent reorganization in promoting proton tunneling; such a phenomenon is found in nonadiabatic electron transfer.[26] Also, the kinetic deuterium isotope effect is readily accommodated within the Hynes model.[22] Figure 4 shows the correlation of the rate constants for proton transfer with driving force when *N*,*N*-dimethylaniline and *N*,*N*-dimethyl-d_6-aniline are utilized. The kinetic deuterium isotope effect varies with ΔG_{RXN}, $k_{pt}/k_{dt} = 1.1-2.0$. Finally, the solvent reorganization energy for proton transfer is strongly dependent upon the polarity of the solvent, and the maximum rate for proton transfer within the correlation is also strongly dependent upon the solvent polarity. For benzophenones/*N*,*N*-dimethylaniline, the solvent reorganization energy increases from $\lambda_s = 8.1$ kcal/mol for tertrahydrofuran to $\lambda_s = 15.6$ kcal/mol for dimethyl sulfoxide.[22] The values for the solvent reorganization energies are derived from the fit of Hynes theoretical model to the experimental data.

These and other studies of ours reveal that the mechanism for proton and deuteron transfer within the ^{3}CRIP involves nonadiabatic transfer where the tunneling occurs from $v_R = 0$ in the reactant state into $v_P = 0$ in the product state.[25] The rate constants are critically dependent upon the solvent reorganization energy as well as the vibrational reorganization energy. There is no evidence for the participation of excited vibrations in the product state. Also, the observed correlation of rate constants with driving force cannot be rationalized within transition state theory with the Bell tunneling correction for this theory does not manifest an inverted region.

Finally, a comment is in order regarding the influence of temperature upon the rate constant for proton transfer. The temperature dependence of the rate constant for proton/deuteron transfer described by eq 2 is complex and does not lend itself to straight-forward experimental analysis. First, both ΔG_{RXN} and λ_S are functions of temperature; how the temperature dependence of ΔG_{RXN} and λ_S should be modeled is problematic. Also, the tunneling term C^2 contains a temperature dependence. Although the tunneling process itself is temperature independent, contained within C^2 are terms relating to low-frequency vibrations associated with hydrogen bonding, which serve to modulate the distance for proton tunneling, and these terms are exponentially dependent upon temperature.[18] Thus, given the complexity of the temperature dependence of the terms ΔG_{RXN}, λ_S, and C^2, studies examining the temperature dependence of the rate constants for proton/deuteron transfer will probably provide little insight into the nature of the phenomenon.

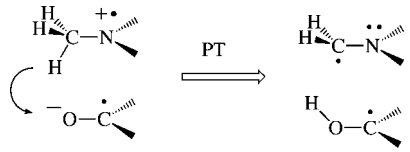
Proton Transfer to a Carbanion

The only other molecular system that displays both a normal region and an inverted region in the correlation of the rate constant for proton transfer with driving force is the reaction of diphenylmethyl carbanion with a variety of acids. Savéant and co-workers used laser flash electron photoinjection to obtain the rate constants for proton transfer to diphenylmethyl carbanion in *N*,*N*-dimethylformamide.[28] The range in driving force of proton transfer was large, varying from $\Delta G = 0$ to -28 kcal/mol. A normal region was observed between $\Delta G = 0$ to -18 kcal/mol followed by an inverted region between $\Delta G = -18$ to -28 kcal/mol. The data correlates with an empirical model that is similar in form to eq 2. Although they did not directly address the nonadiabatic nature of the proton transfer, they did conclude that both solvent and vibrational reorganization are integral in determining the rate of constant for proton transfer, behavior characteristic of nonadiabatic proton transfer.

The Conundrum

The Kiefer−Hynes formulation for nonadiabatic proton transfer that incorporates tunneling transitions to excited vibrations in the product state predicts that the rate constant for proton transfer increases with increasing ΔG_{RXN}. This kinetic

SCHEME 6



characteristic is not to be found in our molecular systems nor in the molecular system of Savéant. The only rational for the kinetic behavior observed in these two sets of experiments is that the proton transfer is occurring via a nonadiabatic process and the dominant transition is from $v_R = 0$ to $v_P = 0$. Our conclusion must be that the transition from $v_R = 0$ to $v_P = 0$ dominates the transition from $v_R = 0$ to $v_P = 1$. However, in the one-dimensional tunneling model employed by Kiefer and Hynes, there is no question that the transition from $v_R = 0$ to $v_P = 1$ should dominate the transition from $v_R = 0$ to $v_P = 0$.

The reconciliation of this inconsistency may lie in the dimensionality of the tunneling transition. The Kiefer−Hynes model assumes a linear geometry for the proton tunneling between the two heavy atoms and thus the tunneling path is one-dimensional.[18] In our molecular system, given the geometrical constraints imposed by the π-stack, the tunneling transition does not entail a linear geometry between the two heavy atoms, Scheme 6. The reaction pathway is curved and thus an appropriate tunneling formalism may require a multidimensional analysis.

Liedl and co-workers have examined the optimal tunneling reaction path for proton transfer within malonaldehyde and found that a multidimensional hydrogen vibrational wave function is required to describe the tunneling process.[36] Hammes-Schiffer recently developed a convenient method for the calculation of a multidimensional hydrogen vibrational wave function for rather complex molecular systems based on Fourier grid Hamiltonian multiconfigurational self-consistent-field (FGH-MCSCF) method.[37] Application of this latter method to proton transfer within the benzophenone/dimethylaniline contact radical ion pairs may reveal that the tunneling transition from $v_R = 0$ to $v_P = 0$ dominates the transition from $v_R = 0$ to $v_P = 1$. The origin of this effect could lie in the partial destructive interference in the overlap of $v_R = 0$ with $v_P = 1$ given the nodal properties of the two wave functions; such an effect is found in the Franck−Condon factors for electron transfer and is requisite for the appearance of the inverted region found in nonadiabatic electron transfer.[26] However, for Savéant's molecular system, the lack of molecular constraints on the reacting entities should allow for a linear geometry in the proton tunneling, yet an inverted region is observed. Clearly, there is something fundamentally lacking in our understanding of the proton-tunneling phenomenon.

Conclusions

Theoretical models have always been central to our understanding of the nature of reaction processes in chemistry and biochemistry. The models serve not only to provide insight into observed molecular phenomena but also to reveal insights beyond that provided by experiment. For example, transition state theory is extensively employed in the analysis of proton/hydrogen/hydride transfer processes in chemistry and biochemistry.[5,6] By combination of experimental data with transition state theory, questions relating to the progress of reaction, the degree of bond breaking and bond making, and the nature of the stabilization of the transition state by the environment can be addressed. These questions are critically important for the development of organic reaction mechanisms and for the development of enzyme catalysis mechanisms.

The recent formulation of adiabatic and nonadiabatic theories for proton/hydrogen/hydride transfer calls into question the conclusions regarding reaction mechanisms of these processes that were developed within the standard model of transition state theory. In the standard model, the transition state is in the bond making and bond breaking coordinate, and it is this assumption that allows for the discussion of changes in bonding during reaction. In the new models, the transition state is in the solvent coordinate, and the making and breaking of bonds is now found in the tunneling transitions or in the adiabatic motion of the reacting particle across the reaction surface. If these new models indeed capture the essence of the reactions paths for proton/hydrogen/hydride transfer, the conclusions for the past 60 years that were based upon transition state theory are in need of reassessment. But before this reassessment is undertaken, much remains to be done to establish the validity of the concepts of nonadiabatic and adiabatic reaction processes.

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BIOGRAPHICAL INFORMATION

Kevin Peters was born in Ponca City, Oklahoma, in 1949. After obtaining his B.S. from the University of Oklahoma in 1971, he pursed his graduate studies with Professor Ken Wiberg in the Department of Chemistry, Yale University, obtaining his Ph.D. in 1975. After three years of postdoctoral studies with Professor Fred Richards at Yale University and with Professor Mereithe Applebury, Princeton University, and Dr. Peter Rentzepis, Bell Labora-

tory, he joined the faculty of the Department of Chemistry, Harvard University, in 1978. He then moved to the Department of Chemistry and Biochemistry, University of Colorado at Boulder, in 1984. His research interests continue to be in the application of laser methodologies to study of organic reaction mechanisms. He is the recipient of the Alfred P. Sloan Fellowship and the Henry and Camille Dreyfus Teacher-Scholar Award.

FOOTNOTES

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