Picosecond Dynamics of Nonadiabatic Proton Transfer: A Kinetic Study of Proton Transfer within the Contact Radical Ion Pair of Substituted Benzophenones/*N*,*N*-Dimethylaniline

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Abstract: Picosecond absorption spectroscopy has been employed in the study of the dynamics of proton transfer within substituted benzophenones/*N*,*N*-dimethylaniline contact radical ion pairs. The reactions were investigated in the solvents cyclohexane, benzene, and dimethylformamide. The correlation of the reaction rates with the change in free energy reveals that the reaction pathway corresponds to a nonadiabatic process, that is the reaction proceeds by proton tunneling. In nonpolar solvents, an "inverted region" is observed in the proton-transfer process.

Introduction

In 1996, we reported a picosecond kinetic study for the effect of solvent upon the dynamics of proton and deuteron transfer between the radical anion of benzophenone and the radical cation of dimethylaniline, which were produced upon the irradiation of benzophenone in the presence of dimethylaniline[1] (Scheme 1).Examining the temperature dependence of the proton transfer, k_{pt}, within an Arrhenius framework, we found that the ratio of *A*-factors for proton transfer, A_H, and deuteron transfer, A_D, are strongly solvent dependent: in benzene $A_H/A_D = 0.6$, and in THF $A_H/A_D = 2.4$. Surprisingly, the standard theoretical framework for proton transfer could not accommodate the solvent dependence for this ratio of *A*-factors. Thus, given the importance of proton-transfer reactions in acid−base chemistry[2] and enzyme catalysis,[3] we have expanded upon our initial study by examining how the rate of proton transfer depends on driving force as well as the solvent and have analyzed these results within newly developed theoretical models for proton transfer.

The standard theoretical framework for the analysis of kinetics for proton/deuteron transfer is transition-state theory.[4−6] In this theory, a classical transition state is defined by the free-energy maximum along the reaction coordinate. Isotope effects are calculated in terms of the difference between the zero-point energies for the transition state and the reactant. In the absence of tunneling, the rate constant ratios k_{H^+}/k_{D^+} are predicted to be in the range of 3−7. These predictions are extensively used as an indicator of mechanism for organic, inorganic, and biochemical reactions in solution. The additional effect of H^+/D^+ tunneling through the barrier is expected to lead to an enhancement in the isotope effect reflecting the greater ease of tunneling by the lighter isotope; approximate theories of this exist based on the work of Bell.[5] The experimental indicators of tunneling are taken to be large k_{H^+}/k_{D^+} ratios and curved Arrhenius plots of ln *k* vs 1/*T*.

Recently, the basic assumptions that underlie transition-state theory have been brought into question.[7−9] Theory has revealed that, in the gas phase, tunneling is the dominant reaction mode for proton transfer, even at ambient temperatures. Extensive calculations show that the standard theory for kinetic isotope effects (KIE) and tunneling can be seriously in error, and thus the entire framework for interpretation of KIE and tunneling in gas-phase reactions is undergoing revision. The corresponding theoretical development for solution-phase reactions has been undertaken by Dogonadze, Kuznetzov, Ulstrup, and co-workers,[10] and then extended by Borgis and Hynes,[11−13] Cukier,[14,15] and Voth.[16,17] Collectively, these theories suggest that when a potential-energy barrier is present in the proton-reaction coordinate, the reaction pathway involves tunneling through the barrier as opposed to passage over the barrier. If experiments are found to confirm these theoretical formulations, which depict the proton-transfer process as occurring exclusively by tunneling at ambient temperatures, studies that use the kinetic isotope effect as an indicator of the nature of the transition state in proton-transfer reactions will need to be reassessed.

There have been in recent years a great number of investigations into the dynamics of proton transfer in the gas phase, in clusters, in solution, and in matrixes.[18−30] However, none of

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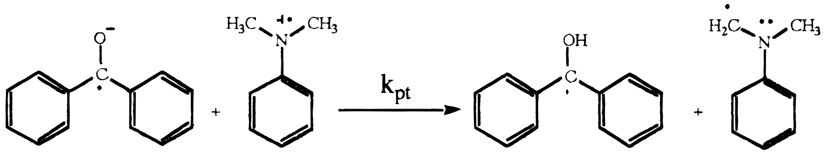
Scheme 1



these studies has been able to fully verify recent theoretical models developed for proton transfer in solution. In the following paper, we will examine the dynamics of proton transfer between the radical cation of dimethylaniline and a series of substituted benzophenone radical anions. This series of reactions will be studied in the solvents cyclohexane, benzene, and dimethylformamide. The correlation of the rate constant for proton transfer with change in energy, as a function of solvent, will then used to assess the recent theoretical models for solution-phase proton-transfer reactions.

Experimental Section

Benzophenone, 4,4′-dichlorobenzophenone, 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 solvents cyclohexane (Mallinckrodt), benzene (Baker), and dimethylformamide (Mallinckrodt) were used without further purification.

The picosecond absorption spectrometer, which employs a Continuum (PY61C-10) Nd:YAG laser producing a 19 ps pulse width, and the methods of data analysis have previously been described.[31] The sample was continuously flowed through a 1 cm quartz cuvette during the experiment. All experiments were undertaken at 23 °C.

Results

For the present experiments, we wished to examine the dynamics of proton transfer within the triplet radical ion pair of the various substituted benzophenones and dimethylaniline. The choice of the triplet state was predicated upon the need to eliminate the competition of back-electron transfer with proton transfer. For the triplet radical ion pair, back-electron transfer is a long time event, >10 ns,[31] while proton transfer occurs on the 100 ps time scale.[1] Thus, to ensure that only the dynamics of triplet radical ion pairs are monitored, it is necessary that the amine concentration should not be in excess of 0.5 M; at higher amine concentrations electron transfer may occur between the excited singlet state of the benzophenones and the amine, thus producing a portion of singlet radical ion pairs whose rate constants for back-electron transfer are competitive with proton transfer. For the following series of experiments, the sample concentrations employed were set to 0.02 M for the benzophenones and 0.4 M for the dimethylaniline. The observed dynamics for the decay of the triplet radical ion pair were found to be independent of the amine concentration over the range of 0.3−0.5 M.[1]

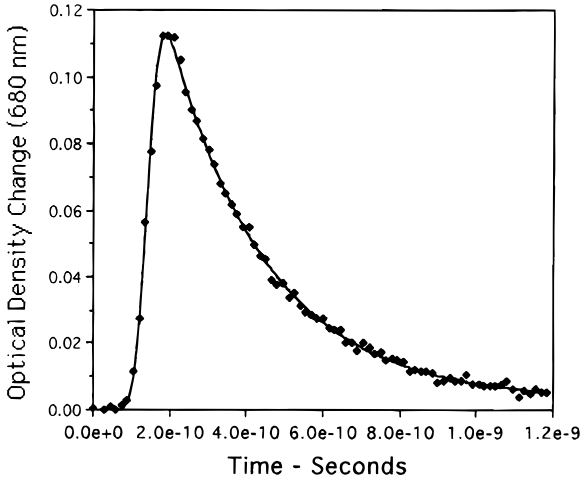


Figure 1. Transient absorption at 680 nm following 355 nm excitation of 0.02 M 4-chlorobenzophenone − 0.4 M *N,N*-dimethylaniline in benzene. (◆) Experimental points, (—) fit to data with $k_{pt} = 4.1 \times 10^9$ s^{-1}.

The dynamics for the decay of the triplet radical ion pair in cyclohexane and in benzene, which is attributed solely to proton transfer, were monitored at 680 nm following the 355 nm irradiation of the corresponding benzophenone.[1] For the samples in cyclohexane and in benzene, the time increments employed in the data acquisition were 15 ps; a total of 80 points were obtained for each run, and a total of four runs were averaged for each sample. The modeling of the kinetic data assumed a single-exponential decay of the contact radical ion pair giving rise to the triplet radical pair. An example of the decay of the 4-chlorobenzophenone/dimethylaniline triplet radical ion pair in benzene and its fit to the model is shown in Figure 1.

For the samples in dimethylformamide (DMF), the time increment for monitoring the dynamics of the radical ion pair at 680 nm was 25 ps; a total of 80 points were obtained for each run, and a total of four runs were averaged for each sample. Given the polarity of DMF, one must take into account the diffusional separation of the contact radical ion pair to form the solvent-separated radical ion pair, as observed in some of our previous studies.[32−36] The modeling of the kinetic data in DMF assumed that there are two decay pathways for the contact radical ion pair; decay of the contact radical ion pair (CRIP) to the radical pair (RP) through proton transfer, k_{pt}, as well as diffusional separation to the solvent-separated radical ion pair (SSRIP), k_{dif}, which cannot undergo proton transfer. Allowing for the collapse of the SSRIP to reform the CRIP did not improve the fit of the kinetic model to the experimental data. Also, in the modeling, it was assumed that the extinction coefficients for the two radical ion pairs are equal, although this is only an approximation as there should be a small difference in the absorption profile for the two species.[37]

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

The optimal value for k_{dif} was was found to be 5.0×10^8 s^{-1}. An example of the decay of the 4-methylbenzophenone/dimethylaniline triplet radical ion pair in DMF is shown in Figure 2. The decay of the 4,4′-dichlorobenzophenone/dimethylaniline triplet radical ion pair to the RP in DMF could not be accurately resolved due to the dominance of the diffusional separation of the CRIP to the SSRIP. The cumulative data for the eight triplet radical ion pairs in the three solvents are displayed in Table 1.

Discussion

In the follow section, we will first present an account of some of the recent theoretical developments relating to nonadiabatic and adiabatic proton transfer. This account will then be followed by a discussion of the procedure for determining the energetics for proton transfer within each radical ion pair. Finally, the correlation of the rate of proton transfer with the energetics will be presented within the context of theory.

Theory of Nonadiabatic Proton Transfer. The model for proton-transfer developed by Dogonadze, Kuznetzov, Ulstrup, and their co-workers assumes that the reaction pathway is a function of the distance of separation, R, between reactants, $\mathrm{AH^+\cdots A}$, Scheme 2.[10] At large distances of *R*, the reaction is thermally activated in the proton-transfer coordinate, *r*, and at the top of the reaction barrier there may be a tunneling contribution of the overall reaction rate. This pathway is that depicted as curve A in Scheme 2. When the distance of reactant separation *R* decreases, the reaction barrier narrows and is reduced, which then leads to a nonadiabatic proton transfer as the predominate reaction mode, that is the proton tunnels from the reactant state to the product state, curve B in Scheme 2. Upon further decrease in the separation distance *R*, as a result of the very strong coupling between the reactant state and product state, the potential-energy barrier in the proton-transfer coordinate is eliminated, and the reaction in the proton coordinate becomes adiabatic, curve C in Scheme 2.

As *R* decreases, the potential-energy barrier in the proton-transfer coordinate decreases, leading to an increase in the rate of reaction but at a cost of increasing the energies of the reactant and of the product states at short distances. Dogonadze, Kuznetzov, and Ulstrup thus defined the rate of proton transfer as[10]

$$k = \int \phi(R) W(\mathrm{R})\, \mathrm{d}R \qquad (1)$$

where $W(R)$ is the transition probability from reactant to product at distance R, and $\phi(R)$ is the distribution function for the molecular species in R.

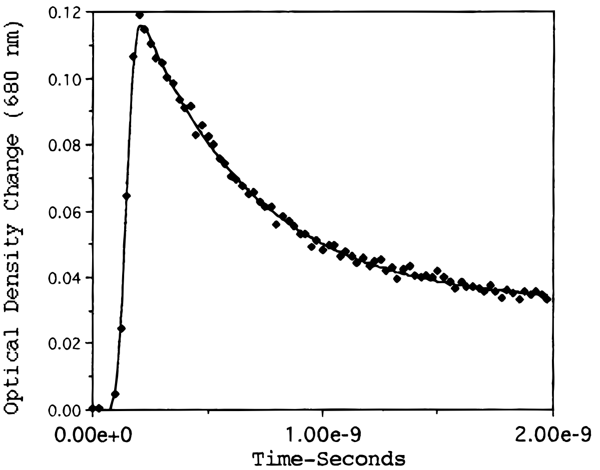


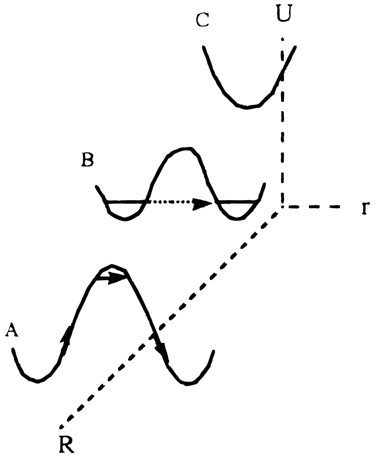
Figure 2. Transient absorption at 680 nm following 355 nm excitation of 0.02 M 4-methylbenzophenone/0.4 M *N*,*N*-dimethylaniline in DMF. (◆) Experimental points, (—) fit to data with $k_{\mathrm{pt}} = 1.5 \times 10^9$ s^{-1} and $k_{\mathrm{dif}} = 5.0 \times 10^8$ s^{-1}.

Table 1. Observed Rate Constants for the Decay of Substituted Benzophenones/Dimethylaniline Triplet Radical Ion Pair (at 23 °C)

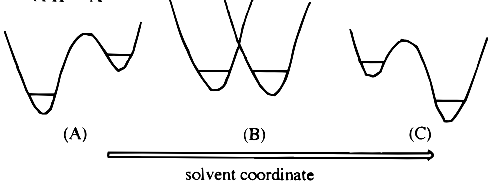
4,4′-benzophenone		cyclohexane	benzene	DMF
4	4′	k_{H} (10^9 s^{-1})[a]	k_{H} (10^9 s^{-1})	k_{H} (10^9 s^{-1})
$\mathrm{CH_3O}-$	$\mathrm{CH_3O}-$	2.9	2.4	1.9
$\mathrm{CH_3}-$	$\mathrm{CH_3}-$	5.9	4.3	1.8
$\mathrm{CH_3O}-$	H	5.4	3.6	1.7
$\mathrm{CH_3}-$	H	8.9	5.8	1.5
H	H	12.0	6.2	0.7
F	H	12.5	5.5	0.5
Cl	H	12.0	4.1	0.3
Cl	Cl	9.1	3.7	*b*

[a] Estimated uncertainties in rate constants ±10% (1σ). [b] Could not accurately resolve decay.

Scheme 2



Scheme 3



The model for nonadiabatic proton-transfer developed by Kuznetsov and his colleagues, depicted as curve B in Scheme 2, is very similar to the model for nonadiabatic electron transfer in its treatment of the involvement of solvent.[10] The fundamental assumption is that when a barrier is encountered in the proton transfer coordinate, instead of the proton undergoing a thermally activated crossing of the barrier, the proton tunnels through the barrier, thus leading to a nonadiabatic process. This assumption is fundamentally different from the Bell picture where proton tunneling occurs only in the region at the top of the reaction barrier. In Kutznetsov model, for the symmetric proton-transfer reaction, $\mathrm{AH^+\cdots A}$ to $\mathrm{A\cdots H^+A}$, when the polar solvent is equilibrated to the reactant, Scheme 3 , surface A, the proton will not be transferred due to an energy mismatch in the reactant and product states. Upon a solvent fluctuation, the energy of

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the reactant and product states become equal, Scheme 3, curve B, and it is in this solvent configuration that the proton tunnels from one side of the well to the other. Finally upon solvent relaxation, the product state is formed, Scheme 3, curve C.

This model leads to the following theoretical formulation for the rate of proton transfer:[10]

$$k = \sum_{n}\sum_{m} \mathrm{P}_n k_{nm} \tag{2}$$

where

$$k_{nm} = 2\pi(C_{nm}/2)^2(\pi/h^2\mathrm{k_B}TE_\mathrm{s})^{1/2}\exp\left(-\Delta G^{\ddagger}{}_{nm}/k_\mathrm{b}T\right) \tag{3}$$

and

$$\Delta G^{\ddagger}{}_{nm} = (\Delta E + E_\mathrm{s} + \Delta E_{nm})^2/4E_\mathrm{s} \tag{4}$$

In eqs 3 and 4, associated with the solvent coordinate is the solvent reorganization energy $\mathrm{E_s}$. The energy difference between the solvent equilibrated reactant state and solvent equilibrated product states is ΔE. The term k_{nm} is the rate constant associated with tunneling of the proton out of the reactant state with n quanta of vibrational energy and into the product state with m quanta of vibrational energy; thus the model allows for the formation of vibrationally excited product. The term P_n is just the thermal average over the vibrational populations of the reactant state. In eq 3, C_{nm} is the proton tunneling probability from the n state of the reactant to the m state of the product when the two states are iso-energetic. Finally for eq 4, $\Delta E_{nm} = (n - m)h\nu$ is the difference between the vibrational energy levels in the reactant state and in the product state.

The initial ideas put forth by Dogonadze, Kuznetzov, Ulstrup, and co-workers for nonadiabatic proton transfer have been extended by Borgis and Hynes where they address the important issue of low-frequency vibrations in promoting proton transfer.[11-13] One striking difference between electron transfer and proton transfer is the extreme sensitivity of the proton tunneling matrix element to distance. The functional form of the tunneling matrix element between the reactant and product state, for moderate to weakly hydrogen-bonded species, is $C(Q) = C_0 \exp(-\alpha\delta Q)$. The decay parameter α is very large, 25−35 Å^{-1}, when compared to the corresponding decay parameter for the electronic coupling in electron transfer, 1 Å^{-1}. It is this feature that makes the dynamics of proton transfer so sensitive to the internuclear separation of the two heavy atoms, A···A. Whereas a decrease of 0.1 Å will increase the rate of electron transfer by a factor of 1.1, a similar distance change in proton transfer will increase the rate by a factor of 20. Thus, in the Borgis−Hynes model, intermolecular vibrations that lead to a decrease in the A···A nuclear separation will significantly enhance the rate of proton transfer.

The Borgis−Hynes model introduces a low-frequency vibrational mode, Q, whose frequency is ω_Q, and the associated vibrational reorganization energy is E_Q.[13] On the basis of a Landau−Zener curve crossing formulation, they derived the nonadiabatic rate constant, k, similar to that of Kuznetsov and co-workers but where the tunneling term C_{nm} is significantly modified. The tunneling term, C_{nm}, is dependent upon a promoting vibration Q

$$C_{nm}{}^2 = C_0{}^2\exp(-\alpha\Delta Q_\mathrm{e})\exp((E_\alpha - E_Q)/h\omega_Q)\,F[L(E_Q, E_\alpha, \omega_Q)] \tag{5}$$

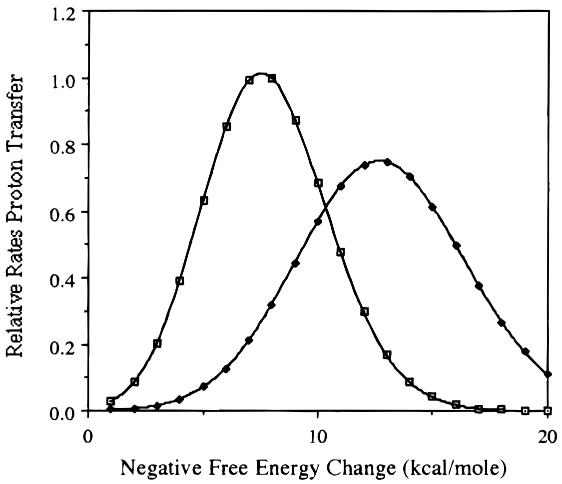

Figure 3. Graph of free-energy dependence ($-\Delta G$ kcal/mole) of the relative rates of proton transfer employing the Borgis−Hynes model, eqs 2−5. $E_\alpha = 2.0$ kcal/mol, $E_Q = 1.0$ kcal/mol, vibrational frequency 300 cm^{-1}, and $\Delta Q_\mathrm{e} = 0.1$ Å. $E_\mathrm{s} = 2.0$ kcal/mol for the larger graph and $E_\mathrm{s} = 7.0$ kcal/mol for the smaller graph.

The energy E_α is a quantum term associated with the proton reaction coordinate coupling to Q vibration, $E_\alpha = h^2\alpha^2/2m$. C_0 is the tunneling matrix element for the transfer from the 0 vibrational level in the reactant state to the 0 vibrational level in the product state. 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. For a thorough discussion of eq 5, see ref 13.

Graphs of the free-energy dependence for the rate of proton transfer within the Borgis−Hynes model, eqs 2−5, assuming a promoting mode of 300 cm^{-1}, are shown in Figure 3; the calculated rate constants, $k/C_0{}^2$, have been normalized. In both plots, the value for E_α is 2.0 kcal/mol and the value for E_Q is 1.0 kcal/mol. They only differ in E_s, the solvent reorganization energy, where for the larger of the two graphs, E_s is 2.0 kcal/mol and for the smaller of the two graphs, E_s is 7.0 kcal/mol. With increasing solvent reorganization energy, the maximum rate constant for a given solvent reorganization energy shifts to larger negative free-energy change and the maximum amplitude is reduced in magnitude as well. This reduction in the maximum rate constant with increasing E_s is the result of the term $E_\mathrm{s}{}^{-1/2}$ in eq 3. Thus, the model predicts that there is an “inverted region” for proton transfer.

Borgis and Hynes have also theoretically examined the situation where A···A internuclear separation is small, so that the electronic coupling between the reactant and product state is large, leading to an adiabatic reaction; the reaction barrier in the proton-transfer coordinate is below the zero-point vibrational energy level of the hydrogen stretch, and thus, no electronic barrier is encountered in the transfer.[13] The adiabatic limit leads to the rate expression

$$k_\mathrm{ad} = (\omega_\mathrm{s}/2\pi)\exp(-\beta\Delta G^{\ddagger}) \tag{6}$$

where ω_s is the solvent frequency and $\Delta G^{\ddagger}$ is the free energy of activation. If the proton-transfer reaction is adiabatic, that is, it does not occur through proton tunneling, then the A-factor will be of the order of 10^{13} s^{-1} or greater.[13]

Energetics for Proton Transfer. To compare theories for proton transfer with experiment, it is necessary to examine how the rate of proton transfer changes with the change in energy for the reaction. This requires an assessment of both substituent and solvent effects for the energy change for the proton-transfer reaction.

To determine the energetics for proton transfer, it is necessary to estimate the energy of the contract radical ion pair as well as the energy of the triplet radical pair relative to the initial reactants so that the difference in energies reflects the energy change for the reaction. First, the energetics for proton transfer in the benzophenone/dimethylaniline contact radical ion pair to form the triplet radical pair in acetonitrile is derived from thermochemical data. Then, the effect of the solvents DMF, benzene, and cyclohexane upon the energy of the contact radical ion pair of benzophenone/dimethylaniline will be estimated from prior studies of solvent dependencies of ion pair energies; we assume the energy of the radical product to be independent of solvent. Then, from redox potentials, we will deduce how the energy of the contact radical ion pair varies with substituent. Finally, the effect of substituents upon the stability of the ketyl radical will be estimated from the kinetic data for the thermal rearrangement of 2-aryl-3,3-dimethyl−methylenecyclopropanes.

The energy of the benzophenone/dimethylaniline contact radical ion pair relative to the reactants, in acetonitrile, has previously been determined by Mataga and co-workers through oxidation and reduction potentials; the derived value is 59.3 kcal/mol.[38] The energy of the radical pair relative to the reactants is obtained from literatures values for the energy for the formation of the ketyl radical[39] and the C−H bond dissociation energy of dimethylaniline[40] through the following thermodynamic cycle.

$$(\mathrm{C_6H_5})_2\mathrm{C{=}O} + \mathrm{H_2} \rightarrow (\mathrm{C_6H_5})_2\mathrm{CHOH} \quad \Delta H = -9 \text{ kcal/mol}$$

$$2\mathrm{H}\bullet \rightarrow \mathrm{H_2} \quad \Delta H = -104 \text{ kcal/mol}$$

$$(\mathrm{C_6H_5})\mathrm{CHOH} \rightarrow \mathrm{H}\bullet + (\mathrm{C_6H_5})_2\mathrm{COH} \quad \Delta H = 78 \text{ kcal/mol}$$

$$\text{dimethylaniline} \rightarrow \mathrm{H}\bullet + (\mathrm{C_6H_5})\mathrm{N(CH_3)(CH_2}\bullet) \quad \Delta H = 91.7 \text{ kcal/mol}$$

$$\text{benzophenone} + \text{dimethylaniline} \rightarrow (\mathrm{C_6H_5})_2\mathrm{COH} + (\mathrm{C_6H_5})\mathrm{N(CH_3)(CH_2}\bullet) \quad \Delta H = 56.7 \text{ kcal/mol}$$

Thus, in acetonitrile, the energy released upon proton transfer is $\Delta H = -2.6$ kcal/mol. In the above analysis, the greatest source of error is associated with the C−H bond energy for diphenylmethanol for, as to our knowledge, this quantity has not been directly measured; the error could be as large as ± 3 kcal/mol. However, what is most important in the present analysis is the change in energy for the proton-transfer reaction with substituents and solvents, not the absolute value for the energy change.

To calculate the solvent dependence for the energetics of proton transfer within the benzophenone/dimethylaniline radical ion pair, we need to estimate how the energy of the contact radical ion pair changes with solvent; we assume that the energies of the product radical species are independent of solvent. Recently Gould, Goodman, Farid, and co-workers determined how the energy of the contact radical ion pair of 1,2,4,5-tetracyanobenzene/hexamethylbenzene varies with solvent.[41] We have taken their data and correlated it with E_T 30 to obtain an estimate of the effect that the solvents, employed in the present study, have upon the energies of the contact radical ion pairs. Relative to acetonitrile, we find that the contact radical ion pair increases in energy by 0.5 kcal/mol in DMF, by 2.8 kcal/mol in benzene, and by 3.6 kcal/mol in cyclohexane. Thus, with decreasing solvent polarity, the energy released upon proton transfer increases to −3.1 kcal/mol in DMF, to − 5.4 kcal/mol in benzene, and to −6.2 kcal/mol in cyclohexane for the benzophenone/dimethylaniline contact radical ion pair.

The effect of substituent upon the stability of the radical ion pair was derived from the study of Arnold and co-workers of the reduction potentials for a variety of 4,4′-substituted benzophenones which included the substituents methoxy, dimethoxy, methyl, and dimethyl.[42] For these substituents they found an excellent linear correlation between the reduction potential and the Hammett σ parameter. Unfortunately, they did not examine benzophenones substituted with either chlorine or fluorine. To obtain the reduction potentials for 4-fluorobenzophenone, 4-chlorobenzophenone, and 4,4′-dichlorobenzophenone, we employed the correlation of reduction potentials with σ to obtain these values. Relative to benzophenone, the subtituents have the following effects upon the stability of the contact radical ion pair: 4,4′-dimethoxy (4.4 kcal/mol), 4,4′-dimethyl (2.1 kcal/mol), 4-methoxy (2.1 kcal/mol), 4-methyl (0.9 kcal/mol), 4-fluoro (−0.5 kcal/mol), 4-chloro (−1.9 kcal/mol) and 4,4′-dichloro (−4.0 kcal/mol). Thus, 4,4′-dimethoxy substitution destablizes the contact radical ion pair by 4.4 kcal/mol, while the 4,4′-dichloro substitution stabilizes the contact radical ion pair by 4.0 kcal/mol.

The effect of substituents upon the stability of the ketyl radical were estimated from the kinetic data obtained by Creary for the thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes, where the mechanism for the isomerization assumes a biradical intermediate.[43] Assuming the kinetic data directly reflects the effect of the substituent upon the stability of the radical intermediate, then the energy associated with the substituent effect can be obtained from the energy of activation. To obtain the energy of activation, it is necessary to have a measure of the A-factor for the thermal rearrangement. Kirmse and co-workers have measured an A-factor of 10^{14} $\mathrm{s^{-1}}$ for the thermal rearrangement of 1-ethoxy-methylenecyclopropane.[44] Finally, in our calculation of substituent effects upon the stability of the ketyl radical, we assumed that the effect of the substituent would be less for the ketyl radical, given its higher degree of delocalization; we arbitrarily assigned a 50% reduction in the substituent effect on the stability of the ketyl radical relative to the substituent effect upon the thermal isomerization of 2-aryl-3,3-dimethyl−methylenecyclopropanes. Thus, we find the following substituents stabilize the ketyl radical: 4,4′-dimethoxy (0.4 kcal/mol), 4,4′-dimethyl (0.2 kcal/mol), 4-methoxy (0.2 kcal/mol), 4-methyl (0.1 kcal/mol), 4-chloro (0.1 kcal/mol), and 4,4′-dichloro (0.2 kcal/mol). The only substituent that destabilizes the ketyl radical is the 4-fluoro (−0.1 kcal/mol).

On the basis of the above analysis of substituent and solvent effects, we have determined the following energetics for proton transfer shown in Table 2.

Comparison of Theory−Experiment. Before we begin to compare the predictions of nonadiabatic proton transfer theory with the present experiments, we need to establish that the reaction conditions are such that adiabatic proton transfer does not intervene. Adiabatic proton transfer may occur when the internuclear separation between the two heavy atoms involved in the proton transfer is small, leading to large electronic

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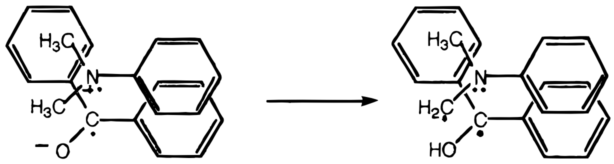
Table 2. Effect of Substitutents upon the Energetics for Proton Transfer[a]

4	4′	DMF	C6H6	C6H12
CH_3O	CH_3O	−7.9	−10.2	−11.0
CH_3	CH_3	−5.4	−7.7	−8.5
CH_3O	H	−5.5	−7.7	−8.5
CH_3	H	−4.1	−6.4	−7.2
H	H	−3.1	−5.4	−6.2
F	H	−2.5	−4.8	−5.6
Cl	H	−1.3	−3.6	−4.4
Cl	Cl	+0.7	−1.6	−2.4

[a] All values are in kcal/mol. Dimethylformamide − DMF, benzene − C_6H_6, cyclohexane − C_6H_{12}

coupling between the reactant and product states. The distance associated with the crossover between nonadiabatic and adiabatic proton transfer has yet to be defined and will clearly be system specific. However, from model calculations, distances in excess of 2.5 Å appear to lead to the realm of nonadiabatic proton transfer.[12]

The geometry of the benzophenone/dimethylaniline contact radical ion pair that undergoes proton transfer is not known. However, from numerous studies of excimers and exciplexes, it is anticipated that the contact radical ion pair would be π-stacked to maximize the Coulombic attraction.



The separation between the π-stack system should be of the order of 3.3 Å based upon studies of the pyrene excimer.[45] Given that both the radical ion of benzophenone and the radical cation of dimethylaniline should be planar molecules, the equilibrium separation between the two heavy atoms involved in the proton transfer, C and O, should be of order of 3.3 Å, although this distance will vary with radical ion pair intermolecular vibrations. Thus, the expectation is that proton-transfer reaction should be nonadiabatic.

Further support for this proposal can be found in our recent investigation of the temperature dependence of proton transfer. For benzophenone/dimethylaniline in benzene and in THF, the temperature dependence of the rate constant for proton transfer was examined within an Arrhenius framework.[1] The *A*-factor, assuming it is independent of temperature, for proton transfer is 2.6×10^{11} s^{-1} in benzene and 6.6×10^{10} in THF. If this reaction were to be attributed to an adiabatic process, as described by eq 6, the expectation is that the *A*-factor should be greater than 10^{13} s^{-1}.[13] Consequently, based upon consideration of the geometry of the contact radical ion pair and the frequency factor for proton transfer, the transfer process should fall in the nonadiabatic regime.

The correlation of the rate constant for proton transfer with changes in free energy for the solvents cyclohexane, benzene, and DMF can be found in Figures 4−6. For the solvents cyclohexane and benzene, as the reaction becomes increasingly exergonic, the reaction rate initially increases, reaches a maximum, and then decreases. Although the free-energy change associated with the maximum rate in proton transfer is not well defined, the maximum rate for proton transfer in both cyclohexane and benzene is approximately −6 kcal/mol. In the solvent DMF, the rate constant for proton transfer increases as the free energy changes from −1 to −5 kcal/mol and then appears to reach a maximum beyond −8 kcal/mol. What is immediately striking when comparing the nonpolar solvents with the polar solvent is a decrease in the proton-transfer rate with a free-energy change of −6 to −12 kcal/mol for the nonpolar solvents, while the rate increases over this range for the polar

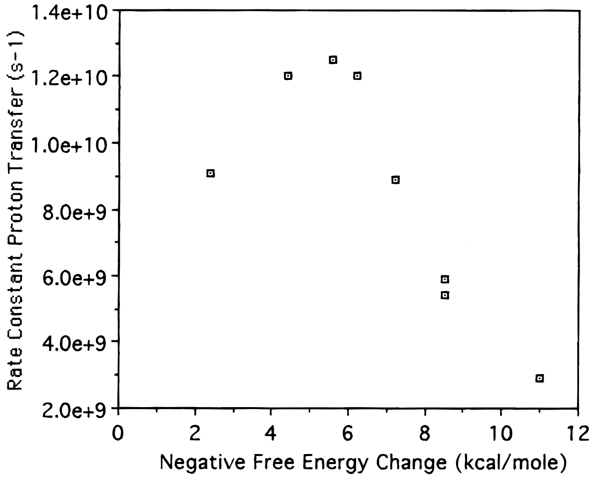


Figure 4. Plot of the rate constant for proton transfer vs free energy change (−ΔG kcal/mol) for solvent cyclohexane.

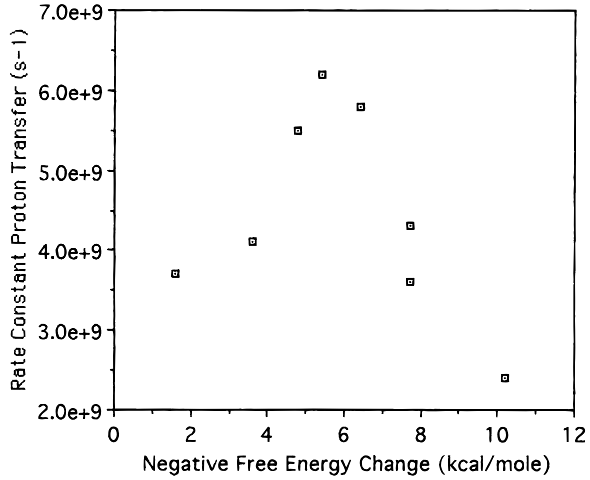


Figure 5. Plot of the rate constant for proton transfer vs free-energy change (−ΔG kcal/mol) for solvent benzene.

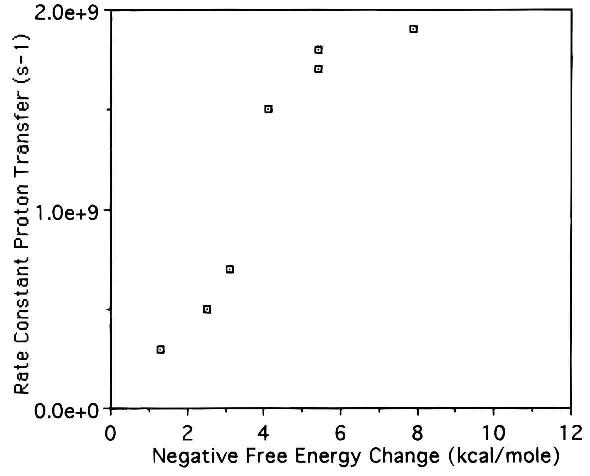


Figure 6. Plot of the rate constant for proton transfer vs free-energy change (−ΔG kcal/mol) for solvent dimethylformamide.

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[45] Birks, J. B. *The Photophysics of Aromatic Excimers*; Birks, J. B., Ed.; Academic Press: New York, 1975.

solvent. The standard model for proton transfer cannot account for this kinetic behavior. Also in the nonpolar solvents, there is a clear manifestation of the "inverted region" for proton transfer as predicted by eqs 2−5.

Qualitatively, the shape of these curves are similar to those predicted by theory, eqs 2−5, although they appear not to be symmetrical about the maximum as predicted by theory, Figure 2. However the theory employed in the development of Figure 2 assumes that only one active vibration is involved in promoting proton transfer. However, more than one vibration may be involved in reducing the two heavy atom, C and O, internuclear separation; thus, the appropriate expression for the rate constant should involve a summation over several vibrational modes, which could lead to an asymmetry in the correlation of the rate constant for proton transfer with change in free energy.

Another apparent inconsistency between theory and experiment is the expectation that the maximum in the rate constant for proton transfer in cyclohexane and in benzene should differ, whereas experiment reveals them to be approximately the same. One parameter that controls the position of the maximum is the solvent reorganization energy, for as the solvent reorganization energy increases, the maximum in the rate constant for proton transfer should shift to larger negative free-energy changes, Figure 2. For the proton-transfer reaction, the solvent reorganization energies for cyclohexane and benzene are not known, but the solvent reorganization energy should be larger for benzene given its somewhat greater polarity. Therefore, it is the expectation that the maximum in benzene should occur at a larger negative free-energy change. However, it is important to note that there is an inherent error in determining the solvent dependence of the free-energy change for proton transfer, and it may be this error that accounts for the same maximum in the two solvents.

Examining how the maximum in the rate constant varies with solvent polarity reveals that in cyclohexane the maximum rate is 1.4×10^{10} s^{-1}, which is reduced to 6.2×10^{9} s^{-1} in benzene, and then further reduced to 1.9×10^{9} s^{-1} in DMF. This in qualitative accord with the predictions of eqs 2−5 as the prefactor to the exponential contains the term $E_s^{-1/2}$. As the solvent reorganization energy increases, the prefactor should decrease, leading to a reduction in the maximum rate constant. There is, however, another factor to consider, for as the solvent polarity increases, the Coulombic attraction in the contact radical ion pair should decrease, leading to an increase in the internuclear separation. The increase in the separation of the contact radical ion pair with an increase in solvent polarity will lead to a reduction in the tunneling matrix element for proton transfer. Therefore, increasing the solvent polarity will increase the solvent reorganization energy and reduce the tunneling matrix element, both having the effect of reducing the maximum rate constant for proton transfer.

Finally it is important to note that the above conclusions regarding the applicability of Borgis−Hynes theory for understanding the dynamics of proton-transfer stands in contrast to our earlier conclusions. In our initial study, ref 1, we suggested that Borgis−Hynes theory, either the adiabatic or nonadiabatic forms, could not account for the observed dynamics of proton transfer within the benzophenone/dimethylaniline contact radical ion pair. This initial conclusion was based upon two observations. First, from temperature-dependent studies, the derived *A*-factor for the solvents benzene and THF is of the order of 10^{11} s^{-1}. Second, the kinetic deuterium isotope effects are small, ranging from 2.0 to 2.4. The *A*-factor analysis appeared to preclude an adiabatic process, for as shown in eq 6 of this paper, the expected *A*-factor for an adiabatic process should be of the order of 10^{13} s^{-1} or greater. Regarding the small isotope effect, we employed a form of the Borgis−Hynes theory whose analytical form is derived from eqs 2−5 of the present paper with the assumption that $\beta(h/2\pi)\omega_Q \ll 1$, resulting in eq 1 in ref 1. Since the prefactor of this equation involves the square of the tunneling matrix element, one would anticipate a large deuterium isotope effect for nonadiabatic proton transfer. However, eq 1 in ref 1 is inappropriate for the analysis of the dynamics of proton transfer under the conditions of our system for term $\beta(h/2\pi)\omega_Q$ is approximately equal to 1.0 as well as eq 1 in ref 1 does not allow for the reaction channel to produce vibrationally excited products, which is clearly an important consideration for proton-transfer reactions that are exothermic. Thus, the full analytical forms of eqs 2−5 of the present study should be employed in the analysis of the kinetic data. Also, recent theoretical studies of kinetic deuterium isotope effects reveal that with the appropriate parameters, eqs 2−5 can produce small kinetic isotope effects.[46] Thus, the presence of a small kinetic isotope effect cannot be used to rule out the intervention of a nonadiabatic proton-transfer process. As a result of these considerations as well as the observed inverted region for proton transfer in the present study, we conclude that the reaction mechanism for proton transfer within the benzophenone/dimethylaniline contact radical ion pair involves the nonadiabatic transfer of the proton.

Conclusion

The goal of the present study was to ascertain if recently developed theories for nonadiabatic proton transfer could account for the effect solvent has upon the dynamics of proton transfer in the benzophenone/dimethylaniline contact radical ion pair. Although qualitatively the correlation between theory and experiment was rather good, a quantitative comparison was not feasible, given the uncertainty in how a number of the parameters integral to theory vary with solvent. However, the results from the present study strongly suggest that, in this particular molecular system, nonadiabatic proton transfer is the dominant reaction mode.

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(46) Professor J. T. Hynes, personal communication. The theory for kinetic deuterium isotope effects will be present shortly.