THE DYNAMICS OF BARRIER CROSSINGS IN SOLUTION: THE EFFECT OF A SOLVENT POLARITY-DEPENDENT BARRIER

Janice HICKS, Mark VANDERSALL, Zoran BABAROGIC [1,2] and Kenneth B. EISENTHAL
Department of Chemistry, Columbia University, New York, NY 10027, USA

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Experiments on the role of the solvent in the dynamics of photoisomerization involving large dipole moment changes are discussed Variation of the photoisomerization dynamics of dimethylaminobenzonitrile in a series of solvents is attributed chiefly to polarity-induced barrier height changes rather than viscosity changes Implications of these findings regarding the use of barrier crossing theories are discussed

1. Introduction

Ultrafast spectroscopic methods have in recent years been used to study rapid structural changes of excited-state molecules in liquids [1–11]. These transitions are usually described as the motion of a particle on a one-dimensional potential surface where the initial and final states are separated by a barrier. The experimentally observed kinetics have been compared to the predictions of barrier crossing theories, which allow for three regions of solute/solvent coupling [12–18]. In the weak coupling limit, the rate of barrier crossing increases with increasing coupling, e.g. with collision frequency and viscosity. In this region, solvent collisions assist the solute in gaining enough energy to reach the top of the barrier. In the intermediate region, the rate approaches a maximum and then decreases with increasing coupling as the solvent collisions begin to impede the progress of the particle over the barrier. Finally, in the high coupling region, the motion becomes diffusive, i.e. the particle takes many small forward and backward steps in crossing the barrier to the final-state structure. The rate becomes inversely proportional to the solvent coupling, and is the so-called Smoluchowski limit.

Although the photoisomerization process seems to be a good model system for testing barrier crossing theories, the problem for experimenters has been to find a probe molecule for which (i) the rate of crossing the barrier can be reliably measured in the various regions of solute/solvent coupling, as described above, (ii) the motion can be described as one-dimensional, and (iii) the method of varying the solute/solvent coupling does not change the barrier height or shape of the potential. Such methods include varying the pressure or temperature, or varying the solvent, generally within a solvent series such as n-alcohols. Molecules such as diphenylbutadiene [1,2], stilbene [3] and 1-(1-pyrene)-3-(4-dimethylaminophenyl)propane [7] have been studied in an alkane series. Binaphthyl [8] and cyclohexane [9] have been studied in various solvent types. Diphenylbutadiene [4], DODCI [5], stilbene [10], and ethyl violet and crystal violet [6] have been studied in an alcohol series. Ethyl violet and crystal violet have also been studied in a single alcohol solvent at different temperatures [11]. In each case, the assumption that the barrier height does not change within each series, or with temperature, has been made. So far, the experimental data have not quantitatively verified the barrier crossing theories over the various coupling regions, though important qualitative experimental support of stochastic models has been obtained for the first time in the weak and intermediate coupling regions for the isomerization of cyclohexane [9]. The

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[1] International Atomic Energy Fellow, Vienna, Austria
[2] Permanent address Institute of Physics, P O. Box 57, 1101 Belgrade, Yugoslavia

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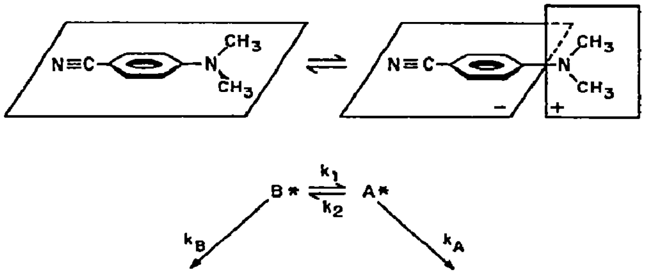
recently reported turn-over behaviour for triphenylmethane dyes in alcohols [11] may be due to polarity-induced barrier height changes, and will be discussed later in this paper. The deviations from theory observed in these various studies have been explained by various models, including frequency-dependent friction [5,19, 20] and changing boundary conditions [6,11]. A key issue is whether the theories break down for these reasons, or do they only appear to break down because the assumptions listed above (i)–(iii) are not valid?

In this paper we consider the role of the solvent in the dynamics of excited-state structural changes, and particularly isomerizations involving significant charge redistribution. The process we have studied is the twisting dynamics of *p*-dimethylaminobenzonitrile (DMABN) (see scheme 1). In the excited state this molecule undergoes a rotation of the dimethylamino group about the amino–phenyl bond. This motion results in a charge separation between the two groups, and thereby generates a large change (≈10 D) in the excited-state dipole moment [21]. In polar solvents the twisted, large dipole form, is stabilized. It produces a new emission in the visible which does not appear in non-polar solvents. Rapid equilibration between the twisted and planar forms in polar media yields a dual fluorescence, one due to the planar form in the UV and the other to the twisted form in the visible. This twisted internal charge transfer (TICT) model, first proposed by Grabowski and co-workers [22], and demonstrated to include rapid equilibration [23,24], accounts, as given in scheme 1, for the dual fluorescence of DMABN in polar liquids.

The absence of the visible emission in non-polar solvents and its appearance in polar solvents indicate that the excited-state potential surface connecting the planar and twisted forms is dependent on the solvent polarity. This polarity dependence of the potential surface can thus play an important role in determining the dynamics of the isomerization. The viscosity of the solvent, though not changing the potential surface for isomerization, is some measure of the solute/solvent coupling and also can be of importance in the isomerization dynamics.



Scheme 1.

In this study, the effect of the solvent viscosity, polarity and temperature on the rate, k_1, of crossing the potential barrier between the B* (planar) and A* (twisted) states are studied in neat nitriles and nitrile/alkane solutions. The value of k_1 is calculated for each solvent at a given temperature from the observables k_{obs} (the rate of fast decay of the B* emission and the rise of the A* emission) and F, the fraction of fluorescence at time zero in the slowly decaying component of the short-wavelength band (the planar B* state). Based on our observation that the sum of the excited-state rates, $k_1 + k_2$, is large compared to the population decay rates of the two states, k_A and k_B, the following equation is obtained (see ref. [23])

$$k_1 = k_{\mathrm{obs}}(1-F) = (k_1 + k_2)(1-F) . \qquad (1)$$

2. Experimental

The dual fluorescence of DMABN was measured with picosecond resolution by using a passively mode-locked Nd^{3+}/glass laser (fwhm of pulse, including detector response function, is 8 ps) and a Hadland Imacon 675 streak camera The apparatus and data handling procedures have been described [23].

Temperature control (±0.1°C) was attained by using a Neslab circulation cooler, model RTE-4, connected to a copper block into which the sample was placed.

DMABN (Aldrich) was purified twice by vacuum sublimation. The nitriles were purified by fractional distillation, and stored over type 4A molecular sieves. The DMABN concentration was 0.25 mM for all samples, and the solutions were sealed and degassed in 1 mm path length quartz cells. Absorption spectra of of the samples taken before and after the laser experiments were identical, indicating that no substantial permanent photochemistry took place.

Viscosity measurements were made using a Cannon-Fenske capillary viscometer with a temperature bath. Solvent polarity values, $E_T(30)$, were obtained by measuring the absorption maximum of the dye, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide [25]. For the dilute nitrile/alkane mixtures, the lipophilic penta-tert-butyl-substituted betaine dye was used [26].

3. Results

For all of the liquids studied the dynamical processes of the DMABN isomerization shown in scheme 1 have been verified. The fluorescence lifetimes for the A* and B* states were measured, and found to be equal (3.0 ± 0.2 ns). This confirms that equilibrium is attained between the excited planar and twisted species during the lifetime of these states. Similarly the observed formation and decay rates (k_{obs}) were found to be equal within experimental error, thus confirming the A* population originates from the B* population. In all cases, single-exponential behaviour for the formation of the A* state and the fast decay component of the B* state was observed. This indicates that no ground-state complexes were present, as were shown to occur in alcohol/alkane mixtures [24]. The presence of hydrogen bonding between the solute and solvent complicates the kinetic behaviour, and will be the subject of another paper.

Since our chief interest in the present work is the dynamics of isomerization, i.e. the formation rate of A*, it is important to determine if the rise times of the A* fluorescence which we measure depend on the fluorescence wavelengths monitored. Two situations could conceivably be the origin of such a wavelength-dependent rise time. If the dipole moment of the molecule continually increases during the course of the isomerization, and the solvent follows this change by relaxing quickly around the evolving dipole, this would give rise to a continually red-shifting spectral change with time. Another situation that could cause this effect would be if the dipole moment of the molecule increases suddenly, and in the short, but measurable time following the change, the solvent relaxes around the molecule, thereby stabilizing it. In both cases there would be different rise times for the blue versus the red ends of the A* band. Using several different filters to isolate the blue and the red spectral regions of the A* band, we observed the same rise times in both spectral regions; this is in agreement with more extensive spectral experiments carried out elsewhere ‡. These results indicate that there is not a continual solvent stabilization in the isomerization process, but rather a rapid jump from the B* state to the A* state. Any subsequent stabilization of A* by the rearrangement of the solvent molecules must also be rapid compared to the isomerization rate constant k_1.

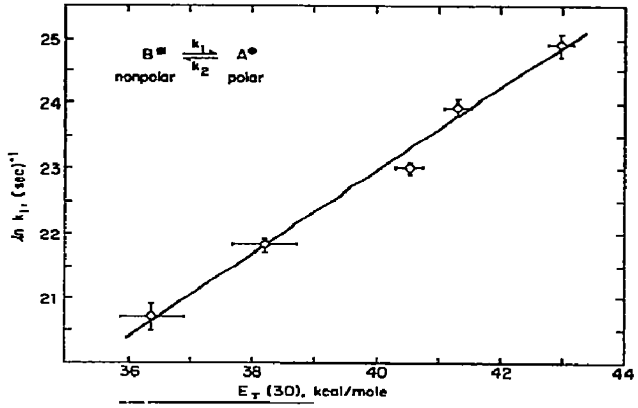


Fig. 1. Plot of logarithm of k_1 for DMABN in butyronitrile/octane mixtures versus the polarity of those mixtures. Slope = 0.641 ± 0.038, intercept = −2.48 ± 1.5, correlation = 0.990.

Having established that the details of the TICT process as given by scheme 1 are valid for DMABN in the solvents we studied, we sought to separate the effects of solvent polarity and viscosity on the isomerization dynamics. Two techniques were used: (i) k_{obs} was measured at room temperature in isoviscous mixtures of a nitrile and an alkane where the polarity of the mixture was controlled by the concentration of the nitrile, and (ii) the temperature was varied for each neat solvent so that the solutions had the same viscosity but different polarity values. In the isoviscosity experiment with nitrile mixtures it was found that there is a linear relationship between the logarithm of k_1 and the solvent polarity parameter, $E_{\text{T}}(30)$ (see fig. 1). To obtain an expression which reflects this exponential dependence of the rate on the solvent polarity, we start with an Arrhenius-type rate equation. The polarity dependence is introduced by making the assumption that the barrier height E_{a} decreases linearly with increasing solvent polarity $E_{\text{T}}(30)$.

$$E_{\text{a}} = E_{\text{a}}^{0} - A[E_{\text{T}}(30) - 30], \qquad (2)$$

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‡ The authors thank Professor J. Clark for showing us a preprint of his work.

where $E_T(30)$ is the solvent polarity parameter, E_a^0 is the activation energy in an alkane solvent having an $E_T(30)$ of 30 kcal/mole, and A is a measure of how strongly the barrier height changes with solvent polarity. The polarity-dependent expression for the rate which can be fit to our data is

$$k_1 = C\exp\{A\,[E_T(30) - 30]/RT\}\exp(-E_a^0/RT). \quad (3)$$

The constant A was determined from the least-squares fit to the data of fig. 1: $A = 0.37 \pm 0.02$. The Arrhenius pre-exponential factor, C, is obtained from the experiment where the temperature is varied, and has a value 1.9×10^{13} s^{-1}, which is in the range of Arrhenius prefactors obtained for other isomerizations such as that of diphenylbutadiene in alkanes [1].

From the isoviscous experiments performed in neat nitriles at different temperatures, we have further evidence that the barrier is strongly dependent on solvent polarity. The data in table 1 show that as the temperature of the medium is lowered, the rate of formation of the charge transfer (A*) state of DMABN increases rather than decreases. If the internal barrier height were independent of solvent and temperature, the rate of the isomerization would decrease as the temperature is lowered. We propose that the anomalous behaviour for DMABN indicates that the barrier is not constant with temperature. This can be traced to the fact that the polarity of the liquids increases as the temperature is lowered. The barrier would therefore not remain constant as the temperature is lowered since the highly polar A* form of DMABN would be stabilized relative to the "non-polar" B* form. The barrier would in fact decrease with increasing polarity, as given by eq. (2), thereby overcoming the usual temperature effect, and causing the increased isomerization rate with decreasing temperature as we observed. To isolate the effect on the height of the barrier, we plot the logarithm of the polarity-corrected rate, κ, versus the inverse of the temperature (see fig. 2).

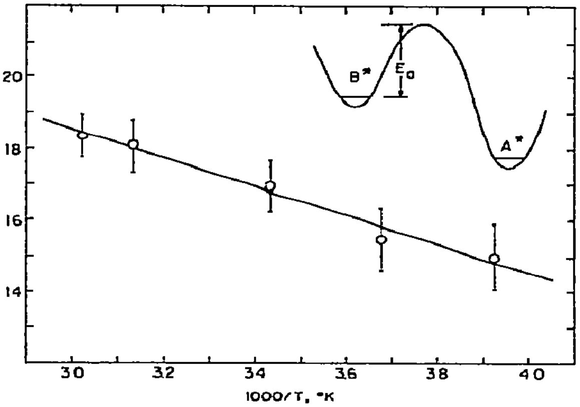

Fig 2. Isoviscosity Arrhenius plot for DMABN in neat nitriles where the rate is corrected for temperature-induced polarity changes $\kappa = k_1 \exp\{-A[E_T(30) - 30]/RT\}$, slope = −4018 ± 350, intercept = 30.58 ± 1.2, correlation = 0.978.

$$\kappa = k_1 \exp\{-A\,[E_T(30) - 30]/RT\}. \quad (4)$$

There are no adjustable parameters in this expression since k_1 and $E_T(30)$ are measured, and A was obtained in a separate set of experiments at a fixed temperature. We now obtain the expected negative slope corresponding to $-E_a^0/R$, the barrier for the isomerization in an alkane solvent divided by the gas constant R. It has a value of $E_a^0 = 8.0 \pm 0.7$ kcal/mole. Using this value of E_a^0, the barrier in a polar solvent such as butyronitrile can now be calculated from eq. (2), and a value of 3.2 ± 0.8 kcal/mole is obtained. From the values for

Table 1
Temperature effects on TICT of DMABN in nitriles: isoviscosity conditions, viscosity = 1.0 cP [a]

Solvent	Temperature (°C)	F	k_{obs} (10^{10} s^{-1})	k_1 (10^{10} s^{-1})	$E_T(30)$
C_4H_7N	−18.5	0.08 ± 0.01	6.25 ± 0.89	5.75 ± 1.0	43.3
C_5H_9N	−1.3	0.08 ± 0.02	6.66 ± 1.0	6.13 ± 1.2	43.7
$C_6H_{11}N$	18.0	0.55 ± 0.01	5.55 ± 0.70	5.27 ± 0.80	42.0
$C_8H_{15}N$	45.7	0.10 ± 0.01	4.00 ± 0.35	4.97 ± 0.93	41.1
$C_9H_{17}N$	57.5	0.19 ± 0.01	4.00 ± 0.35	3.24 ± 0.46	40.3

[a] Error in E_T value is 0.2 kcal/mole. Viscosity values interpolated from data in ref. [27].

the activation energy in a non-polar solvent and in a polar solvent such a butyronitrile we see that the proposal of a barrier whose height changes with the polarity of the medium gives a simple explanation for the appearance of dual fluorescence in polar solvents and a single fluorescence in alkanes or the gas phase: a certain polarity is required before the TICT barrier is low enough to allow the forward TICT process to proceed within the lifetime of the initially excited state. Using eq. (3), we find quantitative support for this statement Calculation of k_1 in an alkane of $E_T(30)$ = 30 kcal/mole yields a value of 2×10^7 s^{-1}, a rate that is slow compared to the rate of decay of the excited B* state, 3×10^8 s^{-1}.

From these kinetic measurements we obtain information not only on the dependence of the barrier height on solvent polarity but on how the free energy difference ΔG_{A*B*} between the planar (B*) and twisted (A*) forms depends on polarity. The dependence of ΔG_{A*B*} on polarity in turn can provide some insight into the change in barrier height, E_a, with polarity. The free energy difference ΔG_{A*B*} is obtained from measurement of the excited-state equilibrium constant K_{eq}. By rearrangement of eq. (1), we find that

$$K_{eq} = k_1/k_2 = (1 - F)/F\,, \qquad (5)$$

where F is the measured fraction of fluorescence at time zero due to the slowly decaying component from the planar (B*) state. The free energy difference is then obtained from the expression $\Delta G_{A*B*} = -RT \ln K_{eq}$ for DMABN in each of the liquids studied. As shown in fig. 3, ΔG_{A*B*} decreases linearly with increasing solvent polarity. The charge transfer state, A*, having the larger dipole moment, interacts more strongly with the polar solvent, and is stabilized relative to the B* state. It has been noted by many authors that as the free energy difference between initial and final states decreases, the barrier between the two may also be lowered [1,28,29]. This can be readily seen if one assumes that the shapes of the potential wells are constant as the energy of the final state decreases. The intersection of the two wells would then occur at lower energies as one well is vertically displaced. In the DMABN case, this change in the relative energy positions of the potential surfaces is brought about by an increase in the solvent polarity.

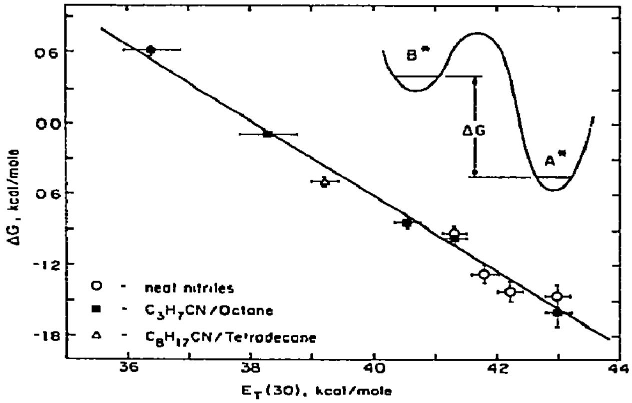

Fig. 3. Free energy difference between the planar and twisted forms of DMABN in neat nitriles (circles), in butyronitrile/octane mixtures (squares), and in 0.8 M octyl cyanide/tetradecane (delta) versus the polarity of those solvents. Slope = −0.321 ± 0.015, intercept = 12.2 ± 0.6, correlation = 0.984.

Having obtained quantitative expressions for the polarity dependence of the rate k_1, we can now correct for the polarity differences in neat nitriles in order to investigate the viscosity dependence of the isomerization. In fig. 4, the logarithm of the polarity corrected rate, κ (eq. (4)), is plotted versus the logarithm of the viscosity. Due to the larger error bars, which originate in the uncertainty in A which is propagated exponentially, it is difficult to report with confidence that there is little or no viscosity dependence of the rate. The best fitted line suggests that there is a zero or even slightly positive dependence of the rate on viscosity; the slope is 0.2 ± 0.9. Experiments designed to better isolate viscosity as a parameter are currently being planned.

If the rate k_1 is plotted against $1/\eta^a$, as is commonly done [30], disregarding changes in the polarity of the solvent, we would find that $a = 0.63 \pm 0.08$. This might be construed (incorrectly) to be the $\eta^{-2/3}$ dependence predicted by the Förster model for energy relaxation

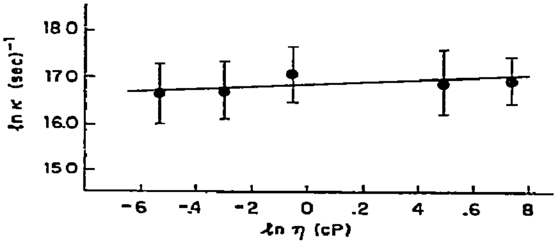

Fig. 4. Plot of ln κ ($\kappa = k_1 \exp\{-A[E_T(30) - 30]/RT\}$ versus ln η. Slope = 0.2 ± 0.9, intercept = 16.8 ± 0.8, correlation = 0.7.

due to isomerization in excited-state triphenylmethane dye molecules [31]. To reach the conclusion that the TICT process for DMABN is viscosity dependent without examining the effects of solvent polarity would be misleading, as we have shown in the above discussion.

For the case of other molecules in polar solvents which have been used to test barrier crossing theories, e.g diphenylbutadiene [4], DODCI [5], stilbene [10], and ethyl violet [6,11], where the transition over the barrier to isomerization probably also involves charge transfer, we suggest that solvent polarity effects on the barrier height might also be important. In the case of diphenylbutadiene, it has been noted that the barrier is lowered in going from alkanes to alcohols, but the solvent polarity changes within the alcohol series have not been considered to be significant [4]. It turns out that the data can also be fitted with polarity effects included. This can lead to a different internal barrier and viscosity dependence and therefore would alter the interpretation of the isomerization dynamics. It would be interesting to see if solvent polarity and viscosity effects both play large roles in the isomerization of diphenylbutadiene, though the viscous drag could dominate since the motion involves a relatively large volume change compared to that of DMABN.

Finally, the occurrence of a negative temperature dependence of the rate of isomerization of ethyl violet in different isoviscous alcohols [6] indicates that a polarity effect is important in this molecule. Upon correcting for the polarity by fitting the data to our model as outlined in this paper, we find that the negative temperature dependence is removed and a positive energy of activation is obtained. While it has been noted that the barrier height for the isomerization of ethyl violet and crystal violet in the lower alcohols increases through the solvent series from methanol to octanol [11], it is not recognized that, even in a single solvent, polarity changes due to temperature influence the rate. We find that the turn-over behaviour observed for ethyl violet and crystal violet in higher alcohols can be explained by barrier height changes due to the variation of temperature. We conclude that, before examining the viscosity dependence of the isomerization rate in a series of polar solvents and over a range of temperatures, it is necessary to consider this polarity effect.

4. Conclusions

We have shown that the polarity of the solvent can play a key role in the isomerization dynamics of molecules where there is a large change in charge distribution. We find that the barrier height for the isomerization changes dramatically with polarity for DMABN in a series of nitriles and nitrile/alkane solutions. The change in barrier height affects the dynamics and this must be taken into account before applying barrier crossing theories to rates of molecules in solution. We also conclude that the twisted internal charge transfer model involving the rapid equilibration between "non-polar" and polar excited states is valid for the isomerization of DMABN in nitrile solutions.

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