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POLARITY-DEPENDENT BARRIERS AND THE PHOTOISOMERIZATION DYNAMICS OF MOLECULES IN SOLUTION

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The dynamics of molecular isomerizations that involve major charge redistributions are studied using picosecond lasers. The usual assumptions that the isomerization barrier is independent of temperature and constant within a solvent series are found to be incorrect due to solvent polarity effects. Polarity and hydrogen bonding effects on isomerizations involving large dipole moment changes (*p*-dimethylaminobenzonitrile) and those involving a polar intermediate (*t*-stilbene) are discussed.

1. Introduction

Efforts to understand solvent effects on chemical reactions have often been directed towards "simple" unimolecular reactions such as photoisomerizations [1–18]. Comparisons of the kinetics of reactions with the predictions of barrier crossing models have been applied to a number of different molecules in a variety of solvents [3–9]. In many of these experimental and theoretical studies, the principal solvent effect that is considered is a collisional or frictional one. The idea is that the solute–solvent collisions interfere with the crossing of the barrier separating the reactant and product structures, and thereby slow the reaction. To study the effects of the solvent on isomerization, the kinetics are often measured in a solvent series, e.g. an alcohol series or an alkane series, where the viscosity increases as one goes to larger members of the solvent series. Implicit in these studies are the assumptions that the isomerization potential energy barriers are the same for the various members of the series, and that it is only the variation in solvent viscosity that is important in affecting the isomerization [‡]. Similarly it is assumed that changing the temperature in a given solvent alters only the solution viscosity and the population at the top of the barrier, i.e. the Boltzmann factor. The potential energy barrier is assumed, therefore, to be independent of the solution temperature.

In this paper we consider isomerizations that involve major charge redistributions, and which consequently experience strong interactions with polar solvent molecules. The idea that the barrier to isomerization remains the same for the different members of a solvent family or for a given solvent at different temperatures cannot be confidently assumed. For polar solute molecules that undergo a very large change in dipole moment on isomerization, such as *p*-dimethylaminobenzonitrile (DMABN) [17], and for non-polar molecules that pass through polar intermediate structures in the course of isomerizing, such as *t*-stilbene [5–16], polarity-dependent barrier effects due to changes in temperature in a given solvent or variation in the energy barrier within a solvent family at a given temperature must be considered.

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. A Nd^{3+}/YAG laser with pulses 30 ps in duration was used to excite the *t*-stilbene, and the fluorescence was detected using a streak

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[‡] Cases where polarity effects through a solvent series or with gas density have been considered include refs. [7,12,18].

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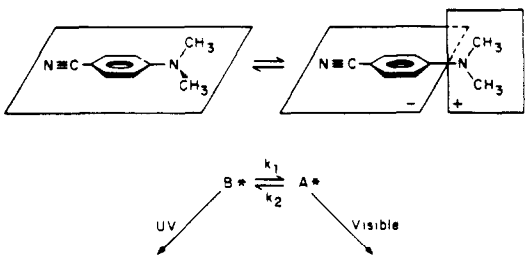
camera, as for DMABN. A polarizer oriented at 54.7° was placed in the collection optics to avoid the effects of time-dependent depolarization of fluorescence. The apparatus and data handling procedures have been described [17,19]. Temperature control($\pm 0.1\,^{\circ}$C) (was attained by using a Neslab circulation cooler connected to a copper block into which the sample was placed. DMABN (Aldrich) was purified twice by vacuum sublimation. *t*-stilbene (Kodak) was scintillation grade and was used as received. Absolute ethanol was refluxed over Mg, and then fractionally distilled under dry nitrogen and used immediately. Propanol, butanol, octanol, and decanol (Gold Label, Aldrich) were allowed to sit over cleaned, activated Type 4A molecular seives, before use. Pentanol and hexanol (Aldrich) were fractionally distilled over P_2O_5 and stored over molecular seives. The nitriles were purified by fractional distillation, and stored over type 4A molecular sieves. A 0.25 mM concentration of DMABN and a 0.05 mM concentration for *t*-stilbene were used for the samples. All solutions were sealed and degassed in 1 mm path length quartz cells.

3. Results and discussion

3.1. DMABN – isomerization of a polar molecule

For a molecule that undergoes a significant charge redistribution on isomerization, the dynamics and even the occurrence of the isomerization can depend on the solute–solvent interactions. A classic example of the effects of charge redistribution on the excited state isomerization is that of *p*-dimethylaminobenzonitrile (DMABN), where a structural change occurs in polar but not in non-polar solvents. From the many studies [19–33] of this molecule a general outline of the dynamics has been developed, scheme 1. The general picture [21,24,25] involves a rotation of the dimethylamino group about the amino–phenyl bond resulting in a charge separation between the two groups and concomitantly a large increase, 10 D, in the excited state dipole moment [25]. In polar solvents the twisted, larger dipole form is stabilized, producing a new emission in the visible that does not appear in non-polar solvents. Rapid equilibration [19] between the twisted and planar forms in polar media yields a dual fluorescence: one band due to the planar form in the UV and the other to the twisted form in the visible.



Scheme 1. Photoisomerization of DMABN.

Having established some of the key ideas of the isomerization, it becomes possible to investigate how the solute–solvent interactions affect the observed kinetics. As we have already noted, a commonly used approach to determine the effects of solution viscosity on the kinetics of a reaction is to carry out measurements in a solvent series, e.g. the linear alcohols, methanol, ethanol, propanol, etc. Following this approach, the forward rate constant k_1 at room temperature yielded a viscosity dependence of $k_1 \approx \eta^{-2/3}$ in the nitrile series [17], whereas in the alcohol series [34] it was roughly η^{-1}. These results could indicate that the frictional effects for DMABN in alcohols were in the Smoluchowski regime of very strong coupling, and in nitriles, in the intermediate coupling region. However, this interpretation is based on the assumption that only the viscosity is important in the structural kinetics. For cases of isomerization where a large change in dipole moment does *not* occur, polarity differences within a series are probably of minor importance. For a polar transition, however, this cannot be assumed to be the case.

3.1.1. Solvent viscosity and polarity effects

To separate the effects of solvent polarity and viscosity, we have used two approaches. In one, the forward rate constant k_1 was measured at room temperature in mixtures of a polar solvent and an alkane solvent having the same viscosity, and for which the mixtures also had the same viscosity. The polarities of these isoviscous solutions were controlled by the concentration of the polar component. In the second approach, the temperatures of the neat solvents were adjusted so that their viscosities were the same, but their polarities differed.

As shown in fig. 1 the isomerization rate constants measured in solutions having the same viscosity and temperature are *not constant*, contrary to the predictions of frictional and collisional theories, but indeed vary exponentially with the empirical solvent polarity parameter $E_T(30)$ [35]. The fitting of the kinetic data with theoretically derived polarity expressions gives the correct trend but the correlation with experiment is not as good as when $E_T(30)$ is used.

3.1.2. Effect of temperature on solvent polarity

Further support for the effects of solvent polarity on the isomerization dynamics is obtained from the second technique, where the same viscosity is obtained in the various neat liquids by adjusting their temperatures. The different rates measured have usually been assumed to be due to the different Boltzmann factors, since the only other factor considered (i.e. the viscosity) is the same in all of the experiments. This can be seen in the following Arrhenius type expression

$$k=Bf(\eta)\exp(-E_a/RT)\,, \qquad (1)$$

where E_a is the barrier height, $f(\eta)$ is the viscosity function (which is a constant for the isoviscosity experiment) and B is the pre-exponential frequency factor. We carried out these measurements in both neat alcohols and neat nitriles, and found for both solvent families that the *rate increases as the temperature is lowered.* This result of a "negative" activation energy is contrary to what would be the case if only Boltzmann factor is changing.

To explain these results, we propose that the barrier height is not independent of temperature, but decreases due to a higher solvent polarity at lower temperatures. This larger solvent polarity at lower temperatures is manifested by an increase in the measured $E_T(30)$ value as well as an increase in the related solution dielectric constant. The polar twisted form of DMABN (A*) is stabilized relative to the initially excited planar form (B*) due to the higher polarity, and thus larger solvation energy at the lower temperature, thereby leading to a smaller barrier (see scheme 2). This decrease in the barrier overcomes the usual Boltzmann effect and is responsible for the increased rate at lower temperature. When we correct for the temperature-induced polarity changes, we

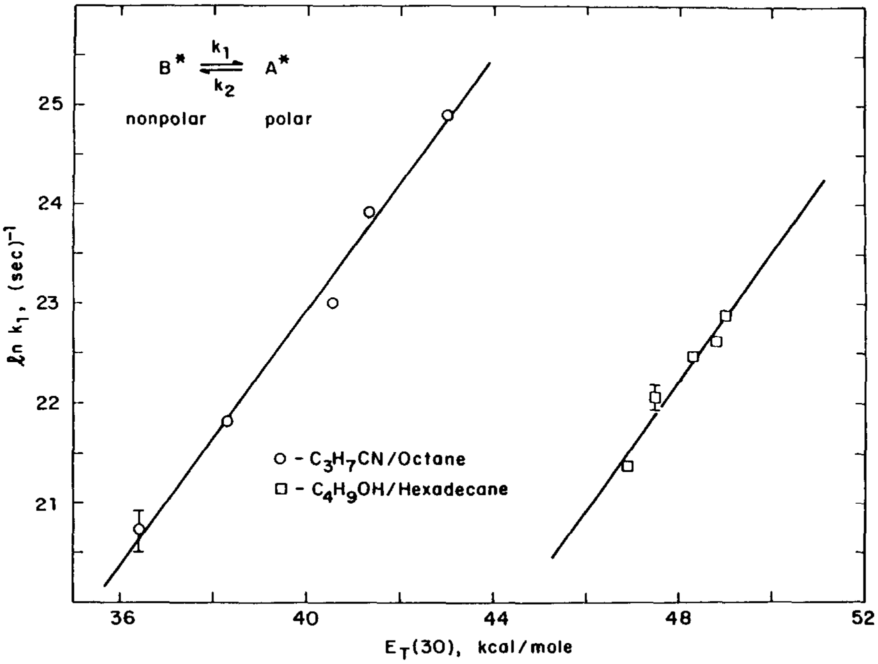
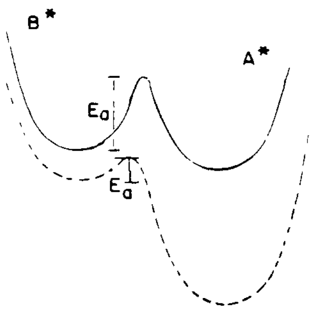


Fig. 1. Plot of ln k_1 versus the solvent polarity parameter $E_T(30)$ for DMABN in butyronitrile/octane and butanol/hexadecane mixtures.



Scheme 2. Dependence of barrier E_a on solvent polarity. An increase in solvent polarity (dashed curve), achieved by lowering the temperature and/or by going to a more polar solvent, preferentially stabilizes the more polar A* state and thereby lowers the barrier E_a.

find that the corrected rate decreases as the temperature is lowered, i.e. a normal positive activation energy is obtained, as seen in fig. 2.

3.1.3. Hydrogen bonding effects on the isomerization

Both the alcohol and nitrile date shown in figs. 1 and 2 can be explained by introducing a polarity-dependent barrier E_a:

$$E_a = E_a^0 - A[E_T(30) - 30] , \qquad (2)$$

where E_a^0 is the activation energy in an alkane solvent having an $E_T(30)$ of 30 and A is an experimentally determined factor that determines how strongly the barrier height changes with solvent polarity. The corrected rate κ, plotted in fig. 2, is

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

$$= C \exp(-E_a^0/RT) , \qquad (3)$$

where C is the Arrhenius pre-exponential factor. The values of E_a^0 are found to be 8.0 kcal/mole in the nitriles and 14.0 kcal/mole in the alcohols. Comparing the nitriles and alcohols at a given solvent polarity, we see that the barrier E_a^0 is higher in alcohols by about 6 kcal/mole. We attribute this to the effects of hydrogen bonding between the dimethylamino group of DMABN and the alcohol hydroxy group. The hydrogen bond withdraws electrons from the electron donating dimethylamino part of DMABN and thereby opposes the electron transfer to the benzonitrile part of DMABN. For the intramolecular charge transfer in DMABN to occur, the hydrogen bond must be broken. This increases the barrier for the

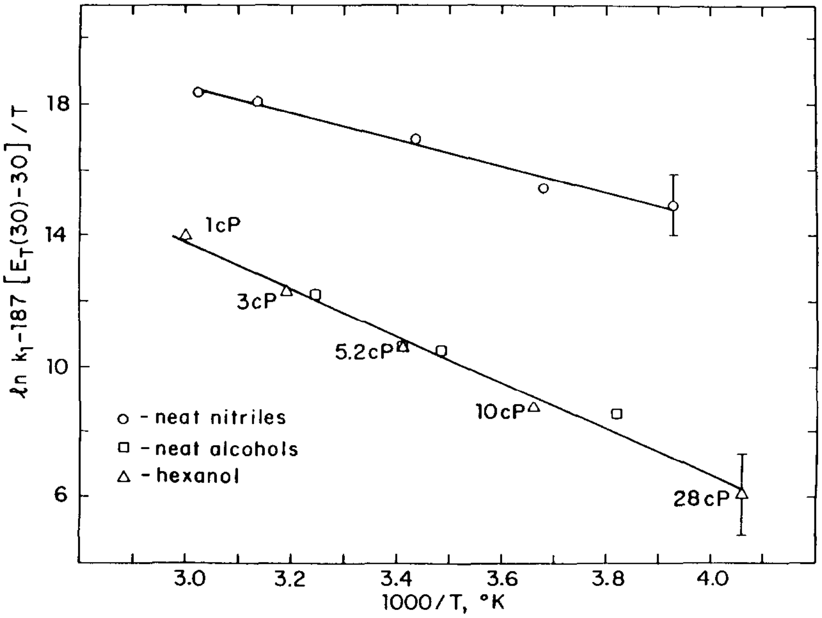


Fig. 2. Arrhenius plot of polarity corrected rate for DMABN in neat isoviscous nitriles (1.0 cP), neat isoviscous alcohols (5.2 cP), and hexanol at the indicated viscosities.

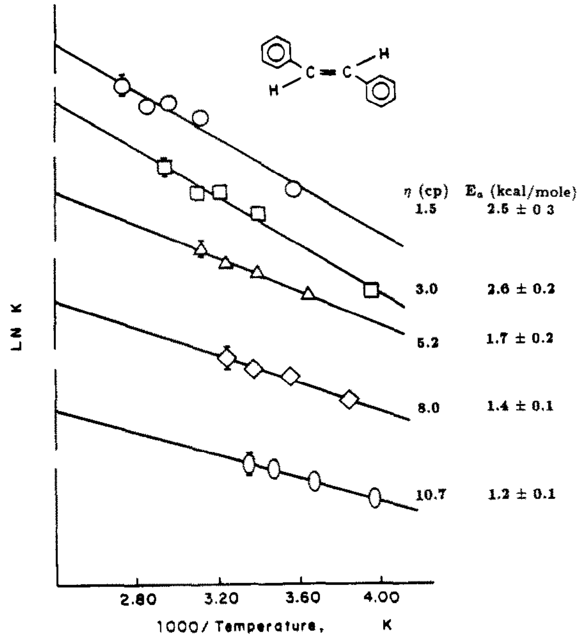


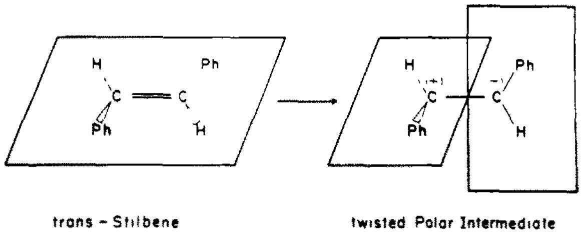
Fig. 3. Plot of ln k versus T^{-1} for *t*-stilbene in isoviscous alcohols; the ordinate axis is offset for each viscosity line for viewing purposes.

isomerization in alcohols relative to nitriles by 6 kcal/mole, roughly the energy of a hydrogen bond.

3.2. Trans-stilbene – isomerization involving a polar intermediate structure

The photoisomerization of *t*-stilbene has been studied by many groups to gain insight into how the solvent affects this simple chemical change [5–16]. The observed rate has been discussed in terms of eq. (1), where $f(\eta)$ is either the Kramers function (which gives poor agreement with the observed rates) or more often $\eta^{-\alpha}$, which can be fit to the data [5,9]. This latter form can be obtained from a free-volume [36] or frequency-dependent model [37–40]. This general equation predicts that at constant viscosity, a plot of ln κ versus T^{-1} should have the slope $-E_a/R$. We have tested this prediction by studying the rates of photoisomerization of stilbene in alcohols at various temperatures under constant viscosity conditions.

In fig. 3 it is shown than the slopes of these lines depend on viscosity, contrary to what the equation predicts. The apparent E_a vary from 2.6 to 1.2 kcal/mole. A further deviation from eq. (1) for $f(\eta) = \eta^{-\alpha}$, is shown by the dependence of the rate on viscosity at different fixed temperatures. We find that the value of α varies by a factor of two over a 50 K temperature range. This result conflicts with the constant α value predicted by the $\eta^{-\alpha}$ dependence of the rate equation.



Scheme 3. Photoisomerization of *t*-stilbene, involving a twisted polar intermediate.

3.2.1. Dynamic polarity effects

To understand these deviations from a frictional model as given by eq. (1), we ask whether polarity-dependent barrier effects are important in the isomerization process, noting that the stilbene isomerization involves an intermediate structure that is highly polar, scheme 3[‡]. That there is a solvent effect on the barrier is seen in the difference between the value for E_a of ≈ 3.5 kcal/mole estimated from isolated supersonic jet beam experiments [10,11] or isoviscosity measurements in liquid alkanes [5,9], and the lower values for E_a we find in the alcohols. It is of interest to note that there is presently discussion [12–15] as to whether the approximately equal values of E_a found in the jet and liquid alkane studies can be interpreted as meaning that the barriers are equal, or whether it is only apparent and that a change in barrier height does occur in going from the isolated stilbene molecule to stilbene in the non-polar environment of liquid alkanes. On the one hand the kinetic data ranging from the jet to the liquid state

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[‡] It should be noted that the barrier in the photoisomerization of trans-stilbene occurs between the planar excited trans-stilbene and the twisted polar intermediate in scheme 3, not the cis-stilbene conformer. The rate limiting step in the isomerization is the barrier crossing to the polar intermediate, which is then followed on a shorter time scale to the ground cis or trans forms of the molecule.

experiments can be interpreted [12] in terms of a constant barrier of 3.5 kcal/mole. This model includes effects such as non-adiabatic and incomplete intramolecular vibrational redistribution, which decrease in importance with increasing density, i.e. collision rate. The alternative explanation [13] that also explains the kinetic data suggests that the potential surface and thus the barrier height is density dependent and does indeed change due to clustering of stilbene with alkanes in the gas phase all the way up to the liquid phase. The results of the present study in alcohols cannot differentiate between these interpretations, though we note that in the alkane-induced barrier change model the estimate of a barrier in liquid alkanes of about 1.4 kcal/mole [15] is lower than, or in the range of, the values we obtain for the alcohols. This is somewhat surprising since we would expect that the strongly polar alcohol solutions would more strongly stabilize the polar intermediate form and thus have a lower barrier than the alkane solutions. However, it should be emphasized that the 1.4 kcal/mole barrier is based on a fitting of high-pressure gas phase data [15]. Changes in some of the fitted parameters, such as the cluster equilibrium constant, could increase the alkane barrier and thereby make the model of alkane-induced barrier shifts more consistent with our alcohol results, without compromising their density-dependent barrier model.

At this point in the discussion we ask whether the variation in barrier heights found in alcohol solutions at different isoviscosities, fig. 3, can be explained by taking into account the variation in solvent polarity within the alcohol family, and the variation in solvent polarity with temperature, as we did for DMABN. Our attempts to fit the stilbene data with a barrier that is the sum of a polarity-dependent part and a polarity-independent part, as in our treatment of DMABN, was not successful. Unlike DMABN we found that static polarity effects, including static viscosity effects, do not explain the kinetic data for stilbene in alcohols.

This finding that a static polarity model is not adequate could be due to a dynamic polarity effect arising from the extensive solvent rearrangements required in crossing the barrier separating the initial planar non-polar trans-stilbene from its twisted charge-separated intermediate form (scheme 3). For DMABN such large-scale solvent motions are not necessary since the isomerization involves an increase in dipole moment along the *same axis* from a polar (6 D) to a more polar (16 D) form. The solvent is already arranged about the large dipole of the initially excited DMABN, and thus very small changes in solvent positions are required in the transition. For stilbene, on the other hand, the solvent arrangement about the initially excited *t*-stilbene is appropriate to a non-polar solute molecule. Thus, extensive rearrangements of the surrounding alcohol molecules are necessary for the transition from the non-polar *t*-stilbene to the zwitterionic intermediate structure. If the solvent motions are slow compared to the isomerization time, which would be the case for the breaking up of the hydrogen bonding network of alcohols, then the isomerization dynamics would depend critically on the dielectric relaxation properties of the solvent [41–47] [#]. The energy barrier separating the trans and the intermediate form would therefore depend upon the positions of the surrounding solvent molecules, and thus be dependent on the rate of change of the solvent arrangement. With these considerations in mind, it is perhaps not surprising that static viscosity and polarity effects are not adequate to explain the isomerization dynamics of *t*-stilbene.

4. Conclusions

We find the isomerization dynamics of molecules that involve a large charge redistribution, such as in DMABN, are strongly dependent on the polarity of the solvent. The solute–solvent interactions can be described in terms of a polarity-dependent barrier that separates the two structural forms of the molecule. In addition to the well-recognized effects of barrier height changes in going from a non-polar to a polar solvent, we find that polarity changes within a series of related polar liquids, e.g. linear alcohols or nitriles, and changes in the polarity of a given solvent with temperature are crucial to the observed kinet-

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[#] The effects of solvent dielectric relaxation time on processes such as barrierless charge transfer reactions, electron solvation, and rotations of dipolar solute molecules, has been the subject of important experimental and theoretical activity (see refs. [34–40]).

ics. We have also found that hydrogen bonding of DMABN with alcohols impedes the isomerization relative to that of non-hydrogen bonding polar solvents such as nitriles.

For *t*-stilbene in alcohols, we have found from measurements at various viscosities and temperatures that the isomerization cannot be described in terms of frequently applied equations that contain and $\eta^{-\alpha}$ power dependence. Although there is a solvent-induced change in the barrier, as seen by the decrease in barrier height in going from the isolated molecule to the solution phase, we find that we cannot fit the data using a static polarity correction as we did for DMABN. The possibility of a dynamic polarity effect due to a large solvent rearrangement in going from the non-polar initially excited *t*-stilbene to the polar-twisted intermediate stilbene structure is discussed.

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