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Evidence for Dynamical Solvent Effects on the Photoisomerization of 4,4′-Dimethoxystilbene

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The photoisomerization dynamics of 4,4′-dimethoxystilbene have been studied in *n*-alkanes and *n*-alkyl alcohols as a function of temperature at ambient pressure. By comparison with unsubstituted stilbene results the influence of the methoxy group, both intramolecular and intermolecular, on the isomerization process has been evaluated. The studies in *n*-alkane solvents reveal larger barrier heights and a weaker viscosity dependence for dimethoxystilbene compared to those of stilbene. This observation is in agreement with earlier ideas concerning frequency-dependent solvent effects but contrary to free volume models of solute–solvent friction. The studies in *n*-alkyl alcohol solvents demonstrate the inability of separating intramolecular from intermolecular effects. The potential energy surface associated with the reaction is strongly coupled with solvent dynamics, hence time dependent. These results demonstrate the importance of understanding microscopic friction and dielectric interactions on ultrashort time scales.

Introduction

Considerable effort has been placed on the investigation of trans–cis photoisomerization of stilbenes[1–8] and a variety of similar molecules in solution. The goal of this work has been to understand the influence of the solvent on the reaction dynamics. Because the isomerization process involves a large-amplitude motion, it is expected to couple strongly with the solvent friction. In most cases the solvent friction has been modeled by the solvent viscosity; however, there are notable exceptions where the reorientation time of the solute has been used as a measure of the solvent friction.[9–11] Because the isomerization involves a polar transition state, dielectric solute–solvent interactions (i.e., "polarity" effects) are found to be important. Initially discussed from a static viewpoint, more recent studies have focused on dynamical dielectric effects.[5,12–14] These efforts as a whole have been fruitful, primarily because they underscore the importance of the very short time solvent response on the reactive process. In this work a study of a stilbene analogue, 4,4′-dimethoxystilbene, is described where the isomerizing moeity now possesses a dipole moment and is expected to displace approximately twice as much solvent volume in the isomerization process as does the unsubstituted stilbene. The goal of this study is to understand how the solute properties modify its interaction with the solvent.

Previous work in this field, both experimental and theoretical, has been reviewed.[1,15–18] The pertinent experimental conclusions can be outlined as follows. Velsko et al.[9,19] showed for the case of diphenylbutadiene in the *n*-alkanes and the dye molecule, DODCI, in the *n*-alkyl alcohols that the intramolecular barrier effects could be separated from the effect of the solvent in the reactive process. The possibility for this separation occurs because models for isomerization rate constants have the form of

$$k_{\text{iso}} = F(\xi)\exp(-E_0/kT) \tag{1}$$

where $F(\xi)$ is a function of the solvent friction, ξ, and solute parameters and E_0 is the free energy barrier height. The exact form of $F(\xi)$ depends on the particular model. This separation was performed via an "isoviscosity" plot; that is, an Arrhenius type plot was made for the isomerization rate constant in different solvents at different temperatures but the same shear bulk viscosity. This approach assumes that a constant shear viscosity results in a constant $F(\xi)$. From the slope of the plot, the activation energy was then interpreted in terms of the intramolecular barrier to isomerization. This separation of the solvent effect from the barrier effect has been an underlying theme in the interpretation of similar experiments.[2–5,8–14,18–21] Variations on this theme have occurred, most notably the work of Hicks et al.[12] in which the effect of the solvation of the isomerizing particle on the activation energy for the reactive process is included. This separation of barrier and solvent effects is not always possible. In particular, researchers have observed a breakdown of this separation in *n*-alkyl alcohol solvents,[5,11,14] and a model for this effect is discussed later.

Once the barrier effect is extracted, the "reduced isomerization rate", $F(\xi)$, can be analyzed and its solvent dependence studied. Most of the experimental studies have focused on the applicability of the one-dimensional Kramers model[22] to describe the isomerization. These investigations have been limited by the modeling of solute–solvent friction when testing the Kramers model. A variety of studies exist where the zero-frequency solvent shear viscosity (a bulk property) is used to model the microscopic friction. Other studies have used both the shear viscosity and the overall rotational diffusion correlation time as measures of the solute–

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solvent friction. In the case of DODCI, Velsko et al.[9] found no difference between these two measures of the friction. In both cases they observed significant deviations from the predicted Kramers behavior. They suggested that the frequency dependence of the friction must be included when modeling the isomerization dynamics. This effect has been discussed by a variety of workers.[2,3,9,10,18] More recently, Courtney et al.[11] and Lee et al.[10] have studied the isomerization dynamics of *trans*-stilbene where the friction is modeled by the shear viscosity and by the rotational diffusion time. Both of these workers find that when the zero-frequency shear viscosity is used, deviation from the Kramers model is observed whereas use of the rotational diffusion time results in good agreement with the Kramers model. This result is reasonable since the rotational diffusion correlation time is a microscopic property and a measure of the microscopic friction on a time scale less far removed from the isomerization time scale than is the zero-frequency shear viscosity. The case of DODCI may be different for two reasons. Firstly, DODCI is charged which would make long-range interactions more important in determining the microscopic friction (hence the viscosity, a hydrodynamic property, a better measure). Secondly, the barrier curvature in the case of DODCI is larger than in stilbene, implying a faster frequency motion and hence a larger time scale separation between the friction experienced via isomerization and that experienced via rotational diffusion. At this time it is still not clear whether the Kramers model in its simple form is adequate. There are three areas which require study: (1) the ability of a one-dimensional picture to adequately describe what must in general be a multidimensional process, (2) the adequacy of various models for the solvent friction, and (3) the importance of a frequency-dependent solvent response.

Our studies with functionalized stilbene should give some insight into the solvent–solute interaction and its influence on the chemical reaction. We have studied the photoisomerization of 4,4'-dimethoxystilbene in both *n*-alkane and *n*-alkyl alcohol solvents as a function of temperature at ambient pressures. Our results in the *n*-alkanes can be analyzed in the sense discussed above (i.e., via "isoviscosity" plots), allowing us to draw comparisons with the work of others on the photoisomerization of *trans*-stilbene.[1-5] The investigations in the alcohol solvents are more complex. When the isoviscosity plots described above are performed, the slopes change as one changes the parameter which measures the solvent friction. We provide evidence that for the alcohol solvents the simple procedure performed above for separating the solvent influence from the intramolecular barrier is inadequate and that in fact the solvent is intimately involved in the potential describing the reaction. Our results show that on the reactive time scale the solvent is never in equilibrium with the solute and the potential energy of the isomerizing species is never well-defined; that is, it changes as the solvent responds to the new orientation of the isomerizing moiety. This effect of the dynamic dielectric response of the solvent has been treated theoretically[23-27] and treated experimentally by Hicks et al.[5] for the case of *trans*-stilbene.

This paper is organized as follows. In the Experimental Section the time-resolved fluorescence apparatus and sample preparation procedures used in this study are discussed. Next the results and their analysis are presented. Subsequently, the results and their analysis are discused in light of available theoretical models. Lastly, a summary of the conclusions of this analysis is presented.

Experimental Section

Because time-correlated single-photon counting has rapidly become a standard technique for the measurement of short fluorescence lifetimes,[28,29] only the relevant specifics of the apparatus are discussed (see Figure 1). The laser system is a synchronously pumped, cavity-dumped ion laser/dye laser system (Coherent Models 468AS mode locker, Innova 90-5 argon ion laser, CR 599 dye laser (extended on optical table), CR 7200 cavity dumper) which generates tunable pulses a few picoseconds duration. The electronics and detection instrumentation consist of an Antel Optronics photodiode (Model AR-55, 140-ps risetime) for the start signal, constant fraction discriminator (Tennelec 454), time-to-amplitude converter (EG&G Ortec 567), and Hamamatsu (R1564U-01) microchannel plate photomultiplier tube, and a Hewlett-Packard (8447D) amplifier for the stop signal. The multichannel buffer is an EG&G ADCAM (918) system with data collection software which interfaces our DEC PRO350

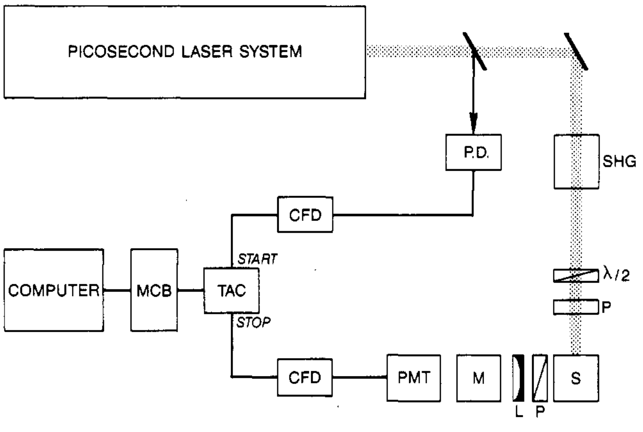

Figure 1. A schematic diagram of the time-correlated single photon counting apparatus is shown: PD, photodiode; SHG, second harmonic generation; λ/2, 1/2 waveplate; L, lens, P, polarizer; M, monochromator; TAC, time-to-amplitude converter; PMT, photomultiplier tube; MCB, multichannel buffer; CFD, constant fraction discriminator; S, sample.

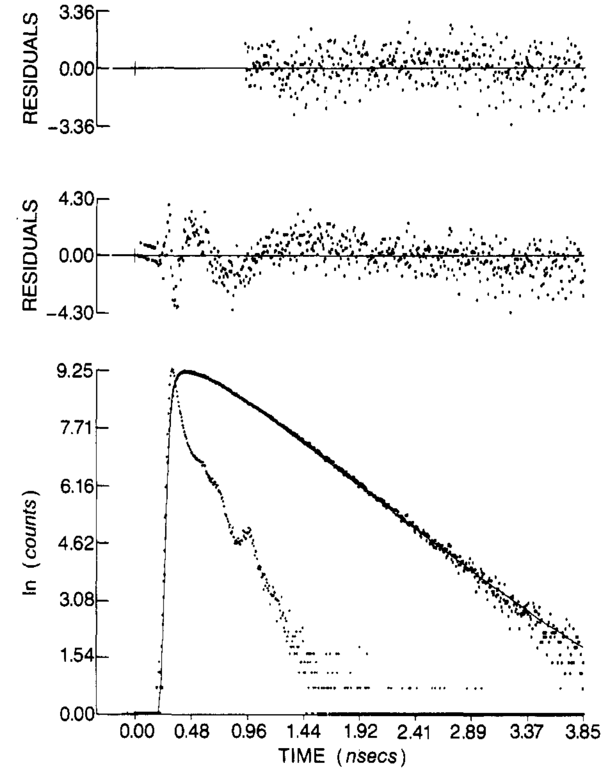

Figure 2. A decay curve is shown for 4,4'-dimethoxystilbene in ethanol at 20 °C. The instrument response function shown has a fwhm ~ 60 ps and a fwtm ~ 140 ps. The solid curve is a fit of the data to a single exponential which is convoluted with the instrument response function. The decay time is 418 ps.

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microcomputer with the multichannel buffer. In these experiments the output of the dye laser was frequency doubled in an angle-tuned $LiIO_3$ crystal. The instrument response function was measured by scattering of the laser pulse in a cuvette filled with a $BaSO_4$–glycerol colloid. Typical response functions had a full width at half-maximum of 60 ps and a full width at tenth maximum of 130 ps (see Figure 2). Count rates in the experiment were kept below 2500 Hz (resulting in a deadtime of less than 2%), and the laser was operated at a repetition rate of 304 kHz. After construction, the apparatus was checked by measurement of lifetimes of known species (stilbene, 9,10-diphenylanthracene, cresyl violet).[28-30]

Steady-state absorption and fluorescence spectra were measured at ambient pressure and temperature. The absorption spectra were measured on a Beckman DU-7 spectrophotometer. The fluorescence spectra were measured in an SLM 8000 (SLM Instruments, Inc.) in the 90° configuration. Relative quantum yields were measured in the same fluorimeter with quinine sulfate in 0.1 N H_2SO_4 as a standard ($\phi = 0.54$).[30-32] The relative quantum yield of anthracene in ethanol (not degassed) was found to be 0.30, in good agreement with literature values of 0.27,[32] and that of 9,10-diphenylanthracene was found to be 0.76 (undegassed), in which literature values range from 0.70 to 0.77.[30]

4,4′-Dimethoxystilbene and all solvents were purified. 4,4′-Dimethoxystilbene was dissolved in hot acetone, washed through activated carbon, and recrystallized from a water/acetone mixture. The purity was checked by a variety of methods, namely, melting point, thin-layer chromatography, mass spectrometry, and NMR. The alcohol solvents were purified by distillation. The alkane solvents were extracted three times (3:1 ratio of alkane:H_2SO_4), washed with deionized water, dried over $MgSO_4$, and passed through a column of silica gel impregnated with silver nitrate. The criterion for purity of the solvents was that fluorescence be low enough to allow measurement of solute fluorescence with minimal solvent interference. Values for solvent properties such as shear viscosity,[33-37] static and optical dielectric constant,[34,35c,35e,39] density,[33,36,40] self-diffusion coefficients,[41,42] and Debye relaxation times[35c,43,44] were taken from the literature. A phenomenological fit of the literature data at various temperatures was performed in order to interpolate the solvent parameter value at the desired temperature.

Fluorescence decay measurements were performed in both the normal alcohol (methanol through decanol) and the normal alkane (pentane through dodecane, tetradecane, and hexadecane) solvents as a function of temperature. The fluorescence decay profiles were fit by iterative convolution of a measured instrument function with a guessed analytical form of the decay (in this case a single exponential). This guessed decay was compared with the measured decay by using the Marquandt–Levenberg algorithm. The specific program used in our fits is that of Cross and Fleming.[45] A sample fit is shown in Figure 2. It was found that the decays were exponential at long time and the decay constants were independent of excitation wavelength (from 315 to 330 nm) and emission wavelength to within our experimental error. Steady-state spectral studies of 4,4′-dimethoxystilbene show that excitation in this region is approximately 30:1 trans:cis.[46] Lifetimes were found to be independent of repetition rate and independent of long irradiation times (up to 8 h). At early times there are marked deviations from single exponentiality which is dependent on emission wavelength. This deviation is attributed to a dynamic Stokes shift (see Figure 3).

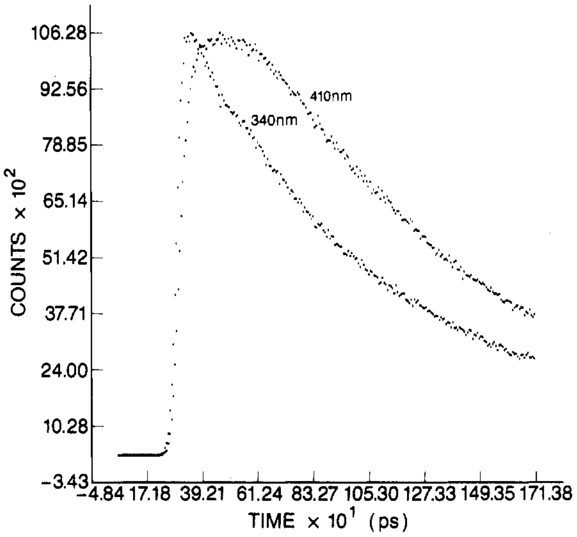

Figure 3. Decay curves for 4,4′-dimethoxystilbene in decanol are shown at two different regions of the fluorescence spectrum. The slower risetime and rounded top of the red emission are the signature of solvent reorganization about the excited state.

TABLE I: Quantum Yields Measured at Room Temperature

solvent	n^2	ϕ	k_r, ns^{-1}
methanol	1.77	0.20 ± 0.01	0.66
decanol	2.06	0.51 ± 0.01	0.53
hexane	1.89	0.72 ± 0.02	0.83
hexadecane	2.04	0.91 ± 0.03	0.93

The isomerization rate constants, obtained from experiment, were fit to various models with analytic functional forms. These fits were performed using the Minpack routines developed by Argonne National Laboratory.[47]

Results

Isomerization Rates. In order to obtain the isomerization rate constants from the fluorescence decay rate constants, it is necessary to know the radiative rate. The radiative rates were obtained by measurement of the quantum yield for four different solvents. The radiative rates obtained are listed in Table I. A radiative rate in the alcohols of 0.32×10^9 s^{-1} and in the alkanes of 0.42×10^9 s^{-1} were used. These values were obtained by dividing the experimental values by the index of refraction squared, n^2, and computing the average. The radiative rate constant in a given solvent at a given temperature was obtained by multiplying the above number by n^2. The isomerization rate constant in a given solvent, at a given temperature, was obtained by means of the following equation

$$k_{iso} = k_F - k_r$$

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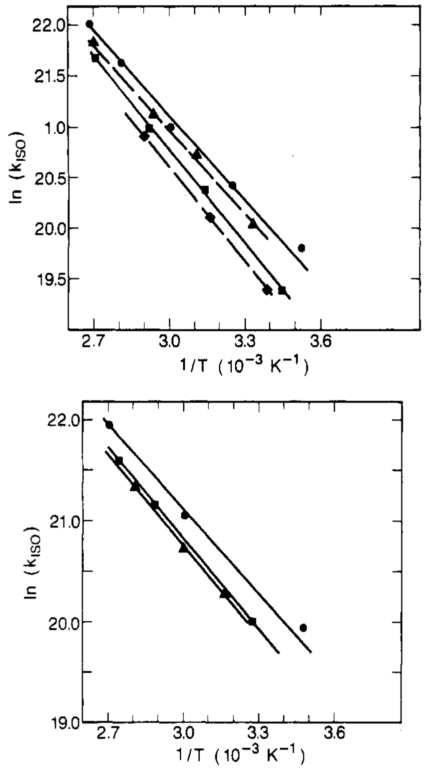

Figure 4. (a, top) Arrhenius type plots at constant viscosity are shown for dimethoxystilbene in the *n*-alkanes. (b, bottom) Arrhenius type plots at constant solvent self-diffusion coefficient are shown for dimethoxystilbene in the *n*-alkanes.

where k_{iso} is the isomerization rate constant, k_F is the fluorescence rate constant, and k_r is the radiative rate constant. This formula assumes that the only nonradiative decay process is isomerization, an assumption which is well-verified for *trans*-stilbene. Previous studies have shown that intersystem crossing should be small for 4-methoxystilbene.[48] Further justification for this assumption can be found in our measured value of $k_F = 0.7 \times 10^9$ s^{-1} in frozen tetradecane, which agrees closely with the radiative rate constant.

Isofriction Plots. Various models of reactive processes in the condensed phase predict a rate constant of the Arrhenius form given by eq 1. It has been common among workers in this field to attempt to separate the solvent effects from the barrier effects by performing an Arrhenius type plot with a constant $F(\xi)$. One method for modeling ξ is to assume that

$$\xi \propto \eta \qquad (2)$$

where η is the solvent shear viscosity which results from a hydrodynamic treatment of the motion of the isomerizing moiety. Other methods may be employed as well. Previous studies[9,11] have measured the overall rotational diffusion coefficients of the solute in the appropriate solvent and used this as a measure of the friction experienced upon isomerization. Ideally, one would like to measure the diffusion coefficients, both translational and rotational, of the moiety undergoing internal rotation and combine these two coefficients to model the friction.

Three types of "isofriction" plots were performed for the alkane data. In the first case, the viscosity was held constant. (Plots were performed between viscosities of 0.35 and 1.5 cP.) This analysis yielded an average slope of 5.66 kcal/mol (see Figure 4a). In the second case, a collision time was computed from the relationship of $\tau_{col}^{-1} = \rho d^2/6\eta$, where ρ is the density and d is the diameter of the solute molecule.[49] The diameter was computed via the van der Waals volume of the solvent molecules and by assuming the solvent molecules are spherical. Despite this crude modeling, Arrhenius plots with constant collision frequency had an average slope of 5.05 kcal/mol. The last approach used the correlation time, τ_{ls}, computed from light-scattering studies of the neat solvent, as a measure of the friction.[41,42] This correlation time has been associated with the rotational self-diffusion coefficient of the solvent molecules. Arrhenius plots at constant τ_{ls} give an average slope of 5.70 kcal/mol (see Figure 4b). The agreement between these approaches to modeling of the friction reflects the insensitivity of the separation of solvent and intramolecular properties to the modeling of the friction.

TABLE II: Isoviscosity Plot Parameters for *n*-Alkyl Alcohols

viscosity, cP	E_{act}, kcal/mol	solvents
0.75	4.62	C_1–C_4
1.0	4.58	C_1–C_4
2.0	3.08	C_2–C_8
3.0	2.82	C_3–C_{10}
5.0	2.84	C_3–C_{10}
7.0	2.69	C_3–C_{10}
9.0	2.61	C_4–C_{10}
10.0	2.47	C_4–C_{10}

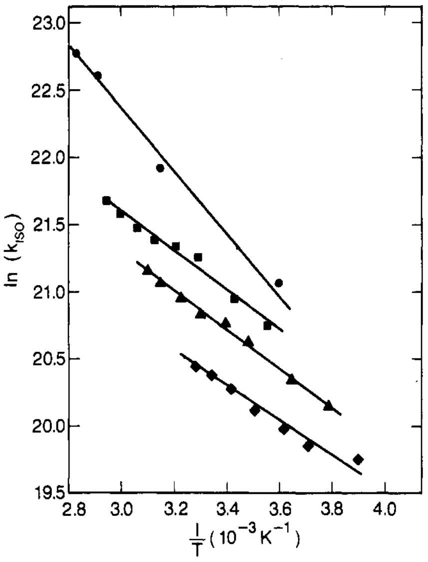

Figure 5. Isoviscosity plots are shown for 4,4'-dimethoxystilbene in the *n*-alkyl alcohols: ●, 0.75 cP; ■, 3.0 cP; ▲, 5.0 cP; ◆, 9.0 cP.

A possible explanation for the lower activation energy from the τ_{col}^{-1} plots is an underestimation of the collision frequency in the longer chain alkanes because of the spherical approximation. The solvent molecules could be better approximated by an ellipsoid, which would have a larger collision frequency for the same volume displaced (because of their larger surface area) than that of the corresponding sphere. An underestimation of the friction would lead to selection of a rate constant which is lower than the true value at the selected friction. Because the more asymmetric molecules are at a higher temperature than the more spherical molecules, this choice would cause the Arrhenius plots to have a shallower slope. As long as the true friction experienced by the solute in the different solvents can be written as a function of the solvent parameter used (η, τ_{ls}, or τ_{col}^{-1}), this approach to separating the barriers appears to be valid. The barrier height used in the rest of this work will be that obtained by using $\xi \propto \tau_{ls}$. It is reasonable to choose this approach because τ_{ls} is a microscopic measure of the solvent/solvent coupling on a time scale more relevant to the isomerization than η. Moreover, τ_{ls} is a nonlinear function of η as one proceeds through the homologous series, although it is linear as a function of η/T within each individual solvent, much like the behavior of the overall rotational diffusion of stilbene in the *n*-alkanes.[3]

In the alcohol solvents, isoviscosity plots lead to a series of lines with different slopes (Table II and Figure 5). In fact, the slope is observed to decrease from 4.62 kcal/mol at 0.75 cP to 2.47 kcal/mol at 10 cP. It is likely that the Arrhenius plots are not linear, but the limited temperature range and small number of

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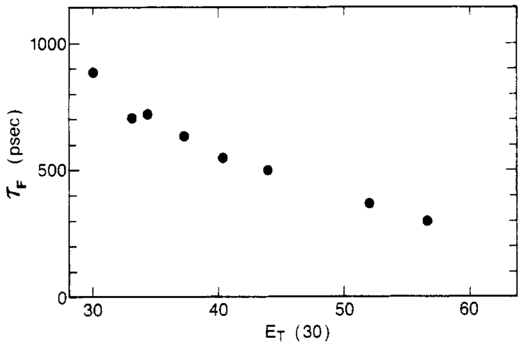

Figure 6. Plot of τ_F versus $E_T(30)$ for dimethoxystilbene in solvents of similar viscosity but varying polarity. In order of increasing $E_T(30)$ the solvents are *n*-decane, mesitylene, xylene, anisole, pyridine, DMF, ethanol, and methanol.

TABLE III: Steady-State Spectral Data in *n*-Alkane Solvents

solvent	λ_{abs}, nm	λ_{fl}, nm	Stokes shift, cm^{-1}
pentane	324.0	370.0	38
hexane	324.7	370.4	1
heptane	324.8	371.0	35
octane	325.3	371.5	24
nonane	325.5	372.0	41
decane	326.3	372.0	−34
dodecane	326.2	372.4	4
tetradecane	327.2	372.8	−61
hexadecane	327.2	373.0	−46

points do not allow us to address this issue. Clearly, the attempt to separate solvent and barrier effects has failed. Previous work by Hicks et al.[12] for *N*,*N*-(dimethylamino)benzonitrile in polar solvents showed that the barrier could be modified by solvation. They showed that rate data could be corrected for this barrier modification and the intramolecular effects separated from the solvent effects. Specifically, they corrected the data using the following expression

$$k_{\text{new}} = k_{\text{iso}} \exp[\alpha(E_T(30) - 30)/kT] \qquad (3)$$

where $E_T(30)$ is an empirical measure of solvent polarity, α is a coupling constant which measures the strength of solvation, and k_{new} is the corrected isomerization rate constant. By measuring the isomerization rate in a series of solvents at constant viscosity with changing $E_T(30)$, it is possible to obtain α for a particular solute species. Figure 6 shows the dependence of τ_F on $E_T(30)$ at constant viscosity and temperature, and α is found to be 0.025. Such a study demonstrates the increase in isomerization rate with an increase in solvent polarity. This behavior is also evident in the large increase in rate constant for the alcohols over that of the alkanes. The alcohol data when corrected in the above manner with the above α do not show parallel isoviscosity lines. In fact, the lines become less parallel. However, if α is used as a parameter and allowed to vary, parallel isoviscosity plots can be obtained, but α has an opposite sign to that obtained experimentally. (That is, the barrier in methanol, the most polar alcohol, is larger than the barrier in decanol, the least polar alcohol.) Similar behavior is observed if one uses other measures of solvent polarity, namely, the fluorescence shift and the Stokes shift defined with respect to the alkane solvents as a reference. The values for the steady-state spectral data are given in Tables III and IV. Similar behavior has recently been observed in the case of *trans*-stilbene by Hicks et al.[5] They suggest that dynamical dielectric considerations may be required to resolve this apparent paradox.

TABLE IV: Steady-State Spectral Data in *n*-Alkyl Alcohol Solvents

solvent	λ_{abs}, nm	λ_{fl}, nm	Stokes shift, cm^{-1}
methanol	324.3	373.0	227
ethanol	325.2	373.4	170
propanol	325.6	373.3	125
butanol	326.0	373.8	124
pentanol	326.5	374.4	119
hexanol	326.6	374.4	110
heptanol	326.8	374.5	98
octanol	327.0	374.4	73
nonanol	327.1	374.6	77
decanol	327.4	374.8	64

Spectral Shifts. The steady-state absorption maxima given in Tables III and IV for the alcohols and alkanes demonstrate that the ground-state dimethoxystilbene is nonpolar and the spectral shift in different solvents is dominated by the change in index of refraction. However, the fluorescence spectra show a larger red shift in the *n*-alkyl alcohols than in the *n*-alkanes. This shift implies a polar excited state; however, because the shifts are relatively small, ≤200 cm^{-1}, the geometry change in the excited state must be limited. This enhanced shift in the alcohols is probably caused by reordering of solvent dipoles around the new electronic state. (Evidence for this is provided below.) The steady-state Stokes shifts reported in Tables III and IV are computed with respect to the average steady-state Stokes shift in the *n*-alkanes. Because of the small spectral shifts and the multiple peaks in the spectra, there is considerable error in the reported Stokes shift (estimated to be ±30 cm^{-1}). It should be noted that the methanol fluorescence spectrum has a slightly different shape from the other *n*-alkyl alcohols. The cause of this difference and its possible association with different solvent structure around the solute have not been explored. The *n*-alkyl alcohol data, from methanol through decanol, shift to the red, implying that the solvation is still strongly influenced by the optical response. If the static response was dominant, the shift would be to the blue as one progresses through the series, because of the decreasing number density of solvent dipoles through the homologous series from methanol to decanol. The steady-state Stokes shift provides a relative measure of the solvent dielectric interaction with the solute caused by solvent structural rearrangement. As dimethoxystilbene isomerizes, the solvent will have to rearrange because of the relative motion of the dipoles on each moiety; the steady-state Stokes shift should provide a *relative* measure of how strongly each solvent interacts with the isomerizing molecule. In other words, the Stokes shift provides information on how the coupling between solute and solvent changes with solvent. It does not, however, provide the absolute magnitude or the frequency dependence of this coupling constant. It provides the long time relative values of the coupling constant, that is, the time scale of fluorescence emission.

As mentioned earlier, the decay profiles did not fit well to a single exponential at early times. Figure 3 shows two decay profiles for 4,4′-dimethoxystilbene in decanol at room temperature. The fast rise in the 340-nm emission compared to the 410-nm emission profile is quite apparent. The time scale of this response is very sensitive to the solvent, whereas the time scale is on the order of 100 ps in decanol at room temperature; it is barely resolvable in methanol at room temperature. This time-dependent red shift in the fluorescence emission is caused by equilibration of the "solute–solvent complex" in the newly created excited state.[50–52] Because the time scale of the Stokes shift is a measure of the time scale for the solvent response to a new solute dipole size or orientation, it is an indicator of the time scale of the solvent response to the isomerization motion. It is evident that the solvent response will be slower than the isomerization motion, which is found to be of the order of 10^{13} s^{-1} in the alkane solvent studies. The frequency will be reduced in the alcohol solvents because of partial solvation.

At this juncture a resolution of the paradox discussed earlier is possible. In the fitting of the fluorescence decay curves information about the long time decay, after the initial trans excited state is equilibrated, is obtained. Because methanol is more polar than the other alcohols, it solvates the excited state better as evidenced by the magnitude of the steady-state Stokes shift.

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Namely, because the methanol solvent better solvates the excited state, dimethoxystilbene has a deeper well out of which to climb than in the other alcohols. This would not be true, however, if the solute was always solvated when isomerizing, because in that case methanol would better solvate the twisted state as well. This solvation effect varies monotonically through the *n*-alkyl alcohol series (see Table III). Because the solvent and solute are out of equilibrium, the solute is only solvated to the extent allowed by the dielectric response of the solvent at a frequency greater than or equal to the frequency of the reactive motion. In the case where an optical dielectric constant (n^2) would be an adquate description, then the solute would be better solvated by decanol than methanol upon barrier crossing. Because the dynamical Stokes shift is a direct measure of the time scale for solvation, the time scale, or frequency, required for the dielectric response is known. At the required frequencies, ranging from 10 GHz to 1 THz, the dielectric constant of methanol is greater than or equal to that of the other alcohols and decreases monotonically through the homologous series.[43,44] The differences in the high-frequency dielectric constant between the alcohols is much smaller than in the static limit, implying that the difference in solvation energies, as one progresses through the homologous series, will be less than in the static limit. This difference results in an effective barrier height which is largest in methanol and decreases through the homologous series. The magnitude of this barrier height change can be modeled quantitatively by using the steady-state spectral properties and is discussed later. An analogous description of this effect which discusses the strength of the solvent polarization field is also possible. Because of the decreasing static dielectric constant as one progresses from methanol to decanol, when the solute isomerizes, the polarization field which lags in the higher static dielectric constant solvent is larger than that in the lower static dielectric constant solvent. The solvent polarization cage supplies a force opposed to isomerization which decreases through the alcohol series from methanol to decanol. This view explains the trends in the isoviscosity plots. Namely, the lower viscosity plots have data from the more polar alcohols whereas the higher viscosity plots have the least polar alcohols (see Table II).

A comprehensive view of the solvation of 4,4′-dimethoxystilbene in the *n*-alkanes and *n*-alkyl alcohols is now possible, at least qualitatively. The alkane solvents solvate the dimethoxystilbene primarily through their high-frequency dielectric response. This may be concluded by the constancy of the steady-state Stokes shift through the *n*-alkane series which implies a weak static solvation; that is, the lack of dipole moment leads to a very weak effect of the solvent structure about the solute. From comparison with studies on stilbene[2,3] and solvatochromism results for the *n*-alkanes,[53] it can be concluded that the energy shifts are relatively small, implying that the barrier height may be near that of the isolated molecule. In contrast, the *n*-alkyl alcohols possess larger high-frequency dielectric constants than the *n*-alkanes,[43,44] which enhances solvation of the transition state for isomerization. Because of the slow time scale for the dielectric response in the alcohols, nonequilibrium solvation is present on the reactive time scale which complicates the dynamics.

Discussion

Alkane Studies. The most widely used model for describing isomerization dynamics is that due to Kramers.[22] In this model, the reactive motion is modeled as the escape of a Brownian particle over a potential barrier in one dimension. Using a Fokker–Planck equation for the time-dependent distribution function of coordinates and momenta, Kramers obtained the expression

$$k_{\text{iso}} = \frac{\omega_0}{4\pi\omega'\tau_v}[(1 + (2\omega'\tau_v)^2)^{1/2} - 1] \exp(-E_0/RT) \quad (4)$$

where ω_0 is the frequency for the harmonic reactant well, ω' is the frequency for the harmonic barrier, E_0 is the potential energy barrier height, and τ_v is the characteristic velocity relaxation time.

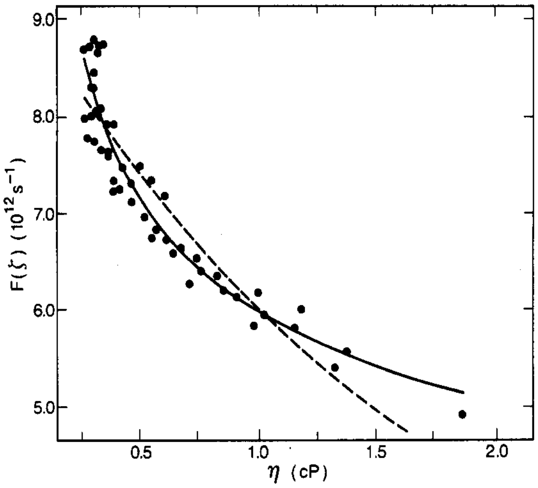

Figure 7. A plot of the reduced isomerization rate versus solvent shear viscosity is shown for the *n*-alkanes. The dashed line is a fit to the Kramers model, and the solid line is a fit to the phenomenological form given in eq 8.

This time scale is assumed to be slow with respect to the time scale of forces acting on the reaction coordinate, and τ_v can be related to the friction by $\tau_v = \mu/\xi$, where μ is the effective mass of the particle. A useful limit of the above expression is where τ_v is much smaller than the time scale of the motion along the reactive coordinate, more precisely ω' the curvature at the barrier. In this (Smoluchowski) limit

$$k_{\text{iso}} = \frac{\omega_0\omega'\tau_v}{2\pi} \exp(-E_0/RT) \quad (5)$$

Although widely used and in many cases in good agreement with experiment, this model has some serious limitations when used to describe stilbene isomerizations. Perhaps most obvious is the one-dimensionality of the model. More recent extensions of this model have attempted to include the effect of other molecular degrees of freedom, both reactive and nonreactive.[54] Also, this model is limited to diffusion along the reaction coordinate, whereas recent studies of rotational reorientation suggest that solute particles of the size of the stilbene moieties may undergo large angle motions.[55] Related to this issue is the assumption of a frequency-independent friction coefficient which corresponds to a separation of time scales between τ_v and the time for solvent force relaxation.[56] Last is the separation of the potential surface from the effects of the bath when in many cases the potential surface is modified by interactions with the bath and in fact can be time dependent.

At this point it becomes necessary to model the friction experienced by the isomerizing moiety. The most common approach is to assume that the friction is proportional to the shear viscosity, η, and reexpress the Kramers expression in a "hydrodynamic" form

$$F(\xi) = \frac{A}{B/\eta}[(1 + (B/\eta)^2)^{1/2} - 1] \quad (6)$$

Other studies have tried to model the friction by measuring the solute particle rotational reorientation time, τ_{or}, and assuming that

$$\tau_{\text{or}} \propto \xi \quad (7)$$

Both of these approaches have had a degree of success in that they were used to fit experimental results to a one-dimensional Kramers expression.[10,11,13] One should not place too much confidence in such results since their relationship to the friction experienced by half the molecule moving in a translational/rotational manner

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along an intramolecular potential is not clear. Proper modeling of microscopic friction is a challenging problem itself and remains a limiting feature in the modeling of isomerization dynamics.

The isomerization data in the *n*-alkanes have been fit to the hydrodynamic Kramers expression (Figure 7). It is evident that the hydrodynamic Kramers expression does not possess the curvature necessary to fit the data. This lack of curvature is qualitatively the same type of disagreement observed by other workers for other systems[3,9-11] and by Rothenberger et al.[2] for stilbene. Following the treatment of Rothenberger et al., the dimethoxystilbene rate constants at high viscosities (>0.5 cP) were fit to the Kramers form (eq 6). The parameters used in this fit were $d = 3.7$ Å, $r = 3.5$ Å, and $I = 4.7 \times 10^{-44}$ kg·m^2. The potential parameters obtained are $\omega_0 = 4.83 \times 10^{13}$ s^{-1} and $\omega' = 2.19 \times 10^{13}$ s^{-1}. The potential parameters obtained in the *trans*-stilbene study were $\omega_0 = 2.9 \times 10^{13}$ s^{-1} and $\omega' = 5.7 \times 10^{13}$ s^{-1}. Comparison of these parameters shows the difficulty of obtaining potential properties from rate constant data; i.e., the barrier curvature is smaller in dimethoxystilbene than in stilbene despite its higher barrier. This behavior could be accounted for by the increased moment of inertia of dimethoxystilbene. Simple comparison of barrier heights with parabolic potentials suggests that the frequency of the dimethoxystilbene barrier (including the increased amount of inertia) should be equal to or slightly higher (1.5 times) than the stilbene frequency.

A much better fit of the data is provided by the phenomenological form of

$$F(\xi) = B/\eta^a \qquad (8)$$

This fit to the dimethoxystilbene data gives the parameters $B = 4.73 \times 10^{13}$ s^{-1} and $a = 0.23$, in contrast to the case of stilbene where $B = 3.5 \times 10^{12}$ s^{-1} and $a = 0.32$.[18] The quality of these fits and the parameters obtained show a behavior similar to that described in earlier studies. Those studies suggest that the frequency-dependent viscosity had to be evaluated at the reactive frequency; i.e., the frequency of the isomerization motion at the barrier top where the reaction is decided. In those studies the same deviations of the Kramers fits from the data were observed whereas the phenomenological form, eq 8, was observed to fit the data well.[9,60] Correlation of data between different systems showed that as the frequency of the isomerization motion (i.e., the curvature of the barrier at the transition state) increased, the value of a in eq 8 decreased, in agreement with our results.

A model of the microscopic friction which has the above phenomenological form is the free volume model of Doolittle.[57] Gegiou et al.[58] use this model to describe the isomerization dynamics of stilbenes. In this model, the solvent shear viscosity is written as

$$\eta = A \exp(V_0/V_F) \qquad (9)$$

where A is a constant, V_F is the free volume per solvent molecule, and V_0 is the critical volume required for translational motion. Because the isomerization requires less solvent displacement than translational solvent motion, Gegiou writes the reduced isomerization rate constant as

$$F(\xi) = k_0 \exp(-aV_0/V_F) \qquad (10)$$

where a is a constant (less than unity) which changes the critical volume, V_0, from one for translational motion to one for isomerization motion, aV_0. Combining these two equations results in eq 8, where $B = k_0A^a$ and a is the weighting factor. The isomerization results for dimethoxystilbene when compared to those for stilbene contradict this model, because the isomerizing moiety in the dimethoxystilbene case is larger than in *trans*-stilbene, and hence a larger value of a would be expected. This result suggests the inadequacy of free volume models. This comparison assumes that the reaction coordinates in the two isomerizing molecules are similar; however, it could possibly change because of the presence of the methoxy group. For instance, the motion could be more of a "fluxional" motion, as with the dark isomerization of azastilbenes,[59] which could result in less solvent displacement. This possibility could be investigated through isotope studies of the isomerization rates. Recent evidence from isotope studies on *trans*-stilbene suggests that the reaction coordinate in the isomerization may not be the simple torsional motion about the ethylenic bond.[60]

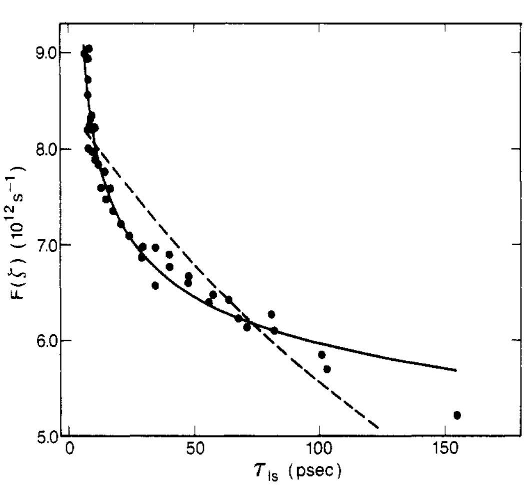

Figure 8. A plot of reduced isomerization rate versus solvent self-diffusion coefficient (light-scattering relaxation time) is shown. The dashed line is a fit to the Kramers model, and the solid line is a fit to the phenomenological form given in eq 8, where η is replaced by τ_{ls}.

An alternative interpretation is present in comparing the isomerization dynamics of dimethoxystilbene and stilbene. It is reasonable to model the distance of the reaction coordinate, from trans to cis, as the same, which implies that the increased barrier height in the dimethoxystilbene case will result in a more curved potential energy surface and hence a higher reactive frequency. This expectation is in accord with the parameters obtained from the fits. Namely, as the reactive motion becomes faster, the slower solvent motions which are contained in the zero-frequency shear viscosity do not contribute to the friction experienced on the reactive time scale. The dependence on the zero-frequency viscosity should then be weaker. This behavior is observed in the shallower dependence on viscosity for 4,4′-dimethoxystilbene, $a = 0.23$, as compared to stilbene, $a = 0.32$. Frequency dependence of the friction has been discussed with regard to isomerization dynamics by a variety of workers,[2,9,10] who observed behavior similar to that seen in this study. This weakening of the dependence on the viscosity must be quite dramatic since dimethoxystilbene is expected to displace approximately twice as much solvent upon isomerization as stilbene. A weakness of this interpretation is that the inertial moments are different in the two cases, and the large change in barrier height results in frequencies which are not dramatically different.

The presence of frequency-dependent friction suggests that an evaluation of the friction on a time scale closer to the reactive time scale is necessary. With this motivation the friction is modeled as being proportional to the correlation time obtained from light-scattering measurements of the pure solvent.[41,42] This correlation time is related to the solvent self-diffusion coefficient for overall rotation. This characteristic time is a microscopic solvent property on a time scale of a few picoseconds. Figure 8 shows the fits of the data where τ_{ls} has replaced η in eq 6 and 8. Once again it is observed that the Kramers expression does not possess the right curvature to fit the data. The phenomenological form shows a good fit, better than that of the viscosity, with parameters of $B = 1.0 \times 10^{14}$ s^{-1} and $a = 0.12$. (B is evaluated at $\tau_{ls} = 1$ ps.) These parameters suggest an even weaker de-

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pendence on friction than the case of the viscosity, in contrast to the intuitive expectation that a high-frequency solvent property which is correlated to the solvent friction would be a better measure of the friction. This result may arise because τ_{ls} is primarily a measure of solvent molecular rotation whereas the shear viscosity is expected to have a large contribution from both solvent translational and rotational modes. Since the isomerization couples to both types of motion, the shear viscosity may be a better gauge of the friction. However, this point remains conjecture.

These fitting results underscore the necessity of being careful about the interpretation of the phenomenological form, eq 8. The parameter a actually becomes smaller for the case of more volume displaced, in direct contrast to free volume theories. The viscosity behavior is consistent with previous results interpreted as being caused by a frequency dependence of the friction. However, the use of a higher frequency measure of the friction (τ_{ls}) provides an even weaker dependence via the a parameter. The reasons for this behavior remain unclear, and more studies are required for the resolution of these issues.

Recent work by Lee et al.[10] and Courtney et al.[11] on photoisomerization of *trans*-stilbene in alkane solvents reveals the importance of proper modeling of the solute–solvent friction. Their studies show that, although modeling the friction with a viscosity leads to disagreement with the Kramers form, modeling of the friction by the overall rotational diffusion of the solute leads to good agreement with the Kramers form. An earlier attempt of this type on the dye molecule DODCI failed to lead to better agreement with the Kramers model.[9] This type of study for 4,4′-dimethoxystilbene in *n*-alkane solvents should provide an interesting test for frequency-dependent effects since its barrier height is intermediate between that of stilbene and DODCI. Although measurement of the overall rotational diffusion coefficient of the molecule is a vast improvement over a hydrodynamic approach, the preferred measurement should be the translational and rotational diffusion coefficients of the isomerizing moiety.

Alcohol Studies. Discussion of the alcohol results requires a more involved theoretical approach to the description of the dynamics. Specifically, in the development of the Kramers expression it was assumed that τ_v was much slower than the time scale of the solvent force relaxation. For the alcohol results this assumption breaks down because the relaxation of the solvent polarization cage about the solute excited state is slow or on the order of the time scale for the solute motion. This type of phenomenon has been treated by Hynes and co-workers[25–27,56] using a generalized Langevin equation approach and by Marcus and co-workers[23,24] for electron transfer.

In particular, Grote and Hynes have found an expression for the reaction rate in terms of a frequency-dependent friction

$$2\pi F(\xi) = \lambda_r = \frac{\omega'^2}{\lambda_r + \xi(\lambda_r)} \tag{11}$$

where λ_r is the reactive frequency, ω' is the barrier curvature, and $\xi(\lambda_r)$ is the friction evaluated at the reactive frequency. This self-consistent relation has been modeled or simulated in a variety of studies[2,61] and is found to yield, qualitatively, the same behavior as is modeled by eq 8. Previous work has suggested that frequency-dependent friction can be quite important for reactive processes with high barriers (more precisely strong curvature). In a series of papers van der Zwan and Hynes[25–27] have treated the frequency-dependent friction coefficient for the isomerization of a dipolar species in a dipolar medium. By evaluating the dielectric friction of the medium on the isomerizing dipoles as well as the potential of interaction with each other, they obtain a variety of expressions for the rate constant depending on the coupling strength to the solvent and the time scale of the solvent relaxation.

Because the *n*-alkyl alcohols are strongly interacting solvents with large frictional forces, the overdamped solvent limit of the van der Zwan and Hynes[25] treatment is considered here. This assumption results in

$$\kappa = \left[\kappa + \frac{\beta x}{1 + \kappa x}\right]^{-1} \tag{12}$$

where the parameter κ is the ratio of the measured rate constant to the transition-state theory rate constant. Namely

$$k_{\mathrm{iso}} = \kappa A \exp(-E_0/RT) \tag{13}$$

where E_0 is an activation energy and A is a parameter which contains information on the reactant frequency and solvent frequencies. The parameter β is a measure of the solute/solvent interaction strength given by

$$\beta = \xi(t{=}0)/\omega_{\mathrm{b,eq}}^2 \tag{14}$$

where $\xi(t{=}0)$ is the dielectric friction at time zero, hence directly proportional to the Stokes shift,[50] and $\omega_{\mathrm{b,eq}}$ is the frequency of the reaction barrier if the isomerizing species were in solvation equilibrium. The parameter x is a measure of the solvent friction and given by

$$x = \omega_{\mathrm{b,eq}}\tau_s \tag{15}$$

where τ_s is a solvent response time which here is assumed to be proportional to τ_l[23–27,62] (or η). Because of the slow time scale of the alcohol solvent response (i.e., slower than the reactive frequency) and the strong interaction of the solvent with the solute, the appropriate expression for the isomerization rate reduces to

$$k_{\mathrm{iso}} \propto \exp(-E_0/RT)/\tau_l \tag{16}$$

This expression assumes a continuum solvent response where the solvent friction is the dielectric friction characterized by τ_l. This limit of the van der Zwan and Hynes model corresponds to the isomerizing moiety being in a polarization field which lags the twisting motion. This lag inhibits the motion; in fact, in the very strong coupling, very slow relaxation limit the solute would be trapped in the polarization cage and only isomerize as the cage fluctuated into the right configuration for barrier crossing. In fact, the limit contained in eq 16 is a static limit of a sort. The more common static limit assumes that the solvent response is fast enough to remain in equilibrium with the solute; i.e., the potential energy barrier is the equilibrium solvated barrier. However, the opposite limit, where the solvent response is much slower than the reactive time scale, also occurs and is quite common in the discussion of electron-transfer reactions.[23–27,63] This analogous view to the charging up of the polarization field in discussion of electron-transfer reactions leads to the expectation that the isomerization will proceed with the decay time of the polarization cage, namely, τ_l.

Fits of the data to the expression in eq 16 give poor agreement. This results because not all of the polarization field lags the dipole. The component of the solvent dielectric response on a fast time scale with respect to the twisting motion results in partial solvation Also, the experimental data is in a variety of solvents, methanol through decanol, which result in differing degrees of solvation, whereas eq 16 is written for a single solute–solvent coupling. As discussed earlier, the steady-state Stokes shift can be used to quantitatively model the change in the solute–solvent coupling between solvents. Modification of eq 16 to account for the differing degrees of solvation results in the following expression

$$k_{\mathrm{iso}} = A\frac{\exp(-(E_0 - \alpha S)/RT)}{\tau_l} \tag{17}$$

where S is the steady-state Stokes shift, measured for each solvent, and α is a parameter which is a measure of the strength of the solute–solvent interaction. A fit of the data to eq 17 is shown in Figure 9. This fit results in activation barriers which range from 2.08 kcal/mol in methanol to 0.26 kcal/mol in decanol. A better fit is obtained if the shear viscosity, η, is used in place of τ_l in eq 17 (see Figure 10). The parameters of this fit result in activation

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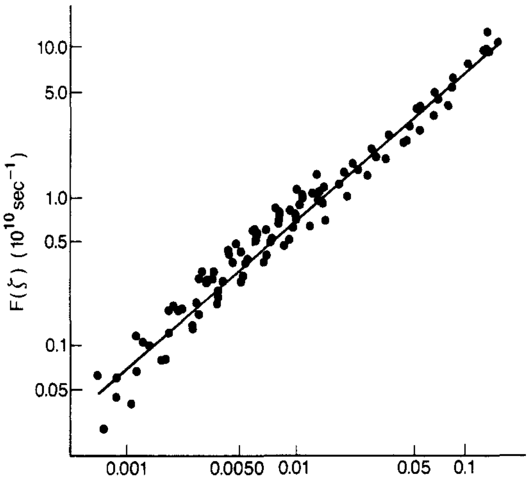

Figure 9. A plot of the preexponential factor versus τ_l is shown for the *n*-alkyl alcohol data. The preexponential factor is obtained after a fit to eq 17. The solid line is the fitted curve.

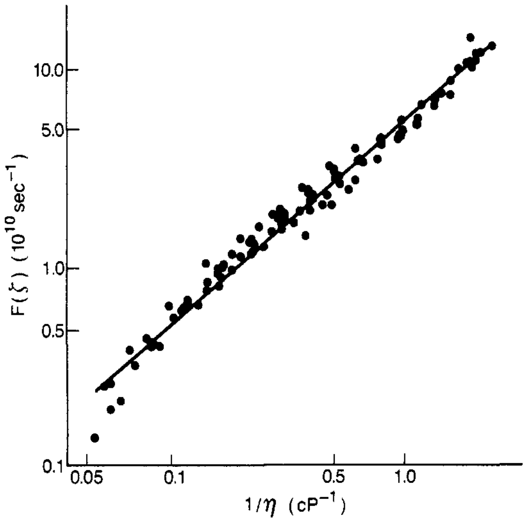

Figure 10. A plot of the preexponential factor versus η is shown for the *n*-alkyl alcohol data. The preexponential factor is obtained after a fit to equations where τ_l has been replaced by η. The solid line is the fitted curve.

barriers which range from 2.1 to 1.26 kcal/mol. In the case of the alcohols τ_l and η are very nearly proportional; however, the difference in fitting is noticeable. Whether this improvement is a result of η containing information about the mechanical friction versus τ_l which is purely dielectric is unclear. In any case, the response of the alcohol solvents is probably dominated by the hydrogen-bonded oligomers whose interactions are manifest in both τ_l and η. The disturbing feature of these fits is the range covered by the barrier heights. These values differ significantly from the range of barrier heights observed in the isoviscosity plots. If the barrier heights are constrained to vary over the same range as the isoviscosity plots, the fits are much poorer than those shown in Figures 8 and 9.

In order to decide whether the limit of strong coupling and high damping is valid, an attempt was made to fit the data to the full expression given by eq 12, but the number of variable parameters and shallow behavior of the function caused convergence problems and a failure to obtain unique parameter values. Instead, the data were fit to the functional form in eq 17 with the preexponential factor replaced by the phenomenological form of eq 8 (B/η^a). Although the fit is somewhat better than the fit to the $1/\eta$ form, it does not appear to be qualitatively improved over the inverse viscosity form. The fitting parameters obtained are $a = 0.72$ and barrier heights which range from 3.30 kcal/mol in methanol to 2.91 kcal/mol in decanol. Although the barrier heights are closer to those observed in the isoviscosity plots, they are still lower and vary over a narrower range. The value of $a = 0.72$ implies that the frictional coupling is an "intermediate" case; i.e., $F(\eta)$ decreases as η increases but not as $1/\eta$. Van der Zwan and Hynes[25] discuss the behavior of eq 12 as β varies, in the context of fits to the phenomenological form.[8] They find that $\beta = 1$, a parameter value which indicates a coupling intermediate between the weak and strong limits, gives a friction dependence which is similar to a fractional power of $^1/_3$. This result implies that the fitted value of 0.72 corresponds to a solute–solvent coupling which is strong but not yet in the Smoluchowski limit of inverse friction.

An important caveat to the comparisons with these models is that the barrier heights and the parameters in the preexponential factors are highly coupled when fitting the data. The range of barrier heights obtained from the isoviscosity plots and the model fits underscore the inability to disentangle the solvent effects from the barrier effects. The attempt to incorporate the dynamical solvent response in a barrier height is equivalent to a strict separation of time scales between the time for solvation and the time for isomerization. Although reasonable fits of the data are obtained, because of the wide variation of barrier heights in the model fits it is not possible to justify this separation. However, the *trend* in the barrier heights is always the same; i.e., it increases as one goes through the homologous series from decanol to methanol. If the barrier height values are constrained to decrease through the series, extremely poor fits are obtained.

Conclusions

These studies on 4,4′-dimethoxystilbene emphasize important aspects of condensed-phase reactions. In particular, they underscore the strong effects of solvation and the influence of fast solvent dynamics on reaction rates. First, these studies reveal that the separation of intramolecular and intermolecular effects is not always possible but that the solvent can be intimately involved in the reaction coordinate. This idea has been treated in recent studies.[5,23–27] Second, these studies demonstrate the importance of accurate modeling of solute–solvent friction when comparing to theoretical models. The alkane results might be explained if an accurate modeling of the friction were available.

In the *n*-alkane solvents, previous methods of separating solvent effects from barrier effects within a homologous series seems to be appropriate. The concept of "isofriction" plots has been tested and extended through the use of different measures of solvent friction, namely, η, τ_{ls}, and τ_{col}^{-1}. It is found that the substitution of a methoxy group in the 4- and 4′-positions of stilbene raises the barrier to isomerization from 3.6 to 5.6 kcal/mol. Since the distance scale of the reaction coordinate is not substantially changed, the frequency of the barrier is expected to increase over that of *trans*-stilbene. This increase in frequency and hence motion of the isomerizing moiety along the potential surface is manifest in a weaker dependence on the bulk shear viscosity for 4,4′-dimethoxystilbene than *trans*-stilbene. This weaker dependence is present even though more volume should be displaced in isomerization of dimethoxystilbene, which would apply a stronger viscosity dependence. Conclusions concerning the adequacy of the Kramers model in describing the isomerization dynamics await more accurate modeling of solute–solvent friction.

In the *n*-alkyl alcohol solvents the simple separation of barrier and solvent effects is no longer possible. The strong dielectric properties of the *n*-alkyl alcohols, intimately related to "polarity", cause strong solute–solvent couplings which modify the potential energy surface for isomerization. This coupling is observed in the Stokes shifts and the isoviscosity plots and has been observed in other systems by Hicks et al.[5,12] Because the *n*-alkyl alcohols are strongly associated solvents with long-lived oligomeric structures (up to many nanoseconds), solvation is incomplete on the relevant time scale as demonstrated by the dynamic Stokes shift measurement. An attempt has been made in this study to incorporate this coupling and nonequilibrium solvation into a modification of the energy barrier. This approach is valid in the limit that the dynamics of isomerization is separated from that of the solvation. It is found that the nonequilibrium solvation results in effective barrier heights which *increase* as the solvent becomes more polar, in contrast to the normal equilibrium solvation picture where the barrier should decrease as the polarity increases, because of increased solvation of the polar transition state. Although models exist which discuss these ideas concerning nonequilibrium solvation, it is difficult to draw quantitative comparisons. Similar behavior to that observed for 4,4′-dimethoxystilbene in *n*-alkyl alcohols has been observed for *trans*-stilbene in *n*-alkyl alcohols by Eisenthal and co-workers,[5] who also suggest nonequilibrium solvation as the cause of changing barrier heights.

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Registry No. 4,4′-Dimethoxystilbene, 4705-34-4; decanol, 112-30-1; hexane, 110-54-3; hexadecane, 544-76-3; pentane, 109-66-0; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; dodecane, 112-40-3; tetradecane, 629-59-4; ethanol, 64-17-5; propanol, 71-23-8; butanol, 71-36-3; pentanol, 71-41-0; hexanol, 111-27-3; heptanol, 111-70-6; octanol, 111-87-5; nonanol, 143-08-8; methanol, 67-56-1.

Identifiability and Distinguishability of First-Order Reaction Systems

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By following the kinetics of a reaction through the use of certain classes of measurable quantities instead of the concentrations of all species, neither the parameter values nor the reaction scheme is necessarily unique. Identifiability deals with the problem of determining whether an experiment is able to supply the desired information on the parameters of an assumed kinetic model, whereas indistinguishability means that two different reaction schemes generate the same values for the observed quantities in any possible experiment. This paper examines these issues for the case of first-order reaction systems, and both problems are solved by the same analytical tools. The method involving Laplace transforms is conceptually simple, is easy to apply, and is also used to derive simple rules to test distinguishability of reaction schemes. Another approach based on similarity transformations is used to generate all the first-order reaction schemes that are indistinguishable from a given one.

I. Introduction

Kinetic experiments are often conducted under conditions such that the reactions are first-order or pseudo-first-order, with rate coefficients proportional to the concentration of a reaction partner in large excess. Interpretation of experimental data by postulating a mechanism and adjusting the values of some unknown parameters has received due attention in the literature.[2-6] The problems usually considered are techniques of parameter estimation and statistical interpretation of the estimates in terms of confidence intervals or joint confidence regions. Kinetists are aware that there remain further fundamental questions to ask.[6] First, are the derived parameters unique, or are there further parameter sets generating the same values for the observed quantities? Second, is the selected model the only plausible one that will give an acceptable fit to the data? These questions of parameter and model uniqueness are not trivial even for very simple mechanisms if not all concentrations are directly observed.

For example, consider the consecutive reaction scheme

$$A \rightarrow B \rightarrow C \qquad (1.1)$$

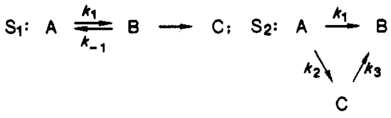
studied in several works[3-5] assuming that initially only A is present in the system and the reaction is followed by observing the single property

$$y = \epsilon_A[A] + \epsilon_B[B] + \epsilon_C[C] \qquad (1.2)$$

which may represent absorbance, conductivity, pH, or ligand release. We regard y as absorbance and ϵ_A, ϵ_B, and ϵ_C as molar extinction coefficients. Frequently the intermediate species B cannot be isolated and separately investigated; hence ϵ_B is an additional parameter to be estimated simultaneously with the rate coefficients k_1 and k_2 from the time-absorbance data. As is well-known,[3-5] under these conditions the solution of the estimation problem is not unique because of the slow-fast ambiguity; thus for any solution $\mathbf{k} = (k_1,k_2,\epsilon_B)^T$ there exists a second solution $\tilde{\mathbf{k}} = (\tilde{k}_1,\tilde{k}_2,\tilde{\epsilon}_B)$ given in terms of k by

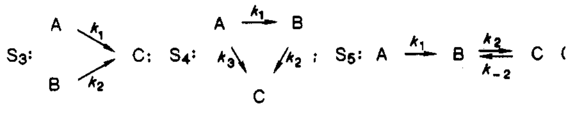
$$\tilde{k}_1 = k_2; \quad \tilde{k}_2 = k_1; \quad \tilde{\epsilon}_B = \epsilon_A + k_1(\epsilon_B - \epsilon_A)/k_2 \qquad (1.3)$$

In addition to nonuniqueness in parameter values there may be ambiguities in the model structure. As emphasized by Milligan et al.,[5] a good fit does not necessarily mean that the model is correct, since there exist further reaction schemes generating the same absorbance curve. They mention the schemes



(1.4)

whereas Jackson et al.[4] claim that the absorbance data can equally be described by adopting the reaction schemes



(1.5)

The purpose of this paper is to present a systematic and rather general analysis of the problems of parameter uniqueness, called identifiability, and distinguishability of different first-order reaction

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