Reorientation and Isomerization of \textit{trans}-Stilbene in Alkane Solutions

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(Received: October 16, 1987)

Rotational reorientation times were obtained for \textit{trans}-stilbene in the series of \textit{n}-alkanes over a wide temperature range by using picosecond anisotropic absorption measurements and fluorescence depolarization measurements. The data show that the coupling of solute and solvent decreases as the size of the solvent increases. However, in a given solvent the reorientation depends linearly on $\eta/\gamma$ over our temperature range. The results are discussed in the context of the free space model of Dote et al. The new data are used to discuss the applicability of current models for activated barrier crossing to the isomerization of stilbene.

Introduction

The qualitative influence of the friction exerted by nonpolar solvents on the photoisomerization of \textit{trans}-stilbene now seems clear.\textsuperscript{1,4} As predicted by barrier crossing theories,\textsuperscript{2} the rate first rises as friction is increased, reaches a maximum, and then turns over and decreases as friction is increased further. The maximum occurs in high-pressure gas phase,\textsuperscript{1,2} and in liquid solutions the rate is a decreasing function of solvent viscosity. Attempts to provide a quantitative description of both rising\textsuperscript{1,6} and falling\textsuperscript{4,5} parts of the curve have met with difficulties. In this paper we concentrate on the high-friction (solution) portion of the curve.

If the stilbene isomerization rate is plotted as a function of viscosity with different viscosities being obtained by change of solvent or temperature, the rate falls off more slowly than is predicted by Kramers' equation if the solvent friction is equated with macroscopic shear viscosity.\textsuperscript{1,5} There are several possible explanations for this behavior: (1) The intramolecular potential surface could be solvent dependent.\textsuperscript{6,8} (2) The solvent viscosity may not be an adequate measure of the friction felt by the isomerization molecule, either because the presence of the intramolecular barrier places an emphasis on the short-time response of the solvent (frequency-dependent friction)\textsuperscript{2} or simply because Stokes's law is inadequate on the molecular scale involved in the isomerization process. (3) Other degrees of freedom than the reaction coordinate may complicate the friction dependence.\textsuperscript{13-15} Perhaps the possible inadequacy of Stokes' law is the most obvious explanation, and recently both Lee et al.\textsuperscript{16} and Courtney et al.\textsuperscript{17} have taken up the suggestion of Velsko et al.\textsuperscript{18} and used rotational reorientation times as a measure of microscopic friction. Both groups found that the Stokes–Einstein relation gave a poor description of reorientation times in a series of alkane solvents at room temperature. Improved fits to Kramers' equation (in the same solvents) were obtained if the inverse reorientation time was used as the friction measure.\textsuperscript{16,17} Thus, much of the failure of Kramers' equation to describe stilbene isomerization in a series of alkanes at room temperature can be traced to the failure of the Stokes–Einstein relation.

The failure of the Stokes–Einstein relation in experimental studies of small-molecule reorientation is well-known\textsuperscript{19,22} and has also been observed for larger molecules in very viscous solutions.\textsuperscript{22} Theoretical approaches to the problem have been discussed by Dote et al.\textsuperscript{19} These authors propose a model in which the coupling between the rotating molecules and the solvent depends on the free space in the solvent. This suggests that the relative size of solvent and solute should be an important parameter. Recently, Zwanzig and Harrison\textsuperscript{25} have also suggested that deviation from the Stokes–Einstein formula should be discussed in terms of an environment-dependent coupling to the solvent, rather than a breakdown of the basic Stokes–Einstein formula. In order to investigate this problem in the case of \textit{trans}-stilbene, we have measured the molecular reorientation in a series of \textit{n}-alkanes over a range of temperatures. Our results support the suggestions of Dote et al. and Zwanzig and Harrison: in a single solvent, over our temperature range, the Stokes–Einstein relation works well. However, the coupling coefficient (slope) is strongly dependent on the solvent and changes by almost a factor of 2 between hexane and hexadecane. We discuss our data in the context of current theories of rotational reorientation and also discuss the implications of our results for the analysis of the isomerization data.

Experimental Section

Two techniques were used to obtain the rotational reorientation times: fluorescence depolarization using time-correlated single-photon counting and anisotropic absorption (polarization spectroscopy) using an amplified colliding pulse mode-locked ring laser. In both cases excited-state reorientation was monitored either via fluorescence or via $S_1-S_0$ absorption. The former technique has been described in detail elsewhere,\textsuperscript{24,25} and details of our results for the analysis of the isomerization data.

\begin{thebibliography}{99}
(7) Kramers, H. A. Physica 1940, 7, 284.
\end{thebibliography}
of the anisotropic absorption experiments are given in ref 17 and 28.

In the anisotropic absorption experiments, the excitation wavelength was the laser second harmonic at 308 nm and generally the probe wavelength was the fundamental (615 nm). The probe was time delayed and had 45° polarization with respect to the pump polarization. The analyzer polarization was set at -45° and detects the signal induced by rotation of probe polarization due to sample dichroism.

The polarizers [Karl-Lambrecht Co.] showed extinction ratios around 3 × 10⁻⁸. It is known that reducing birefringence from external optics may be critical in obtaining an undistorted signal, and we found this indeed is the case for trans-stilbene. We therefore used a free flowing jet instead of a sample cell. The extinction ratio of probe pulse through the analyzer polarization was greater than 2 × 10⁻⁶ with most quartz cells while it decreased to 6.5 × 10⁻⁶ with the jet. A Neslab RTE-5B thermostat was used to regulate the sample temperature. Two thermostats were inserted into the circulating sample line approximately 10 cm before and after the sample. Those two readings were identical to within 0.5°. Most of the alkane solvents made high-quality jets using a Spectra Physics stainless steel dye jet nozzle from Petrich, length difference exists between 615 and 308 nm when a 237° value. ° 22.0 °C value. ° 40.0 °C value.

<p>| TABLE I: Comparison of Measured Decay Times for the Excited-State Anisotropic Absorption Measurements (τ_M*) and the Ground-State Anisotropic Absorption Measurements (τ_M) |
|---------------------------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Solvent</th>
<th>temp, °C</th>
<th>τ_M*, ps</th>
<th>τ_M, ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetradecane</td>
<td>12.5</td>
<td>27.7 ± 0.4°</td>
<td>25.0 ± 2.0°</td>
</tr>
<tr>
<td>17.0</td>
<td>24.6 ± 0.4</td>
<td>21.3 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>17.8 ± 0.3</td>
<td>15.4 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>41.0</td>
<td>17.9 ± 0.3</td>
<td>16.1 ± 1.0°</td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>14.5 ± 0.5</td>
<td>12.9 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>

*Errors represent fit uncertainty. ° 12.0 °C value. ° 22.0 °C value. ° 40.0 °C value.

In the fluorescence depolarization measurements the excitation of trans-stilbene was at 298 nm and the fluorescence was collected at 345 nm after going through an analyzer polarizer. The parallel and perpendicular polarized fluorescence curves are accumulated individually and deconvoluted with an instrument decay curve before being fitted simultaneously until the minimum χ² is reached. In the analysis the initial anisotropy ρ(0) and the reorientation time τ_or for trans-stilbene are correlated. We found that τ_or values fitted with a fixed value of ρ(0) = 0.39 ± 0.01 are in good agreement with the values projected from anisotropic absorption experiments, as shown in Figure 2.

Spectrophotometric grade or gold labeled alkanes were purchased from Aldrich Chemical Co. and used without further purification. The concentration of trans-stilbene, Kodak scintillation grade, was about 2 mM for the anisotropic absorption experiments and approximately 10 μM for fluorescence depolarization experiments. No differences in the measured decay times were observed at concentrations to almost ~5 mM for anisotropic absorption.

Results and Discussion

(A) Rotational Reorientation. Figure 1 shows an anisotropic absorption curve for the excited state of trans-stilbene in decane at 0 °C. The decays in all solvents were well-described by a single-exponential decay. Rotational reorientation times were extracted via eq 1. Following Dote et al. and Zwanzig and Harrison we write:

\[ \tau_{OR} = \left( \frac{V \eta}{kT} \right) \left( \frac{f_{sk}}{C} \right) \]

where \( V \) is the volume of stilbene, \( \eta \) is the shear viscosity, \( f_{sk} \) is a factor dependent on molecular shape, \( C \) is a measure of the coupling between the rotating molecule and its surroundings. Equation 2 provides the motivation to plot \( \tau_{OR} vs \eta/T \) as shown.
in Figure 2 for C₆, C₈, C₁₀, C₁₂, C₁₄, and C₁₆ n-alkanes. Also shown in Figure 2 are least-squares fits to \( \tau_{OR} = S(n/\eta)/T \). The value of \( S \) for each solvent is given in Table II along with the temperature range of the measurements. The dashed line in Figure 2 is a slip boundary condition calculation of \( \tau_{OR} \) using eq 2 and the value of \( \eta \) given by Hu and Zwanzig. To make this calculation, stilbene is approximated as a prolate ellipsoid with a longer semiaxis of 7.4 Å and a shorter semiaxis of 2.8 Å.

Several observations are apparent in Figure 2. First, the reorientation times are similar to slip predictions for the smaller solvents and are below slip predictions (subslip) in the larger solvents and are below slip predictions (subslip) in the larger temperature range, -90-150 °C from H NMR experiments. The apparent validity of the fractional viscosity dependence arises from “accidental” exponential dependence of \( \tau_{OR}^{-1} \) and \( \eta \) on an experimental parameter—in our case the number of carbon atoms in the n-alkane.

Dote et al. have discussed a number of theories for the explanation of the coupling coefficient \( C \). They suggest

\[
C = (1 + \gamma / \eta_{slip})^{-1}
\]

where \( \eta_{slip} \) is the hydrodynamic friction coefficient for slip boundary condition and

\[
\gamma = BkT \eta \eta [4(V_p/V_s)^{3/2} + 1]/V_p
\]

where \( B \) is a temperature-independent parameter, \( k \) is the isothermal compressibility of the solvent, and \( V_p, V_s \) are the volumes of probe and solvent molecules, respectively. Equation 6 suggests that \( C \) should decrease as the size of the solvent molecule becomes larger, which agrees with our experimental observations. However, Dote et al.'s \( C \) (C_{Dote}) varies with temperature in a given solvent through the variation of \( \eta \) and \( C \).

Figure 3 shows the calculated (via C_{Dote}) and experimental \( \tau_{OR} \) values for C₈, C₁₂, and C₁₄. The correct trend is obtained, but the curvature present in the calculated curves is not reflected in our data. This was already noted by Kivelson in the context of the data of Zager and Freed. Kivelson suggests that the failure of eq 5 in predicting \( C \) with the temperature changes arises because the \( BK\eta \eta \) coefficient in eq 6 is a composite of several different theories of liquids. In fact, the coupling constants proposed in several other theoretical models have similar forms to C_{Dote}, namely

\[
C = (1 + \alpha \eta )^{-1}
\]

\[\text{(7)}\]

C from these models should show more curvature than C_{Dote} on
TABLE III: Comparison of $C_{GW}$ Estimated from Gierer–Wirtz Theory with Experimental Values

<table>
<thead>
<tr>
<th>solvent</th>
<th>$C_{GW}$</th>
<th>$C_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>0.18</td>
<td>0.39</td>
</tr>
<tr>
<td>octane</td>
<td>0.15</td>
<td>0.35</td>
</tr>
<tr>
<td>decane</td>
<td>0.13</td>
<td>0.34</td>
</tr>
<tr>
<td>dodecane</td>
<td>0.11</td>
<td>0.30</td>
</tr>
<tr>
<td>tetradecane</td>
<td>0.094</td>
<td>0.24</td>
</tr>
<tr>
<td>hexadecane</td>
<td>0.084</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* $C_{exp} = 2k/(V)_{n}^{(k)}$. 

the $\tau_{OR}$ vs $n/T$ plot because $\alpha$ is virtually temperature independent, while Dote et al.'s consideration of variation of solute-solvent coupling. However, it appears that the data available from these studies, it seems appropriate to reexamine the discussion by Courtney et al. and Lee et al.

These fits are based on the standard expression for barrier crossing,

$$k_{ISO} = F(\delta_{ISO}) \exp(-E_{0}/RT)$$

where $F(\delta_{ISO})$ is a function of solvent friction and $E_{0}$ is the barrier height. $\delta_{ISO}$ is often assumed proportional to solvent shear viscosity $\eta$. Then

$$F(\delta_{ISO}) = F(\eta) = \frac{A}{2\pi(B/\eta)^{2}}[(1 + (B/\eta)^{2})^{1/2} - 1]$$

Following Velsko et al. the assumption is made that

$$\delta_{ISO} = \delta_{OR}$$

and

$$\delta_{OR} = \left(\frac{6kT}{I_{OR}}\right)\tau_{OR}$$

where $\delta_{ISO}$ and $\delta_{OR}$ are the friction coefficients for isomerization and reorientation, respectively, and $I_{OR}$ is the moment of inertia for reorientation. Kramers’ equation can now be rewritten as

$$F(\delta_{ISO}) = \frac{A_{OR}}{B}[(1 + (B/\delta_{OR})^{2}]^{1/2} - 1$$

where $A = (\omega/2\pi)(Q'/Q)$ and $B = 2\omega_{0}/\omega$. Here $f$ is a proportionality constant, $\omega$ is the angular frequency of the reactive mode, $\omega_{0}$ is the frequency corresponding to the barrier curvature. $Q'$ and $Q$ are partition functions for the reactant and transition state, respectively. The prime indicates that the reactive mode has been factored out of $Q$. To compare with our experimental data over a wide temperature range, we calculate the experimental prefactor as

$$F_{exp}(\delta_{ISO}) = k_{nt} \exp(E_{0}/RT)$$

and

$$k_{nt} = \frac{1}{\tau} - k_{r}$$

where we use 3.5 kcal/mol for $E_{0}$ and $6 \times 10^{8} s^{-1}$ for $k_{R}$. Figure 4 compares eq 12 and 15 with viscosity (a) or $\tau_{OR}$ (b) as the friction measure. Using the reorientational data produces a slightly better fit, in particular reducing dispersion between the decane, dodecane, and tetradecane data. However, neither the standard expression nor eq 15 contains enough curvature to fit the data well. The doubt remains, however, that the failure of eq 12 and 15 arises from the use of different solvents.

The excellent straight-line fits in Figure 2 suggest an alternative approach. Since $\tau_{OR} \approx n/T$ in a single solvent, it should be possible to use eq 12 directly in any particular solvent. The ratio $V_{p}/V_{s}$ may be smaller for isomerization than for reorientation, but the data in Figure 2 suggest that, although the coupling constant may decrease, the linear dependence of $I_{OR}$ on $\eta$ should also be pre-
in coupling as solvent is varied. When we apply eq 18 to our trans-stilbene in decane data, we also obtain a good fit (Figure 6b) with similar parameters \(A = 1.06 \times 10^{13} \text{ s}^{-1}, \alpha = 8.0 \times 10^{-12} \text{ cp s}, b = 9.66 \times 10^{-14} \text{ s} \) to the ones reported in ref 44. The form of the friction chosen by Lee et al. has two parts: a part inversely proportional to viscosity which is important at low viscosity and a constant part, \(b\), which takes over at higher viscosities. Lee et al. suggest that this additional term arises from interactions that depend on the intramolecular properties of the solute (e.g., barrier height) but are independent of solvent viscosity. Comparing eq 7 and \(\beta_{\text{iso}} = (a/\eta + b)^{-1}\) and making the identification \(\alpha = b/a\) shows that the form of the friction coming from the free space model of reorientation is the same as that proposed by Lee et al., although the physical reasoning seems rather different. The value of \(\alpha\) required to fit the isomerization data, 12 cp\(^{-1}\), is about 10 times larger than the typical values of \(\alpha\) calculated from Dote et al. For example, Dote et al.’s \(\alpha\) ranges from 1.1 to 2.1 cp\(^{-1}\) in decane over the temperature range of our reorientation studies. The large increase of \(\alpha\) for the isomerization presumably reflects the influence of the intramolecular potential barrier on the friction. In other words, the friction approaches a constant value much more rapidly for isomerization than for reorientation. The greater quantitative success of eq 18 for \(F(\beta_{\text{iso}})\) as compared with eq 7 for \(\tau_{\text{RKR}}\) no doubt stems from the use of three variable parameters in the former case and only fixed parameter values in the latter case. However, it seems clear that the connection between the approaches of Dote et al. and Lee et al. to describing friction in complex solvents deserves further investigation.

**Concluding Remarks**

The data presented here point out the importance of the relative size of a solvent and a moving object in determining friction. Since the relative size of the solvent and the moving group differs substantially between rotational reorientation and isomerization, the process of “calibrating” isomerization friction via reorientation\(^{16-18}\) is not without ambiguity. Our data do show, however, that for trans-stilbene isomerization in n-alkane solvents a linear dependence of reorientation time on \(\eta/T\) does not imply that the friction dependence of the isomerization is adequately described by the Markovian form of Kramers’ equation. Our data, in a single solvent, can be well-fit by both the Grote–Hynes expression and the form proposed by Lee et al.\(^{44}\) In assessing the significance of these fits, it is necessary to bear in mind that we cannot rule out temperature-dependent changes in the potential surface or the possibility that the zero-frequency friction is nonlinear with \(\eta\) in a single solvent for the isomerizing group. Pressure-dependent studies of reorientation and isomerization should help in addressing the former possibility.

Two aspects of the reorientational data are worth noting. It is interesting that the excited state of trans-stilbene appears to reorient about 20% more slowly than the ground state. This implies that either the effective volume of the excited state or the coupling to the medium is larger than that of the ground state. The trend in decreasing coupling with increased solvent size parallels that seen earlier by Waldeck and Fleming\(^{23}\) for the monocation DODCI in alcohol solutions. The decrease is rather larger for trans-stilbene in alkanes, perhaps implying that the stronger intermolecular interactions between the charged molecule and its polar solvent tend to weaken the importance of molecular sizes in determining the friction. Another factor, as recently noted by Ben-Amotz and Scott,\(^{45}\) is that the decrease of coupling in going from alkane to alcohol solvents is rather large for trans-stilbene in alkanes, perhaps implying that the coupling to the medium is larger than that of the ground state. The trend in decreasing coupling with increased solvent size parallels that seen earlier by Waldeck and Fleming\(^{23}\) for the monocation DODCI in alcohol solutions. The decrease is rather larger for trans-stilbene in alkanes, perhaps implying that the stronger intermolecular interactions between the charged molecule and its polar solvent tend to weaken the importance of molecular sizes in determining the friction. Another factor, as recently noted by Ben-Amotz and Scott,\(^{45}\) is that the decrease of coupling in going from alkane to alcohol solvents is rather large for trans-stilbene and becomes less significant for larger solute molecules. This again stresses the importance of the relative size of the probe molecule and the solvent.

**Acknowledgment.** We thank Dr. Scott Courtney and Prof. Daniel Kivelson for many helpful discussions. This work was supported by a grant from the NSF.

**Registry No.** trans-Stilbene, 103-30-0.

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