Dynamics of cis-Stilbene Isomerization in Solution

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Fluorescence lifetime measurements of cis-stilbene show weak
dependence on solvent viscosity and suggest that the reaction coordinate
involves substantial ethylenic hydrogen motion.

1. Introduction

The influence of the solvent on the dynamics of reactive processes
continues to be of great interest [1,2]. The past decade has seen a
substantial increase in our understanding of the effect of solvent friction
on activated barrier crossing processes. The trans-cis isomerization of
stilbene has served as a useful prototype for understanding these types of
reactions [3,4]. Less well understood is the role of the solvent in
reactions for which there is little or no potential energy barrier
separating reactant from products [2]. An example of the latter type of
process is isomerization of stilbene from the cis side. The lack of a
substantial barrier along the reaction coordinate leads to a rapid internal
twisting motion that results in internal conversion ultimately leading to
formation of the trans isomer.

A fundamental difference between barrierless processes and activated
barrier crossing arises from the lack of a clear separation of time scales
between motion along the reaction coordinate and vibrational relaxation of
the remaining orthogonal degrees of freedom in the former case. The
resulting dynamics can be quite complicated and, in the case of stilbene,
can be viewed as a result of the competition between the intrinsic
nonradiative rate from the twisted configuration and the viscous drag
exerted by the solvent on the reaction coordinate.

2. Results and Discussion

We have carried out measurements of the excited state lifetime in both
alcohols and alkanes using the fluorescence upconversion method [5]. In
addition we have measured the fluorescence anisotropy in 2-propanol. A
summary of the lifetimes is shown in Table1. A typical decay curve is
displayed in Fig. 1. We find weak viscosity dependence in both types of
solvents. Additionally, we find that the lifetime is shorter by almost a
factor of two in 2-propanol than in tetradecane though the viscosity of
these two solvents differ by only 3% at room temperature. It is suspected
that these are manifestations of the breakdown of the Stokes-Einstein
relation connecting the microscopic friction with the shear viscosity of
the solvent. Extensive hydrogen bond formation in alcohols leads to a
larger free volume providing less resistance to large amplitude twisting
of the molecule. An alternative explanation can be based on the effect of the polar environment of the alcohol solvents on the reaction coordinate. If the potential surface along which the nuclei relax to achieve the twisted configuration arises from an avoided crossing of the \( S_1 \) and \( S_2 \) surfaces, then differential solvation effects on these two states would lead to a reaction coordinate with a solvent dependent frequency.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (cp)</th>
<th>(400) nm ( \pm ) ps</th>
<th>(430) nm ( \pm ) ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>h12 cis-stilbene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-propanol</td>
<td>2.35</td>
<td>0.76 ( \pm ).10 ps</td>
<td>0.87 ( \pm ).05 ps</td>
</tr>
<tr>
<td>decanol</td>
<td>15.51</td>
<td>1.27 ( \pm ).10 ps</td>
<td>1.47 ( \pm ).10 ps</td>
</tr>
<tr>
<td>hexane</td>
<td>0.32</td>
<td>1.03 ( \pm ).15 ps</td>
<td>----</td>
</tr>
<tr>
<td>tetradecane</td>
<td>2.43</td>
<td>1.38 ( \pm ).10 ps</td>
<td>1.52 ( \pm ).05 ps</td>
</tr>
<tr>
<td>d2 cis-stilbene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetradecane</td>
<td>2.43</td>
<td>1.71 ( \pm ).15 ps</td>
<td>1.75 ( \pm ).10 ps</td>
</tr>
</tbody>
</table>

An important question to consider is the nature of the reaction coordinate. We have found that deuteration of the ethylenic protons leads to a lifetime that is approximately 20\% slower than that for the nondeuterated species indicating the reaction coordinate for this process is indeed more complicated than simple ethylenic torsion. Similar conclusions have been reached by Myers and Mathies [6] and Abrash, et al.[7]. A recent spectroscopic study by Petek, et al.[8] on cis-stilbene analogs that are prevented from isomerizing has concluded that ethylenic-phenyl bending and phenyl torsional modes are strongly displaced in the \( S_1 \) state. The viscosity dependence of these motions should be less pronounced than that for ethylenic torsion and should lead to an isomerization rate that depends weakly on viscosity. This is in accord with our observations.

Regardless of the nature of the reaction coordinate, motion along this coordinate should lead to a rotation of the \( S_1\)-\( S_0 \) transition dipole moment. Fluorescence anisotropy measurements in 2-propanol suggest a fast component in the decay with a lifetime comparable to the magic angle time and an amplitude corresponding to a rotation of the transition dipole of approximately 20 degrees. The presence of a short component in the anisotropy argues that the rate determining step in the electronic relaxation process in 2-propanol is nuclear motion along the reaction coordinate. Recently, Abrash, et al.[7] measured transient absorption decays of cis-stilbene in various alkanes and concluded that a small barrier exists along the reaction coordinate. This is in qualitative agreement with a recent study of cis-stilbene in rare gas clusters by Petek, et al.[9]. It is possible that the slower rates of isomerization in alkanes observed in our studies could arise from a small barrier on the \( S_1 \) surface; however, the anisotropy result suggests that in 2-propanol the process is barrierless. This could arise from changes in the geometry of
the avoided crossing due to solvent polarity. It is known that in trans-stilbene the barrier to isomerization is substantially lower in alcohols than in alkanes due to preferential solvation of the $S_2$ state [10].

3. Conclusion

The weak viscosity dependence of the fluorescence lifetime of cis-stilbene along with the observation of ~ 20% increase in the lifetime in the deuterated species suggest that the reaction coordinate is more complicated than ethylenic torsion and involves a substantial amount of ethylenic hydrogen motion. The rate of isomerization in alcohols is faster than that in alkanes at constant viscosity, though it is not known whether this is a result of a dynamic or static solvent effect. The anisotropy result, though tentative, suggests that the isomerization process in 2-propanol is barrierless and that we are directly measuring motion along the reaction coordinate.

![Image](image-url)

Fig. 1 Fluorescence decay curve of cis-stilbene in 2-propanol at 293 K. Emission wavelength is 430 nm.

References