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ROTATIONAL REORIENTATION AND ISOMERIZATION OF TRANS-STILBENE

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ABSTRACT

We have tested the validity of using solvent shear viscosity as a measure of friction involved in the dynamics of t-stilbene. The rotational reorientation and the isomerization in n-alkanes are considered.

INTRODUCTION

Ultrafast techniques have made it possible to investigate hydrodynamic theories in the picosecond regime. The photoisomerization of t-stilbene has been widely used to test the Kramers theory for barrier crossing. But the small size of the probe suggests that a macroscopic solvent viscosity (η) may not be an adequate measure of the friction. In contrast the rotational reorientation time (τ_{OR}) is expected to provide a more accurate measure of the microscopic friction. We applied this concept to fit the isomerization data of t-stilbene in n-alkanes to the Kramers equation. We also discuss the isomerization in n-alcohols where the dynamic nature of the solvent possibly changes the activation barrier.

LASER SYSTEM

The measurements of τ_{OR} were performed with a CPM ring laser amplified through Nd:YAG pumped dye cells. The 615nm output pulse was frequency doubled and used to induce an excited state anisotropy in the sample. The decay of the anisotropy is monitored via S_1 - S_n absorption by the time delayed fundamental through crossed polarizers. All isomerization data were obtained with a single photon counting system or were taken from other sources.

RESULTS AND DISCUSSION

Figure 1 shows the macroscopic friction (∝ η) is not parallel to the microscopic friction (∝ τ_{OR} T) when the solvent is varied. The longer alkane solvent creates a larger space where t-stilbene can rotate more freely, as reflected in the trend of the slope changes in Figure 1. However, rather surprisingly, Stokes law (τ_{OR} ∝ η / T) appears to hold within a given alkane.

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The data agree qualitatively with a free space model\textsuperscript{3}. But the model predicts a curvature in the plot when applied to a single solvent\textsuperscript{4}. This suggests that the effect of density changes within a given solvent is less important than the theory predicts.

In earlier studies\textsuperscript{5,6}, using $\tau_{OR}$ as a friction measure instead of $\eta$ seemed to improve the Kramers expression when applied to t-stilbene in n-alkanes at room temperature. However, this method fails when the study is extended over a range of temperature (Figure 2). The Kramers equation with the microscopic friction $\zeta_{OR} (=6kT\tau_{OR} T / I_{OR})$ still lacks the necessary curvature. This failure is also seen when the fit is made for a single solvent (Figure 2c) where according to Figure 1 $\eta$ is a suitable parameter. Therefore other forms of the friction (e.g. frequency dependent friction\textsuperscript{7}) should be considered. We also cannot exclude the possibility that the potential energy surface is multidimensional or density dependent.

While isoviscosity plots provide a fixed barrier height (~3.5 Kcal/mol) for the stilbene isomerization in alkanes, they give higher barriers for low viscosity alcohols than high viscosity alcohols (e.g. ~3.5 Kcal/mol at 1 cp and ~2 Kcal/mol at 10 cp). This trend cannot be explained by a static polarity alone.
Fig. 2 Reduced isomerization rate $F(t_{\text{ISO}})$ for t-stilbene plotted versus $\eta(a)$ and $\zeta_{OR}(b)$ with best Kramers fits (solid curves). The plot symbols are given in Figure 1. (c) shows a simple Arrhenius expression (dotted curve) fits the data for a single solvent (decane) better than Kramers equation.

The longitudinal relaxation times ($\tau_L$) of the alcohols are distributed over much wider range than the isomerization lifetimes ($\tau_{\text{ISO}}$) in the corresponding alcohols. For example, on going from methanol ($\tau_L \sim 9$ ps at 20°C) to decanol ($\tau_L \sim 690$ ps at 20°C) $\tau_{\text{ISO}}$ changes from 40 ps to 190 ps. This suggests that only the short alcohols solvate effectively the excited state during the isomerization. This effect, coupled with the static polarity effect, may change the barrier height in a way consistent with the data.

We conclude that in any of the dynamics considered above the macroscopic shear viscosity is not the proper measure of the friction.

REFERENCE