SEARCH FOR THE KRAMERS THEORY TURNOVER:
PHOTOCHEMICAL ISOMERIZATION AT VERY LOW VISCOSITIES

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The rate of photochemical isomerization of diphenyl butadiene has been studied as a function of viscosity and temperature in liquid ethane and propane. The lowest viscosity studied is about one order of magnitude lower than our previous study. No evidence for a turnover or decrease in rate with decreasing viscosity was found.

1. Introduction

There has been considerable recent interest in the low-friction or energy controlled region of activated barrier crossing in solution [1—5]. From the theoretical point of view interest has centered on obtaining rate expressions for the low-friction regime [2,3] and on developing expressions which bridge between the low and high friction solutions obtained by Kramers [6] for the problem of a brownian particle escaping over a potential barrier [4]. Several authors have also considered the consequences of non-markovian friction in the low-friction regime. All these discussions are in accord in predicting, for the one-dimensional problem, that at sufficiently low values of the friction, the barrier crossing rate will stop increasing with decreasing friction (as is observed in photochemical isomerization studies at normal viscosity values [7—10]) and begin to decrease with decreasing friction. The decrease occurs simply because the rate of accumulation of energy in the reaction coordinate becomes rate limiting and as pointed out by Hynes this regime could be regarded as a problem in vibrational relaxation [11]. That the limiting rate at zero friction (for states below the barrier) is indeed zero is confirmed by the supersonic jet studies of stilbene by Syage et al. [12]. These authors found that for cold, isolated stilbene molecules, those molecules excited with excess vibrational energy <1200 cm⁻¹ delayed purely radiatively. For excess energies above this value the radiationless decay rate decreases very rapidly with increasing energy, and Khundar et al. [13] have discussed this excess energy dependence in terms of RRK and RRKM theories.

Jonas and co-workers [14], using high-pressure NMR techniques, have found that the rate of ring inversion in cyclohexane solutions at first increases and then decreases with increasing viscosity. Garrity and Skinner [5] and Carmeli and Nitzan [4] have discussed these results from a theoretical point of view.

In view of the current interest in this problem direct time-resolved studies in the low- and intermediate-friction regimes will be of value. We have extended our earlier measurements of the photochemical isomerization of diphenyl butadiene (DPB) [7] to viscosities one order of magnitude lower than previously by using room temperature liquid ethane and propane as the solvent. We have also studied the temperature dependence of the radiationless process in these solvents. At the lowest viscosity studied (0.04 cP) our solution is only about a factor of two more viscous than air (0.02 cP at 298 K).

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2. Experimental

Fluorescence lifetimes were measured by the time correlated single photon counting technique [15] using the second harmonic of a DCM synchronously mode locked/cavity dumped dye laser as the excitation source. The sample was contained in a specially designed, variable temperature, high-pressure cell. The pressures used were the cylinder pressures for ethane (600 psi) and propane (120 psi). That the sample was liquid was checked visually by observing the meniscus rise in the cell during filling. If the windows are leaking boiling can be observed in the cell. Temperature control was achieved using a Neslab RTE-4 to circulate a water/ethylene glycol mixture through the stainless steel cell block. Temperatures were monitored with a calibrated thermocouple/digital thermometer combination. The temperature range used was -12 to 23°C. The cell was allowed to stabilize for 10-15 min after changing the temperature. The viscosity values were interpolated from ref. [16]. The lifetime and viscosity values are listed in Table 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Viscosity a) (cP)</th>
<th>( \tau_f ) (ps)</th>
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<td>propane</td>
<td>-13</td>
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<td></td>
<td>-10</td>
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<td>145</td>
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<tr>
<td></td>
<td>24</td>
<td>0.039</td>
<td>150</td>
</tr>
</tbody>
</table>

a) Viscosities obtained from ref. [16].

3. Results and discussion

Following our previous procedure [7,8] we first assume that the barrier crossing rate can be written as

\[ k_{nr} = k_{iso} = F(\eta) \exp(-E_0/RT) . \] (1)

The use of (1) relies on three major assumptions: (i) a hydrodynamic model for the friction [7,8], (ii) an \( E_0 \) value that changes little from solvent to solvent, and (iii) a pre-exponential factor with no intrinsic temperature dependence. Our data appear quite consistent with these assumptions. Using \( E_0 = 4.7 \) kcal/mole [7] the plot in fig. 1 was constructed. First we note that the room temperature liquid ethane and propane points fall on the same smooth curve as the room temperature points for the higher linear alkanes studied previously. Here the assumption of an unchanged \( E_0 \) in the two new solvents is irrelevant. Second, when the \( F(\eta) \) values from the temperature dependent studies in ethane and propane are calculated, within our experimental error, they fall on the same smooth curve. Thus the assumption of an approximately constant \( E_0 \) seems well justified. Hence, we are confident in stating that at the lowest viscosity we have studied -0.039 cP (ethane, 24°C) the isomerization rate in DPB is still increasing with decreasing viscosity.

Had we gained access to the low-friction regime of the barrier crossing, the assumption of a temperature independent form for \( F \) in eq. (1) would have been
Fig. 2. Arrhenius plots for the non-radiative rate of DPB in ethane (solid line) and propane (dashed line). The activation energies are given in the text.

invalid. At very low friction Kramers finds

\[ k \propto (\eta/T) \exp(-E_0/RT). \] (2)

In the intermediate (i.e. turnover) region the temperature dependence will be complex since one is switching from a \(\eta/T\) dependence to a \(1/\eta\) dependence at high viscosity. If the viscosity “activation energy” \(E_\eta\) is comparable to \(E_0\), then Arrhenius plots of \(\ln k_{nr}\) versus \(1/T\) should appear curved for measurements in the intermediate region, with slope, \(E_{nr}\), increasing with increasing friction. Fig. 2 shows the Arrhenius plots for DPB in liquid ethane and propane. Although the temperature ranges are not large no evidence for deviation from linearity is observable.

We are currently extending the ethane results over a much wider temperature range. The \(E_{nr}\) values obtained from fig. 2 (\(E_{nr} = 5.3 \pm 0.9 \text{ kcal/mole}\) (ethane), \(5.1 \pm 0.4 \text{ kcal/mole}\) (propane)) are very similar to the \(E_{nr}\) values in the higher alkanes, \(E_{nr} = 5.6 \pm 0.6 \text{ kcal/mole}\) (hexane) = 5.7 \pm 0.7 kcal/mole (octane) = 6.2 \pm 0.7 kcal/mole (dodecane) [16].

Since we do not observe a turnover in our data it may be possible to fit the viscosity dependence to Kramers expression for intermediate and higher friction (valid only for rates which decrease with increasing friction). One way of writing Kramers expression is as the transition state rate \[ k_{TST} = (\omega_0/2\pi) \exp(-E_0/RT) \] times a correction factor:

\[ k_{nr} = k_{TST}(1/2\omega'\tau_v) \{1 + (2\omega'\tau_v)^2\}^{1/2} - 1\}. \] (3)

Here \(\omega_0\) and \(\omega'\) are the frequencies describing the initial minimum and barrier maximum respectively, \(\tau_v\) is the velocity relaxation time for the isomerization motion, and \(E_0\) the barrier height. The factor in braces runs between unity for zero friction (i.e. giving \(k_{TST}\) as an upper limit) and zero for infinite friction. As before [7] we fit to the hydrodynamic form of (3) where \(\tau_v\) is assumed to be inversely proportional to viscosity. Including the new low-viscosity data along with the previous results for DPB in alkanes does not improve the fit of the Kramers function.

The same qualitative failure is observed — the Kramers expression does not curve sharply enough to fit the data over the whole range. The parameters for \(\omega_0\) and \(\omega'\tau_v\) obtained depend on the range of the fit. A reasonable compromise fit is shown in fig. 1 and corresponds to \(\omega_0 = 5.9 \times 10^{13} \text{ s}^{-1}\) and \(\omega'\tau_v = 0.133\) (at 1 cP). At 0.04 cP we then find that the Kramers rate is 86% of the transition state value. In terms of the one-dimensional Kramers model \(k_{TST}\) represents an upper limit but in view of the slope of the curve in fig. 1 at the lowest viscosities, it seems hardly likely that we are within 14% of the maximum rate. In our previous study at higher viscosities we found that a functional form

\[ k = (B/\eta)^a \exp(-E_0/RT) \] (4)

fit our data significantly better than the Kramers equation. The fit including our new data is also shown in fig. 1. It is somewhat better than the Kramers expression in reproducing the very sharp curvature present in our data. The parameters are \(B = 1.53 \times 10^{12} \text{ s}^{-1}\) and \(a = 0.66\) \(^{\ddagger}\). In our previous study and that of Bagchi and Oxtoby the apparent “saturation” of the influence of viscosity in retarding the rate was attributed to the frequency dependence of the medium response [8,17]. Calculations based on the Grote–Hynes model [2] for frequency-dependent friction produced a curve well described by an expression with the form of eq. (4) [17]. At very low viscosities frequency-dependent friction becomes unimportant and the Grote–Hynes expression reduces to the Kramers expression (3) (cf fig. 1

\(^{\ddagger}\) The values are very similar to those in ref. [7]. There is a misprint in this latter article: the value of \(BA^{\ddagger}\) should read \((1.7149 \pm 0.337) \times 10^{12} \text{ s}^{-1}\).
of ref. [17]). We do not ascribe our failure to find a turnover to non-markovian effects in the solvent friction.

There are clearly serious difficulties in applying the standard Kramers treatment to our data. We do not observe a maximum in the rate as a function of viscosity and yet the model parameters derived from our data suggest we have almost reached the maximum model rate. Physically the rising region of the rate dependence on viscosity arises when the rate of accumulation of energy in the reactive coordinate becomes rate limiting (i.e. \( < \omega_0 \) where \( \omega_0 \) is the curvature of the initial minimum). In other words in the energy controlled region a Boltzmann distribution cannot be maintained in the reactive mode. In small molecules vibrational relaxation in liquids can be surprisingly slow [18], however in a large molecule like DPB both inter- and intra-molecular vibrational relaxation (or activation) is likely to be very rapid. The other modes of the molecule will then keep the reactive mode in equilibrium and it will be very much more difficult to reach the energy controlled regime than would be expected from the one-dimensional theoretical models. In DPB, we suggest, vibrational relaxation is sufficiently rapid that energy starvation in the twisting coordinate may not be obtainable in practice in liquid solution. In his review [11] Hynes makes a similar point in noting that internal degrees of freedom will make it more difficult for the reaction to be in the energy controlled region. Very recently Millar and Eisenthal have suggested that binaphyl excited state isomerization is energy controlled below \( \approx 0.5 \text{ cP} \) [19]. Perhaps energy flow into the reactive mode is relatively slow in this molecule. In any case quantification of the ideas discussed here requires more information on inter- and intra-molecular vibrational relaxation processes in large molecules in solution than we currently possess.

Acknowledgement

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References