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## COMMUNICATIONS

## Unimolecular reaction rates in solution and in the isolated molecule: Comparison of diphenyl butadiene nonradiative decay in solutions and supersonic jets

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The recent study of diphenyl butadiene (DPB) in supersonic jets and in solution by Shepanski *et al.*<sup>1</sup> and by Courtney and Fleming,<sup>2</sup> respectively, provides an opportunity to compare the isomerization rates measured in the isolated molecule (jet) with those measured at very low viscosity in solution. These comparisons should shed light on the vibrational energy flows between "optical" and "reactive" modes in the isolated molecule and on the connection between activated, friction dependent, models of barrier crossing in solution,<sup>3-5</sup> and statistical RRK (or RRKM) theories of gas phase unimolecular reactions.<sup>6</sup>

The degree to which all the vibrational modes of the reacting molecule are in rapid communication with each other represents one of the most obvious potential differences between isolated and solvated molecules. In the absence of a significant solvent effect on the potential surfaces, for a given amount of vibrational energy content, we might expect very similar rates of isomerization in an isolated molecule with rapid intramolecular vibrational redistribution and in a molecule in a solution with viscosity sufficiently low that frictional effects are unimportant.

Before comparing the two data sets a few remarks on relevant time scales are in order. The collision rate in liquids<sup>7</sup> can be extracted from the expression  $\tau_{\text{coll}} = (\rho d^2/6\eta)$ , where  $\rho$  is the density,  $d$  the diameter, and  $\eta$  the viscosity. For the lowest viscosity solvent used—room temperature liquid ethane<sup>2</sup>— $\tau_{\text{coll}}$  is  $\sim 460$  fs. The fluorescence lifetime under these circumstances is 150 ps and it seems safe to regard the vibrational population as a Boltzmann distribution characterized by the temperature, since on the average there are 300 collisions during the lifetime.

Assuming a Boltzmann distribution, the average vibrational energy content  $E_v$  for a DPB molecule can be computed using the standard expression<sup>8</sup> (zero point energy is neglected and the harmonic approximation used). To compute  $E_v$  for DPB we used the normal mode vibrational frequencies of Pierce and Birge.<sup>9</sup> At 297 K we obtain  $E_v = 2270$  cm<sup>-1</sup>. Note that  $E_v$  at room temperature is

greater than  $E_0$ , the isomerization threshold in either vapor (1050 cm<sup>-1</sup>) or solution (1650 cm<sup>-1</sup>) phase.<sup>1,10</sup> Figure 1 shows the logarithm of the nonradiative rate vs excess vibrational energy (jet results) and vs the average vibrational energy (solution phase results). For liquid ethane and liquid propane results are shown for a range of temperatures (260–297 K). Also shown are the room temperature data for liquid alkanes C<sub>2</sub>–C<sub>12</sub>.

The most striking feature of Fig. 1 is that the jet and solution results are similar in the low viscosity solvents if  $E_{\text{excess}}$  (jet) is assumed equal to  $E_v$ . The strong influence of solvent viscosity is shown by the vertical line (at  $E_v$

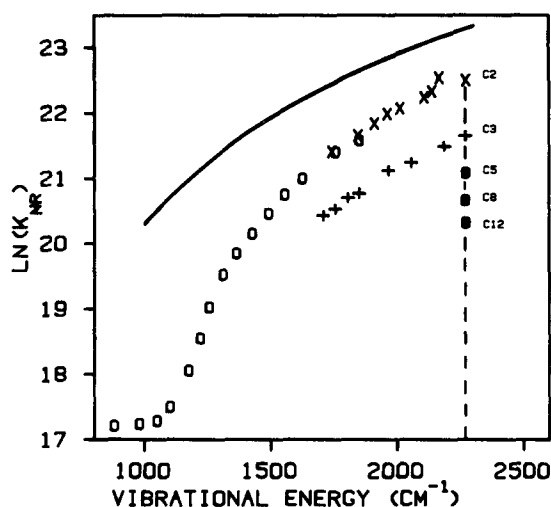


FIG. 1. Rates of photoisomerization of diphenyl butadiene as a function of vibrational energy. The abscissa corresponds to the average vibrational energy for both systems. O—jet results, X—in liquid ethane, +—in liquid propane. The vertical line shows the influence of solvent viscosity at 24 °C ( $E_v = 2270$  cm<sup>-1</sup>). The solid line gives the thermally averaged rates calculated according to the procedure outlined in Ref. 15 and the density of states was calculated using a direct count procedure outlined in Ref. 6. The normal modes frequencies were taken from Ref. 9.

$= 2270 \text{ cm}^{-1}$ ) describing the room temperature decay rates in alkane solution. In fact, we found that even at the lowest viscosity studied the measured rate still correlated strongly with viscosity. If IVR leads to complete equilibration among the different degrees of freedom, the measured rates of isomerization in the isolated molecule should be compared with those measured in solution near zero viscosity. As Fig. 1 shows, the jet results and the liquid ethane data give very similar rates. The fact that the rates in ethane still show viscosity dependence leads us to suggest that at these excess energies IVR<sup>11</sup> from optical modes to the torsional mode involved in the isomerization is not as effective in the isolated molecule as in the solution phase. This assumes that the microcanonical and canonical rates are equivalent when the average vibrational energy is high enough. To compare with solution phase data we also present in Fig. 1 the thermally averaged microcanonical rates. Clearly these averaged rates are higher than both the solution phase and beam data. This is consistent with the finding of a viscosity effect even at 0.039 cp.<sup>2</sup>

Courtney and Fleming<sup>2</sup> have previously argued that the failure to observe the "turnover" predicted by one-dimensional Kramers theory<sup>3,4</sup> at very low viscosities results from efficient intra- and intermolecular vibrational relaxation but no distinction between the two mechanisms was made. From the present analysis it is clear that intermolecular (collisional) "assistance" of IVR can enhance the isomerization rate over the isolated molecule value and that, at least at low viscosities, both mechanisms contribute to the observed rate in solution. At higher viscosities since  $\tau_{\text{coll}}^{-1}$  is now much larger than  $k_{\text{IVR}}$  (e.g., at 1 cp  $\tau_{\text{coll}} \sim 10^{-14}$ s) the collisional process dominates. (At higher viscosities in any case frictional effects, i.e., barrier crossing and recrossing, rather than energy accumulation in the reactive mode, dominate the reaction rate). The effect of higher viscosity solvent in lowering the rates is shown in Fig. 1.

The restriction of IVR<sup>11</sup> to certain modes in the isolated molecule is not surprising. In anthracene, for example, Felker and Zewail found in a dense region of the spectrum that only a few modes are coupled.<sup>12</sup> At higher excess energies IVR becomes very rapid. In stilbene<sup>13</sup> and DPB,<sup>1,14</sup> the emission spectrum become diffuse for excess energies above the threshold for rapid nonradiative decay (the barrier

height), and the rate becomes insensitive to the initially excited vibrational level. In recent studies of stilbene in a bulb, Perry *et al.*<sup>15</sup> suggest that the IVR rate is  $5 \times 10^{11} \text{ s}^{-1}$  at 296 K. In supersonic jets this IVR has a threshold below the barrier for isomerization in stilbene.<sup>16</sup>

In conclusion, the comparison made here between *isolated* molecule and *solution* phase results indicates that intramolecular interactions are important and compete with intermolecular interactions. A precise evaluation of the relative importance of these effects requires a detailed theory of the nature of energy redistribution. A more complete account of this work will be published later, when our data on stilbene and other systems become available.

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