Rates of Photoisomerization of *trans*-Stilbene in Isolated and Solvated Molecules: Experiments on the Deuterium Isotope Effect and RRKM Behavior

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In this paper we consider the dynamics of the photoisomerization of *trans*-stilbene and related molecules. New measurements of the deuterium isotope effect on reaction rates are presented, and details of RRKM behavior in isolated and solvated *trans*-stilbene are discussed. From measurements of fluorescence decay rates as a function of the excess vibrational energy in jet-cooled *trans*-stilbene-d_{12}, an energy threshold to the rates is found at ca. 1200-cm^{-1} excess energy in the first excited singlet state. The threshold behavior is similar to that which occurs in the photoisomerization of *trans*-stilbene-h_{12}. The overall magnitudes of the perdeuterio rates are smaller, however, than the perprotio ones. As with *trans*-stilbene-h_{12} the measured rates are found to be slower than those calculated by *standard* RRKM theory. Nevertheless, the observed slowing of the rates upon deuteration *is* predicted by the theory. The results and their interpretation are discussed in light of the results of other jet studies of *trans*-stilbene derivatives and of studies of the photoisomerization reaction in solution. The role of intramolecular vibrational energy redistribution and the nonadiabatic influences on the reaction are also discussed.

I. Introduction

In previous publications[1-3] we have presented accounts of our study of the photoisomerization dynamics of *trans*-stilbene in supersonic jets (collisionless conditions). Our interest in the problem has focused on measuring rates vs. excess vibrational energy in the isolated molecule,[2,3] on understanding the details of the reaction coordinate,[1,2] on relating the reaction process to the process of intramolecular vibrational energy redistribution (IVR),[1-3] and on relating the measured rates of collisionless and solvated molecules to calculated RRKM rates.[2,4]

From picosecond time-resolved measurements made on the jet-cooled molecule,[2,3] it has been found that the photoisomerization of isolated *trans*-stilbene proceeds at rates which are roughly an order magnitude less than the rates calculated[2,4] by standard RRKM theory. This situation is to be contrasted with that for the reaction in solution, for which measured rates are found to approach rates calculated by using the solution limit of RRKM. It has been argued that this state of affairs is consistent with nonadiabatic influences on the photoisomerization process, although other possible reasons (for example, restricted IVR or reversibility in the reaction) could not be ruled out.[2]

This paper presents experimental and calculational results which further test the applicability of *standard* and *nonadiabatic* RRKM in explaining the reaction rates of *trans*-stilbene. Our principal focus is on measured and calculated reaction rates of jet-cooled perdeuterio-*trans*-stilbene (*trans*-stilbene-d_{12}). Our reason for studying this species stems from the fact that it is expected to have potential energy surfaces virtually identical with those of the perprotio species. Yet, its rate vs. energy behavior may differ from that of *trans*-stilbene-d_{12} because of its different vibrational level structure and vibrational density of states. The detailed form of any such differences in rates can be predicted if one assumes that the reaction can be described by some variant of RRKM theory. Comparisons of observed vs. calculated rate differences for the two *trans*-stilbene species therefore serve as tests of the various RRKM models. A second focus of this paper is on the relation of our results for the *trans*-stilbene species to rates obtained for other *trans*-stilbene derivatives and for diphenylbutadiene, the rationale being similar to that underlying the comparative study between *trans*-stilbene-h_{12} and -d_{12}. Finally, the implications of the isolated molecule results regarding rates for the reaction in solution are discussed.

II. Theory and Methods of Calculation

A. Standard RRKM Treatment of Rates. In the interpretation of our experimental results, it shall be useful to refer to what we

call a "standard" RRKM calculation of *trans*-stilbene reaction rates. In this section, we outline what it is that we mean by this. Also, we outline our determination of the values to be used in performing such calculations.

The basis for our RRKM calculations is the expression[5]

$$k(E_x) = \frac{\int_0^{E_x-E_0} \rho^\dagger(E_v^\dagger)\, dE_v^\dagger}{h\rho(E_x)} = \frac{N^\dagger(E_x - E_0)}{h\rho(E_x)} \quad (2.1)$$

where E_x is the excess vibrational energy in the molecule, E_0 is the reaction barrier energy, $\rho^\dagger(E_v^\dagger)$ is the density of vibrational states for the transition state at an excess vibrational energy (in the transition state) of $E_v^\dagger$, $\rho(E_x)$ is the density of vibrational states of the molecule at energy E_x, $N^\dagger(E_x - E_0)$ is the number of vibrational states in the transition state having energies less than or equal to $E_x - E_0$, and h is Planck's constant.

To evaluate (2.1) one must know (1) the barrier energy E_0, (2) the vibrational frequencies of the reactant species, and (3) the vibrational frequencies of the transition state. For the *trans*-stilbene reaction one can obtain E_0 from measurements of rates vs. excess energy made on jet-cooled molecules (ref 2 and 3 and section IV) and from measurements of fluorescence quantum yields[6,7] made on such samples for different excess energies.[6] We use $E_0 = 1200$ cm^{-1} (for a discussion of this choice, see section V.A). A real problem exists, however, in determining the reactant and transition-state vibrational frequencies. A typical approximation used to ameliorate this problem is one which we make and which, along with eq 2.1, serves as the defining attribute of our standard RRKM calculation: we assume that the frequencies of all the normal modes in the reactant do not change in going to the transition state (except, of course, the frequency ν_{rxn} of the normal mode which corresponds to the reaction coordinate). With this approximation, one in principle can obtain all the frequency values needed from spectroscopic measurements and/or force-field calculations made for the reactant molecule. For *trans*-stilbene-h_{12} we have used vibrational frequencies from three sources: (1) fluorescence excitation spectra,[1] (2) infrared and Raman mea-

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(3) J. A. Syage, W. R. Lambert, P. M. Felker, A. H. Zewail, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **88**, 266 (1982).
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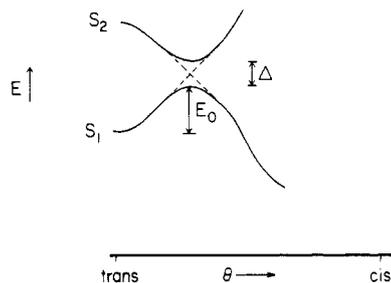(7) T. S. Zwier, E. Carrasquillo M., and D. H. Levy, *J. Chem. Phys.* **78**, 5493 (1983).

Figure 1. Model potential energy surfaces relevant to *trans*-stilbene photoisomerization. The solid lines represent adiabatic surfaces corresponding to the S_1 and S_2 excited electronic states. The dashed lines represent the diabatic energy surfaces which mix strongly at their crossing point and give rise to the avoided crossing of the adiabatic curves. The isomerization reaction is taken to correspond to motion along the lower adiabatic surface. E_0, then, is the energetic barrier to isomerization. Nonadiabatic effects arise because the molecule need not stay on this lower surface but, instead, may undergo a transition to the S_2 curve near the crossing point. The probability of such a jump increases with decreasing energy difference Δ between the curves and with increasing velocity along the reaction coordinate.

surements[8] of ground-state vibrational intervals, and (3) calculated results.[9] In the cases where the frequencies of S_1 modes were not available from jet excitation spectra, the measured S_0 values,[8] reduced by 3% to account for their shifts upon electronic excitation to S_1, were used. Modes without frequencies assigned from experiment were given the values calculated by Warshel.[9] For *trans*-stilbene-d_{12} (1) and (2) above were used. In the rare cases when there were no values available from these sources, the perprotio values were used. All the values used for both species can be found in Appendix I of this paper.

Our choice of ν_{rxn} for *trans*-stilbene-h_{12} is from the infrared–Raman study[8] and is ultimately based on Warshel's calculation[9]—the 410-cm^{-1} b_g fundamental assigned in ref 8 closely corresponds in frequency to the b_g torsional fundamental of ref 9. We have reduced its value by 3% to account for its presumed red shift upon excitation to S_1. (In practice, this adjustment has a negligible effect on the calculated values.) Corresponding to the 410-cm^{-1} band in the *trans*-stilbene-h_{12} IR spectrum is a 408-cm^{-1} band in the *trans*-stilbene-d_{12} spectrum. We reduce this value by 3% to obtain ν_{rxn} for the perdeuterated species.

Using the above values for E_0, ν_{rxn}, and the other vibrational frequencies, we evaluate the $N^\dagger$ and the ρ in eq 2.1 using a direct count procedure with frequency grouping (27 groups). (We discuss the effect that this grouping approximation has in section V.A.)

Clearly, a "standard" RRKM calculation, as first was applied[2,4] to the photoisomerization of *trans*-stilbene, is not the only way to calculate rates using RRKM theory. One particular modification of the procedure is to let the transition-state vibrational frequencies vary (thereby introducing additional parameters) from those of the reactant values. This has been done more recently by Troe[10] in his application of RRKM to *trans*-stilbene photoisomerization. We discuss the validity of this approach in section V.B.

A second possible modification involves changing eq 2.1 to account for nonadiabatic influences on the reaction. As we have argued elsewhere,[2] such influences could be present in the *trans*-stilbene reaction. In the interest of presenting a more quantitative analysis of this possibility, we consider nonadiabatic RRKM theory in the next section and in section V.

Finally, it should be noted that, in all RRKM calculations on *trans*-stilbene described herein or by others, neither the involvement of rotations ($k(E,J)$) nor rotational–vibrational coupling is taken into account.

B. Nonadiabatic RRKM Treatment. Equation 2.1 applies to the situation wherein every reactant molecule that achieves the transition-state configuration proceeds on to products. Now the

barrier to photoisomerization in *trans*-stilbene is assumed to arise from the avoided crossing of two electronic state adiabatic potential energy surfaces[11] (see Figure 1). The initial step to isomerization occurs if a molecule's trajectory along the reaction coordinate remains on the lower adiabatic surface and crosses the barrier on this surface. There is also the possibility, however, that some trajectories will jump from the lower adiabatic surface to the upper one in the region of the avoided crossing. In other words, a nonadiabatic transition may occur. Such nonadiabatic transitions, which increase in probability with increasing "velocity" along the reaction coordinate, serve to decrease the rate of the adiabatic isomerization reaction. The finite probability that the trajectory of the isolated molecule will jump to the upper adiabatic surface is consistent with the overestimation of the rate by RRKM theory, since the theory assumes[5] that every molecule gaining the configuration of the transition state (at the avoided crossing) and moving along the reaction coordinate toward the product configuration will yield a product molecule.

For the situation wherein a nonadiabatic transition competes with the photoisomerization (see Figure 1), there is a velocity-dependent probability (P_{12}) that the trajectory of the molecule will not remain on the lower energy adiabatic surface that leads to isomerization but, instead, will jump to the upper adiabatic surface. An approximate expression for P_{12} is as follows[12-14]

$$P_{12} = \exp\left(-\frac{\pi}{2}\gamma\right) \tag{2.2a}$$

$$\gamma = \frac{1}{\hbar v}\frac{\Delta^2}{|F_1 - F_2|} \equiv \frac{1}{\hbar v}\gamma' \tag{2.2b}$$

where v is the velocity along the reaction coordinate at the avoided crossing, Δ is the energy difference between the two energy surfaces at the avoided crossing, and F_1 and F_2 are the slopes of the two curves there.

Now v is directly related to the kinetic energy ($E_t^\dagger$) of the molecule's motion along the reaction coordinate[15]

$$v = (2E_t^\dagger/\mu)^{1/2} \tag{2.3}$$

where μ is an effective mass (or moment of inertia) for the motion along this coordinate. Also

$$E_t^\dagger = E_x - E_0 - E_v^\dagger \tag{2.4}$$

That is, $E_t^\dagger$ just equals the total amount of energy in the transition-state species minus the vibrational energy of that species. Taking into account the probability of a nonadiabatic, nonreactive trajectory, the integral in (2.1) must include a factor that accounts for P_{12}

$$k(E_x) = \frac{\int_0^{E_x-E_0}[1 - P_{12}(E_x - E_0 - E_v^\dagger)]\rho^\dagger(E_v^\dagger)\,dE_v^\dagger}{h\rho(E_x)} \tag{2.5}$$

or by using (2.2)–(2.4)

$$k(E_x) =$$
$$\int_0^{E_x-E_0}\left[1 - \exp\left\{-\frac{\pi\gamma'}{\hbar 2}\left(\frac{\mu}{2(E_x - E_0 - E_v^\dagger)}\right)^{0.5}\right\}\right] \times$$
$$\rho^\dagger(E_v^\dagger)\,dE_v^\dagger/h\rho(E_x) \tag{2.6}$$

It is (2.6) which we use as the basis for our nonadiabatic RRKM rate calculations. Note that, in the limit of large Δ, γ' goes to

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(15) In the case of the *trans*-stilbene isomerization reaction considered in this paper, the reaction coordinate corresponds to an internal rotational about the ethylene double bond. We assume here that the motion along the reaction coordinate near the activated complex configuration is that of a free rotor. Thus, v is an angular velocity, μ is the moment of inertia of the molecule about the ethylene double-bond axis, and $E_t^\dagger$ is the kinetic energy of the motion.
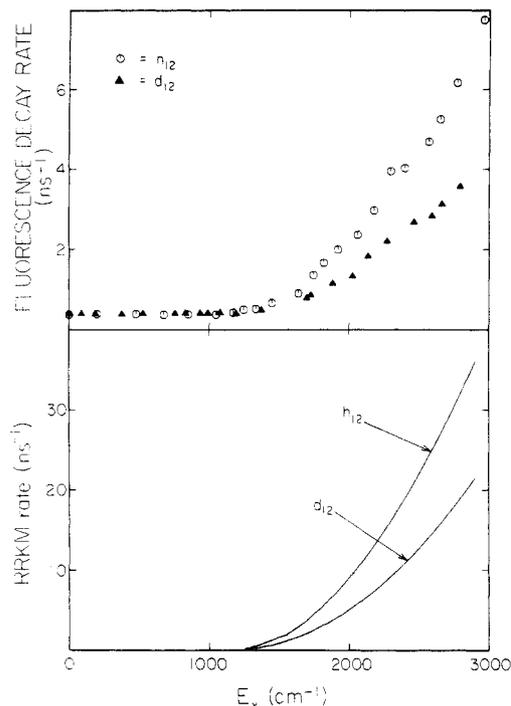
Figure 2. (top) Measured fluorescence decay rates of *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12} as a function of excess vibrational energy in the first excited singlet electronic state. (bottom) Standard RRKM-calculated rates for *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12} as a function of excess energy in S_1. See the text for details of the calculation. Note the change in scale of the ordinate relative to that of the plot of the observed rates (top).

infinity and (2.6) becomes the standard RRKM expression for the rate.

At this point it is pertinent to note the usefulness of measuring rates for *trans*-stilbene-d_{12}, as well as for the -h_{12} species, in testing the applicability of (2.6) and the nonadiabatic RRKM model to the reaction process. This usefulness derives from the similarity of the electronic state potential energy surfaces of the two species. This implies that one value of γ' should apply to both molecules. Measuring rates for the two isotopic species and comparing these rates to calculations performed assuming a particular value for γ' therefore can provide a consistency check on the theory.

The only two parameters needed to evaluate (2.6) which are not needed for (2.1) are γ' and μ. Now, we shall be interested in varying γ' so as to try to fit observed results. μ, however, can be calculated as the moment of inertia about the ethylene double bond by using the geometry of ref 16 (obtained by electron diffraction measurements). Doing so, one finds $\mu = 1033$ and 1141 amu Å^2 for the perprotio and perdeuterio species, respectively.[17]

III. Experimental Section

The experimental apparatus and procedures have been described elsewhere.[18] One difference in the apparatus used in this study as opposed to that used for earlier ones is the replacement of the phototube with a Hamamatsu R1564U multichannel plate. This substitution decreases the temporal width of the response function to ~80 ps. Results obtained previously[2,3] for *trans*-stilbene-h_{12}

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(17) It may be more appropriate to use the so-called reduced moment of inertia for the ethylene torsion, $\mu_{red} = \mu/4$, as done recently in the paper concerning isomerization dynamics by Robinson et al. (see the citation in ref 21). Doing so would give a value for γ' twice that which would be obtained by using μ (see eq 2.6). However, the use of $\mu/4$ does not change any of the conclusions which are drawn below from the derived value for γ'. This is because these conclusions are based on products of the form $\gamma'\mu^{1/2}$. (The derived value for Δ (section V.B4) would change slightly, but it is only quoted in a qualitative sense anyway.)

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TABLE I: Nonradiative Decay Rates as a Function of Energy in the S$_1$ States of Perprotio- and Perdeuterio-*trans*-stilbene in Supersonic Jets

	h_{12}		d_{12}
E_x,^{a} cm^{-1}	k_{nr},^{b} ns^{-1}	E_x,^{a} cm^{-1}	k_{nr},^{b} ns^{-1}
0	0^c	0	0^c
1048	0.0^c	1078	0.02^c
1170	0.06^c	1189	0.01
1246	0.12^c		
1332	0.14^c	1372	0.09
1447	0.29^c		
1638	0.53^c		
1725	1.04	1700	0.39
1820	1.29	1730	0.46
1840	1.35	1885	0.76
1920	1.63		
1940	1.74		
2005	2.13	2025	0.93
2060	1.99		
2095	2.33	2135	1.44
2185	2.76		
2295	3.58	2270	1.63
2395	3.66	2460	2.28
2565	4.32	2590	2.43
		2660	2.74
2770	5.80	2790	3.17
2960	7.38		

^{a} For energies above 1400 cm^{-1}, the error in the quoted values is ca. ±5 cm^{-1}. ^{b} The error is ca. ±5%. ^{c} From ref 2.

by using the photomultiplier tube were reproduced using the faster multichannel plate.

trans-Stilbene-d_{12} was obtained from Merck (98 atom % deuterium) and used without further purification. The carrier gas used in all the experiments reported here was helium.

IV. Experimental Results

Shown in Figure 2 are the experimentally measured fluorescence decay rates as a function of excess vibrational energy for *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12}. One would note several points in comparing the perdeuterio rates to the perprotio ones. Firstly, the low-energy rates are similar for both species. Not only are the two rate vs. energy curves flat from $E_x = 0$ to ~1200 cm^{-1}, but the values for the rates in this energy region are very similar ($k_H = 3.7 \times 10^8$ s^{-1}, $k_D = 4.0 \times 10^8$ s^{-1}). Secondly, the results for the perdeuterio species show an energy threshold at ca. 1200 cm^{-1}, such as has been found to exist for the perprotio species. Finally, at higher energies the perdeuterio rates are significantly slower than the perprotio rates. If one assumes that the radiative rate in the perdeuterio species is simply the low-energy fluorescence decay rate and if one assumes that the increases in the rates at higher energy can be attributed solely to the activation of the photoisomerization nonradiative decay channel, then one can obtain the rates for the initial step of the photoisomerization process. These rates are given in Table I along with rates determined in the same fashion for the perprotio species. (Note that some of the rates for the perprotio species in Table I differ slightly from those quoted in ref 2. This is a reflection of the better time resolution available with the Hamamatsu multichannel plate.)

V. Discussion

A. Standard RRKM-Calculated Rates. We have shown in two previous publications[2,4] that standard RRKM calculations (see section II.A) of reaction rates for the initial step in the photoisomerization reaction of *trans*-stilbene overestimate these rates by a factor of ~6–8, depending upon the vibrational frequencies used in the calculations (accounting for this scaling factor, the fits to the observed rates were shown to be very good). Recently, however, it has been suggested[10] that a sizable fraction of this difference is due to the fact that we have made use of vibrational frequency grouping. Furthermore, differences of opinion as to the appropriate energy values to use for the E_0 of the reaction and the reaction coordinate vibrational mode (ν_{max})

have surfaced. At the outset of this discussion it is useful to address these issues so as to avoid the perpetuation of any confusion they may generate.

Firstly, we maintain that any reasonable grouping of vibrational frequencies does not substantially change the magnitudes of calculated rates from their "true" RRKM values (i.e., the values calculated by using no grouping). Indeed, this is suggested by Figure 3 of ref 4, wherein the rates calculated for *trans*-stilbene photoisomerization using the division of vibrational modes into both 7 and 22 groups are plotted. (The figure shows the results for the two groupings to be quite close except for the periodic fluctuations in the rates for the coarser grouping.) As a definitive test, we have performed RRKM calculations using grouping (27 groups) and using the same E_0 (1180 cm^{-1}) and ν_{rxn} (88 cm^{-1}) used in ref 10, section 3. We find that although the calculation of ref 10 used no grouping of frequencies, our results are *the same* as the results reported there. Clearly, the claim that grouping has a substantial effect is incorrect in this case.

Since frequency grouping has little or no effect on calculated rates, the question then remains as to the source of discrepancy between the rates calculated by Troe (ref 10, section 3) and those calculated earlier.[2,4] It is a difference in the choice of values for the reaction coordinate frequency. In our work we have used values of $\nu_{rxn} \simeq 400$ cm^{-1}. Troe uses $\nu_{rxn} = 88$ cm^{-1}. In general, the smaller ν_{rxn}, the smaller k_{RRKM} is (this may be seen from eq 2.1—ρ increases as ν_{rxn} decreases, whereas the numerator does not change), hence the slower rates of ref 10. (It is pertinent to note that even when the 88-cm^{-1} value for ν_{rxn} is used, the calculated rates are consistently higher than the jet rates by a factor of 2–3.) Our choice of 400 cm^{-1} for ν_{rxn} was made on the basis of the results of Warshel's calculations for the normal modes of *trans*-stilbene. The justification for the 88-cm^{-1} value is not clear. From ref 10 one gets the impression that the experiment of Greene and Farrow[19] establishes 88 cm^{-1} as the proper value for ν_{rxn}. In actual fact, Greene and Farrow *assume* this value based on Warshel's calculations for *cis*-stilbene. Since the value for the ethylene torsion of the trans species is the appropriate one to use for ν_{rxn} in the calculation of trans isomerization rates, we have continued to use the 400-cm^{-1} value in this paper. It is pertinent to add that very recently, from measurements of fluorescence decay rates for *trans*-stilbene in ethane as a function of pressure (0–170 atm), Hochstrasser and co-workers[20] have shown that the reaction coordinate frequency must be greater than 160 cm^{-1} in order for them to explain the turnover in rates at low pressures. This finding is consistent with our choice of 400 cm^{-1} and not with the 88-cm^{-1} value of ref 10.[21]

As a third point pertaining to our standard RRKM calculations, we consider the rationale for our choice of the barrier energy: E_0 = 1200 cm^{-1}. This choice was made on the basis of fluorescence decay rate vs. energy results for the jet-cooled, isolated *trans*-stilbene molecule.[2,3] The results reveal a virtually flat rate vs. energy curve for vibrational energies below 1170 cm^{-1} in the S_1 state. At 1170 cm^{-1} and the next available energy, 1250 cm^{-1}, one finds significant deviations toward faster rates. Notably, this trend of increasing rates with increasing energy continues on past these energies, as we have reported[2,3] previously. There does not appear to us to be any obvious reason to attribute the initial increase in rate at ~1200 cm^{-1} to any process other than that to which we attribute the entire high-energy behavior of the rate vs. energy curve, namely, the photoisomerization process. Our

time-resolved measurements have been shown to be consistent with quantum yield data,[6] and as we[2,4] and Jortner et al.[6,22] have noted, the *optimal* choice for E_0 in RRKM[2,4] and RRK[6] calculations will depend on the details of the model used. The important point here is that the *experimental* threshold at which the rates change is 1200 ± 100 cm^{-1}.

The upshot of the above is that (1) the standard RRKM calculations reported[2,4] previously by us were in fact accurate ones (in the sense that there were no frequency grouping artifacts) which used very plausible values for ν_{rxn}, E_0, and the vibrational frequencies of the molecule and (2) our earlier assertion of the inadequacy of standard RRKM theory regarding *trans*-stilbene photoisomerization (by virtue of a persistent overestimation of rates) still stands.

As an ending to this section, it is pertinent to consider the predictions of standard RRKM theory regarding the per-deuteration effect on the *trans*-stilbene reaction rates. The results of calculations for the two species appear in the bottom half of Figure 2. The decrease in rates upon deuteration is the result of significant decreases in the frequencies of the lowest energy vibrational modes of the molecule. Notably, although the absolute magnitudes of the calculated rates for both species are too high, the magnitude of the perdeuteration effect closely matches the observed effect (Figure 2, top). This suggests that a description of the reaction using a statistical theory indeed is plausible.

In the following section we consider possible reasons for the failure of standard RRKM theory to account for the reaction rates of *trans*-stilbene. We shall argue that a statistical theory does exist whereby calculated rates can be brought into line with observed ones, i.e., nonadiabatic RRKM theory. We shall also discuss other possibilities.

B. Possible Sources of Deviation from Standard RRKM Rates. 1. Modifications of the Transition State: Changes in Vibrational Frequencies. On possible source of discrepancy between standard RRKM values and observed rates relates to one particular assumption which we and others make in doing the rate calculations, namely, that vibrational frequencies (other than the one associated with the reaction coordinate) do not change in going from the *trans*-stilbene geometry to that of the transition state. For most of the lower frequency modes (the modes whose precise frequency values have the most effect on calculated rates) this is probably a safe assumption. However, it is possible that there is an average increase in the frequencies of such modes in the activated state, which increase would lead to a decrease in the RRKM rates. For example, two vibrational modes likely to undergo such a frequency change are the ones corresponding to torsions about the C–phenyl single bonds; steric crowding in the complex might be expected to increase the force constants in the modes.

It is, in fact, possible to calculate RRKM rates which mimic the observed rates by assuming some changes in the frequencies of low-frequency modes. Such an assumption is one of the bases for the "optimized" RRKM calculations of ref 10 and 23, which pertain to the *trans*-stilbene and methyl-*trans*-stilbene and *trans*-1,4-diphenyl-1,3-butadiene (DPB) reactions, respectively. However, either the magnitudes of the changes in frequency required to achieve agreement for *trans*-stilbene are very large (in the case of a change in just one frequency) or they are significant changes (20%) spread out over many (15) modes.[10] There is not any compelling physical reason to assume that such changes occur, aside from the fact that they allow better RRKM fits to measured rates. Moreover, there are a number of problems with the optimized RRKM calculations. Firstly, as stated in ref 10 and 23, such calculations fail to provide the correct high-pressure, thermal rate constants for the *trans*-stilbene and DPB reactions. In the case of *trans*-stilbene, the calculated thermal rate constant is considerably less than measured values for the reaction in solution. Secondly, the optimized RRKM fits to jet data can be

(19) B. I. Greene and R. C. Farrow, *J. Chem. Phys.*, **78**, 3336 (1983).

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(21) The theoretical paper by Robinson et al. (G. W. Robinson, W. A. Jalenak, and D. Statman, *Chem. Phys. Lett.*, **110**, 135 (1984)) indicates that, for a sinusoidal double-well potential of barrier height 1225 cm^{-1} and reduced moment of inertia appropriate to *trans*-stilbene photoisomerization, the value for ν_{rxn} should be on the order of 10 wavenumbers. Nevertheless, this value depends intimately on the details of the shape of the potential, which are not well-known. We use the 400-cm^{-1} value based on the conclusions of ref 20 and calculations of ref 9. Further, we would note that the jet excitation spectra of ref 1 give no evidence for an S_1 vibrational mode of frequency on the order of 10 cm^{-1}.

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made only by assuming vibrational frequency increases in the transition state *accompanied* by increases in the energy barrier to reaction. For the *trans*-stilbene reaction the barrier value necessary to obtain an optimized RRKM fit of the experimental data is $E_0 = 1300 \pm 50$ cm^{-1}. As we have stated in the previous section, the break in the measured rate vs. energy curve occurs at ~ 1200 cm^{-1}. These values, although not drastically different, are enough so to warrant notice. Moreover, there are other indications that E_0 is close to the 1200-cm^{-1} value: (1) Solution-phase results[24] give an activation energy for the nonradiative rate of *trans*-stilbene of between 3.5 and 4.0 kcal/mol (1225–1400 cm^{-1}). These values can be related to the E_0 for the isolated molecule (see eq 4 of ref 4) and give a range $1100 < E_0 < 1230$ cm^{-1}. (2) Troe has taken his optimized RRKM rates, related them to rates in solution (k_∞ of ref 10), and determined an activation energy from these k_∞ values. His predicted value for the activation energy in solution is 1250 cm^{-1}, which is less than his "optimum" value for E_0. However, if anything, the activation energy should be found to be greater than E_0.[4] Significantly, overestimation of E_0 also characterizes the optimized RRKM fit[23] to the measured rates of the DPB reaction. Thirdly, the fractional increases in transition-state frequencies necessary to achieve agreement with measured rates for *trans*-stilbene are different than those increases found to be necessary to achieve agreement with the 4-methyl-*trans*-stilbene measured rates.[10] One would expect, given the similarity of the two molecules in the isomerization dynamics, that the optimal increases would be found to be the same. Finally, we would mention that the sensitivity of calculated rates to changes in the frequencies of vibrational modes is widely recognized. Courtney and Fleming, for example, have noted this in conjunction with calculated photoisomerization rates for *trans*-stilbene (modeling the twisted configuration of the molecule as two benzyl radicals) in media where the molecule is subject to intermolecular interactions.[24] Essentially, this sensitivity means that if one allows vibrational frequencies to change in performing an RRKM calculation, one has a large number of different ways in which to fit the observed data (there are, in the *trans*-stilbene case, a large number of vibrational modes). The fits are therefore not unique, and the parameters derived from the fits have unclear meaning. This lack of uniqueness is evident in ref 10, wherein it is shown that the observed *trans*-stilbene rates can be fit by letting many (the F parameter of ref 10) *or* just one (the G parameter) frequency change. While this does not, by any means, argue against one determining whether modifications of the transition state are consistent with observed data, it does argue for the careful consideration of other possible modifications of standard RRKM behavior.

2. Incomplete IVR. A second possible source of discrepancy between measured and calculated rates involves the breakdown of a fundamental assumption of RRKM theory that vibrational energy is rapidly and statistically partitioned among all energetically accessible vibrational states of the molecule subsequent to excitation. Several groups[25,26] have indicated that if vibrational energy redistribution does not access all energetically accessible states, then, in principle, reaction rates will tend to increase relative to RRKM rates by reducing ρ of eq 2.1. However, it has also been argued by these groups that nonstatistical IVR can lead to decreases in rates if some of the phase space of the transition state is "wasted" ($N^\dagger$ decreases). While we cannot completely rule out the possibility that incomplete IVR might be the source of the calculated vs. observed rate discrepancy for *trans*-stilbene, we can make three points.

Firstly, we have directly observed in time vibrational energy flow in *trans*-stilbene-h_{12}, using fluorescence and MPI techniques.[27,28] In particular, we have found that, for energies as low

as ~ 1250 cm^{-1} in the molecule, IVR is dissipative in nature and occurs on a time scale of 20–50 ps. (Presumably this time scale shortens further with increasing energy.) Thus, the RRKM criterion of fast vibrational energy flow is fulfilled for energies at which photoisomerization occurs. What is not clear is whether the energy flow accesses all available states. It is our opinion that there is no compelling reason why this should not be the case. We say this because an effective restriction on vibrational coupling,[29] that related to symmetry selection rules, would be expected to be essentially inoperable in the relatively asymmetrical[16] *trans*-stilbene molecule.

Secondly, nonexponential kinetics are expected[26] for those cases where incomplete IVR leads to lower rates. Our fluorescence decay results are well fit by single exponentials.

A third and final point is that the observations show a monotonic increase in rate with energy above the barrier of ~ 1200 cm^{-1}. Hence, there is no apparent dependence of the rates on the character of the vibrational motion initially excited. Such a dependence might be expected if less than complete IVR were influencing the reaction rates. (It should be noted that while IVR and quantum beats in *trans*-stilbene have been shown to be mode selective,[27] the isomerization rates, which are much smaller than the IVR rates, are not.)

3. Repeated Crossing (Reversibility) and Complex Reaction Coordinates. In ref 2 and 4 we have discussed another possible reason for the discrepancy between standard RRKM results and experiment—namely, that repeated barrier crossings may be taking place in the reaction (the reaction may be reversible). It is known that when such repeated crossings occur, the standard RRKM rates will be found to be larger than the apparent experimental rates. For the case of *trans*-stilbene we have calculated (using a steady-state approximation in the kinetic analysis) the magnitudes of the reverse rate constants necessary to bring calculated and observed rates into agreement.[4] However, subsequently we have pointed out that such reverse rate constants should, besides reducing apparent rates, also introduce significant nonexponential behavior into measured fluorescence decays.[2] Since there was no evidence for such behavior in our results, we did not favor this mechanism.[2] (In a private communication, Marcus has pointed out to us, however, that if detailed averaging is carried out, it may be that the nonexponential temporal behavior arising from repeated crossings will wash out.)

Another complexity arises if the reaction coordinate is not the simple one-dimensional curve with barrier that we have assumed it to be. If, for instance, the reaction coordinate is multidimensional and involves some inactive pathways,[30] then the observed rates would be less than the standard RRKM rates. This point has been considered for another system for which the pertinent reaction involves a complex (multidimensional) reaction coordinate and for which observed rates are systematically smaller than standard RRKM rates.[30]

4. Nonadiabatic RRKM. A final significant possibility to be considered herein is that nonadiabatic effects influence the *trans*-stilbene photoisomerization reaction. The idea is that the adiabatic energy surfaces corresponding to the reaction are of the form shown in Figure 1. Upon excitation to the lower surface in the trans configuration, the motion along the reaction coordinate can proceed on the lower surface and lead to reaction. Or, in the region of the avoided crossing, there can be a jump to the upper surface (nonadiabatic transition) with subsequent return to the trans configuration, i.e., no reaction.

To assess the possibility of nonadiabatic effects, we have used the nonadiabatic RRKM rate equation (2.6) to calculate rates for *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12} for various values of

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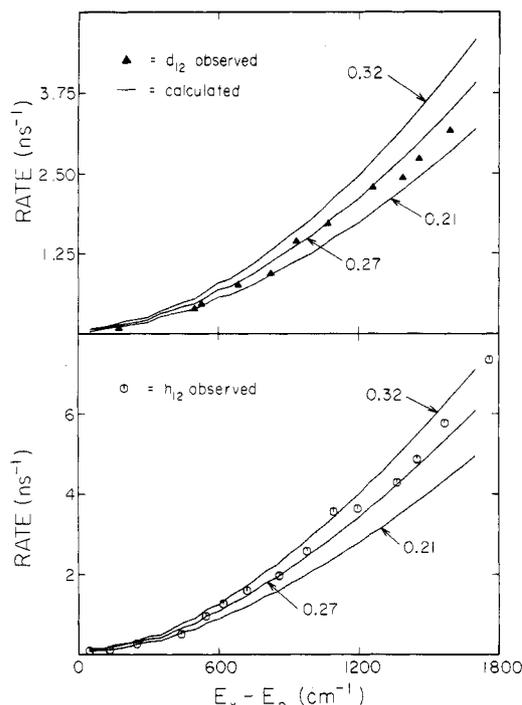(30) J. A. Syage, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.*, **81**, 2233 (1984).

Figure 3. (top) Observed nonradiative decay rates (data points) and reaction rates calculated (lines) by using the nonadiabatic RRKM expression (eq 2.6) vs. S_1 energy for *trans*-stilbene-d_{12}. The numbers labeling the calculated curves correspond to values for the parameter $\Delta^2/|F_1 - F_2|$ in units of cm^{-1} rad. (bottom) Same as for the upper portion of the figure except for *trans*-stilbene-h_{12}.

the nonadiabatic parameter γ' (eq 2.2b). As we have stated above, given nonadiabatic influences on the reaction, one expects that the same value for γ' will allow one to calculate accurate rates for both isotopic species. The results of the calculations are shown in Figure 3. Curves for a number of different γ''s are shown so as to indicate the sensitivity of the results to this parameter (note that we express all energy values in cm^{-1}). Clearly, the curves for

$$\gamma' \equiv \frac{\Delta^2}{|F_2 - F_1|} = 0.27\frac{(cm^{-1})^2}{cm^{-1}/rad}$$

match both the perprotio and perdeuterio results reasonably well. The fact that both sets of rates can be fit with one value of γ' is a significant test of the consistency of the nonadiabatic model. We reiterate that in these calculations we have used the experimental threshold energy ($1200\ cm^{-1}$), a reaction coordinate frequency of $400\ cm^{-1}$ in the reactant, and we have assumed no change of vibrational frequencies in going from the reactant to the transition state.

Assuming the validity of the nonadiabatic RRKM description, one can use the derived value of γ' to obtain parameters associated with the potential curves of the reaction and thereby further check the plausibility of the theory. In a previous paper,[2] using an estimate for $|F_2 - F_1|$ of $15\,000\ cm^{-1}/rad$,[11] we calculated $\Delta \simeq 1500\ cm^{-1}$. This calculation, however, was based on a very rough determination of γ' (an average value for v in eq 2.2b was used and thus P_{12} was taken to be independent of $E_t^{\dagger}$). Using the more rigorously determined value obtained herein, and again using $|F_2 - F_1| = 15\,000\ cm^{-1}/rad$, we now obtain $\Delta \simeq 64\ cm^{-1}$. There are several points that can be made about the derived value for Δ. Firstly, it implies a coupling matrix element of $32\ cm^{-1}$ between the electronic states involved at the avoided crossing. Caution, however, should be taken in using this result for Δ, since the value for $|F_2 - F_1|$ is only approximate and the shape of the surface is not accurately deteremined. Secondly, the ratio $\Delta/|F_2 - F_1| \equiv l_{LZ}$, according to Frauenfelder and Wolynes,[31] defines a charac-

teristic distance scale over which the chances of a nonadiabatic transition are appreciable. In our case $l_{LZ} \simeq 0.0042\ rad$. This value is useful in assessing the influence of solvent on the reaction rates, as we shall see below.

Finally, it should be emphasized that the conventional theoretical explanation[11] for the fact that the reaction barrier in S_1 is much smaller ($E_0 = 1200\ cm^{-1}$) than that in the ground electronic state is that the S_1 barrier arises as a result of electronic state avoided crossing. The nonadiabatic picture discussed in this section is therefore by no means an unphysical one.

C. Comparison with Other Experimental Results. 1. Substituted Stilbenes. Majors et al.[22] have measured fluorescence lifetimes of 4-methyl-*trans*-stilbene and 4-chloro-*trans*-stilbene. They found no significant differences in the behavior of the rate constants vs. excess energy for the two species when compared with *trans*-stilbene. In the particular case of 4-methyl-*trans*-stilbene this was interpreted as an indication of nonstatistical vibrational energy flow in the molecule subsequent to excitation. The observed behavior for the methyl derivative contrasts with the observations reported herein pertaining to the effect of perdeuteration. Moreover, as discussed earlier, IVR in the energy region in which the isomerization reaction occurs has been shown to be dissipative in nature.[27]

Regarding this apparent difference, we would make a number of points. Firstly, there may be, in fact, no discrepancy. That is, although IVR may be statistical in *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12}, vibrational energy flow into the vibrational modes of the methyl moiety from other modes of the 4-methyl derivative could be inefficient.

Secondly, we note that, in contrast to going from the perprotio to the perdeuterio species, the electronic state energy surfaces of *trans*-stilbene can shift significantly upon methylation. Although this does not seem to affect the energy barrier to isomerization,[22] it could influence the degree to which nonadiabatic effects influence the nonradiative rates. An interpretation of *trans*-stilbene rates vs. 4-methyl-*trans*-stilbene rates, along with considering differences in vibrational densities of states between the species, must therefore also consider the possibly different influences on the rates of the potential energy surfaces involved.

Finally, it may be that the increases in the vibrational densities of states upon methylation of *trans*-stilbene are such that the changes in reaction rates would be expected to be very small. For instance, we have found that the RRKM rates for perdeuterio *trans*-stilbene are significantly less than those for the perprotio species, primarily because the lowest frequency modes shift[1] to lower frequency upon perdeuteration (the 95-cm^{-1} mode to $87\ cm^{-1}$ and the 83-cm^{-1} mode to $76\ cm^{-1}$). Based on the excitation spectra of Majors et al.,[22] it appears that there are actually increases in the frequencies of these modes upon methylation. This may offset the effect on the rates of the additional modes introduced by the methyl group.

2. Photoisomerization Rates in Solution and High-Pressure Gases. There exist a body of results[20,24,32-43] pertaining to

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trans-stilbene photoisomerization rates in media where the molecule is not isolated from intermolecular interactions. Examining these data in light of the proposed nonadiabatic influences on the reaction in the isolated molecule is useful in at least two regards. It allows further tests of the nonadiabatic model, and it may reveal some of the ways in which the presence of intermolecular interactions can influence the reaction rates.[44]

We start by assuming that in the presence of solvent local thermodynamic equilibrium is rapidly established in the reactant portion of the reactive surface of *trans*-stilbene subsequent to excitation by light. We further assume, for the moment, that solvent friction has a negligible effect on rate. Then, one can consider two limits to the reaction rate. Firstly, in the absence of nonadiabatic interactions, one obtains an upper limit to the rate in solution (transition-state theory)

$$k_{ad}(T) = \frac{k_B T Q^\dagger e^{-E_0/k_B T}}{hQ} \tag{5.1}$$

where k_B is Boltzmann's constant, T is the temperature, $Q^\dagger$ is the vibrational partition function of the transition state, Q is the vibrational partition function for the *trans*-stilbene "reactant", and E_0 is the energy barrier of the reaction. Equation 5.1 is just the thermally weighted average of the RRKM rate constants[4]

$$k_{AV}(T) = \frac{1}{Q} \int_0^\infty k(E)\, \rho(E) e^{-E/k_B T}\, dE \tag{5.2}$$

where, for $k_{AV} = k_{ad}$, $k(E)$ is given by (2.1). (Note that $k(E)$ is zero for $E < E_0$ and that, therefore, the lower limit on the integration in eq 5.2 could just as well have been set to E_0.) In the case where the vibrational frequencies do not change in going from reactant to the transition state

$$k_{ad}(T) = \frac{k_B T e^{-E_0/k_B T}}{h q_{\nu_{rxn}}} \tag{5.3}$$

where $q_{\nu_{rxn}}$ is the partition function of that vibrational mode in the reactant which corresponds to the reaction coordinate

$$q_{\nu_{rxn}} = \frac{1}{(1 - e^{-h\nu_{rxn}/k_B T})} \tag{5.4}$$

which simply becomes $k_B T/h\nu_{rxn}$ in the high-temperature limit.

A lower limit to the rate (in the absence of friction) is obtained if one assumes that the nonadiabatic influences are the same in solution as in the isolated molecule. In this case

$$k_{nad}(T) = \left[Q^\dagger \exp\left(\frac{-E_0}{k_B T}\right) \times \right.$$
$$\int_0^\infty \left\{ 1 - \exp\left(-\frac{\pi}{2\hbar} \frac{\Delta^2}{|F_1 - F_2|} \left(\frac{\mu}{2E}\right)^{0.5}\right)\right\} \times$$
$$\left. \exp\left(\frac{-E}{k_B T}\right) dE \right] \Bigg/ (hQ) \tag{5.5}$$

which is obtained via (5.2) with $k(E)$ given by eq 2.6. (A derivation of (5.5) is given in Appendix II.) Again assuming no difference in vibrational frequencies between the reactant and the transition state

$$k_{nad}(T) = \left[\exp\left(-\frac{E_0}{k_B T}\right) \int_0^\infty \left\{ 1 - \exp\left(-\frac{\pi}{2\hbar} \frac{\Delta^2}{|F_1 - F_2|} \times \right.\right.$$
$$\left.\left. \left(\frac{\mu}{2E}\right)^{0.5}\right)\right\} \exp\left(-\frac{E}{k_B T}\right) dE \right] \Bigg/ (hq_{rxn}) \tag{5.6}$$

It is instructive to evaluate (5.3) and (5.6) by using the same parameters assumed in the RRKM calculations reported above.

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For $T = 295$ and 350 K, $\nu_{rxn} = 400$ cm^{-1}, $E_0 = 1200$ cm^{-1}, and $\Delta^2/|F_1 - F_2| = 0.27$ cm^{-1} rad (section V.B), the rates for the perprotio species are

$$k_{ad}(295) = 1.54 \times 10^{10}\ s^{-1} \tag{5.7a}$$

$$k_{ad}(350) = 4.30 \times 10^{10}\ s^{-1} \tag{5.7b}$$

and

$$k_{nad}(295) = 2.54 \times 10^9\ s^{-1} \tag{5.8a}$$

$$k_{nad}(350) = 6.59 \times 10^9\ s^{-1} \tag{5.8b}$$

Interestingly enough, most of the experimental reaction rates[20,24,32-43] in hydrocarbon solvents at the appropriate temperatures fall between the calculated values for k_{ad} and k_{nad}. (Some measured rates at room temperature and very low viscosity[40] are slightly greater than (5.7a) but are still very close, within experimental error.) To rationalize this, it is useful to now consider the influence of solvent friction on reaction rates in solution. Frauenfelder and Wolynes[31] have indicated that, for reactions influenced by nonadiabatic factors, an increase in friction forces can increase reaction rates.[45] Such behavior occurs in going from a medium of very low to one of somewhat higher friction. It arises because solvent collisions tend to slow the velocity of the reactant along the reaction coordinate. This slowing inhibits jumps between adiabatic potential surfaces and, thus, increases the adiabatic reaction rate. Now k_{nad} represents a thermal rate for a reaction influenced by nonadiabatic factors at zero solvent friction. One therefore expects a regime of greater solvent friction in which the thermal rate is greater than k_{nad}.

For the case of *trans*-stilbene, experimental measurements of rates in very low viscosity media by Fleming and co-workers[24,40] indicate that if such a regime exists, it occurs at viscosities less than 0.06 cP. In fact, very recent measurements by Hochstrasser and co-workers[20] of the fluorescence lifetimes of *trans*-stilbene in gaseous and liquid ethane at 350 K as a function of viscosity (pressure) provide evidence that the regime *does* exist from 0 to 0.03 cP. Specifically, they find that as the viscosity of the ethane "solvent" changes from 0.01 to 0.04 cP, the isomerization rate increases from $\sim 0.9 \times 10^{10}$ s^{-1} (0.01 cP) to a maximum of 3.4 $\times 10^{10}$ s^{-1} (0.03 cP), at which point it begins to decrease upon further increase in viscosity ($k \simeq 2.7 \times 10^{10}$ s^{-1} at 0.04 cP). Thus, they have found a range over which increases in viscosity increase reaction rates. Furthermore, the absolute magnitudes of their measured rates fall entirely within the range defined by (5.7b) and (5.8b), and their lowest viscosity rate is very close to $k_{nad}(350)$ (eq 5.8b). These facts are entirely consistent with the above picture of a solvent's influence on a reaction inhibited by nonadiabatic effects. In short, measured rates in solution and high-pressure gases[20,24,32-43], especially those of ref 20, taken together with (5.7) and (5.8) provide a strong argument that nonadiabatic influences decrease the rate of *trans*-stilbene (and perdeuterio-*trans*-stilbene) photoisomerization in the isolated molecule, whereas they are turned off via intermolecular (solvent–solute) interactions. Note that in the isolated[2,4] and solvated[24] molecules the values for E_0 are essentially the same (see section V.B-1.)

As a further check on this mechanism, it is useful to compare the characteristic time (τ_{LZ}) that the molecule spends in the region of the avoided crossing with the characteristic times between collisions in various solvent media (τ_{coll}). Above, we have calculated an angular "length" (l_{LZ}) of 0.0042 rad at the avoided crossing, over which the reactant molecule is forced to "decide" which potential curve to continue on. τ_{LZ} can be obtained by dividing l_{LZ} by the average thermal velocity $\langle v \rangle$ along the reaction coordinate.[31] For the perprotio species at 295 K

(45) According to ref 31, the same trend is expected for *adiabatic* reactions, as well. However, recent papers (A. G. Zawadzki and J. T. Hynes, *Chem. Phys. Lett.*, **113**, 476 (1985); M. Borkovec and B. J. Berne, *J. Chem. Phys.*, **82**, 794 (1985)) show that, for molecules with even a modest number of vibrational degrees of freedom, the regime of solvent friction wherein such rate increases occur with increasing friction (before "Kramer's turnover") becomes vanishingly small.

$$\langle v \rangle = (k_B T/\mu)^{0.5} = 4.9 \times 10^{11} \text{ rad/s}$$

With this value

$$\tau_{LZ} \simeq 10 \text{ fs}$$

τ_{coll} can be obtained roughly by using a simple formula quoted elsewhere[44,46]

$$\tau_{coll} = \rho d^2/6\eta$$

where ρ is the density of the solvent, d is an effective diameter for the solvent molecules, and η is the solvent viscosity. For hydrocarbon solvents and viscosities ranging from 0.1 to 1.0 cP (the solvents and the range of viscosities used in the study reported in ref 39, for example), τ_{coll} varies from ~ 100 to 10 fs. Perhaps a more pertinent number is the value $\tau_{coll} \simeq 150$ fs, which corresponds to the experimentally determined rate turnover in liquid ethane at 350 K.[20] Clearly, τ_{LZ} and τ_{coll} are comparable, as should be the case if solvent friction is to have the effect of decreasing the nonadiabatic influence on the dynamics.

A quantity which appears several places in the literature[2,4,44] and pertains to the link between isolated molecule and solution rates is the thermal average of *experimentally measured* isolated molecule rates, $\langle k_{expt} \rangle$ (i.e., eq 5.2 with $k(E)$ given by rates measured for isolated molecules). This calculated rate should equal measured rates in solution *if* the only effect of solvent is to establish rapid thermal equilibrium between degrees of freedom in the molecule. Thus, one expects that $\langle k_{expt} \rangle$ should match the low-viscosity solution rate. Moreover, if the picture of nonadiabatic influences on the *trans*-stilbene reaction is correct, one expects that $\langle k_{expt} \rangle = k_{nad}$. We have calculated $\langle k_{expt} \rangle$ for *trans*-stilbene using the isolated molecule rates shown in Figure 17 of ref 2, using the vibrational frequencies given in Appendix I to calculate $\rho(E)$, and averaging the measured $k(E)$ up to $E = 6000 \text{ cm}^{-1}$. At 295 and 350 K we obtain values of 2.7×10^9 and $5.6 \times 10^9 \text{ s}^{-1}$. These compare well with eq 5.8a and 5.8b, which are thermal averages of nonadiabatic RRKM rates. Furthermore, these values of $\langle k_{expt} \rangle$ are an order of magnitude less than almost all the measured values of solution rates, as noted before.[2] Notably, however, the 350 K value for $\langle k_{expt} \rangle$ agrees well with the value measured[20] recently for the rate at very low viscosity.

In ending this section it is pertinent to calculate the solution rates to be expected in a situation where some of the vibrational frequencies differ in the activated complex and the trans reactant. In particular, we calculate k_{ad} in the case where two of the lowest frequency modes[1] of *trans*-stilbene (83 and 95 cm^{-1}) increase to 200 cm^{-1} each in the activated complex. Such changes in these modes are necessary to bring the RRKM rates for the isolated molecule into agreement with the jet rates. Using eq 5.3 with all the other parameters the same as for the calculation leading to (5.7) gives

$$k_{ad} = 4.89 \times 10^9 \text{ s}^{-1} \tag{5.9}$$

This value for k_{ad} is very close to the k_{nad} of (5.8). Clearly then, this frequency change mechanism predicts rates that are too slow in solution. One might reasonably speculate that any scheme that one might devise to bring the RRKM rates into agreement with jet results by shifting around vibrational frequencies would also tend to predict solution rate constants smaller than are actually observed (except in the higher viscosity solvents).

3. Comparisons with Jet-Cooled and Solvated Diphenylbutadiene Rates. As a final case for comparison with the experimental and theoretical results obtained for *trans*-stilbene, we consider now diphenylbutadiene (DPB). This molecule, which is similar to *trans*-stilbene in that it can undergo trans–cis photoisomerization, is also different in several respects, most notably in that the electronic state ordering of the molecule is $A_g(S_1)$, $B_u(S_2)$,[47–49] the reverse of the *trans*-stilbene ordering.
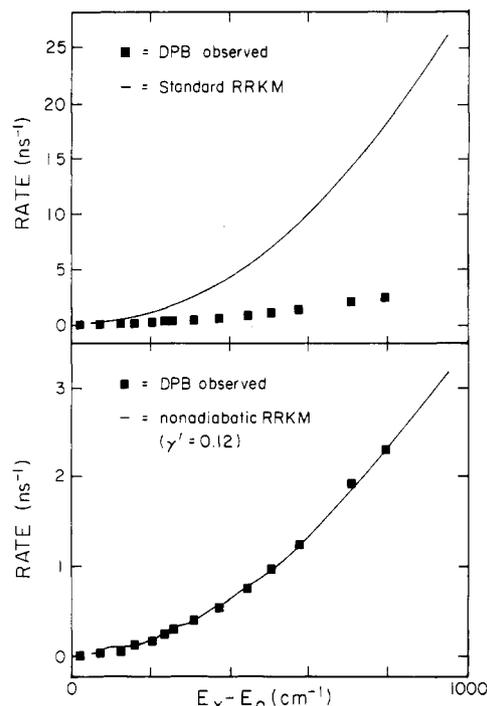

Figure 4. (top) Standard RRKM-calculated DPB rates (line) and measured rates (squares) for isolated DPB (measured rates from ref 47). (bottom) Nonadiabatic RRKM DPB rates (line) calculated with $\gamma' = 0.12 \text{ cm}^{-1}$ rad and measured rates (squares) for isolated DPB.

Fluorescence decay rates as a function of excess vibrational energy (E_x) in jet-cooled DPB were measured by Shepanski et al.[47] over the range 0–1800 cm^{-1}. As with *trans*-stilbene, an energy threshold in the rate vs. energy curve is present, beyond which the rates rapidly and monotonically increase. The behavior has been interpreted[47] in terms of the photoisomerization of the molecule, with the measured energy threshold of $1050 \pm 100 \text{ cm}^{-1}$ giving E_0 for the reaction.

More recently, Amirav and Jortner have measured relative fluorescence quantum yields (by dividing the fluorescence excitation spectrum intensities by absorption spectrum intensities) as a function of E_x (0–7000 cm^{-1}) in DPB.[23] Knowing our $E_x = 0$ fluorescence lifetime for the jet-cooled molecule,[47] they have obtained nonradiative rates as a function of energy that are consistent with our time-resolved data. Moreover, their results reveal no evidence of any abnormal rate behavior, attributable to the electronic state ordering in the molecule, in the energy region corresponding to $E_x \geq 1100 \text{ cm}^{-1}$.

In Figure 4 we show our experimentally determined nonradiative rates of jet-cooled DPB.[47] As with *trans*-stilbene we are interested in comparing these rates to those calculated by standard (eq 2.1) and nonadiabatic (eq 2.6) RRKM theory. These comparisons appear in Figure 4. In calculating the theoretical rates, we have (1) used the vibrational frequencies calculated for DPB by Pierce and Birge,[50] (2) assumed no change in frequencies from the reactant to the transition state, (3) taken $\nu_{rxn} = 407 \text{ cm}^{-1}$ and $E_0 = 1050 \text{ cm}^{-1}$, (4) accounted for the reaction path degeneracy of two,[51] and (5) in the nonadiabatic case, used a value for μ of 1810 amu Å^2, obtained by calculating the moment of inertia about a single ethylene bond in DPB using the geometry of ref 50. As is evident from Figure 4, and similar to our results for *trans*-stilbene (Figure 3), standard RRKM theory predicts rates which are significantly greater than the measured rates. This discrepancy between theory and experiment can be accounted for by a number of possibilities, as discussed in detail in section V.B for *trans*-stilbene. Our primary interest here is to see if, as is the case for

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(51) The RRKM expression applies to the reaction about a single ethylene double bond. Since there are two such bonds in the molecule, the calculated rate must be multiplied by a factor of 2.

trans-stilbene, RRKM theory modified to account for nonreactive, nonadiabatic transitions (eq 2.6) can account for the observed rates. Clearly, the results in Figure 4 show that the nonadiabatic RRKM rates *do* reproduce the observed rates if the nonadiabatic parameter γ' (see eq 2.2b) is taken to be equal to 0.12. Since the barrier to photoisomerization in DPB is expected to arise from an avoided crossing of potential surfaces such as occurs in *trans*-stilbene, the possible presence of nonadiabatic effects is certainly plausible physically. (We note that although the optimal value of γ' for DPB is quite different from the optimal value obtained for *trans*-stilbene, there is no reason to expect them to be the same, since the molecules' potential energy surfaces and the ordering of their A_g and B_u states are different.)

It is also of interest here to compare solution-phase rates obtained for DPB with the limiting rates represented by eq 5.3 and 5.6 and corresponding to a reaction inhibited by nonadiabatic effects. Using $E_0 = 1050$ cm^{-1}, $\nu_{rxn} = 407$ cm^{-1}, $\gamma' = 0.12$, and $T = 297$ K, one finds

$$k_{ad}(297) = 3.33 \times 10^{10} \text{ s}^{-1} \qquad (5.10)$$

and

$$k_{nad}(297) = 3.39 \times 10^{9} \text{ s}^{-1} \qquad (5.11)$$

If one compares these values with the data presented in refs 44 and 52, it is evident that while the adiabatic rate constant is significantly greater than measured rate constants in all solvents studied, $k_{nad}(297)$ is less than or comparable to the measured constants in *low*-viscosity solvents. This is similar to the *trans*-stilbene situation and is consistent with solvent (friction) effects on nonadiabatic influences in the reaction. Of course, in this regard it must be noted that there is strong evidence that solvent, in the DPB case, does more than just serve as a thermal bath and a source of friction. For instance, it seems that solvent-induced potential energy shifts increase the energy barrier to reaction in solution ($E_a = 1650$ cm^{-1}) relative to the barrier in the isolated molecule[47,52] (in contrast to the apparently constant barrier for *trans*-stilbene) and may affect the ordering of electronic states. This situation complicates the meaningful comparison of isolated molecule and solution-phase rates. In short, nonadiabatic RRKM theory can account for the rates of isolated DPB just as it can in the *trans*-stilbene case, but comparison of thermally averaged isolated DPB rates (eq 5.10 and 5.11) with solution–phase values is not straightforward, since solvent interactions may affect the rates.[53]

As a final point, we would note that Troe et al.[23] have fit measured DPB rates using the optimized RRKM theory applied earlier to the *trans*-stilbene reaction.[10] We have discussed problems associated with this procedure in section V.B-1. It is pertinent to reiterate two of these problems here, in conjunction with DPB. Firstly, the increases in transition-state frequencies which must be assumed to achieve agreement with measured rates are not unique. One can let just one, or many frequencies, vary and get good agreement. Secondly, the optimized RRKM fits give E_0 values (1100 cm^{-1}) which are somewhat larger than the measured threshold value (1050 cm^{-1})[47] for the isolated molecule. Also, as with the case of *trans*-stilbene, the solution-phase activation energy derived from the optimized fits is less than the optimized E_0 value for the isolated molecule.[23] As pointed out in section V.B-1, one expects the solution activation energy to be greater than E_0.

VI. Summary and Conclusions

In continuation of our study of the photoisomerization of *trans*-stilbene we have presented new experimental results pertaining to the reaction rates of *trans*-stilbene-d_{12}. We have discussed the rates for the isolated and solvated h_{12} and d_{12} species in terms of RRKM theory, and we have compared our results to

TABLE II: *trans*-Stilbene-h_{12} Normal Mode Frequencies (in cm^{-1}) Used in the RRKM Calculations[c]

83[a]	88[b]	95[a]	105	198[a]	229	233	280[a]
329	400	443	455	512	526	591[a]	596
622[a]	657	673	716	743	818	820	823
849[a]	883	892	938	944	944	957	959
972	973[a]	973	995[a]	1000	1041	1070	1123
1132	1150	1157	1170	1186	1249[a]	1263	1264
1294	1301	1332[a]	1412	1430[a]	1455	1465[a]	1533
1548	1553	1555	1638	2932	2935	2938	2949
2953	2959	2973	2975	2980	2992	3000	3010

[a] S_1 values from ref 1. [b] S_1 value from ref 9. [c] All values, unless indicated otherwise, are S_0 values from ref 8, reduced by 3%. See text for details.

TABLE III: *trans*-Stilbene-d_{12} Normal Mode Frequencies (in cm^{-1}) Used in the RRKM Calculations[d]

76[a]	81[b]	87[a]	97	188[a]	201	207[a]	264[a]
325	396	416	444	453	505	525	531
531	566[a]	580[a]	581	626	641	642	692
695	725	739	741[a]	750	765	765	771
778[a]	801	812	818	823	830[a]	834	860[a]
867[a]	929	934[c]	970	990[a]	1005	1068	1125[a]
1158	1246	1253	1286	1307[a]	1325	1345	1488
1504[a]	1520	1522[a]	1579[a]	2156	2165	2171	2187
2190	2200	2202	2209	2210	2217	2217	2227

[a] S_1 values from ref 1. [b] *trans*-Stilbene-h_{12} value from ref 9 (88 cm^{-1}) reduced by average deuteration shift of low-frequency modes. [c] S_0 values from ref 1 reduced by 3%. [d] All values, unless indicated otherwise, are S_0 values from ref 8, reduced by 3%. See text for details.

results obtained for other molecules thought to undergo trans–cis photoisomerization. Our major conclusions are as follows:

1. The isotope effect on *trans*-stilbene rates is pronounced. Upon perdeuteration the rates decrease by a factor of about 2, even though the reaction barrier height for the perprotio and perdeuterio molecules is the same ($E_0 = 1200 \pm 100$ cm^{-1}). This relative change in rate vs. excess energy curves is predicted by *standard* RRKM theory, although the absolute magnitudes of the rates are *not*.

2. As reported before,[2,4] standard RRKM theory overestimates the reaction rates (whether a reaction coordinate frequency of 400 or 88 cm^{-1} is used). A number of reasons for this overestimation are possible—nonstatistical IVR, repeated barrier crossings, a complex reaction coordinate or a very small reaction coordinate frequency,[21] a "tighter" transition state, nonadiabatic effects—all of which we have discussed. A particularly attractive mechanism is the nonadiabatic one, since it can account for the absolute values of the *trans*-stilbene-h_{12} and -d_{12} jet-cooled molecule rates and for the rates in solution and high-pressure gases. Moreover, the mechanism arises as a result of the same situation which is thought to produce the isomerization barrier in *trans*-stilbene, the avoided crossing of two potential energy surfaces.

3. By appropriate thermal averaging, one can obtain the solution-phase limits of standard and nonadiabatic RRKM rates. For a reaction inhibited by nonadiabatic effects in the isolated molecule, the limit of the standard RRKM rate represents a theoretical upper bound and the nonadiabatic RRKM limit represents a theoretical lower bound (in the low-viscosity regime) to the rate of the reaction in solution. Calculating these bounds by using parameters obtained from our theoretical fits to isolated molecule rates, we find that solution-phase rates do indeed fall within the theoretical range. (Significantly, the thermal average of measured isolated molecule rates matches the nonadiabatic RRKM solution limit.) This is taken to support the presence of nonadiabatic influences on the photoisomerization reaction and the role of solvent in suppressing these influences.

4. The rate behavior exhibited by jet-cooled *trans*-stilbene also occurs for other molecules capable of undergoing trans–cis photoisomerization. We have discussed our stilbene results in light of the behavior of these other molecules. Of especial interest to us has been the case of diphenylbutadiene. As with *trans*-stilbene,

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(53) B. Otto, J. Schroeder, and J. Troe, *J. Chem. Phys.*, **81**, 202 (1984); J. Schroeder and J. Troe, *Chem. Phys. Lett.*, **24**, 453 (1985); G. Maneke, J. Schroeder, J. Troe, and F. Voss, *Ber. Bunsenges. Phys. Chem.*, preprint.

we have found that although standard RRKM theory overestimates the actual rates, nonadiabatic RRKM theory can fit the data. Comparisons with solution-phase DPB rates must be made with care, however, since there is evidence that solvent affects the DPB reaction barrier height and the ordering of electronic states in the molecule.

Appendix I

Presented in Tables II and III are the vibrational frequencies used for *trans*-stilbene-h_{12} and *trans*-stilbene-d_{12}, respectively, in the rate calculations reported herein. A discussion of our choice of these values may be found in section II.A of this paper. It should be emphasized that different choices for the frequencies can yield significantly different values for the calculated densities of states. We have tried to take our values, to the greatest extent possible, from experimental studies (see text). These values yield somewhat different numbers for $\rho(E)$ than when the frequencies are taken from the normal mode calculations of ref 9 (as done in ref 40 for example).

Appendix II

In this Appendix we derive eq 5.5 using (5.2) and (2.6).

Since $k(E)$ in (5.2) is zero for $E < E_0$, the equation is equivalent to

$$k_{\text{nad}} = \frac{1}{Q} \int_{E_0}^{\infty} k(E) \, \rho(E) e^{-E/k_B T} \, dE \qquad (A2.1)$$

Substituting (2.6) for $k(E)$ gives

$$k_{\text{nad}} = \frac{1}{Qh} \int_{E_0}^{\infty} e^{-E/k_B T} \int_0^{E-E_0} \rho^\dagger(E_v{}^\dagger) \times$$
$$\left\{ 1 - \exp\left(\frac{-C}{(E - E_0 - E_v{}^\dagger)^{1/2}} \right) \right\} dE_v{}^\dagger \, dE \quad (A2.2)$$

where $C = (\pi/2\hbar)(\mu/2)^{1/2}\gamma'$. Inverting the order of integration, we obtain

$$k_{\text{nad}} = \frac{1}{Qh} \int_0^{\infty} \rho^\dagger(E_v{}^\dagger) \int_{E_v{}^\dagger + E_0}^{\infty} e^{-E/k_B T} \left\{ 1 - \right.$$
$$\left. \exp\left(\frac{-C}{(E - E_0 - E_v{}^\dagger)^{1/2}} \right) \right\} dE \, dE_v{}^\dagger \quad (A2.3)$$

Substituting $x = E - E_0 - E_v{}^\dagger$ in the integral over E results in

$$k_{\text{nad}} = \frac{1}{Qh} \int_0^{\infty} \rho^\dagger(E_v{}^\dagger) \int_0^{\infty} \exp\left(\frac{-(x + E_0 + E_v{}^\dagger)}{k_B T} \right) \times$$
$$\{1 - e^{-C/x^{1/2}}\} \, dx \, dE_v{}^\dagger \quad (A2.4a)$$

$$k_{\text{nad}} = \frac{e^{-E_0/k_B T}}{Qh} \int_0^{\infty} \rho^\dagger(E_v{}^\dagger) e^{-E_v{}^\dagger/k_B T} \, dE_v{}^\dagger \times$$
$$\int_0^{\infty} e^{-x/k_B T} \{1 - e^{-C/x^{1/2}}\} \, dx \quad (A2.4b)$$

Or

$$k_{\text{nad}} = \frac{e^{-E_0/k_B T} Q^\dagger}{Qh} \int_0^{\infty} e^{-x/k_B T} \{1 - e^{-C/x^{1/2}}\} \, dx \quad (A2.5)$$

which is precisely the form of eq 5.5.

Similarly, the well-known correspondence between the solution limit of RRKM theory and transition-state theory, eq 5.1, can be derived from (5.2) by using (2.1) for $k(E)$. In this case (5.2) becomes

$$k_{\text{ad}}(T) = \frac{1}{hQ} \int_{E_0}^{\infty} \frac{\rho(E)}{\rho(E)} N^\dagger(E - E_0) e^{-E/k_B T} \, dE \quad (A2.6)$$

which can be evaluated by parts to give

$$k_{\text{ad}}(T) =$$
$$\frac{k_B T}{hQ} \left[-N^\dagger(E - E_0) e^{-E/k_B T}\big|_{E_0}^{\infty} + \int_{E_0}^{\infty} \rho^\dagger(E - E_0) e^{-E/k_B T} \, dE \right]$$
$$(A2.7)$$

(since $dN^\dagger(E - E_0) = \rho^\dagger(E - E_0) \, dE$). The first term is zero, while the second integral can be expressed as

$$\int_{E_0}^{\infty} \rho^\dagger(E - E_0) e^{-E/k_B T} \, dE = e^{-E_0/k_B T} \int_0^{\infty} \rho^\dagger(x) e^{-x/k_B T} \, dx =$$
$$e^{-E_0/k_B T} Q^\dagger \quad (A2.8)$$

Thus

$$k_{\text{ad}}(T) = \frac{k_B T Q^\dagger e^{-E_0/k_B T}}{hQ}$$

which is eq 5.1.