PICOSECOND PROCESSES IN THE ISOMERISM OF STILBENES

Robin M. Hochstrasser

Department of Chemistry, Laboratory for research on the Structure of
Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Abstract - Following a review of the problem of stilbene isomerism an
account is given of recent picosecond timescale experiments on this system.
Transient absorption methods are used to expose vibrational relaxation de-
tails for molecules in solution and streak camera measurements of fluo-
rescence decay are presented to demonstrate the irreversibility of the S_1
(trans) decay. A simple statistical mechanical model is presented to
describe the effect of viscosity on the twisting dynamics of trans-stilbene.
A summary of recent experiments involving stilbene in the gas phase is
presented. The isolated molecules twist very rapidly ($15 ps at 265 nm ex-
citation) and display characteristics typical of systems with a potential
barrier. Finally the solution and gas phase processes are contrasted.

INTRODUCTORY REVIEW

It is well known that substituted ethylenes can undergo cis-trans isomerism following optical
excitation. A large literature already exists on this topic and the particular case of
stilbenes (1,2-diphenylethylenes) was recently reviewed by Saltiel and coworkers (1). Phenyl
substituted ethylenes received considerable attention from photochemists because their opti-
cal spectra are in the near ultraviolet, readily accessible to traditional light sources. The
groundwork for understanding the photoisomerism process in solutions was laid on the basis of
conventional (pre-laser) experiments (1,2) but the intrinsic molecular steps involved are now
known from vapor phase studies to be subnanosecond (3,4). The basic model for the isomerism
is that a twisted, less conjugated form of stilbene is formed following optical excitation
(5). This twisted form may then undergo relaxation processes that result in both cis and
trans structures (6). The solvent slows down the isomerization and at sufficiently low
temperature or high viscosity the rate is found to be even slower than the natural radiative
processes (7). The fluorescent properties of the system therefore can be used to monitor the
isomerization. Saltiel and coworkers (8,9) have shown that the principal ultraviolet photo-
chemistry of stilbene arises from the singlet excited surface. The triplet state can be in-
volved when sensitizers are present (9,10), and the ground state pathway requires moderately
high temperatures (1,2). There is also evidence that isomerization is not the exclusive
photoprocess since small yields of rearranged species have been reported (11).

The electronic states of stilbenes were first characterized by their low temperature spectros-
copy in mixed crystals (12). These measurements by Dyck and McClure refer to essentially
planar molecules - so constrained by the host crystal lattice. Under such circumstances the
optical absorption starting at 325 nm exposes a single electronic transition with the bulk of
the intensity appearing in two modes at 1600 cm^{-1} and 212 cm^{-1}. The lower frequency mode
corresponds to an in-plane symmetric bend of the ethylenic portion of the molecule while the
other progression forming mode is a carbon-carbon stretch involving the conjugated backbone
of the molecule. No progressions of low frequency torsional modes are seen in the spectrum
indicating no substantial alteration in planarity of the ethylene system in the excited state.
On the contrary the electronic spectrum of ethylene (13) displays a long Franck-Condon pro-
gression of the out-of-plane bending mode. These experiments show that the relevant states of
ethylene and stilbene are quite different, and indeed this is confirmed by theoretical calcu-
lations as discussed below. Warshel (14) has calculated an equilibrium geometry for stilbene
subject to no anisotropic constraints and finds that the phenyl rings are significantly
rotated from the planar configuration in both the trans and cis isomers. This conclusion is
consistent with electron diffraction studies (15). Elementary considerations suggest that
the repulsion of one ortho and an ethylenic hydrogen would ensure that the molecule will be
nonplanar in the absence of fixed external constraints (cf. biphenyl). The molecular spec-
troscopy of the nonplanar ground states of the stilbene is not structurally informative:
Both the vapor (16) and the solution spectra are sufficiently diffuse that the details of the
vibrational structure are lost. Presumably this situation will be remedied as a result of
future spectroscopic studies in supersonic jets. The calculations of the optical spectrum

based on Warshel's structure (14) indicate that significant changes in the phenyl ring orientations might occur in the electronically excited state. Recent studies of the variation with exciting wavelength of fluorescence from trans-stilbene excited in the region of the 0-0 band (3,4) have indicated that the absorption spectrum of cold molecules should reveal valuable dynamical information. The existence of strong two photon absorption (17) (λ_{max} = 2 x 250 nm) has indicated the presence of a gerade state in stilbene that may be important for the photochemistry of isolated molecules.

Recent theoretical work has attempted to compute the potential surfaces for ground and excited states corresponding to twisting about the ethylenic double bond and internal rotations of the phenyl groups (18-21). A significant advance was made by Orlandi and Siebrand who suggested that the singlet isomerism might be mediated by an avoided crossing of the delocalized $\pi\pi^*$ (first singlet) surfaces with a 'gerade' type state involving mainly two-electron excitation (18). This suggestion is analogous to current views on the isomerism of polyenes (22,23). The avoided crossings of the $\pi\pi^*$ and other types of states having lower energy in the twisted configuration have also been invoked to explain the photoproperties (24). These theoretical calculations suggest that the photoisomerization is an adiabatic process that may involve a small barrier in passing from the trans to the twisted conformation. Although the theories lead to qualitative agreement with earlier experiments, there is as yet little theoretical information on the effects of coordinates other than twisting about the double bond, nor do the calculations lead to strong predictions regarding the depth of the potential minimum of the twisted conformation.

Picosecond laser experiments on the stilbene system have resulted in the confirmation of some of the earlier ideas by allowing direct measurements of subnanosecond fluorescence and singlet state absorption spectra of solutions at room temperature. The fluorescence lifetime was measured as a function of temperature and solvent using streak camera techniques (25-27). Transient absorption of trans-stilbene was discovered at around 550 nm after pumping with the Nd: glass fourth harmonic (28). The decay of this absorption occurred with a lifetime of 90 ps leading to products that were transparent in the region 400-700 nm (28). These measurements probably signal the primary step in the process of isomerism. The cis isomer disappears too quickly to have yet been exposed by short pulse experiments. Estimates based on the absence of transient absorption signals place its lifetime at less than 1 ps in hexane at 300 K (28). At lower temperature in rigid media the cis – singlet lifetime is much longer and both fluorescence and transient absorption have been observed (29). In a recent experiment the trans form was observed to appear in a time less than 20 ps after pumping the cis (30). Further experiments along these lines are needed to elucidate the isomerization dynamics.

TRANSIENT SPECTROSCOPIC TECHNIQUES

Both transient fluorescence and absorption spectra of stilbene have been carried out in this laboratory. For the fluorescence studies we use a GEAR – Pico – V streak camera in conjunction with an optical multichannel analyzer (OMA-II, PAR). A single ca. 7 ps pulse at 1060 nm from a Nd:glass laser frequency quadrupled to 265 nm with KDP can be used to excite the sample of stilbene in hexane. The resulting fluorescence is readily focused onto a portion of the streak camera photocathode. The sweep speed and timing of the spectra are measured by focusing a train of pulses at 530 nm onto another part of the photocathode. This pulse sequence can be obtained by inserting two plane-parallel and partially transmitting plates (Fabry-Perot interferometer) into the 530 nm beam. The streak camera can be triggered by the laser pulse at 1060 nm. The result of a typical single firing of the laser is shown in Figure 1. Already these data are sufficiently accurate to provide a good estimate of the fluorescence decay. The dynamic range is of the order of 10^3. Used in this fashion (Figure 1) the signals contain some background that can be quite accurately subtracted out resulting in a much improved signal-to-noise (31).

The transient absorption spectra are recorded in the manner described by Greene, Hochstrasser and Weisman (32). The spectra are obtained in double beam fashion with the continuum pulse being generated by focusing a 1060 nm pulse into a liquid. One continuum pulse is passed through the excited region and the other through an unexcited region of the sample. Both transmitted pulses are then focused onto the slit of a spectrograph, and an optical multichannel analyzer is used to record and process their images at the focal plane of the spectograph. The time between pumping of the sample and taking the spectra can be changed by means of an optical delay line in the continuum path. The spectra obtained in this way are quite accurate and are reproducible when proper precautions are taken. With the pump beam blocked the measured optical density is in the range 0 ± 0.005, which gives an indication of the expected errors in the wavelength range around 500 nm where the continuum is most intense.

These two techniques are valuable adjuncts to the conventional methods of studying isomerization kinetics. The streak camera provides high signal to noise information with sufficiently large dynamic range that decay functions (i.e. non-exponentiality) can be properly evaluated. By means of appropriately oriented polarizers the effects of anisotropy from the molecular rotation can either be studied or eliminated. The transient absorption method is accurate enough that subtle changes in spectral shape can be followed and accurately documented.
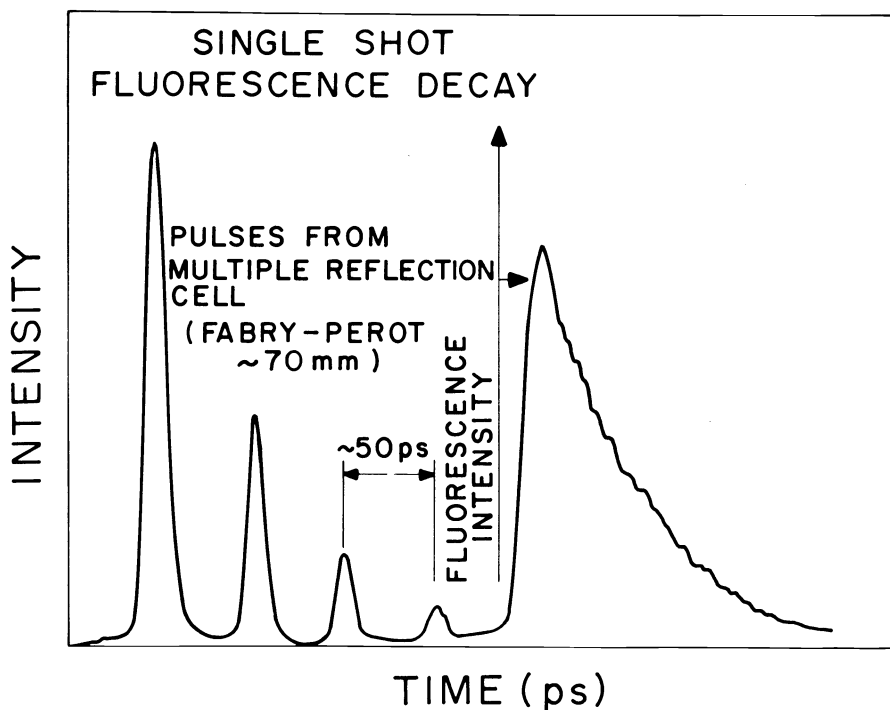
Fig. 1. Streak camera record for a single 265 nm laser shot. Left, Fabry-Perot record; Right, fluorescence from trans-stilbene.

SOLUTION REACTION DYNAMICS

The conventional kinetic studies say very little about the details of processes occurring on the picosecond timescale. From the picosecond transient absorption measurements on trans-stilbene we discovered that the spectrum of the optically pumped singlet state changed markedly over the 50 ps. or so following excitation (28). The spectrum was distinctly wider at the earlier times whereas the accompanying spectral shift was no more than a few nm. A possible interpretation of these results was that the molecules were being observed to cool vibrationally by means of changes in their optical spectra. This appeared reasonable because the excitation at 265 nm is known to introduce - in addition to the thermal energy - about 6450 cm^{-1} of vibrational energy excess onto the S_1 surface. Figure 2 shows a schematic diagram of the relevant states in these experiments. In more recent work we were able to show that excitation at 308 nm yields a transient spectrum that does not show a comparable spectral narrowing (33). The vibrational energy excess in this case is just over 1000 cm^{-1} in addition to the thermal energy content. The main results of these experiments are reproduced in Figure 3. Other possible interpretations of these effects are discussed in the original articles (28,33) but it is argued there that the most plausible explanation involves the occurrence of hot stilbene molecules.

During the period that the vibrational cooling is occurring the population of S_1 states is decreasing. The data in Figure 3 at different times are normalized to the absorption peaks. We have studied both the transient absorption (28) and emission (31) strengths as a function of time. The fluorescence decays are reproduced in Figure 4. It was noted that the fluorescence decay profile (31) shows only a slight deviation from exponential close to t = o. Neither did the absorption spectral decay show a significant rapid component at early time although the kinetic data from absorption are not so reliable as those from emission. These results indicate that the hot molecules that exist in the sample at the earliest times do not undergo isomerism significantly more efficiently than those that are thermalized. The vibrational relaxation is therefore faster than the vibrational energy redistribution leading to isomerism for most of the levels reached in the cascade from the optically prepared state.

At this stage it is apparent that the traditional model for the isomerism is still appropriate. There is no significant thermal reactivation of excited trans molecules occurring on the timescale of five lifetimes. It is also important to remark on the hazards caused by impurities in stilbene samples. The effects of the common interfering impurities are certainly
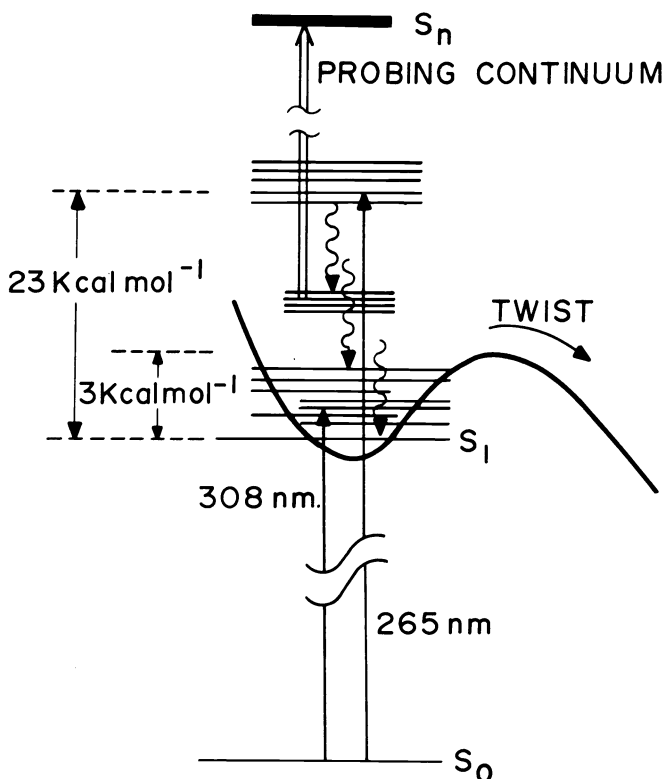
Fig. 2. Schematic diagram of various states and dynamics of trans-stilbene
in solution.

excitation wavelength sensitive. For example in our first picosecond study of stilbene (32)
using 353 nm excitation we were forced to utilize very concentrated solutions in order to
achieve sufficient excitation in a region where the absorption coefficient is very small. The
transient absorption spectrum in that case was quite different from that obtained using
265 nm excitation on the same sample (32). The study by Teschke et al. (34) on trans-stilbene
in which they found a two component decay, used 300 nm excitation. Their results were also
affected by impurities since they found only one component and complete decay of the absorp-
tion signal at 600 nm when the experiment was repeated with material from this laboratory (35).
One way to check the sample purity is to measure the relative fluorescence quantum yield as a
function of excitation wavelength in a fluorimeter. The impurity(s) that competes effectively
for light in the longest wavelength excitation regions has a nanosecond lifetime (32) and
fluoresces brightly. The fluorescence spectrum is also dependent on excitation wavelength in
these samples, whereas the quantum yield of fluorescence trans-stilbene is actually invariant
to the wavelength of excitation (36,37).

ISOMERIZATION DYNAMICS

Figure 5 shows a sketch of the singlet surface on which the various configurational changes
are occurring. Excitation at the trans configuration results first in relaxation at that
configuration. The isomerization then presumably occurs by the transmission of appropriately
activated molecules across the barrier towards the twisted configuration, with the rate being
controlled a Boltzman factor and by the hydrodynamic drag modified by the inertia introduced
through the molecular potential. An important issue concerns the recurrence of excited trans
molecules. If twisted molecules were thermally reformed into excited trans states that could
radiate, then the fluorescence decay should have a nanosecond component. This is the essence
of the Birch and Birks model (38).

Non-exponential decays of trans fluorescence have been reported (25,39) Heisel et al. (27)
suggested that the deviation from exponential was caused by an impurity, but Taylor et al.
(25,39) have gone on to insist that the decay is nonexponential. They claim that their high
repetition rate streak camera has such unique dynamic range that their slow (ca. 1.5 ns)
fluorescence component would not be seen with the conventional streak cameras used by Heisel
et al. We have used our streak camera to investigate the fluorescence of trans-stilbene out
to ca. 5 lifetimes. In this experiment the dynamic range of the system is a few thousand
(not the 'typical' value of 30 quoted in refs. 25 and 31). The results are given in Figure 4
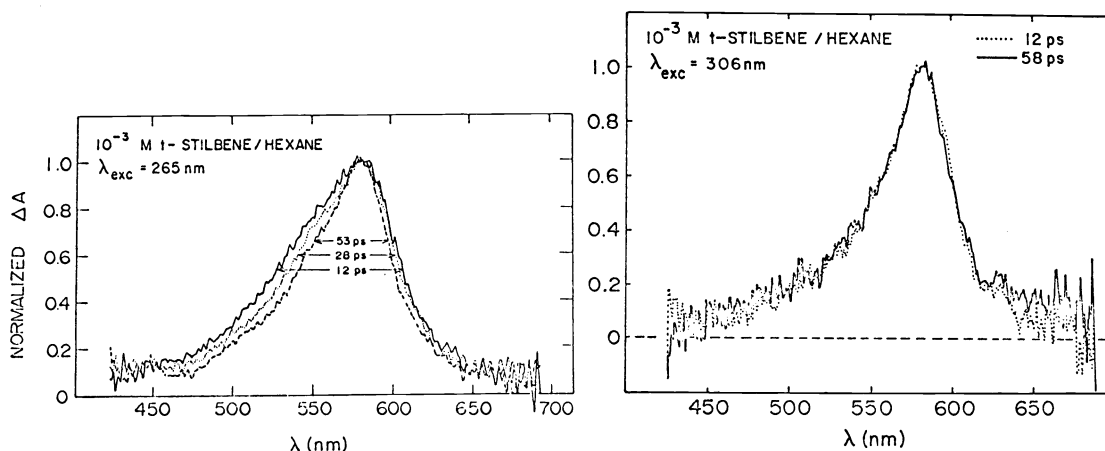
Fig. 3. Transient absorption spectra of stilbene (a) for 265 nm excitation
(after ref. 28) (b) for 308 nm excitation (after ref. 33).

on a semilogplot of the fluorescence decay. These data (OMA output) fit an exponential decay
having the time constant of 68 ps, whereas, the sum of the two exponentials reported by
Taylor et al. (25,39) does not. It is apparent that the conclusions from the previous work
are incorrect, and that there is no significant recurrence of trans molecules on the S_1
surface.

A STATISTICAL DYNAMICAL MODEL

The picosecond results indicate most clearly that the vibrational relaxation of certain
optically achieved modes is very rapid and that complete thermalization occurs before 50 ps
even for the case that the initial vibrational energy excess is large. It certainly appears
that the isomerism is brought about by thermal activation of appropriate modes in a system
where the dynamical interchange of vibrational energy is extremely rapid compared with the
rate at which trans molecules can twist. The results from the studies of isolated molecules
(see below) suggest that indeed there is an intrinsic barrier to twisting away from the trans
configuration. All of these factors suggest that this twisting be described by a moderately
simple statistical mechanical model. One appropriate model is that due to Kramers (40) and
Chandrasekhar (41) which was recently enlarged upon and used by McCaskill and Gilbert (42) to
evaluate the single bond rotational dynamics of 1,1'-binaphthyl in solution. The Kramers
equation relates the time constant (τ) for passing over a hill in the molecular potential to

$$1/\tau = (1/\tau_v) \ (\nu/4\pi \ \nu') \ [(1 + \{\pi\nu'\tau_v\}^2)^{\frac{1}{2}} - 1] \ e^{-Q/kT} \tag{1}$$

the barrier height (Q), the absolute temperature (T), the correlation time (τ_v) for the an-
gular velocity of twisting, and to characteristic frequencies ν' and ν of the piecewise para-
bolic potentials that compose the hill and the valley from which the system evolves. The
velocity correlation frequency $1/\tau_v$ is the ratio of the angular drag coefficient to the mo-
ment of inertia about the axis of rotation. The drag coefficient for spherical objects having
hydrodynamic radius d and radius of gyration r is $4\pi\eta \ dr^2$, with η being the viscosity of the
solvent. When $\nu'\tau_v \ll 1$ equation (1) reduces to a Smoluchowski result for passage over the
barrier, in which τ_v is proportional to the viscosity.

Taylor et al. (25) have measured the decay time of the fluorescence of trans-stilbene as a
function of solvent composition in ethanol-glycerol mixtures. We have evaluated the
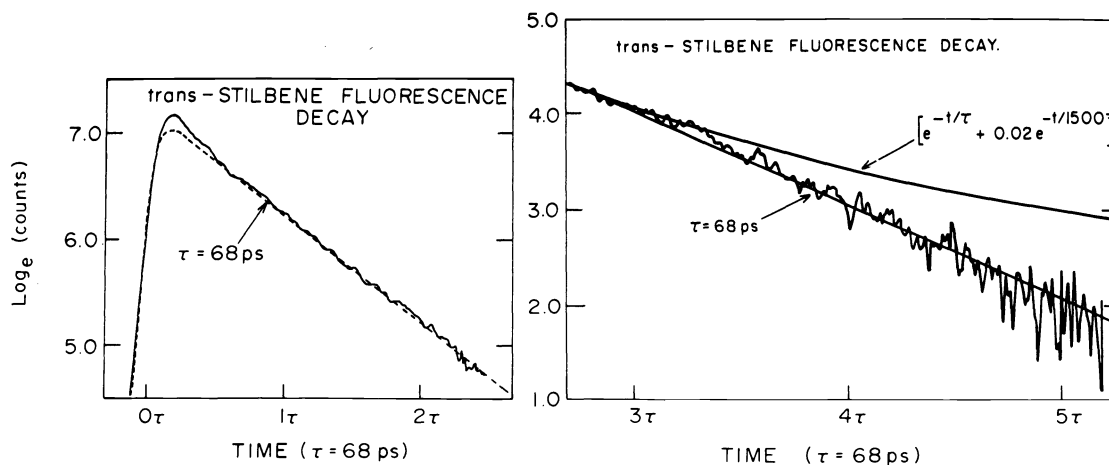
Fig. 4. Streak camera fluorescence decay of trans-stilbene (31)
(a) First three lifetimes (7 shots)   (b) Up to five lifetimes (14 shots).

variation of the faster of the two decays reported by these workers as a function of the
solvent viscosity, and find that $(d\tau/d\eta)$ is approximately constant at 87 ps/poise for vis-
cosities in the range 0.1 to 1.0poise. These results are consistent with equation (1) for
$\nu\nu'/c^2 = 6.6 \times 10^5$ cm^{-2} (we use $I = 9.2 \times 10^{-38}$ gm cm^2; $d = 1.7$ Å; $r = 2.42$ Å; $Q = 2.42$ Å;
$Q = 3.2$ kcal mole^{-1}). A value for ν/c of 450 cm^{-1} is reasonable for the frequency of twist-
int about the double bond according to Warshel (14), so that ν'/c is ca. 1400 cm^{-1}. These
frequencies are significantly less than $1/\tau_v$ for the chosen range of viscosities. The re-
sults are consistent with the isomerism being an essentially classical statistical pro-
cesses understood in terms of a simple separation of stilbene and solvent motions. In this
case, the isomerizing stilbene molecule is subject to large numbers of binary uncorrelated
collisions with the solvent at each angular increment along the twisting coordinate. At much
higher viscosities the values of $(d\tau/d\eta)$ are significantly smaller and the present simple
model appears to be inapplicable. The model stilbene molecule used in the calculations is
shown in Figure 6, and the theoretical parameters are described in Figure 7.

Because of the hydrogen bond network structure of glycerol-alcohol solvent mixtures these
systems are less than ideal for fitting to such statistical mechanical models. It would
certainly be worthwhile to obtain values of the fluorescence lifetime as a function of vis-
cosity in hydrocarbon mixtures. Since the streak camera studies have shown that the radia-
tive lifetimes are not strongly solvent dependent these data could be obtained from measure-
ments of the quantum yield

Since there are no strict symmetry restrictions that would allow the crossing of potential
surfaces of partially twisted stilbenes, we have adopted the view here that the rate of
twisting is controlled by thermal activation to a barrier. Although the barrier is a result
of an avoided crossing (such as in the Orlandi-Siebrand model) the rate of crossing is not
limited by the interaction between the surfaces such as would be the case for a non-adiabatic
tunneling process.

COMPARISON OF ISOLATED MOLECULES WITH THOSE IN SOLUTION

The vibrational energy redistribution leading to isomerization of trans-stilbene with 265 nm
excitation in a low pressure gas occurs in 15 ps (3,4). This indicates that an intrinsically
fast molecular process exists. The overall effect of the solvent seems to slow down the con-
formational change. However, the excess energy dependence of the twisting rate shows that
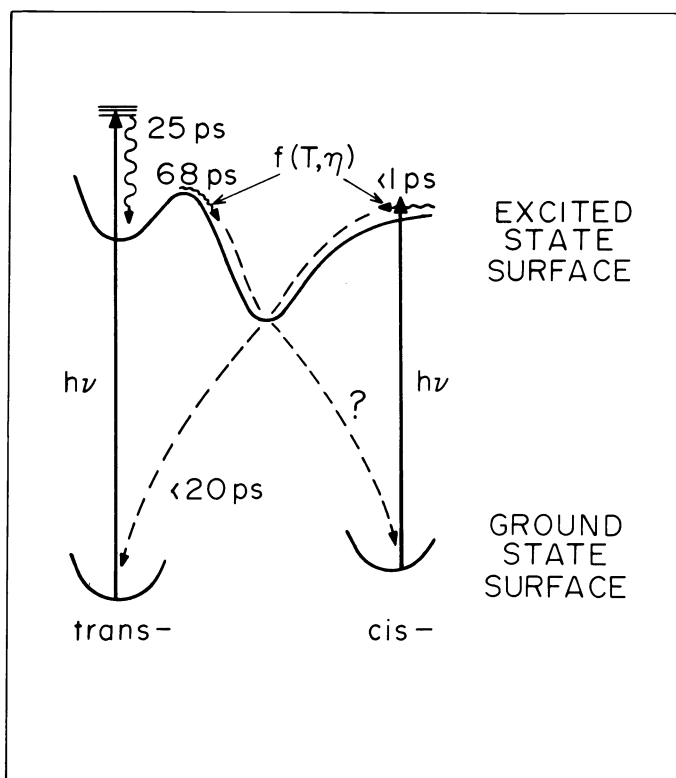
Fig. 5. Schematic diagram of the stilbene dynamics.

for small energy excesses over thermal, the lifetime is lengthened to ca. 1 ns in the iso-
lated molecule (4). Thus the isomerization is initiated in 1000 ps (indicated by the dis-
appearance of the optically prepared state) for the free molecule, whereas the thermally as-
sisted passage over the barrier in hexane solution occurs with a characteristic time of 68 ps
– a time that decreases with decreasing viscosity. Presumably the solution process is ac-
celerated because the thermal distribution is dynamically maintained by exchange of energy
with the medium. In the isolated molecule the isomerization is limited by the rate of vibra-
tional energy redistribution and only those molecules that have sufficient vibrational energy
may isomerize. It is apparent from this discussion that the vapor phase fluorescence decay
could be nonexponential for optical excitations causing low energy excess. Experiments to
observe this were not yet carried out though we assumed in a previous study of the quantum
yields of fluorescence (4) that the decay would be exponential.

An important result of the vapor phase study (3,4) was that the variation with excess energy
of the twisting rate – or rate of vibrational energy redistribution – on the S_1 surface was
indicative of there being a barrier to isomerism even in the isolated molecule. The twisting
rate varied from 15 ps at 265 nm to many ns. for excitation near to the 0-0 transition. It
is apparent that the hot stilbene molecules observed in the solution transient absorption
spectra up to ca. 30 ps must be substantially cooler than these initially formed molecules
since the isomerism in solution is wavelength insensitive.

It can be expected that high resolution spectroscopic studies of stilbene vapor in supersonic
beams and of stilbene in hydrocarbon solvents at low temperature will allow an increasingly
accurate picture of the excited state surface to be developed. A crucial test of the ideas
expressed here will arise when a reasonable potential surface, based on such spectroscopic ex-
periments, is incorporated into a statistical mechanical theory that includes the solvent
dynamics. Of course there are other steps in the isomerism to understand besides passing
over the barrier near the trans configuration. We have adopted the view that this process
is an adiabatic configurational change. However the passage from the twisted form into trans
and/or cis may be a non-adiabatic (curve crossing) process with the rate being controlled by
the interaction between two different surfaces. On the otherhand this process may also be
adiabatic and the molecular structure may not be bottlenecked at the twisted configuration.
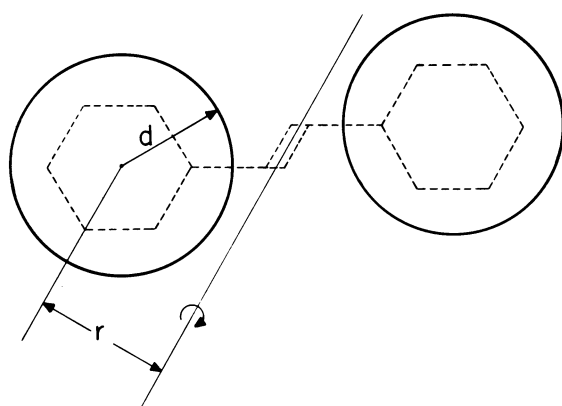Obviously more experiments are needed to explore these concepts.

$$\frac{1}{\tau} = \frac{1}{\eta} \, f \, (\nu, \nu^1) \, e^{-Q/kT}$$

TWISTING COORDINATE

Fig. 6. Model stilbene molecule   Fig. 7. Parameters used in
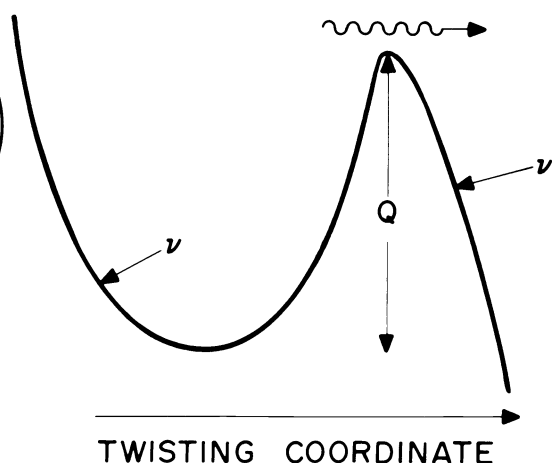for statistical calculation.   Equation (1).

SUMMARY

The main points stressed in this lecture were as follows:

    (a)   The conventional picture of stilbene isomerism is consistent with the experiments. No recurrences are observed on the S_1 surface.

    (b)   Vibrational relaxation is faster than isomerism in solution and the isomerism is restricted by the liquid structure.

    (c)   Molecules of stilbene excited at 265 nm take ca. 25-30 ps to cool in solution.

    (d)   Possibly there is a long (> 300 ps) cross relaxation time in the inhomogeneous distribution of stilbene that exists in solutions.

    (e)   Vibrational energy redistribution in the isolated molecule is strongly dependent on energy excess. The isomerism of isolated molecules shows that the configurational changes can be intrinsically fast.

    (f)   Statistical models should be applied to photophysical processes of this type. In the limit where the inertia of the solute towards conformational change greatly exceeds that of the solvent (such as will arise if there is an intrinsic potential barrier) then simple models are specially valuable.

The research presented in this lecture was carried out with the collaboration of R. B. Weisman, B. I. Greene, F. Doany, Y. Liang and D. Negus. Their efforts formed the basis for this talk.

REFERENCES

1. J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton and O. C. Zafiriou, Org. Photochem., 3, 1 (1973); J. Saltiel and J. L. Charlton in "Rearrangements in Ground and Excited States", Academic Press, New York p.25 (1980).

2. E. Fischer, M. Frankel and R. Holovsky, J. Chem. Phys., 23, 1365 (1955).
3. B. I. Greene, R. B. Weisman and R. M. Hochstrasser, J. Chem. Phys., 71, 544 (1979).
4. B. I. Greene, R. B. Weisman and R. M. Hochstrasser, Chem. Phys., 48, 289 (1980).
5. G. S. Hammond and J. Saltiel, J. Am. Chem. Soc., 85, 2516 (1963).
6. J. Saltiel, J. Am. Chem. Soc., 89, 1036 (1967).
7. G. Fischer, G. Seger, K. Muszkat and E. Fischer, J. Chem. Soc., Perkin II, 1569 (1975).
8. J. Saltiel, E. D. Megarity and K. Kneipp, J. Am. Chem. Soc., 88, 2336 (1966).
9. J. Saltiel, J. Am. Chem. Soc., 90, 6394 (1968).
10. G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, J. Am. Chem. Soc., 86, 3197 (1964).
11. R. Srinivasan and J. C. Powers, Jr., J. Chem. Phys., 39, 580 (1963).
12. R. H. Dyck and D. S. McClure, J. Chem. Phys., 36, 2326 (1962).
13. G. Herzberg, Electronic Spectra of Polyatomic Molecules (New York: Van Nostrand Reinhold Company) pp. 533-5 (1966).
14. A. Warshel, J. Chem. Phys., 62, 214 (1975).
15. M. Traetteberg, E. B. Frantsen, F. C. Nijhoff and A. Hoekstra, J. Mol. Struct., 26, 57 (1975).
16. O. P. Kharitonova, Opt. Spectry., 10, 394 (1960).
17. T. M. Stachelek, T. A. Pazoha, W. M. McClain and R. P. Drucker, J. Chem. Phys., 66, 4540 (1977).
18. G. Orlandi and W. Siebrand, Chem. Phys. Lett., 30, 352 (1975).
19. G. Orlandi, P. Palmieri and G. Poggi, J. Am. Chem. Soc., 101, 3492, (1979).
20. A. Wolf, H.-H. Schmidtke and J. V. Knop, Theoret. Chim. Acta, 48, 37 (1978).
21. P. Tavan and K. Schulten, Chem. Phys. Lett., 56, 200 (1978).
22. B. S. Hudson and B. E. Kohler, Chem. Phys. Lett., 14, 299 (1972).
23. K. Schulten, I. Ohmine and M. Karplus, J. Chem. Phys., 64, 4422 (1976).
24. M. C. Bruni, F. Momicchioli, I. Baraldi and J. Langlet, Chem. Phys. Lett., 36, 484 (1975).
25. J. R. Taylor, M. C. Adams and W. Sibbett, J. Photochem., 12, 127 (1980).
26. M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, Chem. Phys. Lett., 51, 183 (1977).
27. F. Heisel, J. A. Miehe and B. Sipp, Chem. Phys. Lett., 61, 115 (1979).
28. B. I. Greene, R. W. Weisman and R. M. Hochstrasser, Chem. Phys. Lett., 62, 427 (1979).
29. K. Yoshihara, A. Namiki, M. Sumitani and N. Nakashima, J. Chem. Phys., 71, 2892 (1979).
30. M. Sumitani, N. Nakashima and K. Yoshihara, Chem. Phys. Lett., 68, 255 (1979).
31. F. E. Doany, B. I. Greene, Y. Liang, D. K. Negus and R. M. Hochstrasser in "Picosecond Phenomena II"; editors: Hochstrasser, Kaiser and Shank. Springer-Verlag (1980).
32. B. I. Greene, R. M. Hochstrasser and R. B. Weisman, J. Chem. Phys. 70, 1247 (1979).
33. F. E. Doany, B. I. Greene and R. M. Hochstrasser, Chem. Phys. Lett., in press.
34. O. Teschke, E. P. Ippen and G. R. Holtom, Chem. Phys. Letts. 52, 233 (1977).
35. E. P. Ippen, B. I. Greene, private communication.
36. R. M. Hochstrasser, Can. J. Chem., 37, 1367 (1959).
37. G. Bartocci and U. Mazzucato, Chem. Phys. Lett., 47, 541 (1977).
38. D. J. S. Birch and J. B. Birks, Chem. Phys. Lett. 38, 590 (1979).
39. J. R. Taylor, M. C. Adams and W. Sibbett, Appl. Phys. Lett., 35, 590 (1979).
40. H. A. Kramers, Physica 7, 284 (1940).
41. S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
42. J. S. McCaskill and R. G. Gilbert, Chem. Phys., 44, 389 (1979).