Temperature Dependence of Photoisomerization.
VI. The Viscosity Effect[1]

Dina Gegiou, K. A. Muszkat, and Ernst Fischer

Contribution from the Department of Chemistry, The Weizmann Institute of Science, Rehovoth, Israel. *Received June 26, 1967*

Abstract: The quantum yields ϕ_t of the *trans* → *cis* photoisomerization of stilbene and many of its derivatives decrease with increasing viscosity of solvents such as glycerol and glycerol triacetate, in the range of very high viscosities (up to 10^{11} poise). Similar observations were made in other media and also with stilbene derivatives (4-bromo and 4-nitro) in which ϕ_t does not change with temperature in low-viscosity solvents. No similar effect was found regarding the quantum yield of the *cis* → *trans* photoisomerization, ϕ_c, and both ϕ_t and ϕ_c in substituted stilbenes exhibiting steric hindrance, such as 2,2′,4,4′,6,6′-hexamethylstilbene. The viscosity effect is ascribed to an increase in molecular volume somewhere along the path of the *trans* → *cis* photoconversion. Changes in the *shape* of the cavity occupied by the solute, which obviously accompany all isomerizations, therefore seem to play no role in the viscosity effect. The quantum yield of fluorescence of the *trans* isomers (measured in stilbene and in 4-bromostilbene) does not change with the viscosity. It is concluded that intersystem crossing precedes the viscosity-dependent step of the *trans* → *cis* photoisomerization. This step may be either the conversion of the triplet *trans* molecule into an intermediate (triplet?) common to both isomers, or the decay of the latter to the ground state of the *cis* (but not the *trans*) isomer. The observed viscosity dependence of ϕ_t is represented fairly well by an equation based on free-volume considerations.

Photochemical or photophysical processes of excited states are usually characterized in terms of energy, multiplicity changes, and lifetime. In the present paper we wish to introduce an additional classification of these processes according to their spatial requirements and to describe the application of this concept to the study of the mechanism of the direct photoisomerization of stilbenes. This concept is expected to serve as a useful adjuvant in the investigation of radiationless transitions. To this problem the direct spectroscopic methods often cannot be applied.

In the present study the spatial requirements of excited molecules are determined from the dependence of the quantum yields of certain photoisomerizations on the viscosity of the medium, as reported in two preliminary notes.[2] The viscosity is controlled by the nature of the solvent and by the temperature.

Theory

A dependence of the rate constant of a monomolecular rearrangement process on the viscosity of the medium (and on the free volume) may be expected only if the following conditions are met:

(1) the free space required for the motion of parts of the molecule represents a considerable fraction of the mean free space to be found in the solvent in the immediate vicinity of the reacting molecule, (2) a second process that does *not* require additional free space will compete with the rearrangement in the deactivation of the excited molecule, (3) an increase in volume should occur somewhere along the path leading from the excited singlet state of the starting molecule to the ground state of the product. The present work is concerned with the free-space requirements of processes of electronically excited molecules. Certain rearrangements of molecules in their ground state may of course also be expected to depend on viscosity in suitable cases.[2]

The photochemical isomerization of stilbenes is either temperature independent or shows an activation energy of 1–10 kcal/mole. Therefore, the dependence of the rates on the viscosity of the medium can be investigated by changing the temperature and applying, if necessary, a correction for the intrinsic change of the rates with the temperature.

Doolittle[3] has represented the viscosity η of several fluids as a function of the free volume (v_f, per molecule) by an equation of the form

$$\eta = A[\exp(v_0/v_f)] \qquad (1)$$

Here v_0 is the critical volume required for a translatory motion of a molecule and A is a constant. A similar relationship was found by Williams, Landel, and Ferry for several viscous liquids.[4] v_f is manifested by the thermal expansion of the liquid. It is to a good approximation a linear function of the temperature, and therefore the equation that Tammann and Hesse[5] found experimentally for the temperature dependence of the viscosity coefficient η of viscous liquids

$$\ln \eta = A' + B/(T - T_0) \qquad (2)$$

is equivalent to eq 1.

An expression analogous to eq 1 has been derived by Cohen and Turnbull[6] for the free-volume dependence of the diffusion coefficient. According to this approach, $\exp(-v_0/v_f)$ is the total probability factor for a molecular motion process that can take place only if the moving molecule has available a free volume larger than some critical value v_0.

---

[1] Based on a part of the Ph.D. thesis submitted by D. G. to the Weizmann Institute of Science, 1967.

[2] (a) E. Fischer, *Fortschr. Chem. Forsch.*, 7, 605 (1967); (b) K. A. Muszkat, D. Gegiou, and E. Fischer, *J. Am. Chem. Soc.*, **89**, 4814 (1967).

[3] A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

[4] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, 77, 3701 (1955).

[5] G. Tammann and W. Hesse, *Z. Anorg. Allgem. Chem.*, **156**, 245 (1926).

[6] M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).

We assume that the physical process by which parts of a reacting molecule rearrange in solution is similar to the relaxation of stresses in the solvent. This relaxation is responsible for the bulk and shear viscosities. In general, this similarity is expected to hold as long as the duration of the rearrangement of the solute and the duration of the stresses to which the solvent is subjected in the viscosity measurement are comparable. In several associated viscous liquids,[7,8] the high-frequency shear and bulk viscosities and the steady-flow viscosity are of the same order of magnitude and have a similar temperature dependence. In these cases it is justified to treat a rearrangement in the solute molecule in terms of some free-volume function like the steady-flow viscosity, although the time scales of the rearrangement and of the viscosity experiment are quite different. However, in other media, such as noncross-linked polymers (*e.g.*, polyisobutylene), the high-frequency bulk and shear viscosities are low while the steady-flow viscosity is infinite.[9] Such media are expected not to inhibit the rearrangement of the solute molecule as long as the temperature is above the glass transition point.

The critical free volume required for the rearrangement of the solute is composed of two parts: the van der Waals volume occupied by the molecule and some additional free volume provided by the solvent. This additional free volume is expected to be only a fraction of the critical free volume required for the motion of a solvent molecule (or a group of solvent molecules). This fraction will be denoted a and is expected to be considerably smaller than unity, at least in stilbenes. The reason is that the rearrangement in the solute involves only a limited relative motion of parts of the molecule. However, the motion of a solvent molecule requires a free volume at least equal to its own van der Waals volume. Therefore the free-volume-dependent total probability factor for a rearrangement of a solute molecule will be $\exp(-av_0/v_f)$. The rate constant, k, for a process dependent on free volume will be proportional to $\exp(-av_0/v_f)$ through the free-volume-independent factor k_0

$$k = k_0[\exp(-av_0/v_f)] \tag{3}$$

k_0 would be the limiting value of k at low viscosities. k may be expressed in terms of η (eq 4)

$$\ln \eta = \ln A + v_0/v_f \tag{1'}$$

$$\ln k = \ln k_0 - av_0/v_f \tag{3'}$$

$$\ln k = \ln k_0 + a \ln A - a \ln \eta \tag{4}$$

or

$$\ln k = B - a \ln \eta \tag{5}$$

where $B \equiv \ln k_0 + a \ln A$, and ln denotes the natural logarithm. B is not viscosity dependent but may vary with the temperature.

In a rearrangement reaction like the *trans* → *cis* photoisomerization (*cf.* the mechanism suggested below), the isomerization competes with some deactivation process of an excited molecule which is independent on the viscosity and which results in re-formation of the starting isomer. Let the rate constant for the isomerization process be k and that for the competing viscosity-independent process be k'. ϕ' will denote the over-all quantum yield (independent on viscosity) of the steps leading to the excited state from which either isomerization or reconversion to the starting isomer may take place. The quantum yield of the photoisomerization (Φ) will then be

$$\phi = \phi' \frac{k}{k + k'}$$

or

$$\ln [(\phi'/\phi) - 1] = \ln k' - \ln k \tag{6}$$

On substituting for ln k from eq 5, we obtain

$$\ln [(\phi'/\phi) - 1] = \ln k' - B - a \ln \eta = C - a \ln \eta \tag{7}$$

where $C \equiv \ln k' - B$. C is a constant independent of viscosity. a should be dependent both on the solute and on the solvent. For a series of similar solutes (like stilbenes substituted in the 4 position) in one solvent, a would be expected to have approximately the same value.

The free volume and therefore the viscosity also depend on the external pressure.[6] Consequently one may expect certain quantum yields to decrease with increasing pressure. This effect should be particularly pronounced in solvents whose viscosity increases sharply with pressure.[10]

Results

In the present study high viscosities of the various media were achieved by lowering the temperature down to the respective glass points. It was therefore necessary to ascertain first of all if, and to what extent, the quantum yields to be investigated depend on the temperature in similar solvents of *low* viscosity. Yields measured were those for the *trans* → *cis* and *cis* → *trans* photoconversion, ϕ_t and ϕ_c, and that of the fluorescence of the *trans* isomers, ϕ_F. ϕ_t and ϕ_c were measured with light at 313 mμ, while ϕ_F was measured with light at several excitation wavelengths. Two types of behavior of the quantum yields ϕ_t and ϕ_F in low-viscosity hydrocarbon solvents were recognized in previous investigations[11-13] and are exemplified by stilbene and by 4-bromostilbene, respectively.

In a solution of stilbene in a methylcyclohexane–isohexane mixture, ϕ_t drops continuously from 0.50 at +25° to practically zero at −180°, while ϕ_F increases from about 0.05 at room temperature to somewhat less than unity at −180°.[13] ϕ_t of 4-bromostilbene is constant down to −160°, while ϕ_F increases only threefold on cooling from +25 to −180°.[13] ϕ_c for both molecules is constant down to −160°.[13] This investigation of the dependence of the above three quantum yields on temperature in low-viscosity solvents has meanwhile been considerably extended to

---

[7] K. F. Herzfeld and T. A. Litowitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press Inc., New York, N. Y., 1959, Chapter 12.

[8] N. Hirai and E. Eyring, *J. Appl. Phys.*, **29**, 810 (1958).

[9] J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley and Sons, Inc., New York, N. Y., 1961.

[10] E. Kuss, *Angew. Chem. Intern. Ed., Engl.*, **4**, 944 (1965).

[11] R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

[12] S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

[13] S. Malkin and E. Fischer, *ibid.*, **68**, 1153 (1964).

Table I. Quantum Yields of Photoisomerization of Stilbenes, and of Fluorescence of Their *trans* Isomers, at Several Temperatures in Different Media[a]

Stilbene in MCH/IH[b,c]

t, °C	+25	−40	−65	−90	−105	−123	−140	−183
ϕ_t	0.50	0.46	0.31	0.18	0.12	0.07	0.04	0.006
ϕ_c	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.12
ϕ_F[d]	0.06	0.14	...	...	0.55	...	0.73	0.75
ϕ_F[e]	0.05	...	...	(0.35)[f]	0.54	...	...	0.75

Stilbene in Ethanol–Methanol (4:1)

t, °C	+25	−100	−180
ϕ_t	0.50	0.12	0.005
ϕ_c	0.35	0.35	0.20

Stilbene in Ethanol

ϕ_F	0.35 at −80°

Stilbene in Glycerol

t, °C	50	25	10	0	−25	−50	−70	−80
ϕ_t	0.55	0.52	...	0.25	0.10	0.040	0.016	0.010
ϕ_c	0.25	0.24	...	0.26	0.26	0.25	0.29	0.22
ϕ_F	...	0.15	0.16	0.27	0.37	0.42	0.45	0.46

Stilbene in Glycerol Triacetate

t, °C	+25	−25	−75
ϕ_t	0.42	0.22	0.04
ϕ_c	0.19	0.22	0.24

4-Chlorostilbene in MCH/IH[c]

t, °C	+25	−40	−80
ϕ_t	0.60	0.45	0.29
ϕ_c	0.45	0.45	0.50

4-Chlorostilbene in Glycerol

t, °C	+25	−25	−75
ϕ_t	0.33	0.09	~0
ϕ_c	0.53	0.52	0.35

4-Methoxystilbene in Glycerol

t, °C	+25	−25	−75
ϕ_t	0.36	0.08	~0
ϕ_c	0.42	0.38	...

4-Dimethylaminostilbene in Glycerol Triacetate

t, °C	+25	−25	−70
ϕ_t	0.44	0.1[g]	0.004[g]
ϕ_c	0.26	...	...

4-Bromostilbene in MCH/IH[b,c]

t, °C	+25	−40	−115	−135	−155	−183	−183
ϕ_t	0.35	0.35	0.35	0.35	0.35	0.003	0.35[h]
ϕ_c	0.16	0.16	...	0.16	0.19	0.05	0.16[h]
ϕ_F	0.065	0.08	0.11	0.12	0.13	0.17	...

4-Bromostilbene in Glycerol

t, °C	+50	+25	0	−25	−40	−50	−60	−70	−80
ϕ_t	0.51	0.52	0.45	0.20	...	0.045	...	0.02	0.009
ϕ_c	0.28	0.27	0.27	0.28	...	0.31	...	0.31	0.32
ϕ_F	...	0.05	0.075	0.10	0.11	...	0.11	...	0.11

4-Bromostilbene in Glycerol Triacetate

t, °C	+25	−25	−75
ϕ_t	0.51	0.19	0.024
ϕ_c	0.26	0.26	0.26

4-Nitrostilbene in Polyisobutylene[i]

t, °C	−50	−100
ϕ_t	0.14	0.002[g]
ϕ_c	0.20	...

4-Nitrostilbene in Glycerol

t, °C	+25	0	−30	−50	−70
ϕ_t	0.16[g]	0.15	0.06	0.03[g]	0.002
ϕ_c	...	0.20	(0.11)	...	...

2,2′,4,4′,6,6′-Hexamethylstilbene in Glycerol Triacetate[g]

t, °C	+25	−75
ϕ_t	0.5	0.5
ϕ_c	0.5	0.5

2,2′4,4′,6,6′-Hexamethylstilbene in Polyisobutylene[g]

t, °C	+25	−50	−100
ϕ_t	0.50	0.40	0.4

2,4,6-Trimethylstilbene in Glycerol[g]

t, °C	+25	−75
ϕ_t	0.5	0.1

α-Methylstilbene in Glycerol

t, °C	+25	−25	−75
ϕ_t	0.48	0.44	0.33
ϕ_c	0.1	0.1	0.12

Azobenzene in MCH/IH[12]

t, °C	+25	−75
ϕ_t	0.09	0.05
ϕ_c	0.4	0.4

Azobenzene in MCH/IH at 436 mμ[12]

ϕ_t	0.23	0.18
ϕ_c	0.4	0.6

Azobenzene in Glycerol

t, °C	+25	−75
ϕ_t	0.05	0.03
ϕ_c	0.5	...

Azobenzene in Glycerol at 436 mμ

ϕ_t	0.42	0.23
ϕ_c	0.53	...

[a] Light at 313 mμ used unless stated otherwise. 4-Nitrostilbene was isomerized with light at 365 mμ. [b] MCH/IH = methylcyclohexane–isohexane (2:1 by volume); MCH/IP = methylcyclohexane–isopentane (1:3 by volume). [c] These values are taken from ref 13. [d] These are the values reported previously[13] and normalized to $\phi_F = 0.75$ at −183°. [e] Excited at 305 mμ. [f] At −80°. [g] These results are based on estimates from measurements of the composition at photoequilibrium, and therefore their accuracy is lower. [h] The solvent in this measurement was MCH/IP. [i] Oppanol B 200, produced by the BASF Co., mol wt 4.7 × 10^6.

include many other substituted stilbenes.[14] The results of this study have important implications for the elucidation of the mechanism of the photoisomerization. Those which are relevant to the present matter will be briefly mentioned in the discussion to follow.

Several media of widely differing viscosity were used in the course of the investigations described in this part and in parts IV and V in this series.[2,13,14] They were selected so as to demonstrate the effect of only one factor at a time, to the exclusion of the others. These factors were the viscosity, the temperature, and the polarity. The following media were used: (1) a methylcyclohexane–isohexane (MCH/IH) mixture (2:1) (This mixture is fluid down to −170°. Its viscosity increases sharply at lower temperatures.[15] The drop in the values of ϕ_t observed previously[13] in this medium below −160° is now ascribed to the sharp increase in the viscosity under these conditions), (2) a methylcyclohexane–isopentane (MCH/IP) mixture (1:3) (This mixture is completely fluid down to liquid air temperature[15,16] and was used for the study of stilbenes under low-viscosity conditions at temperatures where MCH/

---

(14) Forthcoming publication, part V in the present series.

(15) H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

(16) F. J. Smith, J. K. Smith, and S. P. McGlynn, *Rev. Sci. Instr.*, **33**, 1367 (1962).

IH forms a rigid glass, *i.e.*, below −170°.), (3) ethanol, and an ethanol–methanol mixture (4:1 by volume)[15] (These exhibit low viscosity at −80° and were used to rule out the possibility that the effects observed in glycerol are due to the hydroxylic groups of this molecule. The stilbenes investigated in the present study had about the same temperature dependence of the various quantum yields in ethanol and ethanol–methanol as in MCH/IH.), (4) glycerol and glycerol triacetate (These two solvents were used as high-viscosity media, glycerol as a hydroxylic, and glycerol triacetate[17a] as a nonhydroxylic solvent. The dependence of the viscosity of these two solvents and of ethanol on temperature was studied by Tammann and Hesse.[5] At a temperature of about −80° the viscosity of the first two solvents is about 10^{11} poise.), (5) polyisobutylene (This polymer was used as a high-viscosity hydrocarbon medium.[17b] A high molecular weight grade (Oppanol 200) was used. The glass transition temperature of polyisobutylene is about −80°.[4]).

The values of ϕ_t, ϕ_c, and ϕ_F of stilbene, of 4-chlorostilbene, and of 4-bromostilbene reported previously[13] in MCH/IH, and those now measured in viscous solvents, are collected in Table I, together with ϕ_F values of stilbene measured in MCH/IP and in ethanol, and ϕ_t and ϕ_c values for 4-bromostilbene measured at −183° in MCH/IP. The values listed for 4-nitro-, 2,4,6-trimethyl-, and 2,2′,4,4′,6,6′-hexamethylstilbene are for high-viscosity media. In low-viscosity media both ϕ_c and ϕ_t in these compounds do not change with the temperature.[14]

Conclusions and Discussion

The results presented in Table I may be summarized as follows. (1) The *cis* → *trans* quantum yields (ϕ_c) depend only weakly on the viscosity of the medium, but not on the temperature (down to −160°). (2) The fluorescence quantum yields of the *trans* isomers (measured only in stilbene and in 4-bromostilbene) depend on the temperature and, to a much lesser extent, on the nature of the solvent, and on its viscosity. This conclusion has important mechanistic implications (see below). (3) The quantum yields of the *trans* → *cis* photoconversion can change with the temperature[13,14] and with the viscosity of the medium, depending on the substituents. Accordingly the stilbenes may be classified into three groups, as follows.

a. Stilbene and Stilbenes Substituted at the Rings with Substituents not Affecting the Singlet–Triplet Intersystem Crossing Efficiencies. In these compounds (*e.g.*, stilbene, and its 4-methoxy, 4-dimethylamino, and probably 4-chloro derivatives), the *trans*-to-*cis*-isomerization quantum yields depend both on temperature[14] and on viscosity. In nonviscous media, such as MCH/IH at temperatures well above the onset of high viscosity (*i.e.*, above −160°), ϕ_t falls off sharply in the temperature range +25 to −160°. In the highly viscous solvents glycerol and glycerol triacetate, the values of ϕ_t at −80° are as low as those observed in MCH/IH at −180°.

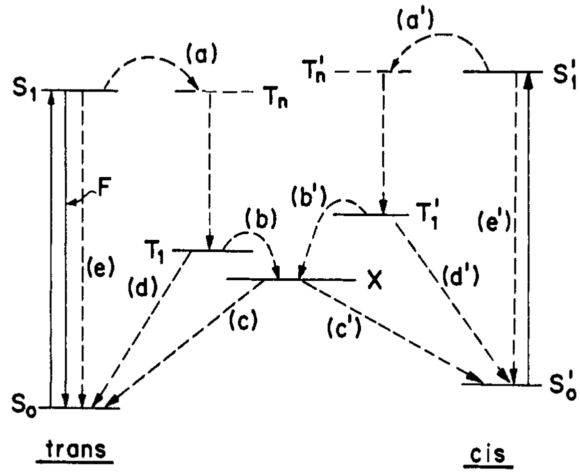
b. Stilbene Substituted at the 4 Ring Position with Groups That Strongly Increase the Singlet-to-Triplet Crossing Efficiencies.[18,19] The effects of the following substituents were examined: bromo,[13] nitro,[14] aceto,[14] and benzoyl.[14] Compounds in this group have ϕ_t values which in nonviscous media do not depend on temperature down to the lowest temperatures studied.[14] The drop in ϕ_t observed[13] with 4-bromostilbene in MCH/IH below −160° was now found to be a viscosity effect. No similar effect was found in a MCH/IP mixture, which stays fluid[15] down to at least −185°. The viscosity dependence observed is as in the first group.

c. Sterically Hindered Stilbenes.[20] In this group we have investigated 2,2′,4,4′,6,6′-hexamethyl-, 2,4,6-trimethyl-, and α-methylstilbene. In these compounds the ϕ_t values in nonviscous media are independent of temperature.[14] In hexamethylstilbene ϕ_t is completely independent of viscosity, while in trimethylstilbene a weak dependence is found.

The present results show that the only quantum yields affected by environmental factors are those of the *trans* → *cis* conversion in groups a and b.

Any mechanism of reversible photoisomerization obviously must include a common intermediate excited state X from which the molecule reverts to the ground state of either the *cis* or the *trans* isomer.[21] In view of the ideas developed above, the fact that only ϕ_t and not ϕ_c depends on the viscosity shows that the conversion *trans* → *cis* is accompanied by an increase in molecular volume, somewhere along the reaction path. If we assume that triplet states of both isomers are involved, as shown in Scheme I, this means that either step b, step c′, or both are viscosity controlled, while the other steps are not. This conclusion is supported by the fact that in solution the molar volume of *cis*-stilbene[22] is larger than that of *trans*-stilbene by about 2.5%, indicating that the van der Waals volume[23] of *trans*-stilbene is smaller than that of *cis*-stilbene. The same probably holds for the *para*-substituted stilbenes.

Scheme I



---

[17] (a) We are indebted to Professor E. Lippert for suggesting glycerol triacetate as a nonhydroxylic solvent of high viscosity. (b) We are indebted to Mr. T. Bercovici who introduced this medium into our laboratory.

[18] D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949); 20, 682 (1952).

[19] M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

[20] For a discussion of steric hindrance in stilbenes see, *e.g.*, H. H. Jaffé and M. Orchin in "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 15.

[21] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[22] K. von Auwers, *Ber.*, **68B**, 1346 (1935).

[23] In the present context this would be the volume that is never penetrated by solvent molecules (see below).

In sterically hindered derivatives such as 2,2,'4,4',6,6'-hexamethylstilbene, ϕ_t is no longer viscosity controlled. We suggest that in these compounds the volume occupied by both isomers is similar, since the solvent molecules are excluded from the vicinity of the molecule in both isomers to a similar extent. Therefore, isomerization in both directions does not require additional free volume to be supplied by the solvent.

The temperature dependence[2,10,14] of ϕ_t in group a is ascribed to a temperature dependence of step a, *i.e.*, the intersystem crossing.[2b,13]

The fluorescence quantum yields of *trans*-stilbene and of *trans*-4-bromostilbene in glycerol are only weakly dependent on the viscosity (Table I), whereas the ϕ_t values are markedly viscosity dependent. Thus fluorescence, which is emitted by the vibrationally relaxed first excited singlet, is under these conditions not dependent on the *trans*-to-*cis* photoisomerization step. Therefore this isomerization proceeds neither in the first excited singlet level nor in a level which is in equilibrium with it. We conclude that intersystem crossing (a) takes place before the actual isomerization, which proceeds from the common (triplet?) level X as indicated in the above scheme.

Additional evidence supporting this mechanism is presented elsewhere.[2b] These conclusions are essentially in agreement with those of other investigations,[13,21,24,25] but disagree with two recent papers,[26,27] in which a singlet mechanism is favored. The level X may be identical with the one obtained by energy transfer from "low-energy sensitizers."[21] Thus in principle it would be possible to identify the viscosity-dependent step (b or c' in the above scheme) by investigating the photosensitized isomerization of stilbenes at high viscosities, provided that the trivial diffusion effect can be eliminated.[27a]

The temperature dependence of ϕ_t in azobenzene and azonaphthalenes has been described before.[12] The present results in viscous solvents indicate only a very slight viscosity effect, both in the n–π^* and in the π–π^* absorption bands.

It is reasonable to assume a close similarity between the geometry of the two isomers of azobenzene and of stilbene. The absence of a viscosity effect in the former may therefore be taken as a further indication[28] that the isomerization of azobenzene does not proceed through rotation around the double bond, as assumed in stilbene and its derivatives, but rather *via* a linear intermediate with a sp^3 nitrogen hybridization, which rearranges by an inversion of the nitrogen trigonal pyramid. This conclusion is also supported by the absence of any substituent effects on the thermal *cis* → *trans* isomerization[28,14] and on the quantum yields of the photoisomerization in azobenzene.[14]

Quantitative Application of Eq 7. This equation was applied to the viscosity dependence of the *trans*-to-*cis* isomerization quantum yields of stilbene and of 4-bromostilbene, in glycerol and in glycerol triacetate. Since only η and ϕ are measurable directly, an estimate of ϕ' has to be made. In view of the development given in the previous section, ϕ' is identical with the intersystem crossing yield, to be denoted ϕ_{ISC}. For *stilbene* in MCH/IH at −180° the rate of step a is zero and therefore $\phi_{ISC} = 0$. The fluorescence yield ϕ_F is about 0.75, so that an internal conversion $S_1 \rightarrow S_0$ (step e), takes place with a yield of about 0.25, *i.e.*, one-third of ϕ_F. In the absence of additional data we assume that this ratio (1:3) is maintained at higher temperatures, and therefore $\phi_{ISC} = 1 - \phi_F - (\phi_F/3)$. The values for ϕ_{ISC} obtained by this procedure for stilbene are listed in Table II.

Table II. Intersystem Crossing Quantum Yields (ϕ_{ISC}) of Stilbene in Glycerol and Glycerol Triacetate at Different Temperatures

t, °C	25	0	−25	−50	−70	−80
ϕ_{ISC}	0.80	0.64	0.51	0.44	0.40	0.39

For *4-bromostilbene* ϕ_{ISC} was assumed to be independent of temperature, and the change of ϕ_F with temperature was ascribed to a competing temperature-dependent internal conversion process, whose quantum yield was taken as zero at −180°. We may take the sum of this yield and ϕ_F as constant and equal to ϕ_F at −180°, *i.e.*, 0.17. Hence $\phi_{ISC} = 1 - 0.17 = 0.83$.

Obviously the derivation of the ϕ_{ISC} values for these two molecules involves some arbitrary assumptions. However, the results of the application of eq 7 to the experimental data are only little affected by the use of somewhat different ϕ_{ISC} values and do not change much even if the radiationless $S_1 \rightarrow S_0$ transition is completely ignored.

The ϕ_t's were measured in both solvents over the temperature range from +50 down to −80°. The required viscosity values (Table III) were obtained from the equation of Litowitz,[29] $\ln \eta = A + B/T^3$, applied to the experimental points obtained by Tammann and Hesse.[5] The viscosity of both glycerol[29] and glycerol triacetate is accurately represented by this equation in the temperature range investigated by these authors,[5] down to −40°. Viscosities at temperatures below −40°, for which no experimental values are available, were extrapolated by this equation.

Table III. Experimental (above −25°) and Extrapolated (below −25°) Values of the Logarithm of the Viscosity Coefficient η (in poise) of Glycerol and of Glycerol Triacetate at Different Temperatures (T, °K)

Temperature		Log η	
t, °C	$10^9 \times T^{-3}$	Glycerol	Glycerol triacetate
50	30	0.09	−3.05
25	38	0.84	−2.05
0	49	1.90	−0.60
−25	66	2.45	1.50
−50	90	5.8	4.75
−70	120	8.6	8.7
−75	129	9.4	9.7
−80	140	10.4	11.2

---

(24) T. Förster, *Z. Elektrochem.*, **56**, 716 (1952).

(25) D. Schulte-Frohlinde, H. Blume, and H. Gusten, *J. Phys. Chem.*, **66**, 2486 (1962).

(26) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Am. Chem. Soc.*, **88**, 2336 (1966).

(27) J. Saltiel, *ibid.*, **89**, 1037 (1967).

(27a) Note Added in Proof. X may also be identical with the minimum of the potential curve of the T_1 state, ^{3}**B** [P. Borrel and H. H. Greenwood, *Proc Roy. Soc.* (London), **A298**, 453 (1967)].

(28) E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967), and previous references listed therein.

(29) T. A. Litowitz, *J. Chem. Phys.*, **20**, 1088 (1952).

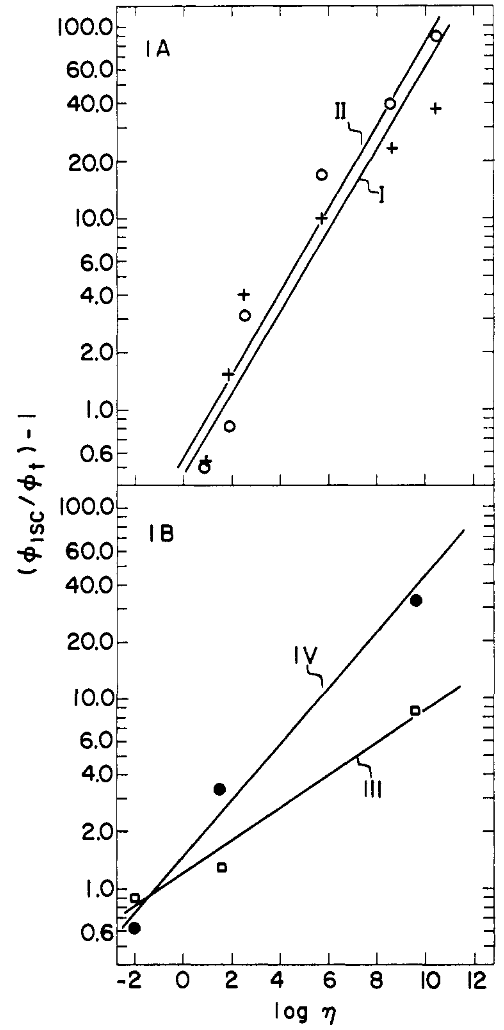


Figure 1. Plot of $[(\phi_{ISC}/\phi_t) - 1]$ *vs.* log η. (A) In glycerol: curve I (+), stilbene, curve II (○), bromostilbene. (B) In glycerol triacetate: curve III (□), stilbene; curve IV (●), bromostilbene.

In Figures 1A and 1B the values of $[(\phi_{ISC}/\phi_t) - 1]$ for stilbene and 4-bromostilbene have been plotted on a semilogarithmic scale *vs.* log η. The medium was either glycerol (Figure 1A) or glycerol triacetate (Figure 1B). From the slopes of these lines the following values were calculated for *a;* stilbene and 4-bromostilbene in glycerol, 0.22; stilbene in glycerol triacetate, 0.086; 4-bromostilbene in the same solvent, 0.15. *a* is thus seen to be smaller in glycerol triacetate than in glycerol. This is probably due to a larger mean molecular free volume (v_f) in glycerol triacetate. The values of the mean thermal expansion coefficients of these liquids support this conclusion[30] (glycerol triacetate, $\alpha = 12.9 \times 10^{-4}$ deg^{-1}; glycerol, $\alpha = 5.76 \times 10^{-4}$ deg^{-1}).

In order to avoid the arbitrariness regarding ϕ_{ISC} in eq 7, this quantity may be eliminated as follows. ϕ_t was equaled previously to the product of ϕ_{ISC} and $k/(k + k')$. Let k be the rate constant of step c′ and k' the rate constant of step c. We thus identify the viscosity dependent step with process c′. (A similar conclusion may be reached assuming that step b, rather than c′, in Scheme I is viscosity dependent.) $k/(k + k')$ is the decay ratio (R) from level X to the *cis* isomer.

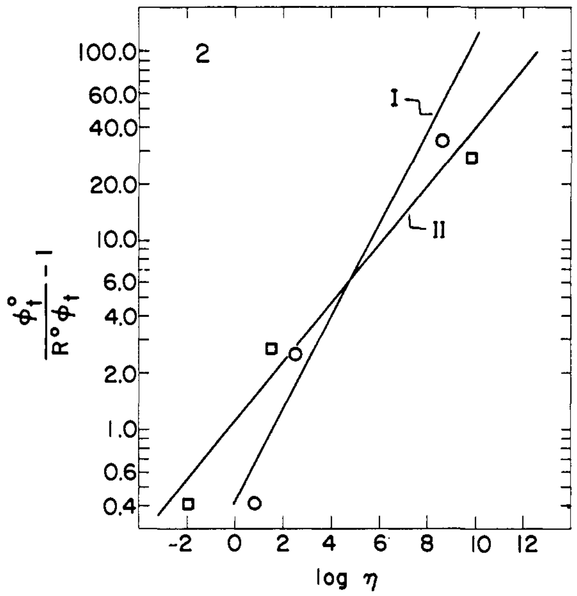


Figure 2. Plot of $[(\phi_t^\circ/R^\circ\phi_t) - 1]$ *vs.* log η for 4-bromostilbene: curve I (○), in glycerol; curve II (□), in glycerol triacetate.

At any temperature T, ϕ_t in a *fluid* reference medium (denoted ϕ_t°) is given by

$$\phi_t^\circ = \phi_{ISC}\frac{k^\circ}{k^\circ + k'} \qquad (8)$$

ϕ_{ISC} is, according to the compound, either constant or temperature dependent.

As long as the medium is fluid, $R^\circ = k^\circ/(k^\circ + k')$ is a temperature-independent constant. At the same temperature T, in a viscous medium, ϕ_t is given by

$$\phi_t = \phi_{ISC}\frac{k}{k + k'} \qquad (8')$$

Equation 8 divided by eq 8′ allows the elimination of ϕ_{ISC}.

$$\phi_t^\circ/\phi_t = R^\circ(1 + k'/k) \qquad (9)$$

A good estimate of R° in stilbenes (room temperature, fluid medium) is 0.5–0.6, based on the prevailing values of ϕ_t.[13] Thus proceeding exactly as for eq 7 we obtain

$$\ln\left[\frac{\phi_t^\circ}{R^\circ\phi_t} - 1\right] = C - a\ln\eta \qquad (10)$$

In Figure 2 the values of $[(\phi_t^\circ/R^\circ\phi_t) - 1]$ for 4-bromostilbene are plotted on a semilogarithmic scale *vs.* log η. R° was taken as 0.5.

Experimental Section

Most of the experimental details are described in previous papers.[13,31] Fluorescence quantum yields and spectra were measured on 6×10^{-6} *M* solutions. Absorption spectra and isomerization quantum yields were in most instances measured on 2–3 $\times 10^{-5}$ *M* solutions. Polyisobutylene films were prepared by evaporating the solvent from solutions of polyisobutylene and the solute in chloroform. The concentration of the solute in polyisobutylene was about 0.5%. Solutions of stilbene and of bromostilbene in glycerol (anhydrous, Fluka) and in glycerol triacetate (BDH) were deoxygenated before use by bubbling prepurified nitrogen for 30 min through the solution (maintained at +50° to obviate trapping of gas bubbles). Deoxygenation is rendered

---

(30) F. M. Jaeger, *Z. Anorg. Allgem. Chem.*, **101**, 1 (1917).

(31) K. A. Muszkat and E. Fischer, *J. Chem. Soc., Sect. B*, 662 (1967).

necessary by the efficient photooxidation of stilbene and bromostilbene to phenanthrene or its derivative.[31]

Solutions of stilbenes in MCH/IP or MCH/IH were dried and deoxygenated by the usual Na-K alloy treatment.[13] Fluorescence spectra were measured at right angles to the exciting light, as described previously.[13] The exciting light was isolated by a Bausch & Lomb 500-mm grating monochromator from a 450-w Osram xenon lamp. No isomerization was observed during the recording of the fluorescence spectra. Fluorescence yields were determined by comparison with a solution of anthracene in ethanol, of absorbance 0.15 at 315 mμ, serving as a standard with $\phi_F = 0.27$.[32]

Photoisomerization quantum yields were measured and calculated by the method of Zimmerman, Chow, and Paick.[12,33] Quantum yields with 313-mμ light in glycerol triacetate were corrected for the absorption of light by this solvent ($D = 0.20$, independent of temperature). The quantum yields of isomerization and of fluorescence are probably accurate to better than ±10%, except the isomerization quantum yields below 0.1, which are much less accurate. Emission and absorption spectra, especially at low temperatures, did not show any evidence of dimerization, association, or aggregation of solute molecules, phase separation of components of the solvent mixtures, or cloudiness due to humidity.

Acknowledgments. The authors wish to thank Professor J. R. Platt and Dr. W. M. Windsor for helpful discussions on several of the topics covered by the present work. They also acknowledge a research grant from the U. S. National Bureau of Standards, which served to finance a part of this investigation.

---

(32) C. A. Parker, *Advan. Photochem.*, **2**, 305 (1964).

(33) G. Zimmerman, L. Chow, and U. Paick, *J. Am. Chem. Soc.*, **80**, 3528 (1958).

Estimation of Particle Dimensions from the Relaxation of Transient Electric Birefringence of Suspensions

Don Ridgeway[1]

Contribution from the Department of Biophysics, Medical College of Virginia, Richmond, Virginia.

Received May 16, 1967

Abstract: Analysis is continued of the relaxation of transient electric birefringence of suspensions of rigid particles. The relaxation curve of suspensions of a rigid particle of arbitrary shape is shown to be describable in general by a sum of two exponential terms, defining two relaxation constants. Apart from a physically unlikely class of exceptions, a relaxation curve consisting of a single exponential term is shown to occur only for an axisymmetric particle, and always in this case. For the asymmetric ellipsoid, combination of the relaxation constants with the particle volume is shown to lead to definition of two reduced relaxation constants which are functions only of the axial ratios of the particle. A procedure is presented for convenient estimation of particle dimensions from relaxation data in terms of these reduced quantities, and necessary computed values required in this procedure are tabulated for a wide range of axial ratios. Finally, the estimation procedure is applied to the protein hemocyanin from the snail, *Helix pomatia*.

Analysis of the relaxation of transient electric birefringence of protein solutions provides a convenient method for study of protein structure if suitable expressions are available to relate the relaxation constants inferred from the data to shape parameters of the individual particles. In an earlier paper[2] (designated in the following as RI), we have obtained a general equation for the birefringence of an oriented suspension of particles in terms of the angular probability density of the particles. Introducing results of the theory of rotational Brownian motion of Perrin,[3] we used this equation to write the specific form for the decay in birefringence of a suspension of asymmetric ellipsoidal particles in free rotation following initial orientation in terms of the optical and frictional properties of individual particles. The present investigation is an extension of the preceding work directed toward its generalization and application in estimation of particle shape.

Numerous problems in application are apparent from the theoretical analysis. The question of the actual amount of information in a relaxation curve gives rise to many of these. In the absence of knowledge about the general form of the relaxation curve, *i.e.*, for particles of arbitrary shape, uncertainty necessarily arises in connection with misinterpretations produced by assumption of an incorrect particle-shape class for the analysis. The lack of utility of definition of an equivalent-spheroid model in the study of protein structure has exemplified this problem in the past. The significance of a simple exponential decay of birefringence, the form observed for some proteins, is of particular interest because of the known result that it can arise in an ellipsoidal model for the monodisperse axisymmetric spheroid. Moreover, one concludes from the analysis of suspensions of the asymmetric ellipsoid that the relaxation curve does not itself contain enough information to specify uniquely the dimensions of an ellipsoid. The relaxation data therefore cannot be applied except in a confirmatory fashion to ellipsoids without determination of what additional observable parameters are required to obtain such specification. Finally, there are already described in the literature birefringence curves which do require the form of the relaxation equation derived for the asymmetric ellipsoid (as opposed to the spheroid) if one assumes the suspensions under study to be monodisperse. It is of interest to evaluate an example of such data in terms of the theory to establish

---

(1) Biomathematics Program, Institute of Statistics, North Carolina State University, Raleigh, N. C.

(2) D. Ridgeway, *J. Am. Chem. Soc.*, **88**, 1104 (1966).

(3) F. Perrin, *J. Phys. Radium*, [7] **5**, 497 (1934); [7] 7, 1 (1936).