High-Pressure Study of the Effect of Viscosity on Fluorescence and Photoisomerization of *trans*-Stilbene

L. A. Brey, Gary B. Schuster,*[1] and H. G. Drickamer*

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801.

Received May 30, 1978

Abstract: The fluorescence quantum yields ϕ_f and the initial photoisomerization rates for *trans*-stilbene in several deoxygenated solvents were obtained as a function of solvent viscosity at room temperature by using pressures to 11 kbar to alter solvent viscosity. It was observed that in solvents of the same viscosity, ϕ_f is generally larger in hydrocarbons than in hydroxylic solvents. Fluorescence lifetimes at 1 atm were measured with a picosecond laser and streak camera allowing calculation of the radiative deactivation rate of the excited singlet state in several solvents. At high viscosities in paraffin oil and glycerol ϕ_f approaches a limiting value associated with the complete inhibition of molecular twist. Analysis of the data gives the rates of intersystem crossing (isc) and of viscosity-dependent deactivation via twist of the planar excited singlet. These parameters indicate that in nonviscous solvents such as *n*-hexane at room temperature, only about 2% of the planar excited singlet states undergo isc. The isc yield in glycerol at room temperature is calculated to be 21% implying significant isomerization via the triplet state in viscous solvents.

The photoisomerization of stilbene is of considerable interest from both a theoretical and a practical point of view, particularly as a prototypical example of polyenes such as vitamin A and the visual pigments which play an important role in photobiology. Light absorption in the stilbene system is followed by a rapid change in molecular configuration due to twisting about the double bond. This change in molecular geometry upon excitation gives rise to the unusual emission properties observed in stilbene and the polyenes. Such a process involving rotation about a double bond has the advantage of possessing a reaction coordinate easily separable from other molecular coordinates, thereby facilitating theoretical description.

Early work by Dyck and McClure[2] and Malkin and Fischer[3] on the temperature dependence of *trans*-stilbene fluorescence and isomerization quantum yields established that almost all decay from the first excited trans singlet ($^1t^*$) can be accounted for by fluorescence or by crossing into the state from which subsequent isomerization occurs. Great controversy arose over the identification of the process competing with fluorescence from $^1t^*$. Fischer[3] advocated a model proposed by Förster[4] in which the process was assigned to intersystem crossing (isc) into the triplet stilbene manifold ($^3t^*$) followed by isomerization via a triplet state common to both isomers. Saltiel[5] assigned the competing process to activated rotation about the central bond to form a twisted (perp) singlet ($^1p^*$) from which isomerization occurs by efficient internal conversion to the ground state S_0. This singlet mechanism (eq 1-5) has received additional theoretical and experimental support and is the currently accepted model for direct *trans*-stilbene photoisomerization.

$$^1t + h\nu \rightarrow {}^1t^* \qquad (1)$$

$$^1t^* \xrightarrow{k_f} {}^1t + h\nu \qquad (2)$$

$$^1t^* \xrightarrow{k_{tp}} {}^1p^* \qquad (3)$$

$$^1t^* \xrightarrow{k_{is}} {}^3t^* \qquad (4)$$

$$^1p^* \xrightarrow{k_d} \alpha\,{}^1t + (1-\alpha){}^1c \qquad (5)$$

A consequence of this mechanism is the prediction of very short lifetimes for stilbene fluorescence at moderate temperatures. This is in conflict with recently reported fluorescence lifetime work by Birch and Birks[6] in which a two-component exponential decay was reported. At room temperature the long component was found to be 1.65 ns and the short component less than 0.2 ns in methylcyclohexane/isohexane. In order to account for this, it was proposed that during the singlet (S_1) lifetime, thermal equilibrium is established between $^1t^*$ and $^1p^*$ by reversible internal conversion across the potential barrier. Preliminary fluorescence data by Teschke and coworkers[7] seem to indicate such an equilibrium between a fluorescing and a nonfluorescing state. However, a recent picosecond study[8] of the effect of temperature on *trans*-stilbene fluorescence lifetimes (in which a careful search for a long decay component was made) and our observations on these lifetimes at room temperature in various solvents show only a single very short simple exponential decay. Until further data are available to resolve this question, we assume that the $^1t^* \rightarrow {}^1p^*$ internal conversion is effectively unidirectional as originally proposed by Saltiel. A small degree of reversibility would not affect the general conclusions reached herein.

Two pieces of evidence were instrumental in establishing the singlet mechanism. One was the observation by Saltiel and Megarity[9] that the effect of azulene on the photostationary states for direct stilbene photoisomerization is small and independent of solvent viscosity, while the effect of azulene on sensitized stilbene photoisomerization is large and viscosity dependent. In the sensitized experiments the azulene acts as an efficient acceptor of triplet excitation from $^3t^*$ at the diffusion-controlled rate resulting in a large enhancement of the amount of trans isomer in the photostationary state mixture. The small, viscosity-independent enhancement of the trans isomer in the direct isomerizations is attributed to long-range singlet–singlet energy transfer. These experiments established that isc is not an important (<5%) decay path for unperturbed *trans*-stilbene in nonviscous solvents at room temperature.

The second key piece of evidence for the singlet mechanism was the observation by Saltiel and D'Agostino[10] that fluorescence and isomerization yields remain coupled in a highly viscous solvent upon lowering the temperature. On the basis of these experiments they postulated the existence in viscous solvents of a viscosity-dependent barrier to $^1t^* \rightarrow {}^1p^*$ rotation giving an overall activation energy for this process of $E^\ddagger = E^\ddagger_t + E^\ddagger_v$ where $E^\ddagger_t$ is the inherent thermal barrier and $E^\ddagger_v$ is the viscosity-dependent barrier. The individual activation energies were then extracted by use of the Arrhenius and Andrade equations to analyze the dependence of the fluorescence quantum yields upon temperature and upon viscosity (at

0002-7863/79/1501-0129$01.00/0

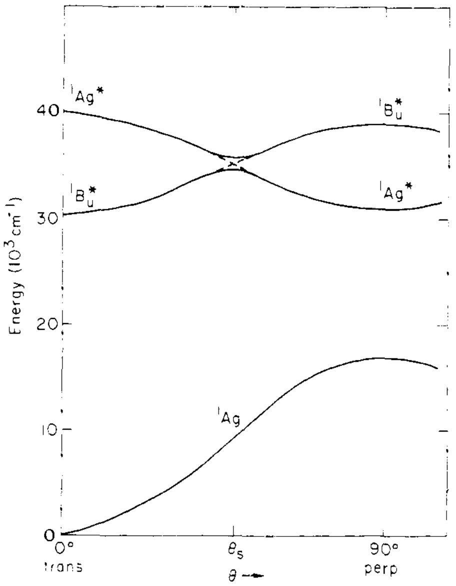

Figure 1. Potential energy diagram of ground and two lowest excited singlet states of *trans*-stilbene as a function of rotation angle θ. After ref 6 and 17.

Table I. Fluorescence Quantum Yields and Lifetimes at 23 °C

solvent	ϕ_f	τ_f, ps
methanol	0.026	
isobutyl alcohol	0.032	58
tert-butyl alcohol	0.035[9]	
glycerol	0.26	650
	0.26 (t = 25 °C)[10]	
n-pentane	0.043 (t = 20 °C)[18]	
n-hexane	0.043	
MCH	0.047	
	0.046 (t = 25 °C)[18]	
HMN	0.048	85
paraffin oil	0.15	

varying temperature and at constant temperature using glycerol/water mixtures).

The ordering of the lowest energy excited singlet states of the all-trans polyenes has been the subject of much study.[11,12] In these molecules the excited $\pi\pi^*$ states are of either A_g or B_u symmetry and the only allowed electric dipole transitions from the A_g ground state are to u states. It was thought that the excited A_g state would be located at much higher energy than the B_u state owing to its doubly excited character, but recent theoretical work has shown that when doubly excited configurations are included in the configuration interaction this state is predicted to exist at an energy much lower than previously supposed.[11-13] In fact these calculations predict that in the higher polyenes the doubly excited A_g singlet should be the lowest singlet lying just below the singly excited B_u state.[12] The B_u state has considerable Rydberg character while the excited A_g state is covalent suggesting that the B_u state is much more sensitive to solvent changes than is the A_g excited state.[11] The very strong solvent dependence of the quantum yields and fluorescence lifetimes of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) has been attributed to the modification of the energy gap between these states by solvent polarity.[14,15]

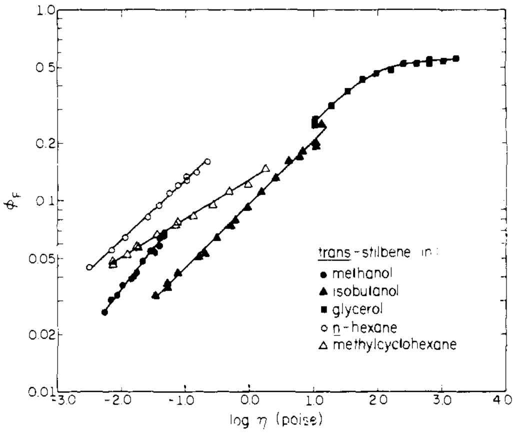

Figure 2. ϕ_f vs. log viscosity: *trans*-stilbene in several solvents.

Orlandi and Siebrand[16] have proposed a potential energy diagram for *trans*-stilbene isomerization based upon such a low-energy doubly excited singlet state. This A_g state, which for *trans*-stilbene arises from an electronic excitation mainly localized in the ethylenic fragment, has higher energy than the lowest B_u state for planar geometry, but lower energy for twisted geometries. The two potentials interesect at some angle $\theta = \theta_s < 90°$ leading to a reversal of the state order. Birch and Birks have used this potential energy diagram in their discussion of stilbene isomerization. Birks[17] has recently presented this semiempirical model in more detail and applied it to the higher polyenes. Figure 1 shows schematically the angular dependence of the ground and excited singlet state potentials in *trans*-stilbene based on this model.

In this report we investigate the effect of solvent viscosity on fluorescence and isomerization quantum yields of stilbene at room temperature by using high pressure to alter solvent viscosities. Viscosities from less than 10^{-2} P to more than 10^3 P were obtained by application of pressures to 11 kbar on organic solvents. The use of pressure allows a clean separation of the viscosity effect from purely temperature and solvent effects—both of which are important in this system.

Results and Discussion

Fluorescence Quantum Yields and Lifetimes. Fluorescence lifetimes and quantum yields obtained for *trans*-stilbene in various solvents at 23 °C (λ_{exc} 295 nm) are shown in Table I. Also shown are quantum yield data from Saltiel's work. Agreement between the two sets of data is very good. Figure 2 shows the fluorescence quantum yield as a function of solvent viscosity at room temperature in several solvents. Figure 3 is a plot of ϕ_f vs. P in 2,2,4,4,6,8,8-heptamethylnonane (HMN) and paraffin oil—solvents for which the pressure dependence of viscosity is not known. The 10-kbar point in HMN was disregarded as it seemed inconsistent with the other data. This was the last point taken and it is likely that some photoisomerization occurred resulting in a low ϕ_f. Solutions were deoxygenated, although fluorescence yields in solution are almost unchanged even under an oxygen atmosphere. $\phi_f^0/\phi_f^{O_2} = 1.03 \pm 0.02$ in *n*-pentane;[18] $\phi_f^0/\phi_f^{O_2} = 1.01 \pm 0.02$ in paraffin oil (this work).

The dependence of the fluorescence yields on viscosity indicates the presence of a viscosity barrier to $^1t^* \rightarrow {}^1p^*$ rotation even in the nonviscous solvents studied. There is also an inherent thermal barrier to the twist which is not addressed in these experiments. It should be noted that even quite nonviscous solvents such as the commonly used 1:1 methylcyclohexane/methylcyclopentane (MCH/MCP) mixture become significantly more viscous at low temperatures. For example, MCH/MCP attains a viscosity of about 10^4 P at -175 °C.[19] When a solvent such as this is used in a low-temperature fluorescence yield experiment to extract the thermal activation energy via an Arrhenius plot, the observed ϕ_f must contain both thermal and viscosity-dependent contributions.

In order to explain the $\eta^{2/3}$ dependence of the fluorescence yield in the triphenylmethane dyes, Förster and Hoffman[20]

Table II. Activation Volumes

solvent	$\Delta V_c^{\ddagger}$ cm^3/mol	solvent	$\Delta V_c^{\ddagger}$ cm^3/mol
methanol	2.2	HMN	9.5
n-hexane	3.5	glycerol	12.9
MCH	3.7	paraffin oil	13.2
isobutyl alcohol	5.2		

proposed a model in which the phenyl rings rotate to a new equilibrium position after excitation at a rate controlled by Stokes-like viscous damping. The nonradiative, viscosity-dependent deactivation rate of the excited singlet was taken to be quadratically proportional to the angle of ring rotation. Although this model accounts for the emission quantum yields, it predicts a fluorescence decay of the form $\exp(-bt^3/\eta^2)$ where b is a constant. However, a simple exponential decay has been observed in the triphenylmethane dye malachite green.[21] It is difficult to see how any model in which there is a time-dependent rate of excited-state deactivation could give rise to a simple exponential fluorescence decay as observed in *trans*-stilbene and malachite green. We, therefore, assume that the rate of viscosity-dependent $^1t^*$ deactivation is time independent and assign it the value k_c. Whether or not this is also the rate of rotation about the central bond k_{tp} as postulated by Birch and Birks,[6] Saltiel and D'Agostino,[10] and others is unknown.

It is evident from Figure 2 that in addition to the viscosity dependence of the fluorescence yields, there is also a strong solvent dependence. For example, at a viscosity of 0.1 P in isobutyl alcohol, MCH, and *n*-hexane, the fluorescence yields are 0.045, 0.080, and 0.13, respectively. This large enhancement of ϕ_f in hydrocarbon solvents over that in polar solvents has received little attention. Saltiel and Megarity[9] noted the low ϕ_f in the viscous *tert*-butyl alcohol in comparison to the higher ϕ_f in the nonviscous *n*-pentane, but attached no particular significance to it. A similar solvent effect has been observed in *trans*-1,1,4,4-tetraphenyl-2-methybutadiene[22] and in DPH.[23]

The solvent effect can be rationalized in terms of Birk's potential diagram (Figure 1). An increase in solvent polarity may decrease the $^1B_u^*$ energy at a geometry near the crossing with $^1A_g^*$ thereby lowering the S_1 potential barrier to rotation. This increases the rate of nonradiative $^1t^*$ deactivation resulting in a lower ϕ_f. Also the angle Θ_x at which the avoided crossing occurs increases—making viscosity more effective at hindering deactivation of $^1t^*$ in a polar solvent than in a nonpolar solvent. This may explain the large slope of the ϕ_f vs. log η plot for the highly polar methanol. As expected, the absorption spectrum of *trans*-stilbene undergoes a bathochromic shift of about 175 cm^{-1} upon changing the solvent from a hydrocarbon to glycerol owing to stabilization of the excited state by the more polar solvent.[10] The findings for the two hydrocarbon solvents *n*-hexane and MCH are rather puzzling. The data show that the slope is larger in *n*-hexane. The smaller ϕ_f in MCH could be due to its greater molecular polarizability (note that at low viscosities the difference in ϕ_f is not large). Phenomenologically, this indicates that an increase in viscosity is much less effective in hindering twisting in MCH than it is in *n*-hexane. This may be connected with the shape of the molecule—the other solvent molecules are much more "cylindrical" than MCH.

Activation volumes $\Delta V^{\ddagger}$ for $^1t^* \rightarrow {}^1p^*$ rotation in each solvent are shown in Table II. The correlation coefficient obtained from the least-squares analysis of the ln k_c vs. P plots was ≥0.995 for each solvent. The large variations in magnitude from solvent to solvent of the $\Delta V^{\ddagger}$ values illustrate the powerful effect of molecular environment upon $^1t^* \rightarrow {}^1p^*$ rotation. The $\Delta V^{\ddagger}$ values are not strongly correlated with solvent viscosity or other physical properties, except that there appears to be some relationship to solvent boiling point.

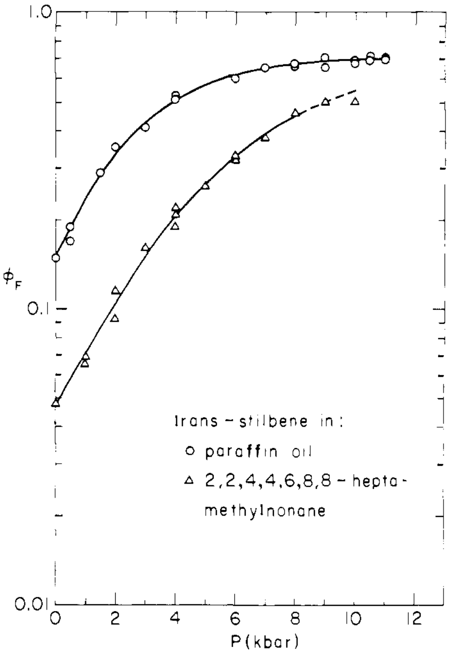

Figure 3. ϕ_f vs. pressure: *trans*-stilbene in paraffin oil and in 2,2,4,4,6,8,8-heptamethylnonane.

From our ϕ_f and τ_f data at room temperature we calculate the radiative rate k_f as 4.0 × 10^8 s^{-1} in glycerol, 5.5 × 10^8 s^{-1} in isobutyl alcohol, and 5.6 × 10^8 s^{-1} in HMN. A theoretical value of k_f in *n*-pentane of 5.9 × 10^8 s^{-1} has been obtained by Marinari and Saltiel[24] from the integrated absorption spectrum using the Birks–Dyson relation.[25] The small solvent dependence observed is supported by the relative insensitivity of the *trans*-stilbene absorption and fluorescence spectra to solvent changes.[9] A similar insensitivity to pressure is the justification for taking k_f to be pressure independent.

Figures 2 and 3 show that at the highest viscosities attained, ϕ_f has reached a limiting value in glycerol and paraffin oil. The ϕ_f in HMN shows signs of limiting at some value near that for the paraffin oil. At these high viscosities the excited *trans*-stilbene molecule experiences hindrance to twisting from the walls of its now rigid solvent cage. The rotational deactivation path from $^1t^*$ is closed off and the excited molecule either fluoresces or undergoes isc to $^3t^*$. The cessation of molecular twist in the excited singlet is consistent with the observation that the excited-state absorption of $^1t^*$ shows no significant decay in the 120 ps after excitation in a polymethyl methacrylate (PMMA) matrix in contrast to the fast decay observed in *n*-hexane solution.[7] It should be noted that the complete inhibition of the $^1t^* \rightarrow {}^1p^*$ rotation does not necessarily mean that trans to cis photoisomerization has also ceased. As Birks has pointed out,[26] isomerization via a triplet mechanism could still occur. The reduction in the rate of the process $^3t^* \rightarrow {}^3p^*$ would be less important than in the corresponding singlet process because of the longer $^3t^*$ lifetime. Such a triplet mechanism is operative in the trans to cis photoisomerization of the styrylnaphthalenes[27,28] which occurs even in rigid media such as polystyrene.[29] A similar triplet mechanism for isomerization also seems to be operative in *trans*-stilbene at high viscosities and at room temperature. Irradiation at these viscosities leads to loss of fluorescence intensity indicative of trans to cis isomerization.

The rate of isc at room temperature k_{is} can be calculated from the limiting ϕ_f values at high viscosity by use of the equation

$$(\phi_f)_{\eta \rightarrow \infty} = k_f/(k_f + k_{is}) \qquad (6)$$

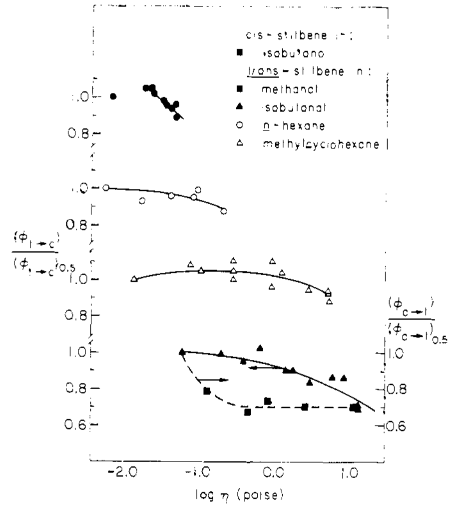

Figure 4. Relative $\phi_{t\to c}$ vs. log viscosity in several solvents and $\phi_{c\to t}$ in isobutyl alcohol.

Calculated k_{is} values are 3.3×10^8 s^{-1} in glycerol and 2.4×10^8 s^{-1} in paraffin oil (using $k_f = 5.6 \times 10^8$ s^{-1} in this solvent). The difference between these values is probably not significant, but both are much larger than the generally quoted values. These range from about 2×10^7 s^{-1} (the value for β-styrylnaphthalene)[30] to about 6.4×10^7 s^{-1} (from computer-assisted curve fitting of ϕ_f vs. T).[18] However, the large k_{is} values obtained are not in conflict with the photochemical behavior of *trans*-stilbene at room temperature (see below). The near unity ϕ_f in hydrocarbon solvents at -190 °C[31] is explained by assuming that k_{is} decreases as the temperature is lowered. At these low temperatures the trans to cis isomerization yield $\phi_{t\to c}$ is small ($\phi_{t\to c} = 0.006$ at -183 °C)[3] so k^0_{is} can be calculated as above. At about -190 °C, $k_f^0 = 5.8 \times 10^8$ s^{-1} from low-temperature ϕ_f[31] and τ_f[8] data giving $k^0_{is} = 3.1 \times 10^7$ s^{-1}.

Knowing k_f, k_{is}, and ϕ_f at some viscosity allows calculation of the rate of configuration-dependent ^{1}t* decay (k_c) via the relation

$$\phi_f = k_f/(k_f + k_{is} + k_c)$$

In *n*-hexane at atmospheric pressure and room temperature, k_c is 1.2×10^{10} s^{-1}. Values in the other nonviscous solvents studied are not far different. Calculation of the isc quantum yield ϕ_{is} in these solvents shows that only about 2% of the ^{1}t* states undergo isc to ^{3}t*. This is well below the 5% isc yield which could have been detected in Megarity and Saltiel's azulene quenching experiments.[9] In glycerol k_c is 8.1×10^8 s^{-1} giving an isc yield of 21%. Thus, the triplet mechanism plays a significant role in *trans*-stilbene photoisomerization in glycerol and other viscous solvents at room temperature. Saltiel and D'Agostino[10] obtained isc yields of 1 and 5% in MCH and glycerol, respectively, from analysis of the temperature dependence of stilbene fluorescence.

Since the yields of *cis*- and *trans*-stilbene from ^{1}p* and ^{3}p* are identical,[32] measurements of the photostationary states in a particular solvent give no information on whether the isomerization proceeds via a singlet mechanism, a triplet mechanism, or both simultaneously. This explains why the same photostationary states are observed in glycerol and in nonviscous solvents. The use of a triplet interception method to determine the isc yield in glycerol would be extremely difficult as the high viscosity would result in a much smaller rate of triplet quenching and thereby cause only slight trans enhancement for reasonable quencher concentrations. The high-pressure technique described here seems the best way to approach the problem.

Initial Isomerization Rates. In Figure 4 the effect of viscosity on the initial rate of trans to cis photoisomerization relative to the initial rate at a viscosity corresponding to a pressure of 0.5 kbar is shown in several solvents at room temperature. The data represent the relative rates during the first 10% of the trans to cis conversion. Also shown are data obtained for the cis to trans conversion in isobutyl alcohol. The fraction (about 0.1) of excited cis molecules which undergo photocyclization and oxidation by traces of oxygen giving phenanthrene seemed little affected by pressure and was ignored in the calculation of the relative rates.

Although there is a fair amount of scatter in the data, several conclusions can be drawn. In all solvents studied, the rate of trans to cis conversion decreases at the highest solvent viscosities showing that ϕ_f and $\phi_{t\to c}$ are indeed coupled in moderately viscous media at room temperature in accordance with the singlet mechanism (eq 1-5). The slope of the $\phi_{t\to c}$ vs. log η plot is greater in methanol than in the other solvents. This is consistent with the large viscosity effect on ϕ_f in methanol as discussed above—solvent viscosity is more effective at hindering ^{1}t* → ^{1}p* in polar solvents. In some cases it appears that at intermediate pressures (2-5 kbar) $\phi_{t\to c}$ actually increases as the viscosity increases. A likely explanation is that pressure alters the cis/trans decay ratio from ^{1}p* further in favor of the cis isomer ($1 - \alpha = 0.59$ in nonviscous solvents at atmospheric pressure).[32] Calculation of $(1 - \alpha)$ from the equation

$$\phi_{t\to c} = \frac{(1-\alpha)k_c}{k_f + k_{is} + k_c} \tag{7}$$

yields values which increase by less than 15% in all solvents studied. The largest increase is in MCH while in isobutyl alcohol $(1 - \alpha)$ is essentially constant. The fast drop in the rate of cis to trans conversion between 0.5 and 4 kbar must therefore be ascribed to the effect of pressure on the rate of ^{1}c* deactivation. From 5 to 10 kbar, $\phi_{c\to t}$ seems independent of both solvent viscosity and pressure. The viscosity independence is in agreement with the results of Gegiou, Muszkat, and Fischer[33] in glycerol at temperatures down to -80 °C implying that the rate of the process ^{1}c* → ^{1}p* is much less sensitive to solvent viscosity than that of ^{1}t* → ^{1}p*. This is illustrated by the observation that the cis to trans conversion occurs rapidly in a PMMA matrix at pressures to 100 kbar as shown by the rapid growth of *trans*-stilbene fluorescence intensity upon irradiation.[34]

Conclusion

trans-Stilbene direct photoisomerization proceeds predominantly via the singlet mechanism (isc yield ≈ 2%) in nonviscous solvents at room temperature. As solvent viscosity is increased at room temperature, isomerization via the triplet mechanism becomes increasingly competitive owing to inhibition of the ^{1}t* → ^{1}p* process. In glycerol at room temperature about 21% of the ^{1}t* states undergo isc to ^{3}t*. If the ^{3}t* → ^{1}t radiationless decay is negligible as suggested by the identical photostationary states observed for perhydro- and perdeuteriostilbenes with high-energy sensitizers[5] then 21% of the isomerization occurs via the triplet mechanism in glycerol. The ability of high pressure to alter solvent viscosities at one temperature is a very useful tool in the investigation of photochemical processes involving changes in molecular geometry upon excitation.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) was recrystallized twice from $CHCl_3$/EtOH and then sublimed. Analysis by GLC showed no volatile impurities other than a trace of *cis*-stilbene. A pure sample of *cis*-stilbene was obtained by preparative GLC. Spectral glycerol (600 mL) (Mallinckrodt) was mixed with 200 mL of water and filtered through activated charcoal to remove UV-absorbing impurities. The anhydrous glycerol was recovered by fractional distillation under high vacuum. Methanol, isobutyl alcohol, *n*-hexane, and MCH were all MCB fluorometric solvents and were used without further purification in the fluorescence experiments. HMN (Aldrich) and paraffin oil (Amoco no. 31, USP) were used to attain high viscosities in a nonpolar solvent. The HMN was used without further purification. The paraffin oil was stirred for 12 h over fuming sulfuric acid (30% SO_3), washed, neutralized, and filtered through silica gel and alumina. This treatment reduced the fluorescence background by a factor of about 20 for 313-nm irradiation. The alcohols for the isomerization experiments were distilled over BaO to remove trace acidic impurities which catalyzed cis to trans isomerization upon concentration of the irradiated solutions. The MCH was distilled to remove small amounts of high-boiling substances which interfered with the GLC analysis.

High-Pressure Viscosities. The pressure dependence of the viscosities of the solvents in Figure 2 is given by Bridgman at 30 and 75 °C.[35] The Andrade equation is used to correct the viscosities to ambient temperature at each pressure. The currently accepted value for the viscosity of glycerol at 30 °C (6.29 P) is used rather than that used by Bridgman (3.8 P), which he took from the International Critical Tables. The more recent work by Zolotykh[36] on the pressure-viscosity relation of carefully dried glycerol to 7 kbar shows excellent agreement with Bridgman's data.

Atmospheric Fluorescence Yields. Fluorescence quantum yields at atmospheric pressure for *trans*-stilbene in methanol were obtained relative to quinine sulfate in 1 N H_2SO_4 ($\phi_f = 0.55$)[37] at 23 °C. Fluorescence spectra of stilbene and the standard were taken on a previously described emission spectrometer[38,39] using photon counting at very low excitation intensities. Loss of fluorescence intensity while the spectrum was being taken (due to trans to cis photoisomerization) was negligible. The relative fluorescence intensities were obtained by integration of the corrected emission spectra. Refractive index corrections were made to adjust for the different solvents used with the standard and the stilbene solution. Concentrations of solutions were adjusted so that optical densities were approximately equal at the exciting wavelength (295 nm) and the fluorescence intensities were corrected for small differences in optical density. Fluorescence quantum yields for *trans*-stilbene in other solvents were determined by comparison with the quantum yield in methanol. This was done on an uncorrected fluorometer (Farrand Mk II) by monitoring the emission intensity at the wavelength of maximum intensity in each solvent and assuming that the intensity is proportional to the area of the emission spectrum in that solvent. (Emission spectra changed only slightly in position and half-width in the solvents studied.) Refractive index corrections were made as above.

High-Pressure Fluorescence Yields. The high-pressure liquid cell and associated emission equipment have been described elsewhere.[38,39] *trans*-Stilbene solutions (4×10^{-6} M) were excited into the absorption band with maximum at about 308 nm. The excitation wavelength (bandwidth 0.5 nm) was adjusted at each pressure and for each solvent to give maximum fluorescence intensity. The shift of the excitation maximum was never more than 3 nm over the 11-kbar pressure range. Photon counting at very low excitation intensities was used to minimize trans to cis isomerization. In order to further reduce the time that the solution was irradiated during a pressure run, only the emission intensity at the wavelength of maximum intensity was taken at each pressure. This emission intensity was corrected for photomultiplier and monochromator response, and taken to be proportional to the area of the emission spectrum at that pressure. The emission spectrum undergoes a red shift with increasing pressure, but the half-width is little changed. Intensities were corrected for the increase in solution concentration due to solvent compressibility using Bridgman's data.[40,41] The compressibility of *n*-heptane was used for HMN and paraffin oil was assumed to be 85% as compressible as *n*-heptane. It is unlikely that these estimated values differ by more than 10% from the actual compressibilities. No correction for the approximately 10% increase in refractive index[42] from atmospheric pressure to 11 kbar has been applied to the high-pressure intensity data. The design of the collection optics in the high-pressure emission equipment makes this correction negligible.

High-Pressure Isomerization Rates. Solutions at pressure were irradiated in a cylindrical stainless steel inner cell designed for high-pressure absorption work[43] with path length of about 1.5 cm. The sapphire window assembly at one end of the cell was replaced with a polished stainless steel plunger to reflect exciting light back into the solution. It was verified that the extent of photoisomerization was directly proportional to irradiation time for small conversions showing the absence of any appreciable dead volume in the cell. All solutions were deoxygenated by bubbling argon through them for several minutes. *trans*-Stilbene solutions (4×10^{-6} M) were irradiated at the wavelength of maximum emission intensity for each pressure and solvent as determined in the fluorescence experiments. *cis*-Stilbene solutions (1×10^{-5} M) were irradiated at 277 nm. A solution was brought to pressure and irradiated for the time necessary to bring about approximately 10% isomerization at 0.5 kbar, the pressure was released, and the sample was set aside while the process was repeated at another pressure. After several pressure runs, the solutions were concentrated on a hot plate under a stream of argon. This treatment was shown not to affect cis/trans ratios if carefully done. The solutions were then analyzed by GLC for the percent conversion (glass 3 ft × 1/8 in. column of 3% SE-30 on Chromosorb P, *T* 155 °C).

Fluorescence Lifetimes. The picosecond laser, streak camera, and digitizing system have been previously described.[44] The Nd^{3+}: YAG laser 4th harmonic (265 nm) was used to excite *trans*-stilbene (5×10^{-5} M) in various solvents at room temperature. Streak camera optics were quartz, allowing observation of the entire *trans*-stilbene fluorescence spectrum. Ten decay curves were obtained in each solvent, summed, and fitted to a single exponential decay. In each case a good fit was obtained.

Acknowledgment. The authors thank Professor G. Weber for use of the Zeiss PMQ II spectrophotometer for optical density determinations, Professor K. Kaufmann for use of his picosecond laser and streak camera to determine the fluorescence lifetimes, and Kevin Smith for measuring the lifetimes. This work was supported in part by the U.S. Department of Energy under Contract EY-76-C-02-1198 and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1977–1979.
(2) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).
(3) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).
(4) T. Forster, *Z. Elektrochem.*, **56**, 716 (1952).
(5) J. Saltiel, *J. Am. Chem. Soc.*, **89**, 1036 (1967); **90**, 6394 (1968).
(6) D. J. S. Birch and J. B. Birks, *Chem. Phys. Lett.*, **38**, 432 (1976).
(7) O. Teschke, E. P. Ippen, and G. R. Holtom, *Chem. Phys. Lett.*, **52**, 233 (1977).
(8) M. Sumitani, N. Nakashima, K. Yoshihara, and S. Nagakura, *Chem. Phys. Lett.*, **51**, 183 (1977).
(9) J. Saltiel and E. D. Megarity, *J. Am. Chem. Soc.*, **94**, 2742 (1972).
(10) J. Saltiel and J. T. D'Agostino, *J. Am. Chem. Soc.*, **94**, 6445 (1972).
(11) B. S. Hudson and B. E. Kohler, *J. Chem. Phys.*, **59**, 4984 (1973), and references cited therein.
(12) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972).
(13) R. B. Birge, K. Schulten, and M. Karplus, *Chem. Phys. Lett.*, **31**, 451 (1975).
(14) J. B. Birks and D. J. S. Birch, *Chem. Phys. Lett.*, **31**, 608 (1975).
(15) J. R. Andrews and B. S. Hudson, *J. Chem. Phys.*, **68**, 4587 (1978).
(16) G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, **30**, 352 (1975).
(17) J. B. Birks, *Chem. Phys. Lett.*, **54**, 430 (1978).
(18) J. L. Charlton and J. Saltiel, *J. Phys. Chem.*, **81**, 1940 (1977).
(19) G. A. Von Salis and H. Labhart, *J. Phys. Chem.*, 72, 752 (1968).
(20) T. Förster and G. Hoffman, *Z. Phys. Chem. (Frankfurt am Main)*, **75**, 63 (1971).
(21) W. Yu, F. Pellegrino, M. Grant, and R. R. Alfano, *J. Chem. Phys.*, **67**, 1766 (1977).
(22) J. Kordas and M. A. El-Bayoumi, *J. Am. Chem. Soc.*, **96**, 3043 (1974).
(23) E. D. Cehelnik, R. B. Cundall, J. R. Lockwood, and T. F. Palmer, *J. Phys. Chem.*, **79**, 1369 (1975).
(24) A. Marinari and J. Saltiel, *Mol. Photochem.*, 7, 225 (1976).
(25) J. B. Birks and D. J. Dyson, *Proc. R. Soc. London, Ser. A*, **275**, 135 (1963).
(26) J. B. Birks, *Chem. Phys. Lett.*, **38**, 437 (1976).
(27) P. Bortolus and G. Galiazzo, *J. Photochem.*, **2**, 361 (1973–1974).
(28) M. Sumitani, S. Nagakura, and K. Yoshihara, *Chem. Phys. Lett.*, **29**, 410 (1974).
(29) N. P. Kovalenko, Yu. B. Shek, L. Ya. Malkes, and M. V. Alfimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 298 (1975).
(30) G. G. Aloisi, V. Mazzucato, J. B. Birks, and L. Minuti, *J. Am. Chem. Soc.*, **99**, 6340 (1977).
(31) S. Sharafy and K. A. Muszkat, *J. Am. Chem. Soc.*, **93**, 4119 (1971).
(32) J. Saltiel, J. T. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).
(33) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 12 (1968).
(34) D. Mitchell, private communication.
(35) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **61**, 57 (1926).
(36) E. V. Zolotykh, *Tr. Inst. Kom. Stand. Mer Izmer. Prib. Sov. Minist. SSSR*, **75**, 123 (1964).
(37) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(38) B. Y. Okamoto and H. G. Drickamer, *J. Chem. Phys.*, **61**, 2870 (1974).
(39) W. D. Drotning and H. G. Drickamer, *Phys. Rev. B*, **13**, 4568 (1976).
(40) P. W. Bridgman, "The Physics of High Pressure", Bell and Sons, London, 1931.
(41) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 129 (1949).
(42) K. Vedam, Proceedings of the 4th International Conference on High Pressure, Kyoto, 1974.
(43) B. Y. Okamoto, Ph.D. Thesis, University of Illinois, 1974.
(44) K. K. Smith, J. Y. Koo, G. B. Schuster, and K. J. Kaufmann, *Chem. Phys. Lett.*, **48**, 267 (1977).

Excited State Adduct Formation between Excited Substituted Quinolinium Cations and Specific Inorganic Anions

S. C. Chao,† J. Tretzel, and F. W. Schneider*

Contribution from the Institute of Physical Chemistry, University of Würzburg, 8700 Würzburg, West Germany. *Received March 22, 1978*

Abstract: Fluorescence enhancement of quinolinium, *N*-ethylquinolinium and pseudoisocyanine cations in the Hammett acidity region of $HClO_4$ and H_2SO_4 is shown to be due to the anions of these acids, ClO_4^- and HSO_4^-, whereas other acids and their anions act as strong quenchers. We propose that excited state adducts are formed specifically with ClO_4^- or HSO_4^- whose quantum yields are larger than those of the corresponding uncomplexed cations. Rate constants for a proposed kinetic mechanism are determined from steady-state and pulse experiments. For quinolinium ions a (second) excited state pK_a* may not be invoked in the Hammett acidity region.

Introduction

In earlier work[1] we measured the relatively low rate constants of proton transfer to a number of cyanine cations acting as carbon acids with pK_a values between 4 and 8 in their electronic ground states. Simple Förster cycle calculations predict these cyanines to be considerably stronger acids in their electronic excited state than in their ground state. In this paper we show that addition of high concentrations of $HClO_4$ or H_2SO_4 leads indeed to a strong increase of fluorescence in the Hammett acidity region without any shift in fluorescence or absorption wavelength. Surprisingly, this observed fluorescence enhancement also occurs with the anions of these acids, i.e., perchlorate or bisulfate ions at low acidities. A similar fluorescence enhancement is observed in the fragment of pseudoisocyanine (1,1-diethyl 2,2-cyanine chloride), namely, *N*-ethylquinolinium ion, whose quaternized nitrogen cannot accept a proton. Thus we are led to conclude that the excited states of these cations interact specifically with the anions of the above acids to form strongly fluorescent ionic adducts. This interpretation may be extended to the dramatic fluorescence enhandement observed for simple quinolinium cations in concentrated $HClO_4$ or H_2SO_4 which has been attributed to a (second) excited state pK_a* in the Hammett acidity region.[2] However, since $NaClO_4$ (or $KHSO_4$) is shown in this work to produce a similar enhancement, an excited-state pK_a* may not be invoked in the Hammett acidity region for the quinolinium ion. On the other hand, a number of other strong acids (e.g., HCl) and their anions are efficient quenchers in solvents of high dielectric constant at room temperature.

We present a mechanism that interprets this novel fluorescence behavior in terms of excited-state adduct formation involving the specific anions ClO_4^- or HSO_4^-. One may visualize the strongly fluorescent excited-state adduct as an excited cation which is "protected" from quenching H_2O molecules through complex formation with a specific anion. Adduct formation may be accompanied by a (partial) substitution of the solvation sphere around the cation by the entering ClO_4^- or HSO_4^-. Thus some but not all water molecules may be displaced in the inner cation solvation sphere resulting in the observed fluorescence enhancement without any fluorescence wavelength shift:

$$\begin{tikzcd}
(A_s^+)^* + S_s^- \arrow[r, shift left, "k_r"] \arrow[d, shift left, "k_f\ k_{nf}"] & (A^+S^-)_s^* \arrow[l, shift left, "k_d"] \arrow[dl, "k'_f\ k'_{nf}"] \\
A_s^+ + S_s^- \arrow[u, shift left, "I"] &
\end{tikzcd}$$

where A_s^+, $(A_s^+)^*$, S_s^-, and $(A^+S^-)_s^*$ are solvated quinolinium (derivative) cations, their solvated excited singlet states, solvated anions, and solvated ionic adducts in the excited state, respectively; k_r and k_d are adduct association and dissociation rate constants, respectively; I is the intensity of the exciting light; k_f and k_f' are fluorescence rate constants of the singlet cation and its ionic adduct, respectively.

We have omitted complex formation in the ground state, since no noticeable shift in absorption frequency or optical density is observed upon addition of the specific anions at room temperature under present conditions. Neither charge transfer nor exciplex formation is indicated. Transient measurements of fluorescence decay and steady-state measurements provide values for the rate constants.

Stern-Volmer experiments *in the absence* of $NaClO_4$ show that methanol and ethanol are stronger quenchers of cation fluorescence than H_2O molecules. The presence of $NaClO_4$ significantly lowers the quenching rate constants of methanol and ethanol due to the "protection" by ClO_4^- through excited-state adduct formation with the cation. Thus, in a wider sense, the observed fluorescence changes are a manifestation of a general solvent substitution effect.

Experimental Section

Reagent grade *N*-ethylquinolinium iodide and quinoline were purchased from K and K Laboratories, Inc., and Matheson Coleman and Bell, respectively. Pseudoisocyanine chloride (1,1′-diethyl-2,2′-cyanine) was kindly provided by Dr. E. Daltrozzo. High-resolution

---

† In partial fulfillment for the Ph.D. degree, 1975.

0002-7863/79/1501-0134$01.00/0