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Influence of solvent viscosity on the photoisomerization of a novel *trans*-stilbene derivative with hindered single bond torsion

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Abstract

Fluorescence life-time measurements were performed at elevated pressure and temperature to examine the viscosity dependence of the rate of photoinduced isomerization, k_{iso} , in a stilbene derivative in which the single bond torsion is hindered by the introduction of CH₂ bridges. The results obtained with *n*-hexane and methylcyclohexane as solvents (0.2 mPa s < η < 2 mPa s) could not be fitted satisfactorily on the basis of Kramers' expression. A good global fit was, however, achieved when applying the empirical relationship $k_{iso} = C \cdot (\eta/\text{mPa s})^{-a} \cdot \exp(-E_A/RT)$. The value for a drops from about 0.30 in *n*-hexane to about 0.15 in methylcyclohexane thus pointing to solvent specific contributions to the friction. The derived activation energies E_A are about 12.8 and 12.5 kJ mol⁻¹ in *n*-hexane and methylcyclohexane, respectively. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the early theoretical work by Kramers [1], the influence of solvents on the rate of chemical reactions has been a main topic of chemical kinetics. Over the years, the photoinduced isomerization of *trans*-stilbene has become the most intensively studied reaction and the major test for theoretical models of activated barrier crossing (for a review see Ref. [2]). The essential result of all studies is that the hydrodynamic Kramers equation does not adequately model the friction dependence. It was therefore suggested to introduce a frequency dependent friction rather than the macroscopic shear viscosity. Although the Grote–Hynes model [3] can adequately describe the course of the rate constant of isomerization, k_{iso} , it suffers from the fact that unrealistically small frequencies are obtained for the barrier. More recently, Anderton and Kauffmann [4] pointed out that, because stilbene is more polar in the transition state than in the (planar) trans configuration, correct evaluations of barrier energies in alcohols require data not only for isoviscous but also isodielectric solvents ('isodielectric-Kramers–Hubbard [5] analysis'). According to Schröder et al. [6,7] the pressure dependence of the isothermal photoisomerization rate reveals a significant change of the activation energy even in *n*-alkanes with solvent density, caused by the electrostatic solute–solvent interactions.

Hynes and co-workers [8,9] and Carmeli and Nitzan [10] investigated a two-dimensional model in which a reactive mode is coupled to a nonreactive

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mode. Both modes feel Markovian friction: however. as the coupling between modes increases, the influence of friction on the reaction rate becomes weaker. Later. Schröder concluded that the observed "deviations from the one-dimensional Kramers model are manifestations of multidimensional barrier crossing processes" [7]. Agmon and Kosloff [11] suggested a model in which the motion is viscosity dependent in only the reaction coordinate and its barrier height dependent on the value of the perpendicular coordinate, e.g. the phenyl twist angle. To provide further evidence for such a model which was adopted by several authors to explain their experimental results [12–14] it seems appropriate to study stilbene derivatives in which the phenyl torsion is hindered. So far. only two derivatives of this kind are available (see Scheme 1). In the first example, termed 'stiff stilbene' by Saltiel et al. [15], the single bonds are bridged by a five-membered ring containing two CH₂ groups, (5(*trans*-1-(1-indanylidene)-indane)). This derivative exhibits an excited state life-time much shorter than *trans*-stilbene [16]. Pump-probe experiments applying high pressure provided evidence for the existence of two excited conformers with different kinetic behaviour [17].

The derivative containing two six-membered rings with three CH₂ groups each, *trans*-1-(1-tetralinylidene)tetralane (6) [18], appeared to be non-fluorescent. Since the oscillatory strength of the S_0-S_1 absorption band is of similar size as in *trans*-stilbene, one can conclude that the excited state life-time



Scheme 1. Structures of compounds referred to in the text and abbreviations used.

is even further reduced than in the five-membered ring derivative (5). In this Letter, we will report on fluorescence life-time measurements performed at variable temperature and pressure aimed at elucidating the influence of solvent viscosity on the isomerization kinetics of the stilbene derivative (4) containing two four-membered rings (one CH_2 group each). According to model calculations, this derivative is essentially planar in the ground state and thus wellsuited to elucidate the role of single bond rotation during the double bond isomerization process.

2. Materials and methods

2.1. Synthesis of new compound

The title compound **4** was synthesized by reductive coupling of the corresponding ketone using low valent titanium species [19].

The McMurry reagent was prepared in the following way [20]: TiCl₄ (0.77 ml, 7 mmol) and subsequently zinc powder (1.33 g, 4 mmol) were carefully added at 0°C to anhydrous THF (75 ml). A solution of benzocyclobuten-1-one [21] (0.708 g, 6 mmol) in THF (25 ml) was added and the resulting black slurry was refluxed for 21 h. After cooling, the reaction mixture was quenched with K₂CO₃ (75 ml of a 10% aqueous solution). The mixture was extracted with diethylether (4 times with 50 ml each). The etheral phase was washed with H₂O, dried over $MgSO_4$, and the solvent evaporated in vacuo. The crude product (0.72 g) was purified by chromatography over silica gel (50 g eluent: *n*-hexane/acetone). Trans-4 and cis-4 (0.42 g, 22%) were obtained as a 1:1 mixture, as shown by GC/MS. A small amount of the mixture of isomers was separated by semipreparative HPL-chromatography: Gilson 350 apparatus with Merck LiChrospher columnn (RP18, particle size 5 μ m), elution with acetonitrile/water 2:1. Pure *trans*-4 was obtained by a modified purification scheme as white crystals; mp 181–183°C, MS: m/e = 204 (74, M⁺), 203 (100), 202 (97). 1 H – NMR (400 MHz, CDCl₃) δ = 3.80 (s, 4 H, 2-H), 7.11-7.33 ppm (ABCD-system, 2 m, 8 H). ¹³C-NMR (100.6 MHz, CDCl₃) $\delta = 145.03$, 144.86 (2s, C-2a, C-6a). 128.07, 127.52 (2s, C-3, C-4), 127.45 (s, C-1), 122.74 (s, C-5), 118.77 (s, C-6), 37.62 ppm (s, C-2). Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92. Found: C, 93.89; H, 6.30.

2.2. Fluorescence measurements

Fluorescence decay curves were recorded by means of a home-built time-correlated single photon counting apparatus using the frequency-doubled output of a cavity-dumped, synchronously-pumped rhodamine 6G dye laser ($t_p \sim 10$ ps, repetition rate 800 kHz)[22]. The fluorescence was dispersed by a Zeiss monochromator and detected by a channel plate multiplier (Fa. Kemnitz, Berlin, model ELDY EM1). In combination with coventional electronics (Tennelec / Ortec) a fwhm of the instrument response function of less than 100 ps was achieved. Data analysis was performed by the usual least-squares fitting procedure assuming a multi-exponential decay law. The high pressure optical cell was built according to a design provided to us by Dr. D. Schwarzer (Max-Planck Institut für Biophysikalische Chemie, Göttingen). It contains three windows at right angles and can be used for pressures up to 3.5 kbar. The sample region and pressure producer are separated by a transducer with the total sample volume being approximately 8 ml.

Stationary fluorescence spectra were recorded at the same excitation wavelength (308 nm) on a Perkin Elmer model LS50 spectrofluorimeter. Solvents were used as provided by the suppliers (*n*-hexane (Ferak), methylcyclohexane (Aldrich)). Solutions were freed of oxygen by bubbling argon through for an extended period of time.

3. Results and discussion

3.1. Stationary absorption and emission spectra

In Figs. 1 and 2, the UV/vis absorption and fluorescence spectra of 4 in *n*-hexane are compared to those of the parent *trans*-stilbene 1. It has been pointed out before [2] that those substitutions which constrain the twisting of the phenyl rings change the spectral features in the absorption spectra such that they become more similar to those observed for



Fig. 1. Comparison of UV/vis absorption spectra of *trans*-stilbene 1 (---) and the bridged derivative 4 (---) in *n*-hexane (for structures see Scheme 1).

trans-stilbene at low temperature in a highly viscous environment. Accordingly, the 0-0 transition appears more pronounced in **4** and the vibrational bands are better resolved. In the room temperature emission spectra, this distinction is conserved in the sense that the 0-0 transition is relatively stronger than in **1**. The fluorescence quantum yields of **4** are higher than those of the parent *trans*-stilbene [23], namely 0.06 versus 0.036 in hexane and 0.05 versus 0.016 in polar solvents.

Recently, Hohlneicher et al. [24] reported the fluorescence spectra of **4** matrix-isolated in argon at 15 K. They analyzed the low frequency modes in comparison with the Raman spectra and found that "the most striking difference with respect to the parent stilbene is the lack of pronounced progressions of low frequency a_g modes in the fused ring derivatives".

3.2. Time-resolved fluorescence measurements

As one may anticipate on the basis of the increase in fluorescence quantum yield, the fluorescence decay times of **4** at ambient temperature and pressure are found to be longer than those of *trans*-stilbene, namely 140 ps in *n*-hexane and 120 ps in methylcyclohexane. As in case of *trans*-stilbene, we find a second component in the fit of the decay curves exhibiting a life-time of about 1.6 ns (fairly independent of pressure and temperature). Since its relative amplitude increases with the length of the measure-



Fig. 2. Fluorescence spectra of *trans*-stilbene 1 (_____) and the bridged derivative 4 (____) in *n*-hexane ($\lambda_{ex} = 308$ nm).

ment (time of irradiation) we assign this component to an unidentified photoproduct. In case of transstilbene, it is well-known that the *cis*-isomer, either present from the very beginning or produced by photoinduced isomerization from the *trans*-isomer, can react via 9,10-dihydrophenanthrene to phenanthrene. The corresponding final products have also been postulated in case of photodegradation of the derivatives with aliphatic bridges [25]. Due to its low amplitude and the large difference in decay time, the presence of this additional component did not influence the result for the fluorescence decay time of the investigated compound. It should also be mentioned that no additional shorter lived component attributable to fluorescence from the *cis*-isomer could be detected.

The rate for isomerization, k_{iso} , is usually derived from the experimentally determined fluorescence decay times $\tau_{\rm F}$ via the relation:

$$k_{\rm iso} = 1/\tau_{\rm F} - k_{\rm r} - k_{\rm ISC} - k_{\rm IC} = 1/\tau_{\rm F} - k^0.$$
(1)

For the numerical evaluation of $k_{\rm iso}$ in *trans*-stilbene and derivatives it is assumed that the rate for internal conversion, $k_{\rm IC}$, can be neglected. The intersystem crossing rate, $k_{\rm ISC}$, was determined as approximately $3 \times 10^8 \text{ s}^{-1}$ [26] and is therefore of the same order of magnitude as the rate for radiative decay, $k_{\rm r}$. The latter is determined with the help of the fluorescence yield $\Phi_{\rm F}$ ($k_{\rm r} = \Phi_{\rm F}/\tau_{\rm F}$) and is assumed to be constant and independent of temperature and solvent viscosity (pressure). Several authors, e.g. Schröder [17] have chosen k^0 as $6.2 \times 10^8 \text{ s}^{-1}$ for *trans*-stil-



Fig. 3. Rate of excited state isomerization, $k_{\rm iso}$, as derived from pressure dependent fluorescence decay times (solvent: *n*-hexane). Solid lines represent a global fit using the parameters given in Table 1.

bene. In an analogous procedure, we have determined $k^0 = 3.6 \times 10^8 \text{ s}^{-1}$ for compound **4** and we will use this value independently of solvent (*n*-hexane or methylcyclohexane) and temperature or pressure.

Consequently, the rates for k_{iso} displayed in Figs. 3 and 4 are based on the equation:

$$k_{\rm iso} = 1/\tau_{\rm F} - 3.6 \times 10^8 [\rm s^{-1}] \,. \tag{2}$$

The necessary values of the solvent viscosity were determined from the published dependencies of η on pressure and temperature [27].



Fig. 4. Rate of excited state isomerization, k_{iso} , as derived from pressure dependent fluorescence decay times (solvent: methylcyclohexane). Solid lines represent a global fit using the parameters given in Table 1.

Inspection of Figs. 3 and 4 immediately reveals that the data points follow in the log/log plot of $k_{\rm iso}$ versus η an approximately linear dependence with slopes around 0.3 (*n*-hexane) and 0.15 (methyl-cyclohexane).

This qualitative finding suggests a (global) fit of the data by means of the generally accepted relationship:

$$k_{\rm iso} = F(\eta) \cdot \exp(-E_{\rm A}/RT) , \qquad (3)$$

with the viscosity dependent term $F(\eta)$ being approximated by a power law [28,29]:

$$F(\eta) = C \cdot (\eta/\mathrm{mPas})^{-a} \text{ with } 0 \leq a \leq 1.$$
 (4)

The solid lines in Figs. 3 and 4 represent the result of a global fit using the same values for a and E_{A} for all temperatures and viscosities. That such a global fit is possible in good quality is astonishing in view of the different results obtained by various groups for the parent *trans*-stilbene. Previous investigations at ambient pressure yielded slopes of a ~ 0.32 in higher alkanes [16,29–33] with viscosities ranging between 0.1 and 4 mPa s. From transient absorption measurements at variable pressure in *n*-hexane, Schröder [17] derived a temperature dependent slope rising from a = 0.29 (T = 298 K) to a = 0.46 (T =453 K). It must, however, be mentioned that the scatter in Schröder's data collected at the highest temperatures (398 and 453 K) is fairly large and consequently the values of the slopes at higher temperatures are subject to some uncertainty.

Sundström and Gillbro [31] probed the transstilbene isomerization kinetics by picosecond transient absorption spectroscopy in longer chain *n*-alkanes (n = 12, 14, 16). Their isoviscosity plot for $\eta =$ 1.64 mPa s yielded an intrinisic barrier for isomerization of only 10.1 kJ/mol. Courtney et al. [32] found an activation barrier of 15 kJ/mol in hexane. In contrast, Park and Waldeck [33] reported a value of about 18 kJ mol⁻¹ as average activation energy for hydrocarbon solvents (350 K < T < 278 K). They found an increase in activation energy with the length of the alkane chain, i.e. with increasing viscosity. The origin of the latter trend was commented as being opposite to that expected for a solvation effect. According to Schröder [7,17], the activation energy in *n*-hexane drops from 14.3 ($\eta = 0.33$ mPa s) to 11.8 kJ/mol ($\eta = 1.15$ mPa s). In methylcyclohexane, he found 12.1 kJ/mol ($\eta = 1.00$ mPa s) and 10.1 kJ/mol ($\eta = 10.0$ mPa s) thus pointing to the importance of the molecular structure and specific properties of the solvent.

If one wants to compare the results obtained in this work for the bridged compound 4 with the many, in part apparently contradictory results for *trans*-stilbene **1**, one should recall that the evaluation of the viscosity and temperature dependence of the isomerization rate as expressed in Eq. (3) is done by using different assumptions. We have chosen to evaluate our data with the minimum set of free fit parameters, i.e. temperature independent values for a and E_{A} (cf. Table 1). It is obvious that by allowing slightly temperature dependent slopes in the single curve fitting we would produce viscosity dependent activation energies from isoviscous Arrhenius plots. Thus, our fits demonstrate that in case of the bridged compound 4 the temperature effects on a and/or E_{A} must be so small that they do not show up at the level of accuracy of our experiment.

With these assumptions, we find that the activation energy of **4** is lower by about 0.3 kJ mol⁻¹ in methylcyclohexane than in *n*-hexane. This trend parallels the finding by Schröder for *trans*-stilbene and points to the importance of specific solute–solvent interactions for the magnitude of the activation barrier.

The small reduction of the activation barrier in 4 when compared to that given by Schröder for 1 (especially in *n*-hexane) is interesting in view of earlier discussions which proposed that the torsion around the single bond could facilitate isomerization around the double bond. On the other hand, in the derivative comprising the five-membered rings, 5, the thermal activation barrier is lowered even more, namely to only about 6.3 kJ mol⁻¹ [15–17]. Since in contrast to the latter compound, the rate for isomer-

Table 1

Parameters derived from a global fit of the pressure dependent rates of isomerization (Figs. 3 and 4) by Eqs. (3) and (4)

	<i>n</i> -hexane	Methylcyclohexane
$C(s^{-1})$	0.93×10^{12}	1.08×10^{12}
а	0.26	0.14
$E_{\rm A}$ (kJ mol ⁻¹)	12.8	12.5

ization is lower in **4** than in **1**, the pre-exponential factor must also be lower. For *trans*-stilbene, Courtney et al. [32] determined $C = 3.5 \times 10^{12} \text{ s}^{-1}$ with the corresponding a = 0.32. Our analysis yields $C = 0.93 \times 10^{12}$ (*n*-hexane) and 1.08×10^{12} (methyl-cyclohexane) (cf. Table 1).

If the value of the exponent a is taken as a measure for the friction effect, then isomerization of **4** is subject to similar interactions as *trans*-stilbene in *n*-hexane, but subject to stronger interaction in methylcyclohexane. Saltiel et al. [34] investigated the isomerization kinetics of trans-stilbene, trans-4.4'dimethylstilbene and trans-4.4'-dimethoxystilbene in a series of *n*-alkane solvents. Applying a viscosity dependent term as given by Eq. (4), the exponents a in that series of compounds decreased from 0.33 via 0.26 to 0.22 in contrast to the expectation of free volume theory. A possible explanation offered by these authors assumes a solvent and temperature dependence of the activation entropy. A solvent mediated entropy change could also possibly explain the differences in the pre-exponential factor of 4 in *n*-hexane and methylcyclohexane.

Before closing the discussion, it should be mentioned that the observed viscosity dependence of k_{iso} could not be fitted by the modified Kramers' expression

$$F(\eta) = A \cdot \left\{ \left[(\eta/B)^2 + 1 \right]^{1/2} - (\eta/B) \right\}, \qquad (5)$$

except if completely unreasonable parameters were used.

4. Summary

In order to learn more about the influence of torsion around the single bonds onto the excited state kinetics of *trans*-stilbene, a new derivative was synthesized in which the torsion around the single bond is hindered by a CH₂ bridge. The fluorescence decay times could be determined in *n*-hexane and methyl-cyclohexane at varying temperatures (283 K $\leq T \leq$ 343 K) and pressures (1 bar $\leq p \leq$ 3600 bar). The analysis of the rates of isomerization suggests that only the power law $F(\eta) = C \cdot \eta^{-a}$ is suited to fit all data points satisfactorily. From the global fits, one can conclude that E_A is slightly smaller in the

bridged compound **4** than in the parent *trans*-stilbene. Whereas for the latter E_A was found to decrease with solvent viscosity, it appeared to be viscosity independent in the derivative **4**. Fits applying Kramers' expression yielded unreasonable values for the barrier frequency ω_0 and too high activation energies E_A .

It has been speculated that a good agreement between Kramers' model and experimental data can be found in two types of cases: first, if the barrier is low enough that other degrees of freedom do not open up comparably efficient pathways. Second, if the isomerization is more clearly restricted to one dimension. Although the latter requirement should be (better) fulfilled in the bridged derivative 4, the simple Kramers' model does not yield a satisfactory description. In our high pressure studies of the harpooning mechanism of semiflexible bridged electron donor-acceptor systems, we found that a proper description of the friction effect on the large amplitude motion is possible by the term $(A/\eta)^{0.7}$ [35]. In contrast to the present results, the same exponent could be used for the fit of rate constants measured in *n*-hexane, *n*-octane and methylcyclohexane. This shows once more that general statements about the proper description of friction effects are impossible.

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References

- [1] H.A. Kramers, Physica 7 (1940) 284.
- [2] D.H. Waldeck, Chem. Rev. 91 (1991) 415.
- [3] H.F. Grote, J.T. Hynes, J. Chem. Phys. 73 (1980) 2715.
- [4] R.M. Anderton, J.F. Kauffman, Chem. Phys. Lett. 237 (1995) 145.
- [5] P. Hubbard, Phys. Rev. 131 (1963) 1155.
- [6] J. Schröder, J. Troe, P. Vöhringer, Z. Phys. Chem. 188 (1995) 287.

- [7] J. Schröder, Ber. Bunsenges. Phys. Chem. 95 (1991) 233.
- [8] R.F. Grote, J.T. Hynes, J. Chem. Phys. 74 (1981) 4465.
- [9] G. van der Zwan, J.T. Hynes, Chem. Phys. 90 (1984) 21.
- [10] B. Carmeli, A. Nitzan, Chem. Phys. Lett. 106 (1984) 329.
- [11] N. Agmon, R. Kosloff, J. Phys. Chem. 91 (1987) 1988.
- [12] J. Schröder, D. Scharzer, J. Troe, F. Voß, J. Chem. Phys. 93 (1990) 2393.
- [13] N.S. Park, D.H. Waldeck, Chem. Phys. Lett. 168 (1990) 379.
- [14] A.Z. Szarka, N. Pugliano, D.K. Palit, R.M. Hochstrasser, Chem. Phys. Lett. 240 (1995) 25.
- [15] J. Saltiel, J.T. D'Agostino, J. Am. Chem. Soc. 94 (1972) 6445.
- [16] G. Rothenberger, D.K. Negus, R.M. Hochstrasser, J. Chem. Phys. 79 (1983) 5360.
- [17] J. Schröder, Habilitationsschrift, Universität, Göttingen, 1991.
- [18] P. Lemmen, D. Lenoir, Chem. Ber. 117 (1984) 2300.
- [19] D. Lenoir, Synthesis (1989) 883.
- [20] J. McMurry, Chem. Rev. 89 (1989) 1513.
- [21] P. Schiess, M. Heitzmann, Angew. Chem., Int. Ed. Eng. 16 (469) (1977).
- [22] W. Jäger, Ph.D. Dissertation, Friedrich-Alexander-Universität, Erlangen, 1997.
- [23] S.L. Murov, J. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd edn., Marcel Dekker, New York, 1993.

- [24] G. Hohlneicher, I. Kautz, B. Tillmanns, D. Lenoir, R. Frank, J. Mol. Struct. 348 (1995) 191.
- [25] C.F. Mallory, F.B. Mallory, Org. React. 30 (1984) 1.
- [26] L.A. Brey, G.B. Schuster, H.G. Drickamer, J. Am. Chem. Soc. 101 (1979) 129.
- [27] D.W. Brazier, G.R. Freeman, Can. J. Photochem. 47 (1969) 893.
- [28] D. Gegiou, K.A. Muszkat, E. Fischer, J. Am. Chem. Soc. 90 (1968), 12, 3907.
- [29] G.R. Fleming, S.H. Courtney, M.W. Balk, J. Stat. Phys. 42 (1986) 83.
- [30] M. Lee, A.J. Bain, P.J. McCarthy, C.H. Ilan, J.N. Haseltine, A.B. Smith III, R.M. Hochstrasser, J. Chem. Phys. 85 (1986) 4341.
- [31] V. Sundström, T. Gillbro, Ber. Bunsenges. Phys. Chem. 89 (1985) 222.
- [32] S.H. Courtney, M.W. Balk, L.A. Philips, S.P. Webb, D. Yang, D.H. Levy, G.R. Fleming, J. Chem. Phys. 89 (1988) 6697.
- [33] N.S. Park, D.H. Waldeck, J. Chem. Phys. 91 (1989) 943.
- [34] J. Saltiel, A.S. Waller, D.F. Sears Jr., E.A. Hoburg, D.M. Zeglinski, D.H. Waldeck, J. Phys. Chem. 98 (1994) 10689.
- [35] S. Schneider, W. Jäger, J.W. Verhoeven, Chem. Phys. Lett. 270 (1997) 50.