

Photoisomerization dynamics of diphenylbutadiene in compressed liquid alkanes and in solid environment

Ch. Gehrke, R. Mohrschladt, J. Schroeder, J. Troe and P. Vöhringer

Institut für Physikalische Chemie der Universität Göttingen, Tammannstr. 6, W-3400 Göttingen, Germany

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The investigation of the pressure dependence of the S_1 photoisomerization of diphenylbutadiene in *n*-alkanes from ethane to *n*-dodecane allows us to differentiate between various models proposed to explain the observed viscosity dependence of the rate coefficient k_{iso} for twisting about one of the double bonds. For each solvent we observe a linear dependence of k_{iso} on the inverse of the solvent viscosity with a slope that increases with solvent size. Comparing this result with models for microscopic friction we find that the observed solvent size effect is significantly stronger than predicted. We conclude that a hydrodynamic description of frictional forces in terms of the zero frequency shear viscosity of the solvent is in agreement with the observed pressure and solvent dependence. We suggest, therefore, that the solvent size effect reflects variations in the shape of the reaction path with solvent that are possibly associated with the multidimensionality of the barrier crossing process. We also report nonradiative rate coefficients for DPB in solid solution.

1. Introduction

The photoisomerization of diphenylbutadiene (DPB) in the first electronically excited singlet state has – besides the corresponding reaction of trans-stilbene – attracted considerable interest as a model system for the study of solvent influence on chemical reaction rates. In particular, the applicability of Kramers' model [1] and its extensions [2–13] has been tested by investigating the dynamics of this reaction under a variety of damping conditions [14–19]. Our study of the pressure dependence in low viscosity supercritical and liquid solvents [20] showed that the variation of the rate coefficient throughout the entire density range extending from the dilute gas to the low viscosity liquid in alkane solvents can be adequately represented by a combination of unimolecular rate theory and the Smoluchowski limit of Kramers equation. The surprisingly strong temperature dependence of the rate coefficient found in the liquid solvent range was interpreted as a manifestation of the multidimensional character of the reaction barrier. Up to solvent shear viscosities of $\approx 10^{-3}$ Pa s (= 1 cP), no significant deviations from the Kramers–Smoluchowski prediction of the dependence of the

rate coefficient on solvent viscosity were apparent.

In this paper we study the pressure dependence at higher viscosities in a series of alkane solvents. As we have frequently pointed out [18,20–23], this approach offers the possibility to separate to a large extent specific solvent effects from dynamical transport effects that may be difficult to distinguish in experiments employing even homologous solvent series. In this sense our experiments complement the extensive fluorescence lifetime study of Fleming and co-workers, who mainly concentrated on the temperature dependence of the radiationless decay in *n*-alkanes [14] and alcohols [15]. In alkane solvents, they found that the observed viscosity dependence was not in accord with the predictions of Kramers equation, and they suggested that either a frequency dependence of the friction or a free volume effect in the liquid might lead to the observed fractional power dependence of the rate coefficient k_{iso} on viscosity [24],

$$k_{iso} \sim \eta^{-a} \quad \text{with } a=0.66. \quad (1)$$

In alcohols the measured rate coefficients were much higher than in the nonpolar environment, and their viscosity dependence could be fitted [24] with $a=0.92$, i.e. they were in the Smoluchowski limit.

This different behaviour in alcohols was attributed to a lowering of the barrier for internal double bond rotation in the S_1 state of DPB, causing a flatter barrier top than in alkanes. Because of its slower motion across the barrier top the system in this case would experience a constant, frequency independent friction.

It was of interest to us, whether the pressure dependence of the fluorescence lifetimes in alkane solvents would be consistent with this interpretation, or whether it would be necessary to consider a breakdown of the Stokes–Einstein relation [19] or a change of solvent influence on the potential energy surface for photoisomerization even within a homologous solvent series [18,25].

Finally, with the intention to carry the viscosity of the environment to extreme limits, we measured the S_1 lifetime of DPB in solid *n*-decane and in a PMMA-matrix at room temperature. In this way – by comparison with the fluorescence lifetimes in highly viscous liquid solvents – we wanted to get further information on the question how structural properties of the microscopic environment influence the photoisomerization dynamics.

2. Experimental

Fluorescence lifetimes of E,E-1,3-diphenylbutadiene (1.3) (trans-DPB) at room temperature ($T=295$ K) were determined by time-correlated single photon counting. Excitation light pulses at 308 nm from a frequency-doubled, synchronously pumped dye laser (Coherent model 702, pulse autocorrelation fwhm 1.4 ps) were used at the full repetition rate of 76 MHz. Fluorescence from the 7 kbar high pressure cell (Nova Swiss model 500.0301.1) was detected perpendicularly to the excitation beam in a “magic angle” arrangement [26].

The fluorescence photons were detected by a low noise, high gain photomultiplier tube (Valvo XP-2020 operated at 2.3 kV) wired according to ref. [27], whose output/pulses were fed into a CF discriminator (Canberra model CFD 2128). The discriminator signals provided the start pulses of the time-to-amplitude converter (TAC; Tennelec model TC 862), which was operated in reverse mode. Measurements were performed at a count rate of ≈ 40 –50 kHz. The

stop signals for the TAC were derived from the synch output of the ion laser mode-locker driver. The TAC output pulses were digitized by a fast PC-AT-based 12 bit A/D converter and stored in computer memory. The fwhm of the response function of the detection system as determined with Ludox scattering solution was 520 ps, its time resolution in conjunction with the high pressure fluorescence cell ≈ 100 ps.

For the analysis of the fluorescence decay histograms we used a convolution and fitting procedure [27] employing the Levenberg–Marquardt algorithm. As the time interval between subsequent excitation pulses was only about 13.2 ns, the fitting procedure was modified to account for the periodicity of the decay signal [28]. Fluorescence lifetimes measured at ambient pressure in a standard quartz fluorescence cell agreed to within 2% with literature data for the lifetime range from 150 ps to 2 ns, thus confirming the internal consistency of the fitting procedure. The data scatter obtained with the high pressure cell was slightly worse, amounting to $\approx 5\%$ at most.

Transient absorption measurements were carried out in a picosecond pump–probe arrangement with a time resolution of 3 ps using an excitation wavelength of 308 nm and a probe wavelength of 616 nm. These experiments were also performed under “magic angle” conditions [26]. The picosecond system has been described in detail elsewhere [20,22].

Solvents were of spectroscopic grade throughout, and DPB was obtained from Fluka (puriss., No. 236589). Further purification had no influence on the fluorescence lifetime signal. DPB-doped PMMA samples were prepared [29] by adding 0.5 g trans-DPB to 50 ml monomer methylmethacrylate solvent containing 17 mg α,α' -azoisobutyronitrile starter. Careful temperature control during polymerization (3 days at 45°C, one day each at 60°C and at 80°C, 1/2 day at 120°C) lead to samples that could be polished to high optical quality. The absorption spectra of the finished sample showed no signs of appreciable trans-DPB loss during the whole preparation procedure.

3. Results

The fluorescence decays obtained for DPB in al-

kane solvents were single exponential throughout the entire pressure range up to 7 kbar. The amplitude of a second decay component with a lifetime in the nanosecond range was of the order of 10^{-3} or less and considered not to be relevant for the S_1 decay of DPB. In table 1 we compare our lifetimes obtained at 1 bar pressure with fluorescence lifetime data from ref. [14] and the decay of the transient S_1 absorption measured in pump-probe experiments [20]. We also list the corresponding lifetimes in liquid ethane and *n*-butane at a pressure of 100 MPa. The agreement is quite satisfactory.

From the first-order decay rate constant $k_r = 1/\tau_r$ we obtained the overall nonradiative rate coefficient k_{nr} for the S_1 state of trans-DPB, $^1\text{DPB}^*$, by subtracting the radiative rate coefficient k_r :

$$k_{nr} = k_r - k_r. \quad (2)$$

The dependence of k_r on solvent polarizability was taken from ref. [14] as

$$k_r = [1.4f(n^2) + 0.43] \times 10^9 \text{ s}^{-1},$$

with $f(n^2) = (n^2 - 1)/(n^2 + 2)$, and n is the refractive index of the solvent. The pressure dependence of the solvent polarizability was calculated from the Clausius-Mosotti equation $f(n^2) = 4\pi[M]N_L\alpha_m/3$ ($[M]$ denotes solvent concentration, N_L Avogadro's constant, and α_m molecular polarizability), and from the pressure dependence of the solvent dielectric constant $\epsilon(p)$ where experimental data were avail-

able. As the dependence of k_r on solvent polarizability is fairly weak, both procedures led to practically identical results. Table 2 shows the pressure dependence of the lifetime τ_r and the nonradiative decay rate coefficient k_{nr} of $^1\text{DPB}^*$ in alkanes obtained from eq. (2). For *n*-octane, Velsko and Fleming [14] have also measured the pressure dependence of k_{nr} at 20°C. As shown in fig. 1, their values decrease slightly less than ours with increasing pressure. The reason for this discrepancy is not clear, but we note that we observe a similar pressure dependence in all alkane solvents from ethane to *n*-dodecane, irrespective of the experimental technique employed.

We also measured the fluorescence lifetime in *n*-decane at 298 K and a pressure of 320 MPa. Under these conditions the solvent solidifies, which leads to a noticeable increase of scattered light from the sample. We obtained a fluorescence lifetime of $\tau_r = 860$ ps, considerably shorter than $\tau_r = 940$ ps in liquid *n*-decane at $p = 260$ MPa. If we assume that the radiative lifetime in the solid environment is not significantly different from its value in compressed liquid *n*-decane, this corresponds to a nonradiative decay rate $k_{nr} = 3.3 \times 10^8 \text{ s}^{-1}$. In solid PMMA matrix at room temperature we measured the $^1\text{DPB}^*$ lifetime by pump-probe absorption spectroscopy to be $\tau_{S_1} = 1.0$ ns. This would correspond to a value of $k_{nr} \approx 1.5 \times 10^8 \text{ s}^{-1}$, if one extrapolates the polarizability dependence of k_r in alkanes to this more polar environment.

Table 1

S_1 lifetimes of DPB from fluorescence (τ_r) and transient absorption (τ_{S_1}) decay of DPB at 1 bar

Solvent	τ_r (ps)		τ_{S_1} (ps) ref. [20]
	this work	ref. [14]	
<i>n</i> -pentane	440	450	440
<i>n</i> -hexane	480	485	
<i>n</i> -octane	565	580	
<i>n</i> -nonane	605		
<i>n</i> -decane	660	630	
<i>n</i> -undecane	680	690	
<i>n</i> -dodecane	725	710	
ethane ^{a)}	416		385
<i>n</i> -butane ^{a)}	540		530

^{a)} $p = 100$ MPa.

4. Discussion

Our experiments in low viscosity alkanes [20] have shown that already for solvent viscosities greater than approximately 0.2 mPa s (= 0.2 cP) the rate coefficient k_{iso} for $^1\text{DPB}^*$ isomerization is well described by the Smoluchowski limit of Kramers equation [1,4,40]

$$k_{iso} = k_{\infty} \omega_B / \beta, \quad (3)$$

where k_{∞} is the thermal high pressure limiting isomerisation rate coefficient, ω_B a parameter describing the shape of the potential energy surface in the barrier region, and β the friction coefficient. Assuming that the potential energy surface does not change with solvent in the series of linear alkanes, β should

Table 2
 Fluorescence lifetimes τ_f and nonradiative rate coefficients k_{nr} of $^1\text{DPB}^*$ in compressed alkanes

	p (MPa)	τ_f (ps)	$f(n^2)$	$\eta^{d)}$ (mPa s)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	k_{nr} (10^9 s^{-1})
<i>n</i> -pentane	0.1	440	0.215 ^{a)}	0.23	5.2 ^{e)}	1.54
	80	574	0.237	0.42	3.5	0.98
	130	629	0.247	0.55	3.0	0.81
	154	660	0.250	0.62	2.6	0.74
	201	705	0.256	0.76	2.1	0.63
	241	742	0.260	0.91	1.7	0.56
	270	755	0.263	1.01	1.5	0.53
	330	804	0.268	1.26	1.1	0.44
	350	824	0.269	1.35	1.0	0.41
	390	839	0.272	1.55	0.85	0.39
	420	825	0.274	1.71	0.74	0.40
	500	835	0.278	2.22	0.51	0.38
	547	855	0.281	2.56	0.41	0.35
	<i>n</i> -hexane	0.1	480	0.228 ^{a)}	0.31	4.2 ^{e,f)}
25		537	0.234	0.38	3.3	1.11
50		576	0.240	0.47	2.8	0.97
75		595	0.245	0.55	2.5	0.91
100		634	0.249	0.66	2.2	0.80
125		682	0.254	0.76	1.9	0.69
150		698	0.258	0.88	1.7	0.64
190		730	0.262	1.07	1.5	0.57
232		758	0.266	1.30	1.2	0.52
300		790	0.272	1.74	0.87	0.46
378		820	0.278	2.36	0.59	0.40
446		848	0.282	3.05	0.43	0.36
492		858	0.285	3.61	0.34	0.34
<i>n</i> -octane		0.1	565	0.240 ^{b)}	0.51	
	80	704	0.256	0.92		0.63
	160	784	0.265	1.71		0.48
	240	852	0.272	2.88		0.37
	340	898	0.278	4.85		0.30
	413	933	0.282	6.82		0.25
	480	938	0.286	9.27		0.24
	501	940	0.288	10.2		0.24
	<i>n</i> -nonane	0.1	605	0.243 ^{b)}	0.67	
50		681	0.253	1.08		0.68
100		746	0.261	1.54		0.55
150		797	0.267	2.31		0.45
200		844	0.272	3.28		0.38
250		859	0.276	4.47		0.35
300		884	0.280	5.85		0.31
350		901	0.284	7.49		0.28
400		947	0.287	9.40		0.22
<i>n</i> -decane	0.1	660	0.248 ^{b)}	0.89	1.2 ^{e)}	0.74
	70	788	0.260	1.62	0.73	0.48
	130	871	0.267	2.70	0.48	0.35
	205	913	0.275	4.68	0.28	0.28
	260	939	0.280	6.55	0.19	0.24

Table 2 (Continued)

	p (MPa)	τ_r (ps)	$f(n^2)$	$\eta^d)$ (mPa s)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	k_{nr} (10^9 s^{-1})
<i>n</i> -undecane	0.1	680	0.249 ^{c)}	1.14		0.69
	60	799	0.261	1.94		0.46
	120	874	0.268	3.29		0.34
	180	943	0.272	5.25		0.25
	240	980	0.275	7.77		0.21
	310	1000	0.276	11.4		0.18
<i>n</i> -dodecane	0.1	725	0.253 ^{c)}	1.42		0.60
	50	838	0.263	2.23		0.40
	100	908	0.271	3.56		0.29
	160	953	0.278	5.84		0.23

a) Calculated from $\epsilon(p)$ [30]. b) Calculated from $\epsilon(p)$ [31].

c) Calculated from Clausius–Mosotti equation. d) Refs. [32–37].

e) Ref. [38], extrapolated for $p > 200$ MPa. f) Ref. [39].

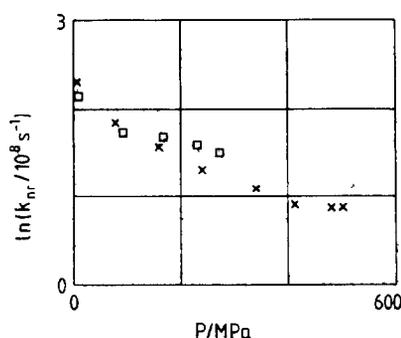


Fig. 1. Pressure dependence of the nonradiative rate coefficient k_{nr} of ¹DPB* in *n*-octane. (×). This work, (□) ref. [14].

be the only solvent dependent quantity in eq. (3). In the simplest approximation β is proportional to the zero frequency shear viscosity of the solvent, and the proportionality constant contains only solute parameters assumed independent of solvent and a constant factor determined by the hydrodynamic boundary condition. On the basis of this picture one expects that

$$k_{iso} = B\eta^{-1} \quad (4)$$

in contrast to the exponent -0.66 found experimentally in ref. [14].

In our experiments we find that within each individual solvent k_{nr} depends linearly on the inverse of the viscosity as illustrated in figs. 2–5. The slopes B_s and the intercepts k_{ic} obtained from fitting the experimental results for the different solvents are listed in

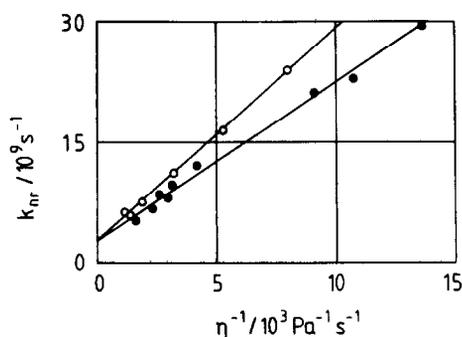


Fig. 2. Dependence of the nonradiative rate coefficient k_{nr} of ¹DPB* on the inverse of the solvent shear viscosity, $1/\eta_s$, in ethane (●) and propane (○) at $T = 298$ K. Solid lines are linear least-squares fits to the experimental data from ref. [20].

table 3 together with the correlation coefficients, which demonstrate that the linear relation

$$k_{nr} = B_s \eta^{-1} + k_{ic} \quad (5)$$

seems to give a very good description of the data. Only the values of k_{nr} in *n*-nonane yielded a slightly worse fit. While the values of B_s increase systematically with the alkane chainlength of the solvent by a factor of ≈ 3 on going from ethane to *n*-dodecane, the intercepts, which are non-zero, vary little from ethane to *n*-nonane and then drop off by a factor of ≈ 2 for the three highest alkane solvents employed. We also list the results of the linear correlation of k_{nr} with the solvent self-diffusion coefficient D , $k_{nr} = B'_s D$, for those

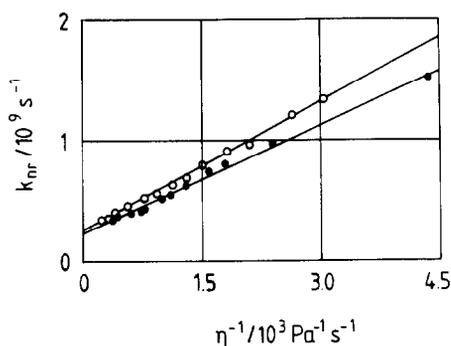


Fig. 3. Dependence of the nonradiative rate coefficient k_{nr} of $^1\text{DPB}^*$ on the inverse of the solvent shear viscosity, $1/\eta$, in *n*-pentane (●) and *n*-hexane (○) at $T=298$ K. Solid lines are linear least-squares fits to the experimental data.

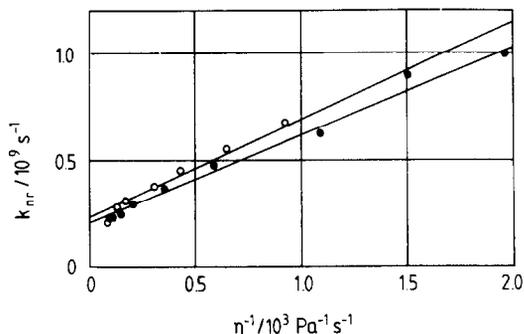


Fig. 4. Dependence of the nonradiative rate coefficient k_{nr} of $^1\text{DPB}^*$ on the inverse of the solvent shear viscosity, $1/\eta$, in *n*-octane (●) and *n*-nonane (○) at $T=298$ K. Solid lines are linear least-squares fits to the experimental data.

solvents where experimental self-diffusion data were available. The constants B_s and B'_s are connected by the relation $B_s/B'_s = \eta D$. The fits are of similar quality, and the intercepts are only insignificantly lower than those obtained from fitting to η^{-1} in view of the experimental accuracy.

The intercepts correspond to the rate coefficient of a nonradiative decay channel still open at “infinite” viscosity, which we attribute to $S_1 \rightarrow S_0$ internal conversion in the all-trans configuration. This assignment is in agreement with conclusions drawn from the temperature dependence of k_{nr} [14] and photoisomerization quantum yields [41,42]. Velsko and Fleming estimated a value of the internal conversion rate coefficient of $k_{ic} \approx 2 \times 10^8 \text{ s}^{-1}$. This compares very

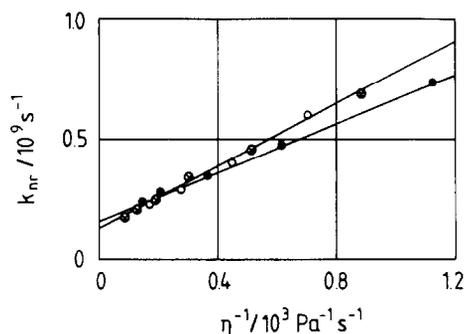


Fig. 5. Dependence of the nonradiative rate coefficient k_{nr} of $^1\text{DPB}^*$ on the inverse of the solvent shear viscosity, $1/\eta$, in *n*-decane (●), *n*-undecane (⊗), and *n*-dodecane (○). Solid lines are linear least-squares fits to the experimental data. (Within experimental uncertainty the rate coefficients k_{nr} in *n*-undecane and *n*-dodecane are fit by the same values of the coefficients k_{ic} and B_s .)

well with the average value from the intercepts in table 3 of $k_{ic} = (2.0 \pm 0.5) \times 10^8 \text{ s}^{-1}$. With this value of k_{ic} one arrives at a quantum yield of internal conversion of 10%, which is considerably lower than a value of 0.34 estimated on the basis of the trans-cis photoisomerization and fluorescence quantum yields in cyclohexane [42]. A reason for this discrepancy between the results from photostationary and time-resolved measurements could be that the usual assumption of equal partitioning from the excited singlet intermediate twisted configuration to the ground state trans-trans and cis-trans conformer does not hold for DPB. A partition ratio of 3 to 4 in favour of coming back to the trans ground state would bring the two observations into agreement. Uncertainties in estimating the pressure dependence of the radiative lifetime cannot account for the low internal conversion yields, as they probably do not exceed 30% [14,43–45]. They could be responsible, though, for the apparent solvent dependence of k_{ic} . Intersystem crossing only plays a very minor role in the decay of $^1\text{DPB}^*$ even at high viscosities [41].

Twisting around one of the double bonds is, therefore, a dominant nonradiative deactivation path even at high pressures. Its rate coefficient is inversely proportional to viscosity:

$$k_{iso} = k_{nr} - k_{ic} = B_s \eta^{-1}. \quad (6)$$

Fig. 6 shows that indeed all rate coefficients are fit

Table 3

Upper part: parameters obtained from a linear fit to the viscosity dependence of the nonradiative rate coefficients k_{nr} of ${}^1\text{DPB}^*$ in compressed alkanes. Lower part: fit parameters obtained by correlating with the solvent self-diffusion coefficient D

Solvent	$r^{a)}$	B_s (MPa)	k_{ic} (10^9 s^{-1})
ethane	0.994	0.20	0.26
propane	0.999	0.26	0.25
<i>n</i> -pentane	0.998	0.31	0.22
<i>n</i> -hexane	0.998	0.34	0.26
<i>n</i> -octane	0.997	0.40	0.21
<i>n</i> -nonane	0.992	0.46	0.23
<i>n</i> -decane	1.000	0.51	0.16
<i>n</i> -undecane	0.998	0.66	0.12
<i>n</i> -dodecane	0.998	0.66	0.12

Solvent	$r^{a)}$	B'_s (10^{18} m^{-2})	k_{ic} (10^9 s^{-1})
<i>n</i> -pentane	0.984	0.20	0.23
<i>n</i> -hexane	0.997	0.36	0.22
<i>n</i> -decane	0.997	0.50	0.13

^{a)} Linear correlation coefficient r .

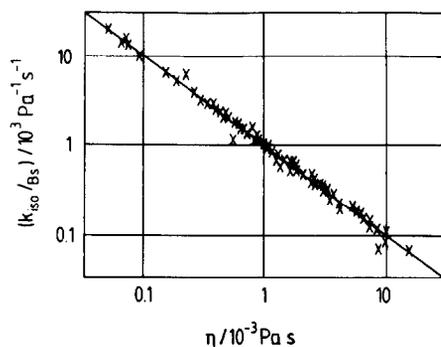


Fig. 6. Viscosity dependence of the solvent scaled rate coefficient k_{iso}/B_s (\times) for twisting about one of the double bonds in ${}^1\text{DPB}^*$ in *n*-alkane solvents from ethane to *n*-dodecane in the pressure range from 0.1 to 650 MPa at $T=298 \text{ K}$. The solid line represents $1/\eta$.

by the expression $k_{iso}/B_s = \eta^{-a}$ with $a=1$ and B_s a solvent dependent constant. This pressure independence of B_s immediately leads to three important conclusions:

(i) The viscosity dependence of the rate coefficient k_{iso} is adequately described by the Smoluchowski limit of the Kramers expression, eq. (3).

(ii) A frequency dependence of the friction coefficient seems to be of no significance for the photo-

isomerization dynamics, because k_{iso} correlates linearly with the zero frequency shear viscosity for each individual solvent.

(iii) Free space models of rotational diffusion [46,47], which would also be able to explain an exponent of $a < 1$ [14], are not consistent with the fact that B_s is independent of solvent pressure.

This behaviour seems to differ substantially from that found for trans-stilbene [48], where k_{iso} was not found to be linearly dependent on $1/\eta$ when the temperature was varied in a single solvent. In that case the rate coefficient could only be fit by Kramers equation when a frequency dependence of the friction was included.

In contrast, the pressure dependence of k_{iso} shows unequivocally that the fractional power dependence of the ${}^1\text{DPB}^*$ photoisomerization on solvent viscosity observed in alkane solvents at ambient pressure results from the solvent dependence of the constant B in eq. (4). Accepting eq. (3) as a valid representation of the rate coefficient k_{iso} , one has to discuss two possibilities to explain the solvent dependence of B :

(i) The hydrodynamic description of the rotational rearrangement in the excited state, relating the frictional drag experienced by the isomerizing DPB molecule to the solvent shear viscosity, is not valid.

This would imply that β no longer scales with solvent viscosity if one changes the solvent.

(ii) The potential energy surface for the reaction could change with solvent. This could affect the barrier height, leading to variations of k_∞ , as well as the effective shape of the barrier which is expressed in the parameter ω_B . This would also include effects due to the multidimensional character of the barrier crossing dynamics.

We first examine the validity of the hydrodynamic model. Based on Stokes' law for hydrodynamic motion of a particle in a continuous fluid, the Stokes-Einstein-Debye equation predicts a simple relation between the rotational relaxation time τ_R of a molecule in a liquid and the solvent viscosity:

$$\tau_R = \frac{1}{6D_{\text{rot}}} = \frac{V_h}{k_B T} \eta f_{\text{stick}} C + \tau_0, \quad (7)$$

where V_h is the hydrodynamic volume of the solute and D_{rot} its rotational diffusion coefficient in the solvent [47,49]. The correction factors f_{stick} and C have been introduced into eq. (7) to account for the non-spherical shape of the solute and the hydrodynamic boundary conditions varying from pure slip to stick, respectively. The constant τ_0 has been included to account for the nonzero intercept for vanishing viscosity found in many experiments. It has been attributed to the solute free rotor relaxation time [50]. Using slip boundary conditions and in the absence of specific solute-solvent interactions or dielectric friction, this hydrodynamic model has been found to hold for the reorientational relaxation times of a large number of even fairly small molecules, the viscosity being varied by changing solvents, temperature or pressure [49,51-54]. There have, however, been some cases where, even in presumably weakly interacting systems such as *p*-terphenyl [54], trans-stilbene [19,48,55], DPB [56] or all-trans-“stiff”-DPB (E,E-ditetrahydronaphthylidene ethane) [19] in *n*-alkanes and others [57-59], deviations from this linear behaviour have been observed when the viscosity was varied by changing solvents. The decrease of τ_R with increasing viscosity tended to saturate as the size of the solvent molecules became comparable to that of the solute. This size ratio effect was attributed to a breakdown of the hydrodynamic boundary condition. Attempts to introduce the microscopic structure of the solute-solvent boundary include models

that treat the effect of the finite size of the solvent molecule [60] and the free space between solvent molecules that allow the solute to rotate “freely” in periods of vanishing contact with the solvent [47]. Both models qualitatively predict the increasingly weaker viscosity dependence with increasing solvent size. From the free space model [47], in addition, one would also expect a similar effect on τ_R as the viscosity of a solvent increases with pressure. For *p*-terphenyl and all-trans-DPB, however, one finds a linear dependence of τ_R on viscosity in compressed *n*-alkane solvents [54,61]. This indicates that the solvent-to-solute size ratio is the more important factor in determining the deviation of the microscopic from the hydrodynamic friction.

A quantitative model for the solvent size effect in microscopic friction was first developed by Gierer and Wirtz [60] for stick boundary conditions and later extended by Dote, Kivelson, and Schwartz to incorporate a more general description of the boundary conditions [47]. In the latter formulation the constant C in eq. (7) becomes:

$$C = \sigma C_0, \quad (8)$$

with

$$\sigma = (1 + 6\sigma_r C_0)^{-1} \quad (9)$$

$$C_0 = \left(\frac{6\sigma_r}{(1 + 2\sigma_r)^4} + \frac{1}{(1 + 4\sigma_r)^3} \right)^{-1}. \quad (10)$$

Here σ_r is the solvent-to-solute ratio of the molecular radii. With these expressions inserted in eq. (7) deviations from the hydrodynamic description due to the solvent-size effect could be qualitatively accounted for [54,57].

If we model the motion of the twisting group in the photoisomerization of DPB as that of a sphere of hydrodynamic diameter σ_{ph} rotated at a distance r from a fixed axis, we obtain for “stick” boundary conditions [62]

$$\beta = \left(\frac{3\pi\sigma_{\text{ph}} r^2}{I_{\text{red}}} + \frac{\pi\sigma_{\text{ph}}^3}{I_{\text{ph}}} \right) \eta, \quad (11)$$

where I_{red} is the reduced moment of inertia for rotation around the double bond and I_{ph} is that for rotation of the phenyl group about its own axis. Applying the appropriate correction factors f_{stick} (for the non-spherical shape of the rotating group) and C (for mi-

crossopic friction) to the rotational term in eq. (11) and correcting the translational part according to Gierer and Wirtz [60] by a factor

$$f_{tr} \approx \left(1.5\sigma_r + \frac{1}{1+\sigma_r} \right)^{-1}, \quad (12)$$

one obtains

$$\beta = \left(f_{tr} \frac{3\pi\sigma_{ph} r^2}{I_{red}} + C f_{stick} \frac{\pi\sigma_{ph}^3}{I_{ph}} \right) \eta. \quad (13)$$

We inserted this expression into eq. (3), calculated a slope B_{calc} of k_{iso} versus $1/\eta$ for each solvent and compared it with the values B_s , obtained from the pressure dependence. The parameters used are given in table 4. (The value of ω_B was adjusted to give $B_{calc} = B_s$ in ethane.) Fig. 7 shows that B_{calc} increases much less with solvent hard sphere diameter σ_s than B_s . The same holds, if we use the microfriction factors empirically estimated from translational diffusion coefficients of toluene in *n*-alkanes, as recently proposed by Sun and Saltiel [65]. Qualitatively, the two methods give very similar results, only the friction coefficients β obtained from the empirical relation are about a factor of three lower due to the neglect of rotational friction. (As Sun and Saltiel are

Table 4
Parameters used for the calculation of B_{calc}

k_{∞} ($T=298$ K; $E_0=850$ cm ⁻¹) = 2.2×10^{10} s ^{-1 a)}		
$\sigma_{ph} = 0.37$ nm	$r = 0.25$ nm	
$I_{ph} = 0.71 \times 10^{-37}$ g cm ²	$I_{red} = 1.5 \times 10^{-37}$ g cm ²	
$\rho_{ph} = 7$ b)		
$f_{stick} = 3.06$ c)		
	σ_{hs} d) (nm)	τ_R e) (ps)
ethane	0.4240	8
propane	0.4773	10
<i>n</i> -pentane	0.5575	15
<i>n</i> -hexane	0.5959	20
<i>n</i> -octane	0.6550	
<i>n</i> -nonane	0.6802	
<i>n</i> -decane	0.705 f)	
<i>n</i> -undecane	0.729 f)	
<i>n</i> -dodecane	0.7529	

a) Ref. [20]. b) Axial ratio for phenyl ring. c) Ref. [63].

d) Hard sphere diameters of alkane solvents; ref. [64].

e) Rotational relaxation times of ¹DBP⁺; ref. [60].

f) Interpolated values.

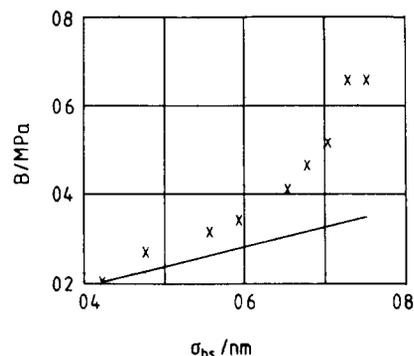


Fig. 7. Comparison of observed and calculated slopes, B_s (\times) and B_{calc} (solid line), as a function of solvent hard sphere diameter σ_{hs} . Values for B_{calc} were calculated by using microfriction factors estimated from the Gierer–Wirtz model [47,60], eqs. (8)–(13) (see text).

implicitly using the “stick” limit, it is surprising that they do not take into account the rotational motion of the phenyl ring about its own axis [62].)

An alternative approach would be to estimate β from the rotational relaxation times. It was first suggested by Velsko et al. in their study of the isomerization of the dye molecule DODCI [66] that there might be an intimate connection between microviscosity effects on rotational relaxation and on the motion along the reaction coordinate in photoisomerization. They used the Hubbard relation [67] to extract a friction coefficient β_R from the rotational relaxation times that was inserted into Kramers equation (eq. (3)). Whereas in the case of DODCI rotational relaxation times obeyed the purely hydrodynamic description and there was no improvement in fitting the Kramers equation to the isomerization rate coefficients observed in a series of alkane solvents, for trans-stilbene [19,48,55] and trans-“stiff”-DPB [19] the data could be fit successfully by employing the friction coefficients derived from rotational relaxation times. If we estimate β_R from τ_R values measured for “stiff”-DPB [19] and DPB [61] in alkanes, we obtain the values of B_{calc} shown in fig. 8. Clearly not even the correct trend of B_s is reproduced. This is not such a great surprise if one considers the viscosity dependence of τ_R for DPB in compressed alkanes from ethane to *n*-hexane [61]: there is no departure from a simple inverse viscosity dependence in this range of solvents that would indi-

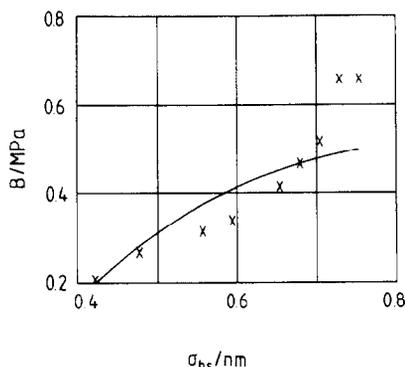


Fig. 8. Comparison of observed and calculated slopes, B_s (\times) and B_{calc} (solid line), as a function of solvent hard sphere diameter σ_{hs} . Values for B_{calc} were obtained by estimating friction coefficients from measured rotational relaxation times of $^1\text{DPB}^*$ [61] and "stiff"- $^1\text{DPB}^*$ [19] (see text).

cate a breakdown of hydrodynamic behaviour whereas already for these small alkanes there is a marked change of B_s with solvent.

Concerning the importance of deviations from hydrodynamic friction models, we can therefore draw two conclusions:

(i) If microscopic friction plays a role in the motion of the isomerizing group, it does not correlate with the friction parameter inferred from overall rotational relaxation of DPB in alkanes. A similar observation was made for trans-stilbene in alkanes [48].

(ii) The solvent size effect as predicted by the Gierer-Wirtz model and its extensions may contribute, but is too small to account quantitatively for the change of B_s with solvent. As no comparable effect is observed for rotational relaxation experiments, one may suspect that deviations from hydrodynamic behaviour play an even minor role.

Assuming that frictional effects are on the whole correctly described by the solvent zero frequency shear viscosity, we are led to the conclusion that solvent effects on the potential energy surface are responsible for the variation of B_s with solvent. As we found in our low density experiments [20] a constant barrier height E_0 in ethane, propane, and *n*-butane, we suggest that, to a first approximation, E_0 remains unchanged also in the other alkane solvents employed here. (From the RRKM analysis of microscopic rate coefficients for DPB photoisomerization [20,68] one may estimate that a decrease of E_0 by

$\approx 25\%$ from ethane to *n*-dodecane would account for the solvent dependence of B_s .) In our model, the solvent dependence of the potential energy surface would then appear as a solvent induced variation of the parameter ω_B . Fig. 9 shows that the fitted values of ω_B , as a function of solvent size, only need to vary by a factor of ≈ 3 to account for the changes in B_s . In view of the strong temperature dependence of ω_B arising from the multidimensionality of the barrier crossing dynamics [20], this comparatively small effect could also be understood as a manifestation of multidimensional Kramers behaviour. This possibility will be discussed in more detail in conjunction with complementary experiments on trans-stilbene [69].

The values of k_{nr} in solid environment give us some hints regarding the microscopic structure experienced by the twisting phenyl group in $^1\text{DPB}^*$. In PMMA we found $k_{\text{nr}} \approx k_{\text{ic}}$, so apparently there is no

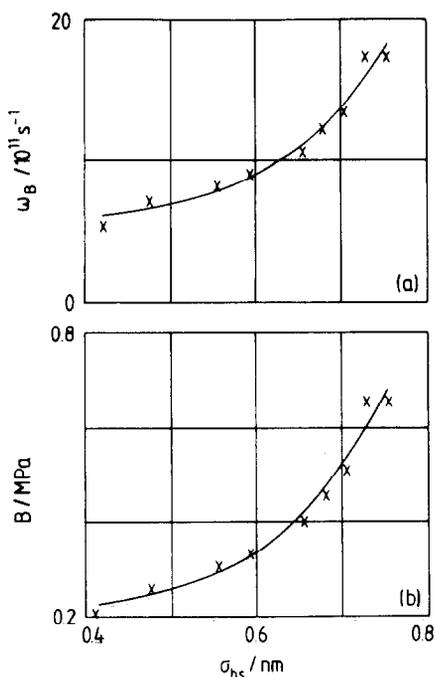


Fig. 9. (a) ω_B values calculated from experimental slopes B_s as a function of solvent hard sphere diameter σ_{hs} . The solid line represents a fit of these values to σ_{hs}^6 . (b) Comparison of observed and calculated slopes, B_s (\times) and B_{calc} (solid line), as a function of solvent hard sphere diameter σ_{hs} . Values for B_{calc} were calculated by using the hydrodynamic friction coefficients and the fitted ω_B values.

“space” for the molecule to isomerize, the strongly interacting solvent holds it in place. In solid *n*-decane, however, $k_{nr} \approx 2k_{ic}$, and there is room enough in the weakly interacting solid solvent to permit the molecule to twist even more rapidly than in liquid *n*-decane at the same temperature and lower pressure. Clearly, more experiments are needed to substantiate the conclusion that there are apparently more holes in solid than in liquid *n*-decane for DPB to photoisomerize in.

5. Conclusion

The investigation of the pressure dependence of ¹DPB* photoisomerization allows us to differentiate between various models proposed to explain the observed viscosity dependence of the rate coefficient k_{iso} for twisting about one of the double bonds. The main result is that for each solvent we observe a linear dependence of k_{iso} on $1/\eta$. However, the slope B_s varies with solvent. From the analysis of the data we conclude that (i) there is no evidence for frequency dependent friction having an influence on the rate coefficients, (ii) a hydrodynamic description of frictional forces on the whole seems to be sufficient, though a solvent size effect as described by the Gierer–Wirtz model may contribute to a minor extent, and (iii) solvent effects on the potential energy surface seem to play the major role in changing B_s with solvent. Whether the latter effect is associated with the multidimensionality of the barrier crossing process remains to be clarified in future experiments.

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