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Barrier crossing and solvation dynamics in polar solvents: Photoisomerization of *trans*-stilbene and *E,E*-diphenylbutadiene in compressed alkanols

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The viscosity dependence of the photoisomerization of *trans*-stilbene in compressed liquid ethanol shows deviations from a simple power law description in the viscosity range from 1 to 4 mPa s. Corresponding deviations are observed in the solvents methanol, *n*-propanol, and *n*-butanol. This behavior is attributed to a competition between solvent relaxation and barrier crossing in the S_1 state of *trans*-stilbene. The relative time scales of barrier crossing and solvent relaxation change as the pressure increases, because the dielectric relaxation rate of the solvent decreases more rapidly with increasing viscosity than the barrier crossing rate. Consequently, the reaction takes place in an increasingly retarded solvent environment which no longer relaxes completely around the changing charge distribution of the solute along its reaction path, giving rise to "dielectric friction." In contrast to *trans*-stilbene, the corresponding reaction of diphenylbutadiene in *n*-alkanols shows a much weaker sensitivity to solute-solvent interaction and, consequently, a simple inverse viscosity dependence of the photoisomerization rate is observed in all alkanols such as described by the Kramers-Smoluchowski theory. This significant difference is probably caused by smaller sudden polarization effects along the reaction path in diphenylbutadiene. The observed dependence of the *trans*-stilbene barrier crossing rate on pressure is compared either to a model with density dependent effective barrier height, or to a simple continuum model of the frequency dependence of the dielectric friction in the limit of weak coupling. Neither model works well unless a very strong viscosity dependence of the dielectric relaxation time of the solvent ($\tau_D \propto \eta^{10}$) is employed to obtain agreement with the observed viscosity dependence of the barrier crossing rate.

I. INTRODUCTION

The photoinduced *cis-trans* isomerization of ethylenic double bonds is a prototype for a large class of processes of biological and practical importance. A model reaction of this kind, which has been studied thoroughly under a great variety of physical conditions, is the S_1 photoisomerization of diphenylpolyenes, in particular, that of *trans*-stilbene¹⁻²¹ and *trans-trans*-1,4-diphenyl-(1,3)-butadiene (DPB).²²⁻²⁵ In many investigations, the influence of solvent friction on these barrier crossing processes has been of main interest.^{2-18,22-24} In particular, the observation of a weak dependence of the barrier crossing rate coefficient k for *trans*-stilbene² and DPB (Ref. 22) on solvent viscosity η in

n-alkanes, following a relation $k \sim \eta^{-\alpha}$ with $\alpha < 1$, has been interpreted in different ways: It was suggested that it is caused by the frequency dependence of the friction coefficient,²⁶ the multidimensional topology of the potential energy surface in the barrier region,²⁷ or by microviscosity effects, i.e., the breakdown of the Stokes-Einstein relation^{9,10} between diffusion coefficients along the reaction path and the medium viscosity.

In general, the effective potential energy surface on which the reaction occurs was assumed to be solvent independent. However, a systematic investigation of the pressure and temperature dependences of the rate coefficient for *trans*-stilbene in *single n*-alkane solvents has shown that the assumption of a constant potential of mean force throughout a homologous solvent series is only a crude approximation.²⁸⁻³⁴ It seems more realistic to assume that the effective barrier to ethylenic bond rotation decreases as the polarizability of the surrounding medium increases. Accounting for this solvent-induced "barrier shift" in a simple

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ad hoc manner, the pressure and temperature dependencies of the rate coefficients could be represented satisfactorily by a combination of Kramers' frictional model with unimolecular rate theory^{33,34} without the need of postulating a breakdown of either the Markovian assumption underlying Kramers' model or the Stokes–Einstein relation.

The latter interpretation receives further support by the observation that the corresponding reaction rates of DPB show a strictly linear dependence on $1/\eta$, if one changes the solvent viscosity by varying the pressure in *single n*-alkane solvents.³⁵ Apparently, the potential energy surface in this case is less sensitive to changes in the electronic environment, and the traditional Kramers–Smoluchowski behavior is recovered. The apparently weaker dependence on viscosity observed in homologous solvent series under ambient pressure,^{21,22} therefore, has to be attributed to a solute–solvent interaction which is solvent dependent. In pressure studies, this leads to solvent dependent slopes of the plots of k vs $1/\eta$. Similar results were obtained for the significantly faster reaction of *cis*-stilbene³⁶ and also for the rate of double bond rotation in tetraphenylethylene.³⁷

In polar solvents, the observed activation energies for *trans*-stilbene photoisomerization are significantly lower than in nonpolar solvents, which is attributed to a much lower effective potential energy barrier in the S_1 state.^{1,3,7,11,16,21} This strong solvent polarity effect could be related to a significant charge separation upon twisting around the double bond in the S_1 state.³⁸ Consequently, the dipole moment of the molecule would change significantly on its way from the planar S_1 equilibrium geometry through the barrier region to the perpendicular conformation of the “phantom” state. Direct experimental evidence for such an effect is difficult to obtain. Recently, however, strong support was provided for the formation of a zwitterionic excited state of tetraphenylethylene.^{39–41} A recent systematic study of the pressure and temperature dependence of *trans*-stilbene photoisomerization in *n*-alcohols⁴² showed that an equivalent picture might also apply to the case of *trans*-stilbene as long as the relaxation of the solvation shell of the molecules along the reaction path is significantly faster than the reactive motion through the barrier region. We concluded that a barrier shift comparable to that observed in alkane solvents occurs also in liquid alkanols, resulting in a similarly weak viscosity dependence of the reaction rates. This can be understood, if the dipolar character of the *trans*-stilbene S_1 excited state increases along the reaction path.

The dynamics becomes more complicated when the time scales of photoisomerization and relaxation of the solvent shell in the excited state begin to overlap such that the reaction has to be considered as a process proceeding on a partially relaxed effective potential energy surface. This conclusion could be drawn from the experiments of Hicks *et al.*¹¹ and Kim *et al.*¹² on the temperature dependence of *trans*-stilbene photoisomerization rates in different *n*-alcohol solutions at 1 bar. The authors concluded that incomplete solvent relaxation of the initially prepared Franck–Condon state in the longer chain alcohols was responsible for the apparent decrease of the potential barrier height in the more viscous alcohols. Furthermore, Kim *et al.* suggested that high fre-

quency components of the solvent dielectric response cause an additional stabilization of the transition state in all alcohol solvents. Thus, to a certain extent, the photoisomerization of *trans*-stilbene can be considered as a model reaction which is sensitive to a loss of solvent synchronism along the reaction path.⁴³ Theoreticians have studied model Hamiltonians describing the influence of the resulting dielectric friction on reaction dynamics,^{44–62} which may be compared with the results of molecular dynamics simulations.^{63,64} While experimental manifestations of this coupling between reaction and solvation dynamics in polar solvents are rare for the type of reaction we are considering here, they are abundant for electron transfer reactions and excited state charge transfer processes where the reaction path is determined by the solvent coordinate, i.e., by the coupling of the electronic states to the nuclear motion of the medium.^{65,66} The nature of this coupling was discussed by comparing excited state electron or charge transfer rates with solvation times obtained from time-resolved fluorescence Stokes-shift measurements^{65,67–69} or ground state electron exchange reaction rates with longitudinal dielectric relaxation times in different solvents.^{70–72}

In the present article, we report results on the pressure dependence in *single* alcohol solvents which show a clear indication for the lack of solvent synchronism in the photoisomerization of *trans*-stilbene. By varying the pressure in a *single solvent*, one can sweep over a wide range of relative time scales, from $1 < k\tau_D$ to $k\tau_D < 1$, where k is the reaction rate coefficient and τ_D the dielectric relaxation time of the solvent. If k was proportional to $1/\eta$ and τ_D to η , this would not be possible. However, in the present case the dielectric relaxation time shows a stronger dependence on solvent viscosity than the reaction rate^{73,74} such that changes of $k\tau_D$ in a single solvent can be realized by pressure variation. As the pressure increases, the solvent eventually starts to lag behind the intramolecular motion along the reaction path such that the apparent viscosity dependence of the reaction rate changes. This phenomenon becomes even more evident, if one compares the pressure dependencies of the reaction rates for *trans*-stilbene and DPB in the same solvent, as in the latter molecule, the extent of charge separation upon twisting around one of the double bonds in the S_1 state appears to be much smaller than in *trans*-stilbene.³⁸ This already led to different *solvent* dependencies of the reaction rates for DPB in polar media which show a significantly stronger dependence on solvent viscosity at 1 bar than for *trans*-stilbene.^{21,23} In the present experiments using variable pressure in *single* solvents, the difference between DPB and *trans*-stilbene is shown to be even more pronounced.

II. EXPERIMENTAL TECHNIQUE

Our picosecond pump–probe spectrometer was described in detail earlier.^{29,31,75,76} The laser system consisted of a hybridly modelocked dye laser pumped by a frequency-doubled, actively modelocked Nd:YLF laser. The dye laser pulses were amplified in a four stage Nd:YAG laser-pumped dye amplifier. UV pump pulses were generated by frequency doubling these amplified pulses to 308 nm, and subsequent reamplification in an XeCl* excimer module. The response function of our apparatus was 1 ps full width at half maxi-

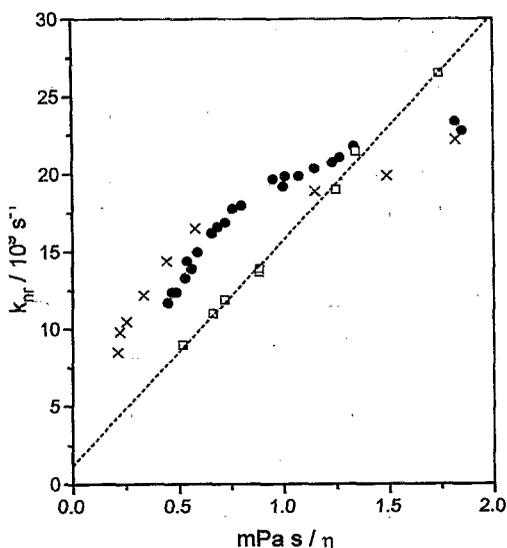


FIG. 1. Nonradiative decay rate coefficients for the S_1 state of *trans*-stilbene and diphenylbutadiene as a function of inverse solvent viscosity η in methanol at 298 K. (\square , diphenylbutadiene, this work; \bullet , *trans*-stilbene, this work; \times , *trans*-stilbene, calculated from Ref. 19. The dashed line represents a linear fit to the rate constants for diphenylbutadiene.)

mum (FWHM) with energies of the pump and probe pulses of 0.3 and 0.05 mJ, respectively. In order to eliminate effects of overall rotational relaxation, the relative orientation of the planes of polarization of the probe and the pump beam was adjusted with a zero-order half-wave plate. Experiments were done with *trans*-stilbene in alcohols from methanol to *n*-butanol and with DPB in alcohols from methanol to *n*-pentanol.

Some rate coefficients for DPB photoisomerization in ethanol to *n*-pentanol were also obtained from fluorescence lifetimes, measured by time-correlated single photon counting using the apparatus and fitting procedures described previously.³⁵ Excitation light pulses were taken from the synchronously pumped dye laser, whose output was frequency doubled, and detected by a XP-2020 photomultiplier tube. The FWHM of the system response function in this second experimental setup was 520 ps. Solvents used were of spectroscopic grade (Merck), DPB was used as supplied (Fluka, puriss., No. 236589), and *trans*-stilbene (Fluka, purum, No. 85870) was recrystallized twice from methanol.

III. RESULTS

Within our time resolution of 1 ps, none of the recorded transient absorption and fluorescence signals showed any significant deviation from monoexponential decay laws. Decay constants obtained from pump-probe experiments agreed within the experimental error of $\pm 5\%$ with those measured by time-correlated single photon counting. The nonradiative rate coefficients k_{nr} were calculated from the first order decay rate coefficients k_{exp} by subtracting the radiative rate constant k_r , which, for *trans*-stilbene, can be estimated from $k_r = [0.72 f(n^2) + 0.37] \times 10^9 \text{ s}^{-1}$ (taking lifetime and quantum yield data from Refs: 19, 77, and 78), and,

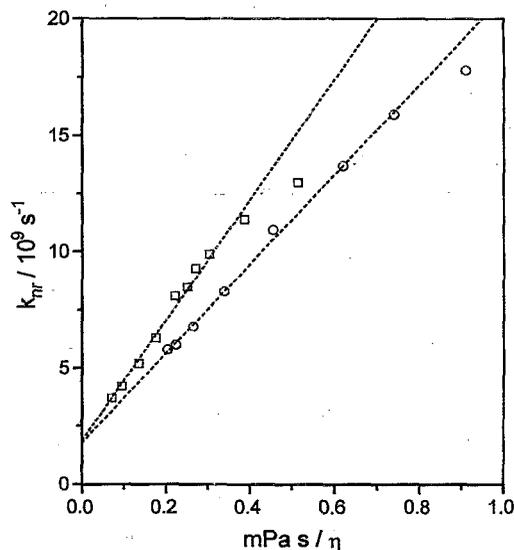


FIG. 2. Nonradiative decay rate coefficients for the S_1 state of diphenylbutadiene as a function of inverse solvent viscosity η in ethanol (\circ) and *n*-propanol (\square) at 298 K. (The dashed lines represent linear fits to the data, disregarding the values obtained at the lowest viscosities, see the text.)

for DPB,²² is calculated from $k_r = [1.4f(n^2) + 0.43] \times 10^9 \text{ s}^{-1}$ with $f(n^2) = [n^2 - 1]/[n^2 + 2]$ (n is the refractive index of the solvent). In Fig. 1 we compare the resulting values of $k_{nr} = k_{exp} - k_r$ at 298 K as a function of $1/\eta$ in methanol for *trans*-stilbene and DPB. (Interpolated viscosities in our experience are accurate to within 4%.) We have also included earlier measurements by Drickamer's group¹⁹ for *trans*-stilbene by calculating nonradiative rate coeffi-

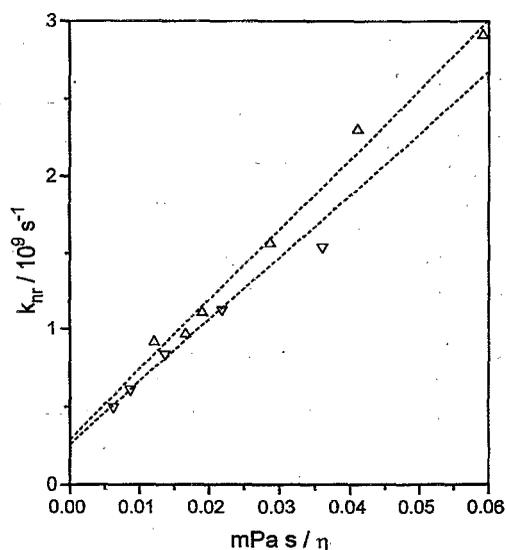


FIG. 3. Nonradiative decay rate coefficients for the S_1 state of diphenylbutadiene as a function of inverse solvent viscosity η in *n*-butanol (Δ) and *n*-pentanol (∇) at 298 K. (The dashed lines represent linear fits to the data, disregarding the values obtained at the lowest viscosities, see the text.)

lients from their pressure dependent fluorescence quantum yields. Considering that the two sets of rates were obtained by different experimental techniques and with twelve years between them, the agreement is surprisingly good, the largest discrepancy being 15%. Our results at ambient pressure also agree to within a few percent with earlier measurements taken under the same experimental conditions.^{3,7,11,16,22,23}

It is evident from Fig. 1 that the nonradiative decay rate constant, for DPB, in methanol is inversely proportional to solvent viscosity while, for *trans*-stilbene, one observes a strongly nonlinear dependence. The picture is analogous to the rate constants for DPB and *trans*-stilbene in *n*-hexane.^{33–35} As we suggested recently,^{28,33,34,42} the nonlinear dependence in the case of *trans*-stilbene is an indication of a decrease of the potential barrier height with increasing solvent density in *n*-alkane as well as in *n*-alkanol solvents. For DPB in *n*-alkanols we observe no such effects, in accordance with our results in compressed alkane solvents.³⁵

A. Results for diphenylbutadiene

The linear extrapolation of the rate constants for DPB to infinite viscosity ($1/\eta=0$) in methanol gives a nonzero intercept $k_{ic}=(1.2\pm 0.4)\times 10^9\text{ s}^{-1}$. In ethanol to *n*-pentanol the rate constants for DPB are also mostly linear in $1/\eta$ as shown in Figs. 2 and 3. Extrapolation to $1/\eta=0$ in ethanol and *n*-propanol yields $k_{ic}=(1.8\pm 0.1)\times 10^9\text{ s}^{-1}$. These intercepts probably correspond to a pressure independent $S_1\rightarrow S_0$ internal conversion in the *all-trans* conformation of DPB. In methanol to *n*-propanol k_{ic} values are in rough agreement with a value of $k_{ic}=1.2\times 10^9\text{ s}^{-1}$ estimated from the fluorescence quantum yield of DPB in ethanol at 77 K.⁷⁹ In the longer chain *n*-alcohols internal conversion apparently is much slower, with rate constants $k_{ic}=(0.30\pm 0.09)\times 10^9\text{ s}^{-1}$ in *n*-butanol and $k_{ic}=(0.26\pm 0.03)\times 10^9\text{ s}^{-1}$ in *n*-pentanol. These values are similar in magnitude to those obtained in nonpolar solvents,³⁵ while in methanol to *n*-propanol, k_{ic} is an order of magnitude larger than in alkane solvents.^{22,35} This polarity effect on the internal conversion rates could be caused by a change in the energy gap between the two lowest electronically excited singlet states of DPB, the 1A_g state and the 1B_u state.

Table I summarizes our results of k_{nr} values for the photoisomerization of DPB in various solvents at varying pressures. The slopes B_s of the plots of k_{nr} vs $1/\eta$, defined by

$$k_{nr}=B_s/\eta+k_{ic}, \quad (1)$$

increase with the molecular size of the solvent. This was also noted in our pressure dependence studies in *n*-alkane solvents and tentatively attributed to solvent-specific changes in the topology of the potential energy surface in the barrier region. The values of B_s in alcohols, however, are about a factor of 50 higher, on average, than in alkanes, ranging from (14.7 ± 0.4) MPa in methanol to (45 ± 3) MPa in *n*-butanol. Table II summarizes B_s values for DPB in the series of alkanes and of alcohols. Also included in Table II are values of the exponents α of a $k\propto\eta^{-\alpha}$ representation obtained from linear fits to the double logarithmic plots of $k=k_{nr}-k_{ic}$ vs η

TABLE I. Pressure dependence of nonradiative decay rate coefficients k_{nr} of the S_1 state of diphenylbutadiene in liquid alcohols at 298 K. Viscosities: interpolated data from Ref. 93.

Solvent	p (MPa)	η (mPa s)	k_{nr} (10^9 s^{-1})	
Methanol	0.10	0.57	26.5	
	75	0.75	21.5	
	95	0.80	19.0	
	220	1.13	13.8	
	375	1.52	11.0	
	485	1.90	9.0	
	Ethanol	0.10	1.10	17.8
		40	1.35	15.9
		85	1.61	13.7
		155	2.11	11.0
265		2.94	8.3	
345		3.75	6.8	
400		4.45	6.0	
<i>n</i> -propanol	0.10	1.94	13.0	
	32	2.58	11.4	
	73	3.29	9.9	
	95	3.69	9.3	
	115	3.96	8.5	
	140	4.50	8.1	
	190	5.65	6.3	
<i>n</i> -butanol	0.10	2.82	10.5	
	4.0	2.70	10.2	
	47	3.85	9.4	
	93	5.11	8.1	
	170	7.60	5.7	
	250	11.2	3.6	
	350	16.9	2.9	
<i>n</i> -pentanol	0.10	3.87	6.4	
	100	8.49	3.6	
	200	16.0	2.2	
	300	27.7	1.54	
	400	45.7	1.13	
	500	73.3	0.84	
	600	115	0.61	
675	159	0.50		

shown in Figs. 5–8. The overall inverse proportionality of k to η for DPB in alkanol solvents in Fig. 4 is illustrated by a plot of $\log(k/B_s)$ vs $\log \eta$.

B. Results for *trans*-stilbene

In methanol, internal conversion and intersystem crossing rates are small in comparison to the barrier crossing rate coefficient k for both DPB and *trans*-stilbene,¹⁹ such that $k\cong k_{nr}$. We, therefore, can represent the results of Fig. 1 in the double logarithmic plot shown in Fig. 5. The weak initial decrease of k for *trans*-stilbene with increasing viscosity, and the sudden turnover into a steeper descent at approximately

TABLE II. B_s values for diphenylbutadiene photoisomerization in liquid n -alkanes (Ref. 35) and n -alkanols at 298 K obtained from linear plots of k_{nr} vs $1/\eta$ according to Eq. (1). Power law coefficients α of $k \sim \eta^{-\alpha}$ obtained from double logarithmic plots in n -alkanols.

Solvent	B_s (MPa)	α	Solvent	B_s (MPa)
Methanol	14.7	1.03 ± 0.04	ethane	0.20
Ethanol	19.2	1.01 ± 0.02	propane	0.26
n -propanol	25.9	0.99 ± 0.03	n -pentane	0.31
n -butanol	45.3	1.03 ± 0.03	n -hexane	0.34
n -pentanol	40.3		n -octane	0.40
			n -nonane	0.46
			n -decane	0.51
			n -undecane	0.66
			n -dodecane	0.66

1.5 mPa s is quite different from the corresponding behavior in DPB. We have recently attributed the weak viscosity dependence of *trans*-stilbene photoisomerization in methanol for viscosities $\eta < 1.5$ mPa s to a reduction of the barrier height with increasing solvent density,^{34,42} an effect caused by solute-solvent interactions obscuring the Smoluchowski type frictional decrease of the rate. In the present work we concentrate on the sudden change from a weak to a very strong viscosity dependence which occurs at higher viscosities. While the photoisomerization rates k of DPB are inversely proportional to η , the rate constants of *trans*-stilbene at viscosities around 2 mPa s approach a power law with $\alpha = 1.3$, i.e., a steeper dependence on η is observed which is parallel to the viscosity dependence of the dielectric relaxation time in methanol such as estimated from the temperature dependence of the dielectric relaxation rates.^{73,74} This is

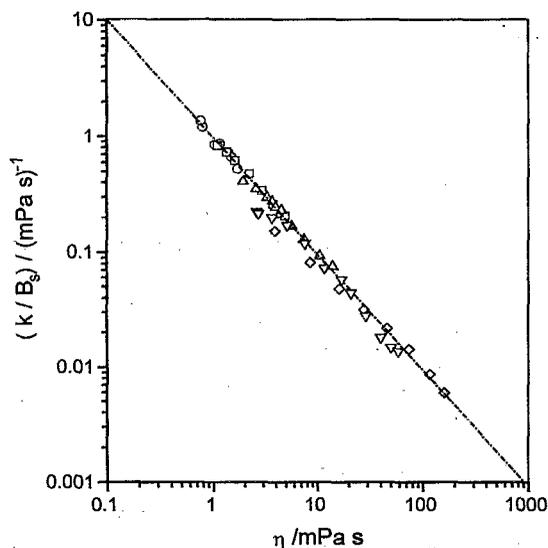


FIG. 4. Reduced photoisomerization rate coefficients k/B_s for diphenylbutadiene in n -alkanol solvents as a function of solvent viscosity η at 298 K [see Eq. (1) with $k = k_{nr} - k_{isc}$; ○, methanol; □, ethanol; △, n -propanol; ▽, n -butanol; ◇, n -pentanol].

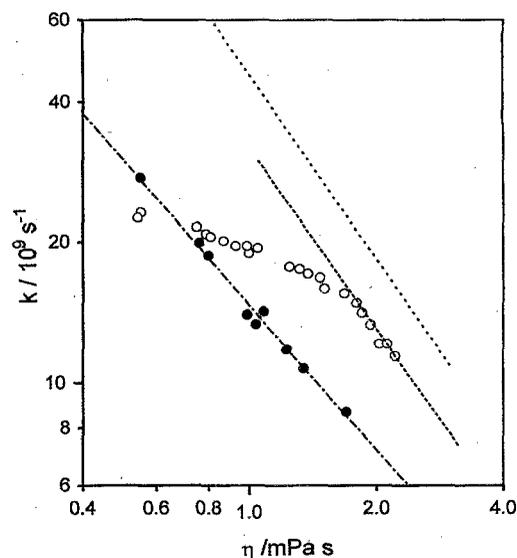


FIG. 5. Photoisomerization rate coefficients k in methanol as a function of solvent viscosity η for *trans*-stilbene (○) and diphenylbutadiene (●). (---) Linear fit to the diphenylbutadiene data; (---) linear fit to the high viscosity *trans*-stilbene data; (···) dielectric relaxation times of methanol (Refs. 73 and 74).

indicated by the dotted line in Fig. 5. (The extrapolation of dielectric relaxation times to higher viscosities should be reliable to within 20%.)

For the solvents ethanol to n -pentanol, one has to account for the rate constant of intersystem crossing k_{isc} . In Figs. 6–8, therefore, we have plotted $k = k_{nr} - k_{isc}$, where k_{isc} was taken to have a value of approximately $2.8 \times 10^8 \text{ s}^{-1}$ in all alcohol solvents.¹⁹ In ethanol, the steep part of the η -dependence of k between 2 and 3 mPa s in Fig. 6 almost exactly coincides with the viscosity dependence of $1/\tau_D$,

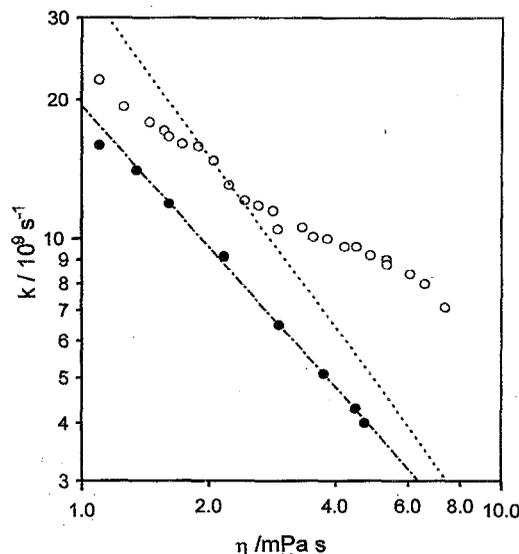
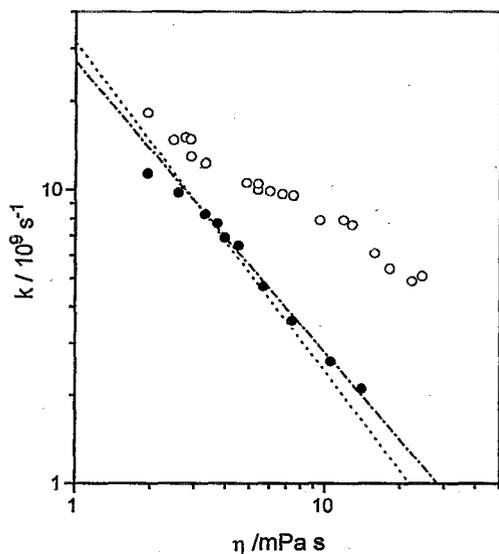
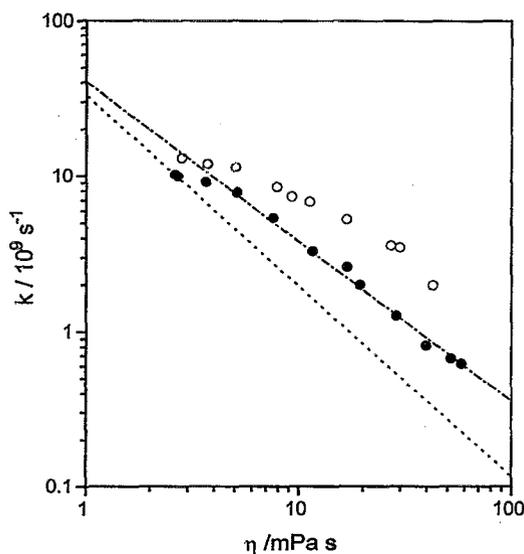


FIG. 6. As in Fig. 5, but in ethanol.

FIG. 7. As in Fig. 5, but in *n*-propanol.

which obeys a power law with $\alpha=1.25$. In *n*-propanol, Fig. 7, reaction rates of *trans*-stilbene are higher than $1/\tau_D$ over the whole viscosity range studied, but the $k(\eta)$ plot has a turning point with an intermediate flat segment. Dielectric relaxation in *n*-butanol finally is always faster than the reaction for *trans*-stilbene and DPB as shown in Fig. 8. For *trans*-stilbene in *n*-butanol, one only finds the weak viscosity dependence indicative of the lowering of the barrier with increasing density, which gradually turns into a steeper dependence, as the barrierless limit is approached.⁴² Table III summarizes our experimental results for k_{nr} of *trans*-stilbene photoisomerization in alcohols.

FIG. 8. As in Fig. 5, but in *n*-butanol.TABLE III. Pressure dependence of nonradiative decay rate coefficients k_{nr} of the S_1 state of *trans*-stilbene in liquid alcohols at 298 K. Viscosities: interpolated data from Ref. 93.

Solvent	p (MPa)	η (mPa s)	k_{nr} (10^9 s $^{-1}$)
Methanol	0.10	0.57	23.1
	75	0.75	21.8
	95	0.80	21.0
	125	0.87	20.4
	165	0.96	19.9
	180	1.00	19.2
	200	1.05	19.7
	275	1.25	18.0
	305	1.32	17.8
	325	1.38	16.9
	355	1.47	16.6
	370	1.51	16.2
	430	1.69	15.0
	460	1.80	13.9
	475	1.85	14.4
	500	1.94	13.3
520	2.02	12.4	
550	2.12	12.4	
575	2.22	11.7	
Ethanol	0.10	1.10	22.4
	25	1.26	19.6
	55	1.45	18.2
	75	1.57	17.5
	84	1.61	17.0
	100	1.73	16.4
	125	1.89	16.2
	150	2.06	15.1
	175	2.24	13.4
	202	2.44	12.4
	225	2.63	12.1
	250	2.85	11.8
	260	2.93	10.8
	305	3.35	10.9
	325	3.55	10.4
	355	3.83	10.3
385	4.20	9.9	
410	4.48	9.9	
435	4.83	9.5	
470	5.28	9.3	
510	6.00	8.65	
545	6.5	8.28	
595	7.3	7.34	
<i>n</i> -propanol	0.10	1.94	18.6
	25	2.47	15.1
	40	2.75	15.4
	50	2.89	14.3
	75	3.31	12.6
	150	4.84	10.9
	175	5.39	10.5
	200	6.02	10.2
	210	6.32	10.3
	225	6.74	10.0
	250	7.47	9.6
	360	11.8	8.2
	385	12.8	7.9
	440	15.8	6.4
	480	18.1	5.6
	530	22.2	5.2
560	24.4	5.4	
<i>n</i> -butanol	0.10	2.82	13.4
	42	3.72	12.3
	92	5.05	11.7
	175	7.87	8.8
	210	9.25	7.7
	250	11.2	7.2
	345	16.8	5.5
	460	27.1	3.9
	490	29.8	3.8
	565	42.7	2.3

IV. DISCUSSION

A. Diphenylbutadiene

The observed linear dependence of k on $1/\eta$ in all solvents, with a solvent dependent slope B_S , is interpreted as follows. In the Smoluchowski limit of Kramers' theory one may write the barrier crossing rate constant k as

$$k = k_{\text{TST}} \omega_B / \beta, \quad (2)$$

where k_{TST} is the transition state theory rate constant, β is the mass weighted friction coefficient, and ω_B is the apparent imaginary harmonic frequency at the top of the potential barrier. We assume that β is proportional to the shear viscosity η of the solvent, i.e., $\beta = C \cdot \eta$, where C is a constant describing the hydrodynamic coupling between DPB and the solvent, and we express k_{TST} by $k_{\text{TST}} = A_{\text{TST}} \exp(-E_0/RT)$, where A_{TST} is the preexponential factor in the TST limit, and E_0 is the barrier height for the reaction. We then have

$$B_S = (A_{\text{TST}} \omega_B / C) \exp(-E_0/RT). \quad (3)$$

The larger values of B_S for alcohols compared to those for alkane solvents can have various origins. The coupling constant C can be affected, ω_B or A_{TST} may change, and the barrier can be lower but pressure independent in polar solvents. We have considered possible variations of C and ω_B with the solvent in the discussion of our experiments with nonpolar solvents;³⁵ we concluded that both factors may contribute only to a smaller extent (up to a factor of three) to the observed increase of B_S , if one compares rate constants in ethane to those in *n*-dodecane.³⁵ If one accepts this order of magnitude also in the case of alcohol solvents, the major part of the increase of B_S in polar solvents must be attributed to an increase of k_{TST} , i.e., mostly via a lowering of the barrier. An increase of k_{TST} by a factor of 50 would correspond to a decrease of the barrier by 9.7 kJ/mol, from a value of $E_0 = 10.2$ kJ/mol in *n*-alkanes⁷⁶ to a value of 0.5 kJ/mol as lower limit, such that DPB photoisomerization in alkanol solvents would be practically barrierless. Of course, this is a preliminary conclusion and, for confirmation, one would also have to measure the temperature dependence of the rate at different pressures. Nevertheless, it seems that DPB photoisomerization in polar solvents is a low barrier crossing process similar to that of *cis*-stilbene³⁶ which exhibits a linear $1/\eta$ dependence of the rate and at the same time obeys a monoexponential decay law in the time domain accessible in our experiments. Figure 4 illustrates this linear dependence for DPB in various alcohols in a double logarithmic plot of k/B_S vs η . According to Fig. 4, the influence of solvent friction on barrier crossing rates seems to be adequately described by Eq. (2).

B. *trans*-stilbene

We have argued previously^{33,34,42} that there should be no fundamental difference regarding the role of friction caused by short range repulsive forces in the barrier crossing process between DPB and *trans*-stilbene. In alcohols, the time scales for the reaction are of similar order of magnitude for both molecules and, therefore, we expect that, although the $k(\eta)$

dependencies look distinctly different for *trans*-stilbene and DPB, representing this "hard-sphere part" of the friction along the reaction path by the shear viscosity of the solvent is also a valid procedure for the barrier crossing process of both molecules in alcohol solvents. Hence, we are led to the conclusion that the observed change of the power α with pressure (in the inverse power dependence $k \sim \eta^{-\alpha}$) for *trans*-stilbene is a consequence of the viscosity dependent dielectric response time of the solvent which, with increasing pressure, causes the reaction to proceed on an increasingly nonrelaxed excited singlet state free energy surface.^{11,16,80} This time lag between the motion of *trans*-stilbene along the intrinsic isomerization coordinate and the reorientation of solvent dipoles around the evolving charge distribution of the solute gives rise to "dielectric friction"⁸¹ which acts on the reacting molecule in addition to the "hard-sphere part" of friction caused predominantly by repulsive forces. The difference in dynamical behavior between DPB and *trans*-stilbene must therefore be connected with a different variation in the intramolecular charge distribution as the system proceeds along the reaction coordinate.

From our experiments, we can distinguish four regimes of the viscosity dependence of the rate coefficient for *trans*-stilbene as the pressure increases: (i) $\alpha \approx 0.4$ at $k < \tau_D^{-1}$, (ii) $\alpha > 1$ at $k \approx \tau_D^{-1}$, (iii) $\alpha \approx 0.3$ at $k > \tau_D^{-1}$, and (iv) α approaching 1 at $k \gg \tau_D^{-1}$.

We do not observe all four regimes in a single solvent, but (i)–(iii) appear in ethanol, i.e., that alkanol on which we will concentrate our discussion. We will identify the different regimes by the headings fast solvent (i), slow solvent (ii), frozen solvent (iii), and frozen solvent-suppressed barrier (iv), and we will discuss our results for stilbene in terms of two simple models—a barrier shift and a dielectric friction model.

1. Barrier-shift model

a. Fast solvent. In the fast solvent regime, orientation of the solvent dipoles around the solute molecule along the reaction path is always sufficiently fast to keep up with the changing charge distribution of the excited state which becomes increasingly polar on its way from the *trans*-conformation to the barrier region. Therefore, the increasing orientational polarization of the solvent dipoles and their electronic polarizability contribute to a lowering of the potential energy in the S_1 state which becomes more pronounced as the dipolar character of stilbene increases towards the barrier. With increasing pressure, i.e., increasing density and viscosity, this polarization effect becomes larger, and the effective barrier height decreases, leading to a fractional power dependence of the reaction rate k on solvent viscosity.^{33,34,42} We have described this effect in terms of a barrier shift proportional to solvent density,

$$E_0([M_r]) = E_0(\text{isolated molecule}) + B_E([M_r]), \quad (4)$$

where $[M_r]$ is the reduced density of the solvent. In methanol, Fig. 5, this regime extends up to about $\eta = 1.8$ mPa s, corresponding to a pressure of $p = 450$ MPa, with $B_E = -2.6$ kJ/mol.⁴² In ethanol, Fig. 6, it covers the range up to $\eta = 2.0$

mPa s, i.e., $p=150$ MPa, with $B_E=-4.4$ kJ/mol,⁴² whereas in *n*-propanol, Fig. 7, and *n*-butanol, Fig. 8, this regime does not appear at room temperature.

The situation is illustrated schematically in Fig. 9 in terms of a simple two-state kinetic model. We have rate coefficients k^* and k^e for barrier crossing along the reaction path in the nonrelaxed and the completely relaxed solvent environment, respectively, and a solvent dipole relaxation rate constant which is given by the inverse of dielectric relaxation time. From this simple kinetic description one would obtain the following time dependence of the total excited state absorbance in the well region S_w of the excited state potential energy surface, $A = A(S_w^*) + A(S_w^e)$:

$$A(t) = a_0(b_1 + l\epsilon^*)e^{-(k^* + 1/\tau_D)t} - a_0b_1e^{-k^*t}, \quad (5)$$

$$b_1 = (l\epsilon^e\tau_D)/(k^e - k^* - 1/\tau_D),$$

with extinction coefficients ϵ^* and ϵ^e in the nonrelaxed and relaxed state, respectively, initial concentration of excited species a_0 , and optical pathlength l in the high pressure cell. In the limit which we consider here, the molecule moves along the completely relaxed reaction path. It starts in the well region at an energy E_w^e and surmounts the barrier at an energy E_b^e and the effective barrier height becomes $E_{\text{eff}}^e = E_b^e - E_w^e$. Equation (5) in this limit reduces to

$$A(t)/a_0l = (\epsilon^* - \epsilon^e) \cdot e^{-l/\tau_D} + \epsilon^e e^{-k^e t}. \quad (6)$$

From the observation of monoexponential absorption decay curves, one may conclude that $\epsilon^* \approx \epsilon^e$ at 616 nm, such that k equals k^e in this case.

b. Frozen solvent. In the *frozen solvent* regime, the solvent dipoles move more slowly such that their orientation virtually does not change before the reaction is completed and the solute molecule has returned to the electronic ground state surface. This means that only the electronic solvent polarizability and a constant, time-independent dipolar term reflecting the solvent equilibrium dipole orientation distribution corresponding to the nonpolar electronic ground state of *trans*-stilbene contribute to the stabilization of the S_1 potential energy surface. This also leads to a weak viscosity dependence of k which is similar to that observed in the *fast solvent* regime. The main difference is that now only the electronic polarizability of the solvent contributes to a lowering of the effective barrier height. In methanol, Fig. 5, this regime is not observed, whereas in ethanol, Fig. 6, it begins near to $\eta=3.5$ mPa s, corresponding to $p=300$ MPa. In *n*-propanol, Fig. 7, it starts to near $\eta=3$ mPa s ($p=60$ MPa) with $B_E=-4.8$ kJ/mol,⁴² and in *n*-butanol, Fig. 8, at room temperature the reaction seems to be in the *frozen solvent* regime at all pressures, yielding a value for the solvent shift parameter of $B_E=-7.0$ kJ/mol.⁴²

In terms of the simple two-state scheme in Fig. 9 this limit can be characterized by the nonrelaxed reaction path where the molecule starts at an energy E_w^* in the well region which is determined by the equilibrium configuration of the solvent shell dipoles corresponding to the charge distribution in the electronic ground state of *trans*-stilbene. As the solvent dipoles do not reorient around the molecule in the well region prior to reaction, the solvation shell maintains an en-

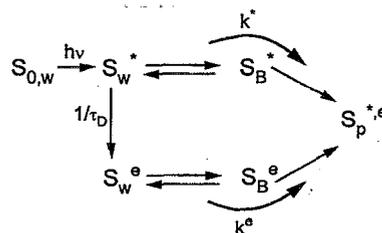


FIG. 9. Scheme of barrier crossing in the S_1 state of *trans*-stilbene. (S_w , S_B , and S_p denote the well, barrier, and perpendicular conformation, respectively. [(*) nonrelaxed solvent medium; (e) equilibrated solvent medium; for details see the text.]

ergetically less favorable configuration along the entire reaction path and, as explained earlier, the molecule passes the potential barrier height at an energy $E_0^* > E_0^e$. The effective barrier height in this case is $E_{\text{eff}}^* = E_b^* - E_w^*$. As in the first case, one observes a weak dependence of k on viscosity with increasing solvent density due to the increasing electronic solvent polarizability.⁴² Assuming $\epsilon^* \approx \epsilon^e$ at 616 nm [see case (i)], Eq. (5) reduces to

$$A(t)/a_0l = (1 + b')e^{-k^*t} - b'e^{-k^e t}, \quad (7)$$

$$b' = \tau_D^{-1}/(k^e - k^*) \leq 10^{-1},$$

such that k can approximately be identified with k^* , and the decays are monoexponential. One could argue that they should show significant deviations from monoexponentiality, because the dipole orientation distribution characteristic for the nonpolar ground state of *trans*-stilbene will be broad, leading to a similarly broad distribution of barrier heights. But one has to keep in mind that the dominant contribution to the barrier shift comes from the electronic polarizability of the solvent,⁴² and the contribution from the dipole term is comparatively small (see the following discussion).

c. Comparison between fast and frozen solvent limit. As the dipolar character of stilbene in the S_1 state is stronger in the barrier than in the well region, the stabilization energy due to interaction with the solvent will always be greater for the barrier than for the well region by a factor $\delta_{b,w} > 1$ which we assume to be independent of the solvent environment. The effective barrier height then can be written as $E_{\text{eff}}^* = E_0^{\text{isolated}} + \Delta E_w(1 - \delta_{b,w})$, where ΔE_w is the stabilization energy of stilbene in the well region. As ΔE_w is smaller in the *frozen solvent* than in the *fast solvent* limit, it follows that, at the same pressure and temperature, $E_{\text{eff}}^* < E_{\text{eff}}^*$, i.e., the effective barrier is smaller along the equilibrium than along the nonequilibrium solvation path. With Eq. (2) it follows that $\ln k^e(\eta) = \ln k^*(\eta) + (E_{\text{eff}}^* - E_{\text{eff}}^*)/RT$. The results in ethanol, Fig. 6, are consistent with this expectation: they show that rate coefficients $k^e(\eta)$ are 23% higher than $k^*(\eta)$, corresponding to an average barrier height difference between the *fast* and *frozen* solvent regime of $(E_{\text{eff}}^* - E_{\text{eff}}^*) \approx 0.5$ kJ/mol, demonstrating that the dipolar contribution to the barrier shift is small compared to that caused by the electronic polarizability of the solvent which, at the solvent density at the transition from the *fast* to the *frozen solvent* regime in

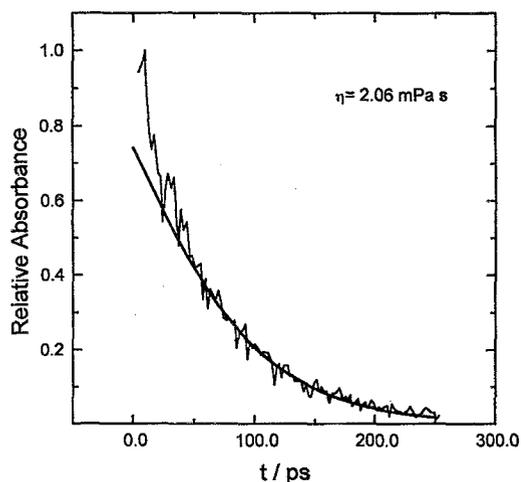


FIG. 10. Measured transient absorbance decay for *trans*-stilbene in ethanol at a pressure of 150 MPa. The smooth solid line is a model calculation according to the simple two-state model (see text).

ethanol, $[M] \approx 0.01875 \text{ mol/cm}^3$, is about 10 kJ/mol, i.e., the solvent dipoles contribute only about 5% to the total lowering of the barrier.

In the fast solvent both electronic and orientational polarizability contribute to the stilbene S_1 stabilization energy; in the *frozen* solvent it is only the electronic polarizability that has an effect. One would expect that, as the pressure is raised, the lowering of the barrier is more pronounced in the *fast solvent*, because both contributions increase proportionally to the solvent density. The exponent α in the inverse power law, therefore, should be *greater* in the *frozen solvent*. In ethanol, however, we observe the opposite: from the experiments we obtain $\alpha^* = 0.41 \pm 0.01$ smaller than $\alpha^e = 0.52 \pm 0.03$. This discrepancy could indicate that the fast solvent limit is not a good approximation to the reaction in ethanol at lower pressures: $1/\tau_D$ is only about a factor of 2 larger than the rate coefficient k , and it could well be that high frequency components of the solvent dielectric response are already freezing out on the time scale of the barrier crossing step, leading to a less pronounced lowering of the barrier height with increasing viscosity and, hence, a larger α . This would also be consistent with the comparatively small contribution of dipole reorientation to the barrier shift—the barrier crossing step just probes a minor portion of the frequency spectrum of the solvent response.

d. Frozen solvent—suppressed barrier. The viscosity dependence of the rate coefficient for *trans*-stilbene in *n*-propanol, Fig. 7, and *n*-butanol, Fig. 8, shows a gradual steepening into a η^{-1} dependence at viscosities $\eta > 10 \text{ mPa s}$. We have discussed this behavior recently⁴² in terms of an approach towards barrierless dynamics due to a complete suppression of the barrier at high solvent densities in these solvents of higher electronic polarizability. In *n*-propanol this leads to an overall viscosity dependence contrasting that in ethanol: At low viscosities the reaction starts in the *slow solvent* regime, turns into the *frozen solvent* regime, and finally approaches the *suppressed barrier* limit

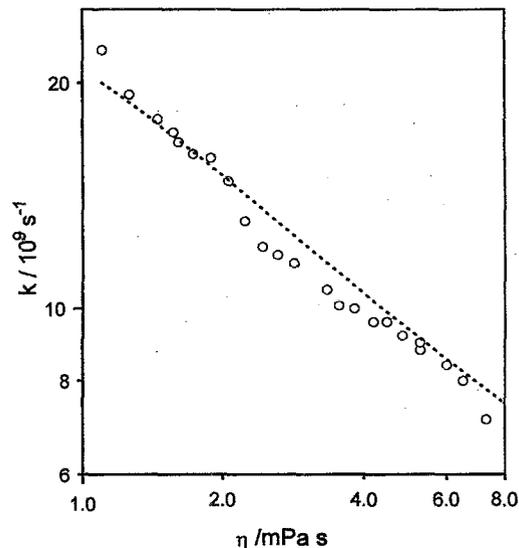


FIG. 11. Viscosity dependence of the rate coefficient k in ethanol. (●), experimental data; dashed line, prediction of the two-state model (see the text).

in a succession of steep, flat, and steep viscosity dependencies. In ethanol we observe the succession of the flat, steep, flat slope corresponding to the sequence of fast, slow, and frozen solvent. In *n*-butanol we only observe the frozen solvent and the turnover into the suppressed barrier limit.

e. Slow solvent. In ethanol, between solvent viscosities of 2 and 4 mPa s, relaxation of the solvent dipole orientation, i.e., the motion of the system along the solvation coordinate, to a large extent, seems to control the reaction dynamics along the reaction path S_w^* to S_w^e to S_B^e in Fig. 9. In this case the simple two state model of Eq. (5) predicts a nonexponential transient absorbance decay. Approximating the viscosity dependencies $k^e(\eta)$ and $k^*(\eta)$ as $k \sim \eta^{-0.43}$ and⁷⁴ $\tau_D(\eta) \sim \eta^{1.24}$, we calculated model decay curves as a function of viscosity, from which we obtained mean first order rate coefficients $k_m(\eta)$. Figure 10 shows, as a representative example, the calculated decay curve at a viscosity $\eta = 2.06 \text{ mPa s}$ (ethanol at $p = 150 \text{ MPa}$) together with the corresponding measured absorbance decay. Even if one takes into account the scatter of the experimental data, the initial nonexponential part of the model decay definitely is not present in the measured curve. In Fig. 11, we compare the viscosity dependence $k_m(\eta)$ obtained from model decays of this type with experimental rate constants $k(\eta)$ of *trans*-stilbene in ethanol. Clearly, the model does not reproduce the characteristic inflection point of the measured $k(\eta)$, but predicts an almost constant power dependence $k \sim \eta^{-0.5}$.

One may improve this simple two-state scheme by considering a continuous evolution of the system on a two-dimensional free energy surface spanned by the solvation and the internal isomerization coordinate. Motion in the direction of the solvation coordinate then leads to a time-dependent barrier height $E_0(t)$ and hence, to a time-dependent rate coefficient $k(t)$. Extending our barrier shift model⁴² we have, for the barrier height,

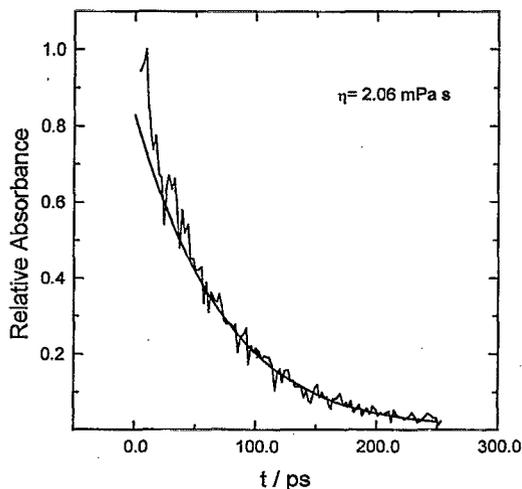


FIG. 12. Measured transient absorbance decay for *trans*-stilbene in ethanol at a pressure of 150 MPa. The smooth solid line is a model calculation according to the time-dependent barrier model (see the text).

$$E_0(t) = E_0 + B[M]_r + B_p[M]_r(1 - e^{-t/\tau_D}), \quad (8)$$

where B characterizes the solvent shift arising from the fast components of the solvent dielectric response, B_p the corresponding contribution from the slower orientational relaxation of the solvation shell. $[M]_r$ is the reduced density of the solvent. For the time dependent rate coefficient we obtain

$$K(t) = k^e \tau_D \left(\frac{t}{\tau_D} + \frac{B_p[M]_r}{RT} (1 - e^{-t/\tau_D}) + \frac{1}{2 \cdot 2!} \left(\frac{B_p[M]_r}{RT} \right)^2 (1 - e^{-2t/\tau_D}) + \frac{1}{3 \cdot 3!} \left(\frac{B_p[M]_r}{RT} \right)^3 (1 - e^{-3t/\tau_D}) + \dots \right). \quad (10)$$

Here k^* and k^e have the same meaning as before. From this model, we have $B_p[M]_r/RT = \ln(k^*/k^e)$ which we obtain from the *fast* and *frozen solvent* limits as $B_p[M]_r/RT \approx 0.05 \ln(\eta/\text{mPa s}) - 0.207$.

Calculated decay curves for this model also are not single exponential, as demonstrated again for $\eta = 2.06$ mPa s in Fig. 12, but the deviation is smaller; this could not be identified in the present experiments due to insufficient signal-to-noise ratios. The predicted viscosity dependence, obtained by fitting the calculated decay curves by single exponentials and using $\tau_D \sim \eta^{1.24}$, is shown as the dashed line in Fig. 13. The steeper transition region is not reproduced by this model either. If one wanted to force the model to account for the observation of the inflection point in the viscosity dependence, one would have to assume that the dielectric relaxation time is proportional to the tenth power of the viscosity, i.e., $\tau_D \sim \eta^{10}$ at least! With this assumption we obtain a viscosity dependence of k corresponding to the solid

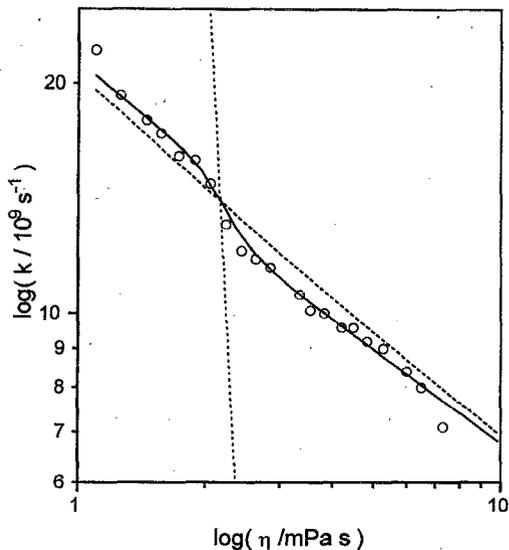


FIG. 13. Viscosity dependence of the rate coefficient k in ethanol (●), experimental data; dashed line, prediction of the time-dependent barrier model calculated with the observed $\tau_D(\eta)$ (see the text); solid line, prediction of the time-dependent barrier model with the dielectric relaxation times indicated by the pointed line (see the text).

$$k(t) = k^* \exp[-B_p[M]_r(1 - e^{-t/\tau_D})/RT]. \quad (9)$$

Integration leads to an approximate expression, $K(t)$, which is proportional to the logarithm of the transient absorbance $-K(t) \propto \ln A(t)$:

line in Fig. 13. In physical terms, such a rapid change of τ_D with η would imply that certain regions of the frequency spectrum of the solvent dielectric response, which are specifically probed by the barrier crossing process in the photoisomerization of *trans*-stilbene, freeze out almost instantaneously at a viscosity near to 2.2 mPa s at 298 K in ethanol—at least in the vicinity of the solvated molecule. Whether such an assumption is realistic, can only be answered either by molecular dynamics (MD) simulations or by measuring the pressure dependence of the high frequency part of the dielectric response spectrum in liquid alcohol solutions.

As a result of this analysis in terms of a simple kinetic barrier shift model, we conclude that a modification of the Kramers–Smoluchowski model with a density dependent barrier height alone only satisfactorily reproduces the observed $k(\eta)$ dependence in the limiting regimes of the *fast* and *frozen solvent* as well as the transition to the *suppressed*

barrier limit. Already on the basis of this simple model, however, one would expect nonexponential decay kinetics in the transition regime, which we were not able to observe at our probe wavelength of 616 nm which is close to the center of the excited state absorption band in alcohols. As the signal decays could also be affected by time-dependent solvent spectral shifts of the transient absorption, measurement of pressure dependent time resolved spectra could clarify this point.

Alternatively, one could try to characterize the dynamics of the reaction more appropriately as a motion of the system on an at least two-dimensional free energy surface with different dynamic friction along the two degrees of freedom.^{80,82,83} On the basis of the viscosity dependence of the rate coefficient alone, however, it is not possible to specify such a surface in reasonable way....

2. Dielectric friction model

In trying to understand the observed viscosity dependence of the rate coefficient k , up to now we have focused attention solely on pressure or density induced changes of the activation barrier for the reaction; an approach following logically from the observation of density dependent barrier heights in a series of nonpolar and polar solvents.^{34,42} Alternatively, one can consider this phenomenon as a deviation from Kramers model caused by non-Markovian dynamics caused by nonequilibrium solvation along the reaction path which leads to a time-dependent dielectric friction coefficient.^{82–84,85}

The general case of frequency dependent friction is described, e.g., by the Grote–Hynes model which, for the rate coefficient, gives an expression of the form⁸⁵

$$k_{\text{GH}} = k_{\text{TST}} \omega_r / \omega_B, \quad (11)$$

where ω_r is the reactive frequency defined by the implicit relation

$$\omega_r = \omega_B^2 / [\omega_r + \zeta(\omega_r)]. \quad (12)$$

Here $\zeta(\omega_r)$ denotes the frequency dependent friction coefficient at the reactive frequency ω_r . For the present system we assume that the friction consists of a dielectric contribution $\zeta_D(\omega)$, mainly due to electrostatic forces between the twisting *trans*-stilbene and the alcohol molecules in the solvation shell, and a “mechanical” contribution $\zeta_m(\omega)$ encompassing the short range, mainly repulsive interactions causing dissipative coupling to the surrounding. On the basis of our previous studies,^{28–37,42} we assume that the latter part is frequency independent and can be replaced by the zero frequency friction ζ_{m0} —this represents the Kramers limit using, e.g., the shear viscosity to describe the friction. At a pressure of, e.g., 1 bar in ethanol, one has $\zeta_D \ll \zeta_{m0}$, and Kramers’ model applies if one includes the lowering of E_0 with increasing solvent polarizability and polarity. As the pressure increases, ζ_D may become comparable to ζ_{m0} , and the rate coefficient given by the barrier shift model, k_{BS} , has to be corrected by a factor κ_{ZH} which accounts for dielectric friction and leads to the stronger viscosity dependence observed in the intermediate range. As the pressure increases further, the influence of dielectric friction apparently decreases again.

This observation suggests that the dielectric friction in this system is caused by weak solvent forces in the limit described by the van der Zwan–Hynes model.^{82,84,85} In the continuum version of this model,⁸⁴ κ_{ZH} with increasing τ_l (the longitudinal dielectric relaxation time) decreases from an initial value of unity at low friction to a limiting value at high friction (large τ_l) given by the expression

$$\kappa_{\text{ZH}}^{\text{min}} = \frac{\omega_r}{\omega_B} = \left(\frac{\omega_B^2 - \omega_s^2}{\omega_B^2} \right)^{1/2}. \quad (13)$$

In Eq. (13) ω_s denotes the electrostatic solvent frequency, defined by the harmonic restoring potential along the solvation coordinate due to the dielectric friction at time zero, $\zeta_D(t=0)$. The limit of weak solvent forces is then determined by the relation $\omega_s \ll \omega_B$. This model describes the physical picture of a frozen solvent such as discussed earlier in terms of a frequency dependent friction. If one wants to specify $\kappa_{\text{ZH}}(\eta)$ and ω_s , one needs a model for the frequency dependent dielectric friction coefficient relevant for the system studied, which could be developed, e.g., from an analysis of molecular dynamics simulations.

Comparing our experiments with the ZH model, we deduce a value of $\kappa^{\text{min}} \approx 0.81$ in ethanol and, from Eq. (13), obtain a value near to 0.6 for the ratio ω_s / ω_B . A rough estimate of ω_s for *trans*-stilbene in ethanol, based on a continuum model for dipole rotation reactions,^{84,87} can be obtained from

$$\omega_s^2 = \frac{2\mu^2(\epsilon_0 - 1)}{(2\epsilon_0 + 1)I}, \quad (14)$$

where μ is the effective dipole moment of *trans*-stilbene close to the barrier, ϵ_0 the static dielectric constant of ethanol at the respective pressure, I the moment of inertia of *trans*-stilbene, and ρ the radius of the cavity occupied by *trans*-stilbene in ethanol. We can estimate the effective dipole moment of *trans*-stilbene in the S_1 -barrier region from our barrier shift in the *frozen* solvent regime of ethanol:⁴² using a cavity radius of $\rho = 8 \times 10^{-8}$ cm (estimated Lennard-Jones radius), we obtain $\mu \approx 7.3 \times 10^{-29}$ Cm or 22 D. Using this value together with $\epsilon_0 = 24.3$ and $I = 1.7 \times 10^{-37}$ g cm², we arrive at a value $\omega_s \approx 1.6 \times 10^{12}$ s⁻¹ and, subsequently, $\omega_B \approx 2.7 \times 10^{12}$ s⁻¹. This result indicates a moderately flat barrier top consistent with the suggestion that the barrier height in ethanol is very small.

In this model, the time scale of the dielectric friction $\zeta(t)$ is given by the relaxation time τ_R which is proportional to the Debye relaxation time τ_D .⁸⁸

$$\tau_R = \frac{3\tau_D}{(2\epsilon_0 + 1)}. \quad (15)$$

For small values of $\omega_B \tau_R$, κ_{ZH} should be proportional to $1/\tau_R$,⁸³ i.e., according to Eq. 15, its viscosity dependence should follow that of ϵ_0/τ_D . Because ϵ_0 increases slightly with increasing density,⁸⁸ one may estimate $1/\tau_R \sim \eta^{-\alpha}$ with $\alpha \approx 1$. With increasing $\omega_B \tau_R$, the factor κ_{ZH} then approaches the limiting value of $\kappa_{\text{ZH}}^{\text{min}} \approx 0.8$. As the overall reaction rate coefficient is given by $k = \kappa_{\text{ZH}}(\eta) k_{\text{BS}}(\eta)$, one can try to fit the data with an expression of the kind

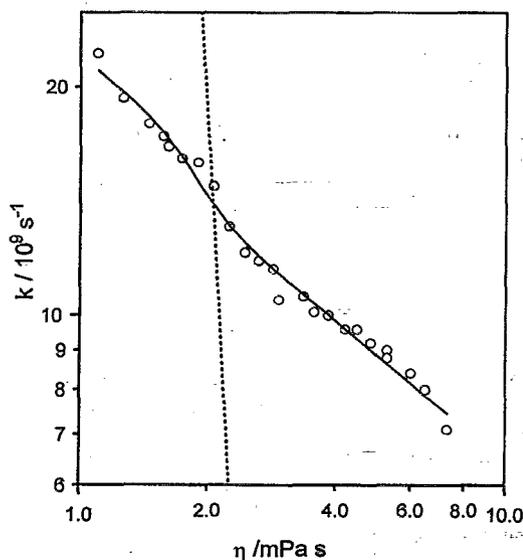


FIG. 14. As in Fig. 13, but for the dielectric friction model.

$k^{\text{fit}} = k^e [0.8 + a/(b\eta + 1)]$, where a and b are adjustable parameters. The factor in square brackets just qualitatively represents the viscosity dependence of κ_{ZH} —the parameters a and b merely set the viscosity range in which κ_{ZH} goes from unity to $\kappa_{\text{ZH}}^{\text{min}}$.

The result of the fit for ethanol is the dashed line in Fig. 14 which shows that we encounter the same difficulty as in the barrier shift model—the viscosity dependence of κ_{ZH} is too weak to be able to account for the observed switch over of the rate coefficient, and, again, one would need to postulate a viscosity dependence of the kind $\tau_R \sim \eta^{10}$ to bring this simple dielectric friction model into accord with the data (solid line in Fig. 14).

The discussion of the results for ethanol also applies to the other alcohols, the only difference being that the viscosity dependent k and $1/\tau_D$ do not cross in these cases. In methanol, the turnover of the $k(\eta)$ curve into the steeper descent occurs at slightly lower viscosities than expected on the basis of dielectric relaxation times. In *n*-propanol the initial steep portion is at somewhat higher viscosities than predicted by the simple picture.⁹⁰⁻⁹² In any case, apparently τ_D can only act as a rough guide to the description of the role of solvation dynamics in the reaction considered here.

3. Interpolation formula

In view of our lack of knowledge concerning the dynamics of solvent motion during the reaction, it may seem sufficient to represent the experimental observations by an interpolation formula of the kind

$$\frac{1}{k} = \frac{1}{k^e} + \frac{1}{k_{rx} + a \cdot k^e} \quad \text{with} \quad k_{rx} = b \cdot (\eta/\text{mPa s})^\beta, \quad (16)$$

where k_{rx} stands for a viscosity dependent rate of solvent dipole rearrangement along the reaction path, and a , b and β are fit parameters. The solid curve in Fig. 15 was obtained

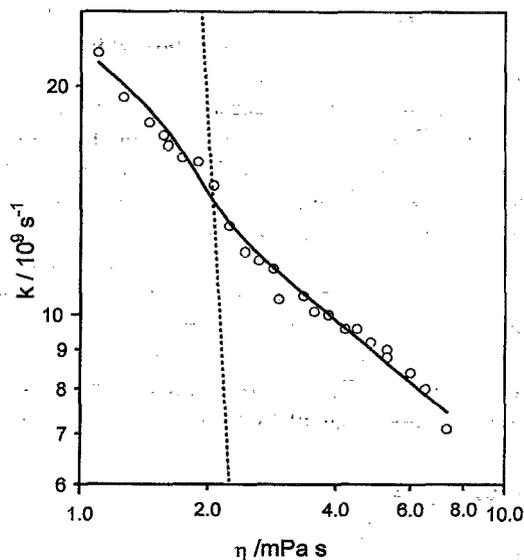


FIG. 15. As in Fig. 13, but for the interpolation formula, Eq. (16).

for $\beta=10$, $a=5$, and $b=5 \times 10^{13} \text{ s}^{-1}$. It empirically fits the experimental data quite satisfactorily.

V. CONCLUSION

We have presented experiments on the photoisomerization of *trans*-stilbene and DPB, which demonstrate that Kramers' model is applicable to this type of barrier crossing reactions in polar solvents, as long as (i) one takes into account the decrease of the barrier height with increasing bulk polarizability of the solvent; (ii) the reaction rate coefficient is not of a similar order of magnitude as the inverse of the dielectric relaxation time τ_D of the solvent.

If condition (ii) is not met, one can either extend the barrier shift model²⁸ to allow for a time-dependent effective barrier height, or describe the lack of synchronism between the motion along the isomerization coordinate and the solvation coordinate by a model including the frequency dependence of the dielectric friction coefficient.⁸³ It remains to be clarified, to what extent both models provide complementary descriptions of the same physical phenomenon. Describing the time scale of motion along the solvation coordinate by experimental viscosity dependent dielectric relaxation times within either of these models, however, does not reproduce the measured viscosity dependence of the reaction rate in the *slow solvent* regime. Instead, one has to postulate a very rapid freezing out of fast parts of the solvent response to obtain agreement with experiment. Whether the nonexponentiality of the absorption decays predicted by the simple models can be detected, has to be tested by experiments with a higher signal-to-noise ratio.

The picture emerging from the present study is in accord with earlier suggestions about the importance of solvation dynamics in the photoisomerization of *trans*-stilbene^{11,16} and dihydroxystilbene.⁸⁰ Our experiments provide unequivocal evidence for the interplay between intramolecular and solvent motion in this type of reaction. We hope to obtain more detailed information on the dynamics from time resolved

subpicosecond transient spectra which would allow to test more elaborate models⁵⁹ of reactions proceeding on partially equilibrated free energy surfaces.

Comparing the results of the pressure dependence studies for *trans*-stilbene and DPB in liquid alcohols with those for liquid and supercritical alkanes,^{28–35} one realizes that the reaction of DPB shows much less evidence for specific solvation effects. Compared to *trans*-stilbene, the barrier in this molecule seems to decrease to a much smaller extent in the clustering range in compressed gases while, subsequently, it vanishes more rapidly with increasing solvent bulk polarizability. It would be interesting to see, whether this striking difference between DPB and *trans*-stilbene is also observed in quantum chemical calculations of excited state solvation.

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