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# From barrier crossing to barrierless relaxation dynamics. Photoisomerization of trans-stilbene in compressed *n*-alkanols

## J. Schroeder, D. Schwarzer, J. Troe, P. Vöhringer

*Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany*
*Max-Planck-Institut für Biophysikalische Chemie, Am Faßberg, D-37077 Göttingen, Germany*

## Abstract

We report the first observation of a reaction which, in a single solvent, starts as a barrier crossing process at low pressure and turns into a relaxation on a barrierless potential at high pressure. The pressure and temperature dependences of trans-stilbene photoisomerization in *n*-alkanols were investigated by picosecond transient absorption spectroscopy. As in *n*-alkane solvents, at constant temperature, the rate coefficients $k$ for rotation about the central double bond in each solvent exhibit a fractional power dependence on solvent viscosity $\eta$, $k \approx \eta^{-\alpha}$, with $0 < \alpha \leqslant 1$. $\alpha$ varies little with solvent, but increases with temperature. This observation is discussed in terms of a solvent shift effect which causes with increasing solvent density a lowering of the barrier height. In *n*-propanol at high pressure the barrier height approaches zero. Even under these conditions, however, the observed decay dynamics remain monoexponential.

## 1. Introduction

The influence of the solvent on the dynamics of chemical reactions in solution continues to attract wide interest. In this field, the isomerization reaction of electronically excited trans-stilbene in a variety of solvents has often served [1,2] as a test for the validity of theoretical models [3,4] [#1] which describe the dependence of unimolecular barrier crossing rates on friction.

In *nonpolar* solvents, the potential energy surface on which the reaction occurs was assumed to be solvent independent. On this basis, threshold energies were identified with activation energies obtained from Arrhenius plots of the rate coefficients at constant viscosity [5–9]. In contrast to this, a detailed analysis of the pressure and temperature dependence of the

rate coefficient in various *n*-alkane solvents suggests that the idea of a constant *effective* potential energy surface, even within a homologous series of solvents, is very crude [10–16]. It was shown that the barrier for rotation about the central double bond depends on the polarizability of the surrounding solvent. Accounting for these solvent-specific barrier shifts in the theoretical model, the entire viscosity as well as temperature dependence of the rate could be represented by a combination of Kramers' frictional model with unimolecular rate theory under hydrodynamic boundary conditions. In this interpretation there is no need to postulate a breakdown of the Markovian assumption implicit in Kramers' model.

In *polar* solvents the dynamics is more complex, because, depending on solvent viscosity and structure, the time scales of photoisomerization and excited state solvation appear to overlap [17–19]. In general, the observed *apparent* activation energies for

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[#1] See also the theoretical chapters in ref. [3].

trans-stilbene photoisomerization are significantly lower in polar than in nonpolar solvents, which is thought to reflect a much lower potential energy barrier in the $S_1$ state [1,2,20,21]. These strong solvent polarity effects have been interpreted in terms of a substantial zwitterionic character of the 90° conformation of the $S_1$ state [22]. Consequently, the dipole moment of the molecule is expected to change significantly on its way from the $S_1$-equilibrium geometry through the barrier region to the perpendicular conformation. If this picture holds and the time scale of the solvent dielectric response overlaps with that defined by reactive motion through the barrier region, the reaction has to be considered as a process proceeding on a partially relaxed potential energy surface.

The extent to which solvent dielectric relaxation controls the photoisomerization rate of trans-stilbene in $n$-alkanols can be tuned by pressure, because, at constant temperature, the dielectric relaxation times of these solvents show a significantly stronger viscosity dependence than the barrier crossing rates of trans-stilbene [23,24]. Therefore, one has the possibility to selectively "freeze out" the slow components of the dielectric response, such that only the fast structural and electronic contributions to the dielectric relaxation can "instantaneously" modify the potential energy surface during the course of the reaction. The situation is then comparable to that in nonpolar solvents, where only the fast electronic part of the dielectric response contributes to the modification of the potential energy surface. Alternatively, one can pressure-tune the viscosity in such a way that one monitors specifically the influence of a slower dipolar component of the dielectric solvent response on the rate of the reaction.

Considerations of this type are to a certain extent supported by experiment. Kim et al. [18] and Hicks et al. [19] investigated the solvent and temperature dependence of trans-stilbene photoisomerization rates in $n$-alcohol solution and concluded that incomplete solvation 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 an additional stabilization of the transition state by high-frequency components of the solvent dielectric response in all alcohol solvents. On the basis of their results, Sundström et al.

[20,25] even arrived at the conclusion that the isomerization of trans-stilbene in $n$-alcohols takes place on a barrierless potential energy surface.

As unambiguous experimental manifestations of this link between reaction and solvation dynamics in polar solvents, which are abundant for electron transfer reactions, are still lacking for the type of reaction we are considering here, we started a systematic experimental investigation of the pressure and temperature dependence of the photoisomerization of trans-stilbene in alcohols. The system was chosen, because, firstly, it appears to be particularly sensitive to solvent–solute interactions, and secondly, the properties of the reaction are particularly characterized by previous work. As stated above, with the high-pressure technique one can separate the influence of the fast electronic solvent response on the barrier crossing process from the purely viscous effect as well as from the slower components of the solvent dielectric relaxation. In this Letter, we concentrate on the instantaneous "static" solute–solvent interaction and show that it gives rise to a barrier shift, such as previously observed in highly viscous nonpolar solvents [15,16]. We demonstrate that the depression of the barrier with increasing density eventually can lead to a barrierless potential energy surface. Changing the density of the solvent thus allows to investigate the dynamics of the same reaction on a continuously changing *effective* potential of mean force, from high to low and, finally, disappearing barrier.

## 2. Experimental technique

Our experimental apparatus was described in detail earlier [13]. In brief, our laser system consisted of a hybridly mode-locked dye laser, operating at 616 nm, which was pumped by a frequency-doubled, actively mode-locked Nd:YLF-laser. The dye laser pulses were amplified in a four stage dye amplifier, pumped by a frequency-doubled, $Q$-switched Nd:YAG laser running at 10 Hz. UV pump pulses were generated by frequency doubling of the amplified light to 308 nm and subsequent amplification in an XeCl* excimer module. The rate coefficients for isomerization in the $S_1$ state of trans-stilbene in alcohols, from methanol to $n$-butanol were measured by picosecond absorption spectroscopy. The re-

sponse function of our apparatus was 1 ps fwhm, the energies of the pump and probe pulses 0.3 and 0.05 mJ, respectively. In order to eliminate effects of overall rotational relaxation, the plane of polarization of the probe beam was varied by means of a zeroth-order half-wave plate. The isomerization rate coefficients $k$ were obtained by subtracting the radiative rate coefficient $k_r$ [26] from the first-order transient absorption decay rate constant $k_f$.

## 3. Results and discussion

In the Smoluchowski limit of Kramers' theory, which is expected to be valid for stilbene photoisomerization in liquid alcohols [21], the dependence of the rate coefficient on solvent friction tentatively is described by [3,4,15]

$$k = k_\infty \omega_B / \beta , \qquad (1)$$

where $k_\infty$ is the ordinary "high-pressure limit" of the unimolecular rate coefficient such as given by the value $k_{TST}$ from transition state theory and $\omega_B$ is the imaginary barrier frequency related to the curvature of the potential energy curve at the parabolic barrier top. $\beta$ denotes the mass-weighted friction coefficient which we assume to be proportional to the solvent shear viscosity $\eta$, which, in the Smoluchowski limit, should give rise to an inverse viscosity dependence of the rate coefficient. As shown in Fig. 1a, our experiments in compressed methanol show marked deviations from this prediction. We stress again that under the conditions of the experiments presented here, the dielectric relaxation time of methanol is significantly shorter than the $S_1$ lifetime of trans-stilbene [24]. (The influence of the solvation *dynamics* on the barrier crossing process will be discussed in a separate paper.) The overall viscosity and temperature dependence of the rate coefficient in methanol resembles that of trans-stilbene isomerization in highly viscous alkanes [5,7,15,16,21,27] where

$$k \sim \eta^{-\alpha} , \qquad (2)$$

with $0 < \alpha < 1$ was observed.

As discussed previously [10,15,16], a value of $\alpha$ smaller than 1 can be the result of a lowering of the reaction barrier with increasing density due to an increase of the high-frequency dielectric constant. In $n$-
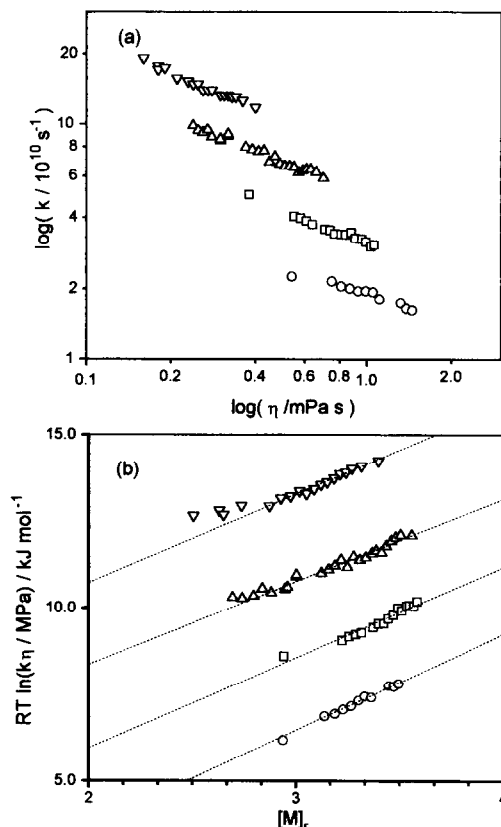


Fig. 1. Trans-stilbene photoisomerization in methanol at temperatures: (○) 298 K, (□) 343 K, (△) 393 K, and (▽) 445 K. (a) Rate coefficients $k$ versus viscosity. (b) Viscosity-scaled rate coefficients $k\eta$ versus reduced solvent density.

hexane solvent, e.g., we concluded that the barrier decreases linearly with solvent density and, therefore, with the solvent bulk polarizability. As a result, in $n$-hexane $\alpha$ practically remains constant over the viscosity range attainable with our high-pressure apparatus, and it is only a function of temperature, changing from a value of 0.29 at 298 K to 0.46 at 453 K. The situation is qualitatively similar in methanol. As is apparent from the slope of the four different isotherms in Fig. 1a, $\alpha$ is somewhat higher and varies less strongly with temperature than in $n$-hexane, increasing from $\alpha = 0.40$ at 298 K to $\alpha = 0.50$ at 445 K.

In ethanol we concentrated on higher temperatures to ensure that solvent dielectric relaxation was sufficiently rapid [23,24]. The results shown in Fig. 2a were obtained under such conditions where one can expect that the potential energy surface in the well
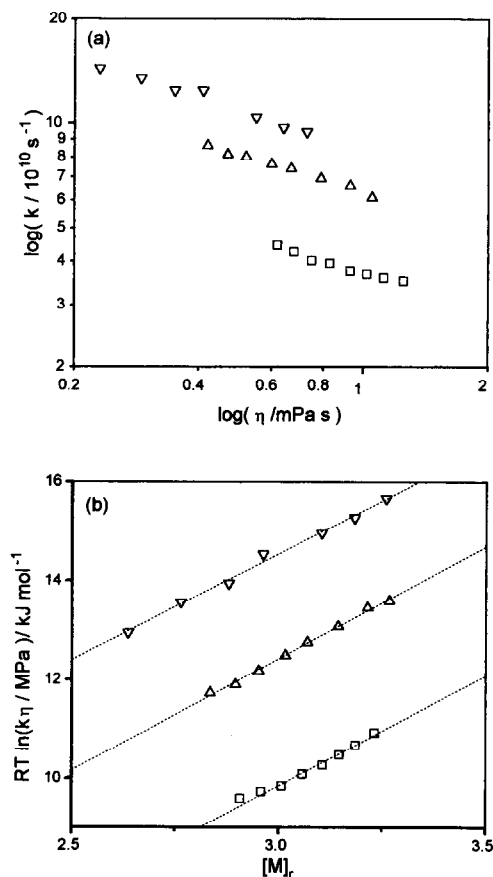
Fig. 2. Trans-stilbene photoisomerization in ethanol at temperatures: (□) 343 K, (△) 393 K, and (▽) 445 K. (a) Rate coefficient $k$ versus viscosity. (b) Viscosity-scaled rate coefficients $k\eta$ versus reduced solvent density.

region is to a large extent equilibrated when the reaction takes place. Again, the isotherms of $k$ versus $\eta$ are well described by the power law, Eq. (2), with $\alpha$ increasing from 0.33 at 348 K to 0.38 at 445 K, values that are close to those found in $n$-hexane.

In $n$-propanol we encountered a different situation. The dielectric relaxation in this solvent is considerably slower [24], so we are working in a regime where, during the barrier crossing process, the solvent is frozen with respect to its dipolar configuration, at least for the temperatures and pressures of our measurements. Also in the well region, only the high-frequency parts of the dielectric response contribute to the stabilization of the potential energy surface. The isotherms of the rate coefficient in $n$-

propanol, shown in Fig. 3a, at lower viscosities exhibit a power law dependence on $\eta$ as in the other solvents, with $\alpha$ ranging from 0.30 at 298 K to 0.39 at 443 K. But as the viscosity is increased further, the isotherms tend to steepen and asymptotically approach $\alpha = 1$ for all four temperatures. At sufficiently high solvent densities, therefore, we find almost $k \sim \eta$, which indicates that there is little further change in the height of the potential barrier.

Arrhenius plots at constant viscosity in methanol to $n$-propanol yield apparent isoviscous activation energies $E_a(\eta)$ which are listed in Table 1. Fig. 4 illustrates the decrease of $E_a$ with increasing viscosity in methanol. As noted before, the values are significantly smaller than in nonpolar solvents [21], but
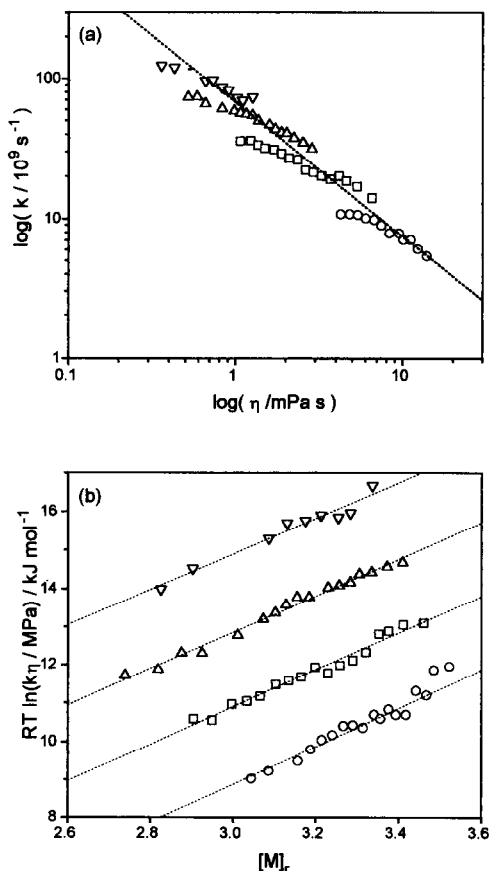


Fig. 3. Trans-stilbene photoisomerization in $n$-propanol at temperatures: (○) 298 K, (□) 343 K, (△) 393 K, and (▽) 443 K. (a) Rate coefficients $k$ versus viscosity; dashed line corresponds to $k \propto \eta^{-1}$. (b) Viscosity-scaled rate coefficients $k\eta$ versus reduced solvent density.

Table 1
Photoisomerization of trans-stilbene in compressed polar solvents: isoviscous activation energies $E_a(\eta)$ in methanol, ethanol, and $n$-propanol

| Solvent | $\eta/$mPa s | $E_a(\eta)/$kJ mol$^{-1}$ |
|---------|--------------|---------------------------|
| methanol | 0.27 | 10.9±1.0 |
| | 0.60 | 10.7±1.0 |
| | 0.70 | 10.1±1.2 |
| | 1.00 | 8.9±1.0 |
| ethanol | 0.60 | 10.6±1.7 |
| | 1.00 | 8.7±0.7 |
| $n$-propanol | 0.50 | 10.1±1.0 |
| | 1.00 | 9.6±1.0 |
| | 3.00 | 8.9±1.0 |

they are also smaller than those reported for the corresponding viscosity range by Kim et al. as well as Hicks et al. [18,19]. All the latter activation energies, however, were derived from Arrhenius plots of rate coefficients measured in different solvents [18–20,25]. As we have shown previously [10], this can be a fallacious procedure, if the effective barrier heights and their density dependences change with solvent. On the other hand, the barrier heights derived here are still finite, and, at a first glance, do not seem compatible with the suggestion that the reaction takes place on a barrierless potential energy surface [20,25].

In order to obtain information on the height of the potential barrier, one has to account for the density dependence of the barrier shift. We express this by writing

$$E_0([M]_r) = E_{0,ref} + \delta E([M]_r), \qquad (3)$$

where $[M]_r = [M]/[M]_c$ is the reduced density, $[M]_c$ the critical density of the solvent, and $E_{0,ref}$ is a fictitious limiting reference value of the barrier height at $[M]_r = 0$. In this sense Eq. (1) can be generalized to give

$$k = \frac{A_{TST} \omega_B}{\beta} \exp\left( -\frac{E_0[M]_r}{RT} \right). \qquad (4)$$

Here, $A_{TST}$ denotes the preexponential factor of the rate coefficient in TST-limit. Assuming the validity of Kramers' equation as well as density-independent potential curvatures $\omega_B$, the following relation should hold:

$$\ln(k\eta) = -\frac{\delta E([M]_r)}{RT} + \text{const.} \qquad (5)$$

Fig. 1b shows the corresponding plot of the four different isotherms measured in methanol. If (i) Kramers' model applied and (ii) there would be no barrier shifts, $RT\ln(k\eta)$ should be independent of solvent density. This is clearly not the case, although for the lowest densities attained in our experiments the density dependence of $k\eta$ tends to become weaker. If one neglects this lower density regime, the data for all four temperatures can be satisfactorily represented by linear fits $\delta E([M]_r) = B[M]_r$ having the same slope $B$ within experimental error.

Our experiments on the isomerization of trans- and cis-stilbene [15,16,28], all-trans-diphenylbutadiene [29], tetraphenylethylene [30], and trans- and cis-"stiff"-stilbene [31] in nonpolar solvents clearly indicated that Kramer model works satisfactorily. As we could show in extensive studies on the isomeri-
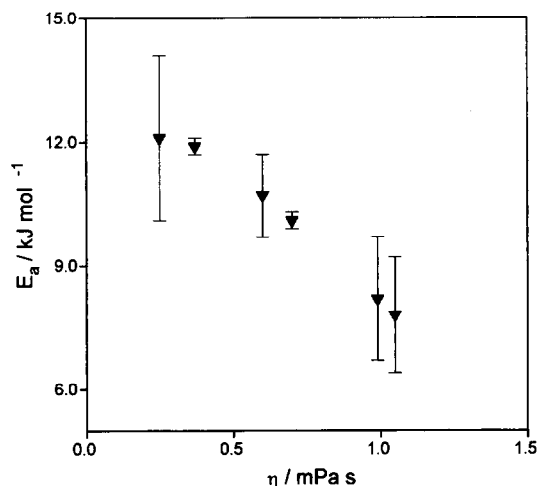
Table 2
Photoisomerization of trans-stilbene in compressed polar solvents: barrier shift parameters $B$, barrier heights $E_0([M]_r=3)$, minimum barrier heights $E_0^{min}$ observed, and extrapolated reduced densities $[M]_r^{extra}$, at which $E_0$ vanishes, see text

| Solvent<br>$(n^2-1)/(n^2+2)$ | $[M]_c$<br>(mol cm$^{-3}$) | $B$<br>(kJ mol$^{-1}$) | $E_0([M]_r=3)$<br>(kJ mol$^{-1}$) | $[M]_r^{max}$ | $E_0^{min}$<br>(kJ mol$^{-1}$) | $[M]_r^{extra}$<br>($E_0=0$) |
|---|---|---|---|---|---|---|
| methanol<br>0.202 | 0.00837 | −2.6±0.2 | 7.0±0.5 | 3.55 | 5.6±0.6 | 5.69 |
| ethanol<br>0.222 | 0.00592 | −4.4±0.2 | 6.9±1.7 | 3.30 | 5.6±1.8 | 4.57 |
| $n$-propanol<br>0.226 | 0.00452 | −4.8±0.2 | 3.5±0.3 | 3.45 | 1.3±0.4 | 3.72 |
| $n$-butanol<br>0.234 | 0.00365 | −7.0±0.3 | | | | |

Fig. 4. Isoviscous activation energies $E_a$ for trans-stilbene photoisomerization in methanol at different viscosities.

zation of diphenylbutadiene in alcohols, Kramers' frictional model holds as well for reactions in polar solvents [32]. In our studies of the pressure and temperature dependence of low barrier processes, so far we have not yet found any indication of a failure of Kramers' model in the intermediate to high damping regime. For this reason, we assume that Kramers' model also works in the present case such that the density dependence of $k\eta$ in Fig. 1b can be interpreted as a density-dependent lowering of the effective potential energy barrier. The same assumption can be made for the measurements in ethanol, Fig. 2b, and $n$-propanol, Fig. 3b. In the latter case, only data in the viscosity range below the onset of the $1/\eta$ dependence of $k$ are shown. The fitted values of the barrier shift parameter $B$ are given in Table 1. For $n$-butanol it was obtained from a single room temperature isotherm.

From the temperature dependence of $k\eta$ at constant density, within our model, we directly obtain the barrier height at the corresponding density,

$$\left(\frac{\partial \ln(k\eta)}{\partial(1/T)}\right)_{[M]} = -E_0([M]_r)/R . \qquad (6)$$

Together with the values for $B$, the effective reaction barrier $E_0([M]_r)$ for the isomerizing molecule at any solvent density $[M]_r$ can be calculated using Eq. (3). Here we neglect any temperature dependence of the apparent barrier frequency $\omega_B$, which seems to be

justified as there is little deviation from linearity in the $k(\eta)$ isotherms [15,16]. The calculated values of $E_0([M]_r=3)$ and $E_0^{min}([M]_r)$ at the highest densities $[M]_r$ reached in methanol, ethanol, and $n$-propanol are listed in Table 1.

If one wants to compare the $E_0([M])$ values obtained in this way with isoviscous activation energies $E_a$, one has to take into account the temperature dependence of $E_0([M])$ at a constant viscosity, which is a consequence of the corresponding temperature dependence of $[M]$,

$$\left(\frac{\partial \ln k}{\partial(1/T)}\right)_\eta = -E_a(\eta)/R$$

$$= -\frac{E_0([M]_r)}{R}\left(\frac{\partial E_0([M]_r)}{\partial(1/T)}\right)_\eta . \qquad (7)$$

From Eq. (7) follows that, under equal conditions, isoviscous activation energies $E_a(\eta)$ always are higher than barrier heights $E_0([M])$. This property is clearly consistent with our experimental results listed in Table 1.

Comparing the barrier parameters obtained in the four alkanol solvents, we note that

(i) the barrier shift parameter $B$ increases with solvent size, and

(ii) the potential barrier height $E_0([M]_r=3)$ is the same in methanol and ethanol, but only half as high in $n$-propanol.

As $B$ increases with solvent size, i.e. solvent polarizability, and not with solvent polarity, one may conclude that only the high-frequency electronic part of the solvent dielectric response is sufficiently rapid to "follow" the motion of the molecule along the reaction coordinate across the barrier top. Only in methanol there is possibly some contribution from dipolar components which are fast enough to respond, as the shift parameter is somewhat higher than one would expect on the basis of the Clausius–Mosotti parameter $(n^2-1)/(n^2+2)$ if a linear relationship between $B$ and solvent electronic polarizability is assumed, as can be seen in Fig. 5.

As pointed out by Kim et al. [18], the barrier height depends not only on the extent of stabilization of the potential energy surface in the barrier region but also in the well region. The latter is determined by the relative magnitudes of the $S_1$ lifetime $1/k$ and the dielectric relaxation time. Under our experimental con-
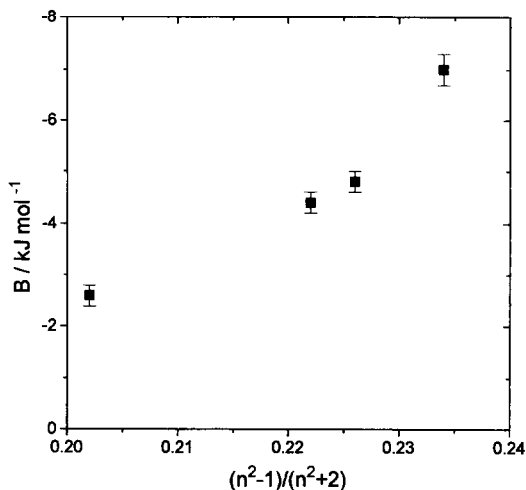
Fig. 5. Solvent shift parameter $B$ versus solvent Clausius–Mosotti parameter at 298 K and 1 bar for the solvent methanol (left) to $n$-butanol (right).

ditions, in methanol and ethanol the latter is shorter than $1/k$, the solvent is completely relaxed around the molecule in the well region. Consequently the barrier is considerably higher than in $n$-propanol, where the slow components of the dielectric response are frozen even on the timescale of the $S_1$ lifetime.

We can use our model parameters to extrapolate to the density, where one would expect the barrier to vanish altogether. The corresponding reduced densities are listed in Table 1. In $n$-propanol the barrier has practically almost disappeared at the densities reached in our experiments, being about at $0.5\,RT$ at room temperature or $0.3\,RT$ at 445 K. Nevertheless, these small barriers seem to be sufficient to create a bottleneck leading to a steady flow across the barrier, as we observed no deviations from simple monoexponential decay laws in our experiments. According to our model, the barrier in $n$-propanol should approach zero at a reduced density of 3.72 which would correspond to a pressure of approximately 6.5 kbar at 298 K.

Although this calculation provides only a rough estimate, it gives an upper limit for the effective threshold energies in the solvated molecule. As we have shown in the analysis of our studies on the pressure and temperature dependence of the isomerization of stilbene [13] and DPB [33] in low viscosity nonpolar solvents, the apparent barrier frequency $\omega_B$ can increase with temperature. We have neglected this

term in the present analysis. The effect would produce an additional decrease of the barrier heights deduced from isoviscosity activation energies. This contribution would further support the assumption of a steadily changing effective energy barrier of the reaction towards a barrierless situation. At this point it may be emphasized that the conclusions drawn from isoviscous solvent studies in $n$-propanol to $n$-hexanol about an essentially barrierless trans-stilbene photoisomerization [20,25] are consistent with our present results.

## 4. Conclusion

We have shown that the apparently weak dependence of the reaction rate coefficient $k$ for trans-stilbene photoisomerization on friction, as in nonpolar solvents, is a consequence of a solvent induced change of the $S_1$-potential energy surface as the system moves along the reaction coordinate towards the more polar intermediate twisted conformation. This leads to an effective lowering of the potential barrier which is approximately proportional to the density in each solvent. Within the alkanol series from methanol to $n$-butanol, the magnitude of this shift increases with solvent polarizability and decreases with solvent polarity, indicating that only the fastest components of the solvent dielectric response are able to track the molecule along its path across the barrier. The solvent polarity leads to stabilization of the molecule in the well region, if the dielectric relaxation time is sufficiently short compared to the $S_1$ lifetime of trans-stilbene. Consequently the barrier heights in methanol and ethanol at a reduced density of 3 are about twice as high as in $n$-propanol where the dielectric relaxation is too slow to allow for a stabilization of the $S_1$ potential in the well region.

We have also demonstrated that, due to these solvent effects, the mechanism of the reaction within a single solvent can change from a unimolecular barrier crossing process to an intramolecular relaxation on a barrierless potential as the pressure increases. According to our model we estimate that the lowest barrier reached in the experiments with $n$-propanol corresponds to $0.3\,RT$ at room temperature. In accordance with our results for cis-stilbene [28], such a small barrier still seems to be sufficient to consti-

tute a bottleneck for the reactive flow as we observe no deviation from monoexponential decay laws on a timescale above 500 fs under these conditions, which might be present, however, on a still shorter timescale.

Our experiments again demonstrate the power of combined pressure- and temperature-dependence measurements which enable a tuning of solvent properties in a controlled manner and allow for a separation of overlapping timescales of competing processes.

## 5. Acknowledgement

## 6. References

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