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The role of solute–solvent interactions in the dynamics of unimolecular reactions in compressed solvents

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Abstract. The role of the solvent in the liquid phase dynamics of unimolecular processes involving small energy barriers is studied by ultrafast laser spectroscopy. Different regions of the interaction potential between the solvent environment and the reactant are characterized by investigating photoisomerization reactions of *trans*-stilbene and related compounds in liquid *n*-alkanes and *n*-alkanols over a wide pressure range. By varying the physical properties of the solvent environment in such a controlled way, aspects of the reactant–solvent interaction which dominate the different density regimes are identified. In particular, the kind of friction acting along the reaction path, the role of solvent-induced changes of the effective potential energy surface for reaction, and the coupling of dielectric solvent shell relaxation and motion along the reaction coordinate are addressed.

The typical pressure dependence of the rate coefficient k for a unimolecular reaction from the low-pressure gas phase to the compressed liquid phase is illustrated in figure 1. At low pressures, where the rate is controlled by thermal activation in binary collisions with the solvent molecules, k is proportional to pressure, i.e. it is in the low-pressure limit k_0 . This regime is followed by a plateau region where k is pressure independent and controlled by intramolecular motion along the reaction coordinate. Here k attains the so-called high-pressure limit k_∞ which can be calculated by statistical theories if the potential energy (hyper)surface (PES) for the reaction is known. If the reaction entails large-amplitude structural changes, further increasing the pressure can lead to a decrease of k as a result of frictional forces retarding the motion along the reaction path. In the simplest approach, k eventually approaches an inverse dependence on solvent viscosity η , the so-called Smoluchowski limit k_{SM} of the reaction rate. The transition from k_∞ to k_{SM} can be described in terms of Kramers' theory [1], and, by using multidimensional unimolecular rate theory on the low-pressure side for the transition from k_0 to k_∞ , one can construct the entire pressure dependence of k [2] knowing the parts of the PES relevant for the reaction, the vibrational frequencies of the molecule, and the pressure dependent viscosity of the solvent. The result can be compared with rate coefficients measured over a wide pressure range in selected solvents to test the assumptions made in the theoretical description.

A well known suitable model reaction for this purpose is the photoisomerization of *trans*-stilbene [3] and similar compounds involving a small energy barrier E_0 in the first excited singlet state whose decay after photoexcitation is directly related to the rate coefficient of *trans*–*cis*-photoisomerization and can be conveniently measured by ultrafast laser spectroscopic techniques.

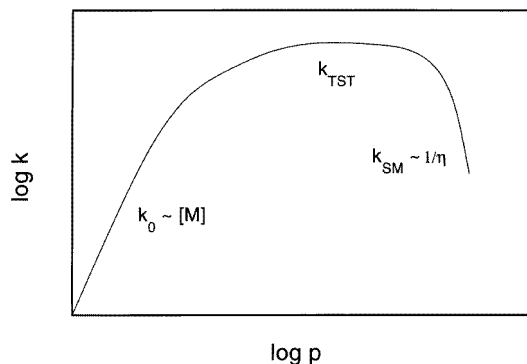


Figure 1. The pressure dependence of the rate coefficient k of a unimolecular reaction. k_{TST} is the high-pressure limit denoted as k_{∞} in the main text. $[M]$ is the density, and η the viscosity of the solvent.

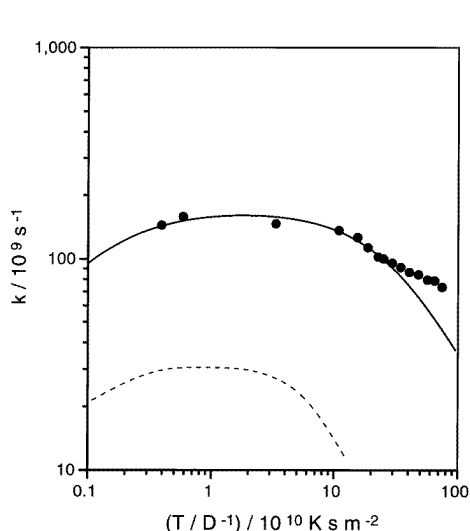


Figure 2. Photoisomerization rate coefficient k of *trans*-stilbene in supercritical *n*-pentane versus inverse self-diffusion coefficient D of *n*-pentane [4]: (●), experiment; —, model fit using lower barrier E_0 ; - - -, model prediction based on isolated molecule data [18].

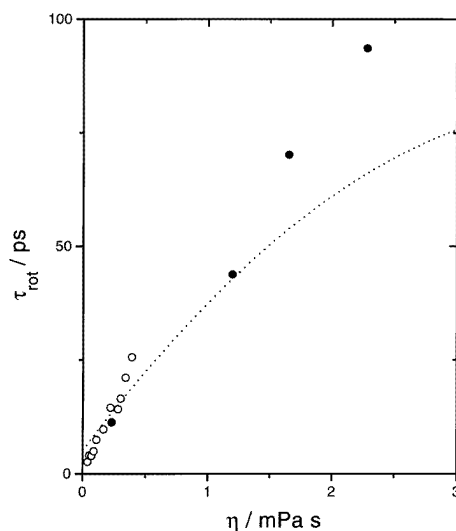


Figure 3. Rotational relaxation times τ_{rot} of *trans*-stilbene versus solvent viscosity in compressed ethane (○) and *n*-octane (●). ·····, τ_{rot} for 'stiff' *trans*-stilbene in the *n*-alkane series at ambient pressure [7].

Figure 2 shows the result of such measurements for *trans*-stilbene in supercritical *n*-pentane [4] and the prediction from the theoretical model which is based on experimentally determined microcanonical rate coefficients in jet-cooled *trans*-stilbene [5]. There are two marked discrepancies between model calculation and measurement: (i) experimental values of k are an order of magnitude higher even at low pressure, and (ii) the decrease of k due to friction is much less pronounced than predicted. The first observation can be explained consistently by a decrease of the effective potential barrier height due to electrostatic solute-solvent interactions enhanced by cluster formation at relatively low pressures [6], and will not be discussed here any further. The weak viscosity dependence, which was first observed

in liquid solution [7], has led to controversial interpretations: (i) the macroscopic solvent viscosity is an inadequate measure for microscopic friction acting along the reaction path [8]; (ii) the multidimensional character of the barrier crossing process leads to a fractional power dependence of k on $1/\eta$ [9]; (iii) as the reaction is very fast, one has to take into account the finite response time of the solvent, i.e. the friction becomes frequency dependent [10]; and (iv) the effective barrier height decreases further with increasing electronic polarizability and polarity of the solvent [11]. We have tested these hypotheses by studying molecular rotational motion and reaction independently in compressed sample solutions. A few examples will serve here to illustrate the main conclusions that we can draw from our experimental results.

(i) *Friction.* Figure 3 shows that the rotational relaxation time τ_{rot} of *trans*-stilbene in compressed liquid ethane and *n*-octane shows a perfectly linear viscosity dependence [12] with a slope that depends on the solvent. One may conclude that the macroscopic solvent viscosity is proportional to the microscopic friction governing molecular rotational diffusion with the relevant solute–solvent coupling changing with solvent. This conclusion should also hold for diffusive motion along the reaction path.

Illustrating results concerning reactive motion, figures 4–6 show examples of the measured viscosity dependence of rate coefficients for the barrier crossing processes in *cis*-stilbene and tetraphenylethylene (TPE). For these molecules as well as diphenylbutadiene (DPB) and ‘stiff’ *trans*-stilbene (where the phenyl ring is fixed by a five-membered ring to the ethylenic carbon atom), we observed in the linear alkane and alkanol solvents a linear correlation between k and $1/\eta$ with a slope that depended on the specific solvent used. The time scale for the motion along the reaction path extends from several hundred picoseconds in DPB to a couple of hundred femtoseconds in *cis*-stilbene. There is no evidence for a frequency dependence of the friction coefficient controlling the barrier crossing. As the time scale for the entirely similar reaction in *trans*-stilbene is between 30 and 300 ps, we conclude that also in this case the dynamics are mainly controlled by the zero-frequency friction, which, in turn, is adequately represented by the macroscopic solvent viscosity. Therefore, the discrepancy between experiment and model calculation observed for *trans*-stilbene in compressed liquid *n*-alkanes does not indicate a breakdown of the simple friction model in the Kramers–Smoluchowski theory. The interpretations (i) and (iii) above, therefore, do not seem to be applicable in this case.

(ii) *Effective barrier height.* Based on our results concerning the order of magnitude acceleration of the reaction rate for *trans*-stilbene in low-density supercritical solutions [4, 6], we measured the pressure dependence of k at different temperatures. An example of the results is given in figure 7, showing that the apparent activation energy at constant viscosity decreases with increasing viscosity. From a detailed analysis [4, 13] one can extract an effective barrier height E_0 along the reaction path that decreases linearly with increasing density of the solvent. The order of magnitude of this barrier shift effect can be illustrated by comparing values of E_0 measured for *trans*-stilbene under different conditions given in table 1. It is interesting to note that in compressed liquid *n*-propanol one almost reaches the regime of barrierless dynamics [14]. This is also evident in the room-temperature $k(\eta)$ isotherm measured in *n*-butanol (figure 8), which turns into linear $k-1/\eta$ dependence at higher pressures, indicating that there is no further decrease of the effective barrier height. Once again we would like to stress that this unexpected dependence of the reaction rate on solvent viscosity is connected with specific properties of the PES of *trans*-stilbene in its first excited singlet state, because corresponding measurements for, e.g. DPB or TPE in *n*-alkanes and *n*-alkanols do not show any evidence for deviations from standard Kramers–

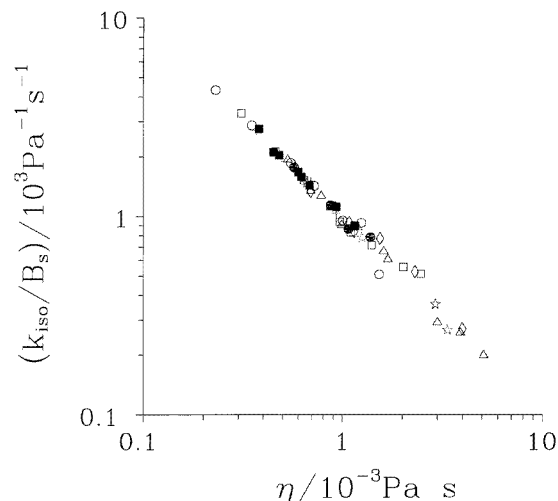


Figure 4. Photoisomerization rate of *cis*-stilbene in various compressed solvents versus solvent viscosity. The double-logarithmic graph shows the viscosity dependence of the rate coefficients divided by the slope B_s of the linear plot in each solvent, k/B_s . The resulting points fall on a straight line with slope -1 , as required by the Kramers–Smoluchowski model. The solvents are *n*-pentane (○), *n*-hexane (295 K) (□), *n*-hexane (390 K) (■), *n*-octane (△), *n*-nonane (◇), methylcyclohexane (★), methanol (●), and acetonitrile (+).

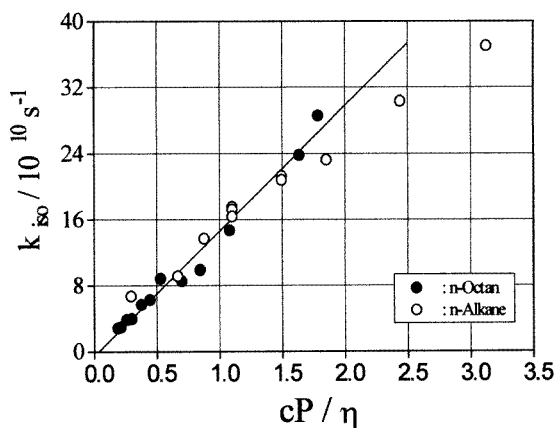


Figure 5. S_1 -barrier crossing rate coefficient k_{iso} of TPE in compressed *n*-octane (●) and in the *n*-alkane solvent series at 0.1 MPa (○) versus inverse solvent viscosity (1 cP = 1 mPa s).

Smoluchowski behaviour.

As a multidimensional PES for the reaction from quantum chemical calculations is not available at present, one does not know the reason for the surprising barrier effect in excited *trans*-stilbene. One could suspect that *trans*-stilbene possesses already a significant amount of zwitterionic character in the conformation at the barrier top, implying a fairly ‘late’ barrier along the reaction path towards the twisted perpendicular structure. On the other hand, it could also be possible that the effective barrier changes with viscosity as a result of a multidimensional barrier crossing process along a curved reaction path [15].

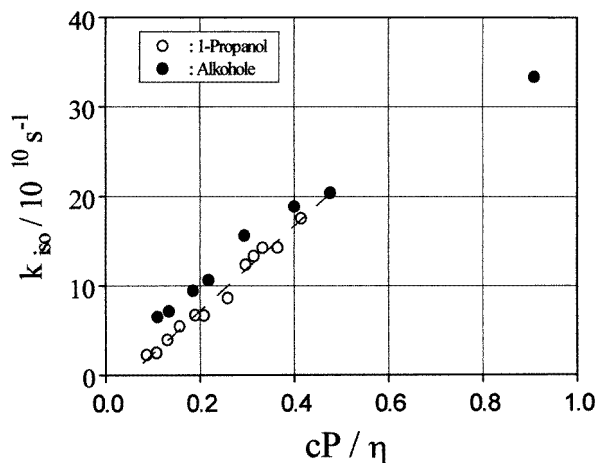


Figure 6. S_1 -barrier crossing rate coefficient k_{iso} of TPE in compressed *n*-propanol (○) and in the *n*-alcohol solvent series (●) at 0.1 MPa versus inverse solvent viscosity (1 cP = 1 mPa s).

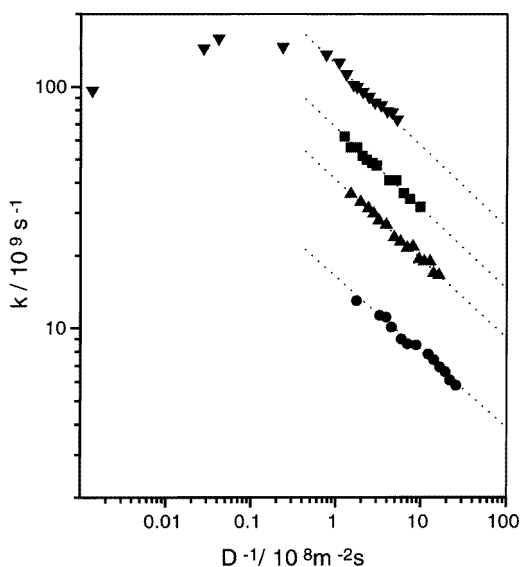
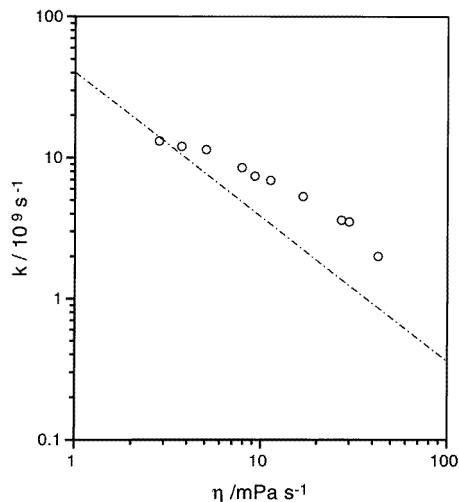


Figure 7. Isotherms of the dependence of the photoisomerization rate coefficient k of *trans*-stilbene in compressed liquid and supercritical *n*-pentane on inverse self-diffusion coefficient. The limiting slopes at high pressure indicated by the dashed lines are of the order of -0.3 and decrease with increasing temperature from -0.311 at 295 K (bottom) to -0.336 at 479 K (top). This demonstrates that the effective potential energy barrier in the S_1 -state becomes smaller as the viscosity (or density) of the solvent increases.

The dependence of k on viscosity becomes even more puzzling when the time scale of motion along the reaction coordinate becomes comparable to that of solvent dipole reorientation around the changing charge distribution within the reacting molecule—in addition to mechanical friction one also has to consider dielectric friction. Figure 9 illustrates this point for the photoisomerization of *trans*-stilbene in ethanol at room temperature. The

Table 1. Effective barrier heights E_0 for *trans*-stilbene photoisomerization in the S_1 -state under different experimental conditions.

Conditions	E_0 (kJ mol ⁻¹)	Ref.
Jet-cooled isolated molecule	15.0	[18]
Jet-cooled 1:1-complex with <i>n</i> -hexane	12	[19]
Supercritical ethane at $\rho_r \approx 0.2$	8	[6]
<i>n</i> -pentane at $\rho_r = 2.62$	6.4	[4]
<i>n</i> -pentane at $\rho_r = 3.43$	5.2	[4]
<i>n</i> -propanol at $\rho_r = 2.92$	3.9	[4, 14]
<i>n</i> -propanol at $\rho_r = 3.72$	1.3	[4, 14]

**Figure 8.** The photoisomerization rate coefficient k of *trans*-stilbene in compressed liquid *n*-butanol (○) at room temperature. The line indicates the Kramers–Smoluchowski limit. It is evident that at higher viscosities η the observed rate coefficients tend to follow the expected $1/\eta$ dependence.

$k(\eta)$ curve exhibits a turning point which is caused by a crossover of competing solvation and reaction time scales: as the viscosity increases the dielectric relaxation time of the solvent increases more rapidly than the typical time necessary for barrier crossing [16]. Gradually, the solvation dynamics starts to freeze out on the time scale of reactive motion, the polar barrier is no longer decreased by solvent dipole reorientation, and the rate coefficient drops more rapidly with increasing viscosity. As soon as the solvent dipoles are completely ‘frozen’, we have the same situation as in a nonpolar solvent, i.e. only the electronic polarizability of the solvent leads to further decrease of the barrier with increasing solvent density.

One can translate this two-dimensional picture as sketched in figure 10 into a simple kinetic model by including a time dependent barrier height $E_0(t)$:

$$E_0(t) = E_0 + B\rho_r + B_p\rho_r(1 - e^{-t/\tau_D}) \quad (1)$$

where B characterizes the solvent shift arising from the fast components of the solvent dielectric response and B_p the corresponding contribution from the slower orientational relaxation of the solvation shell. ρ_r is the reduced density and τ_D the Debye relaxation time

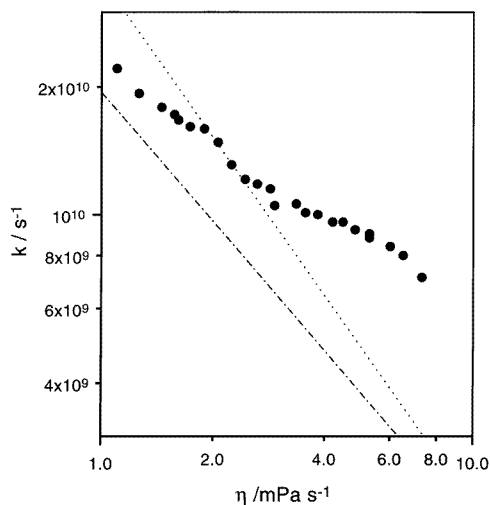


Figure 9. The photoisomerization rate coefficient k of *trans*-stilbene in compressed liquid ethanol (●). The Kramers-Smoluchowski limit is indicated as in figure 8. The viscosity dependence of τ_D (·····) is steeper than $1/\eta$.

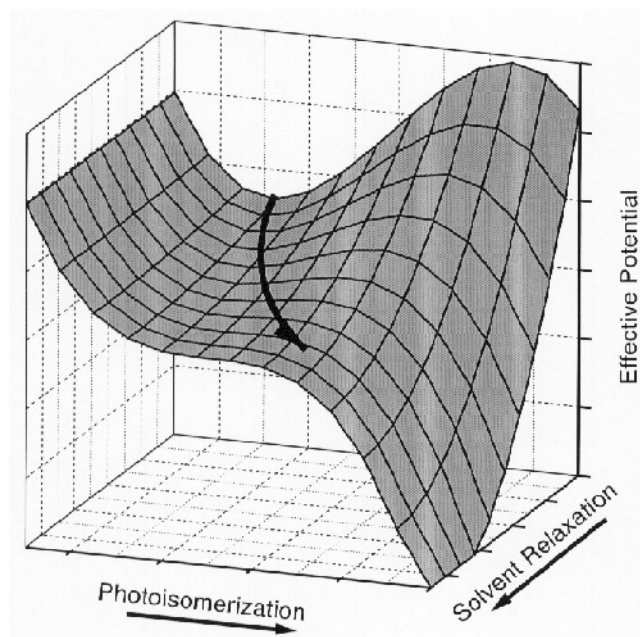


Figure 10. A schematic plot of a qualitative effective potential energy surface including intramolecular reactive motion and the solvation coordinate. The black arrow indicates a possible path of the system if the timescales of relaxation and photoisomerization are of similar magnitude.

of the solvent. This expression obviously leads to a time dependent rate coefficient $k(t)$:

$$k(t) = k^* \exp\left(-B_p \rho_r (1 - e^{-t/\tau_D}) / RT\right) \quad (2)$$

where k^* denotes the rate coefficient for barrier crossing along the reaction path in the

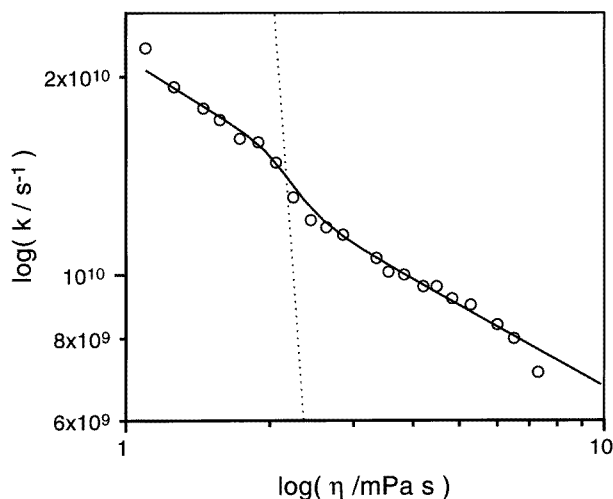


Figure 11. Model fit (solid line, see text) to the viscosity dependence of the photoisomerization rate coefficient k of *trans*-stilbene in compressed liquid ethanol (O). The dashed line indicates the hypothetical increase of τ_D with η^{10} .

orientationally nonrelaxed solvent environment. By integrating this expression one can calculate decay curves at different viscosities and extract from these approximate first-order decay times that may be compared with the experimental values.

However, if one fits this model to the observed inflection point in the viscosity dependence, one finds that the dielectric relaxation time would have to increase with the tenth power of the viscosity. With this assumption we obtain a viscosity dependence of k corresponding to the full line in figure 11. Such a rapid change of τ_D with η would imply that certain parts 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 MD simulations or by measuring the pressure dependence of the high-frequency part of the dielectric response spectrum in liquid alcohol solutions.

The analysis in terms of this simple kinetic barrier shift model shows that a modification of the Kramers–Smoluchowski model with a density dependent barrier height is sufficient to reproduce the entire observed $k(\eta)$ dependence including the transition to the *barrierless* 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 in our pump-probe absorption experiments. 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.

As stated above, one could try alternatively 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. 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.

Finally, it should be mentioned that one could also regard the observed $k(\eta)$ dependence

as a consequence of a breakdown of Kramers' model caused by non-Markovian dynamics of nonequilibrium solvation along the reaction path. Theoretically this situation can be described in terms of a time dependent dielectric friction coefficient [17]. Fitting a corresponding model to the measured rate coefficients, however, yields no additional information concerning the dynamics without knowledge of the PES for the reaction [16].

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