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Isomerization dynamics in solution†

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Recent advances in the dynamics of photochemical isomerization reactions in solution are reviewed. The isomerization reactions in solution show diverse behaviour depending on the nature of the solvent, the viscosity of the solution and the sharpness of the activation barrier. The results of recent time-resolved spectroscopic measurements on several isomerizing molecules in different solvents are discussed. The rate constants of these isomerization reactions lie in the picosecond regime. We briefly discuss the stochastic, Markovian theories of chemical kinetics in solution, including the well known Kramers' theory. Contrary to the traditional belief, recent experiments reveal an apparent breakdown of Kramers' theory at large viscosities. This breakdown is most dramatic for isomerizing molecules with sharp barriers. The failure of Kramers' theory for these cases can be traced to the assumption that the solvent forces on reactive motion are delta-correlated in time. We discuss the recent generalization of Kramers' theory by Grote and Hynes who removed the white-noise assumption of Kramers' theory by including the frequency dependence of friction. This generalized theory can qualitatively explain the new experimental data. We also review both experimental and theoretical studies on isomerization reactions in the absence of an activation barrier. We discuss why the earlier theory of Forster and Hoffmann is inconsistent, and review the recent theory of Bagchi, Fleming and Oxtoby on isomerization in solution in the absence of a barrier. We also discuss the importance of non-equilibrium solvation dynamics on fast isomerization reactions in solution. Recent computer simulation studies are reviewed. Lastly, we discuss the outstanding problems of this field for future work.

1. Introduction

Isomerization reactions in solution constitute an important class of reactions of liquid phase chemistry. And, justifiably, this field is currently enjoying tremendous attention from both the experimentalists and the theoreticians alike. The rapid growth in the experimental research in this field has been fuelled by technological breakthroughs in the generation of ultra-short laser pulses. As a result, it is now possible to study the dynamics of fast reactions with rate constants in the picosecond or even in the subpicosecond regime by time-resolved spectroscopy (Shank *et al.* 1982, Fleming *et al.* 1982, Hochstrasser 1980). The new experimental results have shown the inadequacy of some of the earlier theories and have posed serious challenges to the theoreticians.

On the theoretical side, the advance has been less spectacular. The main difficulty for theoretical studies is that in solution the reacting system is usually strongly coupled to the solvent degrees of freedom. This makes a chemical reaction in solution a dynamical problem of many degrees of freedom. The influence of solvent on a isomerization reaction can be broadly divided into two groups. Firstly, the solvent modifies the reaction potential surface of the isolated molecule. In some cases this

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solvent effect is so strong that it is meaningless to talk of a 'molecular' potential surface. Theoretical treatment of this aspect of solvent effect is usually by using the methods of equilibrium statistical mechanics developed by Chandler and by others (Hansen and McDonald 1976, Chandler 1982). Secondly, solvent dynamics profoundly influences the rate of an isomerization reaction. The best-known manifestation of this solvent effect is the viscosity dependence of the rate. Theoretical analysis of the dynamical solvent effect is based on the methods of time-dependent statistical mechanics, developed by Kubo (1966), Mori (1965) and Zwanzig (1961) in the early sixties.

In this article we review only those isomerization reactions which involve large-amplitude motion of a bulky group, twisting or rotating around a molecular axis. A schematic representative of such a reaction is given in figure 1, where R and R' are bulky groups, usually phenyls or substituted phenyls. The reactive motion is a twist around the C-C axis, as shown by an arrow in figure 1. The reaction coordinate is the dihedral angle between the two planes containing CHR' and CHR moieties. A schematic representation of the molecular potential surface projected along the reaction coordinate is shown in figure 2. In this particular figure, the reactive motion involves the crossing of an activation barrier. However, in some cases isomerization is known to occur in the absence of a barrier. We refer to this case as zero barrier reaction.

The most widely studied aspect of the isomerization reactions in solution is the viscosity dependence of the rate constants. In this article we shall review this aspect at length. The isomerizing molecules show diverse behaviour in solution and it is convenient to adopt a classification scheme to systematize the discussion. The classification can be based on the height of the activation barrier and the viscosity dependence of the reaction. Such a classification of isomerization reactions is shown in table 1. In this table, a high barrier means an activation energy barrier that is larger than or equal to $5k_B T$, where k_B is the Boltzmann constant and T the temperature. Zero barrier implies a barrier height much less than $k_B T$. The significance of the rest of the terms will be made clear (if they are not already obvious) in the next sections.

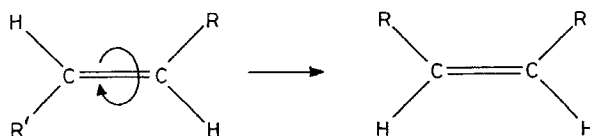


Figure 1. A schematic representation of a *trans*⇌*cis* isomerization reaction. The reactive motion is a twist around the C-C axis, shown by an arrow in the figure.

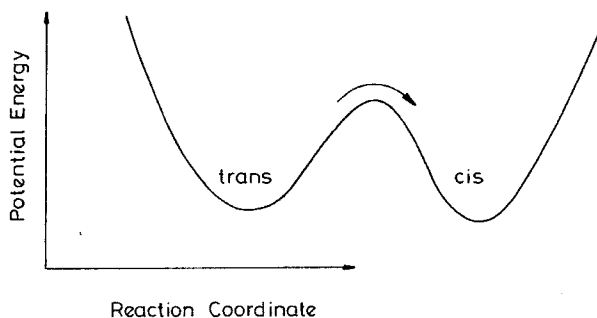


Figure 2. A schematic representation of a one-dimensional molecular potential surface projected along the reaction coordinate.

Table 1. Classification of isomerization reactions in solution.

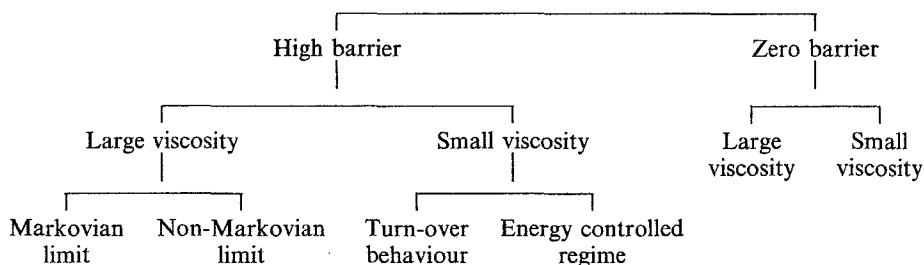


Table 2. Summary of experimental data on isomerizing systems.

Isomerizing molecule	Solvent	Activation energy (in kcal/mole)	Classification
Diphenyl butadiene (DPB) (Excited state)	Alkanes	4.7†	High barrier, non-Markovian
	Alcohols	0.5‡	Zero barrier, large viscosity
DODCI (Dye molecule)	Alcohols	13.5§ (ground state)	High barrier, non-Markovian
		5.4§ (excited state)	
Stilbene (Excited state)	Alkanes	3.5	High barrier, non-Markovian
	Alcohols	<<1¶	Zero barrier, large viscosity
TPM dyes (Ethyl violet, Crystal violet) (Excited state)	Higher alcohols (C ₈ -C ₁₂)	3.6††	High barrier, turnover behaviour at low viscosity
	Lower alcohols (C ₁ -C ₄)	<<1††	Zero barrier, large viscosity

† Velsko and Fleming (1982).

‡ Keery and Fleming (1983).

§ Velsko *et al.* (1983).

|| Rothenberger *et al.* (1983).

¶ Sundstrom and Gillbro (1984 c).

†† Sundstrom and Gillbro (1984 b).

In table 2 we have collected the available experimental informations on those isomerizing systems which have been studied in recent years. We have indicated the classification, according to table 1, wherever possible. One striking feature that comes out from table 2 is that the activation energy is strongly solvent dependent.

The organization of the article is as follows. In Section 2 we have reviewed the traditional, Markovian stochastic theories of chemical reactions in solution. In Section 3, we discuss the recent experimental results on the systems collected in table 2. In Section 4, we discuss the memory effects on isomerization reactions in solution. In Section 5, we consider isomerization in the *absence* of an activation barrier (the zero

barrier case). In Section 6, we discuss equilibrium solvent effects and in Section 7, the effects of non-equilibrium solvation dynamics. Section 8 reviews recent computer simulation results. Section 9 concludes with a discussion on the scope of future work in this field.

2. Theories of activated barrier crossing—Markovian limit

For many isomerization reactions in solution, the reactive motion is a large-amplitude motion of a bulky group twisting around a molecular axis. The rate of isomerization, therefore, depends critically on the forces exerted by the solvent molecules on the twisting group. In most cases, the molecules are initially prepared, optically or by some other means, in the reactant well. At a finite temperature in the liquid state, this is a non-equilibrium situation. In the subsequent development towards equilibrium, a certain fraction of the molecules cross over the product state. In most cases there is an activation barrier which the molecules must surmount in order to form the product state. Naturally, the rate of the isomerization reaction depends critically on the height and the shape of the activation barrier.

The earliest theory for chemical reactions in solution is the transition state theory. The transition state is identified with an imaginary 'dividing surface' separating the reactant and the product states in the configuration space. For a one-dimensional potential surface, the transition state is usually chosen to be the state with the maximum energy in the barrier region. The basic assumption of the TST is that once the reacting system crosses the transition state, it *never* returns to the transition state. The TST rate constant is proportional to the total flux of trajectories from reactant to product side of the dividing surface. The flux can be calculated with a Maxwell-Boltzmann weighting at a given temperature. The TST rate is exact if and only if no trajectory, of any energy whatever, crosses the transition state more than once. It can be shown that when TST is not exact, it *overestimates* the exact, equilibrium rate constant (Wigner 1937, Pechukas 1981).

The general expressions for the transition state rate constant were derived by Eyring and coworkers several decades ago (Laidler 1969). The rate constant is given by

$$k = \frac{k_B T}{h} \frac{Q_{\ddagger}}{Q_R Q_P} \exp(-E_0/k_B T) \quad (1)$$

where Q_{\ddagger} , Q_R and Q_P are the canonical partition functions of the activated complex (the transition state), the reactant and the product, respectively. k_B is the Boltzmann constant, h is the Planck constant and T the temperature. E_0 is the activation energy which in the TST is the amount of energy that the reactant(s) must acquire at 0 K before they can react.

For most chemical reactions in solution, equations (1) is rather useless because of the difficulties in evaluating the partition functions. The usual procedure is to express (1) in terms of thermodynamic functions which may be accessible experimentally. The following well known expression was derived by Wynne-Jones and Eyring (1935)

$$k = \frac{k_B T}{h} \exp(-\Delta S^\ddagger/k_B) \exp(-\Delta H^\ddagger/k_B T) \quad (2)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy of activation and the enthalpy of activation per molecule, respectively. It is a standard procedure to relate the enthalpy of activation to the experimentally observable activation energy (Laidler 1969).

The main advantage of TST expression (2) is that one can, at least formally, include the effects of solvent interactions on the potential energy surface through ΔS^\ddagger and ΔH^\ddagger . However, (2) ignores the dynamical aspect of solvent forces totally. The effects of solvent viscosity on the isomerization reactions, or on any reaction in the condensed phases, find no place in the TST. In solution, the main assumption of TST—that no trajectory crosses the dividing surface more than once—breaks down. The frictional forces exerted by the solvent molecules induce recrossings of the trajectories and reduce the rate below the TST result. For many chemical reactions, including the isomerization reactions, the effects of viscosity on the reaction rate is well documented.

In order to include the dynamical effects of solvent on the reaction rate, Kramers (1940) formulated a theory borrowing ideas from the theory of Brownian dynamics. Kramers' theory played a key role in all the subsequent theoretical development of the activated chemical reactions in solutions and we briefly discuss Kramers' theory and its limitations next.

2.1. Kramers theory

In order to study the effects of frictional forces on the rate of chemical reaction in solution, Kramers modelled the reactive motion as the passage of a Brownian particle over a one-dimensional potential barrier. Kramers assumed that the motion along the reaction coordinate is given by the following ordinary Langevin equation

$$\mu \frac{dv}{dt} = F(x) - \zeta v(t) + f(t) \quad (3)$$

where μ is the effective mass, v is the velocity along the reaction coordinate, $F(x)$ is the force arising from the potential in the barrier region, ζ is the zero-frequency friction parameter and $f(t)$ is the delta-correlated Gaussian white noise. ζ and $f(t)$ are related by the fluctuation dissipation theorem (Kubo 1966)

$$\langle f(0)f(t) \rangle = k_B T \zeta \delta(t) \quad (4)$$

Equation (2.4) is known as the white-noise approximation for the random force. $F(x)$ is assumed to arise from a static potential which is an inverted parabola in the barrier region with barrier frequency ω_b

$$F = \mu \omega_b^2 x \quad (5)$$

In order to calculate the steady state flux of particles across the potential barrier from the reactant to the product side, Kramers solved for the stationary solutions of the Fokker–Planck equation for the phase space probability density function $P(x, v, t)$ which is obtained by standard methods from the Langevin equation (3). The final result of his analysis is the following well known expression for the rate constant k

$$k = \frac{\omega_R}{2\pi\omega_b} \left[\left(\frac{\zeta^2}{4} + \omega_b^2 \right)^{1/2} - \zeta/2 \right] \exp(-E_0/k_B T) \quad (6)$$

where ω_R is the frequency of the (assumed harmonic) reactant well and E_0 is the activation energy of the one-dimensional potential surface.

Equation (6) has the following limiting behaviours. If the barrier frequency ω_b is much larger than the frequency parameter ζ , then we obtain the transition state result

$$k = k^{\text{TST}} = \frac{\omega_R}{2\pi} \exp(-E_0/k_B T) \quad (7)$$

Throughout this review article, we shall refer to k^{TST} as given by equation (7). This is the transition state result when the reactant well is harmonic with frequency ω_{R} and the reactive motion is one dimensional.

In the opposite limit when $\zeta \gg 2\omega_{\text{b}}$, then the rate constant is inversely proportional to the friction parameter

$$k \equiv k^{\text{SL}} = \frac{\omega_{\text{R}}\omega_{\text{b}}}{2\pi\zeta} \exp(-E_0/k_{\text{B}}T) \quad (8)$$

This limit is called the Smoluchowski limit of the rate constant.

The above two limits can be understood from simple physical reasoning. If the barrier is very sharp, then the particle spends too short a time on the barrier top to feel the frictional forces and we get the transition state result (equation 7). On the other hand, if the barrier is flat, then the motion is diffusive on the barrier top and we get inverse friction dependence of the rate.

Equation (6), however, breaks down in the limit of zero friction i.e. the limit (7) cannot be exactly realized. This is because at very small friction, the rate determining step is the accumulation of energy necessary for the solute particle to reach the barrier top. Since the source of the activation energy is the friction itself, the rate will become proportional to friction at very small values of the friction parameter. In a separate treatment, Kramers obtained an approximate expression for k in this low-friction, energy controlled regime and his expression is given by

$$k(\zeta \rightarrow 0) \cong \left(\frac{E_0}{k_{\text{B}}T}\right)\zeta \exp(-E_0/k_{\text{B}}T) \quad (9)$$

Equation (9) correctly predicts that the rate goes to zero as the value of the friction parameter is decreased towards zero.

A comparison of equations (6) and (9) shows that Kramers' theory predicts a 'turnover' of the rate constant as a function of the friction parameter, ζ . Unfortunately, one cannot estimate the value of ζ at which this turnover is expected from Kramers' expressions (6) and (9) because they are not reliable near the turnover region.

Recently Carmeli and Nitzan (1983) solved this vexing problem by obtaining an expression for the rate which is valid for all values of the friction, and yields the Kramers' results both in the $\zeta \rightarrow 0$ and in the $\zeta \rightarrow \infty$ limits. As expected, this solution is not as simple as Kramers' expressions and requires some numerical work to obtain the rate.

In order to use Kramers' expression to interpret experimental results, one must express the friction parameter in terms of the viscosity of the solvent. The usual practice is to use simple hydrodynamic relations to relate ζ to viscosity η . For small molecules, slip boundary condition is known to provide a good description of the frictional force acting on a moving sphere. However, the friction that enters into Kramers' expression is the *friction acting on the reaction coordinate* and not the macroscopic friction experienced by a macroscopic object freely translating or rotating in liquid. For most practical cases, it is a non-trivial exercise to calculate the frictional force on the reaction coordinate, even in the hydrodynamic limit.

Kramers' theory provides us with a simple and elegant expression for the frictional dependence of the rate. It also provides us with a nice physical picture of chemical reactions in solution. Unfortunately, Kramers' theory has some limitations which make it difficult to apply to some realistic cases. These limitations have been discussed in the literature for many years. In the following, we simply list these limitations.

- (1) Kramers' treatment is one dimensional. In isomerization reactions the reactive mode may be coupled to other non-reactive modes. (For instance examples of non-reactive modes may be the vibrational motions in directions perpendicular to the twisting motion.) The multidimensional nature of the potential surface may have an important effect on barrier crossing, especially at low viscosities.
- (2) The assumption that the solvent forces on the reactive motion are delta-correlated in time is suspect for sharp barriers for which ω_b^{-1} is smaller than the 'bath' correlation time at high viscosities. In this limit, the reactant does not stay long enough at the barrier top to probe all the solvent motions. So, the zero frequency friction *overestimates* the solvent drag on the reactive motion, and one must consider frequency dependent friction.
- (3) The Langevin equation description is applicable only to those cases where the isomerizing molecule is much larger than the solvent molecules.
- (4) The influence of the solvent on the reaction potential surface is ignored.

We next discuss an alternative approach to chemical dynamics in solution based on models derived from kinetic theory. This approach was developed by Skinner and Wolynes (1978, 1980), especially for those cases where the masses of the reacting molecule and the solvent molecules are comparable.

2.2. BGK type theories

In many realistic situations the size of the isomerizing molecule is comparable to that of the solvent molecules. In such cases, Kramers' approach of treating the reactant as a Brownian particle is not justified. Skinner and Wolynes (1978, 1980), therefore, adopted a different stochastic approach to the dynamics of chemical reactions in solution. They studied a kinetic model with a phenomenological collision term, given earlier by Bhatnagar *et al.* (1954) which assumes instantaneous collisions which randomize velocities. The model is characterized by an average collision frequency, g , and a parameter γ , which is the analogue of the ratio of the solvent to solute masses (in the original BGK model, $\gamma = 1$). In this model, the limit $\gamma \rightarrow 0$ (solute mass much greater than the solvent molecule mass) corresponds to the Fokker-Planck Brownian motion picture and the limit $\gamma \rightarrow \infty$ (solute mass much smaller than the solvent molecule mass) corresponds to the situation in which reaction takes place surrounded by virtually immobile molecules. This limit is called the Lorentz limit because of its similarity with the Lorentz gas model.

Let us first consider the limit where the solute and the solvent masses are comparable, i.e. $\gamma = 1$ limit. Skinner and Wolynes (1980) obtained a series solution in the power of g^{-1} for this limit. The exact rate constant for this model was obtained by Hynes (1981) for any collision frequency g and his result is given by the following simple expression

$$\frac{k}{k^{\text{TST}}} = 1 - 4\Gamma[\ln 2 + \psi(1 + \Gamma) - \psi(1 + 2\Gamma)] \quad (10)$$

where $\Gamma = g/4\omega_b$ and $\psi(x) = d \ln x! / dx$ is the digamma function. k^{TST} is the transition state result for the parabolic barrier assumed in deriving (10). If we define g by ζ/μ where ζ is the friction constant, then (10) gives results very similar to Kramers' expression (6). Equation (10) predicts Smoluchowski limit for $g \rightarrow \infty$ and TST limit for $g \rightarrow 0$.

Equation (10) breaks down in the very low viscosity region where the rate should be proportional to g . Skinner and Wolynes (1978, 1980) obtained a series expansion in powers of g for this limit. They also proposed some interesting Padé approximants which interpolate between the small viscosity, energy-controlled regime and the large viscosity, diffusive limit. For a symmetric ($\omega_R = \omega_B$) parabolic barrier, the simplest Padé approximant which shows the cross-over behaviour has the following form

$$\frac{k}{k^{\text{TST}}} = \frac{2\pi g}{\omega} \left[1 + \frac{\pi g (2\pi g)^2}{\omega 2\pi\omega^2} \right]^{-1} \quad (11)$$

This form has recently been used by Sandstrom and Gillbro (1984a) to fit the experimental results on isomerization of TPM dyes in alcohol solution.

Skinner and Wolynes (1980) also obtained analytic and numerical solutions for $\gamma \rightarrow 0$ and $\gamma \rightarrow \infty$ limits. The TST was found to be particularly inaccurate in the Lorentz ($\gamma \rightarrow 0$) limit.

Montgomery *et al.* (1979) have performed a stochastic simulation of the BGK model. In the weak coupling limit their results agree well with the analytical studies of Skinner and Wolynes (1978).

3. Experimental studies

In recent years there has been a tremendous growth of experimental research on photochemical isomerization in solution. The advances in laser spectroscopy, especially the availability of ultra-short laser pulses, have played a key role in this growth. The number of molecules that have been studied is rather large. Among them, the cyanine dyes and other substituted polyenes have been studied most extensively in recent years. These molecules undergo large conformational changes upon optical excitation and they provide interesting systems for the study of solvent influences on the excited state decay. In table 2, we have collected the names of the molecules that have been studied in recent years.

The study of photoisomerization of an initially prepared excited state is complicated by several factors. Firstly, there can be several modes of decay of the excited state. The rate of non-radiative relaxation via a large-amplitude motion in the initially prepared excited state is the quantity of interest in most studies. However, the competing influences of direct internal conversion from the initially prepared excited state and of possible intersystem crossings must also be considered carefully before any quantitative measure of the relaxation can be obtained. Secondly, both the solvent and the temperature can adversely affect the rate of radiative decay from the excited state. Thus, one must be careful in choosing solvents. Often it is helpful to restrict the study to one class of solvents, such as n-alkanes or n-alcohols. Within a homologous series, the nature of the solute-solvent interaction may not change significantly and thus a meaningful comparison is possible. Thirdly, the solute molecule may become much more polar on excitation and develop specific interactions with the solvent, which may complicate the analysis of the experimental data.

In order to gain some insight into the physics of photochemical isomerization in solution, let us consider a specific example: the photophysics of the cyanine dye 3,3'-diethyloxadicarbocyanine iodide (DODCI). The mechanism of relaxation of the excited singlet state of this molecule has been investigated in detail and a kinetic scheme has been proposed by Rulliere (1976). According to Rulliere, the excited DODCI undergoes a thermally activated twist to an intermediate geometry which rapidly

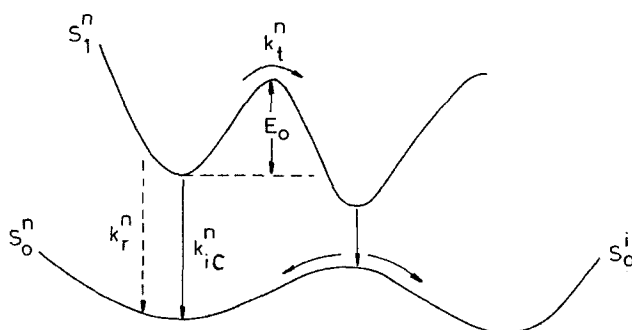


Figure 3. Rulliere model for DODCI photophysics. n , t and i represent normal, twisted and isomer forms of DODCI. k_{iC} , k_r and k_t refers to the rates of internal conversion, radiative decay and twisting, respectively. E_0 is the height of the activation barrier to the twisting motion.

decays to ground state by internal conversion, followed by a branching between the isomer and the normal forms. This scheme is shown pictorially in figure 3.

In figure 3, the non-radiative relaxation of the excited state is governed by the activated barrier crossing from the normal to the twisted state because the internal conversion from the twisted state is very rapid. The large-amplitude motion involved in barrier crossing makes the rate of non-radiative relaxation strongly dependent on solvent viscosity which normally resists the reactive motion. In addition, the polarity of the solvent may profoundly influence the nature of the potential surface of the excited state.

The experimental study of photoisomerization in solution thus consists of several distinct parts. Firstly, one must determine the different channels of decay of the excited state. Secondly, one has to estimate the intrinsic activation barrier E_0 to the non-radiative relaxation. This is usually done by measuring the *isoviscous* rate as a function of temperature and obtaining the Arrhenius parameters by standard procedure. Activation energy obtained in this way contains no contribution from the viscosity activation energy but definitely does contain solvent contributions. Thirdly, one systematically varies the viscosity of the solvent by changing temperature or pressure, or sometimes using different but similar solvents. The reason for using similar solvents is to obtain the variation of rate as a function of viscosity without introducing any undesirable change in solvent effects on the reaction energy surface. Fourthly, one may study the effects of solute-solvent interactions on the potential energy surface by using solvents of dissimilar nature.

Recent investigations have concentrated on two different regimes of solvent viscosity: high viscosity where the reaction is diffusion controlled and where non-Markovian effects become important, and the low-viscosity regime where the reaction is energy controlled. The cross-over between these two regimes of viscosity, characterized by a non-monotonic dependence of the rate on the solvent viscosity, has also drawn considerable attention. In the following we shall briefly review the important results of the recent investigations.

The photochemical isomerization of the dye molecule DODCI has been investigated by Velsko and Fleming (1982 a) and Velsko *et al.* (1983). Their studies concentrated mainly on the high-viscosity regime. Both the ground-state and the excited-state isomerization rate constants were obtained as a function of viscosity in *n*-alcohol solvents. The most important result of their investigation (Velsko and Fleming

1982 a, Velsko *et al.* 1983) is that Kramers' expression fails to describe the viscosity dependence of the twisting rate. If low-viscosity rates were fit to Kramers' expression, then the experimental rates at high viscosities lay consistently higher than predicted by theory. On the other hand, if high-viscosity points were fit to Kramers' expression, the theory predicted too low values for rates at low viscosities. In other words, Kramers' theory does not have the correct *curvature* necessary to describe the experimental results at both low and high viscosities. Velsko *et al.* found that their experimental results could be fitted very well to a viscosity dependence of the following form

$$k = A\eta^{-\alpha} \exp(-E_0/k_B T) \quad (12)$$

where A is a viscosity-independent constant and E_0 is the isoviscous activation energy. The value of the exponent α lie in the range $1 \geq \alpha \geq 0.1$ with $\alpha = 0.26$ for the ground state and $\alpha = 0.43$ for the excited state DODCI. Note that at the high viscosities studied by Velsko *et al.*, Kramers' theory predicts $\alpha = 1$, i.e., the attainment of the Smoluchowski limit. This non-attainment of the Smoluchowski limit is remarkable and will be discussed in the next section.

Velsko and Fleming (1982 b) have also studied photoisomerization of diphenyl butadiene (DPB) in n-alkanes with similar conclusions. In this case they obtained good fit of their experimental results to equation (12) with $\alpha = 0.59$. Rothenberger *et al.* (1983) studied the photoisomerization of *trans*-stilbene in n-alkanes. They also reached the conclusion that Kramers' theory breaks down in the high-viscosity region.

The precise reason for the breakdown of Kramers' theory at high viscosities is still not completely understood. The departure from Kramers' theory obviously implies a reduction of the effect of the macroscopic, zero-frequency viscosity on the reactive motions. A clue to the physical origin of this reduced viscous effect is that magnitude of the exponent α correlates well with the frequency ω_b of the potential barrier. If ω_b is small, then $\alpha \simeq 1$, but if ω_b is large (which implies a sharp barrier), then α is much less than unity. Since ω_b^{-1} is a measure of the 'residence-time' bear the barrier top, it appears that the frequency dependence of solvent friction may play an important role in the breakdown of Kramers' theory. The importance of the frequency dependence of friction was originally suggested by Velsko and Fleming (1982 b) and was later taken up by Bagchi and Oxtoby (1983), Rothenberger *et al.* (1983) and by Grote *et al.* (1984). We shall return to this in the next section where we discuss 'memory effects' in isomerization reactions in solution.

We should also mention at this point that the estimate of ω_b is usually obtained by fitting the experimental results (obtained preferably at low viscosities) to Kramers' expression with the additional assumption $\omega_b = \omega_R$. There is thus considerable uncertainty in the values of ω_b quoted in the experimental literature.

A different kind of behaviour is shown by stilbene in alcohols (Sundstrom and Gillbro 1984 b) and DPB in alcohols (Keery and Fleming 1982). Here the barrier for isomerization is small and the rate of isomerization has a simple inverse viscosity dependence. This kind of isomerization will be discussed in greater detail in Section 5.

Several investigations have been carried out in recent years in low-viscosity solvents in an attempt to realize the energy-controlled regime of the reaction rate. The cross-over to the energy-controlled regime at very low viscosity from the diffusion-controlled regime at higher viscosities should be signalled by a 'turnover' in the rate's dependence on viscosity. In the energy-controlled regime, rate increases with viscosity, whereas in the diffusion-controlled regime, rate decreases.

Courtney and Fleming investigated photochemical isomerization of DPB (1984) and stilbene (1985) in liquid alkanes at low viscosities by time-resolved spectroscopy. Even at very low viscosity (0.039 cp for DPB), no sign of a turnover was observed in their experiments; the rate of isomerization was a monotonically decreasing function of viscosity at the lowest viscosity studied. In an interesting study, Courtney *et al.* (1984) compared the isomerization rates measured for DPB in isolated molecule (Shepanski *et al.* 1983) and in low-viscosity solvent (Courtney and Fleming 1984). Courtney *et al.* (1984) plotted the rates of photoisomerization in an isolated molecule and in solution against the average vibrational energy of DPB. The results for the jet and solution results were found to be strikingly similar. In fact the results lie on a continuous line and the rates are very similar near zero viscosity. This agreement strongly suggests that the failure to observe the 'turnover' predicted by one-dimensional Kramers' theory at very low viscosities arises from the fact that the other degrees of freedom of the molecule act as a 'bath' for the twisting motion. This molecular 'bath' helps efficient intramolecular vibrational relaxation in the reactant well and also provides, by a sudden fluctuation, the energy necessary to climb up to the barrier. Thus, the reaction does not attain the energy-controlled regime even at the very low viscosities.

In contrast to the above results, there are at least two reports in the literature which claimed to have observed the 'turnover' behaviour. Hasha *et al.* (1982), using a high-pressure N.M.R. technique, found that the rate of cyclohexane ring inversion first increases and then decreases slightly as solvent viscosity is increased. Hasha *et al.* (1982) interpreted their results in terms of one-dimensional stochastic models of barrier crossing. Recently Sundstrom and Gillbro (1984a) reported the observation of the 'turnover' behaviour in the isomerization of triphenylmethane dyes in alcohol solutions. The experimental results were compared with the theory of Skinner and Wolynes (1978, 1980) with good qualitative agreement.

The preceding review of the experimental research is very brief and perhaps incomplete. This is an exciting field of research at present and many new results have come out in the last couple of years. They have posed serious challenge to the theoreticians.

4. Memory effects in the isomerization reactions

The rate of a chemical reaction which involves activated barrier crossing depends critically on the shape of the barrier. The shape of the barrier is usually expressed by the harmonic frequency ω_b , which is a measure of the sharpness of the barrier. For an isomerization reaction which involves a twisting motion around a molecule-fixed axis, there is an additional constraint: the reactant and the product states are separated by a fixed angle. This implies that there is a relation between the intrinsic barrier height, E_0 , and ω_b . If E_0 is increased, then ω_b must also increase, that is, the barrier must become sharper. This relationship between E_0 and ω_b was recently addressed by Robinson *et al.* (1984).

Now, the barrier frequency ω_b is a measure of the potential force that acts on the reactant particle near the barrier region. Thus ω_b^{-1} is a measure of the 'residence-time' of the reactant near the barrier region. If the barrier is broad and low so that ω_b^{-1} is much larger than the bath correlation time $\tau (= \mu/\zeta)$, then the reactant molecule stays in the barrier region long enough to probe the dynamics of all the degrees of freedom of the solvent that contribute to the macroscopic shear viscosity. In this case, there is a clear separation of time-scale between the correlation time of the bath molecules and the rate of motion of the reactant molecule in the barrier region so that the assumptions

of ordinary Langevin equation holds and Kramers' theory gives a satisfactory description of the viscosity dependence of the rate constant.

The situation, however, changes drastically when the barrier is high and sharp. When ω_b^{-1} is much smaller than the correlation time τ , the reactant does not stay for sufficient time at the barrier top to probe all the motions of the solvent molecules. Especially, the low-frequency motions will not be able to respond to the fast reactive motion across the barrier if ω_b is sufficiently large. If ω_b is increased (at constant viscosity) by changing the solute particle, then the effect of viscosity on reaction rate should decrease and eventually the rate should approach the transition state result. In the intermediate regime where the 'residence time' of the reactant on the barrier top is comparable to the bath correlation time, the dependence of rate on viscosity of the solvent is non-trivial. In this regime, the reactant molecule can probe only a part of the solvent motions. Therefore, the effective frictional resistance on the reactive motion is different from that given by the zero-frequency friction. This implies that Kramers' treatment is inadequate in the intermediate regime. In particular, the solvent forces on the reactive motion cannot be considered uncorrelated at all times, as assumed in the Kramers' theory. When ω_b is large, the reactive motion feels the correlated motions of the bath degrees of freedom so the memory effects must be taken into account. This implies that we must abandon the white-noise assumption on random forces in the Langevin equation and the friction should become a function of frequency (or equivalently, of time). This calls for a generalization of Kramers' theory. The generalized theory should include the non-Markovian effects. This was accomplished by Grote and Hynes (1980).

4.1. Grote-Hynes theory

In order to include non-Markovian effects, Grote and Hynes (1980) assumed the following generalized Langevin equation (GLE) for the dynamics along the reaction coordinate.

$$\mu \frac{dv}{dt} = F(x) - \int_0^t d\tau \zeta(\tau)v(t-\tau) + f(t) \quad (13)$$

where the different terms have their old meaning. The frequency dependent friction $\zeta(t)$ and the Gaussian random force $f(t)$ are related by the fluctuation dissipation theorem

$$\zeta(t) = \langle f(0)f(t) \rangle / k_B T \quad (14)$$

As before, the systematic force $F(x)$ is one dimensional and in the barrier region it is given by

$$F(x) = \mu \omega_b x^2 \quad (15)$$

From the generalized Langevin equation, one can derive a generalized Fokker-Planck equation for the probability distribution function $P(x, v, t)$ (Addelman 1976). By using the probability distribution solving GLE (13) as an initial value problem, Grote and Hynes 1980 obtained the following simple and elegant expression for the rate constant

$$k = k^{\text{TST}}(\lambda_\tau / \omega_b) \quad (16)$$

where k^{TST} is the transition state rate constant given by equation (7). λ_r is given by the following self-consistent relation

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \hat{\zeta}(\lambda_r)/\mu} \quad (17)$$

where $\hat{\zeta}(p)$ is the Laplace transform of the time dependent friction

$$\hat{\zeta}(p) = \int_0^\infty dt \exp(-pt) \zeta(t) \quad (18)$$

Equation (16) predicts the transition state result for very weak friction ($\lambda_r \sim \omega_b$), and the Kramers' result for low barrier frequency [i.e., $\omega_b \rightarrow 0$ so that $\hat{\zeta}(\lambda_r)$ can be replaced by $\hat{\zeta}(0)$ in (17)]. If the barrier frequency is large ($\omega_b \gtrsim 10^{13} \text{ s}^{-1}$) and the friction is not negligible ($\hat{\zeta}(0)/\mu \sim \omega_b$), then the situation is not so straightforward. In this regime, which often turns out to be the relevant one experimentally, the effective friction $\hat{\zeta}(\lambda_r)$ can be quite small even if the zero-frequency (i.e. the macroscopic) friction (proportional to viscosity) is very large. The non-Markovian effects can play a very important role in this intermediate regime.

In order to apply Grote-Hynes formula (16) to realistic cases, we need a reliable expression for the frequency dependent friction in terms of known quantities, especially as a function of viscosity. In their original paper, Grote and Hynes used some simple parametrized models to show that under certain circumstances k can be quite different from the predictions of Kramers' theory. Bagchi and Oxtoby (1983) used the hydrodynamic expression for the frequency dependent friction (Zwanzig and Bixon 1970) to investigate the effect of the frequency dependence of friction on the rate of photochemical isomerization in solution. As discussed in the last section, recent experiments (Velsko and Fleming 1982 a, b, Velsko *et al.* 1983) have shown a dramatic breakdown of Kramers' theory at high viscosities. The calculations of Bagchi and Oxtoby suggest that the experimentally observed partial saturation effects on rate may arise from the fact that the effective friction in the barrier region is much smaller than its zero-frequency value at high viscosities for barriers characterized by large ω_b .

Hynes and coworkers (Van der Zwan and Hynes 1984, Grote *et al.* 1983) have evaluated the frequency dependent friction for several specific cases which we shall discuss below. Next we discuss the results of the calculation of Bagchi and Oxtoby (1983).

4.2. Frequency dependent friction

Photochemical isomerization processes in molecules like DODCI, DPB, stilbene and 1,1'-binaphthyl involve a twisting motion of bulky groups around a molecular axis. So, as a first approximation this twisting motion can be modelled as the rotational motion of a sphere of hydrodynamic radius R around a molecule-fixed axis; the centre of the sphere is at a distance $(R+l)$ from the axis and l is related to the C-C bond length.

The friction experienced by the moving sphere consists of two parts: one contribution comes from the translational drag which is equal to $(R+l)^2 \hat{\zeta}_{\text{tr}}$, while the second is a pure rotational friction $\hat{\zeta}_r$ due to rotation of the sphere around its own axis. Happel and Brenner (1965) have shown that the coupling between rotational and translational friction for a sphere is zero, so the total friction is the sum of the two contributions

$$\hat{\zeta} = (R+l)^2 \hat{\zeta}_{\text{tr}} + \hat{\zeta}_r \quad (19)$$

The spherical shape, however, may not be a good approximation for many molecules of experimental interest; a spheroidal shape is more realistic for most cases. However, (19) is reasonable as a first approximation since we are mainly interested in the qualitative effects that arise from the frequency dependence of friction. In writing (19), we have also neglected the hydrodynamic interactions arising from the presence of the organic molecule which is considered fixed. Recent calculations of McCaskill and Gilbert (1979) indicate that the hydrodynamic interactions may not be important in isomerization dynamics.

The expressions for the frequency dependent frictions ζ_{tr} and ζ_r can be obtained by solving the generalized Navier–Stokes equation which is obtained by generalizing ordinary hydrodynamics to frequency domain (Zwanzig 1965). For ζ_{tr} , we use the Zwanzig–Bixon (1970) expression (with the correction of Metiu *et al.* (1977)). In the Laplace plane, ζ_{tr} is given by

$$\zeta_{tr}(p) = \left(\frac{4\pi}{3}\right) \eta_s(p) R X^2 [2(X+1)P + (1+Y)Q] \quad (20a)$$

where

$$X = (p\rho_0/\eta_s)^{1/2} R \quad (20b)$$

$$Y = p \left[c^2 + \frac{p\eta_1}{\rho_0} \right]^{-1/2} \quad (20c)$$

$$P = \frac{3}{\Delta} (3 + 3Y + Y^2) \quad (20d)$$

$$Q = \frac{3}{\Delta} \left[3 + 3X + X^2 + \frac{X^2(1+X)}{2 + \beta/\eta_s} \right] \quad (20e)$$

$$\Delta = 2X^2[3 + 3Y + Y^2] + Y^2[3 + 3X + X^2] + \frac{3X^2(1+X)(2 + 2Y + Y^2)}{2 + \beta/\eta_s} \quad (20f)$$

η_s is the frequency dependent shear viscosity, ρ_0 the solvent density, c the velocity of sound and β the slip parameter, zero for slip and infinity for stick boundary conditions. The longitudinal viscosity $\eta_l(p)$ is related to the shear viscosity $\eta_s(p)$ and bulk viscosity $\eta_v(p)$ by

$$\eta_l(p) = \frac{4}{3}\eta_s(p) + \eta_v(p) \quad (21)$$

Equations (7) and (8) are known to give a satisfactory description for the velocity correlation function for small spherical molecules, except for very short times.

The above hydrodynamic expression for $\zeta(p)$ is not reliable for very high frequencies ($p > 10^{13} \text{ s}^{-1}$). For isomerization reactions in solution, the values of the reactive frequency λ_r , given by equation (17), usually lie in the range where the hydrodynamic description is reliable.

For rotational friction, things are somewhat different due to the fact that there is no friction for the perfect slip boundary condition, while the stick limit gives too large values of friction for small molecules. The current approach, of course, is to consider a spheroidal shape since molecules are not perfect spheres. But for this case there is no analytical expression for $\zeta_r(p)$, and even the zero-frequency friction has to be evaluated numerically (Hu and Zwanzig 1974). This problem may not be serious for most cases since ζ_r is generally smaller than ζ_{tr} unless the bulky twisting group is either very large

or carries a charge (as in DODCI (Waldeck and Fleming 1981)) so that stick limit is appropriate. For the perfect stick limit the expression for frequency dependent friction has been given by Montgomery and Berne (1977)

$$\hat{\zeta}_r(p) = \frac{1 + X + \frac{1}{3}X^2}{1 + X} 8\pi\eta_s(p)R^3 \quad (22)$$

where X is given by (20*b*). For DPB, pure slip limit is applicable so that $\hat{\zeta}_r(p)$ is zero, but for DODCI in alcohol solvents, stick limit is appropriate and $\hat{\zeta}(p)$ contains contributions both from $\hat{\zeta}_{\text{tr}}$ and $\hat{\zeta}_r$.

Expressions for the frequency dependent viscosities, $\eta_s(p)$ and $\eta_v(p)$, are needed to evaluate $\hat{\zeta}(p)$. Bagchi and Oxtoby (1983) assumed the simple Maxwell forms

$$\eta_s(p) = \frac{\eta_s^0}{1 + p\tau_s} \quad (23 a)$$

$$\eta_v(p) = \frac{\eta_v^0}{1 + p\tau_v} \quad (23 b)$$

where η_s^0 and η_v^0 are the zero-frequency shear and bulk viscosities. The viscositic relaxation times τ_s and τ_v are physical constants connected to the rate of relaxation of shear and bulk modes of the solvent. The estimation of these relaxation constants poses a problem because for organic liquids like hexane, octane or butanol no reliable experimental data exists for evaluation of τ_s and τ_v by fitting them to equations (23). Bagchi and Oxtoby (1983) used the following semiempirical method to evaluate τ_s and τ_v . For the single relaxation of shear and bulk stresses assumed in writing equation (23), we have the following exact relations for τ_s and τ_v (Herzfeld and Litovitz 1950, Bhatia 1967)

$$\tau_s = \frac{\eta_s^0}{G_\infty}, \quad \tau_v = \frac{\eta_v^0}{K_r} \quad (24)$$

where G_∞ is the infinite frequency shear modulus and K_r is the relaxation part of the bulk modulus. Both G_∞ and K_r are fairly constant for organic liquids over the range of temperature studied in experiments. G_∞ is close to 10^{10} dyn/cm² and K_r related to G_∞ by the empirical relation

$$K_r = \frac{4}{3}G_\infty \quad (25)$$

To evaluate $\hat{\zeta}(p)$, we still need values for a large number of quantities: the variation of η_s^0 , η_v^0 , c , ρ_0 with temperature. Fortunately, extensive tables of experimental values exist for these quantities (Nozdrev 1965). For DPB, we take $R = 3.6 \text{ \AA}$ and use slip boundary condition, while for DODCI, we take $R = 5 \text{ \AA}$ and stick boundary condition ($\beta = \infty$ in (20)). In both cases we use $l = 1.5 \text{ \AA}$.

Figure 4 depicts the behaviour of the frequency dependent friction evaluated using the above hydrodynamic expressions. The parameters used in figure 4 are those for DPB in alkanes with $\omega_b = 5 \times 10^{12} \text{ s}^{-1}$ and the ratio $\hat{\zeta}(p)/\hat{\zeta}(p=0)$ is plotted as a function of frequency p for several values of the shear viscosity. At low viscosities, this ratio changes very slowly, staying close to unity (the Kramers' limit). But as viscosity is increased, $\hat{\zeta}(p)/\hat{\zeta}(p=0)$ shows a sharper fall and at viscosities near 10 cp, the ratio rapidly goes to zero at higher frequencies ($p \approx 0.5\omega_b$). Since the value of the reactive frequency λ_r is expected to be comparable to ω_b (this is confirmed below), the use of zero-frequency friction as a measure of the solvent drag on the reactive motion vastly

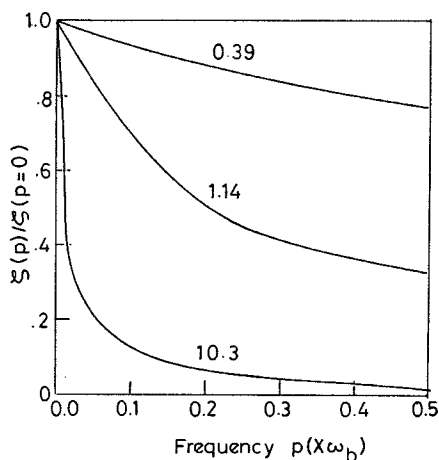


Figure 4. Values of $\zeta(p)/\zeta(p=0)$ are plotted against frequency p for various values of the shear viscosity η_s^0 . The values of η_s^0 (in cp) are indicated on the graph.

overestimates the viscous effect; the effective friction at high viscosities is much smaller than its zero-frequency value. Physically this means that many of the low-frequency motions that contribute to $\zeta(p=0)$ do not affect the reactive motion across the barrier if the barrier frequency is sufficiently high. In long alkane chains, examples of low-frequency motions are those rotations around the backbone which involve cooperative motions of several backbone atoms. These kinds of motions will not respond if the liquid is driven at high frequency.

The above discussion of $\zeta(p)$ is based on a generalized hydrodynamic model. If the barrier frequency ω_b is very large ($\omega_b \gtrsim 10^{14} \text{ s}^{-1}$), then the use of a hydrodynamic model for $\zeta(p)$ is questionable (Zwanzig and Bixon 1970). For chemical reactions in simple liquids, like argon, a reliable expression for $\zeta(p)$ is available from computer simulations (Levesque and Verlet 1970). The Levesque–Verlet friction coefficient has both a short-time collisional part and a long-time hydrodynamic part. The merit of this form is that it can be used for large ω_b cases.

Grote *et al.* (1984) used the Levesque–Verlet friction to estimate the effects of the frequency dependent friction on the rate of barrier crossing. These authors found that for high barrier frequency the rate does not track the long-time hydrodynamics, and the short-time collisional part makes the dominant contribution. They have also obtained a slowing in the rate of fall of the rate constant with viscosity.

4.3. Rate constant results

Several authors have used the Grote–Hynes formula (16) to evaluate the rate constant k . Bagchi and Oxtoby (1983) used it to explain the experimental photoisomerization rate results of Velsko and Fleming (1982, and Velsko *et al.* (1983). Rothenberger *et al.* (1983) have recently used frequency dependent friction in order to describe their experimental results of stilbene isomerization. Below we discuss results of these two investigations.

Bagchi and Oxtoby used the hydrodynamic expression for the frequency dependent friction, as described in the last subsection. Their solution of Grote–Hynes formula (16) and (17) reproduced the qualitative features of the viscosity dependence observed in experiments of Fleming and co-workers. Figure 5 shows the results of their theoretical

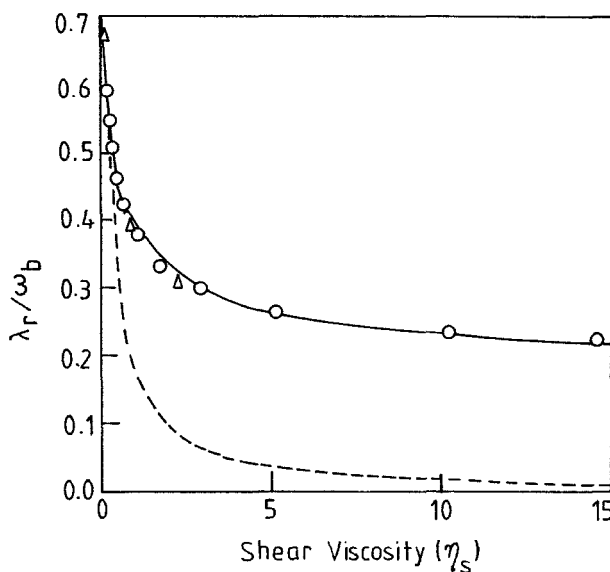


Figure 5. Values of rate parameter $\lambda r / \omega_b$ are plotted against zero frequency shear viscosity η_s^0 for $\omega_b = 6.0 \times 10^{12} \text{ s}^{-1}$. Results are for isomerization in octane (Δ) and in butanol (\circ) are shown. The solid line is a fit of the data to the form $k = A(\eta_s^0)^{-\alpha}$ with $\alpha = 0.25$. The dashed line is the result from Kramer's theory for the same value of the barrier frequency.

calculations for rate ($\lambda r / \omega_b$) as a function of viscosity for DPB parameters with $\omega_b = 6 \times 10^{12} \text{ s}^{-1}$. For comparison, the results of Kramer's theory are also shown in the same graph. As can be seen from the graph, there is a marked slowing in the decrease of the rate at high viscosities, a fact which is in qualitative agreement with experiment and is clearly absent in the Kramer's theory. In this figure, the data for both octane and butanol are used and viscosity is changed by the variation of temperature. If ω_b is held fixed, then the results for these two liquids do not differ at all. However, it has recently been shown that ω_b of DPB can change significantly (Keery and Fleming 1982) from normal alkanes to polar liquids like alcohols. Thus, the effects of solvent interactions at least partly manifest themselves through ω_b .

As can also be seen from figure 5, the results of theoretical calculations can be fitted very well to a form $k_{\text{iso}} = A(\eta_s^0)^{-\alpha}$ (equation (3)) with a value of exponent α significantly less than unity. For $\omega_b = 6 \times 10^{12} \text{ s}^{-1}$, one finds a value of the exponent $\alpha = 0.25$, whereas if we choose $\omega_b = 4 \times 10^{12} \text{ s}^{-1}$, one finds $\alpha \approx 0.64$. The experimental results give a value of $\alpha = 0.59$ for DPB in alkanes (Velsko *et al.* 1983). The theoretical value of ω_b needed to reproduce the experimental value of α is obviously too small, for both DPB and DODCI. This is an important problem in isomerization dynamics in solution and we shall return to it later.

Rothenberg *et al.* (1983) have also attempted to explain their experimental results on photoisomerization of *trans*-stilbene in liquid n-alkanes by using Grote-Hynes theory. They used the same hydrodynamic model as used earlier by Bagchi and Oxtoby with one difference: they evaluated G_∞ and K_r and hence τ_s and τ_v , from Brillouin light scattering experiments of Champion and Jackson (1976). They found values $G_\infty = 7 \times 10^8 \text{ dyn/cm}^2$ and $K_r = 9 \times 10^8 \text{ dyn/cm}^2$. These values of G and K_r are too low; the experimental value of G_∞ for organic liquids, like alkanes, are close to 10^{10} dyn/cm^2 . The reason for this low value obtained by Rothenberg *et al.* is that

Brillouin spectra are of little help in the evaluation of relaxation times when they are in the picosecond regime.

Rothenberg *et al.* fitted their experimental results both Kramers' and Grote-Hynes theory. They obtained better agreement with the latter theory with the values $\omega_b = 1.5 \times 10^{12} \text{ s}^{-1}$ and $\omega_R = 9.6 \times 10^{13} \text{ s}^{-1}$, where ω_R is the harmonic frequency of the reactant well. The value of ω_b is again too low. Even if one uses reasonable values for G_∞ and K_r , the value of ω_b needed to reproduce the experimental results is still too low. This low value of ω_b is hard to imagine when the barrier height is sufficiently large, as in DPB or in DODCI. The theory therefore predicts an unphysical potential surface.

The reason for the unphysical value of ω_b given by the theory is not well understood and this remains an outstanding problem in this field. Among many factors that may be responsible for the failure of theoretical calculations in predicting reasonable value for ω_b , the following three seem most likely:

- (a) The one-dimensional picture of the stochastic theories may not be applicable to the isomerization reactions of the type discussed here.
- (b) The hydrodynamic expression (equations (20)) for the frequency dependent friction and the subsequent approximation in the evaluation of τ_s and τ_v are not reliable.
- (c) There is a 'hidden relationship' between the intrinsic barrier height E_0 and the barrier frequency ω_b . This relationship has recently been discussed by Robinson *et al.* (1984) and is neglected in the fitting of Grote-Hynes theory to experimental data.

The one-dimensional character of Grote-Hynes theory is no doubt an important limitation. Several authors (Carmeli and Nitzan 1984, Grote and Hynes 1981, Fonseca *et al.* 1983) have considered the effects of a coupling between the reactive coordinate and another non-reactive coordinate. The main effect of the non-reactive coordinate is to open a new (non-Markovian) channel between the reactive coordinate and the thermal bath. Thus the multi-dimensional nature leads to a frequency dependent friction even when the random forces acting on the different modes are assumed to be white noise i.e. delta-correlated in time. This introduces a new aspect to the dynamics of isomerization because there can always be coupling between the reactive mode (e.g., the twisting motion of the bulky group) and a non-reactive mode (such as the rotational motion of the bulky group around a different axis). Thus, the non-Markovian theory partly compensates for the multi-dimensional character, but the form of the frequency dependent friction is now different. If the random forces have finite correlations in time, then additional contribution to the frequency dependent friction enters through the multidimensional character of the reaction. A careful analysis of the role of this contribution is yet to be carried out.

We have already discussed some of the limitations of the hydrodynamic treatment of the frequency dependent friction. Rothenberg *et al.* (1983) have suggested that the hydrodynamic friction is unreliable when the solvent molecules are larger than the isomerizing solute molecules. Thus, as the solvent varies from C_4 -alkane to C_{10} -alkane, a qualitative change takes place in the solute-solvent collisional interactions. Clearly, these structural effects are to be incorporated into the theoretical description in order to explain the experimental results quantitatively.

We have already mentioned that due to the geometric constraint on the isomerization processes, the reactant and the product states are separated by a fixed angle. Now, due to rotational symmetry of the intermolecular potential, this angle must

be less than 180° . This implies that there is a relationship between the intrinsic barrier height E_0 and the barrier frequency ω_b . However, the effects of this relationship on the isomerization process, especially in Grote–Hynes theory, is yet to be investigated.

4.4. Validity of the Smoluchowski limit

Experiments of Velsko and Fleming (1982 a, b) and Velsko *et al.* (1983) show that under certain situations the Smoluchowski limit (SL) of Kramers' equation (i.e., $1/\eta_s^0$ dependence of the rate) is not observed even at relatively high values of viscosity ($\eta_s^0 \simeq 20$ cp). This is clearly in contradiction to the traditional belief that at high viscosities, when the bath correlation time $\tau (= \mu/\zeta)$ is small compared to ω_b^{-1} , one obtains Smoluchowski behaviour. Since at the higher values of η_s^0 studied by Velsko and co-workers, τ is much smaller than ω_b^{-1} (a typical value of τ for DPB at 20 cp is 10^{-15} s whereas ω_b^{-1} is about 10^{-13} s), the non-attainment of SL is noteworthy and deserves further investigation.

Bagchi and Oxtoby (1983) suggested that the non-attainment of SL can be explained within Grote–Hynes theory. If the frequency dependent viscosity can be approximated by equations (23) and (24), then a new time constant related to the shear and bulk relaxation times τ_s and τ_v enters the problem. When η_s^0 and η_v^0 become very large, τ_s and τ_v become very large as well, and frequency dependence of the friction become significant. In this limit $p\tau_s \gg 1$, so that

$$\eta_s(p) \simeq \frac{\eta_s^0}{p\tau_s} = \frac{G_\infty}{p}$$

and

$$\eta_v(p) = \frac{\eta_v^0}{p\tau_v} = \frac{K_r}{p}$$

i.e. $\eta_s(p)$ and $\eta_v(p)$ become almost independent of the zero-frequency viscosity η_s^0 . So, if η_s^0 is varied by changing temperature, then $\eta_s(p)$ and $\eta_v(p)$ would change only through the weak dependence of G_∞ and K_r temperature. Therefore, the rate of isomerization would show only a weak dependence on η_s^0 . This is markedly different from the low viscosity behaviour where $p\tau_s < 1$ over the relevant values of p (i.e. close to λ_r) and the frequency dependent rate theory predicts results similar to Kramers' theory. This is indeed observed in numerical evaluation of rate constants; that is, there are two distinct regions of completely different slope in the plot of rate constant versus viscosity and SL is not attained even at viscosities much larger than that predicted by Kramers' theory.

This raises the important question: under what conditions can Smoluchowski behaviour be observed? Experiments (Keery and Fleming 1982) indicate that SL is attained when ω_b is small, which is in agreement with Grote–Hynes theory. But if the barrier is high and sharp, frequency dependence is important and SL may never be realized at arbitrarily large shear viscosity.

The above discussion is of course qualitative because the validity of Maxwell forms (23) is questionable in the high-viscosity regime. Nevertheless, the validity of the above argument seems reasonable in the two extreme limits: $\omega_b^{-1} \gg \tau$ (Kramers' limit) and $\omega_b^{-1} \ll \tau$ (rate becomes independent of η_s^0 for large η_s^0). However, most experimental situations lie in the intermediate regime. Unfortunately, no reliable expression for the frequency dependent friction is available for those liquids which are mostly used; even the hydrodynamic expression needs many simplifying assumptions. In one limit,

however, one can get a definite answer. This is the incompressible limit of the hydrodynamic expression for the frequency dependent friction. In this limit an analytic expression for λ_r can be obtained (Bagchi 1985). This expression clearly reveals three different regions in the rate constant dependence on viscosity. In addition to the TST and SL limits, one obtains a region where $k \propto (\eta_s^0)^{-\alpha}$ with α less than unity.

Grote *et al.* (1984) recently suggested that in certain cases rate constant can even increase with viscosity as opposed to the expected decrease. This fascinating prediction is based on the premise that for high-frequency barriers, the short-time 'collisional' contribution dominates the frequency dependent friction. Theoretically, this is quite plausible. It would be interesting to obtain experimental confirmation of this prediction.

5. Isomerization dynamics in the absence of an activation barrier

There are several important isomerization reactions in solution in which the intramolecular potential surface does not present a significant barrier ($E_0 \ll 1$ kcal/mole) to the motion leading to the isomerization reaction. These isomerization reactions are usually probed by studying the viscosity dependent non-radiative decay of an excited state of the molecule. The rate-determining step in the electronic relaxation process of the initially formed excited state involves large-amplitude motion which is usually rotation of a bulky group around a molecule-fixed axis. Two well documented isomerization reactions in solution where non-radiative relaxation occurs without the intervention of a sizeable activation barrier are the relaxation of triphenylmethane (TPM) molecules in lower n-alcohols (Sundström and Gillbro 1984 b, Cremers 1980, Ippen *et al.* 1976, Yu *et al.* 1977) and the relaxation of *trans*-stilbene in n-alcohols (Sundström and Gillbro 1984 c). Of these two, the former, that is, the case of TPM due molecules, has been studied extensively. Especially, the viscosity dependence has been investigated by a variety of steady-state and time-resolved spectroscopic studies. The experimental findings are summarized below.

- (i) The time dependence of the excited state decay is viscosity dependent. The decay is usually single exponential at low viscosity, but becomes multi-exponential as viscosity of the solvent is increased (Ippen *et al.* 1976, Cremers and Windsor 1980, Sundström and Gillbro 1984 c). This change in the form of the decay curve is an important feature of the radiationless relaxation in the absence of an activation barrier.
- (ii) The fluorescence quantum yield ϕ_f depends on a fractional power of the solvent viscosity. Following the initial suggestion of Förster and Hoffmann that $\phi_f \propto \eta^{2/3}$, several workers have found adequate fits to this form over large viscosity ranges (Förster and Hoffmann 1971, Hirsch and Mahr 1979, Brey *et al.* 1977).
- (iii) Ground-state recovery experiments carried out a range of wavelengths have suggested the existence of a short-lived intermediate in the relaxation process (Sundström *et al.* 1982, Grzybowski *et al.* 1979). Recent studies of Sundström and Gillbro (1984 c) further substantiate this suggestion. They carried out transient absorption measurements by varying the excitation and the analysing wavelengths independently and observed that for crystal violet and for ethyl violet, the radiationless relaxation time constant τ_{nr} depends on the analysing wavelength. In particular, the absorption recovery experiments with $\lambda_{excit} = \lambda_{analyse}$ performed at wavelengths corresponding to short wavelength should, in the absorption spectrum, yield lifetimes approximately twice as long

as those obtained in the long wavelength part of the spectrum. But for some other TPM dye molecules, Malachite Green and Brilliant Green, the relaxation times were independent of wavelength.

The theoretical development of relaxation involving large-amplitude motion in the absence of an activation barrier has lagged behind the experimental research. For a long time, the calculations of Förster and Hoffmann were the only quantitative calculations that were available. Earlier Oster and Nishijima (1956) considered non-radiative relaxation in TPM dyes as a rotational relaxation in the absence of a barrier in which the electronic energy is transferred to bath molecules simply via rotational motion. However, no quantitative treatment of this model or its generalization has yet been carried out. An extensive study of the viscosity dependence of relaxation in TPM dyes has been carried out by Cremers (1980) who solved a system of coupled Smoluchowski equations for the time dependence of the population in ground and excited states. We shall return to the discussion of various theories later.

The kinetics of a chemical reaction in the absence an activation barrier poses interesting theoretical and experimental problems. In the absence of a high barrier, there is no natural separation of time-scales between the motion in the reactive region and in the rest of the potential surface. Therefore, a steady-state Kramers' type calculation is no longer possible and one must solve for the full time-dependent probability distribution function of the system remaining on the excited state surface. If the decay of this probability function is not exponential, which is most often the case in the absence of a sizeable barrier, the definition of a rate constant is not obvious. Another important problem is the characterization of the source of decay from the excited surface. There are several scenarios that are possible. The most widely used model is that of Förster and Hoffmann (1971) who studied relaxation in the absence of a barrier by assuming the existence of a sink at a certain position in the excited-state surface and which gives rise to decay of excited-state population. The sink may be due to a displacement of the minimum of the excited-state surface with respect to the ground-state minimum in such a way that the energy gap between the two surfaces is a minimum at a certain point on the excited surface. Such a situation is described in figure 6. Another model was proposed earlier by Oster and Nishijima (1956) in which the relaxation of the excited state was assumed to take place by a rotational diffusion

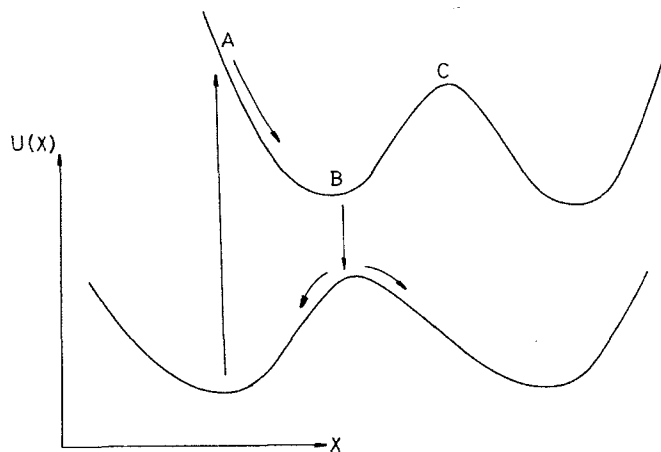


Figure 6. A typical potential surface which can give rise to radiationless relaxation without the intervention of an activation barrier.

process. As pointed out by Sundström and Gillbro (1984 c), the excited-state surface in the Oster–Nishijima model is perfectly flat along the reaction coordinate. However, no quantitative calculation has yet been carried out on this model. In the following, we briefly discuss the recent reformulation by Bagchi *et al.* (1983 a) of the Förster–Hoffmann model and compare the predictions of their calculations with the available experimental results.

Bagchi *et al.* (1983 a) considered a one-dimensional model for the reactive motion on the excited surface. The radiationless relaxation is represented by a coordinate-dependent sink which gives rise to decay in excited-state population. The motion along the potential surface is governed by the force from the potential (approximated as harmonic) and the viscous drag of the solvent. The initial excitation puts the molecule at certain position on the excited surface (position A in figure 6). The subsequent relaxation of the probability distribution function $P(x, t)$ for staying on the excited surface may be modelled by a modified Smoluchowski equation of the following form

$$\frac{\partial p(x, t)}{\partial t} = \frac{k_B T}{\zeta} \frac{\partial^2 p}{\partial x^2} + \frac{\omega^2 \mu}{\zeta} x \frac{\partial p}{\partial x} - k_{nr} S(x) P - k_r P \quad (26)$$

where ω is the frequency of the (assumed) harmonic surface, ζ is the relevant friction coefficient, μ is the reduced mass of the reactive motion and T the temperature. k_{nr} is the magnitude of the radiationless rate at the origin (where $S(x)$ is chosen to be unity) and k_r is the radiative rate constant independent of position.

It is obvious from (26) that the form of the sink function $S(x)$ will play an important role in the formulation of Bagchi *et al.* The precise form of $S(x)$ is, however, very difficult to obtain. It would depend on the details of the forms of the ground and the excited-state potential surfaces, the couplings between them, and also on different channels of non-radiative relaxations. In order to investigate the effects of the sink functions $S(x)$, Bagchi *et al.* (1983) studied three different models for $S(x)$.

- (a) The sink is a pinhole at the origin. This mimics the situation where there is no radiationless transition from anywhere except the origin where the energy gap between the two surfaces may be a minimum and so the decay is very fast. This model may also be relevant to those situations where there is a ‘funnel’ in some region of the potential surface.
- (b) $S(x)$ is a Gaussian function with a maximum at the origin. This is actually quite realistic because the energy difference between two harmonic surfaces in a quadratic function and so an exponential energy-gap law predicts a shifted Gaussian probability distribution between two surfaces.
- (c) $S(x)$ is a Lorentzian function with the transition probability maximum at the origin.

Let us now briefly comment on the relation of the Förster–Hoffmann model with that of Bagchi *et al.* These two models are similar in spirit. But Förster and Hoffmann (1971) chose a quadratic form for $S(x)$ which is entirely unreasonable since it predicts an increase in the rate even when the gap between the ground and the excited surfaces increases. They also assume that all the molecules on the excited surface follow an *average* relaxation pathway rather than allowing for a random distribution of motions on the excited surface. The Förster–Hoffmann model gives a prediction for the viscosity dependence of the quantum yield ($\phi_f \propto \eta^{2/3}$) which is in accord with experiments. However, this agreement is somewhat fortuitous in view of the fact that the time-

dependence of the fluorescence decay given by the model is $\exp(-\alpha t^3)$, which has not been observed experimentally.

Next we briefly discuss the solutions of equation (26) for two choices of the sink function $S(x)$: the pinhole sink and the Gaussian sink. For the pinhole sink, once the solute particle arrives at the origin (point B in figure 6), it decays with unit probability. Mathematically this corresponds to the well known problem of an absorbing barrier at the origin and the solution for $P_e(t)$, the probability of the particle being on the excited surface after time t , can be easily obtained by the method of images (Montroll and West 1979)

$$P_e(t) = \frac{2}{\sqrt{\pi}} \exp(-k_r t) \operatorname{erf}\{Z(t)\} \quad (27)$$

where $\operatorname{erf}\{a\}$ is the error function defined by

$$\operatorname{erf}\{a\} = \int_0^a dq \exp(-q^2) \quad (28)$$

and

$$Z(t) = |x_0| \exp(-Bt) [2A\{1 - \exp(-2Bt)\}/B]^{-1/2} \quad (29)$$

with

$$A = \frac{k_B T}{\zeta}; \quad B = \frac{\omega^2 \mu}{\zeta} \quad (30)$$

Since the error function has the following series expansion

$$\operatorname{erf}(Z(t)) = \sum_{n=0}^{\infty} (-1)^n \frac{(Z(t))^{2n+1}}{n!(2n+1)!} \quad (31)$$

(28) predicts a multi-exponential decay for $P_e(t)$, except for sufficiently long times when the decay becomes single exponential. Since B is inversely proportional to viscosity (equation (30)), the decay of $P_e(t)$ is governed by t/η .

Next we briefly discuss the results for the Gaussian sink. Bagchi *et al.* chose the sink function in the following form

$$S(x) = \exp(-x^2/a^2) \quad (32)$$

where a is the measure of the width of the sink function centred around the minimum of the excited-state potential surface. For this case, it has not been possible to solve the (26) analytically and it has to be solved numerically by a series expansion. The resulting expressions are complicated. Here we briefly summarize the results of the calculations of Bagchi *et al.* (1983).

- (a) For the Gaussian sink, the viscosity dependence of fluorescence quantum yield can be fitted to a form

$$\phi_f = A\eta^\alpha \quad (33)$$

with α in the range $0.5 \lesssim \alpha \lesssim 0.8$. Figure 7 illustrates a representative calculation. The slope of the plot of ϕ_f versus $\ln \eta$ in the lower viscosity range is ~ 0.64 for the parameters chosen. The slope increases in the very low viscosity range ($\eta \simeq 1$ cp) and decreases in the high-viscosity range ($\eta \simeq 10$ poise) where the graph becomes flatter. In fact, a careful analysis of the data shows that the slope

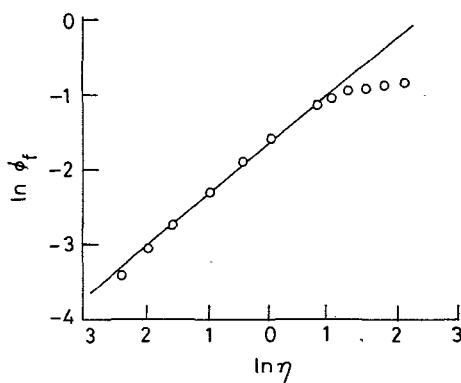


Figure 7. Dependence of fluorescence quantum yield (ϕ_f) on viscosity (η) predicted by the theory of Bagchi *et al.* for Gaussian sink. The values of the parameters are: $a=0.01$, $x_0=0.1$, $k_{nr}=1.0 \times 10^{12}$, $k_r=1.0 \times 10^9$, $\omega=1 \times 10^{12}$. Viscosity (η) is in poise.

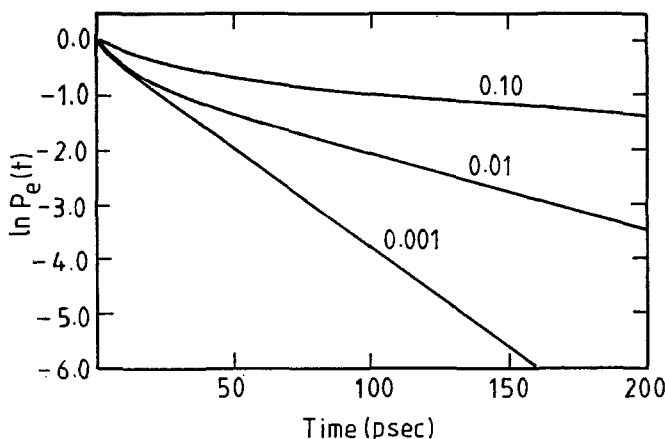


Figure 8. The decay of excited-state population for a Gaussian sink. Parameters are the same as in figure 7 except $k_r=0$. The values of viscosities (in poise) are indicated on the graph.

of the plot ϕ_f versus $\ln \eta$ always changes with viscosity and it may not be meaningful to consider the exponent α in (33) as a constant independent of viscosity. If we set $k_r=0$ to study only the non-radiative decay, we find $\alpha \approx 1$ at large viscosities. So, the saturation mostly arises from competition between the radiative and the non-radiative modes of decay.

- (b) The decay behaviour of $P_e(t)$ is strongly dependent on viscosity. The decay is multi-exponential at all viscosities except in the limit $\eta \rightarrow 0$ where the Smoluchowski equation description is unreliable. Figure 8 describes the behaviour of the decay curve for several values of the viscosity.
- (c) The isoviscous temperature dependence of the rate is weak. The theory predicts a cross-over from a small 'negative' activation energy at small viscosity to a positive activation energy at larger viscosities. This interesting cross-over behaviour arises from the competition between the non-radiative relaxation and the oscillatory motion in the potential well.

- (d) The decay function $P_e(t)$ depends on the wavelength of excitation because light of different wavelengths excites the molecule to different positions on the excited surface. The dependence of the rate constant of non-radiative decay on excitation wavelength, however, is non-trivial. At very low viscosity, the rate constant is independent of excitation wavelength.

Recently, Sundström and Gillbro (1984 b) carried out an extensive experimental study of solvent effects on TPM photophysics. For lower alcohols (C_1 – C_4), the relaxation of the excited state occurs without the intervention of an activation barrier. Sundström and Gillbro compared their results with the theory of Bagchi *et al.* (1983) and found disagreements on several major points. These experiments reveal that the temperature dependence of relaxation, especially the cross-over from small ‘negative’ activation energy to positive activation energy with viscosity, is a solvent-induced effect and is not an intrinsic property of the molecular potential surface as suggested by Bagchi *et al.* The main conclusion of Sundström and Gillbro (1984 b) is that the relaxation rate has an intricate solvent dependence and cannot be described by a simple stochastic theory like that of Bagchi *et al.* (1983). The relaxation kinetics of TPM molecules in alcohol solutions remains a challenging problem to theoreticians and experimentalists alike and future studies on these systems would be worthwhile.

The theoretical analysis of Bagchi, Fleming and Oxtoby is based on the Smoluchowski equation (26). Their results, therefore, are not applicable to very low viscosities where inertial effects become important and one must consider the full phase space Fokker–Planck equation (Chandrasekhar 1943). However, the solution of this equation is very difficult to obtain analytically. Therefore, Bagchi *et al.* (1983 b) solved the Fokker–Planck equation with a Gaussian sink term by generating stochastic trajectories. The main conclusion of their calculations is that the rate constant for population decay is a *non-monotonic* function of solvent friction, as illustrated in figure 9. The value of the rate constant in the $\eta \rightarrow 0$ limit is more than an order of magnitude *lower* than the prediction of the Smoluchowski equation. The Smoluchowski equation description is, however, reliable over virtually the entire experimentally relevant range of viscosity.

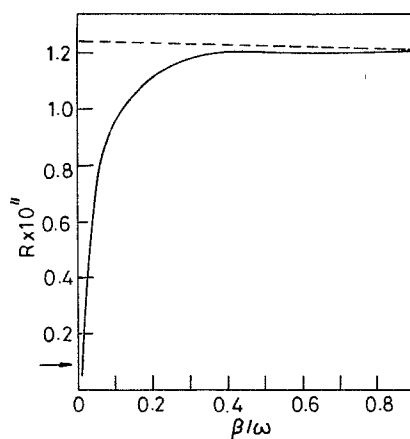


Figure 9. The rate constants of excited state population decay from a Gaussian sink plotted against the friction parameter $\beta(=\zeta/\mu)$. The solid line is the result from the Fokker–Planck trajectory calculations. The Smoluchowski equation result is shown by the dashed line. The analytical estimate for Fokker–Planck description in the $\zeta \rightarrow 0$ limit is shown by an arrow.

Sundström and Gillbro (1984c) also carried out an experimental study of the dynamics of isomerization of *trans*-stilbene in n-alcohols at low viscosities. The activation energy E_0 for non-radiative decay from the excited surface is very small, close to zero. The decay curve was found to be exponential. The time constant τ_{nr} of decay has a linear dependence on viscosity for small values of viscosity, but dependence becomes weaker as η is increased. Bagchi (1985) analysed these experimental results and suggested that they are in good agreement with the theory of Bagchi *et al.* (1983). From the experimental results, he obtained approximate estimates of the frequency ω of the excited surface (assumed harmonic) and of the width a of the sink function $S(x)$, assumed Gaussian (equation (32)). The values are: $\omega = 1.3 \times 10^{12} \text{ s}^{-1}$ and $a = 0.07 \text{ \AA}$. The value of the frequency is rather low which may be due to the poor estimate of the frictional force provided by the hydrodynamic expression used to relate ζ to η . The value of the sink parameter a predicts a narrow sink function which means that the non-radiative decay occurs only from a small region in the excited surface. Further experimental and theoretical work is necessary to verify these predictions.

6. Solvent effects on reaction potential surface

We mentioned in the introduction that the potential energy surface of a reaction may be profoundly affected by the solvent. For isomerization reactions in solution, this effect is most dramatically revealed in those reactions which take place in the optically excited state of the isomerizing molecule. This effect is most easily studied by changing the nature of the solvent. The change in the magnitude of the isoviscous activation energy serves as a good measure of the solvent effects on the potential energy surface. There are several well known isomerization reactions where the isoviscous activation energy changes by several factors in changing the solvent. For example, the activation energy of *trans*-stilbene in normal alkanes is larger by more than an order of magnitude than the same in n-alcohols (Sundström and Gillbro 1984b). Several other examples can be obtained from table 2.

Clearly, a quantitative understanding of the solvent effects on the reaction energy surface is a formidable problem. A chemical reaction in solution is a strongly coupled many-body problem and one must consider not only the coupling between the reactive mode and the solvent molecules but also the couplings between the reactive mode and the non-reactive modes of the reacting molecule; the latter may also be solvent dependent. Thus a first-principles theoretical calculation of solvent effects on the potential surface is prohibitively difficult. The traditional method of including the solvent-induced effects is to write the rate in the following form

$$k = A(\eta) \exp(\Delta S^\ddagger/k_B) \exp(-\Delta H^\ddagger/k_B T) \quad (34)$$

with

- ΔS^\ddagger Entropy of activation of the reaction,
- ΔH^\ddagger Enthalpy of activation,
- $A(\eta)$ Viscosity dependent prefactor, assumed to be given by the Grote-Hynes formula (16)

The solvent effects on potential surface can be studied by changing the solvent while keeping the viscosity of the solvents the same. This leaves the viscosity dependence of $A(\eta)$ in (34) unchanged while ΔS^\ddagger and ΔH^\ddagger may change. We note that $A(\eta)$ also depends on solute-solvent interactions because the frequency parameters ω_R and ω_b depend on potential energy surface. For many purposes ΔH^\ddagger is well approximated by E_0 , the

activation energy of the reaction, because the contribution from the pressure volume term, $P\Delta V^\ddagger$, is small. If we write E_0 in the form

$$E_0 = E_m + \Delta E_{\text{solvent}} \quad (35)$$

where E_m is the intrinsic, molecular, barrier height and $\Delta E_{\text{solvent}}$ is the solvent contribution, then the contributions from the solute-solvent interactions are contained in $\Delta E_{\text{solvent}}$. A similar decomposition can be done for ΔS^\ddagger .

Since the molecular arrangement is different in the activated complex state from that in the reactant, such molecular properties as dipole moment, and polarizability will also be different in these two states. So, the solute-solvent interactions will definitely be different in the two states, leading to a non-zero contribution of $\Delta E_{\text{solvent}}$ to E_0 . Courtney and Fleming (1985) pointed out that the sharp decrease in activation energy for isomerization of DPB in going from normal alkanes to alcohols can be rationalized if the intermediate twisted state (the activated complex) is stabilized in polar solvents. A schematic illustration of such solvent effects is depicted in figure 10. Note that both the barrier frequency ω_b and the reactant-well frequency ω_R are also affected by such solvent effects. Another possible scenario is that the activated state is destabilized by the solvent, thus leading to a higher activation barrier.

The difference in solute-solvent interactions can also affect the entropic contribution, ΔS^\ddagger , to the rate constant. In particular, the activated state may have such a configuration as induces a local order (disorder) in the surrounding solvent, resulting in a negative (positive) entropy contribution to ΔS^\ddagger . Recent computer simulations of Statman and Robinson (1985) of *cis-trans* isomerization in a model system revealed a significant entropy contribution to the rate. These authors attributed the entropy contribution to the change of hydrodynamic volume on isomerization.

The influence of a solvent on the energy and entropy of activation can be significant if the solvent is polar and if the dipole moment of the activated complex is significantly different from that of the reactant. Van der Zwan and Hynes (1982) have investigated these polar solvent effects on solution phase reactions.

Ladanyi and Evans (1983) have investigated the importance of solute-solvent interactions on the potential energy surface of *trans* to *cis* isomerization of stilbene in n-alkanes. They calculated the potential of mean force experienced by the isomerizing molecule *along* the reaction coordinate by using the theory of Chandler and Pratt (1976, 1977) who related the potential of mean force to cavity distribution function. Ladanyi and Evans concluded that for isomerization of *trans*-stilbene in n-alkanes, the solvent influence on the reaction potential surface is negligible.

For many chemical reactions in the liquid phase, an interesting linear relationship between the entropy of activation and the enthalpy activation has been observed (Bell 1937, Eyring and Laidler 1940). This linear relationship is usually written in the form

$$T\Delta S^\ddagger = \alpha\Delta H^\ddagger + \beta \quad (36)$$

with $1 > \alpha > 0$ and $\beta > 0$. Such a relationship has not yet been reported for isomerization reactions in solution. It is an interesting problem to explore.

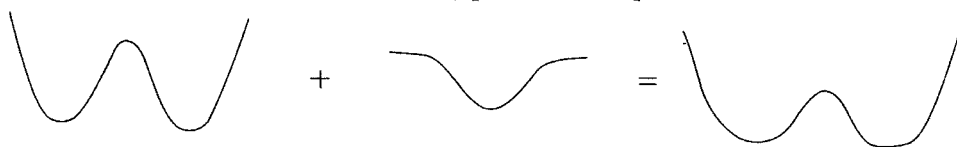


Figure 10. A schematic representation of a probable solvent effect on the reaction potential surface.

7. Non-equilibrium effects in isomerization dynamics

The discussion of the solvent effects on the reaction potential surface in the last section is based on the *assumption* that the solvent molecules are in equilibrium with the reacting system at all times during the reaction. This allows one to describe the solvent effects in terms of the energy and the entropy of activation which are the differences between the energy and the entropy of the activated complex and the reactant, both in equilibrium with the solvent. The dynamical effects of the solvent then enter only through the collisional term, the friction parameter ζ , which at high viscosity hinders barrier crossing by forcing recrossing of the particle back into the reactant region. However, for reactions involving polar or ionic groups in a polar solvent, there is some degree of non-equilibrium solvation in the transition state and its neighbourhood. This is because for a fast reaction, the solvent molecules will not be able to rearrange sufficiently rapidly to follow their equilibrium path to the reactive motion. In such a situation, it will be erroneous to estimate ΔS^\ddagger and ΔH^\ddagger from the solvation values of these quantities for the reactant and the transition state. In addition, qualitatively new effects can arise from the non-equilibrium solvation dynamics (Bagchi 1986).

Recently, Van der Zwan and Hynes (1983, 1984) investigated a simple model for dipole isomerization in polar solvents. In this model the reaction takes place via rotation of two inner reactive dipoles (RDs) by passage over a barrier. The RDs are in turn coupled to two outer solvent dipoles (SDs) by dipolar interactions. The SDs are coupled with the remainder of the solvent by simple frictional damping forces. Van der Zwan and Hynes (1983, 1984) carried out a full dynamical treatment of this problem at the generalized Langevin equation level. Their treatment reveals several interesting solvation regimes where the non-equilibrium effects were important and where the rate constant differs considerably from the traditional transition state theory result. One interesting new result of this work is that the reaction coordinate is determined by the solvent response function at the reactive frequency λ_r .

The above work of Van der Zwan and Hynes constitutes perhaps the first attempt towards a quantitative theory of non-equilibrium solvation effects on isomerization dynamics in solution. Experimental confirmation of the different predictions of this theory is, however, difficult to obtain because there are many competing contributions to rate which may mask the subtle effects predicted by the theory. Further experimental and theoretical work on this interesting problem are needed to understand the non-equilibrium effects.

8. Computer simulations

Computer simulations have played a key role in our understanding of the dynamics of the liquid state (Hansen and McDonald 1976). However, it is only recently (Statman and Robinson 1985) that a full molecular dynamics calculation of an isomerization reaction has been carried out, although several interesting stochastic trajectory calculations were carried out earlier to test the validity of the rate theories (Montgomery *et al.* 1979, 1980). The advantage of a full molecular dynamics simulation of a 'realistic' isomerization reaction is manifold. Firstly, it allows the calculation of the rate for a reaction where the potential parameters are known uniquely. Secondly, it allows a systematic variation of the 'experimental' conditions which is often impossible in real experiments. Thirdly, in case of a disagreement between theory and experiment, it is often possible to pinpoint the cause by analysing the simulation data.

Recently, Statman and Robinson (1985) simulated the isomerization dynamics of a model reaction. In this work, the isomerizing 'molecule' is made up of four Lennard-

Jones atoms bound together by holonomic constraints. The liquid is made up of 50 L-J atoms which interact with the atoms of the reacting 'molecule' via identical potential. The isomerization barrier $V(\theta)$ between the end atoms is defined by

$$V(\theta) = V_0(\sin^2 \theta + 4q \sin^2 V_2 \theta) \quad (37)$$

where θ is the dihedral angle and q is a disymmetry parameter. In the simulation, the model reaction was confined to one dimension by allowing intramolecular vibration only along the reaction coordinate θ . Statman and Robinson found that the friction along the reaction coordinate can be a factor of two *less* than that for the bulk solvent. Another important result of this simulation is that the entropy of activation makes a non-trivial contribution to the rate constant. In this case, the entropy contribution seems to arise from a change of hydrodynamic volume upon isomerization. The modification due to non-Markovian effects was small because the viscosity of the solvent was in the intermediate regime.

The simulation results of Statman and Robinson (1985) indicate that computer simulations can play a very important role in elucidating the role of solvent on the isomerization dynamics. Further work on more realistic systems will certainly be worth while.

9. Conclusions

It is clear from the above review that despite considerable advances in our understanding of the dynamics of isomerization reactions in solution, there are still many questions that are far from understood. In many respects we have just begun to isolate the fundamental problems that must be solved to achieve a satisfactory understanding of these complicated reactions. In the following we discuss some specific problems for future considerations.

(a) *Effects of solute-solvent interactions on reaction potential surface*

The importance of these effects is evident from the large change observed in the activation energy when the solvent is changed from an apolar solvent to a polar solvent. This implies that the polar properties, such as the dipole moment and the polarizability, play an important role in determining the potential surface along the reaction coordinate. The solvent effects are most dramatic for the excited state. It is obvious that the polar properties of the isomerizing molecules change along the reaction coordinate. However, not much is known about this dependence. Measurements of the wavelength dependence of the absorption and the fluorescence spectra in different solvent environments would be helpful to understand this influence of solvent. Theoretically, one needs to do self-consistent quantum chemical calculations for the potential surface of the molecule in the force field of the solvent. Such calculations have been carried out for simple systems (Tapia 1981). However, simple *ab initio* calculations are known to be unreliable for excited states. Further research on this problem would certainly be worth while.

(b) *Multi-dimensional nature of the reaction*

This is currently an active area of research. The treatments of Kramers and of Grote-Hynes are strictly one-dimensional. However, in real systems the reactive mode will be coupled to other non-reactive modes of motion of the molecule. If this coupling is small, then a one-dimensional model is reasonable. However, our knowledge of intra-mode couplings in large molecules is rather poor. If the coupling between the reactive

mode and non-reactive modes is strong, then qualitatively new effects can arise. One such effect is to introduce frequency dependence of friction even when the bath is Markovian (Carmeli and Nitzan 1984, Zwadzki and Hynes 1985).

The importance of the multi-dimensional nature of the potential surface in specific isomerization reactions is still an open problem. It is obviously difficult to ascertain the potential parameters for the non-reactive modes. Thus a quantitative, or even a semi-quantitative, evaluation of the influence of other modes on the rate of isomerization is difficult. At this stage, it is important to understand the couplings for the isolated molecule (e.g. by studies in supersonic jet expansions). These couplings will obviously change in solution, but they can serve as a starting point. Theoretical studies with realistic models for multi-dimensional modes are also necessary to understand this problem.

(c) *Frequency dependent friction*

Since the hydrodynamic expression for the frequency dependence of friction may not be reliable for many cases, we need a reliable way to find the frequency dependent friction. Computer simulation studies can play an important role in this problem, but eventually we would like to have an analytic expression.

(d) *Evaluation of potential parameters*

It is evident from our discussions in Sections 3 and 4 that we need accurate values of the potential parameters ω_R and ω_b in order to make a meaningful comparison between theory and experiment. So far the method has been to fit the experimental data to some particular theoretical expression. This is obviously unsatisfactory. It is imperative that we find an alternative procedure to calculate these parameters. At present this is an open problem.

(e) *Effects of non-equilibrium solvation dynamics*

For a fast isomerization reaction, the solvent degrees of freedom may lag behind the reactive motion. So, it may not be even justified to talk of equilibrium quantities, like entropy of activation, in this case. These effects may be important if the solvent is highly polar and the reactive motion involves large changes in the polar properties of the isomerizing molecule.

(f) *Entropy effects*

This may arise either from change in volume of the isomerizing molecule along the reaction coordinate, or from change in polarity, or from both. Computer simulations of Statman and Robinson (1985) indicate that such effects may play an important role in isomerization dynamics. Further theoretical and experimental, especially computer simulations, studies are necessary to understand this effect.

Note added in proof

Since the time of writing the above review (February to April 1985), a large amount of work has appeared in the literature on various aspects of isomerization dynamics in solution. In the following we briefly discuss some of the new results.

Hicks *et al.* (1985) reported a study of the effects of solvent polarity on photochemical reactions in solution. They studied isomerization kinetics of dimethylaminobenzonitrile (DMABN) in polar solvents and observed that various properties

of the barrier region change significantly with polarity of the solvent. This study suggests that in some cases deviations from Kramers' theory may be due to solvent-polarity-induced changes of the potential surface of the reaction.

A computer simulation study of the non-Markovian activated rate processes has been carried out by Straub *et al.* (1986). These authors calculated the barrier crossing rate constants for a Brownian particle in a double-well potential experiencing a non-Markovian friction. Significant deviations from Grote-Hynes theory (Grote and Hynes 1980) was observed in a physically interesting regime. These authors attributed the deviations to the nonlinearities of the potential surface near the barrier region. The new results of Straub *et al.* (1986) indicate that the role of non-Markovian dynamics on isomerization reactions may have been overestimated in earlier studies (Bagchi and Oxtoby 1983, Rothenberger *et al.* 1983).

Two papers have recently appeared on the dynamics of isomerization in the absence of a barrier. Ben-Amotz and Harris (1985) have studied the ground-state recovery, excited-state absorption and stimulated emission gain temporal profiles of crystal violet in low-viscosity normal alcohol solutions. Viscosity and wave length dependence of dynamics seem to be in agreement with the theory of Bagchi *et al.* (1983 a). Akesson *et al.* (1986) have studied several dye molecules which are characterized by barrierless isomerization in the excited state. The experiments were done in normal alcohol solutions by picosecond absorption spectroscopy. Except for 1,1',4,4'-cyanine dye, the observed behaviour was in agreement with theoretical predictions (Bagchi *et al.* 1983 a, Bagchi 1985).

There has recently been considerable interest in the dynamics of photoisomerization in supersonic beams where excited-state isomerization is studied in 'isolated molecule' conditions (Syage *et al.* 1982, Amirav and Jortner 1983, Majors *et al.* 1984, Scherer *et al.* 1984, Troe 1985). However, a detailed discussion of this subject is out of place here.

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