

Kinetics in highly viscous solutions: dynamic solvent effects in 'slow' reactions*

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Abstract: In combination with viscous liquids, high pressure was effectively used to study dynamic solvent effects on the rate of geometrical isomerization about a carbon-nitrogen and a nitrogen-nitrogen double bond in the molecules at their electronic ground (S_0) state. All of the reactions were slow enough to guarantee the validity of the transition state theory (TST) at atmospheric pressure and the TST-expected pressure effects were observed. However, strong pressure-induced retardations replaced such effects at high pressures. These retardations were concluded as an indication of a shift of the reaction from the equilibrium TST-valid region to the nonequilibrium TST-invalid region. In other words, slow thermal fluctuations of the solvent molecules at high pressures made it possible to observe dynamic solvent effects on unimolecular S_0 -state reactions. Separation of the static pressure effects from the dynamic solvent effects were performed by extrapolations of the rate constant in the TST-valid region to the TST-invalid one. This operation allowed us to make a direct comparison of the observed rate constant with that expected from TST. The results strongly suggest a necessity to separate the chemical and the medium coordinates in the reaction systems studied.

INTRODUCTION

Dynamic solvent effects on unimolecular reactions such as geometrical isomerization about a double or a single bond have been studied extensively in the last two decades [1]. Such studies are expected to yield fundamental knowledge on dynamic details of chemical reactions in solution. Theoretical models may be divided into two classes. In the first model, the climbing of the energy barrier by the reactant, i.e. configurational or conformational movement(s) of atomic group(s) along the reaction coordinate, is assumed to be Brownian motions. In this model, the chemical transformation and the rearrangement of the solvent molecules in the solvation shell are concerted and the reaction can be described by one reaction coordinate. The Kramers model [2] and its modification by Grote and Hynes (KGH model) [3,4] belong to this category. In the second model, chemical transformation and the solvent rearrangement are described by two independent coordinates. If the solvent thermal fluctuations are not fast enough to maintain the thermal equilibrium between the initial and the transition states, the solvent rearrangement in the solvation shell can be rate-determining. Under such circumstances, a reactant molecule has to wait for the formation of the solvation sphere that stabilizes the activated complex before it undergoes chemical transformation. This model was first discussed by Agmon & Hopfield [5,6] and later by Sumi and Marcus [7,8] and also by Berezhkovskii & Zitserman [9,10].

Most of the experimental works performed so far were concerned with molecules at their S_1 state. This is understandable because the reaction usually takes place in the range of 10^{-9} – 10^{-10} s which is only slightly longer than Debye period τ_D or longitudinal period τ_L of common organic liquids and therefore we can reasonably expect that the transition state theory (TST) does not hold in common organic solvents.

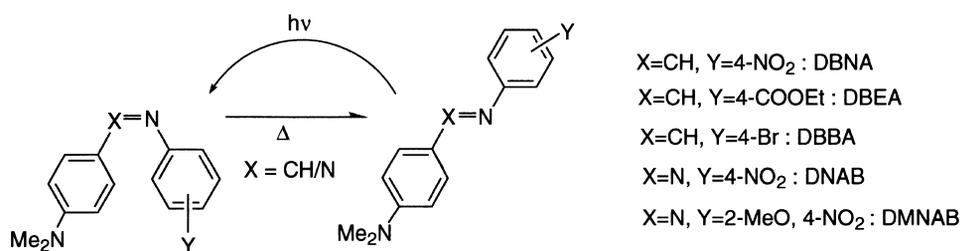
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However, this approach has one significant disadvantage. Since the time range of the chemical conversion and the solvent thermal fluctuations are close to each other, it is difficult to estimate the rate constant expected from TST k_{TST} . Careful works including supercritical fluids as reaction media demonstrated clearly the existence of the so-called Kramers' turnover [11–13] and the maximum rate constant in such experiments may be considered as k_{TST} . However, high pressure was used in those studies to slow down solvent fluctuations and separation of static pressure effects (Eqn 1) from the dynamic solvent effects induced by pressure was difficult because the TST-valid pressure range, if there is any, should not be wide enough to estimate the activation volume ΔV^\ddagger and its pressure dependence.

$$\left(\frac{\delta \ln k}{\delta P}\right) = -\frac{\Delta V^\ddagger}{RT} \quad (1) \quad \frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{TST}}} + \frac{1}{k_f} \quad (2) \quad \eta = \eta_0 e^{\alpha P} \quad (3)$$

A direct comparison of the observed rate constant k_{obs} with k_{TST} is highly desirable for the examination of the two-dimensional reaction-coordinate (AH) model because the model can be approximated to a two-step reaction mechanism (*vide infra*) and the rate expression is given by Eqn 2 where k_f is the rate constant for the fluctuation-limited solvent rearrangement [8]. Such a comparison would be possible if we could cast a 'slow' TST-valid reaction into a TST-invalid conditions by slowing down the solvent thermal fluctuations considerably. High pressure seems to be an ideal tool for this purpose because pressure dependence of the macroscopic viscosity η of liquids is approximately given by Eqn 3 where η_0 is the viscosity at 0.1 MPa [14]. By selecting liquids with branched molecular structures, the pressure coefficient α can be larger than 10/GPa. As a result, it is often possible to make the system more than a million times viscous simply by applying a pressure of several hundred megapascals. Since η is known to be correlated reasonably well with rotational relaxation times of neutral and charged species [15], it may be taken as a measure of the microscopic friction at least in a series of measurements in the same solvent. As mentioned earlier, a pressure increase inevitably affects the reaction rate (Eqn 1). Fortunately, however, kinetic effects of pressure on thermal reactions have been studied in numerous systems. As a result, thousands of activation volumes have been accumulated and their interpretations based on TST are well established [1,16–18]. In other words, it is possible to make a judgment whether the reaction remained in the TST-valid region or went into the nonequilibrium one from the pressure dependence of k_{obs} . Furthermore, empirical functions between k_{obs} and pressure are known [19,20] and therefore reliable estimates of k_{TST} at the TST-invalid conditions are possible. On the basis of these considerations, we decided to study kinetic effects of pressure on S_0 -state geometrical isomerizations shown in Scheme 1. The solvents used were 2-methyl-2,4-pentanediol (MPD), glycerol triacetate (GTA), and 2,4-dicyclohexyl-2-methylpentane (DCMP) for the anils and MPD and GTA for the azobenzenes. Table 1 lists selected η_0 and α values of these solvents estimated from the experimental viscosities at various temperatures and pressures [21–23].



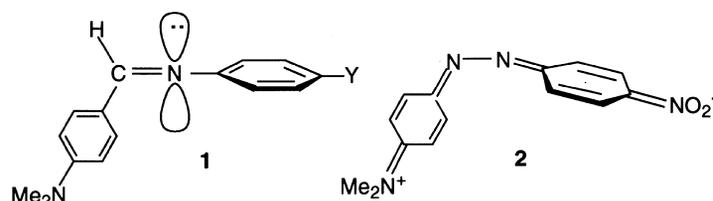
Scheme 1

The reactions were chosen because the activation energies were in the range of 50–70 kJ/mol, considerably larger than those of the S_1 -state reactions ($E_a \leq 15$ kJ/mol), and the half-lives were in milliseconds to seconds. In such slow unimolecular reactions, it is almost certain that the reaction is in the equilibrium region where TST can be applied at least approximately. Another advantage of these reactions was that irradiation of visible light triggers the reaction. The thermodynamically unstable *Z*-isomer can be formed by irradiation *in situ* and the measurements can be repeated for signal

Table 1 Viscosities at atmospheric pressure (η_0 , Pa s) and their pressure coefficients (α , /GPa) of viscous liquids used as reaction media

$T, ^\circ\text{C}$	DCMP		GTA		MPD	
	η_0	α	η_0	α	η_0	α
-5	0.546	53.2	0.146	41.8	0.324	28.3
5	0.156	46.5	0.0608	34.4	0.122	24.1
15	0.0584	41.2	0.0299	28.5	0.0553	20.7
25	0.0267	37.0	0.0168	23.6	0.0288	17.9
35	0.0142	33.7	0.0104	19.6	0.0167	15.6

accumulations. The decay of the *Z*-isomer followed the first-order rate law and therefore the rate constants could be determined unequivocally at all of the conditions studied. The mechanisms of these reactions had been established as a result of the experimental as well as the theoretical studies and in the course of the work, kinetic effects of pressure had been measured carefully [24,25]. The isomerization of the benzaldehyde anils is effected by inversion of the nitrogen atom and the *N*-phenyl group is perpendicular to the carbon-nitrogen double bond in the activated complex **1** [24]. The activation volumes were close to zero [26]. The same inversion mechanism seems to prevail also in azobenzenes [25]. However, when the molecule has an amino and a nitro group in the 4- and the 4'-positions as in DNAB and DMNAB, the reaction proceeds *via* dipolar rotation transition state **2** in polar solvents [25,27]. Because of the increased solvation in the transition state, large negative activation volumes are expected in this mechanism and this expectation was met. Both in the benzaldehyde anils and in the azobenzenes, no indication of viscosity dependence of the reaction rate had been observed in common solvents.

**Scheme 2**

EXPERIMENTAL OBSERVATIONS AND THEIR INTERPRETATIONS

General trends in highly viscous media

Pressure effects on the isomerization rate of DBNA and DNAB in common and viscous solvents with comparable polarities [28] are compared in Figs 1 and 2, respectively [21,29].

In Fig. 1, the solvents were GTA and methyl acetate and in Fig. 2, they were MPD and ethanol. In both reactions, the pressure effects in less viscous solvents were in agreement with the reaction mechanism, i.e. inversion in DBNA and rotation in DNAB. In the former, the pressure effect was almost nonexistent, while in the latter the reaction was strongly accelerated up to 800 MPa. Almost the same pressure effects were observed in GTA and MPD at pressures lower than 200 MPa, showing the validity of TST in these solvents despite their high viscosities. However, strong retarding effects of pressure were observed both in DBNA and DNAB at higher pressures. The most reasonable interpretation of these results is to assume that the reactions shifted from the TST-valid regime to the TST-invalid one because of the slow solvent fluctuations under high pressure, namely dynamic solvent effects were observed in the reactions of molecules in their electronic ground state. The measurements were also performed at several different temperatures and it was found that higher the temperature, higher the pressure of the appearance of the dynamic solvent effect. Two sets of examples are given in Figs 3 and 4 [1]. Qualitatively the same results were obtained in all of the reactions studied.

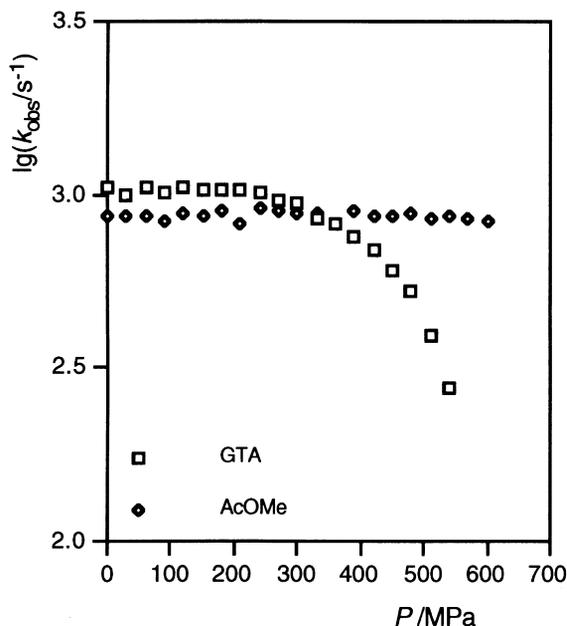


Fig. 1 A comparison of pressure effects on the isomerization of DBNA in GTA and methyl acetate at 25 °C.

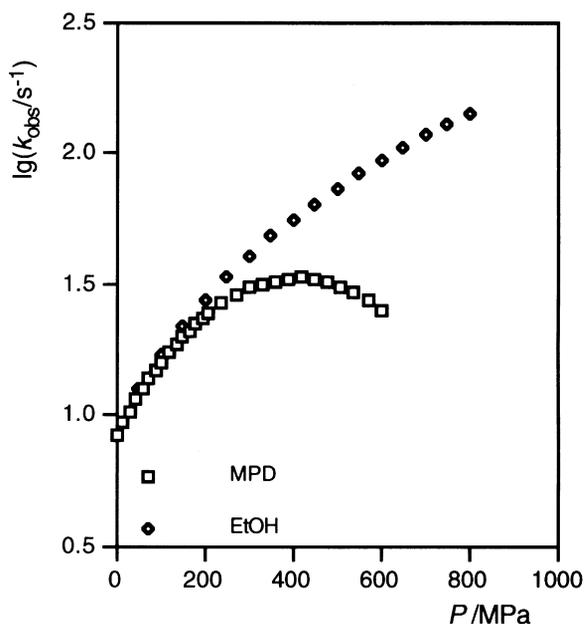


Fig. 2 A comparison of pressure effects on the isomerization of DNAB in MPD and ethanol at 15 °C.

Activation energies at isoviscosity conditions

One of the features of the KGH model is that the energy barrier in the rate determining step is independent of viscosity if we could keep the same potential energy surface at different viscosities. This makes a marked contrast to the AH model. The difference can be seen clearly in Fig. 5, a schematic illustration of the Sumi–Marcus version of the AH model [8] applied to the present reaction.

In this illustration, the reactant and the product energy minima are located in the lower left and the upper right corners, respectively. The ordinate C describes the chemical transformation and the abscissa M describes the medium changes. The borderline T between the two energy surfaces describes the transition state whose energy depends on the position on M . S is the lowest point on T . The zigzag arrows

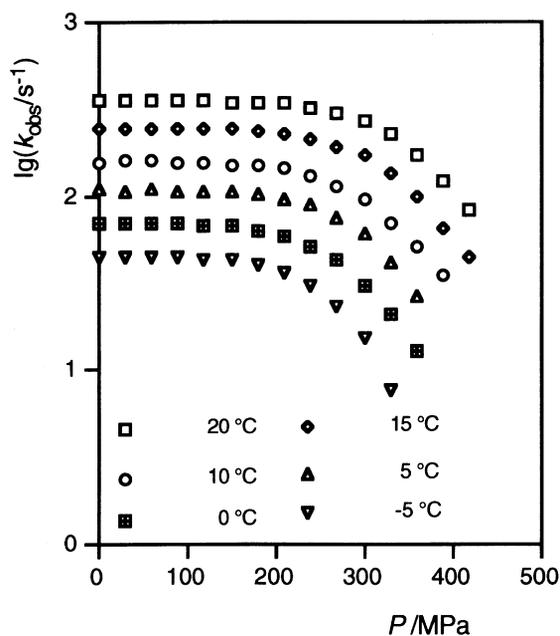


Fig. 3 Pressure effects on the isomerization of DBNA in DCMP at various temperatures.

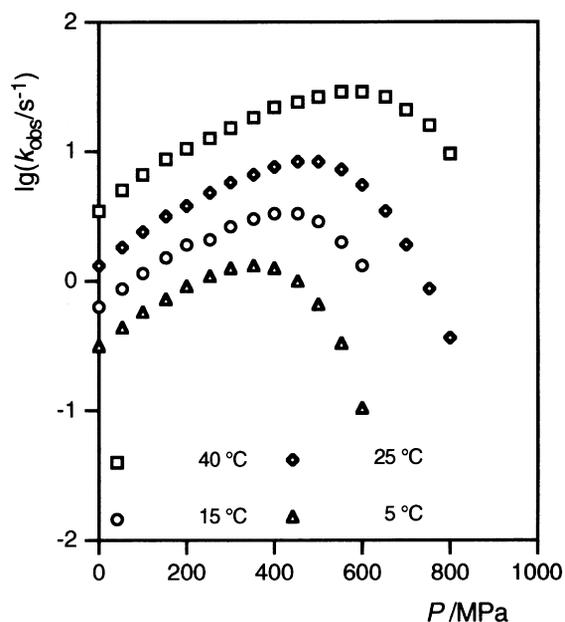


Fig. 4 Pressure effects on the isomerization of DNAB in GTA at various temperatures.

illustrate an example of the reaction paths possible at slow solvent thermal fluctuations. For a reactant to be able to surmount the energy barrier, the solvation shell has to be modified so that the transition state is sufficiently stabilized, i.e. the reactant must move to the right on M prior to the energy barrier crossing and these movements along M can be rate-determining. Z^* describes the reactant molecules with finite probabilities of the energy barrier crossing. An increase in the viscosity will slow down the solvent rearrangements and thus the reaction will be retarded. Compared at the same viscosity, the effect of temperature on this rate constant k_f will be smaller than that on k_{TST} because the energy difference between Z and Z^* , Ea_f , is smaller than that between Z and S , Ea_{TST} . From these considerations, we can predict that if the chemical and the medium coordinates can be independent at high viscosities, the isoviscosity activation energy will decrease as the system shifts from the TST-valid to the TST-invalid

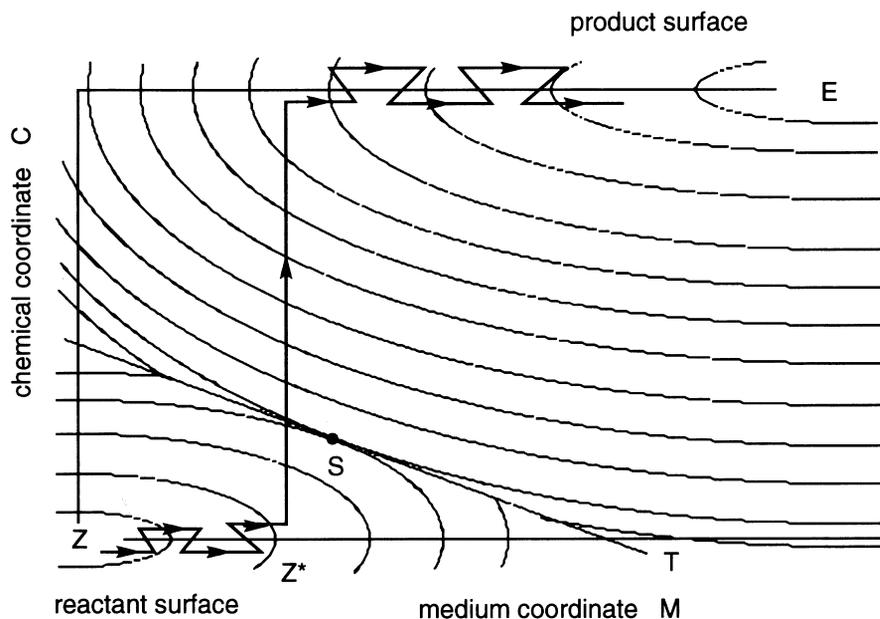


Fig. 5 A schematic illustration of the AH model applied to the *Z/E* isomerization [8].

conditions. In the KGH model, the reaction is assumed to be effected solely by Brownian motions. In other words, movements along *C* take place in concert with changes on *M*. Therefore, the activation energy is independent of the medium viscosity and it is always equal to Ea_{TST} . The rate constants in Figs 3 and 4 are plotted against η in Figs 6 [22] and 7 [21], respectively. It can be seen very clearly that the isoviscosity temperature effect decreases rapidly as the reaction goes into the TST-invalid region. Similar tendency was observed in all of the cases studied. The isoviscous activation energies estimated from these plots are given in Table 2. At high viscosities ($\eta \geq 100$ Pa s) the activation energy decreased rapidly with an increase in η [30]. These results are difficult to reconcile with the KGH model and they seem to indicate a necessity to treat the chemical and the medium coordinates separately.

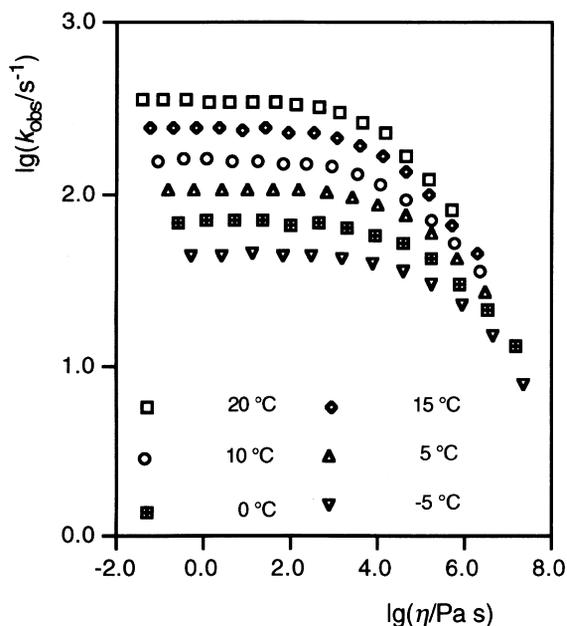


Fig. 6 Viscosity dependence of the isomerization rate of DBNA in DCMP at various temperatures.

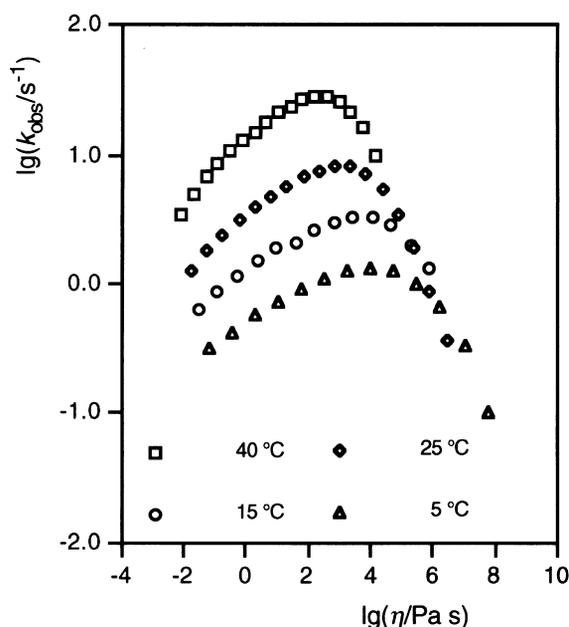


Fig. 7 Viscosity dependence of the isomerization rate of DNAB in GTA at various temperatures.

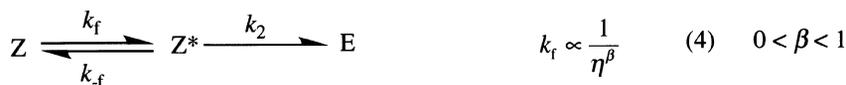
Table 2 The isoviscous activation energies (E_a , kJ/mol) from k_{obs} in the isomerization of DBNA in DCMP and DNAB in GTA

η , Pa s	DBNA	DNAB*	η , Pa s	DBNA	DNAB
0.1	54.8	65.6	10^3	51.7	63.9
1	54.2	68.2	10^4	46.4	45.3
10	53.7	69.9	10^5	36.4	32.2
10^2	53.4	69.8			

*The values at low viscosities are larger than the isopiestic values (50–51 kJ/mol) because they include an apparent contribution from the static effects of pressure. In order to realize the same viscosity, a higher pressure must be applied at a higher temperature. Thus the isoviscous k_{obs} values inherently contain kinetic effects of pressure.

Analyses based on a two-step approximation

The zigzag-arrow reaction route in Fig. 5 can be approximated to Scheme 3. Since k_{TST} is given by $k_2 k_f / k_{-f}$, Eqn 2 is obtained on this scheme by assuming a steady state.



Scheme 3

Extrapolations of k_{obs} in the TST-valid region allow us to estimate the k_{TST} values at the TST-invalid conditions and they, in turn, make it possible to estimate the k_f values. If Scheme 3 is a good approximation, the k_f values thus obtained are expected to give linear Arrhenius plots because thermal fluctuations require thermal activation. Figure 8 shows a set of Arrhenius plots obtained for the reaction of DMNAB in MPD. The plots were satisfactorily linear and the isopiestic activation energies were in the range of 96 (420 MPa) to 107 (600 MPa) kJ/mol. In all of the cases studied, no systematic deviation from the linearity was detected. The validity of the model can be further tested by examining the viscosity dependence of k_f . It has been reported for various fast reactions of S_1 -state molecules that k_{obs} obeyed inverse fractional power law (Eqn 4). It may be safely assumed that those measurements were performed

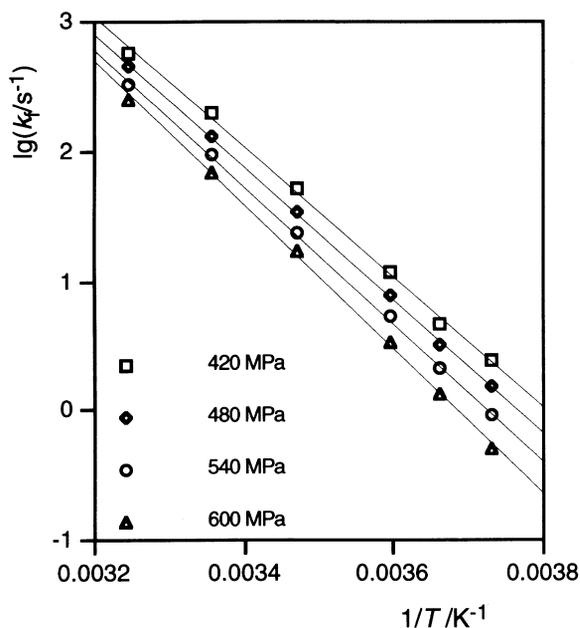


Fig. 8 Arrhenius plots for the fluctuation-limited rate constant k_f in the isomerization of DMNAB in MPD at various pressures.

in the nonequilibrium regime and that k_{obs} is close to k_f in Scheme 3. If these assumptions are valid, our k_f must be inversely proportional to a fractional power of η . Figure 9 shows a typical set of logarithmic $k_f - \eta$ plots. Obviously, the plots are linear and their slopes are smaller than -1 . The β -values for the benzaldehyde anils are listed in Table 3 [22].

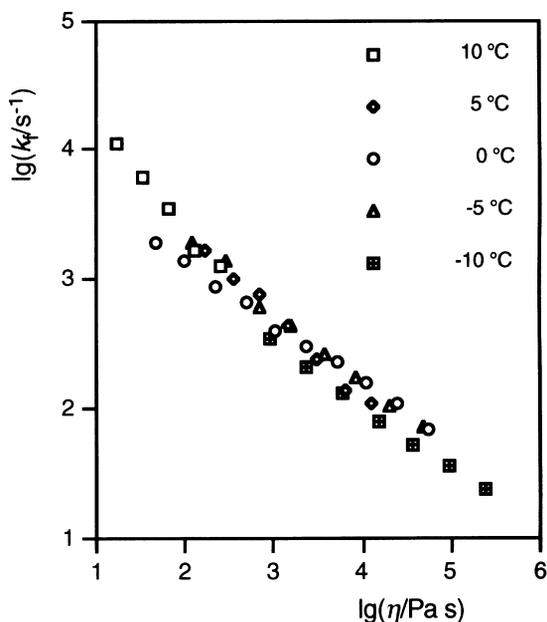


Fig. 9 Viscosity dependence of the fluctuation-limited rate constant k_f in the isomerization of DBNA in MPD at various temperatures.

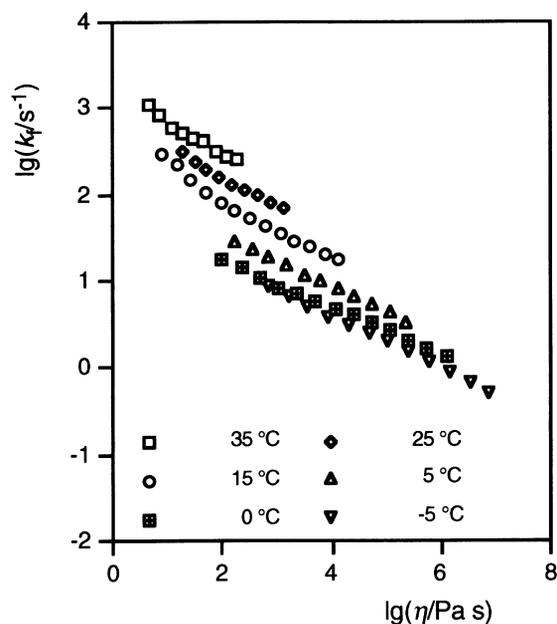
The above-mentioned linearity in the Arrhenius plot and the inverse fractional power dependence of k_f may be considered another evidence for the necessity to treat the chemical and the medium coordinates separately as assumed in the AH model. In other words, the reaction is effected by a combination of the Brownian motions and the following intramolecular atomic vibrations that are not in concert with the

Table 3 Empirical viscosity coefficients β of k_f in the isomerization of the benzaldehyde anils in the three solvents

Solvent	DBNA	DBEA	DBBA
DCMP	0.52	0.56	0.66
GTA	0.66	0.68	0.73
MPD	0.53	0.61	0.67

solvent fluctuations. Solvent rearrangements and the accompanying structural changes in the reactant precede the final energy barrier crossing. When the suitable environment is prepared, the reactant molecule surmounts the barrier to the product surface by a ‘ballistic’ motion of the atomic groups.

Now let us try to extract further information on the reaction mechanism by the analyses based on the AH model. In Fig. 9, k_f shows only small temperature dependence at the same viscosity suggesting that the major part of its large isopiestic temperature dependence ($90 < Ea_f < 100$ kJ/mol) comes from the temperature dependence of the solvent viscosity. Because of the relatively large uncertainties in k_f only rough estimates (10–30 kJ/mol) of the isoviscous activation energies were possible. However, it is almost certain that the energy increase in the reactant during the transformation of the solvation sphere must be much smaller than Ea_{TST} . On the other hand, in the isomerization of the azobenzenes in MPD, k_f showed clear temperature dependence. Figure 10 [21] shows the plots of k_f against η for DMNAB and the isoviscous Arrhenius plots of k_f are given in Fig. 11. Similar results were obtained for DNAB.

**Fig. 10** Viscosity dependence of the fluctuation-limited rate constant k_f in the isomerization of DMNAB in MPD at various temperatures.

The isoviscous activation energies from k_f in MPD are compared with those from k_{TST} in Table 4. As pointed out in the footnote of Table 2, these values include apparent contributions from the pressure-induced accelerations. Therefore, it is difficult to compare Ea_{TST} and Ea_f quantitatively. However, the energy increase of the reactant during the first step must be considerable in the reaction of the push-pull substituted azobenzenes in MPD. As a matter of fact, this energy increase may consist of a major part of Ea_{TST} [31]. Smaller but clear temperature dependence of k_f could be seen in the reaction of DBNA and DBEA in DCMP. The results for DBNA are shown in Fig. 12. The isoviscous Ea_{TST} and Ea_f values for these reactions are listed in Table 5 which also lists the isopiestic activation energies at 0.1 MPa. As can be seen from these Ea_{TST} values, the pressure dependence of the energy surface is relatively small in these

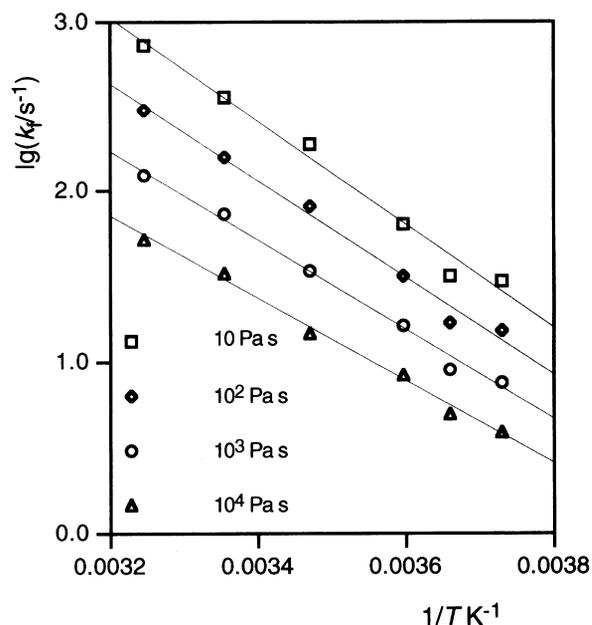


Fig. 11 Isoviscous Arrhenius plots for the fluctuation-limited rate constant k_f in the reaction of DMNAB in MPD.

reactions. Therefore, the Ea_f/Ea_{TST} ratios are supposed to reflect the relative magnitudes of the energy increase in the first step in Scheme 3. The reorganization of the solvation sphere pushes up the Z-isomer to the middle of the uphill road.

Table 4 Isoviscous activation energies (Ea , kJ/mol) from k_{TST} and k_f in the isomerization of DMNAB in MPD.

η , Pa s	Ea_{TST}	Ea_f
10	70	58
10^2	71	54
10^3	72	50
10^4	70	46

Table 5 Isoviscous activation energies (Ea , kJ/mol) from k_{TST} and k_f in the isomerization of DBNA and DBEA in DCMP

η , Pa s	DBNA		DBEA	
	Ea_{TST}	Ea_f	Ea_{TST}	Ea_f
10^4	54.1	31	59.0	23
10^5	54.1	26	59.1	29
10^6	54.1	21	59.2	34
0.1 MPa	54.6		58.6	

Comparisons of the results in different solvents and in different reactions

So far we mainly discussed temperature dependence of the dynamic solvent effect. Here we would like to try to compare the results obtained for a particular reaction in different solvents and for various reactions in the same solvent. In Fig. 13, k_f is plotted against η for the reaction of DBNA at 5 °C. Compared at the same viscosity, the solvent fluctuations are faster in nonpolar DCMP than in the other two polar solvents.

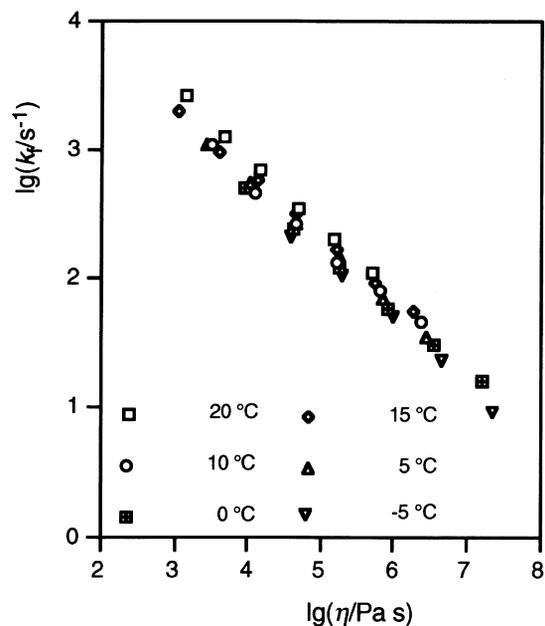


Fig. 12 Viscosity dependence of the fluctuation-limited rate constant k_f in the isomerization of DBNA in DCMP.

Figure 14 seems to be the other side of the coin. In this figure, $k_{\text{obs}}/k_{\text{TST}}$ is plotted against $k_{\text{TST}}\eta$. The latter quantity can be considered as a measure of the balance between the characteristic times of the reaction and the solvent coordinates [32]. Deviations from the TST are smaller in DCMP.

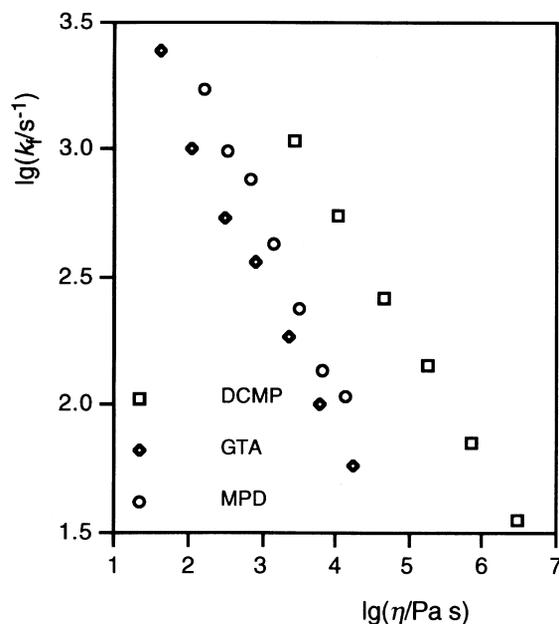


Fig. 13 Plots of k_f against η for the reaction of DBNA at 5°C.

Another example is given in Fig. 15 where the $k_{\text{obs}}/k_{\text{TST}} - k_{\text{TST}}\eta$ plots are compared for three different reactants, i.e. DBNA, DBEA, and 3,3'-diethyloxadicarbocyanine iodide (DODCI) [33]. In DODCI, the reaction is the isomerization about one of the central carbon-carbon double bonds in the cation (Scheme 4). The deviation from TST takes place earlier in this cationic reactant. It is likely that these differences in the dynamic solvent effects are reflections of stronger solute-solvent interactions in polar solvents and in a polar reactant. However, we need information on the

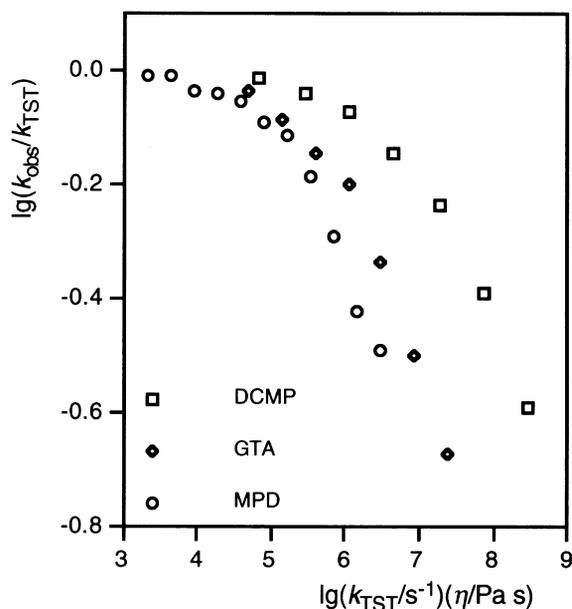


Fig. 14 Plots of $k_{\text{obs}}/k_{\text{TST}}$ against $k_{\text{TST}} \times \eta$ for the reaction of DBNA at 5 °C.

relationship between the bulk viscosity and the microscopic frictions and also on the shape of the energy surface for detailed analyses.

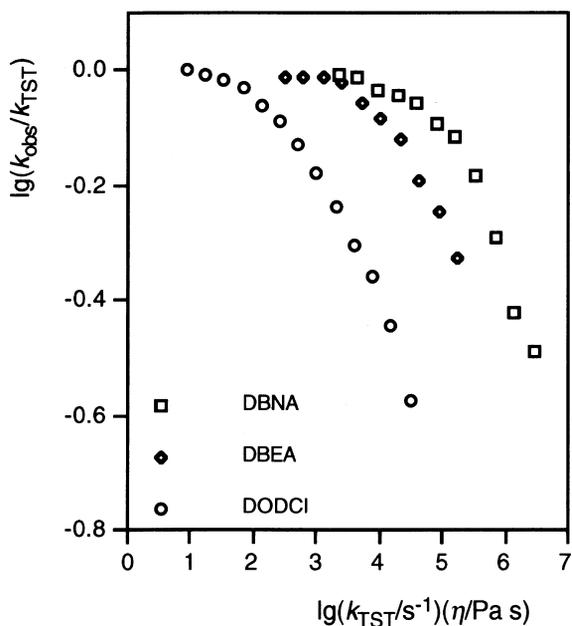
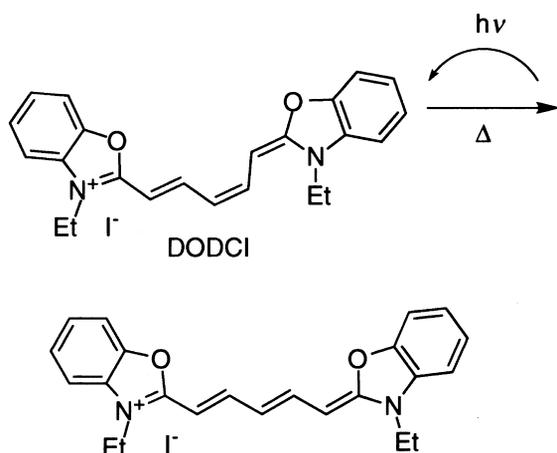


Fig. 15 Plots of $k_{\text{obs}}/k_{\text{TST}}$ against $k_{\text{TST}} \times \eta$ for three different reactants in MPD at 5 °C.

CONCLUSIONS

The experimental results presented here demonstrate that dynamic solvent effects on the TST-valid thermal reactions can be studied in highly viscous environment realized by a combination of high pressure and a viscous liquid. Although it is not possible to dissect the movements of the solvent molecules to each component, the average rate of the most relevant movement(s) seems to be correlated linearly with the macroscopic solvent viscosity η and the results could be analyzed as the viscosity dependence of the rate constant. All of the reactions shifted from the TST-valid region at lower pressures



Scheme 4

to the TST-invalid nonequilibrium region at higher pressures. The isoviscosity activation energies showed clear tendency to decrease with increasing viscosity in the TST-invalid region. This tendency strongly suggests that the one-dimensional reaction-coordinate (KGH) model is not adequate to describe the present reaction systems. The two-dimensional reaction-coordinate (AH) model was reduced to a simple two-step reaction scheme where the first step is the solvent rearrangement with a fluctuation-limited rate constant k_f and the second step is the chemical transformation. In this model, the observed rate constant k_{obs} is related to the TST-expected rate constant k_{TST} and k_f by $1/k_{\text{obs}} = 1/k_{\text{TST}} + 1/k_f$. The k_f values were obtained on the basis of this equation with the k_{TST} values estimated by extrapolations. The $\lg k_f$ values were found to be linearly correlated with $\lg \eta$ and $1/T$ in all of the cases studied as expected for a fluctuation-limited rate process. From these results, we concluded that AH model could better describe our reaction systems than the KGH model.

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