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Effects of Solvent Fluctuations on the Rate of Thermal *Z*/*E* Isomerization of Azobenzenes and *N*-Benzylideneanilines

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Effects of pressure on thermal *Z*/*E* isomerization of substituted *N*-benzylideneanilines and azobenzenes were studied in 2-methyl-2,4-pentanediol. Pressure dependence of the *Z*/*E* isomerization of a substituted azonaphthalene was also studied in glycerol triacetate. From the results in this and earlier papers, the following conclusions were reached. 1) It is possible to cast slow thermal reactions into the state of fluctuation control in highly viscous liquid phase realized by a combination of a viscous liquid and high pressure. 2) The viscosity dependence of the rate constant can be rationalized by the two-dimensional reaction-coordinate model developed by Sumi but not by the Grote–Hynes' theory of frequency-dependent friction. Namely, the energy-barrier crossing takes place after the solvent molecules are rearranged to accommodate the transition state. 3) Whether the solvent rearrangement involves chemical transformations with appreciable energy increases depends on the nature of the reaction and the solvent.

With the development of laser pulse technique, it became possible to study very fast reactions in the 1980's. It has often been observed for solution reactions with low activation energies ($E_a \leq 5RT$) that the fundamental hypothesis of the transition state theory (TST), i.e., the activated complexes are at equilibrium with the reactants, is not valid anymore. In other words, the reaction occurs so rapidly that thermal fluctuations of solvent molecules are not fast enough to realize thermal equilibrium among reactants. Under such conditions, the rate decreases with an increase in the friction between the reactant and the surrounding molecules because thermalization in the reactant state is retarded by the friction. A theory by Kramers[1)] predicts that the rate constant is inversely proportional to the friction in this situation. Since the friction can usually be considered to be proportional to the viscosity of the solvent η, the dependence of the rate constant on the solvent viscosity became a central topic in this new discipline. A large number of experimental works were performed and it was demonstrated that the rate constant k_{obs} is inversely proportional to a fractional power of η in most cases (Eq. 1).

$$k_{\mathrm{obs}} = B\eta^{-\beta} \quad 0 < \beta < 1 \tag{1}$$

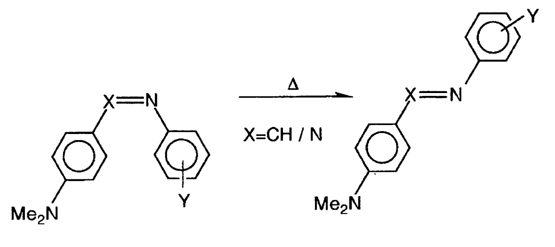
However, the meaning of this deviation from a theoretical prediction (β=1) of Kramers has yet to be clarified. In order to solve this problem, it is highly desirable to extract pure viscosity effect from k_{obs} and for this purpose it is necessary to estimate the TST-expected rate constant k_{TST} in the situations where TST is not valid. As far as we deal with fast reactions, however, it is extremely difficult because TST is easily invalidated even by small frictions. Slow reactions with high activation energies, on the other hand, do not deviate easily from TST even in fairly viscous solvents (vide infra). Therefore, pressure-induced high viscosities seem to provide an ideal opportunity to tackle this problem.

Viscosity increase of liquids with pressure can be described approximately by Eq. 2 where η and η_0 are the viscosities at pressures P and 0, respectively.[2)]

$$\eta = \eta_0 e^{\alpha P} \tag{2}$$

If a liquid with large η_0 and α is used as a reaction medium, pressure would make it possible to render solvent fluctuations so slow that TST could be invalidated even if the activation energy is as large as 20*RT*. Then, a continuous transition from the TST-valid region to the TST-invalid region would be observed and we would be able to estimate k_{TST} values in the latter region by extrapolations from the former region.

We started the study of pressure effects on thermal *Z*/*E* isomerizations about a nitrogen–nitrogen and a carbon–nitrogen double bond, Eq. 3, in viscous liquid several years ago.[3—5)]



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The activation energies for these reactions were in the range of 50—75 kJ mol^{-1} and the half-lives at 25 °C and 0.1 MPa ranged from 7×10^{-4} s to 6.5 s. To the best of our knowledge, effects of high solvent viscosity on such slow molecular reactions had never been considered as a subject of the dynamic solvent-effect study. Several groups of people discussed the correlation between the rate of geometrical isomerizations of molecules at their ground state and the solvent viscosity. For example, Jonas and his co-workers[6] studied pressure effects on inversion of cyclohexane. Since the reaction is a simple structural transformation with little polarity change, similar activation volumes $\Delta V^{\neq}$ are expected in different solvents. However, the value ranged from -1 cm^3 mol^{-1} in methylcyclohexane to -5 cm^3 mol^{-1} in acetone and this solvent dependence was attributed to dynamic solvent effects. The viscosity range studied was relatively narrow [$\eta<0.04$ Pa s (=40 cP)], however, and in the whole range studied, the reaction was accelerated with increasing pressure, i.e., with increasing viscosity. Effects of the chain length of *n*-alcohols on the ground state isomerization of 3,3′-diethyloxadicarbocyanine iodide (DODCI) was studied by Waldeck and his co-workers.[7] Hara and Akimoto[8] studied pressure effects on the same reaction later. The observed rate constants could be correlated to the solvent viscosity. However, the highest viscosities reached in these studies were also low ($\eta<0.03$ Pa s). On the other hand, in our studies[9,10] viscosities higher than 100 Pa s were realized and it was shown that the kinetic effects of pressure were in accordance with the ones observed in "normal" solvents at lower pressures. Retardations of the reactions that could not be interpreted in the framework of TST appeared only at viscosities higher than 50 Pa s. The results allowed us to determine unambiguously k_{TST} values in the TST-invalid region by extrapolation. Dynamical solvent effects, we believe, should be discussed by detecting deviations of k_{obs} from k_{TST}, as in the present work and our previous works.[9,10] In the studies by Waldeck and Hara, however, k_{TST} values were not obtained and, therefore, the analysis inevitably contained ambiguities.

In the previous communication,[10] the results in glycerol triacetate (GTA) were analyzed on the basis of a two-step mechanism, Eq. 4, where Z, E, and M are the initial, the final, and the intermediate state, respectively.

$$\mathrm{Z} \underset{k_{-\mathrm{f}}}{\overset{k_{\mathrm{f}}}{\rightleftarrows}} \mathrm{M} \xrightarrow{k_2} \mathrm{E} \qquad (4)$$

This mechanism is based on a theory by Sumi[11] which assumes a two-dimensional reaction coordinate. One coordinate concerned with rate constants k_{f} and $k_{-\mathrm{f}}$ depicts relatively slow thermal fluctuations (Brownian motions) on the energy surface of the reactant. The movement along this coordinate describes fluctuations of molecular arrangements in the solute–solvent system, and is subject to the frictional retardation. The second coordinate concerned with the rate constant k_2 depicts energy barrier crossing by rapid atomic vibrations that are independent of the friction. In the first step of Eq. 4, the solvent molecules are assumed to be rearranged by thermal fluctuations to form a configuration suitable for the second step while the reactant stays on its energy surface. The chemical change to the product takes place in the second step. At low viscosities, thermal fluctuations are fast enough to make Z and M at equilibrium and TST-expected rate constants are observed, i.e., $k_{\mathrm{obs}}\approx k_{\mathrm{TST}}=k_2k_{\mathrm{f}}/k_{-\mathrm{f}}$.[12] At high viscosities, the first step becomes rate-determining ($k_{\mathrm{obs}}\approx k_{\mathrm{f}}$). At the intermediate viscosity region, k_{f} can be derived from Eq. 5 obtained as the steady-state rate constant in the scheme of Eq. 4.

$$k_{\mathrm{obs}} = 1/(k_{\mathrm{TST}}^{-1} + k_{\mathrm{f}}^{-1}) \qquad (5)$$

The rate constant k_{f} thus obtained was called the fluctuation-limited rate constant. The values at different temperatures at each pressure gave a linear Arrhenius plot and obeyed Eq. 1. It has also been demonstrated[13,14] that the experimental results cannot be described by a theory of Grote and Hynes[15] based on the idea of frequency-dependent friction, which has often been tried to rationalize the deviation from the Kramers' prediction.

In this communication, comparison of the results in GTA and in methyl acetate will be made first in order to further prove that the pressure-induced retardation in GTA is a result of high viscosity of the solvent. Then the results in a protic solvent 2-methyl-2,4-pentanediol (MPD) will be presented and the two theories will be compared. In addition, the results for 4-(dimethylamino)-4′-nitro-1,1′-azonaphthalene (DNAN) in GTA will be presented.

Experimental

Materials. *N*-Benzylideneanilines and azobenzenes have been reported previously.[4,10] DNAN was prepared from *N*,*N*-dimethyl-1-naphthylamine and 4-nitro-1-naphthylamine. Mp 160—161 °C (lit,[16] 156—157 °C). Found: C, 71.49; H, 4.85; N, 15.00%. Calcd for $\mathrm{C_{22}H_{18}N_4O_2}$: C, 71.34; H, 4.90; N, 15.13%.

Kinetic Measurements. The unstable *Z*-isomer was formed by irradiation from a xenon flash lamp and its decay was followed spectrophotometrically. The details of the kinetic measurements were described in the literature.[17] The reaction mixture remained clear and no turbidity was detected at all of the conditions studied, clearly demonstrating the absence of crystallization of the solvent. Deviations from the first-order kinetics as in polymer matrixes[18] were not observed either.

Viscosity Measurements. High pressure viscosities of GTA and MPD were measured by a falling-cylinder viscometer[19] which was calibrated by measuring the falling rate in bis(2-ethylhexyl) sebacate whose viscosity is known.[20] The measurements were performed at 25, 35, 40, 45, and 60 °C and at seven different pressures at each temperature. The highest pressure was 427 MPa.

Results and Discussion

Viscosity of the Solvents at High Pressures. In the previous report,[10] viscosities measured by a falling-ball viscometer[9] were adopted. In that measurements, the sample was kept in a simple piston-cylinder type pressure vessel and it was pressurized by means of a hydrostatic press. The pressure of the sample was estimated from the oil pressure of the press used to raise the ram. In the present experiment, the pressure was directly applied to the sample by a hand-operated pump and measured by a "Heise" Bourdon tube gauge model CM. The high pressure viscosities observed are shown in Figs. 1 and 2. Although the logarithm of the viscosity was linearly correlated with pressure in MPD, slight upward deviations from Eq. 2 were noted in GTA at high pressures. In order to consider this nonlinearity, an empirical equation proposed by Yasutomi and his co-workers[21] was tested. Unfortunately, however, the obtained function resulted in unreasonably large high-pressure viscosities at low temperatures and, therefore, Eq. 2 was adopted also for GTA. In order to estimate the values at the reaction temperature, the observed η_0 and α values were fitted to Walther equation[22] and a linear correlation with the logarithm of the kinematic viscosity, respectively. The values thus obtained are given in Table 1.

Isomerization of DNAB in GTA and Methyl Acetate. Figure 3 shows the pressure dependence of the *Z*/*E* isomerization rate of DNAB in GTA and methyl acetate at 5 °C. At the beginning of pressurization, acceleration of the reaction was observed both in GTA and methyl acetate. This is because of strong electrostriction around a highly dipolar rotational activated complex **1** (Chart 1).[23,24] At higher pressures, pressure-induced retardation was observed in GTA but not in methyl acetate. Electrostatic and specific solute–solvent interactions are expected to be similar in these solvents because both of them are acetates. However, their viscosities at high pressures will be greatly different. Because of its

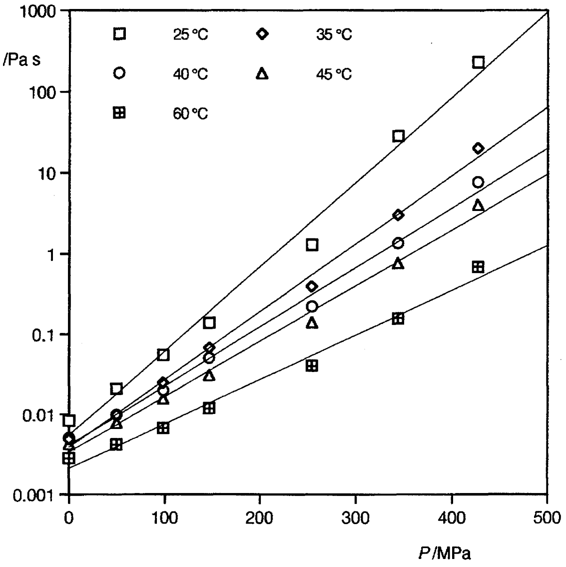

Fig. 1. Pressure effects on the viscosity of GTA at various temperatures.

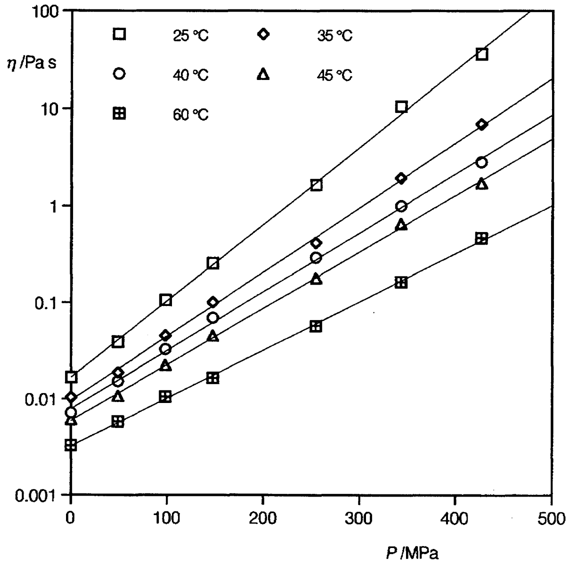

Fig. 2. Pressure effects on the viscosity of MPD at various temperatures.

Table 1. Viscosity Coefficient at 0.1 MPa (η_0/Pa s) and Its Pressure Coefficient (α/GPa^{-1}) for GTA and MPD at Various Temperatures

	GTA		MPD	
T/°C	η_0	α	η_0	α
−10	0.0315	43.8	0.647	32.7
−5	0.0230	40.0	0.311	29.7
0	0.0174	36.5	0.164	27.1
5	0.0134	33.4	0.0931	24.8
10	0.0106	30.6	0.0567	22.8
15	0.00859	28.0	0.0365	21.0
20	0.00706	25.6	0.0247	19.4
25	0.00589	23.5	0.0175	17.9
30	0.00499	21.4	0.0128	16.7
35	0.00427	19.6	0.00964	15.5
40	0.00370	17.9	0.00747	14.5

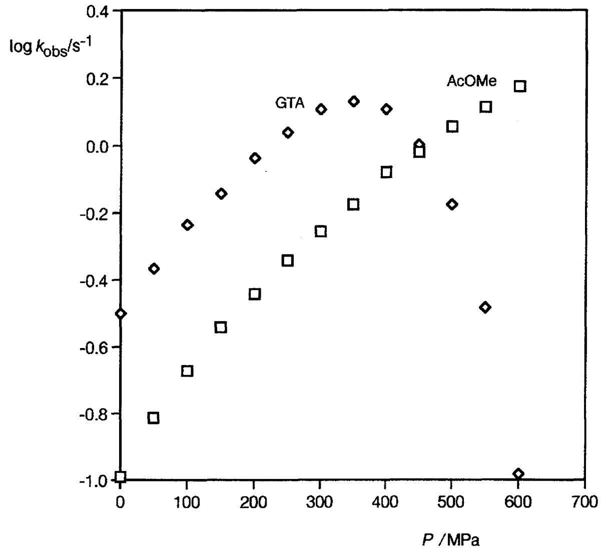

Fig. 3. Pressure effects on the rate of thermal *Z*/*E* isomerization of DNAB in methyl acetate and GTA at 5 °C.

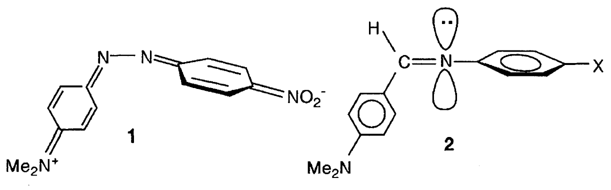

Chart 1.

branched molecular structure, the viscosity of GTA increases rapidly with increasing pressure. For example, at 25 °C, 500 MPa, the viscosity will be 1.3×10^5 times larger than at 0.1 MPa. On the other hand, the pressure coefficient of methyl acetate would be much smaller. Although the direct comparison is not possible, the α value for propyl acetate can be estimated as 8.2 GPa^{-1} at 27 °C from the published data[25] and the viscosity ratio at 500 MPa and 0.1 MPa will be only 60. Therefore, it is reasonable to assume that the observed retardation was caused by slow solvent fluctuations in GTA with high viscosities. This discussion implies that the solvent fluctuations are still fast enough to make TST valid in the current isomerization even at fairly viscous conditions. For example, at 5 °C and 200 MPa, the viscosity is 11 Pa s and the pressure effect still looks normal. Linear Arrhenius plots in Fig. 4 may be considered as a good proof for the validity of TST up to 200 MPa. The plots were linear in methyl acetate even at 600 MPa. The activation energies and the preexponential factors were comparable in these solvents as can be seen from Table 2. These results leave little doubt that the reaction in GTA was activation-controlled (TST-valid) at lower pressures but it shifted smoothly to fluctuation-controlled (TST-invalid) at higher pressures.

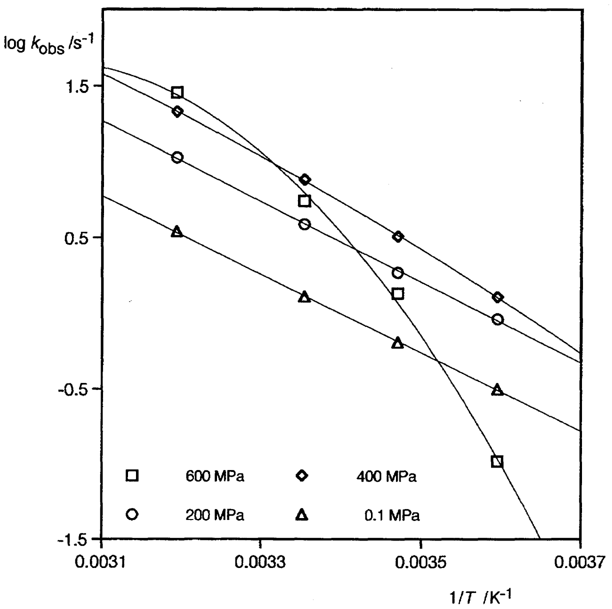

Fig. 4. Arrhenius plots for thermal *Z*/*E* isomerization of DNAB in GTA at various pressures.

Table 2. The Preexponential Factors ν and the Activation Energies Ea_{TST} for Thermal *Z*/*E* Isomerization of DNAB in GTA and in Methyl Acetate at Various Pressures

	GTA		AcOMe	
P/MPa	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}
0.1	6.9×10^8	49.8	1.3×10^8	48.6
100	2.1×10^9	51.0	9.1×10^8	51.3
200	3.4×10^9	51.0	2.1×10^9	52.0
300			2.4×10^9	51.3
400			2.4×10^9	50.4
500			4.3×10^9	51.0
600			4.1×10^9	50.3

Isomerization of *N*-Benzylideneanilines in MPD. Three *N*-benzylideneanilines were studied in MPD. They were *N*-[4-(dimethylamino)benzylidene]-4-nitroaniline (DBNA), *N*-[4(dimethylamino)benzylidene]-4-ethoxycarbonylaniline (DBEA), and *N*-[4-(dimethylamino)benzylidene]-4-bromoaniline (DBBA).[26] These compounds were chosen so as to provide a chance to examine the relation between the magnitude of k_{TST} and k_{f}. The rate constants at 0 °C and 0.1 MPa were 158 (DBNA), 5.58 (DBEA), and 0.0997 (DBBA)/s^{-1}. They vary in their rates because of the difference in the activation energy. The frequency factors and the activation energies at 0.1 MPa in MPD and in GTA are listed in Table 3. The observed pressure effects are illustrated in Fig. 5 for DBNA. They are qualitatively the same with those in GTA.[10] Similar results were obtained also for DBEA and DBBA. The pressure effects were nominal at the beginning of pressurization. The activation volumes calculated by assuming a linear correlation between ln k_{obs} and the pressure were in the range of 0—3.6 cm^3 mol^{-1}. The small activation volumes can be understood in the framework of TST because the reaction was effected by nitrogen inversion and neither charge separation nor bond scission takes place during the formation of the transition state **2** (Chart 1).[27]

Table 3. The Preexponential Factors ν and the Activation Energies Ea_{TST} at 0.1 MPa for the *Z*/*E* Isomerization of *N*-Benzylideneanilines in GTA and MPD

	GTA		MPD	
	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}
DBNA	2.4×10^{12}	53.5	2.7×10^{12}	53.5
DBEA	6.0×10^{12}	62.6	4.8×10^{12}	62.3
DBBA	8.6×10^{12}	71.2	8.5×10^{12}	72.9

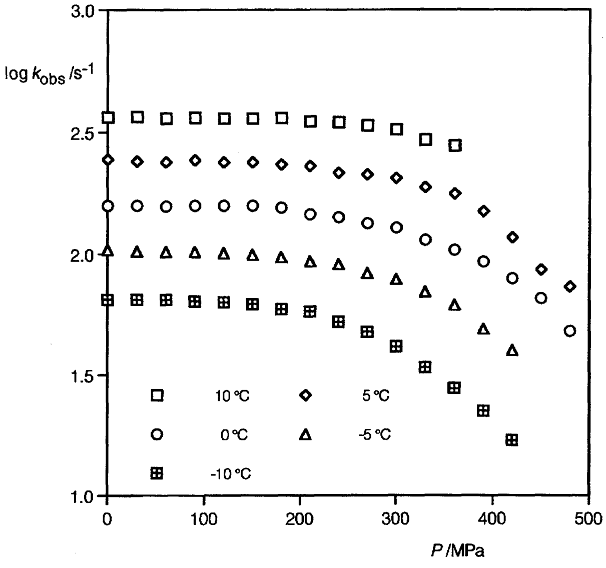

Fig. 5. Pressure effects on the rate of thermal *Z*/*E* isomerization of DBNA in MPD at various temperatures.

As pressure was further raised, strong retardations were observed, suggesting a change in the rate-determining step. The fluctuation-limited rate constants calculated from Eq. 5 with k_{TST} values estimated by a linear extrapolation to high pressures are plotted against solvent viscosity in Fig. 6. As observed in GTA,[10] the points for different reactants flock to separate lines clearly showing the dependence of k_f on the reactant. The temperature dependence of k_f was small when compared at the same viscosity. In other words, the apparent temperature dependence of k_f mainly comes from that of the solvent viscosity suggesting strongly that the energy of the reactant system remains the same and little chemical changes take place during the solvent rearrangement. The β values calculated from all of the data points for different temperatures are given in the Figure. They are slightly smaller than those in GTA, i.e., 0.66 (DBNA), 0.68 (DBEA), and 0.73 (DBBA). Compared at the same viscosity, the k_f values were more or less similar in GTA and MPD as shown in Fig. 7 for DBNA. The hydroxyl groups in MPD did not result in any major difference in the solvent rearrangement during the isomerization of the *N*-benzylideneanilines. The k_f as well as the k_{TST} values were in the order of DBNA>DBEA>DBBA both in GTA and MPD. Obviously the first step is not independent of the second step. According to Sumi,[11] the fluctuation-limited rate constant can be written as

$$k_f \approx \tau^{-\beta'} \nu^{1-\beta'} \exp(-\gamma Ea_{TST}/RT) \quad 0 < \beta', \gamma < 1 \tag{6}$$

where τ is the relaxation time of the solvent fluctuations, β' is a parameter related to the distribution of the intermediate state M (smaller the β', larger the distribution), ν is the preexponential factor of k_{TST} (Eq. 7), and γEa_{TST} is a component of Ea_{TST} brought about by slow solvent motions.

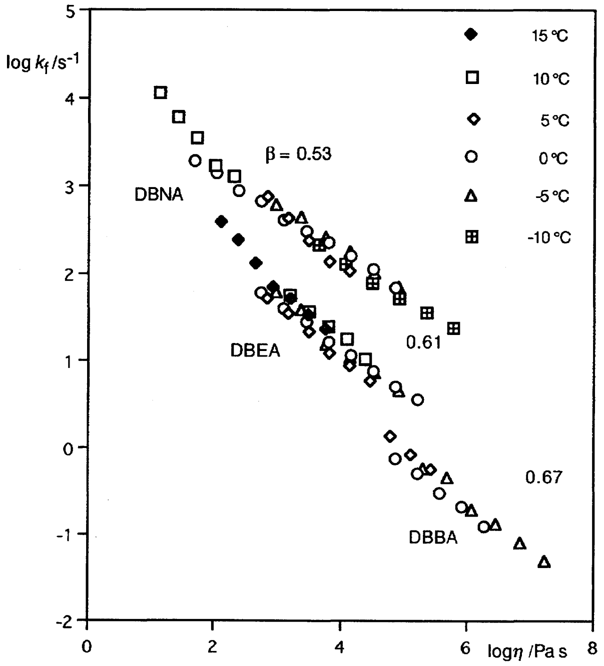

Fig. 6. Plots of the fluctuation-limited rate constant against solvent viscosity for thermal *Z*/*E* isomerization of *N*-benzylideneanilines in MPD.

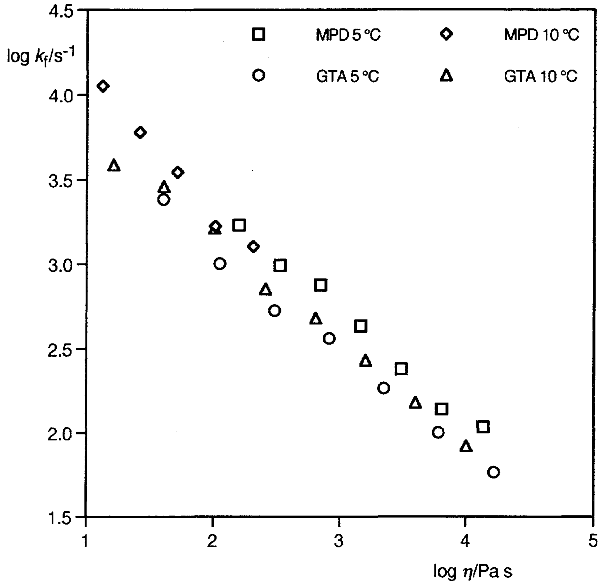

Fig. 7. Comparison of the fluctuation-limited rate constant for thermal *Z*/*E* isomerization of DBNA in GTA and in MPD.

$$k_{TST} = \nu \exp(-Ea_{TST}/RT) \tag{7}$$

Usually τ is proportional to η and pressure dependencies of ν and Ea_{TST} were much smaller than that of η in the isomerization of the *N*-benzylideneanilines. In this case, the β' value in Eq. 6 approximately coincides with the β value in Eq. 1 derived experimentally from the log k_f–log η plot. The β value increased in the order of DBNA<DBEA<DBBA both in GTA and MPD and the preexponential factor ν was in the order of 10^{12} s^{-1} in all of the cases studied. Therefore, the substituent dependence of k_f might be a reflection of the order of $\nu^{1-\beta'}$. On the other hand, the correlation between k_f and k_{TST} could be a result of the difference in the exponential factor in Eq. 6 because the activation energy was considerably different among these reactants. In order to determine which factor is predominant in these reactions, it is necessary to estimate the values of β' and γ. However, it was not possible to do the analysis because the variations of ν and Ea_{TST} with pressure were small and rather erratic.

Isomerization of Azobenzenes in MPD. Two push–pull substituted azobenzenes, 4-(dimethylamino)-4′-nitroazobenzene (DNAB) and 4-(dimethylamino)-2′-methoxy-4′-nitroazobenzene (DMNAB) were studied in MPD. Results for DNAB are illustrated in Fig. 8. The results at low pressures were extrapolated by means of an empirical equation given below where k and k_0 are the observed (TST-expected) rate constants at pressure P and 0, respectively, and a and b are the adjustable parameters.[28]

$$\ln k = \ln k_0 + a \ln(1 + bP) \tag{8}$$

The fluctuation-limited rate constants are plotted against viscosity in Figs. 9 and 10.

There is an important difference between the present re-

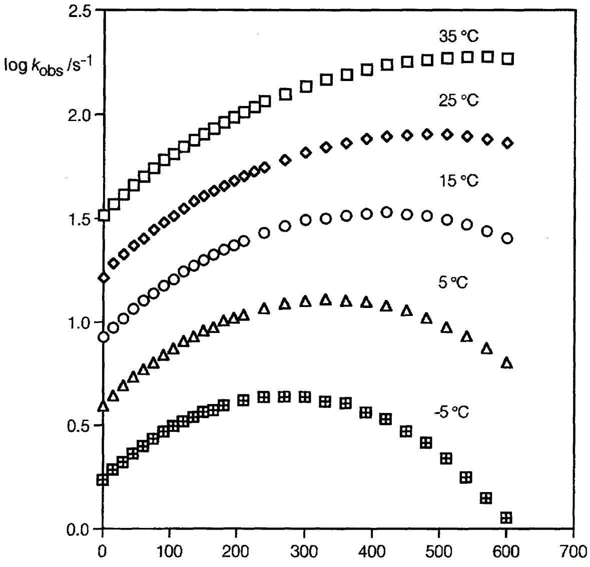

Fig. 8. Pressure effects on the rate of thermal Z/E isomerization of DNAB in MPD at various temperatures.

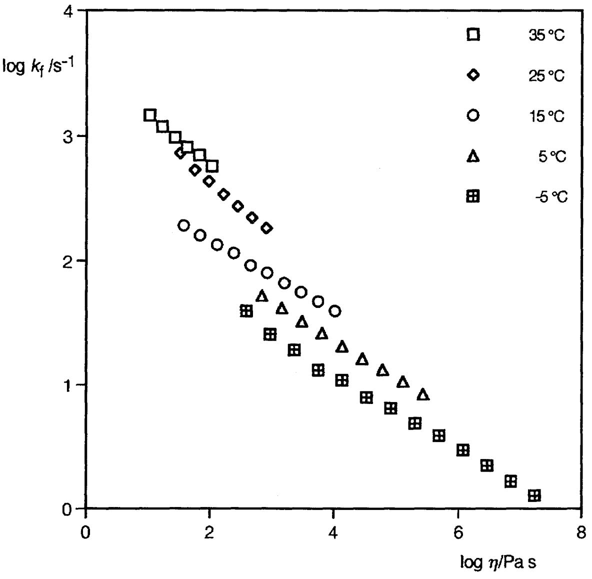

Fig. 9. Plots of the fluctuation-limited rate constant against solvent viscosity for thermal Z/E isomerization of DNAB in MPD.

sults and the ones in GTA reported earlier.[10] In GTA, the plots of $\log k_f$ against $\log \eta$ for different temperatures were close to each other and it was not possible to discuss their temperature dependence. In MPD, however, the same plot gave separate lines for different temperatures as shown in Figs. 9 and 10. Compared at the same viscosity, the first step was faster at higher temperatures. The present reaction is affected by electric fluctuations in polar solvents due to a polarity change during the activation as well as by viscosity related solvent fluctuations. However, it can be considered that τ is determined still by η under highly viscous conditions, as $\tau \propto \eta$, and discussion based on Eq. 6 may be validated. The separate lines in Figs. 9 and 10 indicate that the parameter γ is appreciable in these reactions. Equation 6 is convenient for discussing the τ dependence of k_f when Ea_{TST} and ν are kept unchanged. In the isomerization of DNAB and DMNAB in MPD, however, these activation parameters change considerably with pressure as shown in Table 4 and they are not negligible compared with the variation of τ ($\propto \eta$) in Eq. 6. In order to analyze these results, let us divide Ea_{TST} into two contributions as in Eq. 9 where $Ea_{TST}(0)$ is the activation energy at zero pressure, and $\Delta(P)$ is a pressure dependent part of Ea_{TST} with $\Delta(0)=0$.

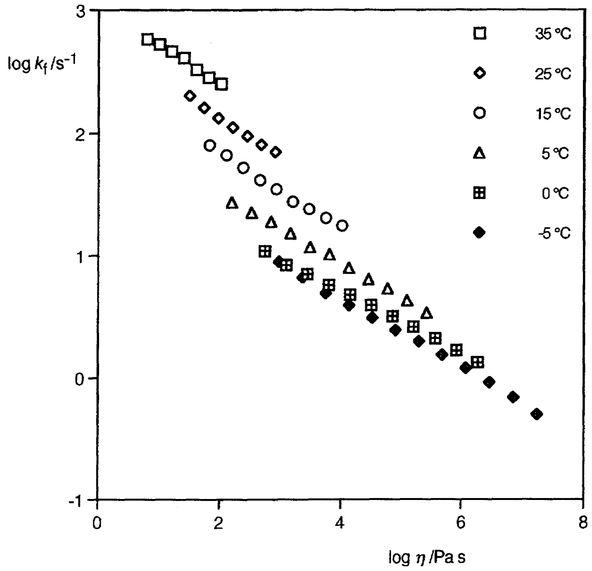

Fig. 10. Plots of the fluctuation-limited rate constant against solvent viscosity for thermal Z/E isomerization of DMNAB in MPD.

$$Ea_{TST} = Ea_{TST}(0) + \Delta(P) \tag{9}$$

Since the intrinsic activation volume must be close to zero in these reactions,[28] the pressure dependent part $\Delta(P)$ is supposed to be mostly related to the pressure dependence of the solvent electrostriction in the activation step. The electrostriction is brought about by slow solvent motions. Therefore, it is reasonable to assume $\Delta(P)$ is, as a whole, a component of the thermal activation energy of k_f. In this case, Eq. 6 should be modified as

$$k_f \approx \tau^{-\beta'} \nu^{1-\beta'} \exp[-\Delta(P)/RT] \ \exp[-\tau Ea_{TST}(0)/RT] \qquad 0<\beta',\gamma<1 \tag{10}$$

Table 4. The Preexponential Factors ν and the Activation Energies Ea_{TST} at Various Pressures for the Z/E Isomerization of Azobenzenes in MPD

	DNAB		DMNAB	
P/MPa	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}
0.1	1.09×10^{10}	50.3	4.25×10^{9}	50.2
150	6.94×10^{10}	52.7	3.71×10^{10}	53.2
300	2.27×10^{11}	54.3	1.20×10^{11}	54.7
450	6.11×10^{11}	55.9	3.30×10^{11}	56.1
600	1.30×10^{12}	57.0	7.40×10^{11}	57.3

where $\gamma Ea_{TST}(0)$ represents a component in $Ea_{TST}(0)$ brought about by slow solvent motions contributing to k_f. The parameters β' and γ are assumed to be independent of pressure and viscosity. This equation explicitly shows that when ν and/or $\Delta(P)$ changes simultaneously with η, it is not possible to determine β' value from the slope of the $\log k_f$–$\log \eta$ plot even if it behaves as Eq. 1. Let us write, here, the k_{TST} value at a pressure P by $k_{TST}(P)$. Then, applying $\nu \exp[-\Delta(P)/RT]=k_{TST}(P)\exp[Ea_{TST}(0)/RT]$ and $\exp[-Ea_{TST}(0)/RT]\propto k_{TST}(0)$ to Eq. 10, we obtain Eq. 11.

$$k_f \propto (\eta\nu)^{-\beta'} k_{TST}(P) k_{TST}(0)^{\gamma-1} \qquad (11)$$

By fitting k_f along with η, ν, $k_{TST}(P)$, and $k_{TST}(0)$ to this equation, it is possible to determine the values of β' and γ simultaneously. They are listed in Table 5 with their standard deviations. The table also contains the values in GTA for subsequent discussion. The results of this treatment can be visualized by plotting $\ln k_f k_{TST}(0)^{1-\gamma}/k_{TST}(P)$ against $\ln \eta\nu$. Such plot must give a straight line with a slope equal to β'. Figure 11 shows plots for the present results. Little systematic deviation from the expected linearity was observed and the correlation was satisfactory. The γ values strongly suggest that a considerable part of Ea_{TST} is related to the slow solvent motions and chemical transformations takes place in association with the solvent rearrangement. Although the pressure dependence of ν and Ea_{TST} (Table 6) and the temperature dependence of the $\log k_f$–$\log \eta$ plot are considerably smaller in GTA, the same treatment was tried to the results in this solvent. The parameters are given in Table 5. The β values were 0.69 and 0.65 for DNAB and DMNAB, respectively and they were larger than the β' values. The differences were less than 10%, however. This is reasonable because the variations in Ea_{TST} and ν amount less than 10% of that in the solvent viscosity η in Eq. 6. The smaller variations in ν and Ea_{TST} inevitably make β' and γ more liable to experimental errors but a qualitative comparison of the parameters would be justified. The γ values were smaller in GTA suggesting chemical changes connected to the solvent rearrangement are less extensive in GTA. Probably, desolvation of the solvent molecules hydrogen-bonded to the dimethylamino group has to take place in MPD and it might induce as well some structural changes in the reactant through the increased electron-donating ability of the substituent. In GTA, there is no specific solvation to the dimethylamino group and movements of solvent molecules are less directly connected to the energy of the reactant system. The smaller β' values in MPD may reflect a difference in the distribution of the intermediate state M on the reactant coordinate. The final transformation to the E-isomer may require less strict solvent arrangement in MPD than in GTA. If M has a wider distribution in MPD, it must be reflected in the preexponential factor of k_{TST} because the distribution of M has to be kept throughout the second step including the transition state. This expectation was met. The isomerization is 10—15 times faster in MPD because of the larger ν values as can be seen from Tables 4 and 6. This view is somewhat different from the traditional understandings of the solvent effects on a reaction with a large polarity increase during activation. It is customarily discussed that an increase in solvent polarity accelerates such reactions because solvation stabilization decreases the activation energy. Undoubtedly, this discussion is correct when a comparison is made for solvents whose polarities are widely different as in hexane and methanol. The activation energies for DNAB in these two solvents were 82.6 and 48.6 kJ mol^{-1}, respectively and the ratio of the k_{TST} value was 23400.[23,29] However, for GTA and MPD, the same rationalization is not applicable. The activation energy in MPD was as large as or larger than that in GTA.

Table 5. Values of the Parameters in Eq. 10 Estimated by Least-Squares Calculations

	Solvent			
	MPD		GTA	
Reactant	β'	γ	β'	γ
DNAB	0.30±0.01	0.76±0.04	0.65±0.03	0.27±0.11
DMNAB	0.30±0.01	0.78±0.03	0.60±0.02	0.47±0.10

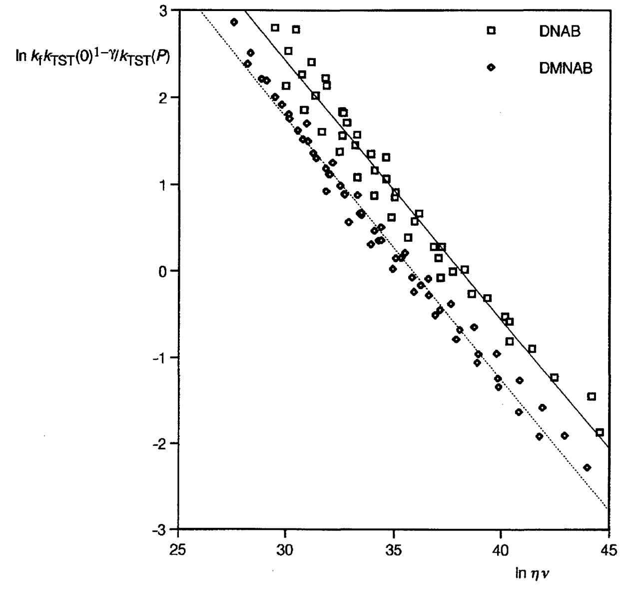

Fig. 11. Plots of $\ln k_f k_{TST}(0)^{1-\gamma}/k_{TST}(P)$ against $\ln \eta\nu$ for the isomerization of DNAB and DMNAB in MPD.

Isomerization of DNAN. Since the solvent rearrangement required for the energy-barrier crossing is expected to

Table 6. The Preexponential Factors ν and the Activation Energies Ea_{TST} at Various Pressures for the Z/E Isomerization of Azobenzenes in GTA.

	DNAB		DMNAB	
P/MPa	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}	ν/s^{-1}	Ea_{TST}/kJ mol^{-1}
0.1	6.90×10^{8}	49.8	3.22×10^{8}	50.8
150	3.18×10^{9}	51.4	6.17×10^{8}	50.0
300	5.85×10^{9}	51.5	1.41×10^{9}	50.5
450	7.01×10^{9}	50.8	3.09×10^{9}	51.1
600	6.60×10^{9}	49.8	4.34×10^{9}	50.9

depend on the steric bulk of the reactant, the isomerization of DNAN was studied in GTA. In DNAN, 1-naphthyl group has to rotate with respect to the nitrogen–nitrogen bond. This group is almost twice as large as the phenyl group and more extensive solvent rearrangement will be required. Therefore, the pressure-induced retardation will appear at lower pressures. The k_{obs} values are plotted against pressure in Fig. 12. The isomerization was much faster than in the azobenzene homologue because of the lower Ea_{TST} (27—30 kJ mol^{-1}) and, as expected, the maximum value in k_{obs} was reached at lower pressures. It was also clear, as can be seen from Fig. 13, that the k_{f} value at the same viscosity was larger in DNAN than in DNAB. Probably, this would be a result of a larger exponential term in Eq. 10. Unfortunately, however, the number of the k_{obs} values used in the extrapolations based on Eq. 8 was small and, therefore, the k_{f} values and their Arrhenius plots at high pressures were subject to large uncertainties. This prevented us from analyzing the results on the basis of Eq. 11. In order to study the pure steric effects on the magnitude of k_{f}, a comparison has to be made for compounds with similar k_{obs} values.

Isoviscosity Rates. In the previous papers,[13,14] it was shown that application of Grote–Hynes' theory to our results yielded unrealistically large values for the correlation time among random forces in the generalized Langevin equation.

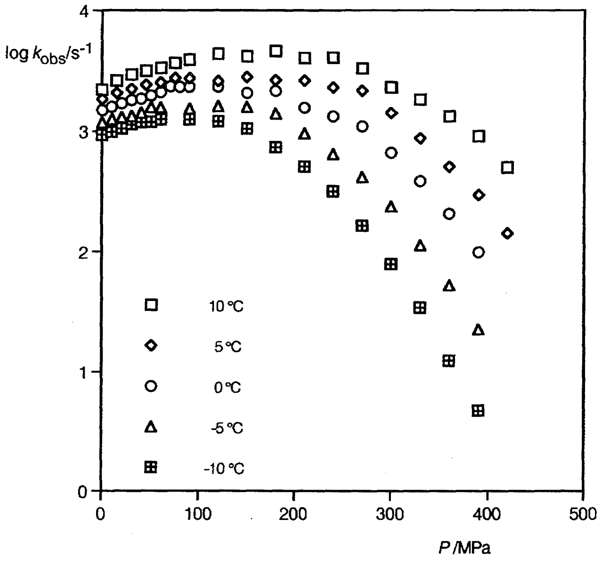

Fig. 12. Pressure effects on the rate of thermal Z/E isomerization of DNAN in GTA at various temperatures.

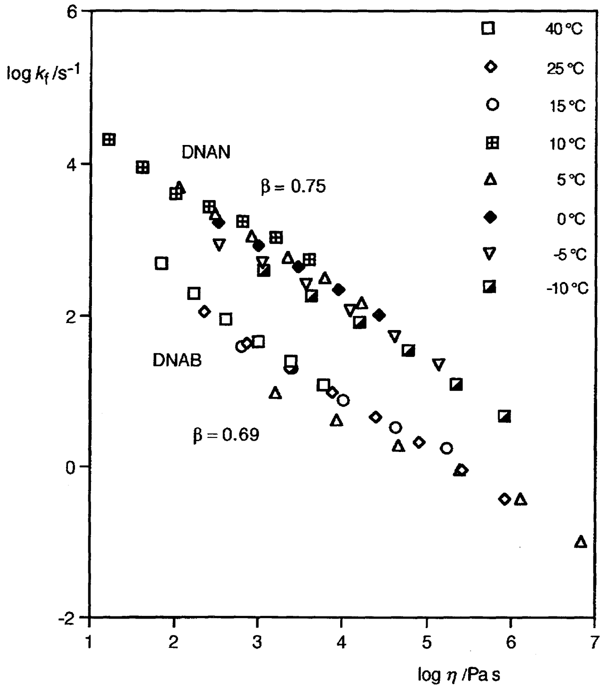

Fig. 13. Comparison of the fluctuation-limited rate constant for DNAN and DNAB in GTA.

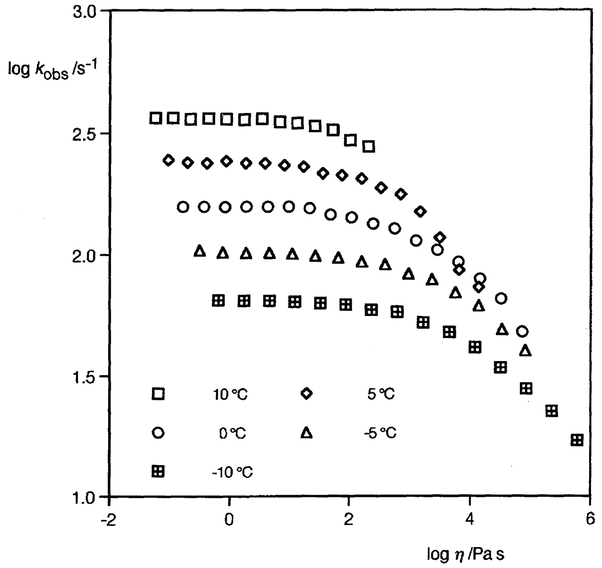

Fig. 14. Plots of the observed rate constant against solvent viscosity for thermal Z/E isomerization of DBNA in MPD.

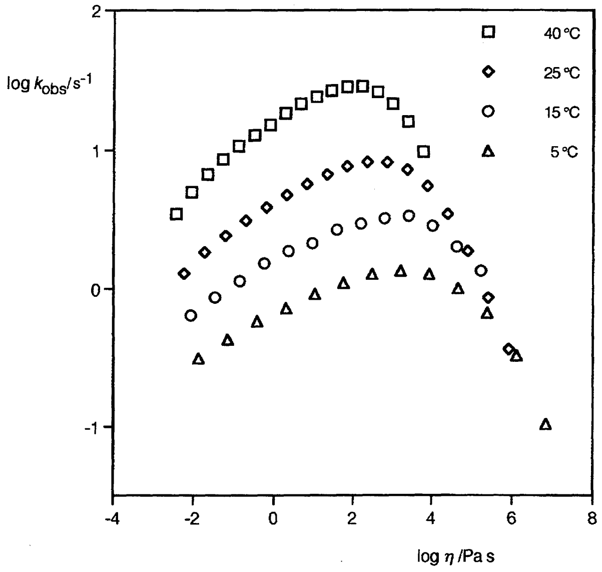

Fig. 15. Plots of the observed rate constant against solvent viscosity for thermal Z/E isomerization of DNAB in GTA.

Here, in this section, we would like to examine the theory from a more chemically oriented point of view. In a single reaction coordinate model of Grote and Hynes, the same barrier must thermally be surmounted for reactions at any situation (see Fig. 2 of Ref. 11). To be more exact, in their model, the viscosity-induced retardations are incorporated as a transmission coefficient $\varkappa$ (Eq. 12) and $\varkappa$ is considered to become inversely proportional to the fractional power of η when the reaction is retarded considerably by slow solvent fluctuations.

$$k_{\mathrm{obs}} = \varkappa k_{\mathrm{TST}} \tag{12}$$

Therefore, the temperature dependence of k_{obs} must be independent of the solvent viscosity so long as it is kept constant. In other words, when $\log k_{\mathrm{obs}}$ is plotted against $\log \eta$ for various temperatures, the curves must stay separated even at high viscosities unless the pressure-induced acceleration in TST-valid region decreases considerably with increasing temperature and, as a result, the sign of Ea_{TST} changes from plus to minus at higher pressures. As can be seen from Figs. 5 and 8, this is not supported by the experimental observations. On the other hand, in Sumi's model, k_{obs} reaches k_{f} at high viscosities and, therefore, the isoviscosity rate constant will have an activation energy considerably smaller than Ea_{TST}. Two examples of $\log k_{\mathrm{obs}}$–$\log \eta$ plots are shown in Figs. 14 and 15. Obviously, the results confirm predictions of Sumi's model but they cannot be rationalized on the basis of the Grote–Hynes model.

Waldeck[7)] and Hara[8)] constructed their discussions on the basis of Eq. 12 and tried to fit the transmission coefficient $\varkappa$ to the Grote–Hynes model. In their studies, however, k_{TST} values have not been obtained, and then the analysis on the basis of Eq. 12 cannot be performed unambiguously. In this situation, we believe, their viscosity variation ranging over only about 10 times was not wide enough to guarantee dynamical solvent effects.[30)] In the present work, on the other hand, the viscosity variations ranges over 10^8 times.

Troe and his co-workers[31—33)] studied photo-induced isomerization of stilbene and 1,4-diphenyl-1,3-butadiene in various media including high pressure gases and liquids. Instead of assuming frequency-dependent friction for $\varkappa$ in Eq. 12, they tried to rationalize their observations by a combination of the Kramers theory giving $\varkappa \propto \eta^{-1}$ and the lowering of Ea_{TST} in k_{TST} caused by a polarizability increase of the solvent. This polarizability dependence of Ea_{TST} was assumed on the basis of the linear correlation of the activation energy determined from isoviscous Arrhenius plots with $(n^2-1)/(n^2+2)$ where n is the solvent polarizability. The viscosity variation ranges over about 10 times still in their studies in the liquid media. Then, studies in a much wider variation may lead to a different conclusion. To be more concrete, we consider that the pressure dependence of k_{obs} in the liquid media shown in Refs. 31 and 33 may be interpreted as data from the end of TST valid region to the TST invalid region. On the basis of Eq. 5, they seem to be in a region where a situation of $k_{\mathrm{f}} \approx k_{\mathrm{TST}}$ changes into that of $k_{\mathrm{f}} < k_{\mathrm{TST}}$. In this region, it is indispensable to use a reliable value of k_{TST} in the analysis of k_{obs} and also a sufficiently wide range of η variations is required to derive a reliable η dependence of k_{f} from k_{obs}. We consider that the data by Troe and his co-workers are not sufficient to prove the validity of their discussion.

Conclusions

The results presented here along with the ones reported earlier demonstrate unequivocally that the rates of *Z*/*E* isomerization of *N*-benzylideneanilines and azobenzenes in highly viscous fluid can be rationalized by Sumi's two-dimensional reaction-coordinate model. It was also shown that whether the solvent rearrangement for accommodating the transition state involves chemical transformations depends on the type of solvent and the reaction mechanism. Similar measurements in nonpolar liquid are under progress and the results will be reported when they are completed.

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3) The *Z*/*E* isomerizations investigated here are single-step processes in which the *Z* isomer continuously transforms itself, by surmounting a potential barrier, to the *E* isomer.[4,5)]

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12) The present reactions are brought about by continuous structural transformation, which is in general composed of solvent motions and much faster intramolecular vibrational motions. To accomplish the whole process, solvent motions must be involved. Then it can be simplified as if it was a two-step process, shown in Eq. 4, composed of slow motions (from Z to M) followed by fast motions (from M to E), although in reality, it must be described by a continuous two-dimensional potential surface spanned by these motions as shown by H. Sumi and R. A. Marcus [*J. Chem. Phys.*, **84**, 4894 (1986)]. In this simplification, the TST-expected rate constant k_{TST} should be obtained by an assumption that M is found in thermal equilibrium with Z in Eq. 4, as $k_{\mathrm{TST}}=k_2\exp(-\Delta G_{\mathrm{M}}/RT)$ where ΔG_{M} represents the free energy of M relative to Z. Since $\exp(-\Delta G_{\mathrm{M}}/RT)=k_{\mathrm{f}}/k_{-\mathrm{f}}$ from the law of mass action, we reach the relation of $k_{\mathrm{TST}}=k_2k_{\mathrm{f}}/k_{-\mathrm{f}}$.

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26) *N*- [4- (Dimethylamino)benzylidene]- 4- (dimethylamino)-aniline was also examined at 15 and 25 °C. However, little pressure-induced retardation that cannot be rationalized by TST was observed. At lower temperatures, the reaction was too slow to obtain accurate thermal reaction rates because of the photo-induced isomerization by the monitoring light.

27) The activation volumes for DBNA in less viscous solvents reported earlier [T. Asano, T. Okada, and W. G. Herkstroeter, *J. Org. Chem.*, **54**, 379 (1989)] were in the range of -1.2—-0.8 $\mathrm{cm^3\,mol^{-1}}$. It is difficult to explain small activation volume differences in various solvents at the present state of our knowledge.

28) In Ref. 10, an empirical Eq.i was used for the extrapolation.

$$\ln(k/k_0) = aP + b\ln(1 + cP) \tag{i}$$

When the present experimental results were fitted to this equation, sometimes the best result was obtained with a negative value for the parameter a. As a result, the extrapolation to higher pressures resulted in an unrealistic maximum value of k just outside the pressure range studied. The term aP is related to the intrinsic activation volume which must be close to zero in the present isomerization because the reaction is unimolecular and all of the atomic groups stay together as one molecule during the activation step. The use of Eq. 8 for the results in GTA gave essentially the same results with the ones obtained by the above equation. Although Eq. 8 is empirical, it can be derived by making the following assumptions [T. Asano, *Rev. Phys. Chem. Jpn.*, **49**, 109 (1979)]. 1. The intrinsic volume change is negligibly small. 2. The isothermal compression of the solvent is described by Tait Eq.ii where V and V_0 are molar volumes at pressure P and 0, respectively, and B and C are the adjustable parameters.

$$V = V_0\left(1 - C\ln\frac{B+P}{B}\right) \tag{ii}$$

3. Solvent molecules in the solvation sphere behave as if they are under the influence of an average extra pressure which is much smaller than B.

29) The mechanism in hexane is the nitrogen inversion and the activation energy for the rotation is expected to be higher than the experimental value.[23)]

30) Judging from the previous and the present results, the ground-state isomerization of DODCI might be in the TST-valid region under the conditions studied. In order to examine this possibility, the present authors are planning to study pressure effects on the ground state isomerization of DODCI and related compounds in MPD. The results will be presented and discussed when the measurements are completed.

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