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Effects of Solvent Fluctuations on the Rate of the Thermal *Z*/*E* Isomerization of *N*-Benzylideneanilines in a Highly Viscous Liquid Hydrocarbon

Tsutomu Asano,* Kohei Matsuo,† and Hitoshi Sumi*,††

Institute for Fundamental Research of Organic Chemistry, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-81

†Petroleum Research Laboratory, Research and Development Division, Japan Energy Corporation, Toda 335

††Institute of Materials Science, University of Tsukuba, Tsukuba 305

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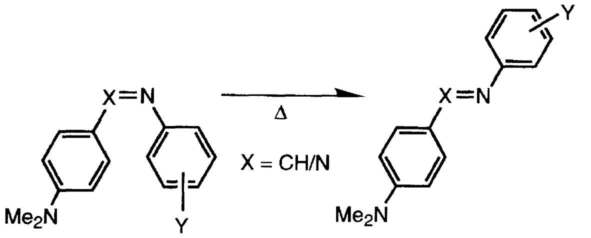
The effects of the solvent viscosity on the thermal *Z*/*E* isomerization of three substituted *N*-benzylideneanilines were studied in a nonpolar aprotic solvent, 2,4-dicyclohexyl-2-methylpentane. By increasing the pressure to several hundred megapascals, the viscosity of the reaction system was raised high enough to retard the isomerization. The viscosity dependence of the observed rate constant was analyzed by assuming a two-step mechanism based on the two-dimensional reaction-coordinate model proposed by one of the present authors. The rate constant of this mechanism is given by $1/(k_{\mathrm{TST}}{}^{-1}+k_{\mathrm{f}}{}^{-1})$, where k_{TST} represents the rate constant expected from the transition state theory, while k_{f} (>0) represents the part controlled by a solvent rearrangement during thermal fluctuations. The k_{f} values were inversely proportional to a fractional power of the viscosity, in agreement with the theory. It was also found that, compared at the same temperature and viscosity, the k_{f} values in the present solvent are larger than those in a polar aprotic solvent, glycerol triacetate, and in a polar protic solvent, 2-methyl-2,4-pentanediol, reported earlier.

In previous papers,[1,2] the effects of the pressure and temperature on the rate of thermal *Z*/*E* isomerization of substituted azobenzenes and *N*-benzylideneanilines in their ground state, Eq. 1, were reported. As the reaction medium, two viscous liquids, glycerol triacetate (GTA, a polar aprotic solvent) and 2-methyl-2,4-pentanediol (MPD, a polar protic solvent) were adopted, and the results were compared with those in less viscous methyl acetate and ethanol.



X=CH, Y=4-NO$_2$: DBNA
X=CH, Y=4-COOEt : DBEA
X=CH, Y=4-Br : DBBA
X=N, Y=4-NO$_2$: DNAB
X=N, Y=2-MeO, 4-NO$_2$: DMNAB (1)

The activation energies of the reaction were close to or higher than 50 kJ mol^{-1} at the ambient pressure (0.1 MPa), and the transition state theory (TST) seemed to be applicable to describe the reaction. In other words, the temperature/pressure dependence of the rate constant at low pressures could be understood on the basis of the free energy difference between the reactant and the transition state. The changes in the solvent viscosity η that inevitably accompany temperature/pressure changes had little effect as long as the viscosity was kept below 10 Pa s ($=1\times10^4$ cP). However, it was clearly demonstrated that the reactions could be retarded by an increase in pressure when the viscosity exceeded several tens of pascal second. Since the retardations were observed only at extremely high viscosities, they were taken to indicate the failure of TST caused by slow solvent fluctuations. In order to examine whether the same phenomenon could be observed in the absence of specific solute-solvent interactions that may exist in GTA and MPD, the effects of pressure on the rate of *Z*/*E* isomerization of the three *N*-benzylideneanilines in Eq. 1 were studied in 2,4-dicyclohexyl-2-methylpentane (DCMP), which is both nonpolar and aprotic; the results are reported here.[3]

Experimental

Materials. *N*-[4-(Dimethylamino)benzylidene]-4-nitroaniline (DBNA), *N*-[4-(dimethylamino)benzylidene]-4-ethoxycarbonylaniline (DBEA), and *N*-[4-(dimethylamino)benzylidene]-4-bromoaniline (DBBA) were reported previously.[6] DCMP was a product of Japan Energy Corporation with a purity of 98.65% (GLC) and was used without further purification.

Kinetic and Viscosity Measurements. These measurements were performed as described in the literature.[2,7] As in the previous measurements, first-order kinetics were followed at all of the conditions studied.

Results and Discussion

Viscosity of DCMP at High Pressures. The pressure dependence of the viscosity of DCMP was measured at several temperatures. The logarithm of the viscosity was almost linearly correlated with the pressure at each temperature, and the results were fitted to the following equation, where η_0 is the viscosity at atmospheric pressure, since $\exp(\alpha P)$ is almost equal to one at 0.1 MPa:

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

In order to estimate the values at the reaction temperature and pressure, the observed η_0 and α values were fitted to the Walther equation[8] and a linear correlation with the logarithm of the kinematic viscosity, respectively. The thus-obtained values are given in Table 1.

Isomerization Rates and Two Reaction Models. The observed rate constants k_{obs} at various temperatures and pressures are listed in Table 2. Despite the large difference in the solvent properties, the pressure effects in DCMP were qualitatively the same as those in GTA and MPD. Namely, at lower pressures, very small kinetic effects of the pressure were observed, as expected from the nature of the reaction. The reaction is effected by an inversion of the imino nitrogen atom without any extensive polarity change in the reactant.[6] Therefore, the activation volume $\Delta V^{\neq}$ must be close to zero, irrespective of the differences in the solvent properties. However, at higher pressures, the activation volume seems to start increasing. The results at 20 °C are illustrated in Fig. 1.

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

T/°C	η_0	α
−5	0.546	53.2
0	0.281	49.6
5	0.156	46.5
10	0.0928	43.7
15	0.0584	41.2
20	0.0387	39.0

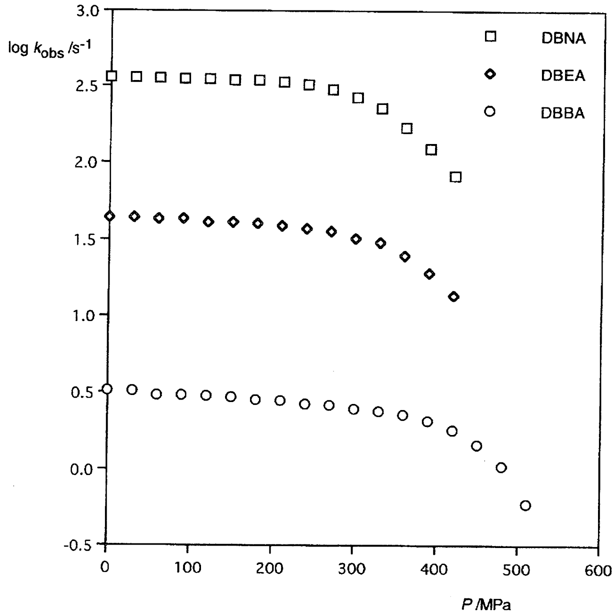


Fig. 1. Pressure effects on the thermal Z/E isomerization of substituted N-benzylideneanilines in DCMP at 20 °C.

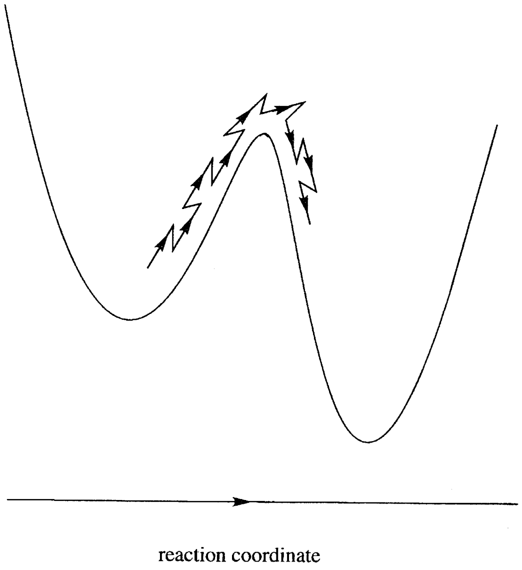


Fig. 2. A schematic illustration of the one-dimensional reaction-coordinate model used by Kramers.

There are two different ways to view the results. One of them is to assume that the reactant climbs up the energy barrier by diffusive motions along a one-dimensional reaction coordinate in tune with the solvent fluctuations, as schematically illustrated in Fig. 2. At low viscosities, the solvent fluctuations are fast enough to maintain thermal equilibrium between the reactant and the activated complex. At high viscosities, however, the solvent fluctuations become so slow that the thermal equilibrium mentioned above cannot be maintained, and the rate constant is given by the following equation, where k_{TST} is the rate constant expected from TST, and the transmission coefficient $\varkappa$ decreases along with an increase in the solvent viscosity η,

$$k_{\text{obs}} = \varkappa k_{\text{TST}}. \tag{3}$$

In the Kramers theory,[9] $\varkappa$ is proportional to η^{-1}, while a slower η dependence of $\varkappa$ might be obtained in the Grote–Hynes theory.[10] Since $\varkappa$ remains constant as long as the viscosity is kept constant in this model, the temperature dependence of k_{obs} will be the same at all viscosities, and it must coincide with that of k_{TST}. Therefore, we would be able to test the validity of the model by plotting k_{obs} at various temperatures against η. If the model is correct, the plots for different temperatures should stay separated throughout the whole range of the viscosity. In our experiments, however, a pressure increase was used to increase the viscosity.

Table 2. The Observed Rate Constants (k_{obs}/s^{-1}) for the Thermal *Z*/*E* Isomerization of *N*-Benzylideneanilines in DCMP at Various Temperatures and Pressures

	DBNA $T/^\circ C$						DBEA $T/^\circ C$					DBBA $T/^\circ C$				
P/MPa	−5	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
0.1	44.1	69.3	108	157	243	360	7.44	12.4	19.4	29.1	43.8	0.425	0.751	1.22	2.00	3.25
30	44.2	69.9	107	160	242	357	7.27	12.3	18.5	28.8	43.8	0.414	0.716	1.15	1.97	3.24
60	44.5	70.6	109	160	244	356	7.08	11.9	17.8	28.1	43.0	0.428	0.688	1.14	1.95	3.03
90	44.0	69.8	107	158	244	352	7.02	11.3	17.9	28.1	43.2	0.404	0.674	1.11	1.87	3.04
120	43.0	66.7	106	156	239	352	6.80	11.6	17.4	27.7	40.9	0.387	0.663	1.08	1.81	3.00
150	42.5	67.3	106	152	242	345	6.72	11.2	17.4	27.4	41.1	0.371	0.652	1.05	1.73	2.95
180	39.8	63.5	103	149	233	346	6.36	10.7	17.0	26.7	40.2	0.372	0.629	0.978	1.73	2.84
210	35.7	58.4	96.1	144	227	337	5.92	10.2	16.4	25.8	39.0	0.364	0.604	1.01	1.68	2.81
240	30.2	51.5	88.4	133	214	323	5.24	9.68	15.0	24.0	37.3	0.350	0.596	0.950	1.63	2.66
270	23.0	42.6	75.0	113	191	299	4.49	8.73	13.9	23.1	35.9	0.331	0.564	0.923	1.60	2.62
300	15.2	30.3	60.5	94.9	170	265	3.32	7.18	12.4	21.1	32.3	0.292	0.536	0.876	1.52	2.47
330	7.73	20.9	42.3	70.2	136	226		4.97	10.2	18.0	30.5	0.258	0.488	0.830	1.46	2.38
360		13.0	26.6	51.9	98.5	169		2.55	7.47	15.4	25.1	0.194	0.421	0.769	1.39	2.27
390				35.3	65.9	123			4.49	10.4	19.3	0.133	0.320	0.619	1.20	2.07
420					45.3	82.5					13.7	0.0711	0.207	0.487	0.988	1.80
450												0.0300	0.0996	0.264	0.762	1.45
480														0.114	0.480	1.05
510														0.0401	0.222	0.597

It is, therefore, necessary to first examine the pressure dependence of the activation energy Ea_{TST}. Table 3 lists the activation energies for DBNA in DCMP at various pressures. Obviously, the activation energy shows no significant pressure dependence. Since this situation was similar in the other *N*-benzylideneanilines, we can safely assume that the barrier height of the present reaction is little affected by the pressure. Figure 3 shows plots of $\log k_{obs}$against $\log \eta$ for DBNA in DCMP at various temperatures. At low viscosities, the plots for different temperatures stayed separated. This means that the temperature effect on k_{obs} was almost constant under the isoviscosity condition. At higher viscosities, however, the temperature effect decreased rapidly, and tended to disappear at the high viscosity end of our experiment. In order to illustrate the situation, Fig. 3 includes the rate constants at 1×10^8 Pa s estimated by extrapolations.[11] The values are in the range of 4.5 and 7.0 s^{-1}. From this and similar results obtained for DBEA and DBBA, we can conclude that the one-dimensional reaction-coordinate model, such as that proposed by Grote and Hynes[10] as well as that by Kramers,[9] cannot be a basis of the analysis of our results. The same conclusion was also reached in GTA and MPD.[2] It was also reached in terms of an unphysically long correlation time of microscopic solvent motions, which was required to describe k_{obs} by the theory of Grote and Hynes.[12]

Table 3. The Preexponential Factors (ν/s^{-1}) and the Activation Energies ($Ea_{TST}/kJ\ mol^{-1}$) for the Thermal *Z*/*E* Isomerization of DBNA in DCMP at Various Pressures

P/MPa	ν	Ea_{TST}
0.1	2.0×10^{12}	54.6
30	1.8×10^{12}	54.4
60	1.6×10^{12}	54.2
90	1.7×10^{12}	54.3
120	2.2×10^{12}	55.0
150	2.0×10^{12}	54.8

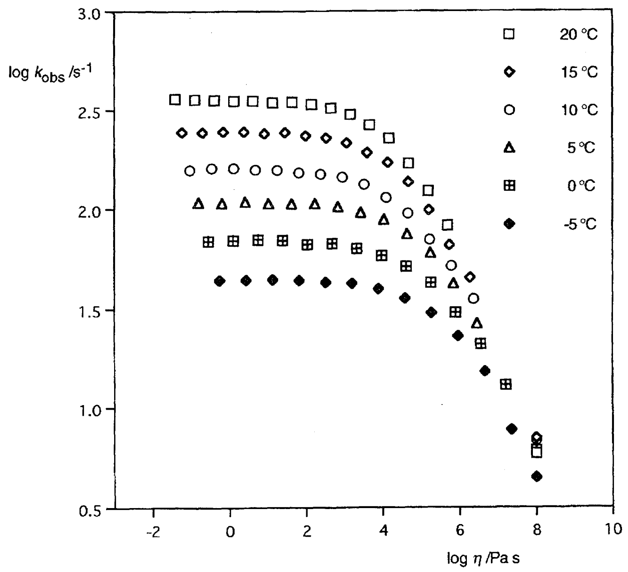


Fig. 3. Plots of $\log k_{obs}$ against $\log \eta$ for the thermal *Z*/*E* isomerization of DBNA in DCMP.

The other way to look at the present data is to assume that the reaction behaves as if it consists of two steps as described below, where the rate-determining step shifts from the second to the first step with increasing viscosity:

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

The physical basis of this scheme is a model developed by one of the present authors, Sumi.[13] In his model, the reaction is described as a motion in a two-dimensional reaction coordinate surface. The first coordinate depicts the solvent rearrangement by relatively slow thermal fluctuations (Brownian motions) on the reactant energy surface. The movements along this coordinate are subject to frictional retardations. The second coordinate depicts an energy barrier crossing by rapid intramolecular atomic vibrations, which are taken to be independent of the friction. The probability of this energy barrier crossing depends on the position on the first coordinate, i.e., on the arrangement of the solvent molecules around the reactant. Before a chemical conversion takes place, solvent molecules around the reactant change their arrangement. In other words, the reactant molecule moves along the first coordinate. At state M in Eq. 4, a reactant molecule is surrounded by solvent molecules that are arranged so as to stabilize the transition state. When the reactant molecule obtains the activation energy there from the environment, an energy-barrier crossing takes place driven by thermal intramolecular vibrations. During this movement, the position on the first coordinate does not change, because the intramolecular vibrations are much faster than the Brownian motions. When the solvent fluctuations are sufficiently fast, the loss of the reactant molecules by chemical conversion at state M is quickly buried, and the distribution of the reactant molecules along the first coordinate is kept thermally equilibrated throughout the reaction. TST is valid under such a condition. The reversible step in Eq. 4 depicts the solvent rearrangement along the first coordinate with the fluctuation-limited rate constants k_f and k_{-f}. The intermediate M corresponds to the reactants at various points on the first coordinate with a finite probability of the energy-barrier crossing. The second step from M to E is a leap along the second coordinate. In this scheme, fast thermal fluctuations make Z and M at equilibrium, and the TST-expected rate constants are observed, i.e., at low viscosities, $k_{obs}\approx k_{TST}=k_2k_f/k_{-f}$, since k_f/k_{-f} gives the thermal-equilibrium populations of the reactants at M from the relation of the detailed balance. At high viscosities, the reaction is retarded because the first step becomes rate-determining ($k_{obs}\approx k_f$), and TST is invalidated. At the intermediate-viscosity region, the observed rate is correlated with k_{TST} and $\mathrm{k_f}$ by the following equation, which can be derived from Eq. 4 by assuming a steady state:

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

With a smooth shift from the TST-valid to the TST-invalid regime, brought about by increasing the viscosity, it would be possible to estimate an expected k_{TST} value in the TST-invalid region by extrapolation. Then, putting the value into Eq. 5 along with k_{obs}, it would be possible to calculate the forward rate constant for the first step k_f. Since a solvent rearrangement by thermal fluctuations requires thermal activation, it is reasonable to expect a linear Arrhenius plot for k_f. Figure 4 shows typical examples. In all of the cases studied, no systematic deviation from the expected linearity was observed, supporting Eq. 4 and Sumi's model upon which Eq. 4 is based. The validity of Eq. 4 can be further tested by checking the viscosity dependence of k_f.

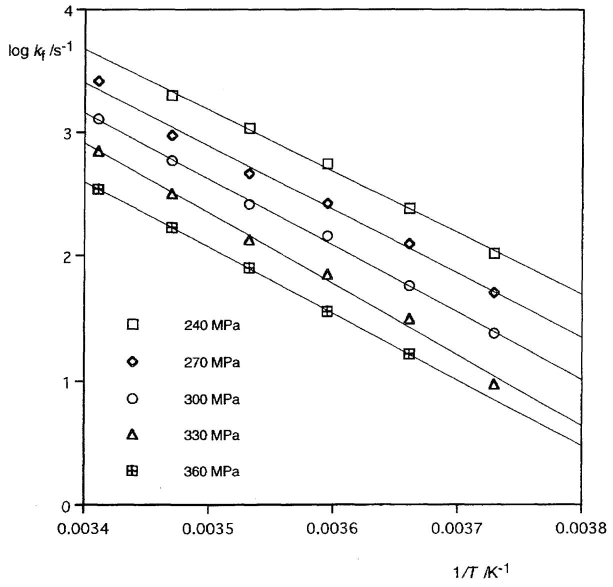


Fig. 4. Arrhenius plots for the fluctuation-limited rate constant k_f for the thermal *Z*/*E* isomerization of DBNA in DCMP.

It has been repeatedly reported that the rate of *Z*/*E* isomerization of molecules at their electronically excited state is inversely proportional to a fractional power of the medium viscosity,[14)]

$$k_{obs} = B\eta^{-\beta} \qquad 0<\beta<1. \qquad (6)$$

The reason for this deviation from the Kramers' theoretical prediction remains an important problem to be solved in the field of chemical kinetics. These reactions are characterized by their low activation energies, and the fundamental hypothesis of TST is expected to be violated even by small frictions between the reactant and the solvent molecules. Therefore, it may be safely assumed that the reactions belong to the TST-invalid regime already at most of the viscosities in their measurements, and that k_{obs} describes k_f in Eq. 4. Figure 5 shows $\log k_f - \log \eta$ plots for the current three *N*-benzylideneanilines at 20 °C. As expected, they are linearly correlated, and the slopes are less than one. These and other similar results reported earlier[1,2)] clearly show the legitimacy of the two-dimensional reaction-coordinate model as a description of the unimolecular reactions in the liquid phase. Kinetic measurements in highly viscous liquids provide new information which has hitherto been unavailable, i.e., the dynamic course of the reaction leading to the transition state.

Temperature and Solvent Effect on k_f. In previous papers it was reported that under the isoviscosity condition the fluctuation-limited rate constant k_f was only slightly temperature dependent for most of the cases in GTA[15)] and for the reaction of the *N*-benzylideneanilines in MPD. A clear temperature dependence was observed only for the isomerization of DNAB and DMNAB in MPD. The temperature dependence of k_f was also found to be small for all three reactants in DCMP. The results for DBNA and DBBA are illustrated in Fig. 6. According to Sumi,[13)] the fluctuation-

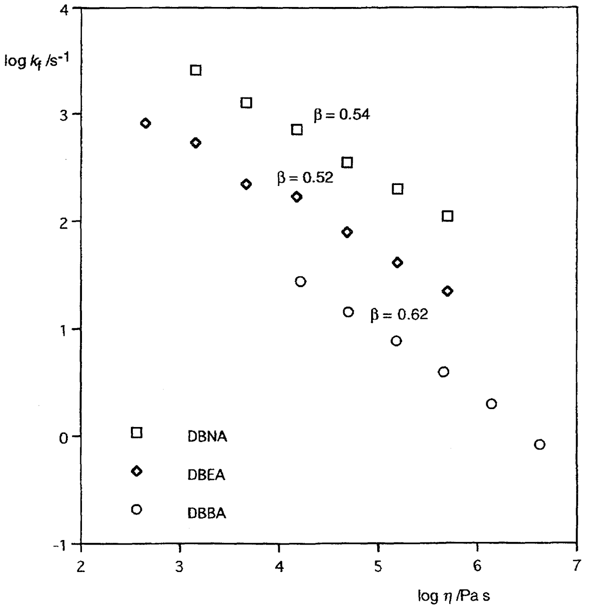


Fig. 5. Plots of log k_f against log η for the the thermal *Z*/*E* isomerization of substituted *N*-benzylideneanilines in DCMP at 20 °C.

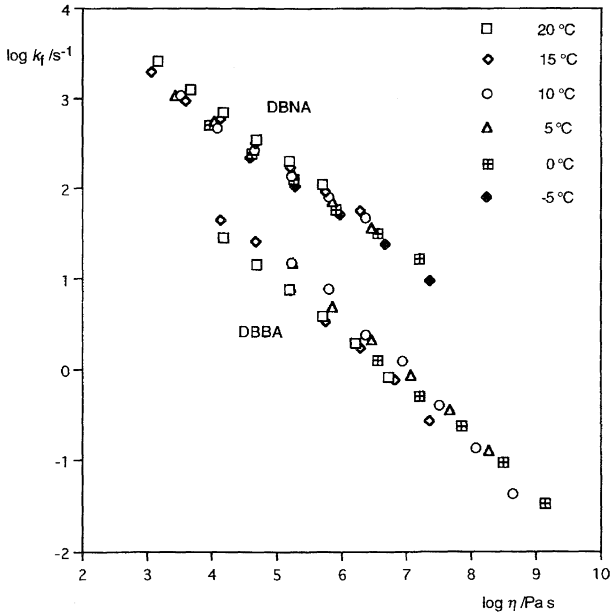


Fig. 6. Plots of log k_f against log η for the thermal *Z*/*E* isomerization of DBNA and DBBA in DCMP at various temperatures.

limited rate constant can be written as

$$k_f \approx \tau^{-\beta'} \nu^{1-\beta'} \exp(-\gamma Ea_{TST}/RT) \qquad 0 < \beta', \gamma < 1, \tag{7}$$

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},

$$k_{TST} = \nu \exp(-Ea_{TST}/RT), \tag{8}$$

and γEa_{TST} is a component of Ea_{TST} brought about by slow solvent motions. The small temperature dependence of k_f under the isoviscosity conditions in the isomerization of *N*-benzylideneanilines means $\gamma \approx 0$ in Eq. 7. This strongly suggests that solvent molecules are rearranged with only minor structural changes in the reactant in all of the solvents, i.e., protic (MPD), aprotic polar (GTA), and nonpolar (DCMP) solvents. Since the pressure dependence of ν was also found to be small (Table 3 and Ref. 2), the empirical parameter β may be considered to be approximately the same as β' in Eq. 7. Table 4 lists the β values in the three solvents calculated on the basis of all k_f values at various temperatures. In all of the solvents, the β value was in the order DBNA<DBEA<DBBA, and, for the same reactant, it was larger in GTA than in the other two solvents. These tendencies indicate that the requirement on the solvent arrangement depends on both reactant and solvent structures. However, in order to clarify physical meanings behind these facts, a further accumulation of experimental data is required. It was also found that, compared at the same temperature and viscosity, k_f is in the order GTA≤MPD<DCMP in all three compounds. The results for DBNA and DBBA at 5 °C are shown in Fig. 7. The viscosity coefficient β cannot rationalize this tendency. According to Eq. 7, k_f will be larger with a

Table 4. Empirical Viscosity Coefficient β for the Fluctuation-Limited Rate Constant k_f in the Isomerization of *N*-Benzylideneanilines in Various Solvents

	DBNA	DBEA	DBBA
DCMP	0.52	0.56	0.66
GTA[a)]	0.66	0.68	0.73
MPD[a)]	0.53	0.61	0.67

a) From Ref. 2.

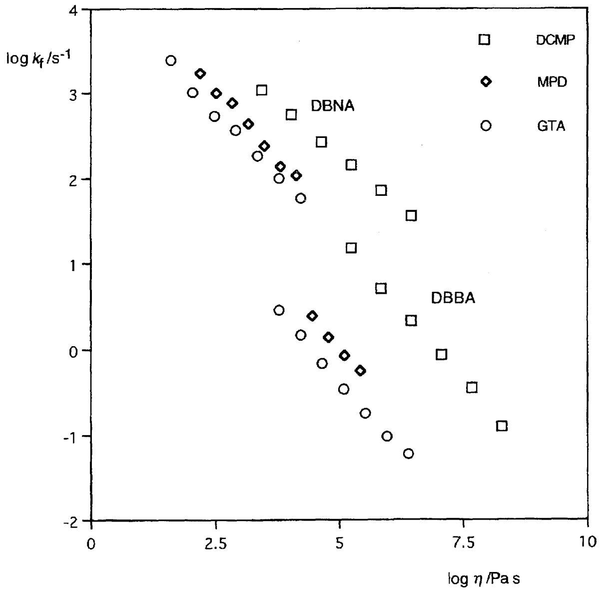


Fig. 7. Plots of log k_f against log η for the thermal *Z*/*E* isomerization of DBNA and DBBA at 5 °C in the three solvents.

smaller β' ($\approx\beta$) value and β is the largest in GTA. However, the coefficients for DCMP and MPD were similar in DBNA and DBBA, failing to rationalize the larger k_f in DCMP. It is also difficult to attribute the solvent dependence of k_f to the variation in the activation parameters ν and Ea_{TST}. As can be seen from Table 5, the activation energy was the highest and the frequency factor was the smallest in DCMP in the isomerization of DBNA. Therefore, the reasons for the the larger fluctuation-limited rate constant in DCMP have to be sought in the solvent. Any further discussion inevitably becomes speculative. However, one possibility may be pointed out: a disparity between the macroscopic viscosity and the microscopic friction between the molecules. The macroscopic solvent viscosity is a property of the solvent itself. The friction between the moving body in the liquid used as a sensor, e.g., a steel ball in the present measurement, should not affect the measured viscosity. On the other hand, the microscopic friction depends on both the friction between the solvent molecules and that between the solvent molecule and the reactant. The latter friction may be larger in polar solvents, such as GTA and MPD, than in the nonpolar DCMP compared at the same viscosity. This difference may result in a faster solvent rearrangement in DCMP.

Conclusions

With the present results, a series of measurements of dynamic solvent effects on thermal *Z*/*E* isomerization about a carbon–nitrogen and a nitrogen–nitrogen double bond has been completed. A combination of high pressure and a viscous liquid effectively rendered TST-valid "slow" unimolecular reactions TST-invalid, and opened a new way to study dynamic solvent effects. Qualitatively, the same dynamic solvent effect was observed in protic, aprotic polar, and nonpolar solvents. All of the results could be rationalized on a two-step reaction scheme, Eq. 4, based on the two-dimensional reaction-coordinate model proposed by Sumi. A simple one-dimensional reaction coordinate model failed to provide a theoretical basis for an analysis of the present and the previous observations. The fluctuation-limited rate constant k_f for the preliminary solvent rearrangement gave new information concerning the solvent dynamics in chemical reactions. In reactions where the solute–solvent interactions in the initial and the transition state are not greatly different, as in the isomerization of the *N*-benzylideneanilines, the energy of the system changes only slightly during the solvent rearrangement before the energy barrier crossing. In other words, the solvent rearrangement induces only minor structural changes in the reactant. In the *Z*/*E* isomerization of push-pull substituted azobenzenes, where the solvation of the transition state is much stronger than in the initial state,[4)] the solvent rearrangement was accompanied by a considerable energy increase in the reactant in MPD, but not in GTA. A rearrangement of the alcohol molecules results in changes in the specific solvation and, in turn, causes structural changes. The accumulation of additional experimental results will provide more detailed information concerning dynamic solvent effects in organic reactions.

Table 5. The Preexponential Factors (ν/s^{-1}) and the Activation Energies (Ea_{TST}/kJ mol^{-1}) at 0.1 MPa for the *Z*/*E* Isomerization of *N*-Benzylideneanilines

	DBNA		DBEA		DBBA	
Solvent	ν	Ea_{TST}	ν	Ea_{TST}	ν	Ea_{TST}
DCMP	2.0×10^{12}	54.6	1.2×10^{12}	58.6	3.0×10^{12}	67.2
GTA[a)]	2.4×10^{12}	53.5	6.0×10^{12}	62.6	8.6×10^{12}	71.2
MPD[a)]	2.7×10^{12}	53.5	4.8×10^{12}	62.3	8.5×10^{12}	72.9

a) From Ref. 2.

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