Kinetics in Highly Viscous Liquid Phase Realized under High Pressure

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Effect of pressure on the rate of relatively slow thermal *Z* to *E* isomerizations was studied in viscous organic liquids. The results clearly demonstrated that the reactions were transferred from the "activation limited" to the "solvent-fluctuation limited" regime by an increase in the solvent viscosity. The viscosity dependence of the observed rate could be analyzed by assuming a two-step mechanism based on the two-dimensional reaction coordinate model proposed by one of the present authors. A recent Biswas-Bagchi prediction of an inverse logarithmic dependence of rate was not born out by our experimental results. A single case of a "multi exponential" decay is also reported. [chemical reaction, dynamic solvent effect, viscosity, solvent fluctuation, two-dimensional reaction coordinate]

1. Introduction

Dynamic solvent effect is one of the most active fields in the current studies of chemical kinetics and high pressure has been employed as a tool to manipulate the medium viscosity by several groups [1, 2]. However, the viscosity is usually kept at relatively low level ($\eta < 1$ Pa s) and reaction dynamics in highly viscous media was left untouched until recently. In this paper, the experimental results of kinetics in highly viscous conditions ($\eta \geq 10$ Pa s) will be presented and a rationalization will be proposed.

2. Results and Discussion

a. Reactions and Their Mechanisms The rate of the thermal *Z/E* isomerizations in eq 1 were measured in three viscous liquids, i.e., polar and protic 2-methyl-2,4-pentanediol (MPD), polar but aprotic glycerol triacetate (GTA), and nonpolar and aprotic 2,4-dicyclohexyl-2-methylpentane (DCMP), at various pressures and temperatures. Furthermore, similar isomerization of *N,N'*-dimethylindigo (DMIG) was also studied in GTA (eq 2). The reactions in eq 1 obeyed the first-order rate law at all conditions studied, while in eq 2, a deviation from a single-exponential decay was observed at high pressures (*vide infra*).

The isomerization of DMIG is expected to proceed by means of a homolytic cleavage of the carbon-carbon π bond and the activation volume will be a small positive value [3]. In the push-pull substituted azobenzenes, on the other hand, the reaction is characterized by a large negative activation volume because of the heterolytic cleavage of the nitrogen-nitrogen π bond [4]. In *N*-benzylideneanilines, the isomerization is effected by the inversion of the nitrogen atom leaving the carbon-nitrogen double bond intact. Because of the absence of a major polarity change in such a mechanism, the

activation volume is close to zero [5]. In all of the cases studied, pressure effects consistent with these mechanisms were observed at the beginning of pressurization. Therefore, it can be safely concluded that the transition state theory (TST) is applicable even in viscous liquids used in our experiments as far as the pressure is kept at a relatively low level ($P \leq 150$ MPa).

b. Pressure-Induced Retardations Despite the TST-expected pressure effects at low pressures, all of the reactions were found to be strongly retarded by an increase in pressure at higher pressures ($P > 200$ MPa). Such kinetic effects were observed only in viscous liquids and we concluded that the reactions were converted from "activation limited" to "solvent-fluctuation limited" by a pressure-induced increase in the solvent viscosity. Figures 1 and 2 illustrate two sets of examples of the viscosity dependence of the observed rate constant. A large thermal activation energy (≈ 50 kJ mol⁻¹) is the reason for the temperature dependence of the rate at the isoviscosity conditions in the TST-valid region. However, the temperature effect decreases rapidly with increasing viscosity in the region where TST is considered to fail. This tendency can hardly be rationalized in the one-dimensional reaction-coordinate model where the reaction is accomplished as a result of energy-barrier crossing by diffusive Brownian motions of the reactant atomic groups. In such a model, in fact, the rate constant at high viscosities is given by the Smoluchowski limit of the Kramers equation (eq 3) where k_{TST} is the rate constant expected from TST and ω_b is the imaginary frequency of the energy barrier and ζ is the microscopic friction constant.

$$k_{\text{obs}} = k_{\text{TST}}(\omega_b/\zeta) \quad (3)$$

If this equation holds, the temperature effect at isoviscosity conditions must be the same with that on k_{TST} throughout the whole range of the viscosity because ζ must stay constant as far as the viscosity is kept constant. Our observations were in an obvious contradiction to this expectation.

c. Two-Step Mechanism The other way to look at the present results is to assume that the structural conversion along the reaction coordinate is much faster than the solvent diffusive fluctuations and the solvent molecules have to be rearranged prior to the chemical conversion [6]. This

Fig. 1. Dependence of the Z/E isomerization rate of DBNA on the solvent viscosity in DCMP at various temperatures.

Fig. 2. Dependence of the Z/E isomerization rate of DNAB on the solvent viscosity in GTA at various temperatures.

assumption will be correct if the movement of the reactant atomic groups along the reaction coordinate preserves the nature of the intramolecular vibrations and slow solvent fluctuations are required to form a favorable solvation sphere at the transition state. This model can be applied to our systems by assuming eq 4 where the first step describes the slow reversible solvent rearrangement by diffusive fluctuations characterized by the rate constants k_f and k_{-f} . The

Fig. 3. Viscosity dependence of the fluctuation-limited rate constant k_f in the Z/E isomerization of *N*-benzylneanilines in DCMP at 0°C.

second step is the energy barrier crossing with a rate constant k_2 . The intermediate M is the state where the reactant molecule has a solvation shell that accommodates/stabilizes the transition state. By assuming a steady state, eq 5 can be derived where k_{TST} is equal to $k_2 k_f / k_{-f}$.

$$1/k_{obs} = 1/k_{TST} + 1/k_f \quad (5)$$

Since k_{TST} at TST-invalid viscosities can be estimated by extrapolations, eq 5 enables us to estimate k_f values. The rate constants thus obtained gave linear Arrhenius plots and they were inversely proportional to a fractional power of the viscosity as observed in many fast reactions [1, 2] where TST is expected to fail. A few examples of the latter correlation are illustrated in Figure 3. These results strongly suggest the validity of eq 4 and the two-dimensional reaction coordinate model which eq 4 is based on.

d. Biswas-Bagchi Prediction Recently, Biswas and Bagchi [7] predicted that the isomerization rate in highly viscous conditions ($\eta > 1$ Pa s) would be inversely proportional to the logarithm of the viscosity. This prediction was made by assuming that the rate of such a reaction is given by the Smoluckowski limit with the Enskog friction Γ_E of hard-sphere liquid (eq 6) and Γ_E is proportional to $\log \eta$.

$$k_{obs} = k_{TST}(\omega_p/\Gamma_E) \quad (6)$$

In Figures 4 and 5 the transmission coefficient κ ($= k_{obs}/k_{TST}$) is plotted against $1/\log \eta$. The viscosity ranges were set so that $\log k_f - \log \eta$ plot mentioned above was linear. If Biswas and Bagchi were correct, the plot must give a straight line going through the origin. As can be clearly seen from the figures, the plots were nonlinear. They must become sigmoidal if the measurement could be extended to the higher viscosities because κ must be zero at infinite viscosity. Considering the fact that the $\log k_f - \log \eta$ plot was linear in these viscosity ranges, we believe that the plots

Fig. 4. Plots of κ against $1/\log \eta$ for the isomerization of DBNA in DCMP at various temperatures.

Fig. 5. Plots of κ against $1/\log \eta$ for the isomerization of DMNAB in MPD at various temperatures.

presented here lend further support to our discussion for the two-dimensional reaction coordinate model. Similar nonlinear plots were obtained in all of the cases studied.

e. Reaction of *N,N'*-Dimethylindigo As a part of our efforts to extend our study to the reactions other than those in eq 1, we studied thermal *Z/E* isomerization of DMIG in GTA. Although the reaction was much slower than those in eq 1, similar viscosity-induced retardation was observed. However, there was one important difference, i.e., a deviation

Fig. 6. First-order rate plots in the *Z/E* isomerization of DMIG in GTA at 5 °C.

from the first-order kinetics at high viscosities. An example is illustrated in Figure 6. In order to fit the data at 510 MPa, at least two exponential terms were necessary (eq 7).

$$A_{\infty} - A_t = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (7)$$

This may be an example of a conversion of a reaction from "single exponential" to "multi exponential" caused by extremely slow solvent thermal fluctuations. The rate constant for the faster process k_2 estimated by fitting the results into eq 7 was found to be larger than the k_1 value at 0.1 MPa. However, at this state of our knowledge, it is not possible to discuss the detailed mechanism of the reaction and why such a deviation from the first-order kinetics did not take place in the reactions of eq 1.

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