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Dynamic solvent effects on the thermal cyclization of a hexadienone formed from a diphenylnaphthopyran: An example of a system with distinctly separate medium and chemical contributions to the overall reaction coordinate[†]

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Pressure effects on the rate of thermal fading of a colored hexadienone formed from 3,3-diphenyl-3 *H*-naphtho[2,1-*b*]pyran were measured at various temperatures in three highly viscous solvents, *i.e.*, 2,4-dicylohexyl-2-methylpentane, glycerol triacetate, and 2-methylpentane-2,4-diol, as well as in their chemically similar nonviscous counterparts, such as methylcyclohexane, methyl acetate, and ethanol. Both experimental data and quantum-mechanical calculations are in agreement with formation of a cyclic activated complex. In the viscous solvents, high viscosities resulted in retardations of solvent thermal fluctuations which, in turn, slowed down the cyclization. The analysis of experimental results unequivocally demonstrated that the dynamic solvent effects in the present systems have to be described by a two-dimensional model that includes separately defined chemical and medium coordinates. Predictions of an alternative one-dimensional model with a diffusion-controlled reaction coordinate are not supported by the experimental data.

Introduction

Transition state theory (TST) describes effects of pressure on reaction rates in terms of a volume of activation, ΔV^{\neq} , related to the pressure derivative of the observed rate constant, $k_{\rm obs}$, by equation^{2–4}

$$\left(\frac{\partial \ln k_{\rm obs}}{\partial P}\right)_T = -\frac{1}{RT} \left(\frac{\partial \Delta G^{\neq}}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT}.$$
 (1)

Defined as a difference between the partial molar volumes of activated complex and the reactant(s), ΔV^{\neq} gives important information on the structural changes that occur in the reaction system as well as on the involvement of solvent molecules in the reaction. However, the validity of eqn. (1) is essentially restricted to the cases where an equilibrium between reactants and activated complex is maintained in the course of reaction. No information on the involvement of solvent molecules in the dynamics of activation is thus contained in this equation. High-pressure kinetics in highly viscous solvents is one of the experimental ways to study how solvent molecules are involved in the activation step. In highly viscous solvents, solvent viscosity rapidly increases with increasing pressure⁵ and thermal fluctuations become too slow to maintain thermodynamic equilibrium between the initial state and the transition state (TS). Under such circumstances, the reaction rate is limited by the rate of solvent thermal fluctuations and a so-called dynamic solvent effect is observed.

As we reported in our previous studies of the pressure effects on the kinetics of Z/E-type isomerizations,^{6–10} even relatively slow reactions ($k < 10^3 \text{ s}^{-1}$) demonstrated a significant departure from the TST and eqn. (1) in highly viscous media. The observed viscosity dependence of the rate constant could not be rationalized if we assumed that chemical transformations are completely coupled with solvation changes. These two components of solution reactions had to be treated as independent coordinates, *i.e.*, the chemical coordinate which described atomic movements of a reactant molecule and the medium coordinate which described solvation changes.

As a part of our efforts to examine the limit of the validity of this conclusion, we extended our measurements to yet another unimolecular rate process, cyclization of a thermodynamically unstable species 1 (R=Ph), photochemically generated *in situ* from 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran 2, into 2 (Scheme 1). First, we discuss the nature of the chemical coordinate on the basis of quantum-mechanical calculations of the gas-phase potential energy surface (PES), then present kinetic effects of pressure in nonviscous solvents and, finally, we describe pressure effects in viscous solvents.

Gas-phase calculations

To study the gas-phase reaction mechanism, AM1 and B3LYP/ $6-31G^{**}$ calculations were performed with Gaussian 98^{11} for somewhat simplified models with R being either CH₃ or C(CH₃)=CH₂, and the second of the fused rings of the naphthalene system removed. The results of calculations indicate that the reaction coordinate is initially represented by rotation around the single C–C bond of the exocyclic diene

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Scheme 1

system, τ_{CC} , followed by C–O bond formation along distance coordinate R_{CO} (Scheme 1). A two-dimensional projection of the AM1 PES on $\tau_{CC}-R_{CO}$ coordinate subspace is shown in Fig. 1 and relative B3LYP/6-31G** and B3LYP/6-31+G** energies for reactants, TSs, and products are listed in Table 1.

Experimental section

3,3-Diphenyl-3H-naphtho[2,1-b]pyran 2 was prepared from 2-naphthol and 1,1-diphenylprop-2-yn-1-ol as described in the literature.¹² The hexadienone **1** was photochemically generated in situ from 2 and its decay was followed spectrophotometrically. The experimental details were described elsewhere.¹³ To study the nonequilibrium effects of viscous solvents, we used 2,4-dicyclohexyl-2-methylpentane (DCMP), glycerol triacetate (GTA), and 2-methylpentane-2,4-diol (MPD) whose viscosities at various temperatures and pressures were reported previously.⁹ In order to measure the equilibrium pressure effects, similar measurements were also performed in nonviscous solvents, such as methylcyclohexane (c-HexMe), methyl acetate (AcOMe), and ethanol (EtOH). No dynamic solvent effects were observed in these solvents. At all conditions studied, the reaction obeyed the first-order rate law and the rate constants could be determined unequivocally.

Experimental results and discussion

Nonviscous solvents

Pressure dependences of the first-order rate constant k_{obs} in methylcyclohexane are illustrated in Fig. 2. Similar pressure dependences were also observed in methyl acetate and ethanol. The results were fitted to eqn. $(2)^{13}$ (k_P and $k_{0.1}$ refer to the rate constants at pressures *P* and 0.1 MPa, respectively) by adjusting parameters *a*, *b* and *c*. The activation volume at zero pressure, ΔV_0^{\neq} , was then estimated from eqn. (3), that can be obtained from eqn. (2) by differentiation with respect to pressure.



Fig. 1 A 2D projection of the AM1 PES for the model reaction (Scheme 1, the second ring removed, $R:C(CH_3)=CH_2$). Energy grid – 10 kJ mol⁻¹.

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$$\ln \frac{k_P}{k_{0.1}} = aP + b\ln(1 + cP) \tag{2}$$

$$\Delta V_{\rm o}^{\neq} = -(a+bc)RT \tag{3}$$

The values at 25 °C were -6.1 (c-HexMe), -6.3 (AcOMe) and -8.8 (EtOH) cm³ mol⁻¹. These results are in agreement with the mechanism of Scheme 1. The product-like activated complex has a smaller internal freedom of motion than the openchain reactant 1 and the volume of the reactant is expected to decrease during the activation.¹⁴ This decrease in the freedom of motion in the activation step is also reflected in relatively small preexponential factors which correspond to activation entropies of $-34 \sim -54$ J K⁻¹ mol⁻¹. The experimental activation parameters are listed in Table 2. The activation energies are in reasonable agreement with the calculated gas-phase values of Table 1. Rate constants at 25°C and 0.1 MPa (0.143 in c-HexMe, 0.100 in AcOMe, and 0.0828 in EtOH) clearly indicated the absence of a major polarity change during the activation step as usually observed for electrocyclic reactions. As can be seen from Table 2, the reaction barriers were only marginally affected by the external pressure.

Viscous solvents

The observed rate constants k_{obs} in DCMP and GTA are plotted against pressure in Figs. 3 and 4. The results in MPD were qualitatively the same.¹ For the sake of comparison, rate constants in less viscous media were also plotted in these Figures for 25 °C.

An increase in pressure resulted in similar magnitudes of acceleration of the reaction at lower pressures. The activation energies at 0.1 MPa (69.0 kJ mol⁻¹ for DCMP, 67.5 kJ mol⁻¹ for GTA, and 66.1 kJ mol⁻¹ for MPD) were also very close to the values in the corresponding nonviscous solvents (Table 2), clearly indicating the validity of TST even in the viscous solvents up to a few hundred MegaPascals (MPa). At higher pressures and lower temperatures, however, pressure-induced retardations were observed. Since these retardations were observed only in viscous media, it is reasonable to assume that TST became invalid for these systems because of high viscosities at high pressures.

Theoretical models

Two different models have been proposed to describe the dynamic effects of medium in solution reactions. The first model, proposed by Kramers¹⁵ and later modified by Grote and Hynes^{16,17} (KGH model), describes the progress of a reaction in terms of a single coordinate that represents a con-

Table 1 Relative $B3LYP/6-31G^{**}$ and $B3LPY/6-31+G^{**}$ (in brackets) energies (kJ mol⁻¹) calculated for model reaction systems

	R:CH ₃	R:C(CH ₃)=CH ₂		
Reactant, 1	0	0		
TS	57.8[58.3]	70.6		
Product, 2	-76.4[-71.4]	-51.0		



Fig. 2 Pressure dependence of the cyclization rate constant (k_{obs}/s^{-1}) of 1 in methylcyclohexane at various pressures.

certed Brownian motion of both the reaction system and the solvent. Fig. 5 shows an example of a 2D PES for a typical KGH-type system.

Due to a strong coupling between the chemical and the medium coordinate, the reaction cannot occur without simultaneous restructuring of the solvation shell. All reaction trajectories must therefore pass through the TS region.

The second model, proposed by Agmon and Hopfield^{18,19} (AH model) and further developed by Sumi and Marcus,^{20,21} Berezhkovskii *et al.*,^{22,24} and by Basilevsky *et al.*,^{25,26} assumes that the two coordinates are independent of each other. As a result, the reactant and product valleys are parallel to each other, as illustrated in Fig. 6, and the reaction can occur simultaneously at various configurations of the solvent. The overall reaction is thus represented in the AH model as an ensemble of simultaneous reactions taking place along the chemical coordinate at various configurations of the solvent. Therefore, reaction trajectories can deviate substantially from the TS region. As a result of the above differences, the two models make totally different predictions about the viscosity dependence of the activation energy. In the KGH model, the reactant particle is pushed back and forth by solvent molecules while it gradually climbs up the energy barrier. The viscosity changes the rate of diffusion of the system along the joint chemical-medium coordinate, but it does not affect the height of the energy barrier since all trajectories have to pass through the TS region. As a result, the KGH model predicts that, in the limit

Table 2 Preexponential factors (A/s^{-1}) and activation energies $(E_a/kJ \text{ mol}^{-1})$ for thermal ring closure of **1** in nonviscous solvents at various pressures (P/MPa)

	c-HexMe		AcOMe		EtOH		
<i>P/</i> MPa	$\frac{10^{-11}A}{s^{-1}}$	$E_{\rm a}/{ m kJ\ mol^{-1}}$	$\frac{10^{-11}A}{s^{-1}}$	$E_{\rm a}/{ m kJ\ mol^{-1}}$	$\frac{10^{-11}A}{s^{-1}}$	$E_{\rm a}/{ m kJ\ mol^{-1}}$	
0.1	1.2	68.1	0.97	68.5	0.28	65.9	
150	2.1	68.7	1.3	68.3	0.34	65.3	
300	2.4	68.5	1.4	67.9	0.40	64.8	
450	2.5	68.1	1.3	67.0	0.43	64.2	
600	3.0	68.2	1.3	66.5	0.44	63.6	



Fig. 3 Pressure dependence of the cyclization rate constant (k_{obs}/s^{-1}) of 1 in DCMP at various temperatures.

of high viscosity, the observed rate constant is represented by a product of the TST rate constant k_{TST} for the given physical conditions by a transmission coefficient $f(\eta)$ that decreases as $\eta^{-\beta}$ (0 < β < 1) in the high viscosity limit:²⁷

$$k_{\rm KGH} = k_{\rm TST} f(\eta) \tag{4}$$

Since the value of $f(\eta)$ is solely determined by η , the temperature dependence of k_{KGH} must be identical with that of k_{TST} if viscosity is kept constant. An isoviscous Arrhenius plot of k_{KGH} should therefore give an isoviscous activation energy $E_{a,\text{KGH},\eta}$ equal to $E_{a,\text{TST},\eta}$.



Fig. 4 Pressure dependence of the cyclization rate constant (k_{obs}/s^{-1}) of 1 in GTA at various temperatures.



Fig. 5 A 2D PES for a KGH-type model.

In the AH model, although the reaction can occur at a variety of different solvent configurations, usually only one configuration gives the dominant contribution to the overall rate constant. A balance between the rate of the diffusion-type solvent reorganization along the medium coordinate and the rate of barrier crossing along the chemical coordinate determines this configuration. The situation is schematically illustrated in Fig. 7.

The reaction starts from the lower left corner and the reactant moves back and forth along the medium-coordinate valley up to point 1* which gives the dominant contribution to the overall rate constant. We do not have direct information on the structure of the reactant at point 1*. However, since it is in a solvation shell which stabilizes the activated complex, it seems reasonable to speculate that 1* has a conformation with a considerably smaller dihedral angle (Fig. 1). If 1* acquires enough energy for surmounting the barrier, one fast movement along the chemical coordinate brings it to the product valley as shown by a long curly arrow. This movement is assumed to take place in a frozen solvent cage. In other words, the movement along the reaction coordinate is considered to be much faster than thermal fluctuations of solvent molecules and the solvent viscosity does not influence this transformation.

At low viscosities, diffusion along the medium coordinate is relatively fast so that point 1* opposes the true saddle point of the PES. Under these conditions, the major contribution to the overall rate constant comes from the TS flux and the reaction







Fig. 7 A reaction trajectory in the AH model.

rate can be described by the TST. As the viscosity increases, the rate of diffusion decreases which reduces the TS flux. However, in contrast with the case of the KGH model where the TS flux is the sole contributor to the overall rate constant, in the AH model the overall process is represented by an array of parallel fluxes crossing the ridge at different points. Therefore, as the TS flux "dries out", the location of point 1* where the dominant flux originates shifts down to the starting point 1 along the bottom of the reactant valley. This alleviates the negative impact of viscosity on the overall rate and thus the viscosity dependence of the AH rate constant k_{AH} is expected to be weaker than that of k_{KGH} .

The isoviscous temperature dependence of k_{AH} should also be different from that of k_{KGH} . Under isoviscous conditions the rate of diffusion along the reactant valley would demonstrate a much weaker temperature dependence than the rate of the barrier crossing. Therefore, an increase in temperature will shift point 1* further towards the starting point 1. As a result, the direct positive effect of the temperature on k_{AH} will be partly compensated by the negative effect of the increase in the barrier height and the overall effect of temperature on k_{AH} will be weaker than that on k_{TST} , *i.e.* the isoviscous activation energy for $E_{a,AH,\eta}$ is expected to be lower than $E_{a,TST,\eta}$. Thus, comparing the observed isoviscous activation energies to the $E_{a,TST,\eta}$ values should allow one to discriminate between KGH- and AH-type behavior.

Isoviscous activation energies

If viscosity could be manipulated without affecting other physico-chemical properties of the system, the isoviscous $E_{a,TST,\eta}$ would be the same as the isobaric $E_{a,TST}$. However, in reality, viscosity change is inevitably accompanied by changes in other physical and chemical properties, *i.e.*, if temperature and viscosity are chosen as independent parameters, pressure becomes a function of these parameters: $P = P(T, \eta)$. If activation energies are determined from the Arrhenius plots, an isobaric E_a and an isoviscous $E_{a,\eta}$ can be defined as derivatives

$$E_{\rm a} = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_P$$
 and $E_{{\rm a},\eta} = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_\eta$.

Since
$$P = P(T, \eta)$$
,
 $E_{a,\eta} = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_{\eta} + RT^2 \left(\frac{\partial \ln k}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\eta}$.

The first term in the right-hand side of this equation is E_a , the isothermal pressure derivative of k is related to ΔV^{\neq} by eqn. (1), and

$$\left(\frac{\partial P}{\partial T}\right)_{\eta} = -\left(\frac{\partial \eta}{\partial T}\right)_{P} / \left(\frac{\partial \eta}{\partial T}\right)_{T}.$$

Therefore,

$$E_{\mathrm{a},\eta} = E_{\mathrm{a}} + \Delta V^{\neq} T \left(\frac{\partial \eta}{\partial T}\right)_{P} / \left(\frac{\partial \eta}{\partial P}\right)_{T}.$$
 (5)

Thus, both $E_{a,obs,\eta}$ and $E_{a,TST,\eta}$ values contain effects of the activation volume.

Viscosity increases with pressure and decreases with temperature, therefore the ratio of derivatives in the second term in the right-hand side of eqn. (5) is negative. Since at low viscosities the ΔV^{\neq} values are negative for the present reaction, the isoviscous activation energies are expected to be larger than the isobaric ones in the TST-valid region. At high viscosities, however, the apparent values of ΔV^{\neq} become positive (k_{obs}) decreases with pressure) and the isoviscous activation energies are expected to be smaller than the isobaric ones. Figs. 8 and 9 illustrate the viscosity dependence of k_{obs} at various temperatures in DCMP and GTA, respectively. From these plots, rate constants at a constant viscosity were estimated for different temperatures by fitting k_{obs} to cubic equations of η and isoviscous Arrhenius plots were constructed. The activation energies thus obtained are listed in Table 3 for all the three viscous solvents studied.

For comparison, we need the corresponding values of $E_{a,TST,\eta}$ which can be obtained from isoviscous Arrhenius plots for k_{TST} . The necessary values of k_{TST} are not immediately available for the entire pressure range, as the TST fails at higher viscosities. However, as mentioned above, even in the viscous solvents, the TST is valid at low pressures. The rate constants obtained for this TST-valid pressure region were fitted to eqn. (2) and the resultant equation was then used to estimate k_{TST} and the activation parameters for the entire pressure range. The activation energies $E_{a,TST,\eta}$ thus obtained are



Fig. 8 Viscosity dependence of the cyclization rate constant (k_{obs}/s^{-1}) of 1 in DCMP at various temperatures.



Fig. 9 Viscosity dependence of the cyclization rate constant (k_{obs}/s^{-1}) of 1 in GTA at various temperatures.

listed in Table 4. As can be seen from the data of Tables 3 and 4, $E_{a,obs,\eta}$ are smaller than $E_{a,TST,\eta}$ at viscosities where TST is expected to fail, which is consistent with the prediction of the AH model. Since $E_{a,KGH,\eta}$ is expected to be equal to $E_{a,TST,\eta}$ at any viscosities, all of these observations strongly suggest that the AH model describes the present system better than the KGH model.

As expected, the $E_{a,obs,\eta}$ values show a clear tendency to decrease with increasing η in DCMP and GTA, whereas the $E_{a,TST,\eta}$ values increase with increasing viscosity.

Conclusions

Slow thermal rate process study at highly viscous conditions again unequivocally demonstrated that the medium and the chemical coordinate have to be treated separately. In order to obtain the information on the extent of coupling between these coordinates, further analyses based on the theoretical models are in progress and the results will be reported shortly.

Table 3 Isoviscous activation energies obtained from k_{obs} ($E_{a,obs,\eta}/kJ$ mol⁻¹) for the cyclization of **1** in viscous solvents at various viscosities (η/Pa s)

η	10^{-1}	10^{0}	10^{1}	10 ²	10 ³	10^{4}	10 ⁵	10 ⁶
DCMP			74	72	69	65	58	50
GTA		77	76	71	64	56		
MPD	74	76	76	76				

Table 4 Isoviscous activation energies obtained from k_{TST} ($E_{a,\text{TST},\eta}/kJ$ mol⁻¹) for the cyclization of **1** in viscous solvents at various viscosities ($\eta/\text{Pa s}$)

η	10^{-1}	10 ⁰	10 ¹	10 ²	10 ³	10 ⁴	10 ⁵	10 ⁶
DCMP	73	74	74	74	75	75	75	76
GTA	77	78	81	83	85	87	90	92
MPD	74	77	79	81	83	86	88	91

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