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Citation: *The Journal of Chemical Physics* **90**, 5386 (1989); doi: 10.1063/1.456445

View online: <http://dx.doi.org/10.1063/1.456445>

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# Dynamical solvent effects on conformational isomerization of cyclohexane and 1,1-difluorocyclohexane

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(Received 19 December 1988; accepted 2 February 1989)

The effect of pressure on the conformational isomerization of cyclohexane in *n*-pentane- $d_{12}$  solvent has been investigated by using the high-resolution, high-pressure nuclear magnetic resonance (NMR) technique. The isomerization rate of cyclohexane increases with increasing pressure at 218 K. The experimental data are interpreted in terms of stochastic models for isomerization reactions, and the results show that cyclohexane isomerization in *n*-pentane- $d_{12}$  exhibits behavior typical for low-friction, energy controlled regime. The effect of temperature and pressure on the conformational isomerization of 1,1-difluorocyclohexane in solution has been investigated with the use of  $^{19}\text{F}$  Fourier transform (FT) NMR spectroscopy. The solvents used in this study are *n*-pentane, acetone- $d_6$ , and methylcyclohexane. Similarly, as in the case of cyclohexane, the ring inversion in 1,1-difluorocyclohexane is accelerated when pressure is increased, and this pressure dependence is nonlinear. The interpretation of the experimental data for 1,1-difluorocyclohexane depends critically on the estimate of  $\Delta V^\ddagger_{\text{TST}}$  which value is not known at the present time. Therefore, it is impossible to determine whether isomerization of 1,1-difluorocyclohexane exhibits the Kramers turnover.

## I. INTRODUCTION

In view of its fundamental importance for understanding of chemical reactions in solution, it is not surprising to find that the problem of barrier crossing for chemical reactions in solution has recently been investigated in many theoretical and experimental studies.<sup>1-20</sup> One of the key issues is the observation of so called Kramers' turnover for isomerization reactions in liquid solutions.<sup>3,11</sup>

At very low friction the reaction rate will increase with increasing collision frequency (friction) and this low-friction regime is sometimes referred to as energy controlled. In contrast at high friction the rate of barrier crossing begins to decrease with the increasing collision frequency (friction). The system is in the so called high friction or diffusive regime. There is a nonmonotonic "turnover" between the low- and high-friction regimes.

In our earlier study<sup>11</sup> of conformational isomerization of cyclohexane in several solvents we followed the pressure and temperature dependence of cyclohexane isomerization in three solvents of different shear viscosity: acetone- $d_6$ , carbon disulfide, and methylcyclohexane- $d_{14}$ . We observed that the cyclohexane ring inversion is accelerated when pressure is increased, and this pressure dependence of the rate constants was nonlinear.

The experimental data were interpreted in terms of stochastic models of isomerization reactions with the conclusion that Kramers' turnover was observed in the system studied. It was not surprising that these findings were not readily accepted because in the case of photoisomerization of stilbene and diphenylbutadiene the Kramers' turnover was not observed even in low viscosity solvents.<sup>12,13</sup> In addition, an nuclear magnetic resonance (NMR) study examining the isomerization of cyclohexane in the gas phase as a function of filler gas ( $\text{N}_2$  or Ar) pressure did not reveal the rate dependence typical for low-friction energy controlled re-

gime.<sup>14</sup> These observations<sup>15,17</sup> suggested that in the condensed medium, the low-friction regime is essentially a problem of internal energy redistribution rather than collisional interaction between the solute and solvent molecules.

A theoretical interpretation of cyclohexane isomerization study has very recently been provided by Chandler *et al.*<sup>18</sup> who performed a multidimensional Bhatnagar, Gross, and Krook (BGK) stochastic molecular dynamics study of cyclohexane isomerization. The most important results of this study was the conclusion that the Rice, Ramsperger, Kassel, and Marcus (RRKM) picture of unimolecular kinetics does not describe the cyclohexane isomerization in liquid solutions. They showed that the energy exchange between the molecule and the stochastic bath occurs with similar ease as the energy rearrangement among intramolecular modes.

Recently, the polarity effects have been brought in to attention by van der Zwan and Hynes.<sup>19</sup> They found that when large dipolar change or charge redistribution is involved in the reaction process the polarity effects can play a significant role in departing from the Kramers' prediction. Polarity effects have been experimentally observed in the recent study of the photoisomerization in *p*-dimethylaminobenzonitrile<sup>20</sup> and in 4,4'-dimethoxystilbene.<sup>32</sup>

The initial skepticism about our result that the cyclohexane isomerization shows inertial behavior in acetone- $d_6$  solvent provided the main motivation for the present set of experiments. Therefore, we selected another low viscosity solvent, *n*-pentane- $d_{12}$ , and investigated the pressure effects on cyclohexane isomerization in this solvent by using high-resolution high-pressure NMR techniques. In addition, we investigated the pressure dependence of the isomerization of 1,1-difluorocyclohexane (DFCH) in the solvents of *n*-pentane, methylcyclohexane, and acetone- $d_6$ . The purpose of choosing the dipolar solvent acetone is to determine if we can observe any polarity effects in this system. The experimental

results of cyclohexane isomerization in *n*-pentane-*d*<sub>12</sub> confirm our earlier findings that cyclohexane isomerization in low viscosity liquid solvents exhibits behavior typical for the low-friction regime. For 1,1-DFCH, the interpretation of the experimental results depends strongly on the estimation of the  $\Delta V_{\text{TST}}^\ddagger$  value. Upon changing the  $\Delta V_{\text{TST}}^\ddagger$  value from  $-1.0$  to  $-2.0$  cm<sup>3</sup>/mol the viscosity dependence of the normalized transmission coefficient changes from a non-monotonic bell-shaped characteristic for a Kramers' turn-over to a monotonic decrease typical for a diffusion controlled regime.

## II. EXPERIMENTAL

"Photrex" grade cyclohexane was obtained from J. T. Baker Chemical Co., and the solvents were obtained from other commercial sources (*n*-pentane-*d*<sub>12</sub> from Cambridge Isotope Inc.; methylcyclohexane from Eastman Kodak and acetone-*d*<sub>6</sub> from Aldrich). 1,1-DFCH was synthesized according to the literature.<sup>21</sup> It was purified by distillation (boiling point 100–102 °C). Cyclohexane was used as received. All solvents were dried over molecular sieves (Linda 4A), and all solutions used in this study were made at a molar concentration of 5%. Each solution was degassed and then transferred in to an high-pressure NMR cell under an inert atmosphere. The isomerization rate constants of cyclohexane were obtained by analyzing the line shapes of its high-resolution proton NMR spectra and the high-resolution <sup>19</sup>F NMR spectra were used for DFCH. The description of the high-resolution high-pressure NMR probe and the discussion of the NMR line shape analysis were given in detail in our earlier studies.<sup>22,23</sup> The probe frequency was 180 MHz for the proton resonance and 169.2 MHz for fluorine using the spectrometer system described earlier.<sup>22</sup> The variable temperature NMR spectra at ambient pressure were collected on a JEOL FX60 spectrometer for DFCH in acetone-*d*<sub>6</sub> and methylcyclohexane solvents, and on a Nicolet 360 NMR spectrometer for DFCH in *n*-pentane.

The input spectral parameters used in the analysis of NMR line shapes were the chemical shift and the natural linewidth in the absence of exchange. The chemical shift in the absence of exchange was determined at low temperatures where no significant isomerization exchange occurs and the natural linewidth was set at 20 Hz. The chemical shift of DFCH did not exhibit a temperature dependence and the rate constants at ambient pressure were obtained by using rate constant and the peak area as two variables in the line shape analysis. The chemical shift though shows a moderate decrease with increasing pressure at a rate of  $\sim 1\%/1000$  bar in the solvents of acetone-*d*<sub>6</sub> and *n*-pentane. This pressure dependence of the chemical shift has been accounted for in the line shape analysis. For DFCH in methylcyclohexane solvent, the pressure dependence of the chemical shift was found to be negligible. Also, within the experimental error the chemical shift for cyclohexane in *n*-pentane-*d*<sub>12</sub> exhibited no pressure dependence.

The temperature control was achieved with a Brinkmann thermostat circulator model NB and the temperature was monitored by a copper–constantan thermocouple inside

the high pressure vessel near the NMR sample cell. The temperature was held constant to within  $\pm 0.2$  °C.

The variable pressure shear viscosity of *n*-pentane at 218 K was measured using a rolling-ball viscometer described earlier,<sup>24</sup> and the viscosity of perdeuterated *n*-pentane was calculated by applying the usual correction. Other viscosity data were either quoted from literature or interpolated from our previous data.<sup>33</sup>

## III. RESULTS AND DISCUSSION

### A. Variable temperature measurements at atmospheric pressure

The temperature dependence of the rate constant for the chair to chair isomerization in DFCH is shown in Fig. 1. The activation enthalpies obtained from these Arrhenius plots are  $9.0 \pm 0.2$  kcal/mol in methylcyclohexane,  $9.1 \pm 0.5$  kcal/mol in acetone-*d*<sub>6</sub>, and  $9.1 \pm 0.4$  kcal/mol in *n*-pentane. Within the experimental error, the barrier height for the isomerization in DFCH is not different from one solvent to the other. In view of the *p*-dimethylaminobenzonitrile results reported by Eisinger *et al.*,<sup>20</sup> this observation of no change in the barrier height for changing solvent from non-polar to polar can be related to the fact that DFCH molecule possesses a dipole moment but its change during the isomerization process is very small.

### B. Variable pressure measurements

The analysis of the experimental data followed the same approach as used in our earlier study.<sup>11</sup> In the following, we mention only the equations necessary for understanding the data treatment.

The stochastic models<sup>3,4</sup> introduce a transmission coefficient to account for the collision effect as

$$k_{\text{obs}} = \kappa \cdot k_{\text{TST}}, \quad (1)$$

where  $k_{\text{obs}}$  is the observed isomerization rate and  $k_{\text{TST}}$  is that predicted by the classical transition state theory given by

$$k_{\text{TST}} = \frac{k_b T}{h} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right), \quad (2)$$

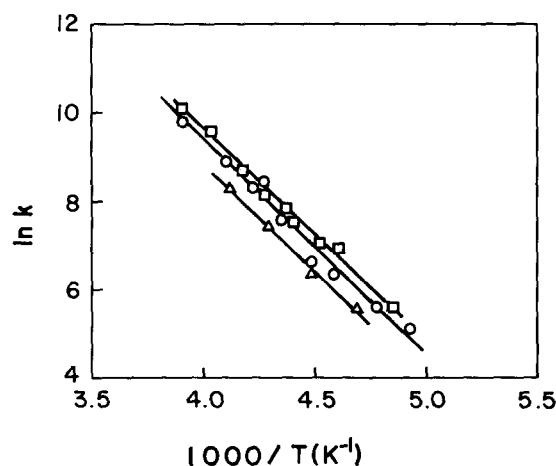


FIG. 1. Temperature dependence of the isomerization rate of 1,1-DFCH in the solvents of acetone-*d*<sub>6</sub> (○), *n*-pentane (△), and methylcyclohexane-*d*<sub>14</sub> (□). *P* = 1 bar.

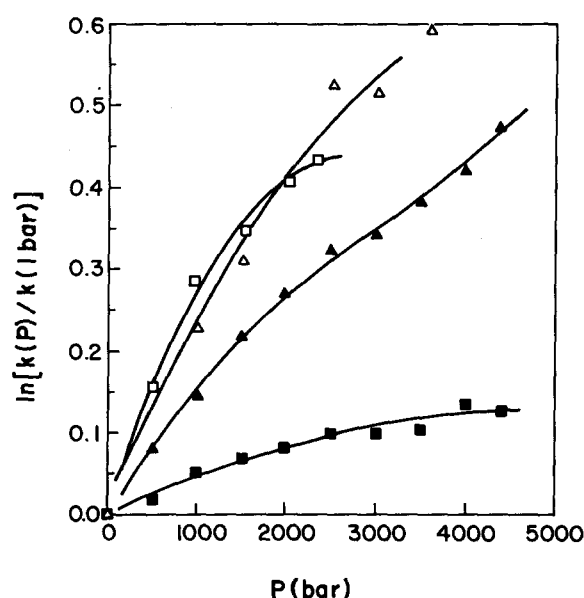


FIG. 2. Pressure dependence of the cyclohexane isomerization rate in the solvents of *n*-pentane-*d*<sub>12</sub> (Δ), acetone-*d*<sub>6</sub> (□), carbon disulfide (▲), and methylcyclohexane (■). *T* = 218 K.

with the symbols having their usual meaning. The transmission coefficient  $\kappa$  is a strong nonmonotonic function of the coupling strength between the reaction coordinate and the surrounding medium. For the cyclohexane isomerization the coupling strength is given by the collision frequency  $\alpha$  which can be related through simple hydrodynamic arguments to the solvent shear viscosity  $\eta$ .<sup>25-27</sup> In the low-friction regime,  $\kappa$  is proportional to  $\alpha$  or  $\eta$ . At higher collision frequency in the high-friction or diffusive regime the rate is inversely proportional to  $\alpha$  or  $\eta$ .

Due to the coupling between the reaction coordinate and surrounding medium the pressure dependence of the isomerization rate no longer follows the Arrhenius relationship. The experimental data is fit to a quadratic equation of the form

$$\ln k(P) = A_0 + A_1P + A_2P^2, \quad (3)$$

where  $P$  is the solvent pressure and  $A$ 's are adjustable constants. In agreement with our earlier observation of the pressure effects on the cyclohexane isomerization in acetone-*d*<sub>6</sub> solvent we observed an acceleration of the isomerization rate in pentane-*d*<sub>12</sub> solvent as pressure is increased. The pressure dependence of the rate constant for cyclohexane isomerization in pentane-*d*<sub>12</sub> is shown in Fig. 2. For comparison, we also give our previous results in acetone-*d*<sub>6</sub>, CS<sub>2</sub>, and methylcyclohexane-*d*<sub>14</sub>.<sup>11</sup> The similarity between the two isotherms in *n*-pentane-*d*<sub>12</sub> and acetone-*d*<sub>6</sub> suggests that the isomerization of cyclohexane in *n*-pentane-*d*<sub>12</sub> falls in the low-friction energy controlled regime. The pressure dependence of the isomerization rate of DFCH in *n*-pentane, acetone-*d*<sub>6</sub>, and methylcyclohexane is shown in Fig. 3. In both cyclohexane and its difluoro analog, the pressure dependence of the isomerization rate deviates the most from the linear relationship in methylcyclohexane, and the pressure dependences in *n*-pentane and acetone-*d*<sub>6</sub> are similar to each other. The experi-

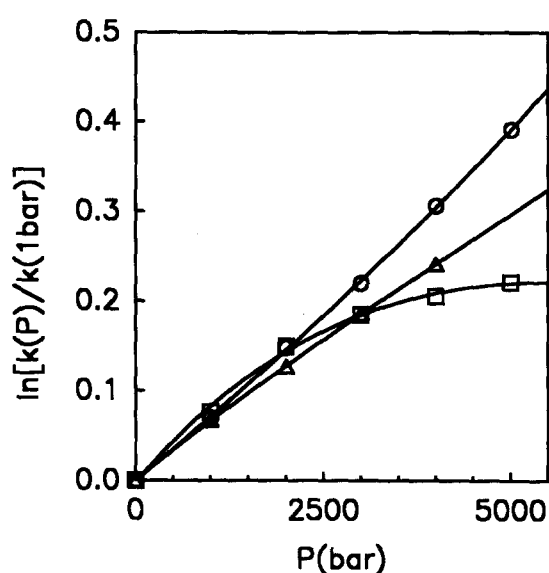


FIG. 3. Pressure dependence of the isomerization rate of 1,1-DFCH in the solvents of acetone-*d*<sub>6</sub> (Δ, 237 K), *n*-pentane (○, 237 K), and methylcyclohexane (□, 253 K).

mental data can be well fitted by Eq. (3) and the fitting parameters are listed in Table I.

As discussed in our previous paper<sup>11</sup> the observed activation volume is the sum of two contributions:

$$\Delta V_{\text{OBS}}^{\ddagger} = \Delta V_{\text{TST}}^{\ddagger} + \Delta V_{\text{COLL}}^{\ddagger}, \quad (4)$$

where

$$\Delta V_{\text{TST}}^{\ddagger} = -RT \left( \frac{\partial \ln k_{\text{TST}}}{\partial P} \right),$$

$$\Delta V_{\text{COLL}}^{\ddagger} = -RT \left( \frac{\partial \ln \kappa}{\partial P} \right).$$

The experimental determination of  $\Delta V_{\text{TST}}^{\ddagger}$  is difficult. Theoretically, the  $\Delta V_{\text{TST}}^{\ddagger}$  is considered to be the sum of two contributions<sup>28</sup>: (i) intrinsic part due to geometric changes in the isomerization process; and (ii) a solvation term due to

TABLE I. Parameters for the cubic fit of  $\ln k$  vs pressure using Eq. (3).

Solvent	<i>T</i> (K)	<i>P</i> <sub>max</sub> (bar)	<i>A</i> <sub>0</sub>	<i>A</i> <sub>1</sub> (× 10 <sup>4</sup> ) (bar <sup>-1</sup> )	<i>A</i> <sub>2</sub> (× 10 <sup>8</sup> ) (bar <sup>-2</sup> )
Cyclohexane					
<i>n</i> -Pentane- <i>d</i> <sub>12</sub>	218	3000	4.22	2.493	-2.758
1,1-DFCH					
<i>n</i> -Pentane	225	3250	6.76	1.039	-1.006
	237	5000	7.81	0.686	0.193
	253	5000	9.44	0.635	-0.374
Acetone- <i>d</i> <sub>6</sub>	218	2350	5.87	0.619	-1.008
	225	3250	6.74	0.034	0.331
	237	5000	7.87	0.670	-0.173
C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	253	5000	9.44	0.582	-0.064
	237	5000	8.14	0.347	-0.239
	253	5000	9.39	0.895	-0.915

TABLE II. Solvent shear viscosity, rate constant, and normalized transmission coefficient for 1,1-DFCH and cyclohexane isomerization, given as function of pressure and temperature.

Solvent	$T$ (K)	$P$ (bar)	$\eta$ (cP)	$k$ (s <sup>-1</sup> )	$\kappa(\eta)/\kappa(3\text{ cP})^a$
Cyclohexane					
<i>n</i> -Pentane- <i>d</i> <sub>12</sub>	218	1	0.69	67.1	0.77
		500	1.04	78.7	0.87
		1000	1.42	84.5	0.89
		1500	1.98	91.5	0.93
		2000	2.16	100.8	0.98
		3000	4.11	112.3	1.00
1,1-DFCH					
Acetone- <i>d</i> <sub>6</sub>	218	1	0.88	354.3	1.04
		500	1.16	368.5	1.05
		1000	1.48	379.3	1.05
		1500	1.80	372.2	1.01
		2000	2.23	392.3	1.03
		2350	2.54	388.5	1.00
	225	1	0.76	843.1	1.02
		500	1.04	853.7	1.01
		1000	1.34	881.7	1.01
		1500	1.65	886.6	0.99
		2000	1.97	936.3	1.02
		2500	2.35	911.4	0.97
	237	3000	2.94	967.2	1.00
		3250	3.12	979.0	1.00
		1	0.67	2 631	0.96
		1000	1.11	2 813	0.98
		2000	1.59	2 986	0.99
		3000	2.12	3 169	1.00
	253	4000	2.96	3 348	1.00
		1	0.51	12 634	0.97
1000		0.85	13 100	0.96	
2000		1.25	14 296	1.00	
3000		1.78	14 809	0.98	
4000		2.43	15 691	0.99	
$\text{C}_6\text{H}_{11}\text{CH}_3$	237	5000	3.67	16 365	0.99
		1	2.10	3 408	1.01
		715	4.35	3 606	1.02
		1790	12.8	3 614	0.97
		2860	36.6	3 695	0.94
	253	3570	62.2	3 813	0.94
		1	1.42	12 054	0.97
		1000	3.98	13 010	1.00
		2000	9.73	14 000	1.02
		3000	18.9	14 500	1.01
Pentane	225	4000	38.5	14 802	0.98
		5000	71.4	15 042	0.95
		1	0.57	870.1	0.93
		1000	1.03	929.8	0.94
		2000	1.86	1 031.4	0.99
	237	3000	3.35	1 083.4	0.99
		4000	5.01	1 108.6	0.96
		1	0.52	2 473.8	0.93
		1000	0.93	2 651.8	0.95
		2000	1.66	2 867.9	0.97
253	3000	2.71	3 082.6	0.99	
	4000	3.99	3 359.4	1.03	
	5000	5.65	3 657.8	1.06	
	1	0.47	12 626	1.00	
	1000	0.82	13 377	1.01	
	2000	1.37	13 994	1.01	
	3000	2.12	14 829	1.02	
	4000	3.05	15 246	0.99	
	5000	4.09	15 729	0.98	

<sup>a</sup> For cyclohexane,  $\kappa(\eta)/\kappa(3 \text{ cP})$  was calculated by using  $\Delta V_{\text{TST}}^\ddagger = -1.5 \text{ cm}^3/\text{mol}$  and for 1,1-DFCH,  $\Delta V_{\text{TST}}^\ddagger = -1.0 \text{ cm}^3/\text{mol}$ .

the difference in the solute-solvent interactions between the ground state and the transition state. It is generally assumed that this solvation term is negligibly small for nonpolar processes.<sup>29</sup> In the chair to chair inversion of DFCH, the distortion in the FCF angle is small and change in the dipole moment is small. It is unlikely that the solvent shell structure is greatly altered during the isomerization process. This argument is supported by the observation that the barrier height is solvent independent in DFCH. Therefore,  $\Delta V_{\text{TST}}^\ddagger$  is mainly due to the geometrical difference between the transition state and the ground state.  $\Delta V_{\text{TST}}^\ddagger$  has been estimated to be  $-1.0 \text{ cm}^3/\text{mol}$  by LeNoble<sup>30</sup> for cyclohexane ring inversion. In our previous study of cyclohexane isomerization, a lower limit was estimated for cyclohexane to be  $-2.5 \text{ cm}^3/\text{mol}$ , and  $\Delta V_{\text{TST}}^\ddagger = -1.5 \text{ cm}^3/\text{mol}$  was adapted in the calculations. To compare the experimental data of cyclohexane in *n*-pentane-*d*<sub>12</sub> to our previous results, we used  $\Delta V_{\text{TST}}^\ddagger = -1.5 \text{ cm}^3/\text{mol}$  in the calculation of  $\kappa(\eta)/\kappa(\eta_0)$  for cyclohexane. For DFCH isomerization, we assumed that  $\Delta V_{\text{TST}}^\ddagger$  is similar to that for the cyclohexane isomerization. In our calculation, we took  $\Delta V_{\text{TST}}^\ddagger = -1.0 \text{ cm}^3/\text{mol}$ . Choosing an alternate value for  $\Delta V_{\text{TST}}^\ddagger$  would merely shift  $\Delta V_{\text{coll}}^\ddagger$  up or down. However, its effect on the normalized transmission coefficient is much greater, and we will discuss this further.

The relationship between the transmission coefficient  $\kappa$  and the solvent viscosity provides a practical way to discuss the isomerization dynamics. Since  $\kappa$  and  $k_{\text{TST}}$  cannot be determined independently, we must evaluate the ratio of  $\kappa(\eta)/\kappa(\eta_0)$ . The normalized transmission coefficient can be obtained from

$$\frac{\kappa(\eta)}{\kappa(\eta_0)} = \frac{k(\eta)}{k(\eta_0)} \exp\left(\frac{(P - P_0)\Delta V_{\text{TST}}^\ddagger}{RT}\right), \quad (5)$$

where  $\kappa(\eta_0)$  and  $k(\eta_0)$  are the transmission coefficient and the observed rate constant at a chosen reference point.  $P_0$  is

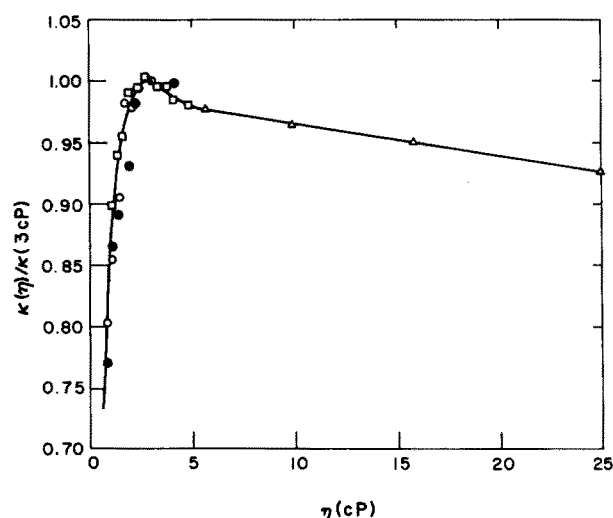


FIG. 4. The transmission coefficient normalized to  $\eta_0 = 3 \text{ cP}$  as a function of the solvent viscosity for cyclohexane in the *n*-pentane-*d*<sub>12</sub> solvent (●), compared to our previous results. Open symbols represent previous results (Fig. 9 in Ref. 11).  $T = 218 \text{ K}$  and  $\Delta V_{\text{TST}}^\ddagger = -1.5 \text{ cm}^3/\text{mol}$ .

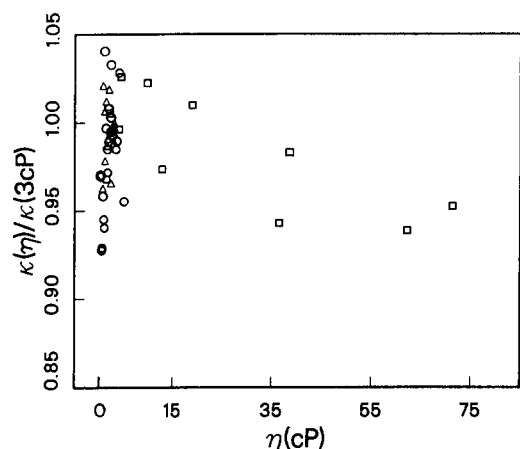


FIG. 5. Relationship between the transmission coefficient normalized to  $\eta_0 = 3$  cP and the solvent viscosity for 1,1-DFCH isomerization.  $\Delta V_{\text{TST}}^\ddagger = -1.0$  cm<sup>3</sup>/mol. Solvents: acetone-*d*<sub>6</sub> ( $\Delta$ ,  $T = 218, 225, 237, 253$  K); *n*-pentane ( $\circ$ ,  $T = 225, 237, 253$  K); methylcyclohexane ( $\square$ ,  $T = 237, 235$  K).

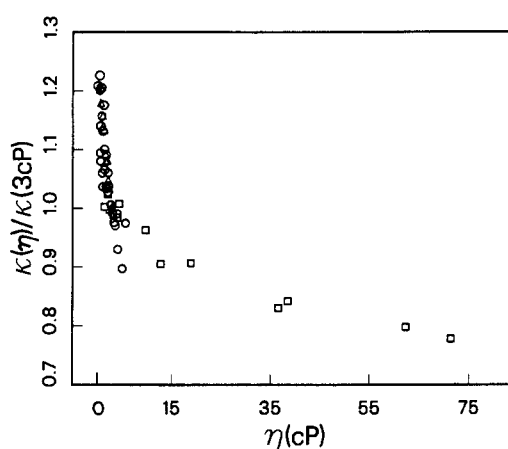


FIG. 6. Transmission coefficient normalized to  $\eta_0 = 3$  cP as a function of the solvent viscosity for 1,1-DFCH isomerization calculated by using  $\Delta V_{\text{TST}}^\ddagger = -2.0$  cm<sup>3</sup>/mol in acetone-*d*<sub>6</sub> ( $\Delta$ ,  $T = 218, 225, 237, 253$  K); *n*-pentane ( $\circ$ ,  $T = 225, 237, 253$  K), and methylcyclohexane ( $\square$ ,  $T = 237, 253$  K).

pressure at the reference point. The experimental results of  $\kappa(\eta)/\kappa(3 \text{ cP})$ , along with the rate constant and the solvent viscosity are given for both cyclohexane and DFCH systems in Table II.

For the cyclohexane isomerization in *n*-pentane-*d*<sub>12</sub>,  $\kappa(\eta)/\kappa(3 \text{ cP})$  vs  $\eta$  plot follows the same trend as we found in acetone-*d*<sub>6</sub> (Fig. 4). In view of the theoretical results by Chandler *et al.*,<sup>18</sup> we may conclude that cyclohexane isomerization in the low viscosity solvent, *n*-pentane-*d*<sub>12</sub>, exhibits dynamic behavior typical for the low-friction energy controlled regime.

The plot of  $\kappa(\eta)/\kappa(3 \text{ cP})$  for the DFCH chair to chair isomerization is shown in Fig. 5. Comparing to our previous results for the cyclohexane experiment,<sup>11</sup> the data in Fig. 5 appears to have larger experimental error. This is partially due to the incorporation of different isotherms. In spite of the relatively large experimental error, Fig. 5 still shows a characteristic correlation between the normalized transmission coefficient and the solvent viscosity. The results in Fig. 5 indicate that the viscosity dependence of the transmission coefficient follows the prediction of the stochastic models and shows Kramers' turnover.<sup>3</sup>

Due to the exponential term associated with the activation volume in Eq. (5), the calculated values of the transmission coefficient are very sensitive to  $\Delta V_{\text{TST}}^\ddagger$  and choosing a different value for  $\Delta V_{\text{TST}}^\ddagger$  leads to a very different result in the relationship between the normalized transmission coefficient and the solvent viscosity. Figure 6 shows the normalized transmission coefficients in DFCH as a function of the solvent viscosity calculated by using  $\Delta V_{\text{TST}}^\ddagger = -2.0$  cm<sup>3</sup>/mol. The viscosity dependence of  $\kappa(\eta)/\kappa(3 \text{ cP})$  shown in Fig. 6 exhibits a typical diffusion controlled behavior. It is unlikely that the  $\Delta V_{\text{TST}}^\ddagger$  for DFCH isomerization is greatly different from that of cyclohexane which is estimated to be  $-1.0$  cm<sup>3</sup>/mol. However, we can not rule out the possibility of the existence of a large negative  $\Delta V_{\text{TST}}^\ddagger$ , and therefore we can not rule out the possibility that the chair to chair isomer-

ization in DFCH falls into the diffusion controlled regime.<sup>31</sup> The conclusion reached in our earlier communication<sup>31</sup> that DFCH isomerization exhibits diffusive behavior may be correct but the arguments used in the interpretation of the experimental data lacked rigorous physical basis.

## ACKNOWLEDGMENT

This research was partially supported by the National Science Foundation under Grant No. NSF CHE 85-09870.

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