

ULTRASONIC DISPERSION STUDIES IN CYCLOHEPTANONE

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ABSTRACT

The ultrasonic dispersion in cycloheptanone has been studied from the ultrasonic velocity measurements over a frequency range 1 to 8 MHz and over a temperature range 303.15 K to 343.15 K. The frequency dependence of velocity observed is that of a single relaxation process. From the experimental data the relaxation parameters are evaluated. These values are used to evaluate the energy parameters associated with the molecular phenomena.

INTRODUCTION

THE ultrasonic relaxation phenomena in cyclic compounds (such as substituted cyclohexanes, etc.) have been investigated earlier¹⁻⁶. The molecular mechanism of the relaxation process considered was the perturbation of the equilibrium proportion of axial and equatorial isomers by the ultrasonic wave.

Physico-chemical evidence indicates that the skeletal structure of substituted cyclic compounds takes mainly a chair configuration, with the substituent atom in the equatorial position. This isomer is believed to be in equilibrium with another having a chair configuration and an axial substituent, the two isomers being rapidly interconvertible by a process often called ring inversion, in which no bonds are broken. The energy differences between the isomers can be evaluated from the measured variation with temperature of the magnitude of velocity dispersion. The barrier hindering rotation can be found from the associated variation of the relaxation frequency with temperature.

In the present work the dispersion and relaxation frequencies for cycloheptanone at different temperatures were calculated from ultrasonic velocity measurements. These values were used in the evaluation of energy parameters associated with molecular phenomena.

EXPERIMENTAL

Ultrasonic velocity was measured using a multi-frequency ultrasonic interferometer at frequencies 1, 2, 4, 5, 6 and 8 MHz. To obtain the measurements at different temperatures, water from a thermostatic water bath whose temperature can be maintained with an accuracy of $\pm 0.01^\circ\text{C}$ is allowed to pass through the circulating tubes fitted to the interfero-

meter cell. The accuracy in velocity measurement is $\pm 0.003\%$.

THEORY

The equilibrium between the equatorial and axial conformers is equivalent to a two-state process of the kind $A \rightleftharpoons B$, with A having lower energy. Such a two-state process is characterized by a single relaxation time, and at any given temperature the ultrasonic relaxation arising from the perturbation of the above equilibrium is accompanied by a variation of velocity with frequency in accordance with equation 1.

$$(C_\infty^2 - C^2)/(C_\infty^2 - C_0^2) = 1/[1 + (f/f_r)^2], \quad (1)$$

where C is the velocity at frequency f , C_0 is the velocity at low frequencies ($f \ll f_r$), C_∞ is the velocity at high frequencies ($f \gg f_r$) and f_r is the relaxation frequency. If C_2 , C_4 and C_6 are the velocities at 2, 4 and 6 MHz respectively, substituting these values in (1) we get,

$$C_\infty^2 = \frac{5C_4^2C_6^2 + 3C_2^2C_4^2 - 8C_2^2C_6^2}{8C_4^2 - 3C_6^2 - 5C_2^2}. \quad (2)$$

Using (2), C_∞ is calculated from the experimental data.

The equilibrium parameters ΔH_0 , ΔG_0 , ΔS_0 and ΔV_0 the difference in enthalpy, Gibbs-free energy, entropy and volume respectively between one mole of the axial and equatorial isomers, are related to C_0 and C_∞ as follows:

$$F = [2C_p^2 J(C_\infty - C_0)C_r^2 \theta^2 RTM]^{1/2} \quad (3)$$

$$= \left[\frac{\Delta H_0}{RT} - \frac{C_p \Delta V_0}{V_0 RT \theta} \right] \frac{\exp(\Delta G_0/2RT)}{1 + \exp(\Delta G_0/RT)}. \quad (4)$$

Assuming ΔV_0 equal to zero (4) becomes

Table 1 Ultrasonic velocity variation with frequency and temperature in cycloheptanone

Temp K	Ultrasonic velocity m/s					
	$f = 1$ MHz	$f = 2$ MHz	$f = 4$ MHz	$f = 5$ MHz	$f = 6$ MHz	$f = 8$ MHz
303.15	1437.61	1441.38	1444.04	1444.48	1444.74	1444.98
313.15	1393.06	1396.46	1399.11	1399.65	1400.00	1400.36
323.15	1356.79	1359.19	1362.11	1362.79	1363.24	1363.72
333.15	1316.66	1318.48	1320.79	1321.71	1322.12	1322.85
343.15	1279.66	1280.62	1282.56	1283.29	1284.01	1284.89

$$F = \left[\frac{\Delta H_0}{RT} \right] \frac{\exp(\Delta G_0/2RT)}{1 + \exp(\Delta G_0/RT)} \quad (5)$$

Here C_p represents the molar specific heat capacity at constant pressure, J the conversion factor from Joules to ergs, θ the thermal expansion coefficient, R the gas constant, T the absolute temperature, M the molecular weight, V_0 the molar volume and C_t is equal to $(C_\infty + C_0)/2$. If ΔH_0 and ΔS_0 are both independent of temperature, the algebraic solution of (5) is

$$\Delta G_0/RT = 2 \ln \{ (\xi_1 + 1) + [F_1^2 + (\xi_1 + 1)^2]^{1/2} \} / F_1 \quad (6)$$

and,

$$\Delta H_0/RT = 2[F_1^2 + (\xi_1 + 1)^2]^{1/2} \quad (7)$$

where

$$\xi_1 = (T_1/F_1)[dF/dT]_1$$

In the above equations (6) and (7) the subscript 1 refers to the value for a given temperature T_1 . The value of ΔS_0 is obtained from the relation

$$\Delta S_0 = (\Delta H_0 - \Delta G_0)/T \quad (8)$$

If $\exp(-\Delta G_0/RT) \ll 1$ and we assume an Eyring type of rate equation, the relaxation frequency is related to the kinetic parameters of the relaxation process as follows

Table 2 Relaxation frequencies and dispersion parameters in cycloheptanone

Temp K	f_r MHz	C_∞ m/s	C_0 m/s	$C_\infty - C_0$ m/s	μ_{\max}	F
303.15	1.41	1445.37	1433.87	11.50	0.0251	1.1354
313.15	1.82	1400.89	1390.56	10.33	0.0233	1.1135
323.15	2.40	1364.46	1355.44	9.02	0.0208	1.0866
333.15	3.16	1324.04	1315.95	8.09	0.0193	1.0625
343.15	4.47	1286.75	1279.33	7.42	0.0182	1.0455

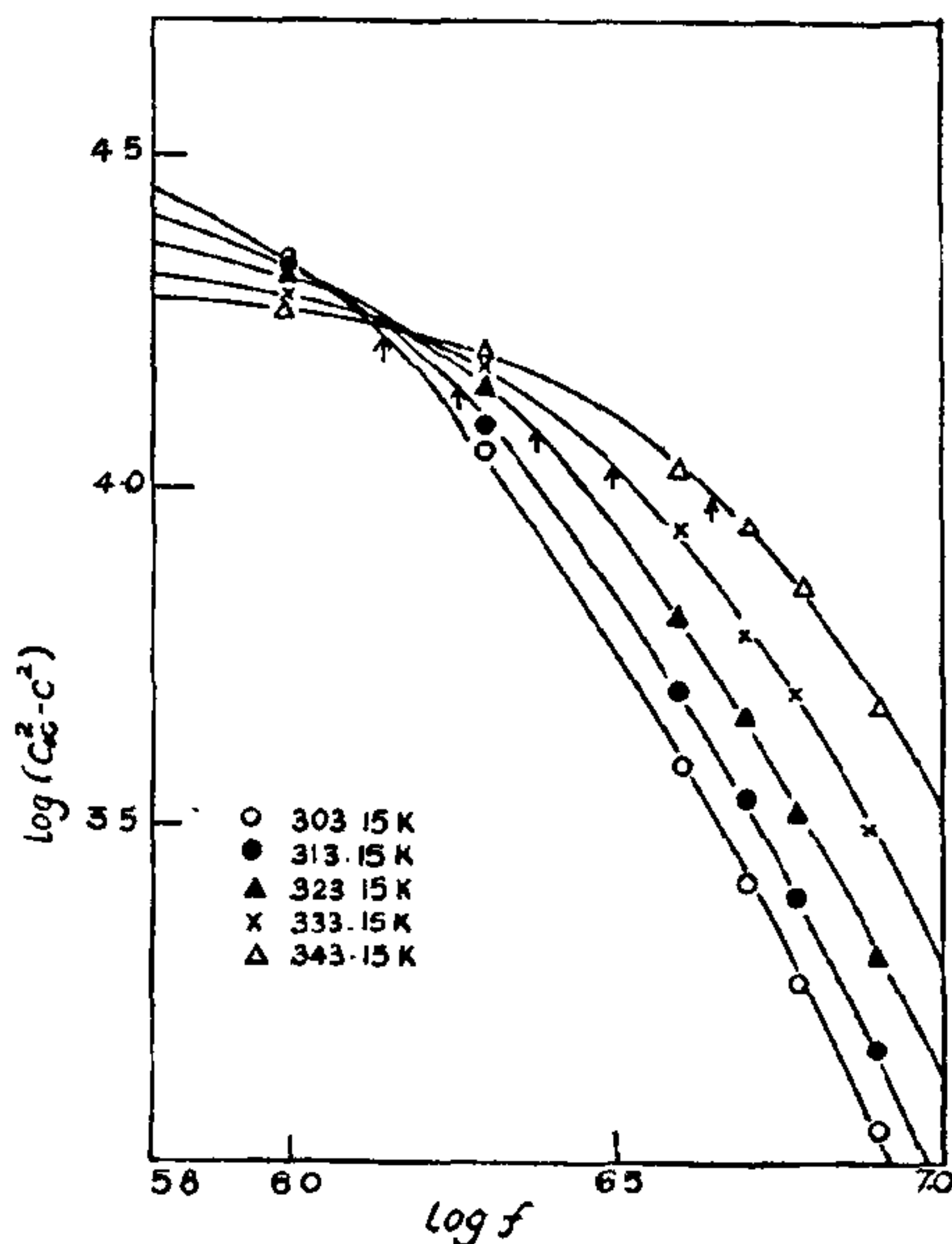
$$f_r = \frac{KT}{2\pi h} [\exp - (\Delta H^* - T\Delta S^*)/RT], \quad (9)$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation respectively for the isomer of higher energy, K is the Boltzmann constant and h the Planck's constant. The slope of the plot of $\log f_r$ against $1/T$ yields the value of activation enthalpy of the backward reaction.

RESULTS AND DISCUSSION

For a given temperature and pressure for a single relaxation process, the shape of the $\log(C_\infty^2 - C^2)$ vs $\log f$ curve is independent of the numerical value of the relaxation parameters f_r and $(C_\infty^2 - C_0^2)$. Hence a template of this theoretical curve with the relaxation frequency marked on it is made using a transparent material. This template is moved parallel to the axis and the theoretical curve best fitting the experimental data is drawn. The relaxation frequency is then directly read from the graph. The value of the ordinate asymptote attained at $f \ll f_r$, as read from the graph, gives the $(C_\infty^2 - C_0^2)$ value. C_∞^2 is calculated using (2).

The velocity data measured at different frequencies from 1 to 8 MHz and at different temperatures from 303.15 K to 343.15 K are presented in table 1

**Figure 1.** Velocity dispersion in cycloheptanone.

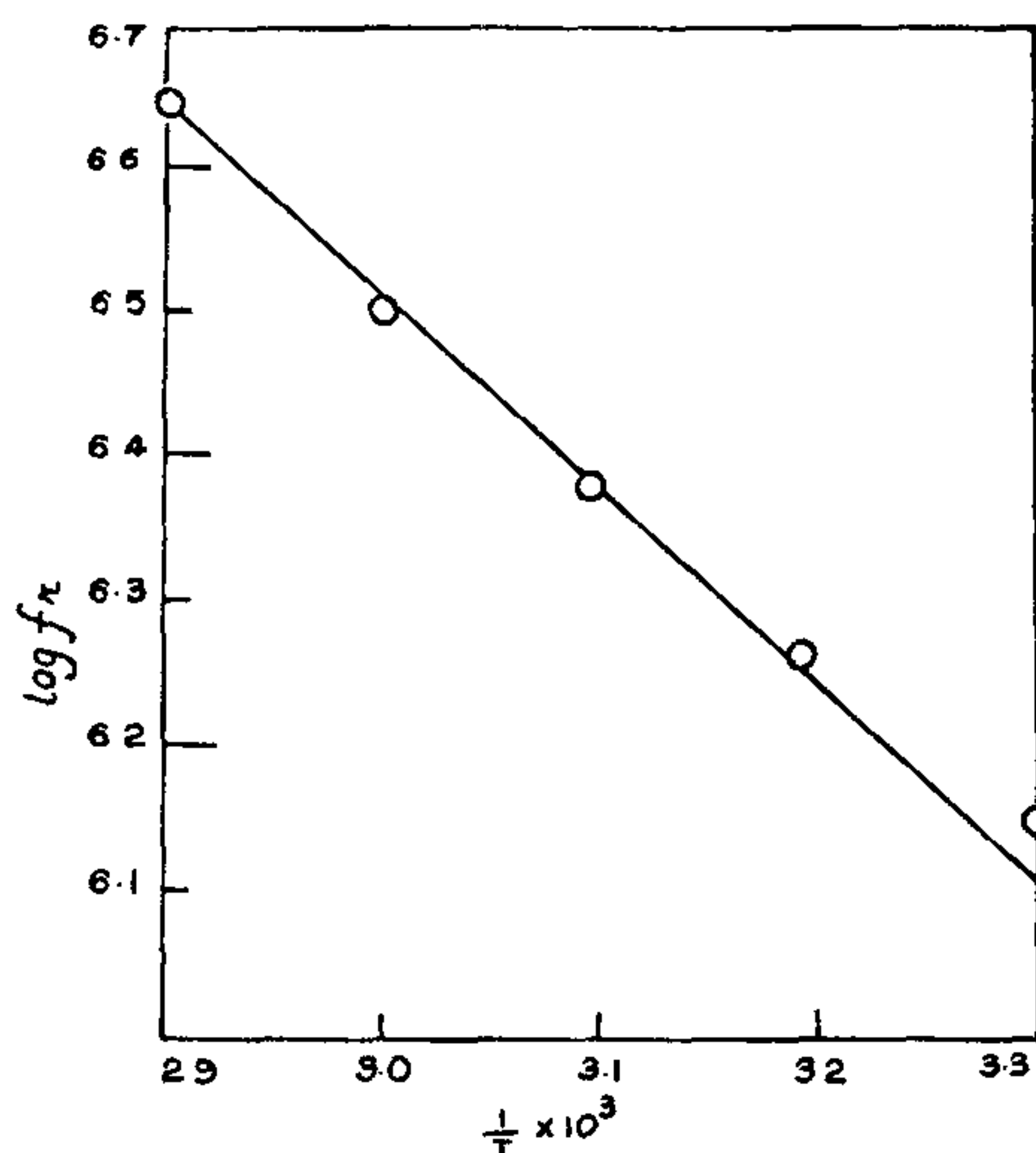


Figure 2. Variation of $\log f_r$ vs $1/T$ for cycloheptanone.

and the relaxation parameters evaluated are given in table 2.

The plots of $\log(C_{\infty}^2 - C^2)$ vs $\log f$ at different temperatures for cycloheptanone are shown in figure 1. The plot of $\log f_r$ vs $1/T$ is shown in figure 2. The changes in free energy, enthalpy and entropy between the two isomers, evaluated from equations (6)–(8), are 1.35 kcal/mol, 2.32 kcal/mol

and 3.20 cal/mol/°K. The activation enthalpy obtained from the plot of $\log f_r$ vs $1/T$ is 6.84 kcal/mol. The magnitude of the relaxation frequency observed in cycloheptanone is of the same order^{7,8} as that observed for substituted cyclohexanes and cycloheptanes. Hence the molecular mechanism of the present relaxation process may be attributed to ring inversion in cycloheptanone.

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