

CONFORMATIONAL STUDIES IN CYCLOHEXYLBROMIDE

T S REDDY and N P RAO

Department of Physics, S. V. University P. G. Centre, Kavali 524 202, India

(Received 30 March 1988; Accepted 16 June 1988)

The ultrasonic dispersion in cyclohexylbromide has been studied from the ultrasonic velocity measurements over a frequency range 1 to 8 MHz and over a temperature range 323.15 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 utilized in evaluating the energy parameters associated with the molecular phenomena.

Key Words : Cyclohexylbromide; Ultrasonics; Velocity

INTRODUCTION

THE ultrasonic relaxation phenomena in cyclic compounds (such as substituted cyclohexanes etc.) have been investigated by a number of workers.¹⁻⁶ 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 the 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 isomers can be evaluated from the measured variation with temperature of the magnitude of dispersion, and 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 cyclohexylbromide 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 measurements were made using a multi frequency ultrasonic interferometer at frequencies 1, 2, 4, 5, 6, and 8 MHz. For obtaining the measurements at different temperatures, water from a thermostatic water bath whose temperature can be maintained with an accuracy of ± 0.01 °C is allowed to pass through the circulating tubes fitted to the interferometer cell. The accuracy in velocity measurement is ± 0.003 per cent.

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 characterised 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 eq. 1.

$$\frac{C_{\infty}^2 - C^2}{C_{\infty}^2 - C_0^2} = \frac{1}{1 + (f/f_r)^2} \quad \dots(1)$$

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 eq. 1 we get

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

Using the above equation 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.

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

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

Assuming ΔV_0 equal to zero eq. 4 becomes

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

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_i is equal to $(C_{\infty} + C_0)/2$. If ΔH_0 and ΔS_0 are both independent of temperature the algebraic solution of eq. 5 is

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

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

where
$$\xi_1 = \frac{T_1}{F_1} \left(\frac{dF}{dT} \right)_1.$$

In the above eqs. 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

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

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 :

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

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 is 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 eq. 2.

The velocity data measured at different frequencies from 1 to 8MHz and at different temperatures from 323.15 K to 343.15 K are presented in Table I and the relaxation parameters evaluated are given in Table II.

TABLE I

Ultrasonic velocity variation with frequency and temperature in cyclohexylbromide

Temp K	Ultrasonic velocity m/sec					
	$f = 1$ MHz	$f = 2$ MHz	$f = 4$ MHz	$f = 5$ MHz	$f = 6$ MHz	$f = 8$ MHz
323.15	1094.88	1096.24	1098.01	1098.49	1098.81	1099.15
333.15	1063.11	1064.73	1066.41	1066.87	1067.39	1067.84
343.15	1034.71	1035.00	1036.72	1037.04	1037.83	1038.20

TABLE II

Relaxation frequencies and dispersion parameters in cyclohexylbromide

Temp K	f_r MHz	C_∞ m/sec	C_0 m/sec	$C_\infty - C_0$ m/sec	μ_{\max}	F
323.15	2.82	1099.77	1093.03	6.74	0.0193	1.8352
333.15	3.98	1068.82	1062.73	6.09	0.0180	1.8336
343.15	5.01	1039.62	1034.24	5.38	0.0163	1.8324

The plots of $\log (C_{\infty}^2 - C^2)$ vs $\log f$ at different temperatures for cyclohexylbromide are shown in Fig. 1. The plot of $\log f_r$ vs $1/T$ is shown in Fig. 2. The changes in free energy, enthalpy and entropy between the two isomers, evaluated from eq. 6-8 are 0.64kcal/mole, 2.54kcal/mole and 6.25 cal/mole/ $^{\circ}$ K.

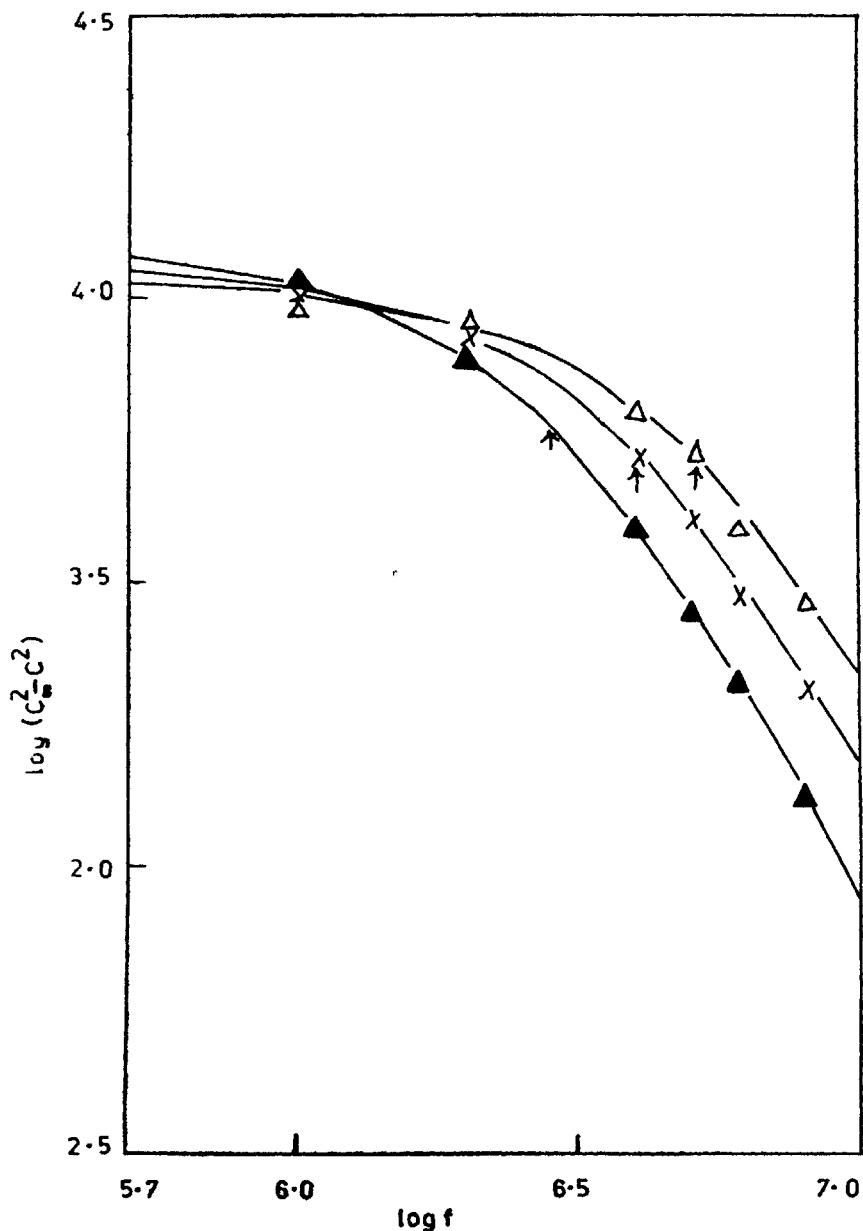
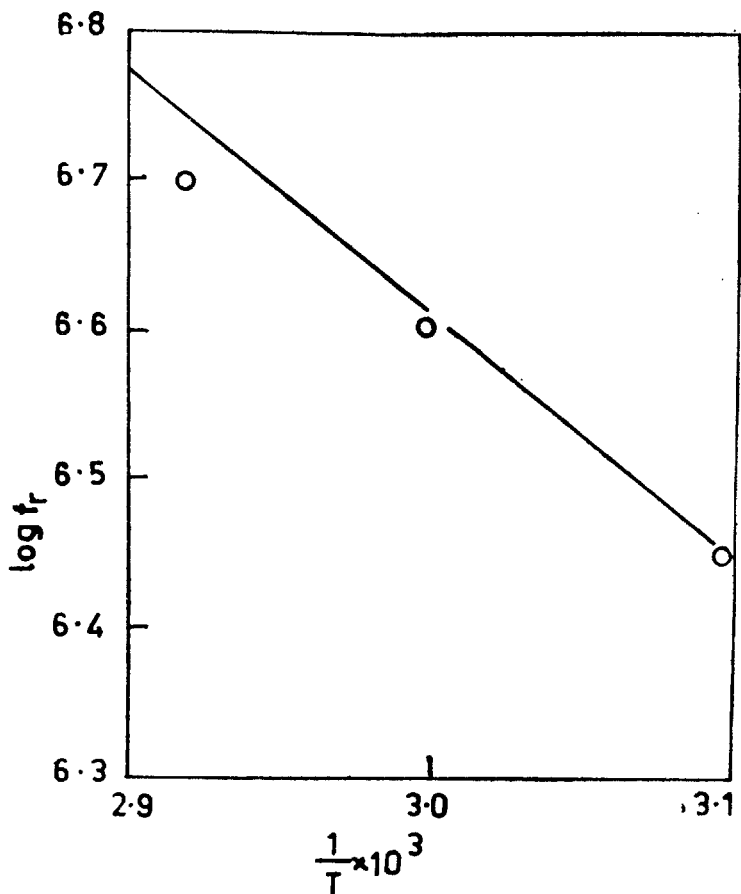


FIG 1 $\log (C_{\infty}^0 - C^2)$ vs $\log f$

FIG 2 $\log f_r$ vs $1/T$

The monosubstituted cyclohexane compounds takes the chair conformation.⁷ In the chair conformation of cyclohexane, there are two types of bonds, 'equatorial' and 'axial'. Thus there exist two conformational isomers of the chair form of monosubstituted cyclohexane and these can be interconverted by a process of ring inversion in which no bonds are broken. The ΔG_0 value of 0.64 kcal/mole for cyclohexylbromide of the present investigation is in reasonable agreement with the ΔG_0 values obtained from other studies.⁸⁻¹⁰

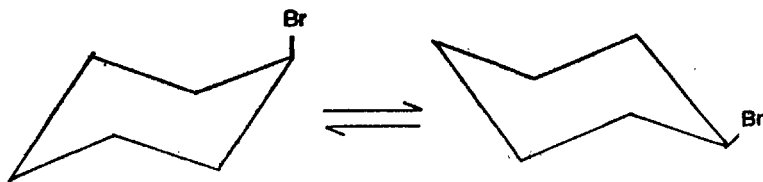


FIG 3 Ring inversion in cyclohexylbromide

The activation enthalpy obtained from the plot of $\log f_r$ vs $1/T$ is 8.45 kcal/mole. This value is in the same order to that of monosubstituted cyclohexane compounds where inversion phenomenon is observed. Hence, the molecular mechanism of the present relaxation process may be attributed to ring inversion in cyclohexylbromide as shown in Fig. 3.

ACKNOWLEDGEMENTS

The authors thank Professor V Padmanabha Sharma for his encouragement and interest in this work. One of the authors (TSR) is thankful to the University Grants Commission, New Delhi for the award of Junior and Senior Research Fellowships.

REFERENCES

- 1 J Karpovich *J chem Phys* **22** (1954) 1967
- 2 J E Piercy *J acoust Soc Am* **33** (1961) 198
- 3 E Rajagopal *PhD Thesis* submitted to *S V Univ* (1972)
- 4 J E Piercy and S V Subrahmanyam *J chem Phys* **42** (1965) 4011
- 5 N Prabhakara Rao and K C Reddy *Acustica* **40** (1978) 54
- 6 V Hyderkhan and S V Subrahmanyam *Acustica* **29** (1973) 350
- 7 M Hanack *Conformation Theory* Trans by Vaumann, Academic Press New York (1965) 103
- 8 H J Schneider and V Hoppen *Tetrahedron Lett* (1974) 579
- 9 J Stokr, H J Schneider and J Jakes *J mol structure* **15** (1973) 87
- 10 W Caminati, D Damiani and F Scappini *J mol Spectrosc* **104** (1984) 183