RELAXATION PROCESSES IN POLYSTYRENE MATRICES

A Thesis Submitted By:

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RELAXATION PROCESSES IN POLYSTYRENE MATRICES

H. A. KHWAJA

M.Sc. Thesis 1977

SUMMARY

Dielectric absorption of aromatic and aliphatic molecules containing the rotatable substituent group and of some analogous rigid molecules in solutions of polar solutes dispersed in an atactic polystyrene matrix are studied. Preparations of these solutions as solid disks and the dielectric measurements using a General Radio 1615-A capacitance bridge and a Hewlett-Packard Q-meter with appropriate temperature-controllable cells are described.

Dielectric relaxation times and energy barrier parameters of a fairly wide range of rigid molecules, viz., halobenzenes, p-halotoluenes and p-halobiphenyls are determined. The results of these rigid molecules are used to suggest a possible correlation between enthalpy and entropy of activation; enthalpy of activation and volume needed for the reorientation of molecules; and a molecule's moment of inertia and relaxation time.

Of the dialkyl and diaryl disulfides examined, an intramolecular rotation around S — S bond is detected in all the dialkyl disulfides and in some diaryl disulfides. The enthalpy barrier to this relaxation process is found to be ~ 29 kJ mol^{-1}.

Rotation of the ester group is examined in aromatic esters and some related compounds. The enthalpy barrier to intramolecular rotation of the ester group is found to be ~ 32 kJ mol^{-1}, and the entropy of activation is determined to be 27 J K^{-1} mol^{-1} in dimethyl terephthalate.

For heterocyclic aldehydes, the activation enthalpy of aldehyde group relaxation is found to be much larger than the usual group value in aromatic aldehydes, and is explained in terms of increased conjugation in the former. Measurement of crotonaldehyde provided a considerably high value of ΔH_E for aldehyde group relaxation, which is accounted for by the enhanced conjugation as reflected in its low carbonyl stretching frequency.

The contribution of the intramolecular rotation of a variety of segments, including the —CHO group, to the absorption of long-chain aliphatic aldehydes is indicated by the relaxation parameters.

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TABLE OF CONTENTS

PAGE

CHAPTER I

CHAPTER II

Experimental Procedures

CHAPTER III

Whole Molecule Relaxation of Some Rigid Molecules

CHAPTER IV

Intramolecular Relaxation of Some Disulfide Compounds

PAGE

CHAPTER V

Ester Group and/or Molecular Relaxation of Some Aromatic Esters

CHAPTER VI

Relaxation Process of Some Heterocyclic Aldehydes

CHAPTER VII

Dielectric Relaxation of Some Unsaturated and Saturated Aldehydes

CHAPTER VIII

Dielectric Relaxation of Some Long-Chain Aliphatic Aldehydes

LIST OF TABLES

List of Tables continued...

LIST OF FIGURES

PAGE

List of Figures continued...

TO MY PARENTS

CHAPTER I

INTRODUCTION

The dielectric absorption technique has been the subject in dealing with a variety of problems; on the one hand, studies of the properties and uses of commercial dielectric materials, and on the other, investigating the foundations of dielectric theory. However, a large amount of effort has gone into physico-chemical studies[1], where the means existed mainly to understand the structure and molecular forces. A vast majority of dielectric studies[2,3] for gaining information of the molecular structure in dilute solutions of a polar substance in a non-polar liquid or in pure polar liquids have been carried out at microwave frequencies. Aromatic molecules containing rotatable polar groups have been studied[4] extensively by the dielectric absorption technique. Information about the dielectric properties of agricultural materials has also been the subject of applied studies[5,6] in this area. Considerable information has also been obtained from dielectric absorption measurements of polymers and their aqueous solutions.[7]

Recently, considerable amount of effort has gone on the materials of biological interest.[8,9] Dielectric measurements[10] have provided a sensitive means of investigating the properties and uses of commercial dielectric materials in solid phase. In recent years, the dielectric absorption studies of polar solutes dispersed in polystyrene matrices have received considerable attention in the literature. This method has proved its success for determining the reasonable intramolecular energy barriers[11,12], which can also be obtained with the other relaxation techniques.[13] The main advantage of this technique is that for a non-rigid polar molecule, where there exists a possibility of simultaneous molecular and intramolecular processes, the relaxation time for the former process can be increased to such an extent that either it may be slowed down considerably or may even be eliminated owing to the highly viscous surrounding medium (polystyrene matrix), so that the contribution of molecular and/or intramolecular relaxation to dielectric absorption may be studied separately. Such a technique appeared more straightforward in comparison to the dielectric solution studies, since in this latter situation the molecular and intramolecular processes overlap, necessitating the use of a Budó analysis for the interpretation of relaxation data, which in a number of cases is now known to be unsatisfactory.[14] In addition, owing to the inadequate frequency and temperature ranges, the relaxation times and energy barriers cannot be deduced with reasonable accuracy. However, these obstacles do not seem to be in the way of the polymer matrix technique, as different instruments can be used to cover a wide frequency range of investigations over a broad range of temperature (i.e., from the lowest liquid nitrogen temperature to the glass transition temperature of the matrix). Thus, it seemed that the dielectric absorption work employing the matrix technique would provide a sound basis for determining the activation parameters, comparable with those determined by the relaxation methods.

The basic theories and related equations for dealing with dielectric absorptions are now well established. Dielectric dispersion is a phenomenon which occurs in materials containing polar molecules. A polar molecule is one which has a permanent electric dipole moment. For a dipolar molecule the so-called dielectric constant is no longer a constant, but varies with the frequency of an applied electromagnetic field. This frequency dependence arises from the inability of the dipole orientation to keep pace with the changes in the direction of the applied field at higher frequencies ($> 10^8$ c/s), and as a result the permittivity (dielectric constant) decreases with increasing frequency in the region of anomalous dispersion. This phenomenon of the permittivity falling off with increasing frequency is accompanied by the absorption of energy and is known as "dielectric dispersion".

In the frequency region, where the dispersion occurs, the dielectric constant is a complex quantity, ε^*.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad \text{I-1}$$

The real permittivity, ε', is commonly called the dielectric constant (even though it is not a constant), ε'' is the imaginary part or loss factor, and is a measure of the conductance of the medium and its ability to dissipate energy, and $i = \sqrt{-1}$.

For a simple system, the frequency dependence of ε' and ε'' for a single relaxation process 'τ' may be expressed[3] by Eqn: 1-2;

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1+i\omega\tau} \quad , \qquad \text{1-2}$$

where ε_0 and ε_∞ are the low and high frequency limiting value of ε^*, respectively, ω is the angular frequency in rad s^{-1}, and τ is known as the relaxation time in s and defined as the time in which the polarization is reduced to 1/e times its original value, where 'e' is the natural logarithmic base.

Combining Eqns. 1-1 and 1-2 and separating into real and imaginary parts yields the Debye-Pellat equations 1-3 and 1-4.

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1+\omega^2\tau^2} \qquad \text{1-3}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty).\omega\tau}{1+\omega^2\tau^2} \qquad \text{1-4}$$

From Eqn. 1-4 it is evident that ε'' is a maximum for $\omega\tau = 1$ and

$$\varepsilon''_{max} = \frac{(\varepsilon_0 - \varepsilon_\infty)}{2} \qquad 1\text{-}5$$

Thus, measurements of ε' and ε'' at frequencies in the absorption region permit the evaluation of relaxation time. By elimination of the frequency and relaxation time variables from Eqns. 1-3 and 1-4, the following Eqn. 1-6 is obtained, which is the basis of the Cole-Cole complex plane plot:

$$\{\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\}^2 + (\varepsilon'')^2 = \{\frac{\varepsilon_0 - \varepsilon_\infty}{2}\}^2 \qquad 1\text{-}6$$

A plot of ε'' against ε' in the complex plane gives a semicircle with radius $\frac{(\varepsilon_0 - \varepsilon_\infty)}{2}$ and its centre is on the abscissa at a distance $(\varepsilon_0 + \varepsilon_\infty)/2$ from the origin.

The above equations apply to both liquids and solids, although different models have been used in their derivation and as mentioned are valid for systems having a single discrete relaxation time, i.e., a "Debye process".

For many systems these equations may be satisfactorily valid, but for the systems, where more than one relaxation process is involved in the dielectric absorption, the analysis of experimental data becomes more complicated. Thus, for the simplest system, which has contributions from two distinct relaxation processes, Budó has shown that Eqns. 1-3 and 1-4 may be modified to include a weighted sum of two terms, one for each process, and thus for two different processes with relaxation times, τ_1 and τ_2, we have Eqns. 1-7 and 1-8:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \qquad 1\text{-}7$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \qquad 1\text{-}8$$

where C_1 and C_2 are normalizing constants, such that $C_1 + C_2 = 1$. The relaxation times can thus be obtained from the complex plane plot for such systems which will depend on the relative magnitudes of τ_1, τ_2, and C_1 but may often be approximated by a sector of a semicircle. It is to be noted that, when neither Debye-Pellat nor Budó analysis is suitable for any system, several modified relations could be employed for the analysis of experimental data, such as the Cole-Cole equation, the Cole-Davidson equation, or the Fuoss-Kirkwood equation.

For many systems, the dielectric absorption is not characterized by a single discrete relaxation time. Cole and Cole[15] considered the case of a continuous distribution of relaxation times about a most probable value, τ_0, and after modification of Eqn. 1-2 obtained Eqn. 1-9:

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1+(i\omega\tau_0)^{1-\alpha}} \qquad 1\text{-}9$$

where $i = \sqrt{-1}$, α is known as the Cole-Cole distribution parameter, an emperical constant which measures the width of the distribution and may take values between 0 and 1.

The Eqn. 1-9 may be rationalized[1] to yield Eqn. 1-10 and Eqn. 1-11:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1+(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)}{1+2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1\text{-}10$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)}{1+2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1\text{-}11$$

For $\alpha = 0$, the equations reduce to the Debye-Pellat Eqns. 1-2, 1-3, and 1-4. For non-zero values of α, the Cole-Cole complex plane plot of ε'' against ε' retains the semicircular form, but the centre lies below the ε' axis on a line drawn in the positive ε' direction from ε_∞ but rotated in a clockwise direction about this point by the angle $\frac{\alpha\pi}{2}$ radians.

Further, a distribution similar to a right skewed arc may also be well represented by the Cole-Davidson distribution function[16], Enq. 1-12, which may be rationalized to Eqns. 1-13 and 1-14.

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{(1+i\omega\tau)^h} \qquad 1\text{-}12$$

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos^h(\phi)\cos(h\phi) \qquad 1\text{-}13$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos^h(\phi)\sin(h\phi) \qquad 1\text{-}14$$

where $i = \sqrt{-1}$, ϕ = arc tan($\omega\tau$), and 'h' is again a constant which may have values $0 < h \leq 1$, with $h = 1$ corresponding to the Debye Eqn. 1-2. The shape of the complex plane plot described by these equations is a skewed arc with the maximum value of ε'' occurring to the right of the centre of the arc, and this is often taken to indicate that the dielectric absorption arises from a relaxation mechanism which involves co-operative motion of the surroundings of the dipolar molecule.

For systems, where the dielectric absorption are much broader than a Debye curve owing to the presence of a range of relaxation times, then Fuoss-Kirkwood's equation[17] can frequently be employed: Eqn. 1-15.

$$\varepsilon''_{obs} = \varepsilon''_{max} \ \mathrm{sech} \ \{\beta \ \ln \ (\frac{f_{obs}}{f_{max}})\} \qquad 1\text{-}15$$

where 'f' is the frequency in c/s and f_{max} is the frequency of maximum absorption. 'β' varies between unity for a single relaxation (in the Debye case) and zero for an infinite range, and $(1/\beta)$ measures the width of the absorption relative to the simplest (Debye) process.

CHAPTER II

EXPERIMENTAL PROCEDURES

INTRODUCTION

The dielectric properties of polar materials have been seen to arise from the ability of their dipoles to reorientate in the presence of an applied electric field. Consider the application of a static electric field to a dipolar material, composed of randomly orientated electric dipoles between the plates of a condenser. Thus, the dielectric constant or permittivity of the materials, ε_0, which is a frequency-dependent quantity and is characteristic of the medium between two charges may be defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. The permittivity, ε_0, is also given by the ratio of the capacitance of a condenser with material, C, between the parallel conducting plates to the capacitance of the same condenser when the material is replaced by a vacuum, C_0, Eqn. II-1:

$$\varepsilon_0 = \frac{C}{C_0} \qquad \text{II-1}$$

If a low-frequency sinusoidal e.m.f. is applied to a dipolar material, then it may cause the molecules partly to reorient before the field reverses. This reorientation of the dipoles is the molecular process transmitting the electromagnetic energy through the medium and is equivalent to an electric current. It is known as the displacement current in the "dielectric". When there is no lag between the orientation of the molecules and the variations of the alternating voltage, then the displacement current will be 90°

out of phase with the e.m.f., the former being ahead of the latter. In the phase diagram (Figure II-1), it seems that there is no component of the current in phase with the e.m.f., so the Joule heating measured by the product e.x.i. is zero in the system. This system corresponds to an ideal dielectric in which the electric energy is transmitted without loss.

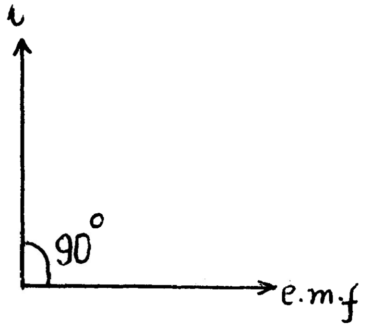

Fig. II-1

As the frequency of an applied electric field for a dipolar material increased, from a static field up to the microwave region, the reorientation of dipoles in the field will, at some stage, lag behind the voltage oscillations. The resulting phase displacement (δ) leads to a dissipation of energy, such as Joule heating in the medium. This is measured by the dielectric loss (ε'') defined as Eqn. II-2:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad \text{II-2}$$

where ε' is the real part of the dielectric constant, $\tan\delta$ is the loss tangent or the energy dissipation factor, and ε'' is the loss factor. It is a measure of the conductance in the medium, and so is directly proportional to the concentration of the polar material in the dielectric. In this frequency region the dielectric constant is a complex quantity as given by Eqn. I-1. The relationship between ε', ε'' and δ is shown by the diagram:

Fig. II-2.

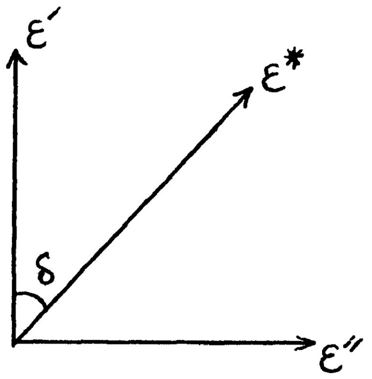

Fig. II-2

All the dielectric measurements depend to a large extent on the above mentioned principles. A considerable variety of experimental methods is available for measuring ε' and ε'': they differ according to the frequency region being covered. However, for the present study, the dielectric measurements have been made on a General Radio capacitance bridge, type 1615-A, and the Hewlett-Packard Q-meter, type 4342-A.

APPARATUS

The General Radio Bridge

The General Radio capacitance bridge has a useful frequency coverage, from 50 to 10^5 Hz, if it is used in conjunction with their model 1310-B sine wave signal generator and model 1232-A tuneable amplifier/null detector. The signal generator output was divided into two parts: one part was allowed to go to the capacitance bridge input terminals and the other part was used to supply the horizontal deflection signal of the oscilloscope. The vertical deflection signal for the oscilloscope was provided by the amplified bridge unbalance signal from the output terminals of the model 1232-A detector. This was connected to the ground lead with a small capacitor to avoid the possibility of errors due to ground loop currents. Thus, the vertical amplitude of the oscilloscope pattern reflected the magnitude of the bridge imbalance. The oscilloscope pattern allows one to see more easily the average value of the signal to judge whether the null balance has been achieved or not, so that any imbalance of bridge controls could be corrected easily to achieve the desired null condition. More importantly, it has an advantage at low frequencies, where environmental noise makes a contribution to the total signal displayed by the null detector. In addition, at these frequencies, the transformer core in the bridge may become saturated if the generator supplies a high signal power. This condition may be indicated by a severe distortion on the oscilloscope pattern. Thus, the oscilloscope allows the user to set the signal generator output to the maximum possible level without causing errors due to transformer core saturation.

The General Radio bridge measures the capacitance and conductivity of the capacitor. Then with the help of these quantities, the real and imaginary parts of the permittivity result from the following equations, II-3 and II-4:

$$\varepsilon' = \frac{C}{C_0} \qquad \text{II-3}$$

$$\varepsilon'' = \frac{G}{\omega C_0} \qquad \text{II-4}$$

where 'G' is the conductivity of the system, $\omega = 2\pi f$ = angular frequency of the applied field, and the other terms are as mentioned previously.

The capacitor measured by the GR bridge consisted of the polystyrene matrix disk clamped between the high and low electrodes. The measurement of C_0 is difficult, as it would require the electrodes to be arranged exactly as they were when they contained the sample, but without the sample, C_0 values may be calculated from the relation[25] Eqn. II-5:

$$C = \frac{0.2244\ A_1}{d_1} \qquad \text{II-5}$$

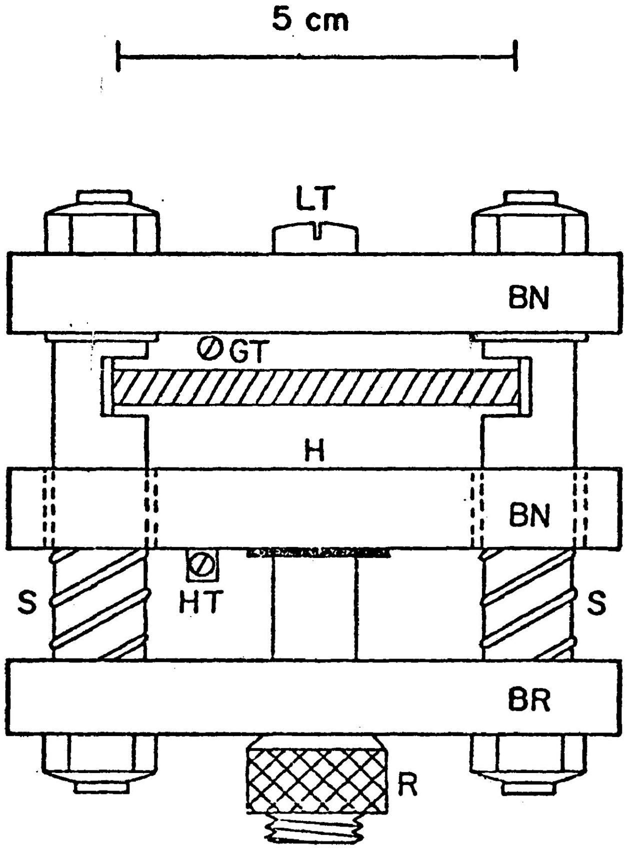

Figure II-3 Three-terminal electrode assembly for dielectric measurements on solid disks.

Key:	
LT	Low electrode connection terminal
BN	Boron Nitride insulating support plates
GT	Guard ring connection terminal
H	High electrode
HT	High electrode connection terminal
BR	Brass support plate
R	Release nut
S	Steel clamping springs

where A_1 is the effective area of the plates in ins.^2, C is the capacitance in units of picofarads, and d_1 is the spacing of the plates in ins.

In view of convenience for the handling of experimental data, Eqns. II-3 to II-5 can be combined, which leads to the following Eqns. II-6 and II-7:

$$\varepsilon' = \frac{Cd_1}{0.2244\ A_1} \qquad \text{II-6}$$

$$\varepsilon'' = \frac{\varepsilon' G}{\omega C} \qquad \text{II-7}$$

where 'G' is the conductivity in picomhos, and the other terms have the same units.

The capacitance of the cell containing a standard quartz disk of diameter 2.0 inches, thickness 0.0538 inches (supplied by the Rutherford Research Products Co., Rutherford, New Jersey, U.S.A.) and with a dielectric constant of 3.819 was measured. This value was then used to determine the effective area of the cell electrode plates 'A_1'.

A schematic diagram of the electrode assembly is shown in Fig. II-3[*], which is a three terminal assembly with an outer diameter of 2.0 ins. The low electrode had a diameter of about 1.5 ins. and was surrounded by a guard ring electrode of outer diameter of 2.0 ins. The electrodes, which were held together by four brass rods of 0.5 ins. diameter passing through the four corners, were mounted on two square blocks of boron nitride. The electrodes maintain pressure on the ca. 0.07 in. thick sample disk by springs on each of the four rods. This type of arrangement for the electrode assembly overcomes considerably any errors due to fringing of the electric field at the edges of the measurement area. Thus, the measured capacitance is solely that between high and low electrodes. The electrode assembly was mounted in an air-tight aluminum chamber with walls 0.5 ins. thick which could be sealed off from the atmosphere. Two sealed tubes provided connections to the electrodes, and two more tubes provided the chamber to be purged with dry nitrogen gas and then maintained a slight positive pressure to avoid the inlet of atmospheric moisture during low-temperature measurements. The exterior of the chamber was surrounded by a heating coil of nichrome wire. The heater resistance was about 2 ohms, so that a 12 volt supply provided a heating power of about 70 watts. Temperature control of better than 0.1 K could be achieved by connecting the heater to the output of a Beckmann/RIIC model TEM-1 temperature controller. Cooling of the chamber was accomplished by conduction from a flat-bottomed aluminum container with liquid nitrogen which was placed on its flat-

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[*] Reproduced by the courtesy of C.K.McLellan of this laboratory.

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Key to Figure II-4 on facing page

SB	Spring bellows
L	Low electrode in contact with case
CP	Centre plate
H	High electrode
I	Insulating supports for high electrode (four)
G	Locating guides for centre plate (three)
TC	Thermocouple in well
H	Handle for operation of switch
N	Nitrogen gas inlet (outlet not shown)
S	Switch assembly
BP	Banana plug connectors for low (case) terminal
HC	High electrode connection strip
Q	Quartz spacer
SA	Sample (2" dia. disk) location
E	Electric heater coil

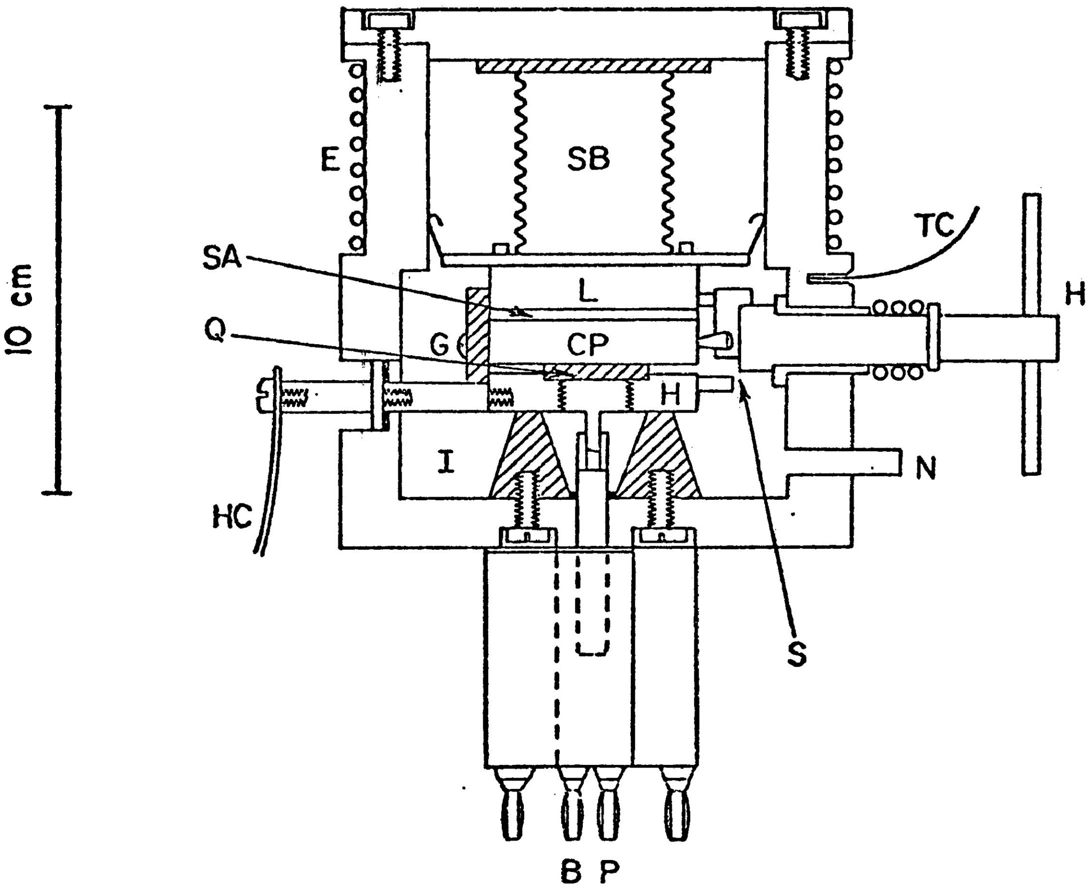

Figure II-4 The Morgan tri-electrode cell for Q-meter.
(key on facing page)

plated, flexible metal strip. The cell consists of two capacitors, sharing a common plate between the sample on one side and an air gap partially filled with a 1 in. diameter quartz disk on the other side, serving as the reference capacitors. The sample and the reference capacitors are placed inside the low and high electrodes, respectively. The sample or the reference capacitor can be examined separately with the help of a switch arm, mounted on the common central plate by allowing this plate to be connected either to the low or the high side. When it is connected to the low plate of the sample capacitor, the common plate then becomes the low plate for the reference capacitor, and the sample capacitor is removed from the circuit. When the common plate is connected to the high plate of the reference capacitor, this capacitor is removed from the circuit, and the common plate becomes the high plate of the sample capacitor. Thus, in this manner the switch provides the Q-meter to examine either the reference capacitor or the sample capacitor. The whole cell assembly was insulated with styrofoam. The cooling of the chamber, the arrangement for the stabilization of temperature, and the cell case were similar to those for the General Radio bridge.

At the start of a set of measurements, the sample disk is placed in the appropriate position, and the air spacing is adjusted between the reference capacitor plates, so that the two capacitors have about the same capacitance value. This can be judged by their ability to achieve resonance of the Q-meter circuits at the same settings of the meter's capacitance controls for both capacitors. Principally, the capacitance difference between reference and sample capacitors could be related to the dielectric constant of the sample if this parameter is known for at least one frequency.

However, these data were not used, as this information gave no consistent values for the dielectric constant of the sample. Thus, for the present work, the values of dielectric loss factor, ε", as a function of frequency were evaluated. One assumes that the conductivity, G, of the measurement system is composed of two additive components, one each for the sample and the measurement system alone, then Enq. II-8 can be obtained. This is accomplished by Eqns. II-3 and II-4, bearing in mind the definitions of loss tangent and of Q.

$$(\tan\delta)_s = \frac{G_x - G_r}{\omega C} = \frac{G_x}{\omega C} - \frac{G_r}{\omega C}$$

$$= \frac{1}{Q_x} - \frac{1}{Q_r}$$

$$= \frac{Q_r - Q_x}{Q_x} \text{ X } \frac{1}{Q_r}$$

Therefore: $$(\tan\delta)_s = \frac{\Delta Q}{Q_x} \text{ X } \frac{\Delta C_r}{2C_r} \qquad \text{II-8}$$

where $(\tan\delta)_s$ = $\tan\delta$ for the sample only,

Q is the Q value for the capacitor being examined,

ΔQ is the Q readings difference for sample and reference,

C_r is the capacitance of the reference capacitor,

ΔC_r is the width of the peak of Q vs C for the reference

capacitor, measured at $Q_r/\sqrt{2}$,
and the subscripts 'x' and 'r' refer to the corresponding values when measured for the sample and reference capacitors, respectively.
The value of C_r is now not known, but it was adjusted to be equal to the value of the sample capacitor, C_x.

Now, by applying Eqns. II-3 and II-5 and then II-2, we can obtain Eqn. II-9:

$$\varepsilon''_s = \frac{(\Delta Q)(\Delta C_r)(d_1)}{(Q_x)(2)(0.2244\ A_1)} \qquad \text{II-9}$$

where ε''_s represents the dielectric loss factor of the sample,
d_1 = sample thickness in inches,
A_1 = effective area of the cell electrodes in one of the capacitors, and the remaining quantities have similar meanings as defined previously in Eqn. II-8.

Preparation of Polystyrene Matrix Sample

The samples used for the present study were all solid disks consisting of polar solutes dispersed in polystyrene matrices. The procedure employed for the preparation of the matrix was similar to that described by Davies and Swain.[11] The desired amount of solute to make about 5 mole percent in the matrices was placed in a ceramic crucible, and to this the required weight of atactic polystyrene pellets (Monomer-Polymer Laboratory, Philadelphia, M_w = 236,000) was added. This mixture was then dissolved in 10 ml of a non-polar solvent, trans-1,2-dichloroethylene (b.p. 320.7K). The mixture was thoroughly stirred until it dissolved, and then the crucible was placed in a drying oven at about 100°C. After sufficient evaporation of the solvent, when the mixture became an extremely viscous mass, the crucible was removed from the oven and allowed to cool so that the viscous mass could be gently pried away from the crucible walls by using a stainless steel spatula. Then, it was rolled into a flat disk and was placed on a teflon sheet in a vacuum oven at about 85°C, and the pressure reduced by a single-stage rotary pump. Repeated checks by heating to constant weight in a vacuum oven at 85°C, ensured that the polystyrene matrix contained the least amount of the solvent (<1%). The procedure was altered for a few cases where the solute molecules were very volatile (b.p. < 125°C). In these cases, no solvent was used. The desired weight of polystyrene was dissolved directly in a large excess of the solute (which was in the liquid state), and the same evaporation process was carried out. The final evaporation in the vacuum oven was then made until the total sample weight indicated that the polystyrene matrix contained the desired amount of solute.

Finally, the matrix material was placed in a stainless steel die with polished tungsten carbide die faces of 2 inches diameter. The die was heated to a temperature of about $115^{\circ}C$ for 20 minutes necessary to melt the matrix material. The sample was then pressed by applying a pressure of about 5 tons after which the die was cooled under pressure with a fan for about 30 minutes. The specimen was finally pushed out as a glass-like circular disk of about 0.07 inches thick. The edges of the sample disk were lightly smoothed with a sharp knife blade, and its average thickness was measured with a micrometer. The sample weight was also noted, and then solute concentration in a polystyrene disk was calculated in moles per litre by using the formula:

$$\text{Concentration} = \frac{\text{wt. of solute used}}{\text{M. wt. of solute}} \text{ X } \frac{\text{wt. of disk}}{\text{Wt. of p.s. \& solute}} \text{ X } \frac{1}{\text{Vol. of disk}}$$

Samples of pure solids were prepared by grinding the solid with a mortar and pestle, placing the powder in the die, and pressing it at room temperature with a pressure of 30 tons. The concentrations of the pure solids were calculated in a similar way by measuring the weight and thickness of the disk.

All the polymer disks used for this work had low solute concentrations ($\sim$5% by weight). The polar solutes are monomolecularly dispersed in the matrices, so that any strong internal electric field, for example, in the crystalline solids is largely eliminated. In addition, such low concentrations would not affect appreciably the relaxation process, as Borisova and Chirkov[24] have shown for small molecules dispersed in a polystyrene matrix that the energy barrier for molecular relaxation in these molecules is independent of concentration (<5-7 mole percent).

Evaluation of Results

For the work of this thesis, the real and imaginary parts of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ have been measured for dilute solutions of several polar molecules in a polystyrene matrix over suitable ranges of temperatures and frequencies. This was accomplished by using the General Radio bridge and in some cases the Q-meter. The dielectric loss factor of the pure solute was obtained by subtracting the loss factor of pure polystyrene (obtained through similar measurements) from that observed for the matrix solutions $\{\varepsilon''_{\text{solute}} = \varepsilon''\ (\text{matrix}) - \varepsilon''\ (\text{polystyrene})\}$. For analysis, the experimental data as functions of temperature and frequency were fed into a series of computer programmes written in the APL language. These programmes, written in this laboratory, were used throughout this work, and may be available on request from the Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada, P7B 5E1.

For each measurement of temperature, the data of dielectric loss factor as a function of frequency were analyzed by the computer according to the Fuoss-Kirkwood Equation, I-15, by a procedure employed by Davies and Swain.[11] By iteration the programme finds that value of ε''_{max} which provides the best linear fit to the plot of $\cosh^{-1}(\varepsilon''_{max}/\varepsilon'')$ against ln(f). From the slope of this line the value of the distribution parameter, β, is deduced. The frequency of maximum dielectric loss, f_{max}, is obtained from this slope and the intercept of the line on the $\cosh^{-1}$ axis. Sample plots of dielectric loss, ε'' against $\log_{10}(f)$ for solutions of solute molecules in polystyrene are given in each chapter.

The Fuoss-Kirkwood equation (Eqn. I-15) does not take into account the real part of the complex permittivity, nor its limiting values at low and high frequencies, ε_0 and ε_∞, respectively. However, for each dielectric absorption process, the total dispersion is given by Eqn. II-10:

$$\Delta\varepsilon' = \varepsilon_0 - \varepsilon_\infty = \frac{2\varepsilon''_{max}}{\beta} \qquad \text{II-10}$$

The Cole-Cole[15] Equation (I-9), is also frequently used to describe the frequency dependence of dielectric permittivity in a system involving a distribution of relaxation times. The Fuoss-Kirkwood distribution parameter, β, may be related to the Cole-Cole distribution parameter, α, by an equation given by Poley:[2]

$$\beta = \frac{1-\alpha}{\sqrt{2}\cos\{\frac{\pi(1-\alpha)}{4}\}} \qquad \text{II-11}$$

Therefore, the Fuoss-Kirkwood analysis was supplemented by the Cole-Cole equation, (I-10), to obtain ε_∞. Several estimates of ε_∞ were obtained by using Eqns. I-10 and II-11 in conjunction with experimental values of ε' at different frequencies by a computer program. The average of these estimates were calculated along with a value for ε' at the frequency of maximum dielectric loss, ω_{max}.

The calculation of the effective dipole moments involved in the dielectric relaxation process was made by using the Debye[18] equation II-12 and the Onsager[19] Equation II-13:

$$\mu^2 = \frac{27000\ kT\ (\varepsilon_0 - \varepsilon_\infty)}{4\pi Nc(\varepsilon'+2)^2} \qquad \text{II-12}$$

$$\mu^2 = \frac{9000\ kT\ (2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{4\pi Nc\ \varepsilon_0(\varepsilon_\infty+2)^2} \qquad \text{II-13}$$

where $(\varepsilon_0 - \varepsilon_\infty) = 2\varepsilon''_{max}/\beta$, (Fuoss-Kirkwood Eqn. II-10),

ε' = value of ε' at $\omega_{max} = \frac{1}{\tau_0}$,

ε_0 = static dielectric constant derived from the estimated average of ε_∞ and Eqn. II-10,

N = Avagadro's number (6.022×10^{23} molecules mol^{-1}),

c = Solute concentration in moles per litre,

k = Boltzman constant (1.38×10^{-16} erg K^{-1}),

T = Temperature in K.

These equations yield μ in units of e.s.u. -cm, but commonly this parameter is expressed in Debye units, where 1 D = $1\text{x}10^{-18}$ e.s.u. -cm.

The Fuoss-Kirkwood analysis and the calculations of ε_∞ and μ were made at each measured temperature. The values of ε_∞ and μ were not calculated from Q-meter data, since ε' from Q-meter measurements was unreliable. The results of these analyses from several temperatures were used for further processing.

Thus, the values of the observed dipole moment at different temperatures were fed in a separate computer program to estimate the extrapolated values of the dipole moment at temperatures above those of measurement. This technique is similar to that employed by Davies and Swain [11] and was based on the assumption that the dipole moment is a linear function of temperature. It seemed from their work that this method yielded reasonable results, although there is little theoretical basis for such a procedure. However, in many cases, it is well established that the variation of ε_0 and ε_∞ with temperature may be described by an equation of the form $\log(\varepsilon) = aT + b$.[20] The extrapolated ε_0 and ε_∞ values, obtained in this manner have been used in conjunction with Eqn. II-12, to calculate dipole moments at warmer temperatures, as well as the Davies and Swain technique.

The energy barrier which must be surmounted in the motion of the dipole was evaluated in terms of the Eyring enthalpy of activation, ΔH_E, by using the Eyring rate expression Eqn. II-14, a procedure commonly used in dielectrics work:[11,21]

$$\tau = \frac{1}{\text{rate}} = \frac{h}{kT}\left[\exp\left(\frac{-\Delta G_E}{RT}\right)\right]$$

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta H_E}{RT}\right)\exp\left(\frac{-\Delta S_E}{R}\right) \qquad \text{II-14}$$

which can be rearranged to the linear form as:

$$\ln(T\tau) = \frac{\Delta H_E}{RT} - \{\frac{\Delta S_E}{R} - \ln(\frac{h}{k})\} \qquad \text{II-15}$$

The plots of $\log(T\tau)$ against T^{-1} yielded good straight lines, and from the slope and intercept of this line, the values of the enthalpy of activation, ΔH_E, and the entropy of activation, ΔS_E, respectively, were evaluated with the help of a computer program.

The program also calculates the relaxation times 'τ' and the free energies of activation 'ΔG_E' (= $\Delta H_E - T\,\Delta S_E$) at different temperatures.

Finally, the plots of $\ln(\varepsilon''_{max}\,T)$ against T^{-1}, according to the following equation II-16, as employed by Meakins,[22] were used to obtain the energy difference, V, between the two sides of the activation energy barrier:

$$\varepsilon''_{max} = \frac{B}{kT}\ \exp\,(-\,V/_{RT}) \qquad \text{II-16}$$

where 'B' is a simple proportionality constant. It is to be noted that in most cases the computer analyses of the present data have yielded energy difference values (V) less than the mean thermal energy and therefore, according to Meakins, could not be considered reliably to be different from zero. The results of the analyses of dielectric data to obtain Fuoss-Kirkwood parameters $\log_{10}(f_{max})$, ε''_{max}, and β, the relaxation times, τ, the limiting high frequency dielectric constants, ε_{∞}, and the effective dipole moments, μ, are collected in the tables in each chapter. The results of Eyring analyses of these data are also presented in each of the following chapters.

Standard statistical techniques[23] provide a means of estimating errors in fitting a straight line to a set of graph points. A computer program FUOSSK calculated intervals of 90%, 95%, 98%, and 99% confidence for both the Fuoss-Kirkwood distribution parameter, β, and $\log_{10}(f_{max})$. The 95% confidence interval was chosen as a good representation of experimental error, typical values for $\log_{10}(f_{max})$ being ±0.05 to ±0.10.

The 95% confidence intervals calculated for $\log_{10}(f_{max})$ were then compared to the differences between observed and calculated values of $\log(T\tau)$ from the computer program for the Eyring rate equation analysis. Any experimental point which deviated from the calculated line by more than its allowed confidence interval was deleted from a repeat run of the Eyring rate equation analysis.

The same technique was adopted to calculate the 95% confidence intervals for both ΔH_E and ΔS_E. A smaller error is to be expected from the use of a larger number of points on the Eyring plot. In the present work, the maximum error in ΔH_E is hardly greater than ±10%. It is of similar order of magnitude to that reported by Davies and Swain,[11] while that of ΔS_E may be as high as ±50% in cases where fewer than six temperatures were employed for the acquisition of dielectric data. The values of activation enthalpies and entropies have been quoted in this work to round figures for comparative purposes only.

The structural diagrams of some typical molecules investigated are given in Appendix 1.

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CHAPTER III

WHOLE MOLECULE RELAXATION OF SOME RIGID MOLECULES

INTRODUCTION

A number of attempts has been made to investigate the parameters, which depend on dielectric relaxation times and the enthalpy of activation of rigid dipolar molecules. Amongst the effects investigated are the entropy of activation (ΔS_E), size and shape of the polar molecules, volume swept out by the molecules in their reorientation process, moments of inertia, viscosity of the medium, and the direction of the dipole within the molecules.

In an earlier investigation, Higasi[1] showed almost a linear dependence of entropy of activation (ΔS_E) upon the corresponding enthalpy of activation (ΔH_E) for a variety of organic molecules. He tentatively postulated from this linear dependence that, "the entropy change is zero or has a small negative value, if ΔH_E is below 13.4 kJ mol^{-1}".

Further, Kalman and Smyth[2] examined 2,2-dichloropropane, 2,2-dinitropropane, camphor, α-chloronaphthalene, isoquinoline, 4-bromobiphenyl, and acridine in nujol solution at 293, 313, and 333K. They obtained values of ΔH_E and ΔS_E for these molecules as 6.7 and -0.6, 8.3 and -0.7, 10.1 and -1.2, 15.2 and 0.5, 18.9 and 4.0, 37.6 and 11.5, 45.9 and 19.8 kJ, respectively. The increase in the activation energies and entropies from the spherically shaped molecules toward the more elongated ones is in line with the investigation of Higasi.[1] Davies and Edwards[3] have also indicated a similar relationship between Eyring enthalpy and entropy of activation for polar molecules of various sizes and shapes of the types, viz., camphor, anthrone, cholest-4-ene-3-one, tetracyclone, and β-naphthol. By the plotting of Eyring parameters ΔS_E against ΔH_E of Edward's[3] data, together with Levi's[4] data, an appreciable linear relation exists between these two parameters. The confirmity is understood qualitatively if the activation energy is largely needed to displace adjacent solvent molecules: the larger the energy required for ΔH_E, the larger the local reorganization ΔS_E.

The dependence of dielectric relaxation time and enthalpy of activation upon molecular rotational volume, viscosity of the medium, position of the dipole moment within the solute molecule, and the molecular inertia has been explored little by little by many investigators.

Crossley and Walker[5] studied three non-spherical rigid molecules, quinoline, isoquinoline, and phthalazine in cyclohexane solution at 323K. In these solute molecules of almost identical size and shape, the direction of the dipole moment is varied. It appeared in these molecules that no significant variation of relaxation time was detectable within the limits of the accuracy of measurement.

Dicarlo and Smyth[6] measured 4-iodobiphenyl and 2-iodobiphenyl in the viscous nujol at 293K and obtained values of enthalpy of activation as 31.8 and 25.9 kJ mol^{-1}, respectively. The 4-iodobiphenyl molecule, having its dipole moment along the long axis, had a six times longer molecular relaxation time than that of 2-iodobiphenyl. This was attributed to a greater volume being swept out by the former molecule in orienting about its two short axes in comparison with 2-iodobiphenyl, where the principal component of the dipole lies along a short axis of the molecule, and relaxation occurs predominantly by rotation around the long axis. The larger value of enthalpy of activation (ΔH_E = 31.8 kJ mol^{-1}) for 4-iodobiphenyl than that of 2-iodobiphenyl (ΔH_E = 25.5 kJ mol^{-1}), is qualitatively consistent with the longer relaxation time of the former molecule from its rotation about the short molecular axes. However, it is notable that in the same medium the value of ΔH_E = 31.8 kJ mol^{-1} for 4-iodobiphenyl is smaller than the measured value of ΔH_E = 37.6 kJ mol^{-1} for 4-bromobiphenyl.[2]

Pitt and Smyth[7] in a study of three rigid ketone molecules of fairly similar size and shape of the type, viz., anthrone, fluorenone, and phenanthrenequinone in benzene solution at 293K, 313K, and 333K, obtained values of enthalpy of activation as 8.8, 8.4, and 10.9

kJ mol^{-1}, respectively. These workers have shown that the larger value of ΔH_E = 10.9 kJ mol^{-1} and longer relaxation time of phenanthrenequinone can be attributed to a greater volume being swept out by this molecule in rotation about the long axis. They also demonstrated from calculated values of moment of inertia of these solute molecules that phenanthrenequinone had a considerably larger moment of inertia about its long axis than the other two molecules. Also, a mean moment of inertia about axes a and c was in the order of progression of the observed relaxation time, which supports the investigation of the effect of molecular moment of inertia on relaxation time.

Pitt and Smyth[8] have also shown in a study of two large oblate ellipsoidal molecules of the types, metal-free heptaphenylchlorophenylporphyrazine and of ferric octaphenylporphyrazine chloride in benzene solution that the relaxation time of the latter was about 5/2 times that of the former. A surprising result was that both the compounds have about the same values of enthalpy of activation, (∿10.9 kJ mol^{-1}). However, the difference in relaxation time was attributed to the dipole moment of the metal free complex lying in the plane of the molecule while that of the ferric complex is perpendicular to the molecular plane.

Some aromatic halides have been measured by Hassell[9] in p-xylene at 288K. He reported the values of enthalpy of activation for fluoro-, chloro-, bromo-, and iodobenzenes as 5.9, 6.7, 8.4, and 9.2 kJ mol^{-1}, respectively. This indicates a slight increase in ΔH_E with increase in size of the molecule. However, a reasonable correlation was found between molecular relaxation time and the volume of the molecule for substituted mono-halobenzenes, o-dibenzenes, m-dibenzenes, and naphthalenes. In addition, Cooke[10] demonstrated for dilute solutions of substituted mono-halobenzenes, ortho and metadihalobenzenes in p-xylene, that there is within the limits of measurement, a linear relationship between the volume swept out and the activation energy.

In view of the existence of preceding correlations, it was thus thought that a closer examination on the dielectric behaviour of a series of rigid dipolar molecules belonging to the same family (the dipole moment lying along the longest axis) should be made. Thus, the present investigation was undertaken to study a fairly wide range of rigid molecules of progressively increasing molecular size in a considerably higher viscous medium, with a view to estimate any correlation between the enthalpy and entropy of activation, the enthalpy of activation and volume needed for reorientation of the solute molecules, and the dependence of molecular relaxation time on moment of inertia.

The rigid molecules chosen were of the type halo substituted benzenes and toluenes as well as some large molecules of the type halo substituted biphenyls. In order to increase the viscosity of the medium, this study was made by trapping solute molecules in a polystyrene matrix. One of the aims of this investigation was also to gain knowledge on the relaxation of a series of rigid polar molecules in such a matrix, since little data are available, and such data are necessary in the studies made in molecules which exhibit both molecular and intramolecular relaxation processes.

EXPERIMENTAL RESULTS

The dielectric measurements of halobenzenes, p-halotoluenes, and p-halobiphenyls molecularly dispersed in a polystyrene matrix were made in the frequency range of 10^2 - 10^5 Hz, and in one case (fluorobenzene) also in the range of 2.2×10^4 - 2.2×10^7 Hz.

The apparatus and procedures employed in the dielectric measurements, and the preparation of a polymer matrix have been described in a previous chapter (ChapterII).

The methods employed for the evaluation of relaxation and activation parameters have also been described previously (Chapter II).

All compounds used were purchased either from Aldrich Chemical Company or K & K Laboratory and were dried prior to use.

Experimental values of τ, $\log_{10} f_{max}$, β, ε''_{max}, ε_∞, and μ at various temperatures obtained for a series of rigid dipolar compounds are listed in Table III-1.

Table III-2 collects the values of ΔH_E, ΔS_E, along with

ΔG_E and τ values at 150K, 200K, and 300K for every system.

The plot of loss factor {$\varepsilon'' = \varepsilon''$ (obs) - ε'' (polystyrene)} against logarithm (frequency) for p-fluorobiphenyl is being given as a sample plot in Figure III-1. Figure III-2 shows a plot of $\log T\tau$ vs T^{-1} for p-fluorobiphenyl.

DISCUSSION

From good straight line plots of $\log T\tau$ as a function of reciprocal temperature, T^{-1} (e.g., Figure III-2 for p-fluorobiphenyl), the corresponding enthalpies and entropies of activation for fifteen rigid polar molecules of type halobenzenes, p-halotoluenes, p-bromoethylbenzene, p-halobiphenyls, p-nitrobiphenyl, and p-fluoronitrobenzene were obtained as listed in Table III-2.

The low values (range 0.13 - 0.26) of the distribution parameter 'β' (which imply a wide range of relaxation times) for all the rigid dipole molecular motion in a polystyrene matrix, agree well with the observations by Davies and Edwards,[3] and Davies and Swain[11] for a series of rigid molecules. The only exception being the fluorobenzene where 'β' ranges from 0.29 - 0.35. The higher values of 'β' for this molecule would not seem unreasonable, since the shape of fluorobenzene is almost spherical, and the dielectric absorption of this molecule would tend to show a Debye behaviour.

Table III-1 indicates that for each system studied, the temperature dependent 'β' values seem not to vary significantly over the temperature range in which full absorption curves have been observed.

Previous studies of halobenzenes in p-xylene solution at 288K by Hassell[9] have yielded the values of relaxation time, activation enthalpy, entropy, and free energy as given in Table III-3.

TABLE III-3

Molecule	ΔH_E (kJ mol^{-1})	ΔG_E (kJ mol^{-1})	ΔS_E (e.u)	$\tau \times 10^{12}$ (s)
Fluorobenzene	5.8	9.2	-2.4	6.8
Chlorobenzene	6.7	9.9	-2.5	10.2
Bromobenzene	8.3	10.6	-2.0	14.0
Iodobenzene	9.2	11.2	-1.6	18.0

The present study of fluoro-, chloro-, bromo-, and iodobenzenes dispersed in a polystyrene matrix yielded the enthalpy of activation as ∿9, 9, 13, and 16 kJ mol^{-1}, respectively. The results of halobenzenes in a polystyrene matrix differ from p-xylene solution studies mainly owing to an increase in viscosity of the medium, as the viscosity of polystyrene is considerably larger than that of p-xylene. This leads to larger values of enthalpy of activation in polystyrene matrix. The enthalpy of activation of 13 kJ mol^{-1} and 16 kJ mol^{-1} for bromo- and iodobenzenes, respectively, is to be compared with the values of 16.4 kJ mol^{-1}, [11] and

17.1 kJ mol^{-1}, [11] respectively, obtained for molecular relaxation in fairly similar sized cyclohexylchloride and cyclohexylbromide molecules in a polystyrene matrix. It is also to be noted that the temperature and frequency ranges for molecular relaxation in halobenzenes are very close to the corresponding values in the two halocyclohexanes.

It is notable (Table III-2) that for halobenzenes, p-fluorotoluene, and p-chlorotoluene, negative ΔS_E values are associated with small ΔH_E values. This is understandable in molecular terms as, if the rotation can occur for small excess energies, 'ΔH_E', then it is likely to involve the minimum of molecular reorganization 'ΔS_E' in the medium. This finding is also supported by Higasi's[1] earlier investigation, in which he examined 120 substances for which ΔH_E and ΔS_E are available for molecular relaxation processes, and tentatively postulated that: "the entropy change ΔS_E is zero or has a small negative value, if ΔH_E is below 13.4 kJ mol^{-1}". In addition, negative entropies of activation for a molecular relaxation process are also found in the literature. For example, Tay and Walker[12] reported for 1-bromonaphthalene (-3.8 J.K^{-1} mol^{-1}); for 2-fluoronaphthalene (-8.4 J.K^{-1} mol^{-1}); and for 2-chloronaphthalene (-10.5 J.K^{-1} mol^{-1}) in a polystyrene matrix. Moreover, Davies et al.[3,11] have reported that the ΔS_E values for molecular relaxation of cyclohexylchloride, cyclohexylbromide, anthrone, and camphor in a polystyrene matrix are -12.6, -20.0, -33.5, and -31.4 J K^{-1} mol^{-1}, respectively.

It can be seen (Table III-2) that in the temperature range of maximum absorption, the enthalpy of activation (ΔH_E) increases on passing from p-fluorotoluene to p-iodotoluene. The increasing sequence of ΔH_E values of 13, 26, 33, and 41 kJ mol^{-1} for p-fluoro-, p-chloro-, p-bromo-, and p-iodotoluenes, respectively, can be interpreted in terms of the increasing size of the molecule with increasing dimensions of the halogen atom. In addition, it should be noted (Table III-2) that the increase in ΔS_E values in halotoluenes is consistent with increasing size of the halo substituent.

Comparison of activation enthalpies for p-chloro- and p-bromotoluenes (Table III-2) in polystyrene with that of solution data [10] shows that the increase in ΔH_E by changing the medium (i.e., from p-xylene to polystyrene matrix) is appreciably larger, since the activation enthalpies for these two rigid molecules in p-xylene are 7.5 kJ mol^{-1} and 10.5 kJ mol^{-1}, respectively. Thus the change in ΔH_E for these molecules from p-xylene to polystyrene is $\sim$19 kJ mol^{-1} and $\sim$23 kJ mol^{-1}, respectively, whereas for chlorobenzene and bromobenzene it is ∿2 kJ mol^{-1} and ∿4 kJ mol^{-1}, respectively. Moreover, the values of ΔH_E and ΔS_E for p-chlorotoluene (26 kJ mol^{-1}; -9 J K^{-1} mol^{-1}), and p-bromotoluene (33 kJ mol^{-1}; 16 J K^{-1} mol^{-1}) agree well with the corresponding values for m-dinitrobenzene[13] (25 kJ mol^{-1}; -2.6 J K^{-1} mol^{-1}), and p-nitrotoluene[23] (35.1 kJ mol^{-1}; 15.6 J K^{-1} mol^{-1}) in polystyrene matrices, respectively, where the solute rigid molecules are of similar size.

It can be seen (Table III-2) that p-halosubstituted biphenyls have considerably larger values of temperature range, enthalpy of activation, and entropy of activation than those for halobenzenes and p-halotoluenes. This may be explained, as the dipole moment is directed along their long axis, and these molecules could have an appreciable contribution from an end-to-end tumbling motion. Such a relaxation contribution would lead the solute molecule to sweep out a larger volume, which could in turn lead to its experiencing a greater viscous drag from the polystyrene matrix, and hence reflects the larger ΔH_E and ΔS_E values for these molecules.

In general, one may note from the results of Table III-2 for halo substituted benzenes, toluenes, and biphenyls in the polystyrene matrices that the relaxation time and enthalpy of activation for the molecular process is very much dependent on the molecular size. For example, the relaxation time for p-fluoro-, p-chloro-, p-bromo-, and p-iodobiphenyls at 300K, each differed by a factor of ∿10. This could be explained by an increase in size of halo atom encountering a greater resistance with the molecular environment, provided by polystyrene, as a result increase in relaxation time and enthalpy with increasing molecular size. Such an effect was also noted by Tay and Walker[12] for halonaphthalenes. It is also apparent from the values of the relaxation time (τ at 200K) and enthalpies of activation(ΔH_E) for bromobenzene (6.5×10^{-8} s, 13 kJ mol^{-1}), p-bromotoluene (1.7×10^{-5} s, 33 kJ mol^{-1}), p-bromoethylbenzene (6.9×10^{-4} s, 38 kJ mol^{-1}), and p-bromobiphenyl (2.3×10^{4} s, 90 kJ mol^{-1}), respectively, that these two parameters are very sensitive to the length of the molecule on the long principal axis. The increase in length of the molecules on the long axis would lead to a greater swept volume around short axes, so that long molecules as p-bromobiphenyl shows a longer relaxation time and a larger enthalpy of activation than those of small bromobenzene molecule. However, the relaxation time, τ(200K), and the enthalpy of activation, ΔH_E, from the smallest molecule (fluorobenzene) to the largest molecule (p-iodobiphenyl) ranges from 10^{-9} to 10^{6} s and from 9 to 102 kJ mol^{-1}, respectively.

Smyth et al.[2] reported the enthalpy of activation and relaxation time for p-bromobiphenyl in nujol solution as 37.8 kJ mol^{-1} and 2580 x 10^{-12} s, respectively. A slight increase in the viscosity of the medium (polystyrene matrix) for p-bromobiphenyl yields appreciably large values of enthalpy (ΔH_E = 90 kJ mol^{-1}) and relaxation time (τ_{293K} = 5.9 x 10^{-4} s). On the other hand, in one of the less viscous mediums (p-xylene at 288K), the small chlorobenzene molecule has an enthalpy (ΔH_E = 6.7 kJ mol^{-1})[9] and a relaxation time (τ = 10.2 x 10^{-12} s).[9] In the polystyrene matrix it has (ΔH_E = 9 kJ mol^{-1}) and (τ_{288K} = 9.0 x 10^{-9} s), respectively. Thus, the comparison of these results for the small chlorobenzene molecule reveals that the increase in enthalpy and relaxation time from a p-xylene to a polystyrene medium is not very large. In view of the above comparison with solution data, it appears that the increase in a viscous molecular environment, provided by polystyrene matrix, would enhance the enthalpy and relaxation time by a larger factor for elongated molecules than those of small molecules. The reason is that the dipole direction in long molecules would involve extensive displacement of neighboring molecules with consequently greater dependence on the viscosity of the medium than that of small molecules.

It is to be noted that the p-halobiphenyls have much longer relaxation times at a given temperature than the corresponding relaxation times for o-halobiphenyls.[24] For example, the relaxation times of p-chloro-, p-bromo-, and p-iodobiphenyls at 300K in a polystyrene matrix are 3.6 x 10^{-5} s, 2.4 x 10^{-4} s, and 1.1 x 10^{-3} s, respectively. At the same temperature and medium, o-chloro-, o-bromo-, and o-iodobiphenyls have relaxation times of 1.4 x 10^{-7} s, 6.3 x 10^{-7} s, and 1.1 x 10^{-6} s, respectively. It is evident from these results that o-halobiphenyls have shorter relaxation times than those of the corresponding values for p-halobiphenyls. This observation could be explained by the fact that the dipoles in p-halobiphenyls are directed along their long axis. Thus relaxation of these molecules will likely occur by rotation about the short axes of the molecule, involving extensive displacement of surrounding polystyrene segments, and as a result this would give rise to longer relaxation times. In contrast to p-halobiphenyls, the principal component of the dipole in o-halobiphenyls lies along the short axis of the molecule. The relaxation of these molecules can occur also about the long axis, which would involve less rotational volume thus in turn lead to short relaxation times in o-halobiphenyls.

Figure III-3 shows the plot of entropy change of the activation process, ΔS_E, upon the corresponding enthalpy of activation, ΔH_E, for a series of rigid molecules, where the dipole moment lies along the principal axis. It would appear likely from Figure III-3, that within the accuracy of ΔH_E and ΔS_E values, a remarkably good linear correlation exists between enthalpy and entropy of activation for a given type of rigid molecules examined in a polystyrene matrix. The increase in ΔS_E values with the ΔH_E values, from halobenzenes to p-halobiphenyls, may be attributed as the rotation of larger molecules need larger volumes to sweep out, as a result; the larger the energy required for ΔH_E, the greater would be the local reorganization in the medium, ΔS_E. However, with the help of slope and intercept of a linear relation (Figure III-3), which the present molecular dipole relaxations provide, an equation has been derived which corresponds to:

$$\Delta S_E\ (\mathrm{J\,K^{-1}\ mol^{-1}}) = -72 + 2.2\ \Delta H_E\ (\mathrm{kJ\ mol^{-1}}).$$

Tay and Walker[12] found a linear relationship between the enthalpy of activation for the reorientation process and the volume swept out by the molecule for some halonaphthalenes dispersed in a polystyrene matrix.

In view of this correlation, it seemed worthwhile to test the relationship for a wide range of rigid molecules such as halobenzenes, p-halotoluenes, and p-halobiphenyls dispersed in a polystyrene matrix, where the dipole moment lies along the longest axis.

The molecular axes are represented as x, y, and z, which have lengths in the order of x > y > z. Figure III-4 illustrates the molecular axes, the position of the molecular dipole in the molecules, and the possible rotational axes.

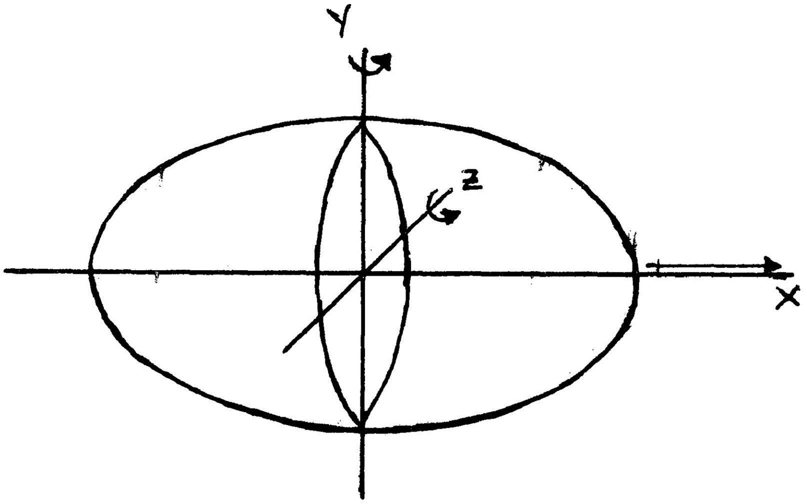


FIG III- 4

Since the dipole moment lies along the longest x-axis, so the rotation of the molecule may give rise to two extreme types of swept volume; one involves large displacement of surrounding molecules, corresponding to out-of-plane rotation, the other, a planar rotation involves less displacement of adjacent molecules. The axes about which dipole reorientation is possible presumably pass through the centre of mass. The centre of mass, effective radius and the length of the rotating species were determined either from molecular models or scale drawings, constructed from known bond lengths and bond angles.[14] The volumes of revolution were assumed to be cylinders. Hence, with the aid of known radius and length of rotating species, the volumes swept out by dipole reorientation about the two axes, perpendicular to the molecular moment, for 180^0 have been evaluated. Since the point about which the molecular rotation occurs is not known, the volumes swept out for rotation about the centre of volume were also calculated.

For rotation, either about the centre of mass or centre of volume, the swept volume is composed of two half cylinders, the radii of which were taken to be the maximum lengths of the molecule in each direction from the point of rotation and the cylinder lengths to be the length of the molecule in the direction parallel to the axis of rotation, Figure III-5.

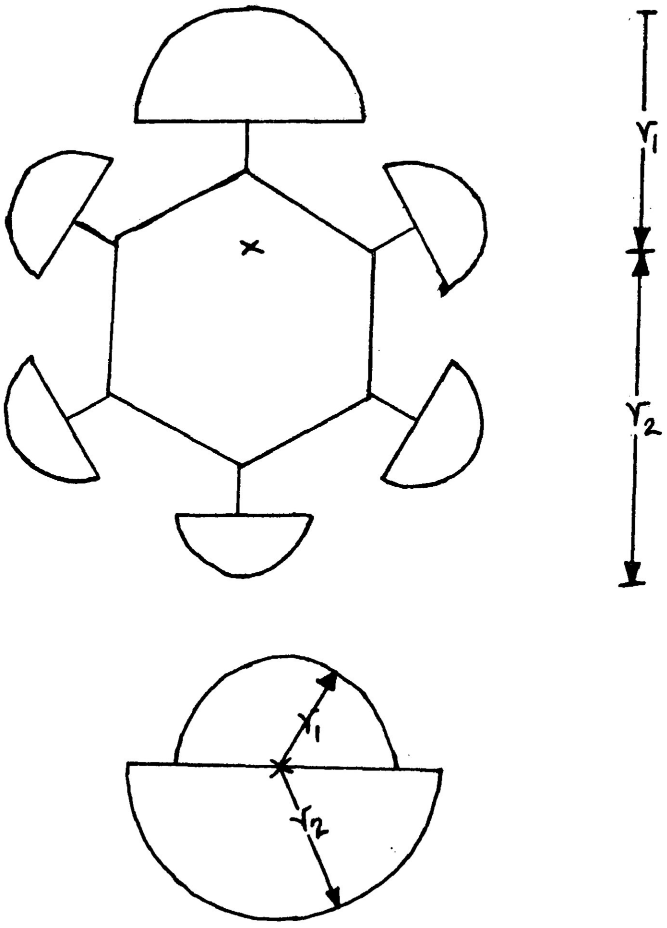


FIG III-5 VOLUME SWEPT OUT BY A ROTATING MOLECULE.

The volumes (V_y and V_z) swept out in molecular reorientation around the molecular axes y & z, respectively, are given in Table III-4.

When the enthalpy of activation and swept volumes for given types of molecules as halobenzenes, p-halotoluenes, and p-halobiphenyls are compared, it may be noted that these two parameters increase as the molecular size increases. This could be explained, for example, in p-halotoluenes, different halogen substitution would shift the centre of mass along the principal axis, thus leads to a larger effective radius. As a result there is an increase in rotational volume and a resultant increase in enthalpy of activation.

It should also be noted that small halobenzene molecules, such as fluorobenzene, with a contribution to its relaxation either from in-plane or out-of-plane rotation, would sweep out the smallest volume and presumably the least energy barrier. On the other hand, larger ΔH_E values for p-halobiphenyl molecules indicate that the relaxation of these molecules involves an appreciable contribution from an end-to-end tumbling motion. This would lead a larger swept volume, and in turn lead to its experiencing a greater viscous drag from the polystyrene matrix, as a result larger ΔH_E values for p-halobiphenyls. In addition, it is notable that at a given temperature, p-halobiphenyls have a relatively longer relaxation time, and also they have a larger variation in this parameter by varying the size of the molecule in comparison with those for halobenzenes and p-halotoluenes. This could be linked up, as in the former case the molecule with a larger halo atom leading to a larger swept volume for in-plane rotation and end-to-end out-of-plane rotation, thus resulting in a longer relaxation time and a larger enthalpy of activation. Such contribution seems to be comparatively much smaller in small halobenzene and p-halotoluene molecules.

The volumes are considered to be more accurate than ±10%. The enthalpies of activation were plotted against rotational volume about the z axis, V_z; the y-axis, V_y; and the mean volume, $V_{mean} = \frac{V_z + V_y}{2}$, for rotation about the centre of volume. Figures III-6 and III-7 show the plots of ΔH_E (kJ mol^{-1}) and logarithm of relaxation time (τ_{200K}) against the mean rotational volume 'V'_{mean} for rotation about the centre of volume, respectively.

A reasonable linear relationship between relaxation time and mean rotational volume is seen for all the molecules (Figure III-7). It can also be seen from Figure III-6 that there is almost a linear relationship between the volume swept out and the enthalpy of activation. However, it was found that some molecules deviate from this linear relation which is prone to be a larger error, either of two parameters or to their non similarity in shape.

Nevertheless, when graphs of enthalpy of activation, ΔH_E, were plotted against rotational volume about the z-axis, V_z, the largest rotational volume i.e., about y-axis, V_y, and the mean volume, $V_{mean} = V_y + V_z /2$, for rotation about the centre of mass. It would seem more likely that a linear correlation exists between ΔH_E and the local volume needed for reorientation of a given series of molecules having a similar shape factor.

In general it was found that plots for rotation about the z-axis were not as satisfactory as those observed for the y-axis volume, 'V_y', and the mean volume, 'V'_{mean}'. Figures III-8 and III-9 show the plots of ΔH_E against V_{mean}, and of ΔH_E against V_y for halobenzenes, p-halotoluenes, p-halobiphenyls, benzaldehyde, α,α,α-trichlorotoluene, p-fluoronitrobenzene, p-bromoethylbenzene, and p-nitrobiphenyl, for rotation about the centre of mass.

It can be seen from the plots (Figures III-8 and III-9) that, within the limits of experimental error, an appreciable linear correlation exists between the enthalpy of activation (ΔH_E) and the rotational volume. An emphasis is placed on a series of molecules having similar shape. This linear dependence of two parameters for molecules of similar shape is in good agreement with the observation by Davies et al.,[3] where cholest-4-ene-3-one departs from linear relation owing to its unusual shape compared with those of the other four molecules.

However, it can be seen from the Figures III-8 and III-9 that, for a given series of molecules, as the size of the molecule increases by different halogen substitution, there is an increase in the rotational volume, and hence an increase in the enthalpy of activation. The significant increase in the values of enthalpy of activation and rotational volume, on passing from fluoro- to iodobenzene, from p-fluoro- to p-iodotoluene, and from p-fluoro- to p-iodobiphenyl are in the correct sequence.

Figures III-10, III-11, and III-12 show the plots of the free energy of activation, ΔG_E (200K), versus the mean volume, V_{mean}, and the largest possible rotational volume, V_y. A reasonable linear relationship is again seen for halobenzenes, p-halotoluenes, and p-halobiphenyls.

DEPENDENCE OF RELAXATION TIME ON THE MOLECULAR MOMENT OF INERTIA

Many theoretical attempts have been made to prove that the dielectric behaviour of molecules may depend upon their moment of inertia.

Firstly, in Debye's theoretical model, the mean orientation moment of molecules in time-dependent fields has been evaluated in terms of orientational diffusion, expressed by a probability function 'f'. The dissipative character of the problem is introduced by a molecular resistive constant 'ζ', which relates torque 'L' of the molecular field to the angular velocity $\delta\theta/\delta t$ by:

$$L = \zeta \left(\frac{\delta\theta}{\delta t}\right) \qquad \text{III-1}$$

With a sinusoidal field $F = F_0 e^{i\omega t}$, the torque on a molecule of dipole moment μ at θ to this field is:

$$L = -\mu F \sin\theta \qquad \text{III-2}$$

Consideration of the equation of continuity in configuration space and the assumption that 'f' reduced to a linearized equilibrium Boltzmann function led Debye to the solution:

$$4\pi f = \frac{1 + \mu F_0 \cos \theta}{kT\,(1 + i\omega\tau)} \qquad \text{III-3}$$

the molecular relaxation time being defined by:

$$\tau = \frac{\zeta}{2kT} \qquad \text{III-4}$$

It was first noted by Rocard,[15] referred to by Whiffen,[16] that Debye's equation does not take into account inertia effect in Eqn. III-1, and a modified form was later suggested by Powles[17] as:

$$I\frac{d^2\theta}{dt^2} + \zeta\frac{d\theta}{dt} = L \qquad \text{III-5}$$

where 'I' is the "effective molecular moment of inertia". Powles considered this effect of molecular inertia in dilute solutions of a polar solute in a non polar solvent, and obtained a relationship:

$$\frac{\tan\delta}{\tan\delta_{I=0}} = \frac{\{1 + (1 - \alpha)x\}\{1 + (\omega\tau)^2\}}{\{1 - x(\omega\tau)^2\}^2 + (\omega\tau)^2\,\{1 + (1 - \alpha)x\}^2} \qquad \text{III-6}$$

where $\tan\delta$ = loss tangent = $\frac{\varepsilon''}{\varepsilon'}$, α, ω, and τ having normal dielectric meaning, and, $x = \frac{I}{2kT\tau^2}$

or, $I \alpha 2kT\tau^2$ III-7

Gross[19] and Sack[18] found that the corrections required by the Debye relaxation formulae were relatively small, being largest for frequencies near the absorption maximum ($\omega\tau \approx 1$). However, the modified Debye equation that these authors obtained is in agreement with that of Powles[17] (Eqn. III-7).

Bauer[20] presented a theory of dielectric relaxation, closely analogous to Eyring's rate theory of dielectric relaxation, and expressed the relaxation time as

$$\tau = \left(\frac{2\pi I}{kT}\right)^{\frac{1}{2}} \left(\frac{\sigma_1\sigma_2}{\sigma_1+\sigma_2}\right) \frac{1}{L} \exp\left(\frac{E_m}{kT}\right) \qquad \text{III-8}$$

where σ_1 and σ_2 are configuration partition functions corresponding to two equilibrium positions. L = effective length of the potential barrier. E_m = Energy barrier separating the initial and final orientations of the dipole.

Later, Hill _et al._,[21] by considering that there is little prospect of achieving specific values for σ_1, σ_2 and 'L' in a liquid or a solution state, and might be $\sigma_1 \simeq \sigma_2$, modified Bauer's rate expression Eqn. III-8 to the form:

$$\tau = \left(\frac{2\pi I}{kT}\right)^{\frac{1}{2}} \exp\left(\frac{-\Delta S^*_B}{R}\right) \left(\frac{\Delta H^*_B}{RT}\right) \qquad \text{III-9}$$

However, in this expression Eqn. III-9, the change in the moment of inertia accounts for the difference in τ. In view of this expression (Eqn. III-9), together with the preceding discussion of the theoretical models, and with the increased dielectric data now available, It seemed worthwhile to examine these theoretical correlations paractically to determine whether experimentally observed 'τ' is dependent on the moment of inertia 'I' for a series of rigid molecules dispersed in a polystyrene matrix.

The molecules examined here are halobenzenes, and p-halotoluenes. The centre of mass co-ordinates for all the molecules were calculated by the usual manner.

$$X_{cm} = \sum_{i=i}^{i=1} \left\{\frac{M_i\ x_i}{Mi}\right\} \qquad \text{III-10}$$

$$Y_{cm} = \sum_{i=i}^{i=1} \{\frac{M_i Y_i}{Mi}\} \qquad \text{III-11}$$

where X and Y are the co-ordinates of the individual atoms, and 'M' their atomic weights.

The principal moments of inertia (I_a, I_b, and I_c) of the molecules by the use of atomic spacings as derived from i.r. and diffraction measurements[14], were estimated from the equation:

$$I_a = \{ \sum_{i=i}^{i=1} M_i r_i^2\} \times \frac{10^{-16}}{N} \quad \text{g. cm}^2 \qquad \text{III-12}$$

where 'M' has the same meanings as before,

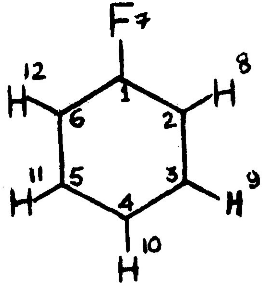
'r_i' = the distance in Ångstrom units from the 'a' axis to the centre of mass of the ith atom,

'N' = Avagadro number.

The axes a, b, and c all meet at the centre of mass. Since the molecules have been assumed to be planar, then the moment of inertia about the axis perpendicular to the plane of the ring (I_c) is equal to the sum of the other two in the plane of the ring, i.e., $I_c = I_a + I_b$. As the resultant dipole moment in these molecules lies along the a - axis, and as there is no orienting torque about this axis, only the remaining two moments of inertia, I_b and I_c, were used in averaging for "I".

Figure III-13 shows a sample calculation of the moment of inertia for fluorobenzene.

FIGURE III-13 Moment of inertia calculation for Fluorobenzene



The atoms are numbered as shown in the figure. Thus, co-ordinates of C_1 and C_2 are $x_1\ y_1$ and $x_2 y_2$ respectively.

Centre of mass co-ordinates $X_{cm} = 0$

and $$Y_{cm} = \frac{\{M_C(Y_1+2Y_2+2Y_3) \ + \ M_H(2Y_8 + 2Y_9 - Y_{10}) + M_F Y_7\}}{6M_C + 5M_H + M_F}$$

Moments of inertia = 1 Å = 10^{-8} cm

$$I_a = \{4\ M_C\ X_2^{\ 2} + 4\ M_H\ X_8^{\ 2}\} \times \frac{10^{-16}}{N}$$

$$I_a = 144.5 \times 10^{-40} \text{ gm cm}^2$$

$$I_b = \{M_C \{ (Y_{cm}-Y_1)^2 +2 (Y_{cm}-Y_2)^2 +2 (Y_{cm}-Y_3)^2 + (Y_4)^2 \}$$

$$+ M_H \{ 2 (Y_{cm}-Y_8)^2 +2 (Y_{cm}-Y_9)^2$$

$$+ (Y_{10})^2 \} +M_F (Y_7 -Y_{cm})^2 \} X \frac{10^{-16}}{N}$$

$$I_b = 332.6 \times 10^{-40} \text{ gm cm}^2$$

As the molecule is considered to be planar;

$$I_c = I_a + I_b$$

$$I_c = 477.1 \times 10^{-40} \text{ gm cm}^2$$

and the mean moment of inertia is:

$$I = \frac{I_b + I_c}{2} = 404.85 \times 10^{-40} \text{ gm cm}^2.$$

Table III-5 lists the values of principal moments of inertia and molecular relaxation times for monohalobenzenes and p-halotoluenes in a polystyrene matrix.

A good agreement of the ones calculated by these procedures with those determined by other workers, where data are available, can be seen in Table III-6.

TABLE III-6: Comparison of calculated "I" values (x 10^{40}) with those of other workers.

gm. cm^2

Compound	This Study	References		
		(9)	(22)	(17)
Fluorobenzene	404.8	403.85	402	--
Chlorobenzene	607.5	616 95	615	--
Bromobenzene	934.1	930.5	940	912
Iodobenzene	1214.5	1154.5	1210	--
p-Chlorotoluene	944.2	911.5	--	--
p-Bromotoluene	1391.5	1346.6	--	--

It should be noted that all the molecules have considerably larger moments of inertia about their axes perpendicular to the plane of the ring, i.e., "I_c" than the other two axes (I_a and I_b) in the plane of the ring and have much smaller values for the moment of inertia about the axis "a", i.e., I_a.

The square root of the arithmetical mean ($I = \frac{I_b + I_c}{2}$) and the geometric mean $\sqrt{I_b I_c}$ are almost similar within the limits of error, so in all the plots the arithmetical mean has been used. Graphs of the mean moment of inertia "I" and the square root of "I" against the logarithm of the relaxation time at 200K have been plotted for halobenzenes, and p-halotoluenes, as shown in Figures III-14 and III-15. It also seems that such a plot of "I" or $\sqrt{I}$ vs $\log\tau$ has an advantage on other molecular factor, that the moment of inertia calculation is solely based on the axes about which molecular rotation may occur.

However, it may be noted that both the plots (Figures III-14, and III-15) show similar trends; molecules having halo substituents on 1 or 4 positions of the aromatic ring give considerably constant $I/\log\tau_{200K}$ and $\sqrt{I}/\log\tau_{200K}$ ratios. From Table III-5, it would seem that the mean moment of inertia "I" governs the magnitude of the relaxation time at a given temperature (τ at 200K) and the enthalpy of activation (ΔH_E) for a given type of molecules. For example, the p-iodotoluene molecule has a comparatively greater value of "I" (1786.9×10^{-40} gm cm^2), resulting in higher values of the relaxation time and enthalpy of activation than those of other molecules. However, on passing from fluorobenzene to p-iodotoluene, the mean moment of inertia "I" (about axes b and c) is in the order of progression of the observed relaxation times (τ_{200K}), the exceptions being p-fluoro- and p-chlorotoluenes, as the former molecule is very similar in size to chlorobenzene, thus having approximately closer values of 'τ'$_{200K}$ and 'I'.

Figure III-16 shows the plot of log $\sqrt{I}$ against ΔH_E for halobenzenes and p-halotoluenes. It is seen that the enthalpy of activation is dependent upon the moment of inertia. Thus, increasing the size of the molecule by halogen substitution leads to an increase in the enthalpy of activation, ΔH_E, which was observed in all the molecules examined. However, it can be seen from Figure III-16 that, within the limits of experimental error, a linear correlation exists between the enthalpy of activation (ΔH_E) and the moment of inertia (log $\sqrt{I}$) for a series of rigid molecules where the shape is very similar.

The plots of I and $\sqrt{I}$ against logτ are seen to predict the effect of the moment of inertia on relaxation time. However, from our plots (Figures III-14 and III-15), it appears that, within the accuracy of two parameters, a remarkably good correlation exists between the moment of inertia and the relaxaton time for a given type of molecule with its dipole moment along the principal axis. This observation is supported well by the theoretical approaches to the dependence of molecular inertia on relaxation time.

In conclusion, it would seem likely that there is within the limits of measurement, a linear relationship between ΔH_E and ΔS_E, ΔH_E and rotational volume, and ΔH_E and log $\sqrt{I}$ in a wide range of rigid molecules dispersed in polystyrene matrices. In addition, dependence of relaxation time on the molecular moment of inertia was also found for the molecules examined. In view of these findings, it would seem worthwhile to carry out further investigations by changing the inclination of the dipole to the axis of rotation on the relaxation parameters.

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TABLE III-1 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS FOR SOME RIGID DIPOLAR COMPOUNDS IN POLYSTYRENE MATRICES AT A VARIETY OF TEMPERATURES

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.95M Fluorobenzene				
94.0	1.15	5.14	0.36	26.8	--	--
97.0	0.582	5.44	0.32	27.9	--	--
101.5	0.391	5.61	0.31	29.4	--	--
104.3	0.231	5.84	0.29	30.9	--	--
118.4	0.083	6.28	0.36	32.2	--	--
		0.62M Chlorobenzene				
89.1	119.4	3.12	0.14	6.2	2.52	0.546
94.3	42.8	3.57	0.13	6.5	2.51	0.597
97.0	21.5	3.87	0.15	6.8	2.51	0.576
102.0	13.1	4.09	0.18	7.1	2.52	0.551
108.0	7.4	4.33	0.20	7.5	2.53	0.549
114.8	4.71	4.53	0.23	7.8	2.53	0.543
118.9	3.57	4.65	0.24	8.0	2.54	0.541
124.5	2.69	4.77	0.26	8.0	2.54	0.537
		0.53M Bromobenzene				
101.2	221.0	2.86	0.19	5.5	2.62	0.500
104.3	137.7	3.06	0.18	5.7	2.62	0.523
108.9	64.8	3.39	0.19	6.0	2.62	0.533
112.6	42.7	3.57	0.19	6.2	2.62	0.553
119.8	14.6	4.04	0.20	6.7	2.62	0.586
126.0	8.55	4.27	0.21	6.9	2.63	0.591
129.8	7.14	4.35	0.23	7.1	2.63	0.586
		0.49M Iodobenzene				
128.7	177.0	2.95	0.23	4.8	2.73	0.487
137.0	64.9	3.39	0.23	5.1	2.73	0.519
142.4	41.9	3.58	0.23	5.4	2.73	0.546
147.9	23.5	3.83	0.22	5.6	2.73	0.576
152.3	15.3	4.02	0.22	5.7	2.73	0.591
157.7	8.94	4.25	0.21	6.0	2.73	0.627
163.4	6.01	4.42	0.21	6.2	2.73	0.647

TABLE III-1 continued.....

T(K)	$10^6\tau$(s)	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
0.64M p-Chlorotoluene						
162.9	258.0	2.79	0.19	13.9	2.63	0.908
166.7	177.2	2.95	0.18	14.3	2.63	0.957
176.6	54.1	3.47	0.19	15.3	2.63	1.00
180.8	36.8	3.64	0.18	15.7	2.63	1.02
185.1	21.1	3.88	0.19	16.1	2.63	1.04
195.5	8.80	4.26	0.21	17.1	2.64	1.05
0.46M p-Bromotoluene						
176.2	284.7	2.75	0.17	12.7	2.57	1.16
182.9	133.3	3.08	0.17	13.2	2.57	1.20
189.4	54.7	3.46	0.16	13.7	2.56	1.24
197.0	22.0	3.86	0.16	14.2	2.55	1.30
203.6	10.2	4.20	0.17	14.7	2.55	1.32
210.2	5.8	4.37	0.17	15.0	2.54	1.35
214.0	3.6	4.55	0.17	15.4	2.54	1.37
0.50M p-Iodotoluene						
198.5	313.1	2.71	0.18	9.6	2.58	0.988
205.8	156.9	3.01	0.18	10.0	2.57	1.03
213.0	77.8	3.31	0.17	10.3	2.56	1.10
220.4	30.5	3.72	0.16	10.6	2.55	1.15
228.0	13.8	4.06	0.17	11.0	2.55	1.18
235.3	6.11	4.42	0.17	11.4	2.54	1.22
240.9	3.25	4.69	0.16	11.7	2.53	1.26
0.62M p-Fluorobiphenyl						
256.1	320.0	3.00	0.20	15.1	2.68	1.14
263.2	93.2	3.23	0.21	15.3	2.68	1.17
268.0	56.5	3.45	0.21	15.5	2.68	1.19
272.5	36.7	3.64	0.20	15.6	2.68	1.22
277.7	21.2	3.88	0.21	15.9	2.68	1.22
283.0	12.5	4.11	0.21	16.1	2.68	1.23
287.8	8.22	4.29	0.22	16.3	2.67	1.24
292.8	5.28	4.48	0.22	16.4	2.67	1.24
297.9	3.81	4.62	0.23	16.5	2.68	1.22

TABLE III-1 continued.....

T(K)	$10^6\tau$(s)	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
0.58M p-Chlorobiphenyl						
282.7	233.0	2.83	0.21	14.1	2.63	1.21
287.6	151.4	3.02	0.20	14.3	2.62	1.26
294.0	70.3	3.35	0.20	14.6	2.62	1.29
300.2	36.8	3.64	0.19	15.0	2.61	1.34
305.0	20.7	3.89	0.20	15.2	2.61	1.36
0.48M p-Bromobiphenyl						
303.1	163.2	2.99	0.22	11.8	2.64	1.25
305.9	119.0	3.13	0.21	12.0	2.63	1.28
310.2	71.9	3.35	0.21	12.3	2.63	1.30
313.3	52.4	3.48	0.21	12.4	2.63	1.33
316.1	38.1	3.62	0.21	12.6	2.63	1.34
319.9	23.2	3.84	0.21	12.9	2.63	1.37
0.39M p-Iodobiphenyl						
312.6	212.5	2.87	0.21	9.7	2.68	1.27
315.3	157.0	3.01	0.23	9.9	2.68	1.24
318.0	110.4	3.16	0.23	10.0	2.69	1.25
326.1	44.6	3.55	0.21	10.6	2.69	1.34
328.5	29.0	3.74	0.19	10.9	2.69	1.43
331.1	22.8	3.84	0.21	11.3	2.70	1.42
0.53M p-Fluoronitrobenzene						
152.1	313.3	2.71	0.18	17.2	2.66	1.11
156.6	201.9	2.90	0.17	18.0	2.66	1.16
164.1	97.2	3.21	0.17	19.1	2.65	1.24
171.4	36.5	3.64	0.17	20.1	2.65	1.29
178.3	15.3	4.02	0.17	21.3	2.65	1.33
184.5	8.47	4.27	0.19	22.4	2.66	1.34
190.0	5.84	4.44	0.20	23.1	2.67	1.35
195.8	3.35	4.68	0.20	24.0	2.67	1.37

TABLE III-1 continued.....

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
		0.50 p-Bromoethylbenzene				
206.2	291.1	2.74	0.20	13.3	2.65	1.10
209.4	236.4	2.83	0.20	13.8	2.66	1.12
217.3	119.8	3.12	0.19	14.3	2.65	1.20
224.2	58.4	3.44	0.18	14.9	2.65	1.26
231.6	26.6	3.78	0.17	15.4	2.64	1.34
238.9	12.9	4.09	0.18	16.0	2.64	1.38
246.2	7.43	4.33	0.18	16.5	2.65	1.40
253.7	4.25	4.57	0.19	17.0	2.65	1.42

NOTE: A blank space (--) indicates that the information was not available.

TABLE III-2 EYRING ANALYSIS RESULTS FOR SOME RIGID DIPOLAR COMPOUNDS IN POLYSTYRENE MATRICES

			τ(s)			ΔG_E(kJ mol^{-1})		ΔH_E	ΔS_E
Molecule	T(K)	150K	200K	300K	150K	200K	300K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Fluorobenzene	94 - 118	9.1×19^{-9}	1.2×10^{-9}	1.4×10^{-10}	13	14	17	~ 9	
Chlorobenzene	89 - 125	4.3×10^{-7}	5.7×10^{-8}	6.8×10^{-9}	18	21	27	9	-60
Bromobenzene	101 - 130	1.1×10^{-6}	6.5×10^{-8}	3.5×10^{-9}	19	21	25	13	-41
Iodobenzene	129 - 163	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	22	24	29	16	-43
p-Fluorotoluene*	101 - 145		7.0×10^{-8}	3.7×10^{-9}		21		13	-41
p-Chlorotoluene	163 - 196	1.6×10^{-3}	5.8×10^{-6}	1.9×10^{-8}	28	28	29	26	- 9
p-Bromotoluene	176 - 214	1.8×10^{-2}	1.7×10^{-5}	1.4×10^{-8}	31	30	28	33	16
p-Iodotoluene	199 - 241	1.7	3.1×10^{-4}	5.1×10^{-8}	37	35	32	42	33
p-Fluorobiphenyl	256 - 298	1.1×10^{5}	6.0×10^{-1}	3.0×10^{-6}	50	48	42	59	57
p-Chlorobiphenyl	283 - 305	1.2×10^{9}	2.2×10^{2}	3.6×10^{-5}	62	57	48	76	93
p-Bromobiphenyl	303 - 320	2.0×10^{12}	2.4×10^{4}	2.4×10^{-4}	71	65	53	90	123
p-Nirtobiphenyl*	290 - 315		1.5×10^{4}	4.6×10^{-4}		64	54	86	106
p-Iodobiphenyl	313 - 331	1.5×10^{15}	1.4×10^{6}	1.2×10^{-3}	79	72	57	102	152
p-Fluoronitrobenzene	152 - 196	4.8×10^{-4}	2.4×10^{-6}	1.1×10^{-8}	26	27	28	25	- 9
p-Bromoethylbenzene	206 - 254	1.9	6.9×10^{-4}	2.2×10^{-7}	37	36	35	38	9

*Data provided through the courtesy of A. Lakshmi and T. Vincenzoni of this laboratory.

NOTE: A blank space indicates that the information was not available.

TABLE III-4 ROTATIONAL VOLUMES (Å^3 per molecule) ABOUT THE MOLECULAR AXES FOR A NUMBER OF RIGID MOLECULES

MOLECULE	Effective radius (Å)	Swept volume about centre of mass			Swept volume about centre of volume		
		V_y	V_z	$V_{mean} = \frac{V_y + V_z}{2}$	V_y	V_z	$V_{mean} = \frac{V_y + V_z}{2}$
Fluorobenzene	5.43	364.5	200.22	282.36	279.62	153.59	216.6
Chlorobenzene	6.06	453.12	248.9	351.01	339.73	186.61	263.17
Bromobenzene	8.12	814.02	477.62	645.82	363.57	213.32	288.44
Iodobenzene	8.46	882.94	544.72	713.83	396.14	244.39	320.26
p-Fluorotoluene	5.56	380.83	198.79	289.81	343.32	179.21	261.26
p-Chlorotoluene	6.41	506.12	285.96	396.04	409.56	231.4	320.48
p-Bromotoluene	7.75	739.38	432.76	586.07	439.48	257.23	348.35
p-Iodotoluene	8.62	915.77	551.54	733.65	471.22	283.8	377.51
p-Fluorobiphenyl	7.95	778.3	383.4	580.9	682.2	336.1	509.1
p-Chlorobiphenyl	8.62	916.1	517.8	716.92	775.8	438.5	607.1
p-Bromobiphenyl	9.87	1200.9	706.45	953.67	812.95	478.25	645.6
p-Iodobiphenyl	11.03	1497.55	926.85	1212.2	859.0	531.65	695.3
p-Nirtobiphenyl	9.14	1102.5	610.2	856.35	786.4	453.37	619.88
p-Fluoronitrobenzene	6.4	404.11	293.71	348.91	299.75	217.85	258.8
p-Bromoethylbenzene	8.21	653.15	562.05	607.6	442.85	381.05	411.95
α,α,α,Trichlorotoluene	8.37	869.8	654.1	761.95	383.64	288.5	336.07
Benzaldehyde	6.0	399.3	261.02	330.16	307.8	201.2	254.5

TABLE III- 5 PRINCIPAL MOMENTS OF INERTIA AND MOLECULAR RELAXATION TIMES (τ at 200K) OF SOME RIGID MOLECULES IN POLYSTYRENE MATRICES

	$\times 10^{40}$ gm cm^2				$\times 10^{20}$ (gm cm^2)$^{1/2}$		
MOLECULE	I_a	I_b	I_c	$I = \frac{I_b + I_c}{2}$	$\sqrt{I}$	$\sqrt{I_b I_c}$	τ_{200K} (s)
Fluorobenzene	144.5	332.6	477.1	404.85	20.12	19.95	1.2×10^{-9}
Chlorobenzene	144.5	535.3	679.8	607.55	24.64	24.56	5.7×10^{-8}
Bromobenzene	144.5	861.8	1006.3	934.05	30.56	30.51	6.5×10^{-8}
Iodobenzene	144.5	1142.2	1286.7	1214.45	34.84	34.81	5.7×10^{-7}
p-Fluorotoluene	150.96	591.42	742.38	666.9	25.82	25.74	7.0×10^{-8}
p-Chlorotoluene	150.96	868.69	1019.65	944.17	30.72	30.67	5.8×10^{-6}
p-Bromotoluene	150.96	1316.03	1466.99	1391.51	37.3	37.27	1.7×10^{-5}
p-Iodotoluene	150.96	1711.4	1862.36	1786.88	42.2	42.25	3.1×10^{-4}
Benzaldehyde	175.32	515.73	691.05	603.39	24.56	24.43	-----

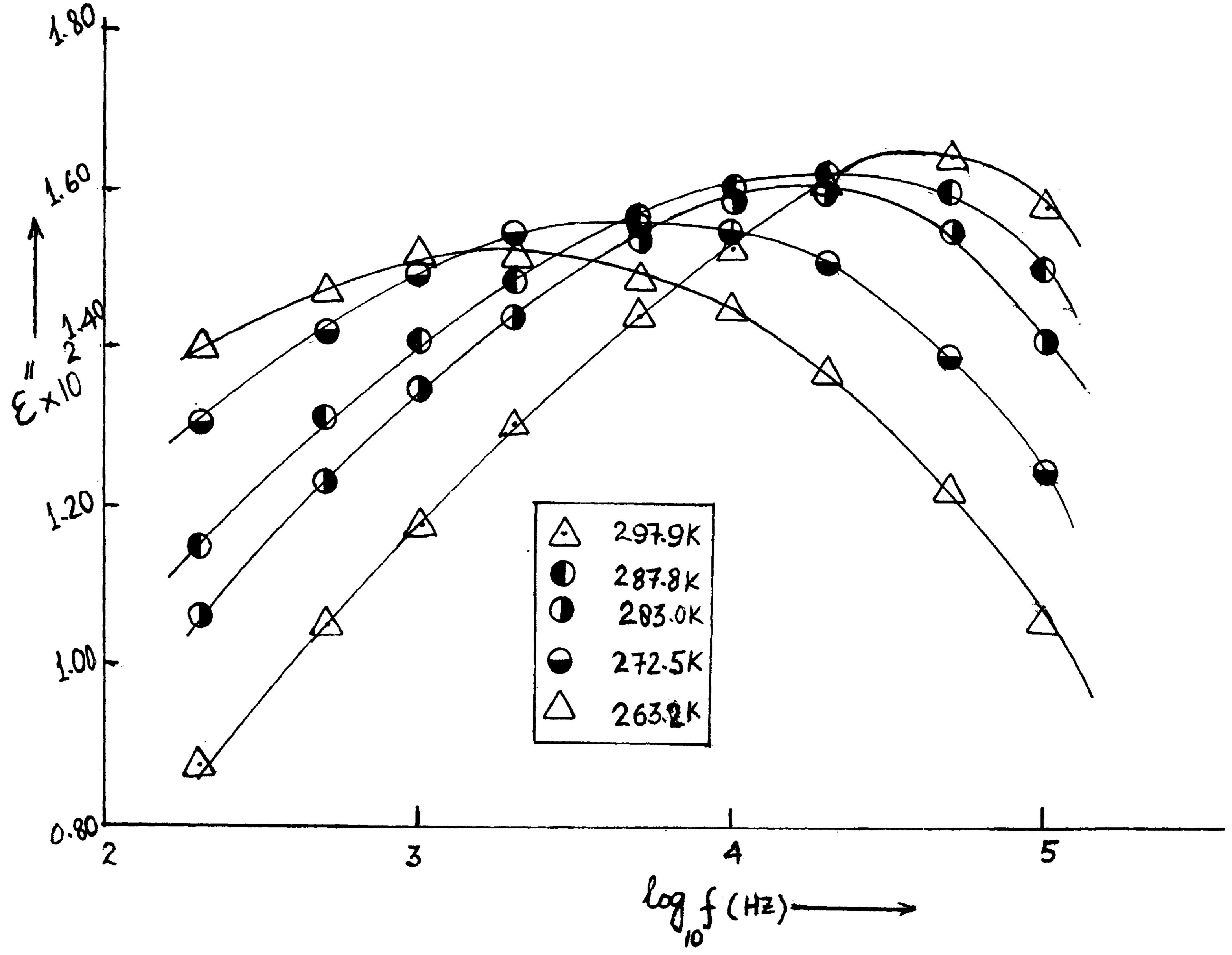


FIG III-1 Plot of Dielectric loss factor vs $\log_{10} f$ for p-Fluorobiphenyl in Polystyrene

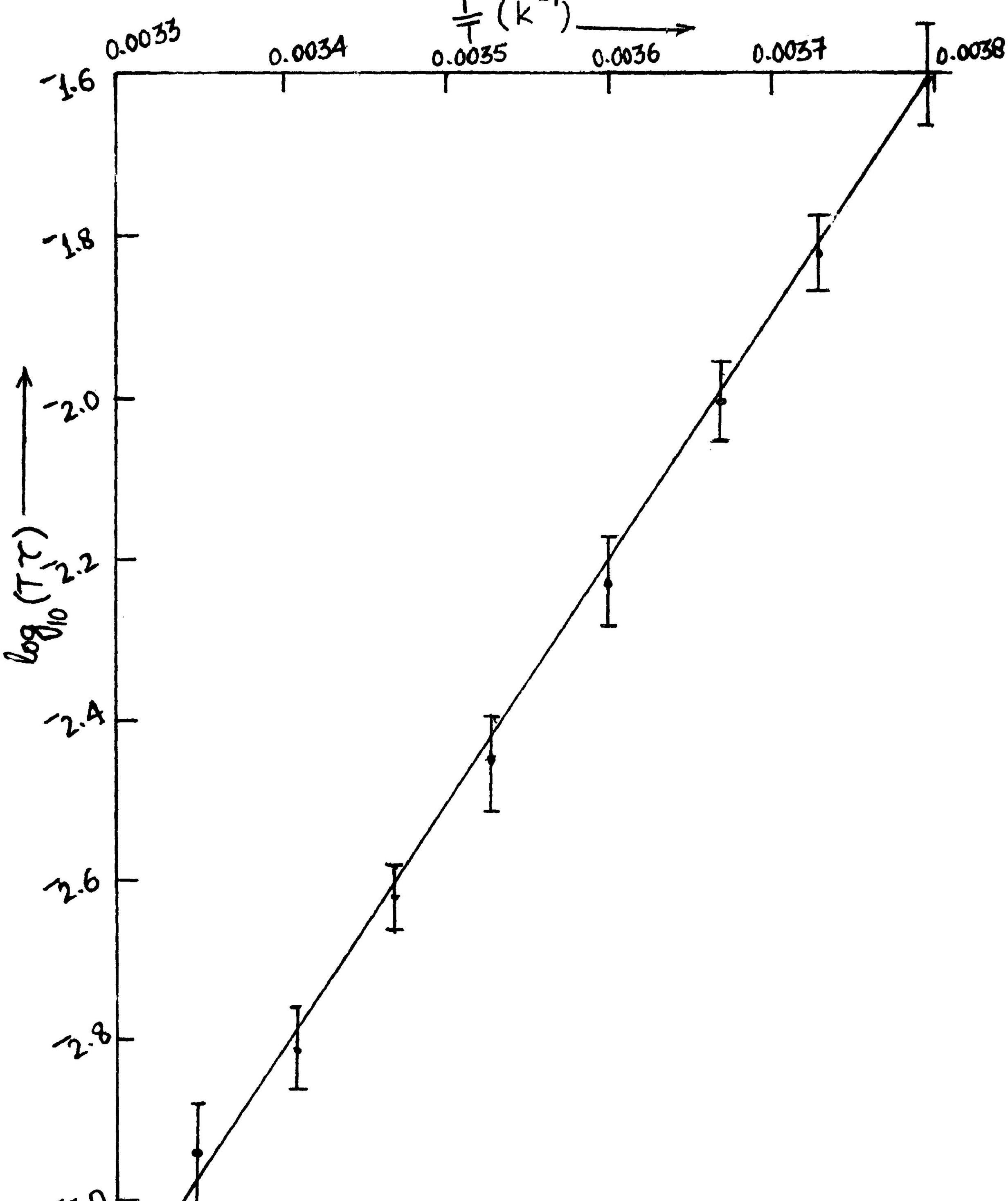
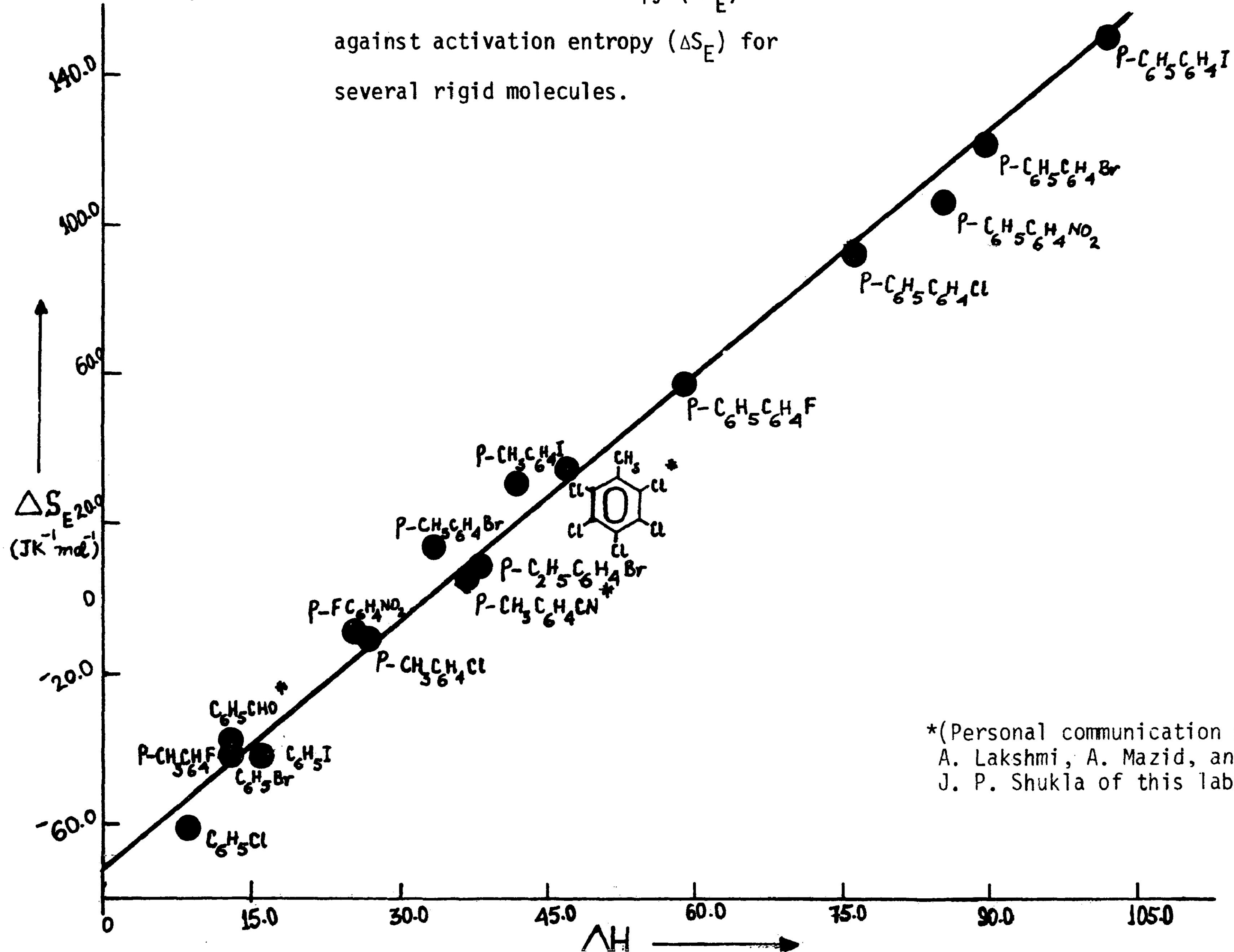


FIG III-2

Eyring plot of $\log_{10}$ ($T\tau$) vs $\frac{1}{T}$ for p-fluorobiphenyl in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values.

FIGURE III-3: Plot of activation enthalpy (ΔH_E) against activation entropy (ΔS_E) for several rigid molecules.



*(Personal communication with A. Lakshmi, A. Mazid, and J. P. Shukla of this laboratory.)

FIGURE III-6: Plot of activation enthalpy (ΔH_E) against mean volume swept out (V_{mean}) about the centre of volume.

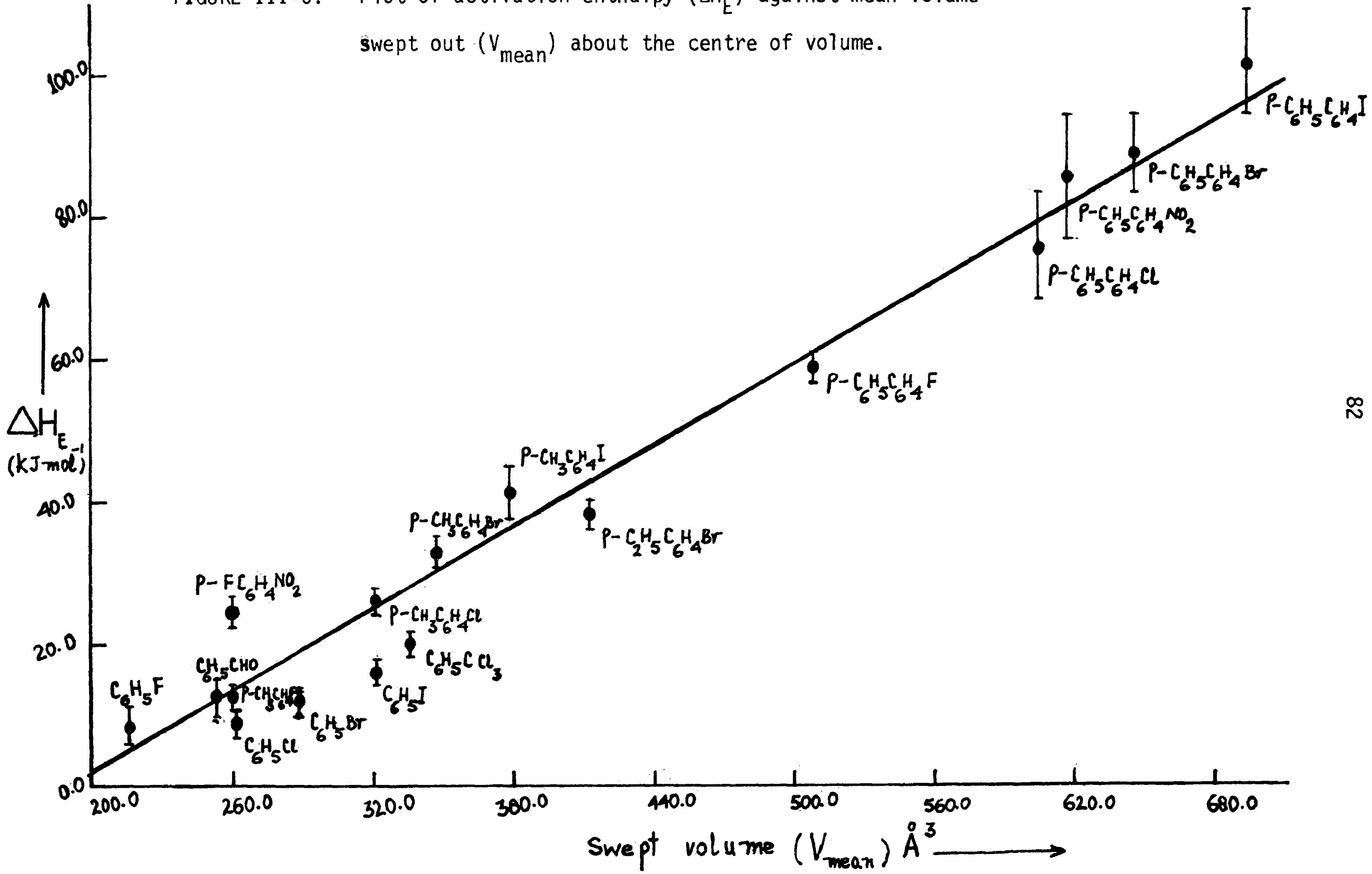


FIGURE III-7: Plot of logarithm relaxation time ($\log_{10}\tau_{200K}$) against mean volume swept out (V_{mean}) about the centre of volume.

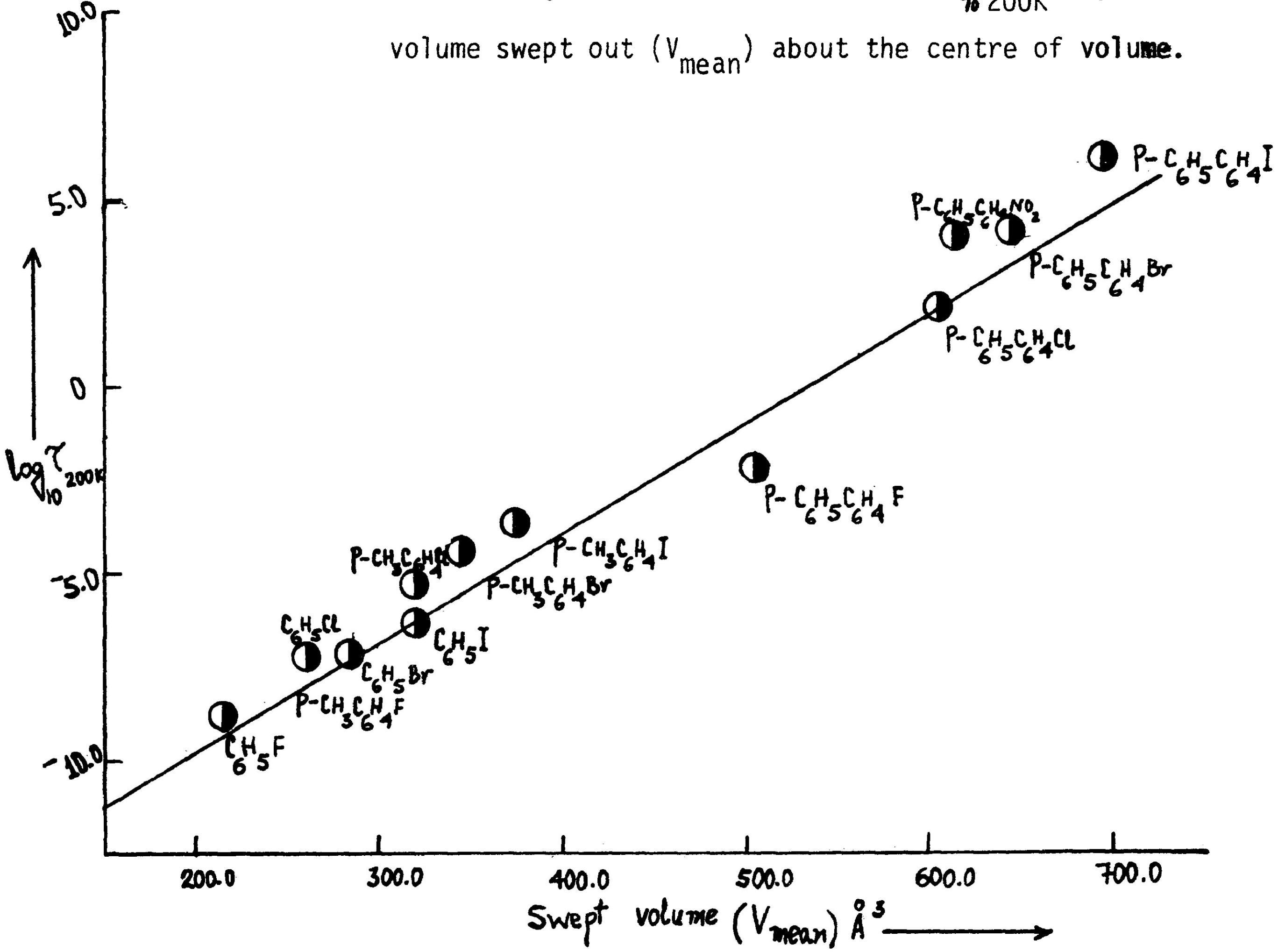


FIGURE III-8: Plot of activation enthalpy (ΔH_E) against mean volume swept out (V_{mean}) about the centre of mass.

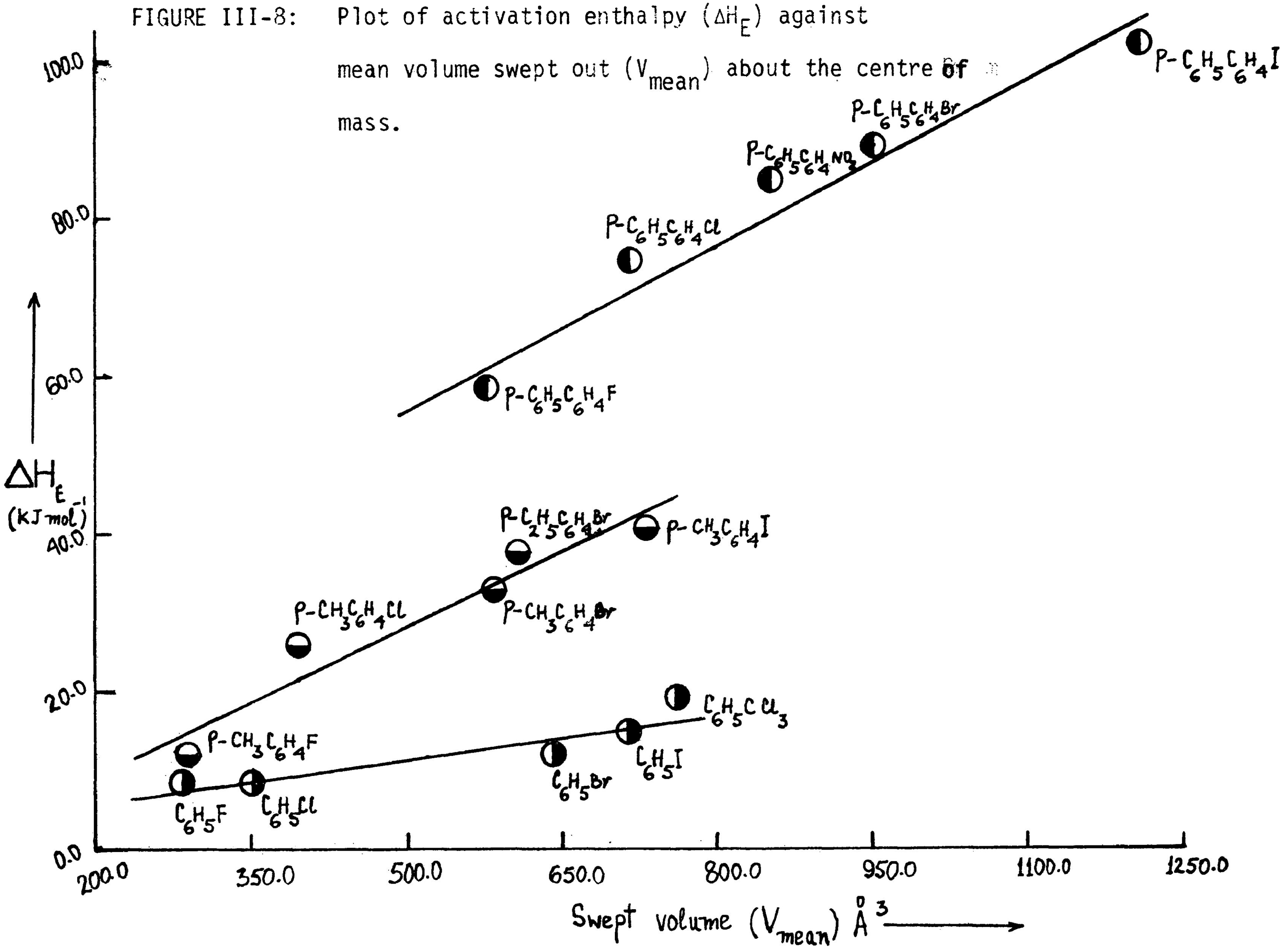
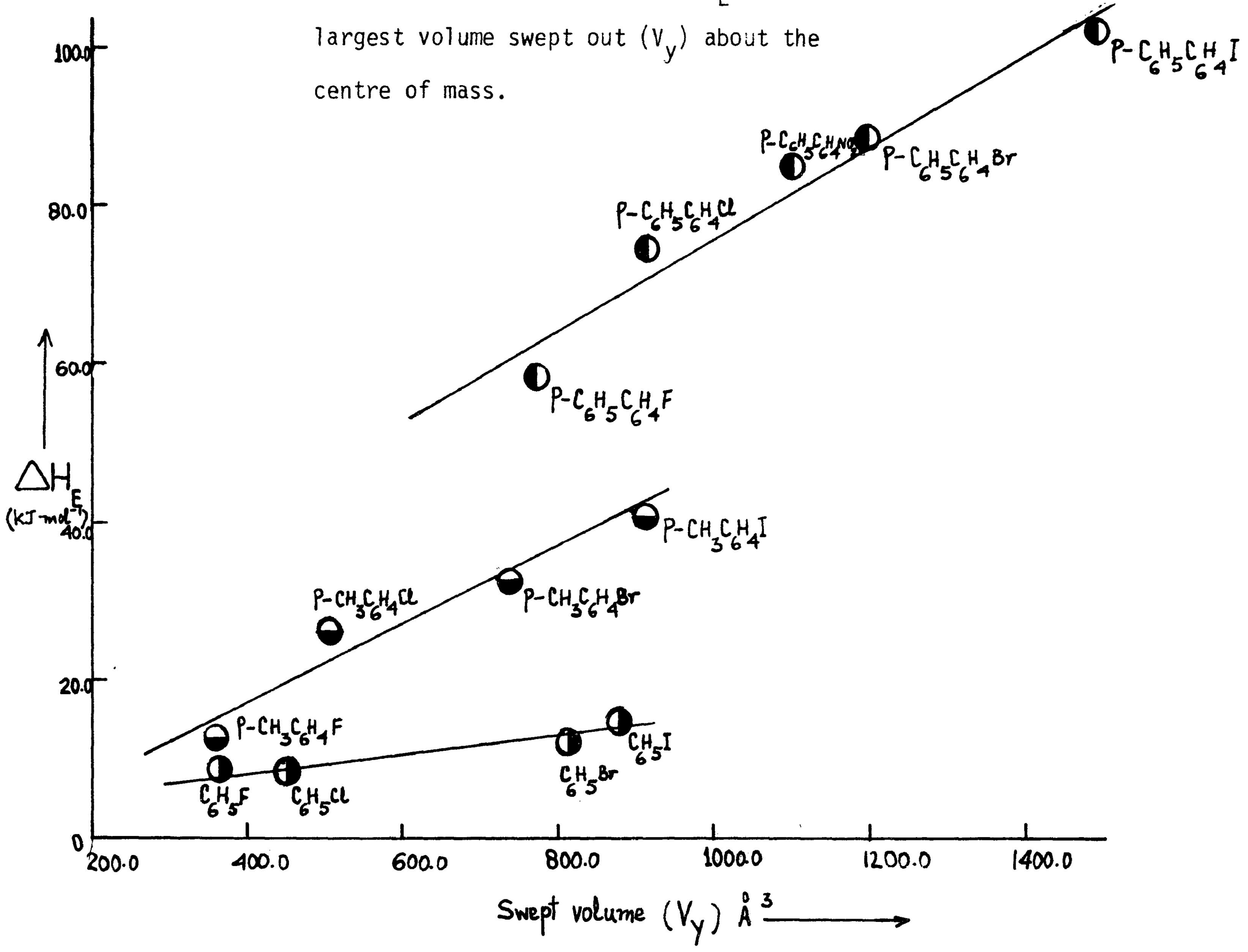


FIGURE III-9: Plot of activation enthalpy (ΔH_E) against largest volume swept out (V_y) about the centre of mass.



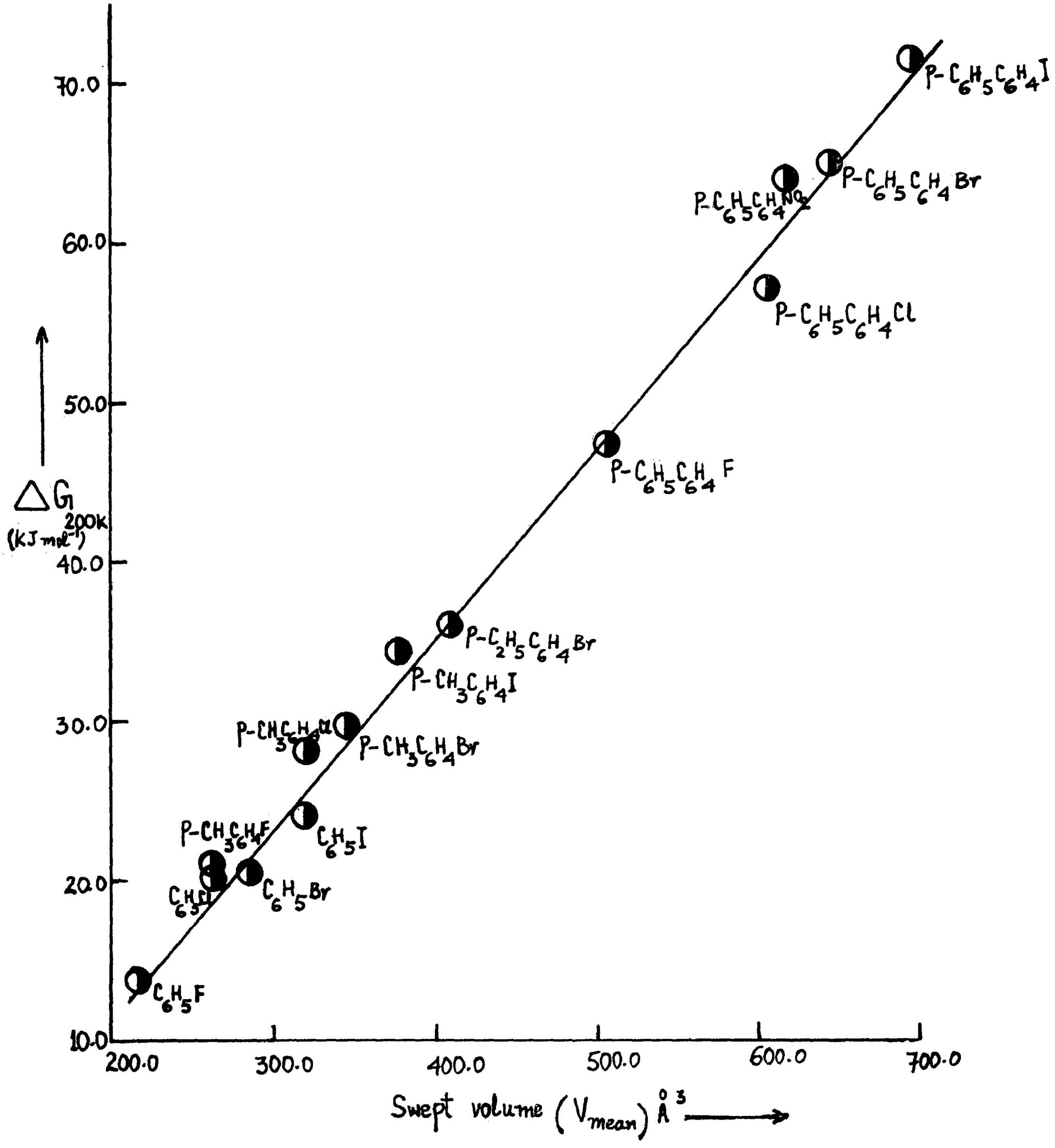
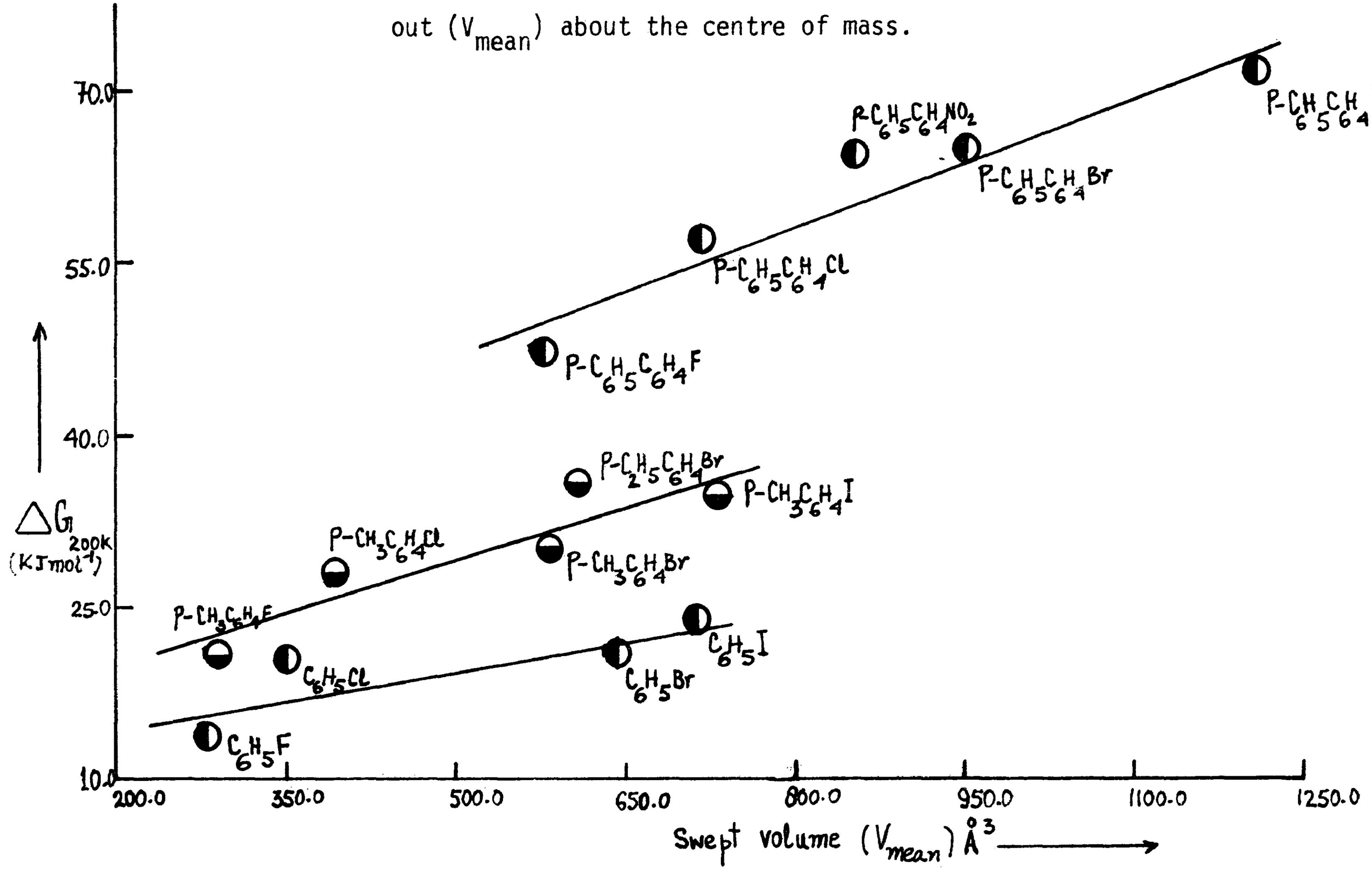


FIGURE III-10: Plot of free energy of activation (ΔG_E) against mean volume swept out (V_{mean}) about the centre of volume.

FIGURE III-11: Plot of free energy of activation (ΔG_E) against mean volume swept out (V_{mean}) about the centre of mass.



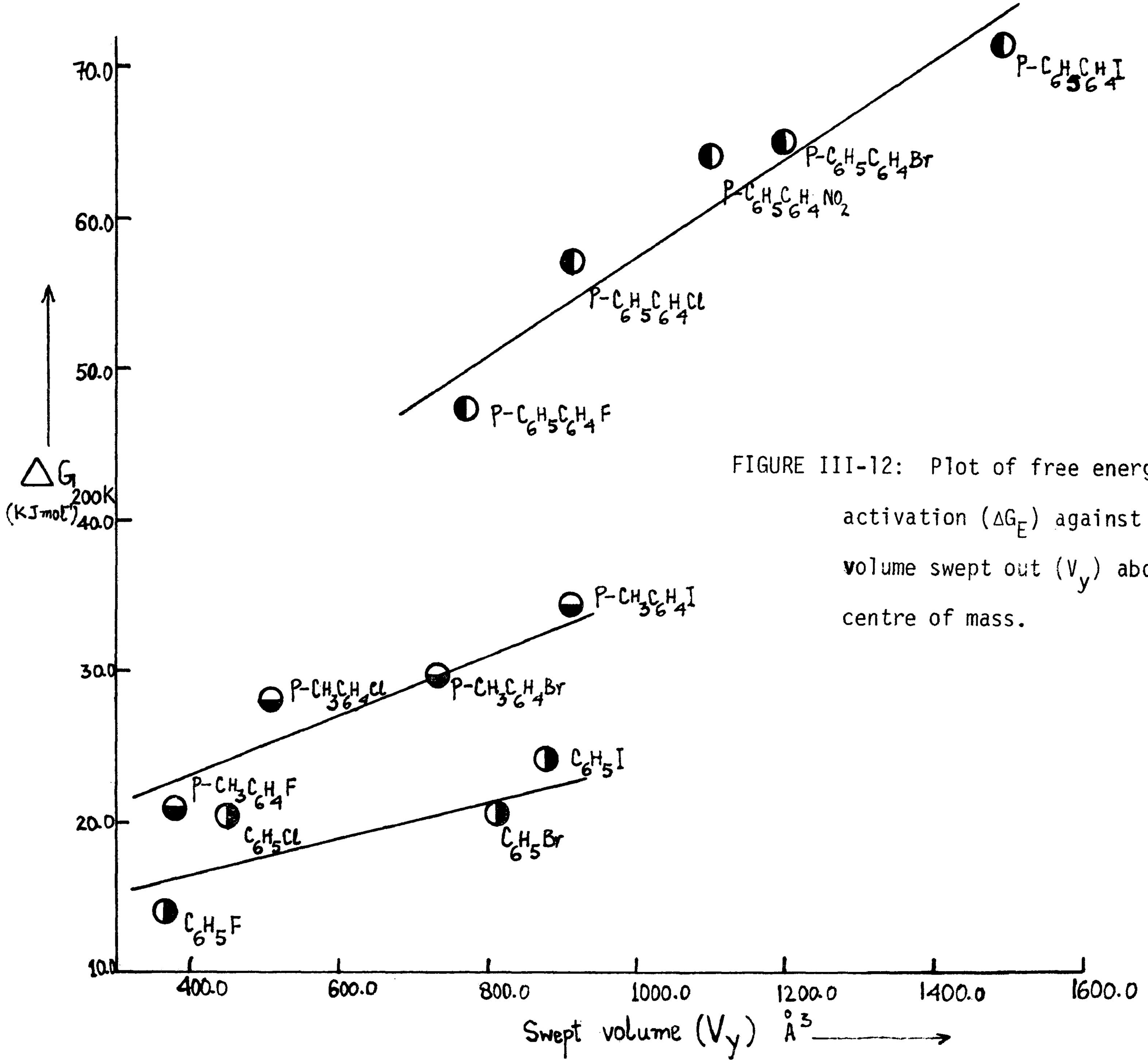


FIGURE III-12: Plot of free energy of activation (ΔG_E) against largest volume swept out (V_y) about the centre of mass.

FIGURE III-14: Plot of '$\log_{10}\tau_{200K}$' against 'I' for halobenzenes and p-halotoluenes.

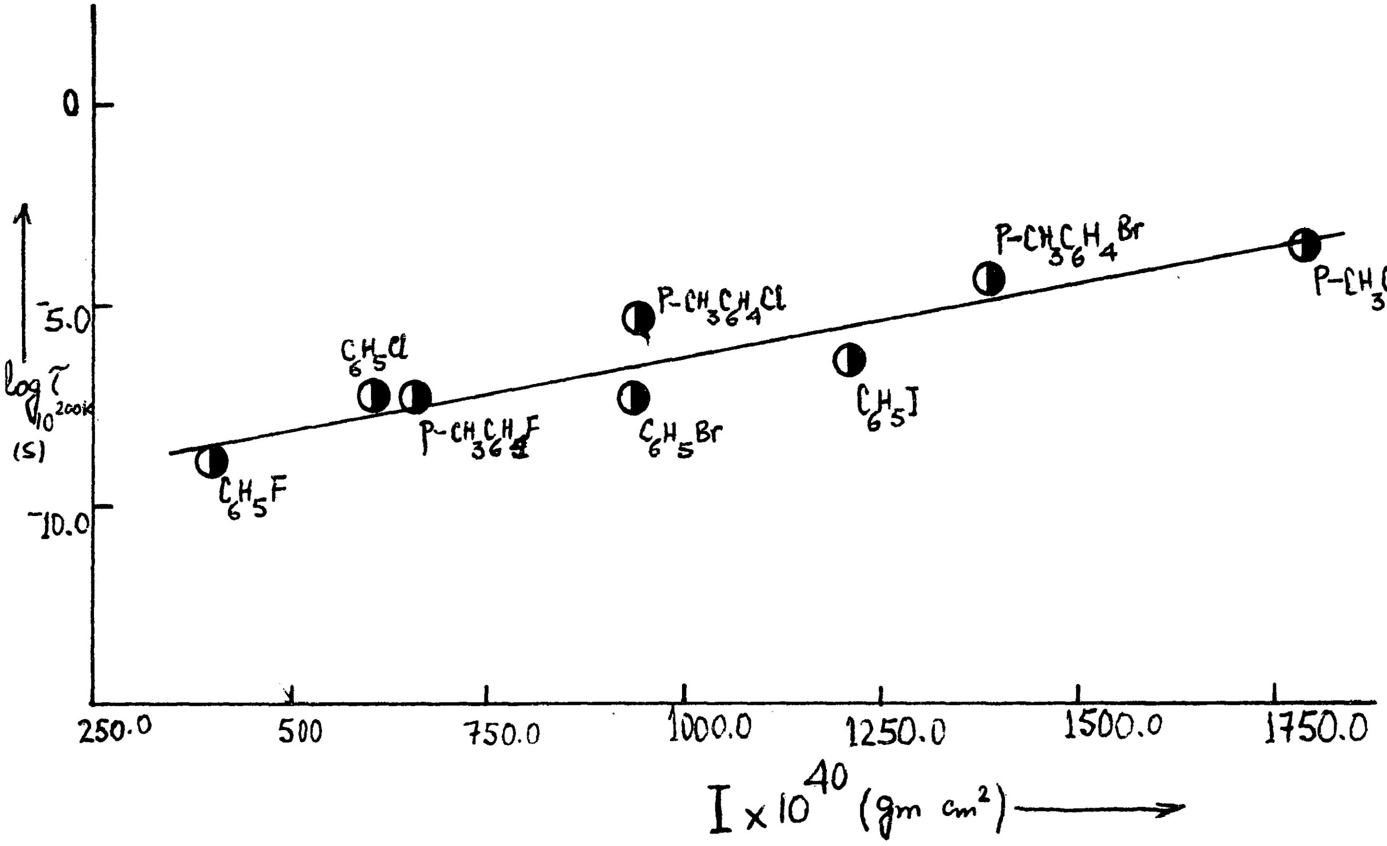


FIGURE III-15: Plot of $\log \tau_{200K}$ against $\sqrt{I}$ for halobenzenes and p-halotoluenes.

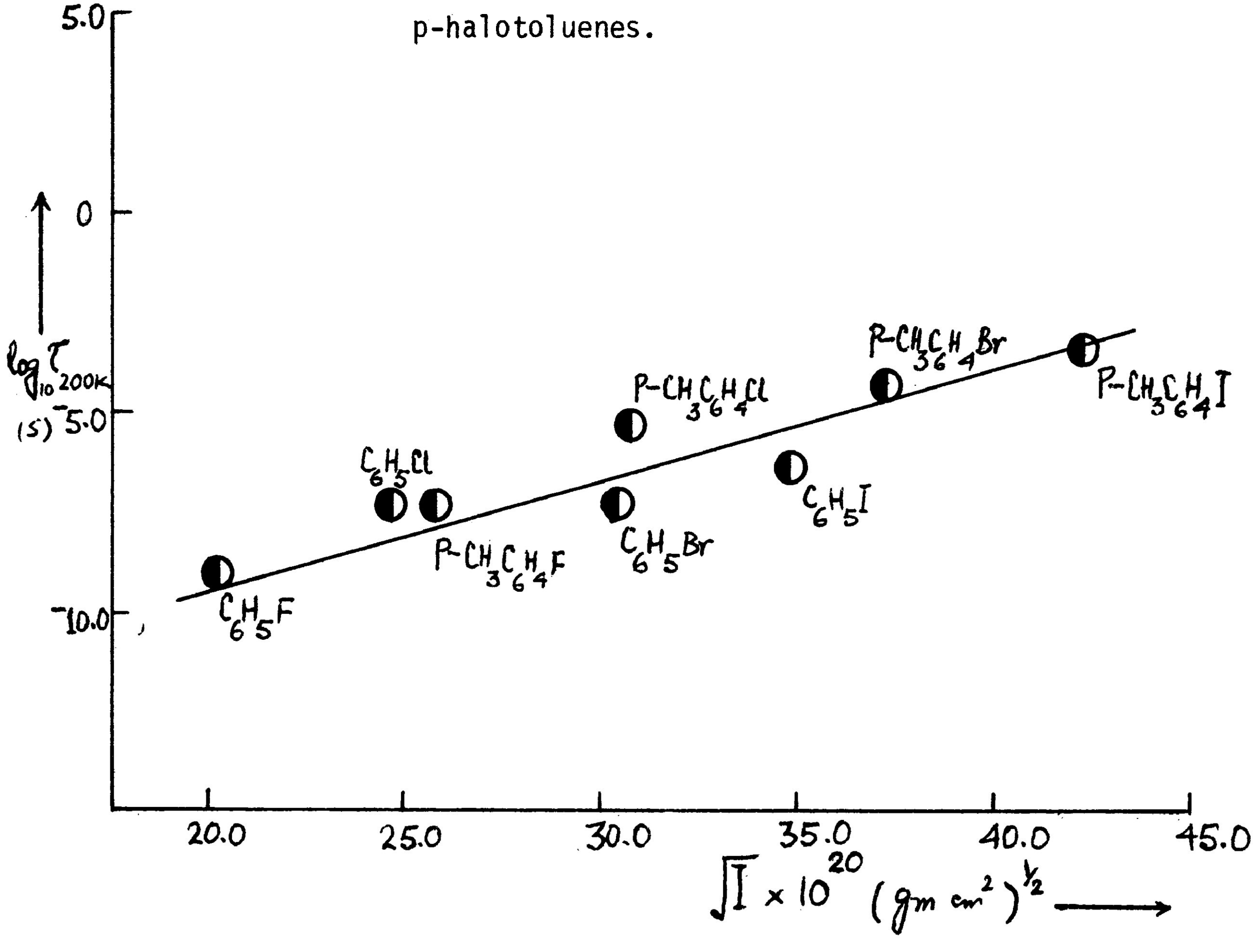
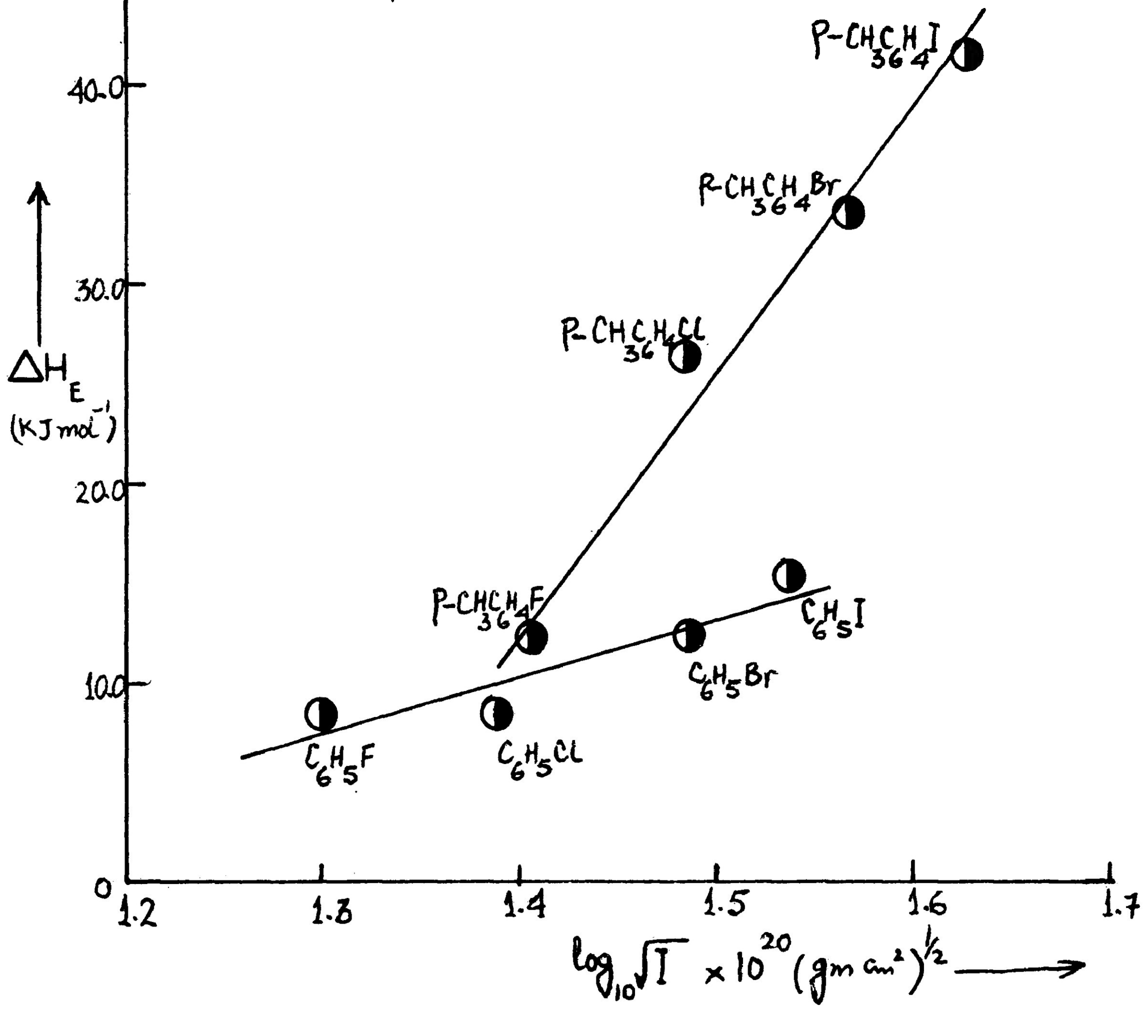


FIGURE III-16: Plot of 'ΔH_E' against $\log_{10}\sqrt{I}$ for halobenzenes and p-halotoluenes.



CHAPTER IV

INTRAMOLECULAR RELAXATION OF SOME DISULFIDE COMPOUNDS

INTRODUCTION

The disulfides constitute a large class of sulfur containing molecules, which are of substantial chemical and biochemical interest. For example, certain disulfide compounds are used as additives to lubricating oils, since their presence increases the load bearing properties of the oil. The disulfide linkage is also important in proteins, enzymes, antibiotics, and other biomolecules.

Dialkyl disulfides and diaryl disulfides are thought to show a stereochemical preference for the skew configuration, similar to that proposed by Penney-Sutherland model for hydrogen peroxide.[1] This is due to the lone pair repulsions which are minimal when the planes containing the two R-S-S groupings are inclined at an angle of $\sim 90^o$.[2-6] Figure IV-1 represents a structure of dimethyl disulfide. The methyl hydrogens are assumed to be staggered with respect to the S-S bond. The numbering of the atoms in dimethyl disulfide is shown in Fig. IV-1, in which the S_1, S_2, and C_3 atoms are assumed to be in the xz plane, while the S_1, S_2, and C_4 atoms are in the xy plane. These two planes are separated by an angle of 'ϕ' ($\sim 90^o$ in disulfides). Here it is also to be noted that dihedral angles of 0^o to 180^o are equivalent to angles of 0^o to -180^o, on account of the C_2 symmetry of the molecule. Table IV-1 collects the molecular geometries for some disulfides, where the data are available.

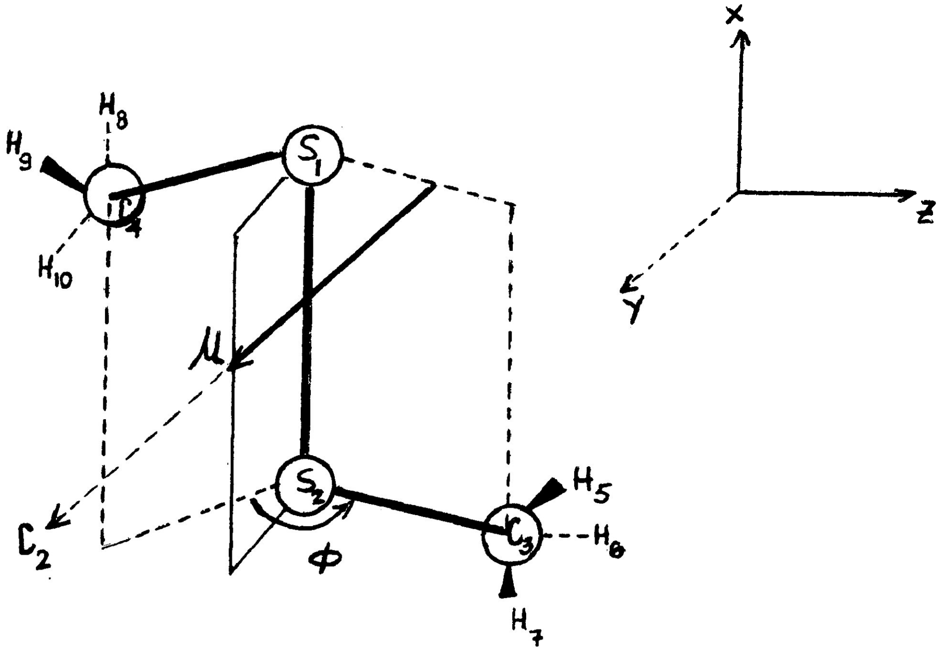


FIG IV-1

TABLE IV-1 Dihedral Angles and Group Moments of Some Disulfides (R-SS-R)

R=	ϕ (R_2S_2) (deg)	μ (R-S) (D)	Ref
Methyl	83.9 68	--- 1.22	15 3
Ethyl	74	1.35	3
Iso-propyl	74	1.40	3
n-Butyl	71	1.35	3
tert-Butyl	83	1.32	3
Phenyl	85	1.29	16
Benzyl	60	1.13	3
β-Naphthyl	78	1.29	16

The structural and conformational investigation of the disulfide moiety has been the subject of a wealth of papers in the recent literature, not only on small model compounds such as dimethyl disulfide, but also on complex ones such as proteins.

The existence of a barrier to rotation about the S-S link of a disulfide was established over 20 years ago, but experimental estimates of its magnitude vary between 25 - 67 kJ mol^{-1}, somewhat depending on the experimental method used to obtain the data. However, it is found that in most of the cases cis and trans barriers were not separately identified, although it was commonly thought that the stable conformation of several dialkyl disulfides would be gauche.

Earlier, the infrared spectra of several dialkyl disulfides were studied by Thompson and Trotter[7] and by Sheppard[8]. Later, Scott et al.[9] reported the vibrational assignments of dimethyl disulfide,[9a] diethyl disulfide,[9b] and di-n-propyl disulfide,[9c] together with the collection of early data of infrared and Raman frequencies for their thermodynamic studies. The infrared and Raman spectra of di-tert-butyl disulfide were also measured by Scott et al.[9h] in detail. These investigations showed the presence of rotational freedom about the S-S link. In addition, Nelson and Smyth[11] reported that the dielectric relaxation behaviour of diphenyl disulfide suggests that a significant degree of intramolecular relaxation takes place about the S-S link.

However, Scott _et al_.[9c] and Foss[9d] reported the barrier height for rotation about the S-S bond of dimethyl disulfide with the help of calculated and observed data for the entropy and heat capacity as 28.4 kJ mol^{-1}. From infrared data[9i] a barrier height of 30.5 kJ mol^{-1} was obtained. An n.m.r. study of less hindered acyclic disulfides was made by Fraser _et al_.[9j] They reported values ranging from 29-39 kJ mol^{-1} for barrier to rotation about the S-S link. But Raman data yielded somewhat larger barriers as for dimethyl disulfide[9a], 39.7 kJ mol^{-1}, and diethyl disulfide,[9b] 55.2 kJ mol^{-1}. An even larger barrier (cis barrier), 51.4 kJ mol^{-1} has been estimated from n.m.r. data.[9e]

Of the existing data on this rotational process, an interesting result is provided by Kessler and Rundel.[9f] By means of d.n.m.r. measurements they found a barrier of 65.5 kJ mol^{-1} in bis (4-methyl- 2,6-di-tert- butyl phenyl) disulfide. From the investigation of the millimeter-wave rotational spectrum of H_2S_2,[9g] it was concluded that the barrier to internal rotation is very high, much higher than the analogous H_2O_2 molecule (cis barrier, 29.3 kJ mol^{-1}, trans barrier, 4.6 kJ mol^{-1}).[12]

In addition to the above experimental studies, a vast amount of quantum mechanical calculation has also been carried out on the investigation of energy barrier to rotation about the S-S link. The computed barrier heights span quite a range, depending on the method used.

Several investigations[10(a,c,d,e,f,h)] by MO methods have been carried out on H_2S_2 molecule. They predict barrier heights in the ranges 11.3 - 45.6 kJ mol^{-1} (cis) and 3.3 - 25.1 kJ mol^{-1} (trans).

From EH calculations, Boyd[10g] reported somewhat lower barriers for H_2S_2 i.e., 6.3 kJ mol^{-1} (cis barrier) and a trans barrier of 3.8 kJ mol^{-1}. Numerous molecular orbital studies have also been carried out on dimethyl disulfide. Previous calculations on the conformation of dimethyl disulfide by the PCILO method[10b] showed a preferred dihedral angle of 100^o, a cis barrier of 12.1 kJ mol^{-1}, and a trans barrier of 5.4 kJ mol^{-1}. However, the EH calculations[10g] produced an equilibrium dihedral angle of about 90^o, staggered methyl groups, and reported a barrier height of 29.3 kJ mol^{-1} (cis barrier) and 9.2 kJ mol^{-1} (trans barrier). A recent suggestion by Allinger _et al_.[10j] implies a barrier height of 41.8 kJ mol^{-1} (cis barrier) and a barrier height of 29.3 kJ mol^{-1} (trans barrier) for dimethyl disulfide. It is to be noted that the trans barrier height of 29.3 kJ mol^{-1} is in good agreement with those found from calorimetric data,[9c,9d] and infrared data[9i].

Furthermore, Bergson[10a] has derived expressions which give the energy barrier to internal rotation around the S-S link. From these expressions he finds that p-orbital repulsion causes a barrier of 57.7 - 65.6 kJ mol^{-1}, and sp^3 orbital repulsion causes a barrier of 25.9 - 29.3 kJ mol^{-1}.

In diphenyl disulfide, the barrier height was calculated to be 62.7 kJ mol^{-1} for rotation about the S-S link, by the $\frac{CNDO}{2}$ method.[10i] In the literature, barrier height to rotation about the C-S link in some disulfides has also been reported. From the calorimetric value of entropy,[9a] a barrier height for methyl group rotation in dimethyl disulfide was found to be 4.8 kJ mol^{-1}. The EH calculation[10g] reported that when the CSSC dihedral angle is large enough to avoid steric hindrance between the methyl groups, the barrier to rotation around C-S bonds in $(CH_3)_2\ S_2$ is 5.0 kJ mol^{-1}, which was found similar to the experimental[13] barrier of 6.7 kJ mol^{-1}. Recently, Aroney et al.[14] made dielectric loss measurements of some dialkyl and diaryl disulfides in benzene solution at 293K, and at only three frequencies, i.e., 1.14, 3.04, and 8.54 GHz. However, the results were not very conclusive, which could be related to the limited frequency coverage.

From the preceding review, though a vast amount of experimental and theoretical work has been carried out on the investigation of the rotational barrier around the S-S link, it seems that conformational analysis of the disulfides is far from complete. This is due to paucity of experimental data concerning the energy barrier and also of some limitations in the technique employed. Therefore, it seemed highly desirable to investigate this problem with the aid of the "dielectric relaxation technique", by trapping solute molecules in a polystyrene matrix, as this method has proved successful in determining intramolecular energy barriers when the intramolecular relaxation can be completely separated from the molecular process.

EXPERIMENTAL RESULTS

The dielectric loss measurements in the frequency range of 10^2 - 10^5 Hz have been made by using a General Radio 1615A capacitance bridge. For dimethyl disulfide, additional measurements have also been made on a Hewlett-Packard 4342A Q-meter in the frequency range of 2.2 x 10^5 Hz to 2.2 x 10^7 Hz. The disulfides studied here have general structure R-SS-R (where R is methyl, ethyl, isopropyl, n-butyl, tert-butyl, n-octyl, phenyl, benzyl, 4-tolyl, 3-nitro phenyl, and 4-aminophenyl) that is all the solute molecules have been examined in a polystyrene matrix. A sample plot of loss factor $\{\varepsilon'' = \varepsilon''(\text{obs}) - \varepsilon''(\text{polystyrene})\}$ against logarithm frequency is given in Fig. IV-2 for $(CH_3)_2 S_2$. Similar dielectric loss measurements have also been carried out on di-β-naphthyl disulfide as pure polycrystalline powder pressed into a disk. In addition, p-chlorothioanisole was also examined in a polystyrene matrix. The results of Fuoss-Kirkwood analyses for the molecules examined are collected in Table IV-2. The results of Eyring equation analyses for these molecules are presented in Table IV-3. The relaxation times calculated from these analyses at three temperatures (100K, 200K, and 300K) are also given.

DISCUSSION

In symmetrical disulfide compounds, the components of the dipole moment of the two substituent groups along the long axis of the molecule (along the S-S bond) cancel each other. This results in a permanent molecular dipole of zero magnitude along that axis; thus leaving only the perpendicular components of the dipole moment to contribute to an intramolecular mechanism. This is a similar case to that of terephthaldehyde,[17] and 1,4-diacetyl benzene,[23] where only the aldehyde group and acetyl group relaxation have been observed in the polystyrene matrices. Thus it appears that the most likely relaxation candidate is intramolecular relaxation around the S-S bond.

The dialkyl disulfides examined here in a polystyrene matrix showed two dielectric absorptions. The only exceptions here were the diethyl- and di-isopropyl disulfide, where the third dielectric absorption around room temperature was also observed. In addition, the low temperature absorption, as observed in all the other dialkyl disulfides, could not be observed in the case of dimethyl disulfide.

From good linear plots of $\log T\tau$ as a function of reciprocal temperature (T^{-1}) (for example, Fig. IV-3 for dimethyl disulfide), the corresponding enthalpies of activation, ΔH_E (kJ mol^{-1}), were 28, 26, 31, 32, 30, and 28 for a high temperature absorption of dimethyl-, diethyl-, di-isopropyl-, di-n-butyl-, di-tert-butyl-, and di-n-octyl disulfides, respectively. All these dialkyl disulfides exhibited dielectric absorptions in the similar ranges of temperature (∿180K) at a given frequency range.

In addition, a low temperature dielectric absorption is also observed in all the dialkyl disulfides, with the exception of dimethyl disulfide. The activation enthalpies for this process were diethyl disulfide, 11 kJ mol^{-1}; di-isopropyl disulfide, 18 kJ mol^{-1}; di-n-butyl disulfide, 18 kJ mol^{-1}; di-tert-butyl-disulfide, 12 kJ mol^{-1}, and di-n-octyl disulfide, 25 kJ mol^{-1}, respectively.

The high temperature absorption has significantly high values of 'β' of about (0.4) for the distribution parameter of dialkyl disulfides. This is similar to that observed by Davies and Swain[18] for the intramolecular process when the absorption occurred at a relatively high temperature, and under such conditions the larger values of β suggest an intramolecular dipole process.

The value of 28 kJ mol^{-1} obtained by this study for dimethyl disulfide for a high temperature absorption is in good agreement with a study by calorimetric data.[9c] This yielded an energy barrier of 28.4 kJ mol^{-1} for rotation about the S-S bond in dimethyl disulfide. In addition, the present value of 28 kJ mol^{-1} for dimethyl disulfide agrees well with those found for dimethyl disulfide from EH calculations,[10h] 29.3 kJ mol^{-1} and from infrared data,[9i] 30.5 kJ mol^{-1}, respectively, for rotation about the S-S bond.

It can be seen from Table IV-2 that the value of maximum dielectric absorption (ε''_{max}) for the high temperature process in dimethyl disulfide decreases with increasing temperature, which is in line with the observation of Davies and Swain,[18] in which the ε''_{max} value for an intramolecular process in cyclohexyl chloride and cyclohexyl bromide decreases with increasing temperature.

Further, it may be noted (Table IV-2) that for high temperature absorption in dimethyl disulfide, the variation in observed dipole moment values with temperature is not very significant. Even when extrapolated at 300K, $\{\mu_{extpd}=0.6D\}$ it could not attain the observed value of dipole moment in benzene solution at 303K, $\{\mu_{LIT} = 1.97\ D\}$. Hence these considerations suggest that the relaxation in this molecule occurs by an intramolecular process around the S-S bond.

The low temperature dielectric absorption was not observed in dimethyl disulfide. It was measured on both the General Radio bridge and the Q-meter within our limits of temperature (liq N_2 temperature) and frequency of the instrument.

As it may be seen from Table IV-3, in dimethyl disulfide a dielectric absorption was measured at a higher temperature range 273 to 311K, giving ΔH_E = 57 kJ mol^{-1} and ΔS_E = 41 J K^{-1} mol^{-1}. It is to be noted (Table IV-3) that the values of relaxation time (τ = 1.1 s), free energy of activation (ΔG_E = 49 kJ mol^{-1}) at 200K, and the enthalpy of activation, ΔH_E = 57 kJ mol^{-1} obtained for this molecule are considerably higher. This would not be expected for molecular relaxation of such a small molecule. However, since this dielectric absorption occurs at a much higher temperature (> 300K), it appears that the absorption might have arisen due to the lowering of glass transition temperature. A co-operative motion of the whole molecule together with the segments of the polymer chain occurs for this high temperature process of dimethyl disulfide. A number of similar systems has been examined in this laboratory by Walker et al.[21] who obtained a relation: ΔS_E (J K^{-1} mol^{-1})= -150 + 3.24 ΔH_E (kJ mol^{-1}), corresponding to the co-operative motion of molecules in the polymer. Hence, as the values of ΔH_E and ΔS_E for the higher temperature process of dimethyl disulfide fit into this relation within experimental error, this gives additional support of a co-operative molecular process in polystyrene for the higher temperature process of dimethyl disulfide.

The next member of the dialkyl disulfide series, i.e., diethyl disulfide, exhibits the higher temperature dielectric absorption in a similar range of temperature (275 - 311K) as observed for dimethyl disulfide. This yielded values of activation enthalpy and entropy as 62 kJ mol^{-1} and 60 J K^{-1} mol^{-1}, respectively, which fit into the above relation[21] for a co-operative molecular process in polystyrene. In addition, it is seen (Table IV-3) that the τ and ΔG_E values (300K) for the higher temperature process of diethyl disulfide are all similar to the corresponding values obtained for the higher temperature process of dimethyl disulfide. Thus, these observations indicate that this absorption in diethyl disulfide arises because of the lowering of glass transition temperature and is attributed to a co-operative motion in polystyrene.

In addition to this absorption, diethyl disulfide shows two sets of absorption, one at high temperature (∿180K), which is in similar ranges of temperature and frequency as in dimethyl disulfide, and the other being the low temperature absorption (∿85K), which was not observed in dimethyl disulfide.

For the high temperature process of diethyl disulfide the distribution parameter, β (0.40 - 0.45) values are appreciable. This is similar to the observation of Davies and Swain[18] for an intramolecular relaxation process. It is also notable (Table IV-2) that for high temperature absorption, maximum loss factor, ε''_{max}, decreases with the rise of temperature. This is in accord with the high temperature process of dimethyl disulfide. The free energy of activation (ΔG_E = 28 kJ mol^{-1}) and the relaxation time (τ = 4.6 x 10^{-6} s) at 200K for diethyl disulfide are found to be closer than the corresponding parameters for dimethyl disulfide (ΔG_E = 26 kJ mol^{-1}; τ = 1.7 x 10^{-6} s). The difference in the extrapolated value of the observed dipole moment at 300K {μ_{extpd} = 0.52 D} and the literature value in benzene solution at 298K {μ_{LIT} = 1.99 D} for the high temperature process of diethyl disulfide is quite significant. In addition, the observed dipole moment value of 0.52 D at 200K is to be compared with the corresponding value of 0.87 D at 200K, typical for an intramolecular relaxation process in an aliphatic system (butyraldehyde).

The activation enthalpy (ΔH_E = 26 kJ mol^{-1}) for diethyl disulfide for a high temperature absorption is ~2 kJ mol^{-1} less than the corresponding value of 28 kJ mol^{-1} in dimethyl disulfide. This is mainly due to the decrease in entropy of activation in the former rather than in the latter. However, this difference in ΔH_E values between dimethyl- and diethyl disulfides may be considered within the limits of experimental error.

It is apparent from Table IV-3 that in diethyl disulfide, the magnitude of enthalpy of activation, $\Delta H_E = 26$ kJ mol^{-1}, is less than the free energy of activation at a given temperature (200K), $\Delta G_E = 28$ kJ mol^{-1}, so that the entropy of activation is negative. According to Branin and Smyth,[20] "negative entropy of activation indicates that there are fewer configurations possible in the activated state and for these configurations the activated state is more ordered than the normal state". As mentioned at the beginning of the discussion, for symmetrical disulfide compounds, only the perpendicular components of the dipole moment would be responsible for the relaxation mechanism. The horizontal components along the long axis of the molecule (S-S bond) are equal and opposite and cancel each other, leaving no horizontal component of the dipole moment to contribute to the molecular relaxation. Thus it would appear that the possible relaxation candidate for the low temperature absorption of diethyl disulfide could be segmental relaxation. The assignment of the low activation enthalpy of 11 kJ mol^{-1} to the segmental rotation in diethyl disulfide appears to be consistent with the observation in this absorption of a large distribution parameter ($\beta \sim 0.3$), small values of relaxation time ($\tau = 5 \times 10^{-10}$ s) and free energy of activation ($\Delta G_E = 13$ kJ mol^{-1}) at 200K, and the observed dipole moment value of 0.8 D at 200K. Hence, in view of the flexibility of the alkyl chain and the above considerations, it would seem reasonable that the segmental reorientation contributes to the low temperature dielectric absorption in diethyl disulfide.

For the high temperature absorption of di-isopropyl disulfide, the observations, i.e., the temperature range of absorption (∿180K), significantly high 'β' values (∿0.4), and the decrease in ε''_{max} with the rise of temperature are all similar to that observed for the high temperature process of dimethyl- and diethyl disulfides. Further, the observed dipole moment decreases with the increase of temperature. When extrapolated to 300K, the difference in the value of dipole moment with that observed in benzene solution is quite significant (Table IV-2). An activation enthalpy of 31 kJ mol^{-1} has been obtained for this high temperature absorption of di-isopropyl disulfide. This may be explained as the enhanced inductive effect which in this molecule would lead to a greater electron density around the S-S bond in comparison with the dimethyl disulfide. Hence, a slightly larger enthalpy of activation than for dimethyl disulfide (ΔH_E = 28 kJ mol^{-1}) would result. Further, the larger free energy of activation at 200K (ΔG_E = 30 kJ mol^{-1}) in the former occurs over that of the latter (ΔG_E = 26 kJ mol^{-1}).

A low temperature dielectric absorption in di-isopropyl disulfide was measured in the temperature range of 101 - 125K, yielding an activation enthalpy and entropy of 18 kJ mol^{-1} and 10 J K^{-1} mol^{-1}, respectively. It is seen (Table IV-3) that for this absorption, the distribution parameter, ($\beta \sim 0.3$), the relaxation time, and free energy of activation at 200K ($\tau = 3 \times 10^{-9}$ s, ΔG_E = 16 kJ mol^{-1}), respectively, are in accord with the corresponding parameters for the low temperature absorption of diethyl disulfide. This suggests a segmental relaxation process for the low temperature absorption of di-isopropyl disulfide. Apart from above mentioned dielectric absorptions for di-isopropyl disulfide, a similar higher temperature absorption ($\sim$300K) was observed for this molecule as in the case of dimethyl- and diethyl disulfides. This absorption yields considerably high values of activation enthalpy, ΔH_E = 138 kJ mol^{-1}, and activation entropy, ΔS_E = 325 J K^{-1} mol^{-1}. This, however, should not be considered reliable, as during the course of dielectric measurements capacitance readings were unstable. They may be attributed to the onset of the glass transition temperature. Such systems would appear to give much flexibility to the polymer segments in the medium, which would in turn lead to greater disorderliness in the medium. Thus, the dielectric measurements are made more difficult. However, the values of activation enthalpy and entropy for di-isopropyl disulfide have been tested in the relation[21] recently derived for the co-operative molecular process. The fact that the higher temperature process obeys this relationship suggests that co-operative motion may occur.

The increase in chain length in the dialkyl disulfide series, i.e., di-n-butyl disulfide and di-tert-butyl disulfide, again shows two regions of absorption.

The temperature range of absorption in a given frequency range and the larger Fuoss-Kirkwood distribution parameter ($\beta \sim 0.4$) for the high temperature absorption in di-n-butyl- and di-tert-butyl disulfide are similar to that found for a high temperature process in dimethyl-, diethyl-, and di-isopropyl disulfide, where the absorption is attributed to an intramolecular relaxation process around the S-S bond. The decreasing behaviour of ΔG_E and observed dipole moment with the rise of temperature is also found in these molecules, which is a common aspect in the preceding dialkyl disulfides, the exception being the diethyl disulfide, where owing to the negative entropy of activation, the value of ΔG_E increases with temperature. It is to be noted (Table IV-3) that di-n-butyl disulfide yields an $\sim$4 kJ mol^{-1} higher enthalpy of activation (ΔH_E = 32 kJ mol^{-1}) than that of dimethyl disulfide (ΔH_E = 28 kJ mol^{-1}), which is not significantly different and may be considered within the limits of experimental accuracy. However, on the other hand, this small difference may be due to the variation in size of the substituent 'R' in RSSR moiety, as the larger substituent would be expected to enhance the barrier to intramolecular rotation around the S-S bond. Similarly, as the size of tert-butyl substituent seems larger than the isopropyl substituent in the RSSR moiety, one might expect a larger activation enthalpy for intramolecular rotation around the S-S bond in di-tert-butyl disulfide than that of di-isopropyl disulfide. However, the enthalpies of activation for the high temperature process of di-tert-butyl- and di-isopropyl disulfides are found to be 30 kJ mol^{-1} and 31 kJ mol^{-1}, respectively, which is not a significant difference within the limits of experimental error. Nevertheless, a little increase in ΔH_E value for the latter molecule with that of the former could also be explained, as the di-isopropyl disulfide has greater steric interaction and a larger group moment (1.4 D) due to an enhanced inductive effect, whereas the di-tert-butyl disulfide has a significantly lower group moment (1.32 D) due to an increase in the dihedral angle ($\phi = 83^{0}$). This reveals that the former molecule has a larger energy barrier to intramolecular rotation around the S-S bond than that of the latter molecule. In addition, the free energy of activation, $\Delta G_E = 30$ kJ mol^{-1} at 200K for di-isopropyl disulfide, is found to be larger in comparison with the corresponding value of 29 kJ mol^{-1} for di-tert-butyl disulfide. It can also be explained in terms of its larger moment and its enhanced inductive effect, which would lead to a greater electron density around the S-S bond. Thus, a slightly larger energy barrier to intramolecular rotation around the S-S bond in di-isopropyl disulfide than in di-tert-butyl disulfide could be explained.

The low temperature dielectric absorption of di-n-butyl disulfide yields an activation enthalpy and entropy as 18 kJ mol^{-1} and 5 J K^{-1} mol^{-1}, respectively, while di-tert-butyl disulfide yields the corresponding parameters as 12 kJ mol^{-1} and -15 J $K^{-1}mol^{-1}$, respectively. It may be noted (Table IV-3) that the temperature range of absorption, the activation enthalpy and entropy, the values of relaxation time, and the free energy of activation at 100K for the low temperature absorption of di-n-butyl disulfide are in accord with the corresponding parameters for the low temperature absorption of di-isopropyl disulfide. For di-tert-butyl disulfide these parameters show resemblance with that of the corresponding parameters for the low temperature absorption of diethyl disulfide. However, when the flexibility of the alkyl chain in these dialkyl disulfides is borne in mind, the variation in the relaxation parameters can be accounted for by the involvement of segments of different size in these molecules. It is also to be noted that the variation in the values of ΔH_E, ΔS_E, τ, and ΔG_E at 100K for the low temperature absorption of di-ethyl-, di-iso-propyl-, di-n-butyl-, and di-tert-butyl disulfides is not in accordance with the size of the molecule. This would not be expected if it had been a molecular relaxation process. Hence, it would seem reasonable to interpret the segmental relaxation within the alkyl chain for the low temperature process of di-n-butyl disulfide and di-tert-butyl disulfide. This interpretation is similar to that observed in diethyl disulfide and di-isopropyl disulfide.

It should be noted that Aroney et al.[14] obtained a relaxation time of 4.0 psec and 7.9 psec for a predominantly molecular relaxation process in dimethyl disulfide and di-tert-butyl disulfide, respectively in benzene solution at 293K. However, since only a limited frequency range was employed in these measurements, a contribution from relaxation about the S-S bond could not be excluded at a higher frequency range.

When the chain length is increased to di-n-octyl disulfide two regions of absorption are again obtained. It should be noted that the values of relaxation time ($\tau = 3.6 \times 10^{-5}$ s) and free energy of activation ($\Delta G_E = 31$ kJ mol^{-1}) at 200K for the high temperature absorption of di-n-octyl disulfide are in harmony with the corresponding parameters of 1×10^{-5} s , 29 kJ mol^{-1}; 1.1×10^{-5} s , 29 kJ mol^{-1}; and 1.5×10^{-5} s, 30 kJ mol^{-1}, respectively, obtained for the intramolecular rotation around the S-S bond in di-n-butyl-, di-tert-butyl-, and di-isopropyl disulfides, respectively. In addition, it is apparent from Table IV-3 that the free energy of activation increases with the rise of temperature, and the enthalpy of activation ($\Delta H_E = 28$ kJ mol^{-1}) is found to be less than the free energy of activation at a given temperature (200K). This is due to its negative entropy of activation. Similar behaviour was found for a high temperature process of diethyl disulfide. It may also be seen that the magnitude of enthalpy of activation (28 kJ mol^{-1}) is about the same order as for other dialkyl disulfides for a high temperature absorption.

Hence, the above considerations suggest that high temperature absorption of di-n-octyl disulfide could be attributed to an intramolecular rotation around the S-S bond, which has been observed in all the other dialkyl disulfides.

An activation enthalpy of 25 kJ mol^{-1} and an activation entropy of 23 J K^{-1} mol^{-1} have been obtained for the low temperature absorption of di-n-octyl disulfide. They would appear to correspond to the segmental relaxation process as observed in diethyl-, di-isopropyl-, di-n-butyl-, and di-tert-butyl disulfides. However, it seems profitable to note that the sequence of increasing ΔH_E, ΔS_E, ΔG_E, and τ at 100K for the low temperature process of diethyl disulfide, di-n-butyl disulfide and di-n-octyl disulfide was 11, 18, and 25 kJ mol^{-1}, respectively; -8, 5, and 23 J K^{-1} mol^{-1}, respectively; 12, 17, and 23 kJ mol^{-1}, respectively; and 8.9 x 10^{-7}, 5.3 x 10^{-4}, and 2.8 x 10^{-1} s, respectively. This sequence of increasing relaxation parameters with increasing chain length of dialkyl disulfides may be related to the increasing length of the alkyl chain with its increased possibilities of intramolecular relaxations. For example, in di-n-octyl disulfide, the larger alkyl units which would be expected to encounter a greater resistance from the surrounding medium. As a result, relatively larger relaxation parameters have been obtained for this molecule than those of diethyl- and di-n-butyl disulfides.

The di-n-butyl-, di-tert-butyl-, and di-n-octyl disulfides were carefully measured at higher temperatures, up to the limit of our high temperature range (i.e., glass transition temperature), to examine the type of absorption, which was observed in dimethyl-, diethyl-, and di-isopropyl disulfides which appears to be attributable to a co-operative molecular process in polystyrene. However, the higher temperature absorption was not observed for these three molecules.

In general, apart from dimethyl disulfide, all the dialkyl disulfides show two regions of absorption. The exceptions are the diethyl- and di-isopropyl disulfides, where the third dielectric absorption (∿300K) was also observed. For dimethyl disulfide, two sets of absorption were found, one around 180K which is common to all the dialkyl disulfides, and the other at ∿300K, which was observed only in diethyl- and di-isopropyl disulfides. The low temperature absorption could not be observed although a very careful and detailed study was made.

The higher temperature absorption of dimethyl-, diethyl-, and di-isopropyl disulfides appears to have arisen owing to the lowering of the glass transition temperature. This may be attributed to a co-operative molecular process in the medium, since the values of ΔH_E and ΔS_E have been examined in the relation[21] recently derived for the co-operative molecular process.

All the dialkyl disulfides, R_2S_2 (where R = CH_3, C_2H_5, $CH(CH_3)_2$, C_4H_9, $C(CH_3)_3$, C_8H_{17}) show high temperature absorptions in the same temperature region ($\sim$180K) for the given frequency range. They have significantly high Fuoss-Kirkwood distribution parameters ($\beta \sim 0.4$), the exception being di-n-octyl disulfide. Further, the values of activation enthalpy for all the molecules do not show any significant variation, and if one examines these values, they all fall in the range 29 ±3 kJ mol^{-1}. This should be considered within the limits of experimental accuracy, and for the values of activation entropy it would appear to tend to zero. It is to be noted (Table IV-3) that di-isopropyl disulfide, di-tert-butyl disulfide, and di-n-butyl disulfide yield virtually identical values of relaxation time ($\sim 1 \times 10^{-5}$ s) and free energy barriers ($\sim$29 kJ mol^{-1}) at a given temperature (200K). It may also be noted (Table IV-3) that the relaxation times and free energy barriers at 200K apparently show an increasing behaviour with increasing size of the rotatable unit, that is in the order of dimethyl-, diethyl-, di-n-butyl-, and di-n-octyl disulfide. However, the variations in these parameters are not very significant, which could be taken to be within the limits of experimental error. The common features found for a high temperature process amongst dimethyl disulfide and the other dialkyl disulfides reveal that the same intramolecular relaxation process around the S-S bond has been observed in all the dialkyl disulfide molecules.

The low temperature dielectric absorption undoubtedly arises from segmental relaxation in these dialkyl disulfides. The variation in relaxation parameters can be accounted for by the involvement of a variety of segments in these molecules. The values of activation enthalpy and relaxation time at 100K (Table IV-3) are not in accord with the size of the molecule. This observation is in contrast to the molecular relaxation process. The absence of low temperature absorption in dimethyl disulfide gives additional support to the above interpretation of segmental relaxation for the low temperature process of dialkyl disulfides. In view of this the Eyring parameters derived for the low temperature absorption may well not be meaningful since more than one relaxation process may be involved.

In addition to the study of dialkyl disulfides, some symmetrical diaryl disulfides have also been examined in the polystyrene matrix. In symmetrical diaryl disulfides, similar to the dialkyl disulfides, there would be no horizontal component of the dipole moment to contribute to the molecular relaxation process. Only the perpendicular components of the dipole moment can contribute. Thus, the possible relaxation candidate could be intramolecular relaxation around the S-S bond in these diaryl disulfides.

In the literature, it is thought that less hindered diaryl disulfides show hindrance to rotation about the C-S bonds only.[9f]

Further, Ronsisvalle *et al.*[22] derived expressions and suggested that the possibility of free rotation of the phenyl groups about the C-S bonds in molecules of the diphenyl disulfide type may be excluded. However, Gruttadauria *et al.*[10i] by using the $\frac{\text{CNDO}}{2}$ method, tentatively reported a rotational barrier for diphenyl disulfide about the C_{Ar}-S link as 238.3 kJ mol^{-1}.

The first molecule of a diaryl disulfide series studied in a polystyrene matrix is diphenyl disulfide. In this molecule only one absorption measured from 219 - 264K was found, having a high distribution parameter, ($\beta \sim 0.3$) and an activation enthalpy of 33 kJ mol^{-1}. It is apparent from Table IV-3 that free energy of activation increases with the rise of temperature. The enthalpy of activation (ΔH_E = 33 kJ mol^{-1}) is found to be less than the free energy of activation (ΔG_E = 38 kJ mol^{-1} at 250K), so that the entropy of activation is negative (ΔS_E = -18 J K^{-1} mol^{-1}). It is seen from Table IV-2 that the extrapolated value of the observed dipole moment at 300K provides a value of only 0.73 D in comparison with the observed value of dipole moment in benzene solution as 1.92 D at 293K. This difference in dipole moment values supports the intramolecular relaxation process in diphenyl disulfide molecule. The reason is that, in the case of the complete relaxation of the dipole by the whole molecule motion, the extrapolated value of the observed dipole moment at a given temperature should attain a closer value to the solution value.

The diphenyl disulfide and o-hydroxy benzophenone*

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*Data is provided through the courtesy of M. Desando of this laboratory.

(which is regarded as a rigid molecule) are fairly similar in size. Each molecule would be expected to have a similar enthalpy of activation for the whole molecular relaxation. However, the value of ΔH_E for o-hydroxy benzophenone is $\sim$25 kJ mol^{-1} greater than that for the diphenyl disulfide molecule. This would not be expected if the process were molecular relaxation in each case. A further comparison with a rigid molecule, dibenzothiophene sulfoxide * (which can be taken as a lower limit for a molecular relaxation enthalpy of activation) has yielded ΔH_E = 39 kJ mol^{-1} for a molecular relaxation process. This is again 6 kJ mol^{-1} greater than that for diphenyl disulfide (ΔH_E = 33 kJ mol^{-1}). Thus, consideration of the enthalpy of activation, ΔH_E for diphenyl disulfide molecule and the corresponding values for the similar sized rigid molecules, o-hydroxy benzophenone and dibenzothiophene sulfoxide, suggests that most likely intramolecular rotation around the S-S bond occurs in the diphenyl disulfide molecule. Further, the free energy of activation, ΔG_E = 36 kJ mol^{-1}, at 158K for diphenyl disulfide would seem reasonable for comparison with the n.m.r. value of ΔG_E = 32 kJ mol^{-1} at coalescence temperature, obtained by Fraser et al.[9j] for an intramolecular rotation around the S-S bond for ($C_6H_5CH_2SSC_6H_5$) in liquid solution.

The dibenzyl disulfide shows only one absorption in nearly the same temperature region as diphenyl disulfide. This molecule, similar to diphenyl disulfide, shows a significant difference between the extrapolated value of the observed dipole moment at 300K (μ_{extpd} = 0.9 D) and the value in benzene solution (μ_{LIT} = 1.9 D at 298K). The relaxation time ($\tau = 4 \times 10^{-4}$ s) and free energy of activation (ΔG_E = 35 kJ mol^{-1}) for dibenzyl disulfide at 200K are found to be smaller than those for diphenyl disulfide, where the values of relaxation time and free energy of activation at a given temperature (200K) are $\tau = 1.1 \times 10^{-3}$ s and ΔG_E=37 kJ mol^{-1} , respectively. It is notable that the values of relaxation time and free energy of activation at a given temperature (200K) did not show any increase with increasing size of the molecule, (i.e., on passing from diphenyl disulfide to dibenzyl disulfide) and rather decreased within the limits of experimental accuracy, which bears out the fact that the same intramolecular process, i.e., rotation around the S-S link in dibenzyl disulfide, is occurring.

In addition, a good correspondence is found between our value of free energy of activation, ΔG_E = 36 kJ mol^{-1} for dibenzyl disulfide at 145K in the matrix, and the corresponding n.m.r. value of ΔG_E = 30 kJ mol^{-1} at 145K for an intramolecular rotation around the S-S bond in dibenzyl disulfide in liquid solution. Hence, this agreement between ΔG_E values obtained from dielectric and n.m.r. techniques also adds support to the above interpretation for an intramolecular process around the S-S bond for the dibenzyl disulfide molecule.

In the case of 4-4'diaminodiphenyl disulfide again a single dielectric absorption was detected. As for this molecule one should expect a relatively higher energy barrier to rotation around the S-S bond in comparison with the diphenyl disulfide molecule. The amino substituents on the para position of the phenyl rings have a high mesomeric moment (+M type) that will direct charge towards the S-S link. This would make much more conjugation along this bond. Thus, owing to the enhanced conjugation, the relaxation time, $\tau = 4.6 \times 10^{-3}$ s (200K) and the enthalpy of activation, $\Delta H_E = 37$ kJ mol^{-1} for 4-4'diaminodiphenyl disulfide appear to be larger in comparison with the corresponding parameters of 1.1×10^{-3} s and 33 kJ mol^{-1}, respectively for an intramolecular process around the S-S bond in diphenyl disulfide.

It is notable that the entropies of activation for diphenyl disulfide and 4-4'diaminodiphenyl disulfide are negative. When consideration of the previous comparison between rigid molecules and diphenyl disulfide is taken into account, the possibility of a molecular relaxation process in 4-4'diaminodiphenyl disulfide could be ruled out, as by introducing the amino groups in the aromatic ring, one should expect the enthalpy of activation to go up significantly owing to an increase in the size of the molecule. Thus, these observations support the assignment of an intramolecular rotation around the S-S bond to this process of 4-4'diaminodiphenyl disulfide.

For 4-tolyl disulfide only one absorption measured from 265 - 303K was found, yielding an enthalpy of activation, $\Delta H_E = 60$ kJ mol^{-1}, a large positive entropy of activation, $\Delta S_E = 55$ J K^{-1} mol^{-1}, and the breadth of the absorptions (low β values $\sim$0.2). One should expect a similar value of relaxation time and enthalpy of activation for 4-4'diaminodiphenyl disulfide and 4-tolyl disulfide for a molecular relaxation process, as both the molecules are fairly similar in size and shape. In contrast, one might expect smaller values of τ and ΔH_E in the latter molecule than in the former, if both molecules exhibit the same intramolecular relaxation process around the

S-S bond as the amino group is more electron donating than the methyl group. This would make far much more conjugation with the S-S bond, and hence a larger energy barrier for an intramolecular process around this bond.

However, significantly larger values of relaxation time, (τ = 2 s at 200K) and enthalpy of activation, (ΔH_E = 60 kJ mol^{-1}) for 4-tolyl disulfide than that for 4-4'diamino-diphenyl disulfide, where the respective values are τ = 4.6 x 10^{-3} s and ΔH_E = 37 kJ mol^{-1}, reveal that two different processes have been observed in these molecules. It is worth noting (Table IV-3) that the temperature region of absorption, relaxation time, and free energy of activation at 300K, and the values of activation enthalpy and entropy for 4-tolyl disulfide are all of the same order as those obtained for the higher temperature absorption of dimethyl-, and diethyl disulfides, where most likely absorption arises owing to a co-operative molecular process in polystyrene.

The bis(3-nitrophenyl) disulfide also shows one set of absorption, having enthalpy of activation, ΔH_E = 71 kJ mol^{-1} and a large positive entropy of activation, ΔS_E = 97 J K^{-1} mol^{-1}. The temperature range, magnitude of relaxation time, and free energy of activation at 300K (Table IV-3) for bis(3-nitrophenyl) disulfide appear to be in close similarity with the corresponding values for 4-tolyl disulfide. In addition, the activation enthalpy, and entropy values for 4-tolyl disulfide and bis(3-nitrophenyl) disulfide are found, in each instance, to fit very well within experimental accuracy to a relation[21] corresponding to a co-operative motion in polymer. This further supports the view that the co-operative motion of the molecule with the segments of the polymer chain make a contribution to the dielectric absorption of 4-tolyl disulfide and bis(3-nitrophenyl) disulfide.

The last molecule of the diaryl disulfide series studied was di-β-naphthyl disulfide. The pure crystalline solid sample of di-β-naphthyl disulfide showed only one absorption and gave a significantly low value of $\Delta H_E = 14$ kJ mol^{-1} in the temperature range of 194 - 229K. A significantly high 'β' value (0.29 - 0.59), (which is the characteristic of intramolecular dipolar motion),[18,19] and a large negative entropy of activation, $\Delta S_E = -93$ J K^{-1} mol^{-1} are found in di-β-naphthyl disulfide.. It is to be noted that the free energy of activation, ΔG_E, at 200K in di-β-naphthyl disulfide is about the same order of magnitude as in dialkyl disulfides for a high temperature intramolecular process. The enthalpy of activation is found to be less than the free energy of activation, owing to a larger negative entropy of activation. Thus from previous consideration of its 'β' and ΔG_E values, the most likely interpretation is that some form of intramolecular motion of naphthyl groups around the S-S bond occurs in di-β-naphthyl disulfide.

The last molecule for which the data are given in Table IV-3 is p-chlorothioanisole, although it is not a member of disulfide moiety. However, a study of this molecule may provide some information for future work in this series.

The p-chlorothioanisole shows two sets of absorption. The higher temperature absorption was measured from 209 - 243K, giving 'β' = 0.17 - 0.19, ΔH_E = 41 kJ mol^{-1} and ΔS_E = 25 J K^{-1} mol^{-1}. The values of relaxation time ($\tau_{200K} = 8.0 \times 10^{-4}$ s) and enthalpy of activation (ΔH_E = 41 kJ mol^{-1}) for p-chlorothioanisole are to be compared with the respective values of ($\tau_{200K} = 3.1 \times 10^{-4}$ s) and (ΔH_E = 42 kJ mol^{-1}) for almost a similar sized rigid molecule, p-iodotoluene. In addition, the values of free energy of activation (at 200K) and entropy of activation for the former molecule are found to be, ΔG_E = 36 kJ mol^{-1} and ΔS_E = 25 J K^{-1} mol^{-1}, respectively. In the latter rigid molecule, these values are 35 kJ mol^{-1} and 33 J K^{-1} mol^{-1}, respectively. Hence, this close similarity of relaxation parameters between p-chlorothioanisole and a rigid p-iodotoluene molecule strongly favoured a molecular relaxation process for p-chlorothioanisole. The low temperature absorption of p-chlorothioanisole was measured on a Q-meter in the temperature range of 90 - 116K, yielded an activation enthalpy of 7 kJ mol^{-1} and an activation entropy of -43 J K^{-1} mol^{-1}. This may be attributed to an intramolecular process around the C_{Ar}-S bond. Farmer and Walker[24] reported a barrier height of 5.4 kJ mol^{-1} for methoxy group rotation, but Katritzky _et al_.[25] estimated a rotational barrier of 10.8 kJ mol^{-1} for methoxy group rotation. Thus, in the light of these reported values of the rotational barrier for the methoxy group, our value of activation enthalpy, ΔH_E = 7 kJ mol^{-1} for an intramolecular process in p-chlorothioanisole seems quite reasonable.

Altogether, from the preceding discussion on the experimental data, the conclusion may be drawn that in all dialkyl disulfides an intramolecular relaxation process around the S-S bond has been observed at a temperature ∿180K, having an enthalpy of activation, ∿29 kJ mol^{-1}.

The segmental relaxation contributes to the low temperature dielectric absorption of diethyl-, di-isopropyl-, di-n-butyl-, di-tert-butyl-, and di-n-octyl disulfides. The disappearance of this absorption in dimethyl disulfide gives additional support to the above interpretation of segmental motion in these dialkyl disulfides. Further, the ΔH_E values for this process for the diethyl-, di-isopropyl-, di-tert-butyl-, and di-n-butyl disulfides favour an intramolecular rather than a molecular process.

The higher temperature absorption of dimethyl-, diethyl-, and di-isopropyl disulfides is coupled with a co-operative motion of molecules with the polymer segments.

In diaryl disulfides, the relaxation time and enthalpy data favour intramolecular relaxation around the S-S bond in diphenyl disulfide, dibenzyl disulfide, 4-4'diaminodiphenyl disulfide, and di-β-naphthyl disulfide. The relaxation in 4-tolyl disulfide and bis(3-nitrophenyl) disulfide seems to be due to the co-operative molecular process in polystyrene. A value of ΔG_E = 36 kJ mol^{-1} for dibenzyl disulfide at 145K in the matrix agrees well with the n.m.r. value of ΔG_E = 30 kJ mol^{-1} at 145K for an intramolecular process around the S-S bond in dibenzyl disulfide in liquid solution. In p-chlorothioanisole a separate molecular relaxation process and an intramolecular relaxation process have been observed.

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TABLE IV-2 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS FOR SOME DISULFIDE MOLECULES AND A p-CHLOROTHIOANISOLE MOLECULE IN POLYSTYRENE MATRICES, AND FOR DI-β-NAPHTHYL DISULFIDE IN A PURE CRYSTALLINE SOLID

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.95M Dimethyl disulfide High Temperature Absorption				
158.1	187.6	2.93	0.37	11.02	2.79	0.458
161.3	118.1	3.13	0.37	11.09	2.79	0.463
165.3	71.7	3.35	0.36	10.99	2.79	0.470
169.4	41.4	3.59	0.37	10.97	2.79	0.474
174.7	22.8	3.84	0.36	10.95	2.79	0.483
179.2	13.6	4.07	0.36	10.86	2.79	0.486
187.8	5.19	4.49	0.37	10.57	2.79	0.485
		0.72M Diethyl disulfide Higher Temperature Absorption				
274.7	76.9	3.32	0.15	3.67	2.65	0.651
280.0	46.5	3.53	0.15	3.55	2.64	0.643
295.0	11.4	4.14	0.18	3.35	2.62	0.586
300.0	7.29	4.34	0.17	3.26	2.61	0.600
304.8	4.36	4.56	0.16	3.19	2.60	0.614
310.8	3.11	4.71	0.15	3.15	2.60	0.647
		High Temperature Absorption				
161.3	245.9	2.81	0.40	10.48	2.61	0.519
165.8	140.4	3.05	0.40	10.40	2.61	0.525
170.3	83.5	3.28	0.40	10.35	2.61	0.528
175.6	46.5	3.53	0.40	10.17	2.62	0.529
186.2	16.3	3.99	0.41	9.89	2.62	0.530
193.6	7.88	4.31	0.41	9.59	2.64	0.532
199.9	4.65	4.53	0.45	9.47	2.64	0.510
		Low Temperature Absorption				
80.9	26.5	3.78	0.24	8.18	2.45	0.439
83.6	14.9	4.03	0.24	8.49	2.45	0.448
84.2	14.0	4.06	0.23	8.62	2.45	0.454
86.8	7.75	4.31	0.25	8.98	2.45	0.459
89.6	4.41	4.56	0.25	9.33	2.45	0.471
90.8	3.83	4.62	0.26	9.45	2.45	0.469
92.1	3.27	4.69	0.27	9.69	2.45	0.470

TABLE IV-2 continued...

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
		0.56M Di-isopropyl disulfide Higher Temperature Absorption				
283.4	58.8	3.43	0.12	2.72	2.66	0.730
288.1	16.2	3.99	0.09	2.69	2.64	0.815
293.8	12.4	4.11	0.11	2.65	2.65	0.744
297.8	2.26	4.85	0.08	2.62	2.62	0.908
		High Temperature Absorption				
176.0	226.9	2.85	0.32	10.69	2.68	0.676
180.5	126.8	3.10	0.35	10.57	2.68	0.655
185.1	69.3	3.36	0.34	10.36	2.68	0.666
190.5	42.0	3.58	0.37	10.08	2.69	0.635
195.0	23.4	3.83	0.36	9.84	2.69	0.631
199.6	16.2	3.99	0.39	9.67	2.69	0.622
204.7	10.0	4.20	0.39	9.42	2.69	0.620
209.5	6.59	4.38	0.40	9.17	2.69	0.615
		Low Temperature Absorption				
100.6	211.2	2.88	0.24	9.83	2.60	0.580
104.3	107.4	3.17	0.24	10.41	2.60	0.601
106.4	72.9	3.34	0.24	10.76	2.60	0.618
110.9	28.8	3.74	0.24	11.46	2.60	0.653
113.6	18.4	3.94	0.25	11.90	2.60	0.663
115.9	12.1	4.12	0.25	12.33	2.60	0.680
121.1	4.86	4.51	0.26	13.28	2.60	0.711
125.1	2.97	4.73	0.27	14.04	2.60	0.720
		0.48M Di-n-butyl disulfide High Temperature Absorption				
173.8	217.9	2.86	0.30	11.72	2.68	0.791
178.0	122.9	3.11	0.30	11.89	2.68	0.800
182.7	63.1	3.40	0.29	12.07	2.69	0.834
187.0	38.9	3.61	0.31	12.14	2.69	0.817
191.5	23.1	3.84	0.33	12.30	2.70	0.809
197.0	13.5	4.07	0.35	12.39	2.71	0.797
201.6	8.52	4.27	0.37	12.45	2.71	0.789
206.6	5.68	4.45	0.38	12.36	2.72	0.780

TABLE IV-2 continued....

T(K)	$10^6\tau$(s)	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		Low Temperature Absorption				
101.8	328.3	2.69	0.29	7.50	2.50	0.511
105.3	175.5	2.96	0.29	7.96	2.50	0.537
109.3	83.7	3.28	0.29	8.42	2.50	0.567
113.3	40.9	3.59	0.28	8.92	2.50	0.596
115.3	27.2	3.77	0.28	9.18	2.50	0.609
120.6	11.5	4.14	0.29	9.89	2.50	0.638
125.4	5.23	4.48	0.29	10.51	2.50	0.670
128.5	3.54	4.65	0.30	10.99	2.50	0.682
		0. 48M Di-tert-butyl disulfide High Temperature Absorption				
170.6	280.5	2.75	0.34	8.16	2.68	0.611
175.0	161.7	2.99	0.35	8.14	2.68	0.610
180.4	82.7	3.28	0.36	8.07	2.68	0.614
184.9	50.3	3.50	0.37	8.00	2.68	0.609
190.3	28.5	3.75	0.39	7.89	2.68	0.597
195.7	16.5	3.99	0.40	7.82	2.68	0.593
199.8	11.3	4.15	0.41	7.76	2.68	0.591
205.9	6.51	4.39	0.43	7.60	2.68	0.583
		Low Temperature Absorption				
85.8	46.3	3.54	0.19	4.59	2.60	0.451
90.6	19.0	3.92	0.19	4.91	2.61	0.468
94.3	9.51	4.22	0.19	5.19	2.61	0.488
99.2	4.28	4.57	0.20	5.53	2.61	0.506
101.3	3.22	4.69	0.20	5.59	2.61	0.519
		0.30M Di-n-octyl disulfide High Temperature Absorption				
181.3	230.2	2.84	0.24	6.28	2.57	0.851
185.4	150.3	3.02	0.26	6.44	2.57	0.828
190.8	82.5	3.29	0.26	6.66	2.57	0.867
194.4	61.9	3.41	0.24	6.69	2.57	0.906

TABLE IV-2 continued....

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.30M Di-n-octyl disulfide High Temperature Absorption (con't)				
199.8	35.6	3.65	0.23	6.88	2.57	0.957
205.9	21.7	3.87	0.23	7.12	2.57	0.991
210.5	14.9	4.03	0.22	7.24	2.57	1.027
216.0	9.27	4.23	0.21	7.43	2.57	1.081
		Low Temperature Absorption				
130.4	204.3	2.89	0.34	7.17	2.52	0.649
135.6	86.2	3.27	0.33	7.53	2.52	0.694
140.3	39.0	3.61	0.34	8.03	2.52	0.721
144.8	18.6	3.93	0.34	8.41	2.52	0.749
149.8	9.15	4.24	0.36	8.92	2.53	0.761
155.0	4.41	4.56	0.36	9.35	2.53	0.784
157.9	3.37	4.67	0.39	9.69	2.53	0.776
		0.41M Diphenyl disulfide				
219.3	177.7	2.95	0.25	3.39	2.68	0.561
224.6	113.0	3.15	0.25	3.48	2.68	0.581
229.9	66.7	3.38	0.27	3.57	2.69	0.570
234.7	53.1	3.48	0.28	3.64	2.69	0.575
239.5	37.5	3.63	0.27	3.67	2.69	0.591
244.1	23.7	3.83	0.27	3.74	2.69	0.610
253.8	12.9	4.09	0.25	3.83	2.69	0.642
263.7	6.63	4.38	0.27	3.96	2.69	0.651
		0.44M Dibenzyl disulfide				
214.9	94.4	3.23	0.16	5.95	2.67	0.889
219.8	50.1	3.50	0.18	6.17	2.67	0.882
224.8	30.3	3.72	0.19	6.40	2.68	0.883
229.9	15.8	4.00	0.19	6.62	2.68	0.904
239.2	7.73	4.31	0.20	7.00	2.68	0.907
248.7	3.95	4.61	0.22	7.37	2.69	0.905
253.8	3.62	4.64	0.25	7.52	2.70	0.881

TABLE IV-2 continued....

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
		0.34M 4,4'-diaminodiphenyl disulfide				
239.4	101.9	3.19	0.22	7.33	2.78	0.998
249.2	45.2	3.55	0.21	7.79	2.78	1.055
258.9	21.2	3.88	0.22	8.32	2.78	1.097
266.2	12.4	4.11	0.22	8.81	2.79	1.135
273.5	7.87	4.31	0.22	9.38	2.79	1.180
280.4	5.61	4.45	0.23	9.89	2.79	1.200
286.8	3.90	4.61	0.24	10.61	2.79	1.234
		0.35M 4-tolyl disulfide				
265.1	184.9	2.93	0.19	4.95	2.68	0.922
268.0	150.0	3.03	0.19	5.07	2.67	0.958
273.0	97.1	3.21	0.17	5.25	2.67	1.026
277.6	59.7	3.43	0.21	5.53	2.68	0.956
281.9	38.7	3.61	0.21	5.79	2.67	0.981
287.5	22.2	3.86	0.20	5.98	2.67	1.051
294.2	11.7	4.13	0.19	6.35	2.66	1.116
302.9	5.72	4.44	0.16	6.71	2.66	1.249
		0.35M Bis-(3-nitrophenyl disulfide)				
258.2	349.0	2.66	0.18	28.63	2.70	2.18
262.9	189.3	2.92	0.19	29.93	2.70	2.21
270.5	84.3	3.28	0.18	31.78	2.70	2.33
278.1	32.3	3.69	0.19	34.08	2.69	2.39
285.5	14.9	4.03	0.21	36.52	2.70	2.40
290.1	8.80	4.26	0.21	37.96	2.69	2.48
294.1	5.07	4.50	0.21	39.70	2.68	2.55
		Di-β-naphthyl disulfide				
194.3	119.2	3.13	0.29	1.77	-	-
199.8	79.9	3.30	0.60	2.64	-	-
204.4	90.9	3.24	0.60	3.02	-	-
209.7	48.7	3.51	0.56	2.81	-	-
214.5	44.9	3.55	0.45	2.66	-	-
219.8	42.4	3.57	0.48	2.85	-	-
244.3	35.7	3.65	0.54	3.56	-	-
229.2	22.7	3.85	0.41	3.02	-	-

TABLE IV-2 continued....

0.55M p-Chlorothioanisole
High Temperature Absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
209.1	252.9	2.80	0.19	11.85	2.63	1.027
214.1	133.6	3.08	0.19	12.18	2.63	1.050
219.6	81.9	3.29	0.18	12.54	2.62	1.113
223.9	53.2	3.48	0.18	12.77	2.61	1.142
228.7	31.7	3.70	0.18	13.07	2.61	1.163
233.7	19.1	3.92	0.17	13.31	2.60	1.207
238.4	12.6	4.10	0.17	13.51	2.60	1.228
243.7	6.83	4.37	0.17	13.74	2.60	1.262

Low Temperature Absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
90.0	1.85	4.93	0.12	1.44	-	-
95.4	0.682	5.37	0.16	1.54	-	-
101.7	0.666	5.38	0.17	1.80	-	-
103.1	0.426	5.57	0.27	1.87	-	-
116.8	0.127	6.10	0.16	2.12	-	-

NOTE: A blank space (-) indicates that the information was not available.

TABLE IV-3 EYRING ANALYSIS RESULTS FOR DISULFIDE AND p-CHLOROTHIOANISOLE MOLECULES IN POLYSTYRENE MATRICES, AND AS COMPRESSED SOLID FOR DI-β-NAPHTHYL DISULFIDE

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		100K	200K	300K	100K	200K	300K		
Dimethyl disulfide	273 - 311	1.4×10^{15}	1.1	8.8×10^{-6}	53	49	44	57	41
	158 - 188	7.6×10^{1}	1.7×10^{-6}	3.9×10^{-9}	27	26	25	28	10
Diethyl disulfide	275 - 311	8.4×10^{16}	2.7	7.2×10^{-6}	56	50	44	62	60
	161 - 200	5.9×10^{1}	4.6×10^{-6}	1.7×10^{-8}	27	28	29	26	- 9
	80 - 92	8.9×10^{-7}	5.3×10^{-10}	3.7×10^{-11}	12	13	14	11	- 8
Di-isopropyl disulfide	283 - 298	9.8×10^{42}	3.5×10^{6}	2.1×10^{-6}	106	73	41	138	325
	176 - 210	3.2×10^{3}	1.5×10^{-5}	2.2×10^{-8}	30	30	30	31	4
	101 - 125	2.6×10^{-4}	3.1×10^{-9}	5.9×10^{-11}	17	16	15	18	10
Di-n-butyl disulfide	174 - 207	3.9×10^{3}	1.0×10^{-5}	1.2×10^{-8}	31	29	28	32	13
	102 - 129	5.3×10^{-4}	6×10^{-9}	1.1×10^{-10}	17	17	16	18	5
Di-tert-butyl disulfide	171 - 206	1.2×10^{3}	1.1×10^{-5}	2×10^{-8}	30	29	29	30	1
	85 - 101	3.8×10^{-6}	1.6×10^{-9}	1.0×10^{-10}	13	15	16	12	-15
Di-n-octyl disulfide	181 - 216	1.8×10^{3}	3.6×10^{-5}	8.2×10^{-8}	30	31	33	28	-15
	130 - 158	2.8×10^{-1}	4.7×10^{-8}	2.2×10^{-10}	23	20	18	25	23
Diphenyl disulfide	219 - 264	1.2×10^{6}	1.1×10^{-3}	9.4×10^{-7}	35	37	39	33	-18
Dibenzyl disulfide	215 - 254	3.3×10^{6}	4×10^{-4}	1.7×10^{-7}	36	35	35	37	8

TABLE IV-3 continued...

Molecule	T(K)	τ(s) 100K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 100K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
4,4'Diamino diphenyl disulfide	239 - 287	4.9×10^{7}	4.6×10^{-3}	1.8×10^{-6}	38	39	40	37	-11
4-Tolyl disulfide	265 - 303	2.5×10^{16}	2.0	7.4×10^{-6}	55	50	44	60	55
Bis(3-nitro phenyl) disulfide	258 - 294	4.5×10^{19}	7.0	3.1×10^{-6}	61	52	42	71	97
Di-β-naphthyl disulfide	194 - 229	9.3×10^{-1}	8.9×10^{-5}	3.4×10^{-6}	24	33	42	14	-93
p-Chloro-thioanisole	209 - 244 90 - 117	1.0×10^{8} 5.8×10^{-7}	8.0×10^{-4} 3.4×10^{-9}	1.3×10^{-7} 5.2×10^{-10}	39 12	36 16	34 21	41 7	25 -43

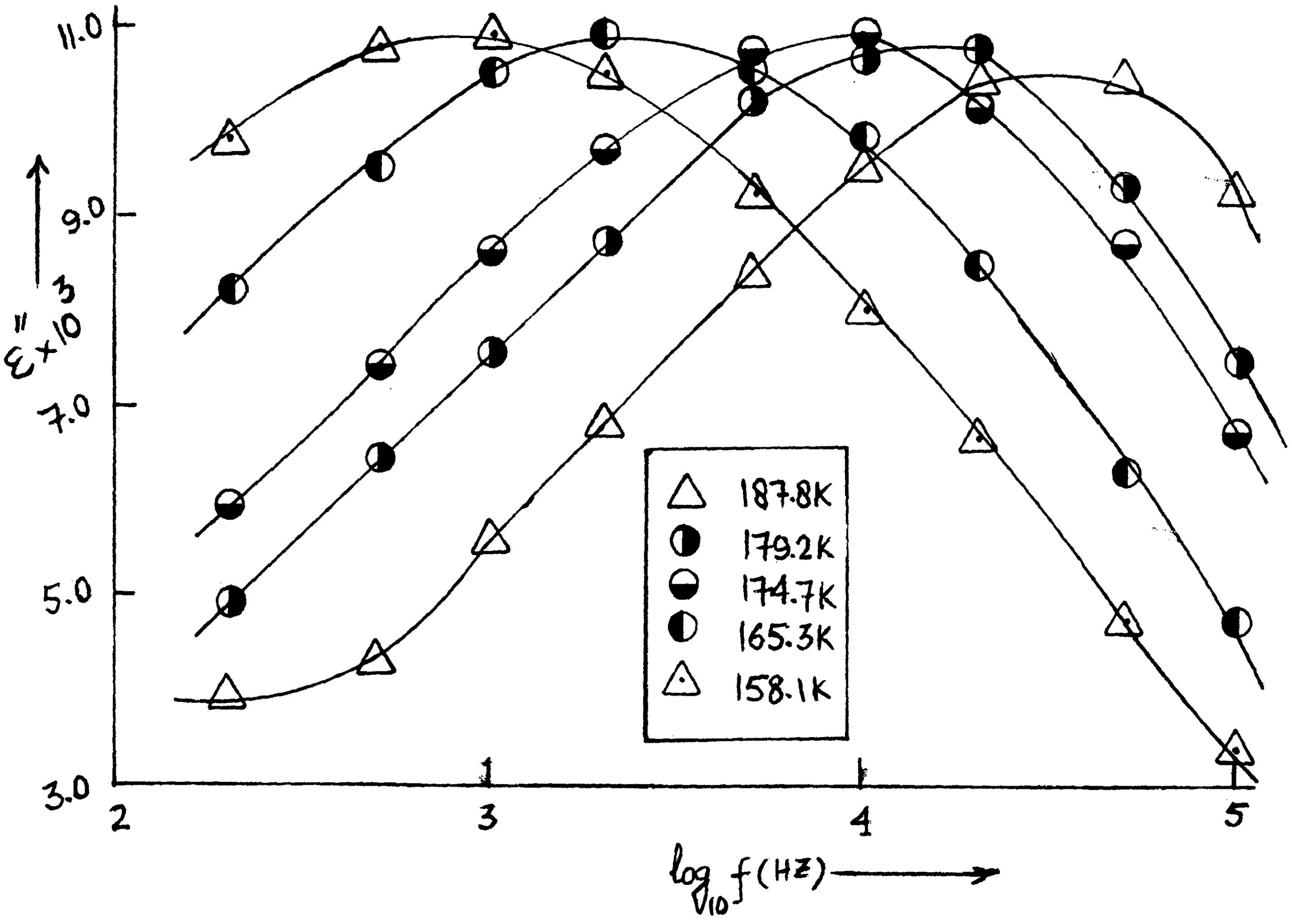
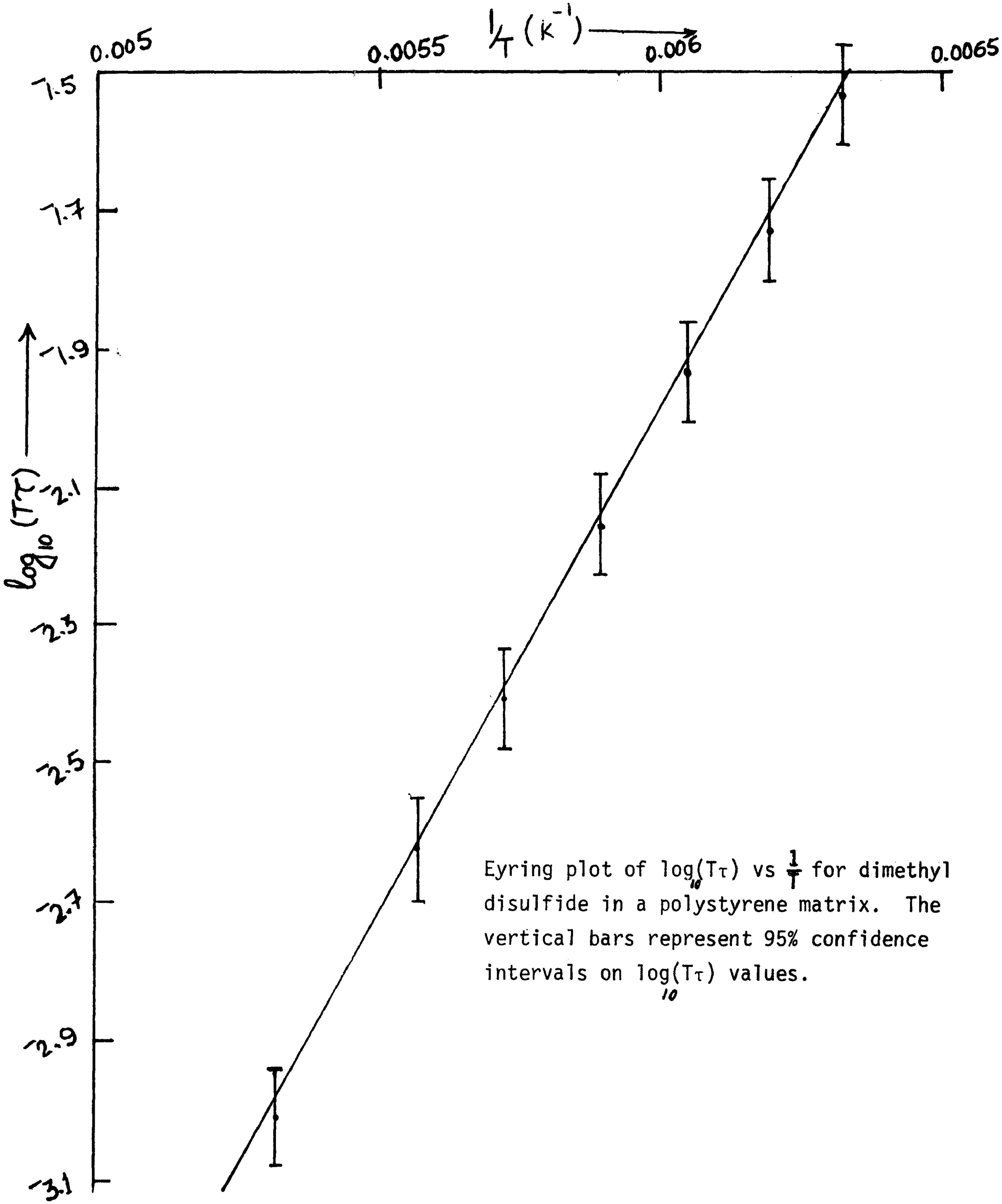


FIG IV-2 Plot of Dielectric loss factor vs $\log_{10} f$ for Dimethyl disulfide



Eyring plot of log$_{10}$(Tτ) vs $\frac{1}{T}$ for dimethyl disulfide in a polystyrene matrix. The vertical bars represent 95% confidence intervals on log$_{10}$(Tτ) values.

FIG IV- 3

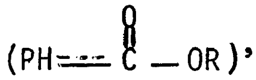
CHAPTER V

ESTER GROUP AND/OR MOLECULAR RELAXATION OF SOME AROMATIC ESTERS

INTRODUCTION

Considerable interest has been shown by chemists in the behaviour of the ester group on aromatic molecules. In the literature there appears to be disagreement among investigators as to whether or not there is electronic interaction between the aromatic ring and the attached carbonyl group in alkyl benzoates. Smyth,[1] and Krishna and Upadhyay[2] suggested that the dipole moments of aromatic esters give no evidence of interaction between the polar group and the aromatic ring. Guryanova and Grishko[3] stated that free rotation about the C_{Ar}—— C bond was unlikely because of the presence of π electrons at C_{Ar} and CO_2 carbon atoms. Le Fevrè and Sundaram[4] stated that the "effective" conformation appeared to be that in which maximum π-electron overlap or conjugation between the benzene ring and the carbonyl group occurred with the C = O atoms in the plane of the ring, and this corresponded to a potential energy minimum.

An increase in the electric dipole moments of a series of alkyl benzoates over the corresponding alkyl acetates was interpreted by Pinkus and Ellen[5], in terms of conjugative interaction with the phenyl ring supplying electrons to the electron-deficient carbonyl carbon.

Hasan *et al.*[6,7] made dielectric measurements in some monocarboxylic esters in the liquid state. They observed that, although the dielectric data in benzyl formate, benzyl acetate etc., could be analyzed in terms of both molecular and group relaxation, in the methyl- and ethyl benzoates the data were consistent with one relaxation process only. It was proposed that in the methyl- and ethyl benzoates,  $(PH{=\!=}\overset{\overset{O}{\|}}{C}-OR)$, the C = 0 dipole is adjacent to the benzene ring and that it imparts double bond character to the C — 0 bond owing to resonance, thus inhibiting the rotation of the OR group around the C—— OR linkage. Further[8], these workers extended the dielectric studies in the microwave region to the case of propyl- and butyl benzoates, finding no group rotation in these molecules. This supports the hypothesis of these workers (Hasan *et al.*)[6,7] in the cases of methyl- and ethyl benzoates.

A dipole moment study of benzyl benzoate, 2-naphthyl benzoate, and o-hydroxybenzyl benzoate in benzene solution by Krishna and Upadhyay[2] gave values for the energy barriers (ΔH_E) of 8.3 kJ mol^{-1}, 8.2 kJ mol^{-1}, and 8.8 kJ mol^{-1}, respectively, and relaxation times (τ) of 7.0 ps, 6.69 ps, and 8.5 ps, respectively. From the comparatively small values of ΔH_E and τ, these workers proposed a possibility of restricted rotation of the -OR group in these molecules about the position of minimum potential energy.

Krishna et al.[9] made a dielectric study of methyl-p-nitrobenzoate, methyl-m-nitrobenzoate, ethyl-m-nitrobenzoate, ethyl-o-nitrobenzoate and methyl-o-aminobenzoate in benzene solution at 303K. They reported barrier heights (ΔH_E) as 9.6 kJ mol^{-1}, 9.2 kJ mol^{-1}, 10.0 kJ mol^{-1}, 8.4 kJ mol^{-1}, and 9.2 kJ mol^{-1}, respectively. From the comparison of observed and theoretically calculated electric dipole moment values, they proposed the absence of intramolecular rotation in these esters except for methyl- and ethyl-m-nitrobenzoates. Thus, the relaxation time in these esters was ascribed to overall rotation of the molecule in the solvent.

Grindley, Katritzky and Topsom[10] have estimated the energy barriers to rotation about the C_{Ar}-C bond to be 22.2 kJ mol^{-1} and 24.7 kJ mol^{-1} for the CO_2Me and CO_2Et groups in methyl benzoate and ethyl benzoate, repsectively; they assumed the strain energy to be zero. In view of the foregoing review of the literature, information about the experimental determination of energy barrier to ester group rotation in alkyl benzoates is lacking so far. Therefore, the present dielectric relaxation study of various aromatic esters and some related compounds in polystyrene matrices was initiated, since it seemed that determination and interpretation of the dielectric relaxation parameters might throw some light on the intramolecular rotation in aromatic esters. This procedure offered the possibility of separating the group relaxation contribution from the molecular relaxation.

EXPERIMENTAL RESULTS

The dielectric measurements for several aromatic esters in polystyrene matrices have been made over suitable ranges of temperature and frequency using the General Radio capacitance bridge, and in one case by using the Hewlett-Packard Q-meter, as described in Chapter II. The present study includes the investigation of dimethyl terephthalate, dimethyl 2,6-naphthalenedicarboxylate, methyl benzoate, ethyl benzoate, ethyl-p-nitro-, ethyl-p-amino-, ethyl-m-amino-, ethyl-p-(N,N-dimethyl amino)-, ethyl-p-fluoro-, ethyl-p-chloro-, ethyl-p-cyanobenzoates, ethyl cinnamate, ethyl-p-nitro cinnamate, ethyl-2-furoate, ethyl-5-norbornene-2-carboxylate, ethylindole-2-carboxylate, and polymethyl methacrylate in a polystyrene matrix. A sample plot of loss factor ($\varepsilon'' = \varepsilon''(obs) - \varepsilon''(p.s)$) against logarithm (freq) is shown in Figure V-1 for dimethylterephthalate.

The samples used in the experiments were commercial products (Aldrich Chemical Company) and were dried appropriately prior to use.

The Fuoss-Kirkwood analysis parameters for several aromatic esters and some related ester molecules at various temperatures are listed in Table V-1. Table V-2 shows the values of 'ΔH_E' and 'ΔS_E' evaluated from dielectric data as well as 'ΔG_E' and 'τ' values, calculated from these analyses at 150K, 200K, and 300K.

DISCUSSION

The good straight line plots of $\log T\tau$ against T^{-1} (for example, Figure V-2 for dimethyl terephthalate) have yielded enthalpies of activation (ΔH_E) for dimethyl terephthalate of 32 kJ mol^{-1} and for dimethyl 2,6-naphthalenedicarboxylate of 35 kJ mol^{-1}, respectively, in polystyrene matrices. Thus, these two esters exhibited dielectric absorptions in similar ranges of temperature and frequency, yielding ΔH_E values in good agreement, well within our estimate of experimental error.

For the cases of dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate, in the absence of stable polar (e.g., cis) forms over the period of measurement, the components of the dipole moments of the two substituent ester groups along the long axis of the molecule are equal and opposite, therefore cancelling out one another. In this case only the components of the dipole moments perpendicular to this axis may contribute to the relaxation mechanism. If, though, a stable cis form existed in sufficient concentration then this could contribute to the dielectric absorption. However, a stable cis form would imply a high energy barrier opposing group relaxation, probably considerably higher than that estimated[10] for ester group rotation.

It is profitable to note that the relaxation times for the slightly smaller p-bromoethylbenzene molecule in a polystyrene matrix (τ_{150K} = 1.9 s; τ_{200K} = 6.9 x 10^{-4} s, and τ_{300K} = 2.2 x 10^{-7} s, respectively) were longer by a factor of $\sim 10^2$ than that of the corresponding values of 2 x 10^{-3} s; 2.4 x 10^{-6} s; and 2.5 x 10^{-9} s, respectively, for dimethyl terephthalate. This would not be expected if the process were molecular relaxation in each case. However, there is no doubt that in p-bromoethylbenzene the process is that of molecular relaxation. The fact that both dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate have about the same values of enthalpy of activation rules out their both being attributed to molecular relaxation, since the latter molecule is appreciably larger in size. Thus, it would have a considerably larger enthalpy of activation than the dimethyl terephthalate for a molecular relaxation process. In addition, it can be seen (Table V-2) that, for dimethyl 2,6-naphthalenedicarboxylate, the temperature region in which absorption occurs, and the relaxation times at 150K, 200K, and 300K are similar to those observed for dimethyl terephthalate. This close similarity of the results for dimethyl 2,6-naphthalenedicarboxylate and dimethyl terephthalate in polystyrene bears out that the same relaxation process (i.e., ester group relaxation) has been observed in both the molecules.

There may also be a possibility of methoxy group relaxation in dimethyl terephthalate. This possibility can be ruled out by considering the results for 2,6-dimethoxynaphthalene (Table V-2), a molecule appreciably larger in size where the component of the substituent group moments along the long axis of the molecule cancel out one another. Thus, only methoxy group rotation is responsible for the dielectric absorption, which was observed at a very low temperature (i.e., 91 - 108K) and yielded an activation enthalpy of 11 kJ mol^{-1}. This value is considerably smaller than that of 32 kJ mol^{-1} obtained in dimethyl terephthalate. However, it should be noted that the value of activation enthalpy, ΔH_E = 32 kJ mol^{-1}, for dimethyl terephthalate in a polystyrene matrix is consistent with the activation enthalpies of 29.3 kJ mol^{-1} (23), and 29 kJ mol^{-1} (26), for aldehyde and acetyl group relaxations in terephthaldehyde and 1,4-diacetylbenzene in polystyrene matrices, respectively, where all three types have a keto group linked to a phenyl group. Therefore, from the above considerations, it appears that the most likely source of dielectric absorption for dimethyl terephthalate in a polystyrene matrix is due to the rotation of the ester group. An enthalpy of activation ∿32 kJ mol^{-1} may serve as a standard for ester group relaxation in an aromatic ester where no enhanced conjugation occurs.

Methyl benzoate and ethyl benzoate showed absorptions in the same temperature range as did dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate for the given frequency range. They yielded enthalpies of activation of 31 kJ mol^{-1} and 33 kJ mol^{-1}, respectively. However, it is noteworthy that Tay et al.,[16] employing techniques similar to those of this work, were able to observe only the group relaxation process in 2,6-dinitro- and 2,6-dinitro-p-methyl phenols. Similarly, Davies and Swain[11] examined ten flexible molecules in polystyrene matrix, finding that only two showed a molecular relaxation process, whereas the intramolecular relaxation was observed in each case. There would appear to be two possible sources of dielectric absorption in these aromatic esters, one being the group and the other molecular relaxation. For molecular relaxation the enthalpy of activation (ΔH_E) tends to increase, and the relaxation time (τ) tends to become longer, as molecular size is increased (cf: Chapter III). Since the molecules of methyl benzoate, ethyl benzoate, dimethyl terephthalate, and dimethyl 2,6-naphthalenedicarboxylate differ appreciably in size, one would expect the values of these parameters to differ, if these four molecules exhibit the same molecular relaxation process. However, values of ΔH_E, and τ at 200K for these ester molecules were 31 kJ mol^{-1} and 3.3×10^{-6} s; 33 kJ mol^{-1} and 3.6×10^{-6} s; 32 kJ mol^{-1} and 2.4×10^{-6} s; and 35 kJ mol^{-1} and 3.6×10^{-6}s, respectively. The close similarity in ΔH_E and τ values for methyl-and ethyl benzoates with those of dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate favours ester group relaxation in the former molecules as observed in the latter molecules. In addition, the free energies of activation (ΔG_E) at 200K for methyl benzoate, 27 kJ mol^{-1}, and for ethyl benzoate, 27 kJ mol^{-1}, were found to be in good agreement with those of 27 kJ mol^{-1} and 27 kJ mol^{-1}, respectively, for dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate. In the latter molecules the process has been ascribed to ester group relaxation. It may also be seen (Table V-2), that the values of entropy of activation (ΔS_E) for these four ester molecules lie in the range 27 ±9 J K^{-1} mol^{-1}.

Further, the calculation of $\mu_{\parallel}$ (the component of the substituent ester group dipole moment along the long axis of the molecule) and $\mu_{\perp}$ (the component of the dipole moment perpendicular to this axis, responsible for group relaxation) has been made for methyl benzoate. The details of which are shown below.

In methyl benzoate (a monosubstituted benzene molecule whose resultant moment is not along a symmetry axis), if it is assumed for the moment that the ester group is free to rotate, then the dipole moment of molecule can be resolved into two components. One is along the carbon-1——carbon-4 axis ($\mu_{\parallel}$), and the other is parallel to the carbon-2——carbon-6 axis ($\mu_{\perp}$) perpendicular to the former. The latter component ($\mu_{\perp}$) will govern the group relaxation process, while the former, $\mu_{\parallel}$ will govern relaxation of the whole molecule.

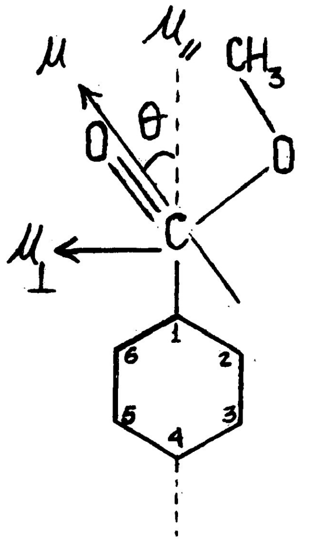
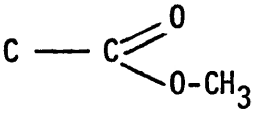


FIG V-3

(Figure V-3). The weight factor (C_2) for the group process will be proportional to $\mu_{\perp}^2$, while (C_1) for the molecular process will α $\mu_{\parallel}^2$. It is to be noted that the weight factors 'C_2' and 'C_1' depend on the angle of inclination, θ, that is the angle of the ester group moment to the long C_1 — C_4 axis. The weight factors 'C_1' and 'C_2' are represented as:

$$C_1 = \frac{\mu_{\parallel}^2}{\mu_{\parallel}^2 + \mu_{\perp}^2} \quad \text{and} \quad C_2 = \frac{\mu_{\perp}^2}{\mu_{\parallel}^2 + \mu_{\perp}^2}$$

where $\mu_{\perp} = \mu \sin\theta$ and $\mu_{\parallel} = \mu\cos\theta$, and thus $C_1 + C_2 = 1$.

For methyl benzoate the angle, θ, subtended by the  $C-C(=O)O-CH_3$ group moment to the major axis of the ring was taken as 69^o 14',[18] and the ester group moment as 1.83 D.[19] With the help of the above equations the values of $\mu_{\parallel}$ and $\mu_{\perp}$ are found to be 0.65 D and 1.71 D, respectively. The calculation produced a molecular weighting factor, $C_1 = 0.13$ and a group weighting factor $C_2 = 0.87$. This suggested that there may be a little contribution from molecular relaxation. It may also be noted that the extrapolated value of the observed dipole moment at 300K ($\mu_{extpd} = 1.5$ D) for methyl benzoate is in reasonable agreement with the perpendicular component ($\mu_{\perp} = 1.71$ D).

There was no indication of any other dielectric absorption corresponding to a molecular relaxation in methyl- and ethyl benzoates, although a detailed and careful measurement over the entire temperature range of 80 - 350K was made. Therefore, it appears that either the molecular absorption occurred within a temperature region similar to that of the group process and with a similar energy barrier, so that both the molecular and group processes overlapped, or that the small magnitude of the weight factor for the molecular process ($C_1 \approx 0.13$) resulted in an absorption too small to be detected. The former possibility may be ruled out by comparing the enthalpy of activation for methyl benzoate (ΔH_E = 31 kJ mol^{-1}) with the values of activation enthalpy for a slightly smaller rigid molecule, iodobenzene (cf: Chapter III) (ΔH_E = 16 kJ mol^{-1}), and with an approximately similar sized rigid molecule, α,α,α-trichlorotoluene (ΔH_E = 20 kJ mol^{-1}).[20] In the latter molecules the process is only that of molecular relaxation.

Thus, all the above considerations seem to indicate that predominantly ester group relaxation contributes to the dielectric absorption of methyl- and ethyl benzoates.

Ethyl cinnamate (a molecule where the ester group is not directly attached to the benzene ring) in polystyrene exhibited two distinctly separate regions of dielectric absorption. One is in the temperature range of 159 - 188K covering a $\log_{10}f_{max}$ range of 2.8 - 4.4, and the other is in the temperature range of 286 - 311K covering a $\log_{10}f_{max}$ range of 2.7 - 4.2 (Table V-2). It is to be noted that the low temperature dielectric absorption for ethyl cinnamate was measured in the same temperature range as that for dimethyl terephthalate for the given frequency range. This yielded an activation enthalpy of 30 kJ mol^{-1} and an activation entropy of 22 J K^{-1} mol^{-1}, comparable to the values of

$\Delta H_E = 32$ kJ mol^{-1} and $\Delta S_E = 27$ J K^{-1} mol^{-1} for dimethyl terephthalate, where the process is most likely an ester group relaxation. For this low temperature dielectric absorption, there may also be a possibility of an intramolecular process around the C_{Ar}——C_{aliph} bond. However, a further comparison of the similar relaxation times and free energies of activation at 200K for ethyl cinnamate and dimethyl terephthalate, which are 1.5×10^{-6} s and 26 kJ mol^{-1}, and 2.4×10^{-6} s, and 27 kJ mol^{-1}, respectively, suggests ester group relaxation as the source of the low temperature absorption in ethyl cinnamate.

An activation enthalpy of 91 kJ mol^{-1} and an activation entropy of 143 J K^{-1} mol^{-1} was found for the high temperature absorption of ethyl cinnamate. These may be attributed to a molecular relaxation process, as the observed activation entropy, $\Delta S_E = 143$ J K^{-1}mol^{-1}, agrees well within experimental accuracy with that of $\Delta S_{calcd} = 128$ J K^{-1} mol^{-1} obtained from the relation: ΔS_E(J K^{-1} mol^{-1}) = $-72 + 2.2\ \Delta H_E$ (kJ mol^{-1}) (cf: Chapter III) corresponding to a molecular relaxation process. Moreover, the extrapolation of the observed dipole moment at 288K for the low temperature process gives $\mu_{\perp} = 1.23$ D, whereas for the high temperature process the extrapolated value of observed dipole moment at 288K is $\mu_{//} = 1.19$ D. Thus, the resultant dipole moment $\sqrt{(1.23)^2 + (1.19)^2} = 1.71$ D, which is in good agreement with the literature value of 1.79 D[17] for a benzene solution at 288K. Such good agreement suggests that the component dipole moments so obtained are reasonably reliable.

Ethyl p-nitrocinnamate also shows two regions of dielectric absorption. The high temperature absorption for ethyl p-nitrocinnamate was found at a relatively higher temperature range than that for ethyl cinnamate. The former molecule yields considerably higher values of activation enthalpy, ΔH_E = 105 kJ mol^{-1} and activation entropy, ΔS_E = 154 J K^{-1} mol^{-1} in comparison with the corresponding values of 91 kJ mol^{-1} and 143 J K^{-1} mol^{-1}, respectively, obtained for the molecular relaxation process in the latter. This would seem reasonable since one would expect for the former molecule that the enthalpy of activation, ΔH_E, and entropy of activation, ΔS_E, would be greater owing to the insertion of a p-nitro substituent in ethyl cinnamate if both molecules exhibit the same molecular relaxation process. The experimental activation entropy of ΔS_E = 154 J K^{-1} mol^{-1} further supports the view that molecular relaxation has been observed for the high temperature absorption of ethyl p-nitrocinnamate. This is evident from the magnitude of activation entropy, ΔS_{calcd} = 159 J K^{-1} mol^{-1}, calculated from the relation (cf: Chapter III) for a molecular relaxation process, which is in excellent agreement with that of the observed value.

For the low temperature process of ethyl p-nitrocinnamate, there may be a possibility of either intramolecular relaxation around $C_{Ar} — C_{aliph}$ bond or an intramolecular relaxation of the ester group.

In the former case one should expect a higher energy barrier to intramolecular rotation than that of the ester group rotation (ΔH_E $\sim$32 kJ mol^{-1}) owing to the larger size of rotatable unit. However, a lower activation enthalpy of 28 kJ mol^{-1} and an activation entropy of 9 J K^{-1} mol^{-1} were found for this low temperature process of ethyl p-nitrocinnamate. These may be compared with the corresponding values of 32 kJ mol^{-1} and 27 J K^{-1}mol^{-1} obtained for the ester group relaxation in dimethyl terephthalate. The apparently lower values of ΔH_E and ΔS_E in the former molecule may be accounted for by the presence of an electron withdrawing p-nitro group which is known to pull the charge towards itself. The -M effect may influence the energy barrier to group rotation, resulting in a slight decrease of the value of activation enthalpy for ester group relaxation in the former molecule compared to that of the latter. Nevertheless, it is noteworthy (Table V-2) that the temperature range of absorption ($\sim$180K), the relaxation time, τ = 1.9 x 10^{-6} s, and the free energy of activation, ΔG_E = 26 kJ mol^{-1}, at 200K for the low temperature process of ethyl p-nitrocinnamate are in good agreement with the corresponding values for dimethyl terephthalate. Here the temperature range of absorption is ∿180K, and the values of τ and ΔG_E at 200K are 2.4 x 10^{-6} s and 27 kJ mol^{-1}, respectively, for ester group relaxation. Hence, these results suggest that ester group relaxation contributes to the low temperature dielectric absorption of ethyl-p-nitrocinnamate.

Ethyl-p-(N,N-dimethylamino)-benzoate in polystyrene exhibits two distinctly separate dielectric absorptions. The enthalpy and entropy of activation for the high temperature process of this molecule was found to be 97 kJ mol^{-1} and 152 J K^{-1} mol^{-1} respectively. The values of relaxation time, τ = 1.5 x 10^{-4} s and free energy of activation, ΔG_E = 52 kJ mol^{-1} at 300K for ethyl-p-(N,N-dimethylamino)-benzoate may be compared with the values of τ = 1.2 x 10^{-3} s and ΔG_E = 57 kJ mol^{-1} at 300K for a slightly larger rigid molecule, p-iodobiphenyl (cf: Chapter III), where the process is only a molecular relaxation. Thus, when it is borne in mind that the large positive entropy of activation, typical for a molecular relaxation process as observed in p-halobiphenyls (cf: Chapter III), the

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PAGE NUMBERING

respective values of, ΔH_E = 32 kJ mol^{-1} and ΔS_E = 27 J K^{-1} mol^{-1} obtained for ester group relaxation in dimethyl terephthalate. Nevertheless, it is noteworthy (Table V-2) that the relaxation time, τ = 2.6 x 10^{-4} s and free energy of activation, ΔG_E = 35 kJ mol^{-1} at 200K for the former molecule are considerably greater than those of τ = 2.4 x 10^{-6} s and ΔG_E = 27 kJ mol^{-1}, respectively, at 200K for the latter molecule. Thus, the increased values of τ and ΔG_E for the former may be explained by the increased conjugation. It is to be noted (Table V-1) that the experimental dipole moment at 200K (∿0.84 D) for the low temperature process of ethyl-p-(N,N-dimethylamino)-benzoate agrees well with the corresponding value of ∿0.97 D at 200K, typical for ester group relaxation, in dimethyl terephthalate. Therefore it appears that the most likely source of the low temperature dielectric absorption for ethyl-p-(N,N-dimethylamino)-benzoate was to be attributed to the rotation of the ester group.

In contrast to ethyl-p-(N,N-dimethylamino)-benzoate, ethyl-p-amino- and ethyl-p-nitrobenzoates exhibited only single dielectric absorptions in polystyrene matrices in the same temperature region (∿290K) for the given frequency range. This yielded activation enthalpies of 76 kJ mol^{-1} and 73 kJ mol^{-1} and activation entropies of 110 J K^{-1} mol^{-1} and 95 J K^{-1} mol^{-1}, respectively. It may be seen (Table V-2) that both the ΔH_E and ΔS_E for these molecules are significantly larger than the corresponding values for ester group relaxation in dimethyl terephthalate. Taking into consideration the -M effect of the p-nitro group in ethyl-p-nitrobenzoate, one might expect a lower activation enthalpy for ester group relaxation in this molecule than that of dimethyl terephthalate (ΔH_E = 32 kJ mol^{-1}). On the other hand, owing to the +M effect of the p-amino group in ethyl-p-aminobenzoate, an increase in activation enthalpy for ester group relaxation would be expected. Nevertheless, the enthalpies of activation for ethyl-p-nitro- and ethyl-p-aminobenzoates were found to be the same within the limits of experimental accuracy. Further, the values of relaxation time and free energy of activation at 300K (Table V-2) for the former molecule were comparable with those of the latter. This would seem reasonable as both the molecules are fairly similar in size.

Hence, all the above considerations lead to the conclusion that the molecular relaxation contributes to the dielectric absorption of both the molecules. Further, the calculated values of activation entropy for ethyl-p-nitrobenzoate (ΔS_{calcd} = 89 J K^{-1}mol^{-1}) and ethyl-p-aminobenzoate (ΔS_{calcd} = 95 J K^{-1} mol^{-1}), from the relation given earlier in the discussion for a molecular relaxation, seem to be in good agreement with the observed values of ΔS_{obsd} = 95 J K^{-1} mol^{-1} and ΔS_{obsd} = 110 J K^{-1} mol^{-1}, respectively, for these molecules. This observation gives additional support to the above interpretation for a molecular relaxation process for both the molecules.

In ethyl-m-aminobenzoate only one dielectric absorption measured from 240 - 264K was found. It was characterized by a low value of the distribution parameter (β = 0.12 - 0.16) and by an activation enthalpy of ΔH_E = 78 kJ mol^{-1}. The values of relaxation time and free energy of activation at 200K for ethyl-m-amino benzoate (Table V-2) were found to be significantly larger than those for ester group relaxation in dimethyl terephthalate, whereas they seem closer to those for ethyl-p-aminobenzoate. It should be noted that the magnitudes of ΔH_E and ΔS_E for this molecule fit precisely in the relation mentioned earlier for a molecular relaxation process within experimental error. Thus, evidence here seems in support of a molecular process for ethyl-m-aminobenzoate.

It is to be expected that placing in the para position an electron withdrawing substituent such as the cyano group in ethyl benzoate would lower the energy barrier for ester group relaxation. However, for ethyl-p-cyanobenzoate only one dielectric absorption was found. This was observed in the same frequency and temperature range as for ethyl-p-nitro- and ethyl-p-aminobenzoates, yielding an activation enthalpy, ΔH_E = 78 kJ mol^{-1}. This is about the same as obtained in the latter molecules within our limits of experimental accuracy. It may be noted (Table V-2) that the values of relaxation time and free energy of activation at 300K, and the entropy of activation for ethyl-p-cyanobenzoate were found to be close to the corresponding values for ethyl-p-nitro-, and ethyl-p-aminobenzoates, where the process is likely one of molecular relaxation. Further, it is notable that the weight factor for the molecular process is found to be C_1 = 0.80, whereas for the group process, C_2 = 0.20 (These were calculated on the basis of the ester group moment, of ∿1.83 D,[19] a cyano group moment of 4.05 D,[19] and assuming an angle of 'θ' of 69^0 14' [18] between the ester group dipole moment direction and the major axis of the ring). This indicates that the molecular weight factor is large enough to obscure the group process and hence makes it undetectable. Therefore, the above considerations favour the assignment of a molecular relaxation process to the dielectric absorption of ethyl-p-cyanobenzoate.

Ethyl-p-fluorobenzoate exhibited only a single absorption in the polystyrene matrix, giving an activation enthalpy of 43 kJ mol^{-1} and an activation entropy of 36 J K^{-1} mol^{-1}. It is important to note (Table V-2) that the temperature region of absorption, enthalpy of activation, relaxation time, and free energy of activation at 200K were all found to be higher for ethyl-p-fluorobenzoate than corresponding values for dimethyl terephthalate. This would not be expected if the former molecule also shows the same ester group relaxation which was the main relaxation mechanism for the latter molecule. The ethyl-p-fluorobenzoate molecule is comparable in size to that of the rigid molecule p-iodotoluene (cf: Chapter III). It may be noted that the values of activation enthalpy of 43 kJ mol^{-1} and an activation entropy of 36 J K^{-1} mol^{-1} obtained for the former molecule are in agreement with the values of ΔH_E = 42 kJ mol^{-1} and ΔS_E = 33 J K^{-1} mol^{-1}, respectively for molecular relaxation in the latter molecule. Further, the magnitudes of the relaxation time and the free energy of activation at 200K for the former molecule agree well with those of the respective values for the latter molecule. In additon, the absorption occurs in the same temperature region for both the molecules. It is noteworthy (Table V-2) also that the enthalpy of activation and free energy of activation (200K) appear to increase with increasing size of the molecule, that is, in the order of ethyl-p-fluoro-, ethyl-p-amino-, and ethyl-p-(N,N-dimethylamino)-benzoates. Therefore, the above considerations seem more in favour of a molecular relaxation process for the dielectric absorption of ethyl-p-fluorobenzoate. However, a contribution from ester group relaxation may not be completely ruled out.

Ethyl-p-chlorobenzoate in polystyrene shows a dielectric absorption in the temperature range of 153 to 199K covering a $\log_{10}f_{max}$ range of 2.7 to 4.8, and yielding an activation enthalpy of 24 kJ mol^{-1} and an activation entropy of -17 J K^{-1} mol^{-1}. It is not clear whether this absorption is due solely to a group relaxation or to an overlap of both group and molecular relaxation processes.

For ethyl-p-chlorobenzoate, one should expect a higher activation enthalpy because of its larger size in comparison with that of ethyl-p-fluorobenzoate, if both molecules exhibit the same molecular relaxation process. However, the enthalpy of activation for the former molecule was 19 kJ mol^{-1} smaller than that for the latter molecule. This would not be expected if the process were molecular relaxation in each case. It is, however, profitable to note (Figure V-4) that for ethyl-p-chlorobenzoate, there is a divergence in the Eyring plot at temperatures below 174K, which might be described by two straight lines of limiting slopes to account for an overlapped absorption due to the group and whole molecular relaxation processes.

The dielectric data, at a lower temperature range of 153 to 174K, yield an activation enthalpy of 11 kJ mol^{-1}. The assignment of this lower temperature dielectric relaxation to a group rotation would seem reasonable, as it is to be expected that the para substituent chlorine atom, which is known as an electron-withdrawing substituent, would lower the electron density between the bond connecting the aromatic benzene ring and the ester group. This would in turn lower the enthalpy of activation for ester group relaxation owing to the decreased double bond character of this bond. This observation is supported by the results of Miller et al.,[21] who, by employing far infrared techniques, evaluated the energy barriers, V_2, for aldehyde group relaxation in benzaldehyde, p-fluoro-, p-chloro-, and p-bromobenzaldehydes in the vapor and liquid phases. The respective values are 19.5, 15.0, 11.8, and 9.9 kJ mol^{-1}, while for the pure liquids they are 28.0, 21.9, 19.2, and 15.6 kJ mol^{-1}, respectively. This shows a decrease in the energy barrier, V_2, in the order H > F > Cl > Br. These workers suggested that para-substituents can influence the barrier height only through electronic interactions, The analysis of the dielectric data for ethyl-p-chlorobenzoate at a higher temperature range of 174 - 199K has yielded an activation enthalpy of 39 kJ mol^{-1} and an activation entropy of 61 J K^{-1} mol^{-1}. This may be attributed to an overlap of both group and molecular relaxation processes with the latter predominating in this temperature region. Further, dielectric measurements for this molecule were also made on the Q-meter, yielding activation enthalpy and entropy values of 39 kJ mol^{-1} and 52 J K^{-1} mol^{-1}, respectively. They may be considered to be the same, within the accuracy of measurements, as those obtained from the higher temperature, G. R. bridge data.

For ethyl-p-chlorobenzoate, the weight factor for the group process is $C_2 = 0.77$, whereas for the molecular process, $C_1 = 0.23$ (calculation of weight based on the group moments of ester, $\mu \sim 1.83$ D[13] and of chlorine, $\mu_{C-C\ell} = 1.58$ D,[19] and the angle of inclination 'θ' of 69^{o} 14',[18] which the ester group makes with the major axis). Thus the group relaxation contribution would be expected to be greater than the molecular process contribution to the dielectric absorption of this molecule.

From the foregoing arguments for ethyl-p-chlorobenzoate, it would appear that mainly ester group relaxation contributes to the absorption at a lower temperature range (below 174K) whereas both group and molecular relaxations produce overlapping absorptions at temperatures higher than 174K.

In order to study an ester group attached to a polymer backbone, polymethyl methacrylate was measured in a polystyrene matrix. The purpose was to investigate the activation enthalpy for ester group relaxation in an aliphatic system. One should expect the ΔH_E for such motion to be less than that in aromatic systems, because of the conjugative interaction and other factors in the latter case. There may be two relaxation candidates in this molecule, one being the methoxy group relaxation and the other ester group relaxation. However, only one dielectric absorption at very low temperature was found for this molecule; this was characterized by larger values of the distribution parameter ($\beta \sim 0.3$), a low enthalpy of activation, $\Delta H_E = 4$ kJ mol^{-1}, and a large negative entropy of activation, $\Delta S_E = -100$ J K^{-1} mol^{-1}.

The magnitude of the enthalpy of activation, $\Delta H_E = 4$ kJ mol^{-1}, for this molecule would seem reasonable on comparison with the corresponding value of 11 kJ mol^{-1} for methoxy group rotation in an aromatic system, 2,6-dimethoxynaphthalene,[20] in a polystyrene matrix. In contrast, it is notable (Table V-2) that the relaxation time and free energy of activation at 150K for the former compound are significantly greater than the corresponding values of the latter molecule. Thus it seems difficult to distinguish clearly the mechanism of the dielectric absorption for polymethyl methacrylate in a polystyrene matrix. It would appear equally probable that either methoxy or ester group relaxation (or both) could account for the absorption in this case.

For ethyl-5-norbornene-2-carboxylate, in which the dipole relaxation may occur by either or both the rotation of the group and that of the molecule as a whole. Only a single dielectric absorption measured from 90 - 115K was observed, yielding ΔH_E = 15 kJ mol^{-1} and ΔS_E = -3 J K^{-1} mol^{-1}. Molecular relaxation as a possibility may be considered by comparison with the results for 5-norbornene-2-carbonitrile[25] (Table V-2), a rigid molecule of slightly smaller size. It absorbs at a higher temperature range of 117 - 149K, with a considerably longer relaxation time, τ_{150K} = 4.9 x 10^{-6} s, greater free energy of activation, ΔG_{150K} = 21 kJ mol^{-1}, and greater enthalpy of activation, ΔH_E = 23 kJ mol^{-1}, than the respective values of τ_{150K} = 6.2 x 10^{-8} s, ΔG_{150K} = 15 kJ mol^{-1}, and ΔH_E = 15 kJ mol^{-1} obtained for ethyl-5-norbornene-2-carboxylate. This would not seem reasonable if the process were molecular relaxation in each case. However, it should be noted (Table V-2) that the temperature region, relaxation time, and free energy of activation at 150K, and the activation enthalpy for this molecule are in good correspondence with those of 91 - 108K, $\tau_{150K} = 1.0 \times 10^{-7}$ s, $\Delta G_{150K} = 16$ kJ mol^{-1}, and $\Delta H_E = 11$ kJ mol^{-1}, respectively, for methoxy group relaxation in 2,6-dimethoxynaphthalene[20] in polystyrene. This close similarity to the results of both the molecules suggests that ethoxy group relaxation contributes to the dielectric absorption of ethyl-5-norbornene-2-carboxylate.

Some values of the activation enthalpy for aldehyde group relaxation in heterocyclic aromatic systems are: furan-2-carbaldehyde, $\Delta H_E = 46$ kJ mol^{-1},[22]; thiophen-2-carbaldehyde, $\Delta H_E = 44$ kJ mol^{-1} (cf: Chapter VI); and N-methylpyrrole-2-carbaldehyde, $\Delta H_E = 53$ kJ mol^{-1} (cf: Chapter VI), all in polystyrene matrices. These are considerably greater than that of $\Delta H_E = 29.3$ kJ mol^{-1} in the simple aromatic system terephthaldehyde[23] in polystyrene. Such differences may be attributed mainly to the increased double bond character of the bond connecting the ring and the aldehyde group in furan-, thiophen-, and N-methylpyrrole-2-carbaldehydes as a result of the increased conjugation in the heterocyclic rings.[24] Therefore one may also expect an increased activation enthalpy for ester group relaxation in ethyl indole-2-carboxylate compared to the value in dimethyl terephthalate, since in the former, the ester group is directly attached to an heterocyclic ring. However, ethyl indole-2-carboxylate in polystyrene, in which the possibility of either or both the group and molecular relaxation as a whole exists, exhibited a single dielectric absorption in the temperature range of 273 - 304K. It yielded significantly larger values of activation enthalpy, ΔH_E = 62 kJ mol^{-1} and activation entropy, ΔS_E = 62 J K^{-1}mol^{-1}. These may be compared to the corresponding values of ΔH_E = 32 kJ mol^{-1} and ΔS_E = 27 J K^{-1} mol^{-1} for ester group relaxation in dimethyl terephthalate. It is possible that the intramolecular process is responsible in the ethyl indole-2-carboxylate and that the increment in the ΔH_E & ΔS_E values may be attributed to enhanced conjugation. The experimental dipole moments (0.97 - 1.19 D) support the view that ester group relaxation may contribute to the absorption of ethyl indole-2-carboxylate. This is evident from the extrapolated dipole moment at 300K (∿1.18 D) which is of the same order of magnitude as the extrapolated dipole moment at 300K (∿1.48 D), typical for ester group relaxation in dimethyl terephthalate.

On the other hand, it may be seen that the enthalpy of activation, ΔH_E = 62 kJ mol^{-1}, the relaxation time, τ = 1.9 s, and the free energy of activation, ΔG_E = 49 kJ mol^{-1} at 200K for ethyl indole-2-carboxylate are comparable with the corresponding values of ΔH_E = 54 kJ mol^{-1}, $\tau = 1.1 \times 10^{-1}$ s, and ΔG_E = 45 kJ mol^{-1}

at 200K for a similarly sized rigid molecule, 2-cyanonaphthalene,[13] where the process can only be molecular relaxation. Further, the observed activation entropy of $\Delta S_{exp} = 62$ J K^{-1} mol^{-1} for this molecule is in remarkably good agreement within experimental error, with the value of $\Delta S_{calcd} = 64$ J K^{-1} mol^{-1}, which was calculated from the relation (cf: Chapter III) which holds for a molecular relaxation process. It seems feasible that an overlap of group and molecular relaxations are responsible for the dielectric absorption of ethyl indole-2-carboxylate.

The last molecule for which the data are given in Table V-2 is ethyl-2-furoate. For this molecule a single dielectric absorption from 211 - 246K was observed, having $\Delta H_E = 44$ kJ mol^{-1} and $\Delta S_E = 44$ J K^{-1} mol^{-1}. It is seen (Table V-2) that this absorption was characterized by a significantly large Fuoss-Kirkwood distribution parameter ($\beta \sim 0.3$), which is suggestive of an intramolecular relaxation process.[11] It should be noted that the activation enthalpy of ~ 38 kJ mol^{-1} for acetyl group rotation and an activation enthalpy of ~ 43 kJ mol^{-1} for aldehyde group rotation have been found in 2-acetyl furan[14] and 2-furan aldehyde.[15] Thus, in the light of these data for acetyl group and for aldehyde group relaxations, it seems reasonable to attribute the present value of $\Delta H_E = 44$ kJ mol^{-1} in ethyl-2-furoate to ester group relaxation. Moreover, the molecular process for this small molecule would be expected to occur at a much lower temperature and have a much smaller ΔH_E.

Altogether from the foregoing discussion, the conclusion may be drawn that the origin of the dielectric absorption of dimethyl terephthalate and dimethyl 2,6-naphthalenedicarboxylate in polystyrene matrices is ester group relaxation around 180K with an activation enthalpy of $\sim$32 kJ mol^{-1}.

The relaxation time and enthalpy data also suggest at least an appreciable contribution from ester group relaxation to the dielectric data in methyl- and ethyl benzoates.

Both ester group and molecular relaxation processes appear to contribute to the dielectric absorption of ethyl cinnamate, ethyl-p-nitrocinnamate, and ethyl-p-(N,N-dimethylamino)-benzoate. For ethyl-p-chlorobenzoate, it seems probable that an overlap of both group and molecular relaxation processes have been observed. The ethyl-p-fluoro-, ethyl-p-amino-, ethyl-m-amino-, ethyl-p-nitro-, and ethyl-p-cyano benzoates each seem to show a molecular process.

Both methoxy and ester group relaxation seem equally probable as the source of the dielectric absorption of polymethyl methacrylate. It seems likely that ethoxy group relaxation contributes to the absorption of ethyl-5-norbornene-2-carboxylate. The overlap of both ester group and molecular relaxation seems to have been observed in ethyl indole-2-carboxylate. Increased conjugation in ethyl-2-furoate might have yielded an increased value of activation enthalpy for ester group relaxation.

In general it would seem that much further work is necessary on aromatic esters containing substituents of electron-donating and electron-withdrawing characteristics in order to investigate the conjugative and inductive influence on the energy barrier to ester group relaxation.

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TABLE V-1 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS FOR AROMATIC ESTERS AND SOME RELATED COMPOUNDS IN POLYSTYRENE MATRICES AT A VARIETY OF TEMPERATURES

T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.43M Dimethyl terephthalate				
163.3	196.7	2.91	0.16	5.9	2.59	0.799
167.5	137.1	3.06	0.16	6.1	2.59	0.839
173.0	64.9	3.39	0.15	6.4	2.58	0.888
177.5	32.7	3.69	0.14	6.6	2.58	0.959
179.8	22.4	3.85	0.14	6.7	2.58	0.967
187.4	7.89	4.30	0.15	7.2	2.57	0.989
194.4	4.04	4.60	0.17	7.7	2.57	0.987
201.6	2.23	4.85	0.19	8.1	2.57	0.972
		0.44M Dimethyl-2,6-naphthalenedicarboxylate				
170.8	192.0	2.92	0.14	1.9	2.64	0.497
174.0	113.4	3.15	0.15	1.9	2.64	0.486
176.6	61.0	3.42	0.16	2.0	2.64	0.480
183.9	19.1	3.92	0.19	2.1	2.64	0.467
191.5	6.16	4.41	0.20	2.3	2.63	0.474
199.4	3.37	4.67	0.23	2.4	2.63	0.463
213.4	1.35	5.07	0.29	2.6	2.62	0.448
		0.59M Methylbenzoate				
165.3	175.7	2.96	0.20	13.5	2.61	0.932
170.6	102.5	3.19	0.19	14.0	2.60	0.977
174.7	60.7	3.42	0.19	14.5	2.60	1.00
179.7	29.7	3.73	0.19	15.0	2.59	1.03
184.6	16.9	3.97	0.20	15.6	2.59	1.04
189.4	10.20	4.19	0.20	16.1	2.59	1.05
194.0	5.56	4.46	0.21	16.6	2.59	1.07
205.1	2.00	4.90	0.23	17.8	2.58	1.10
		0.59M Ethylbenzoate				
171.3	121.9	3.12	0.18	10.5	2.68	0.858
175.4	57.9	3.44	0.17	11.1	2.67	0.908
180.4	32.9	3.68	0.17	11.7	2.66	0.961
193.6	7.88	4.31	0.17	13.0	2.65	1.05
198.2	3.94	4.61	0.17	13.8	2.64	1.09
203.0	2.67	4.77	0.18	14.3	2.65	1.09

TABLE V-1 continued...

$T(K)$	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
0.56M Ethylcinnamate High Temperature Absorption						
285.8	260.3	2.79	0.16	10.2	2.67	1.20
289.3	140.4	3.05	0.17	10.4	2.66	1.19
295.2	73.2	3.34	0.16	10.1	2.66	1.20
300.7	40.6	3.59	0.17	10.2	2.66	1.19
305.4	21.6	3.87	0.18	10.5	2.66	1.19
310.8	9.44	4.23	0.17	10.7	2.65	1.25
Low Temperature Absorption						
158.5	204.1	2.89	0.21	6.0	2.67	0.606
164.0	109.3	3.16	0.22	6.4	2.67	0.620
168.7	59.2	3.43	0.21	6.6	2.66	0.657
174.2	25.1	3.80	0.19	6.8	2.66	0.712
178.9	15.6	4.01	0.21	7.1	2.66	0.696
183.9	7.38	4.33	0.20	7.4	2.65	0.737
187.5	5.46	4.46	0.21	7.6	2.65	0.737
0.39M Ethyl-p-nitrocinnamate High Temperature Absorption						
319.4	213.1	2.87	0.25	32.2	2.49	2.19
322.4	170.8	2.97	0.24	33.3	2.47	2.29
324.5	124.5	3.11	0.24	34.4	2.47	2.34
327.0	96.5	3.22	0.23	35.7	2.46	2.45
330.0	62.2	3.41	0.23	37.8	2.45	2.55
332.9	42.5	3.57	0.22	41.0	2.45	2.71
Low Temperature Absorption						
150.8	141.7	3.05	0.21	2.9	2.67	0.497
169.9	46.1	3.54	0.23	3.0	2.66	0.504
174.3	25.5	3.80	0.22	3.0	2.66	0.527
179.4	13.4	4.07	0.22	3.1	2.66	0.545
197.3	2.43	4.82	0.26	3.6	2.65	0.558

TABLE V-1 continued...

T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
0.45M Ethyl-p-(N,N-dimethylamino)-benzoate High Temperature Absorption						
298.2	177.6	2.95	0.18	29.2	2.56	2.16
302.8	108.1	3.17	0.18	29.9	2.55	2.19
307.6	60.3	3.42	0.19	31.0	2.54	2.24
312.3	33.1	3.68	0.18	32.2	2.53	2.32
317.2	17.3	3.96	0.18	33.8	2.52	2.39
321.9	9.39	4.23	0.18	35.8	2.51	2.52
Low Temperature Absorption						
202.5	170.8	2.97	0.23	8.3	2.64	0.848
204.4	148.4	3.03	0.23	8.4	2.64	0.849
209.9	112.4	3.15	0.21	8.8	2.64	0.927
215.2	87.9	3.26	0.19	9.3	2.63	1.00
219.6	52.3	3.48	0.20	9.5	2.63	1.03
224.9	41.5	3.58	0.16	10.0	2.61	1.18
232.3	17.2	3.97	0.17	10.6	2.61	1.20
240.2	8.59	4.27	0.15	11.3	2.59	1.32
0.49M Ethyl-p-aminobenzoate						
269	203.4	2.89	0.13	24.4	2.62	2.11
273.6	119.7	3.12	0.13	25.5	2.63	2.12
278.5	57.7	3.44	0.14	26.6	2.63	2.10
288.3	18.9	3.92	0.16	29.2	2.63	2.10
295.5	8.54	4.27	0.17	30.8	2.63	2.17
300.9	5.05	4.50	0.17	32.2	2.63	2.19
0.47M Ethyl-p-nitrobenzoate						
270.7	263.6	2.78	0.22	42.2	2.60	2.18
277.4	112.3	3.15	0.22	44.3	2.59	2.25
282.4	71.6	3.35	0.21	45.8	2.57	2.37
288.7	34.9	3.66	0.21	47.6	2.55	2.48
295.6	16.4	3.99	0.22	49.8	2.55	2.52
300.5	9.77	4.21	0.21	51.2	2.53	2.59
306.2	5.05	4.50	0.21	53.1	2.52	2.67

TABLE V-1 continued...

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.52M Ethyl-m-aminobenzoate				
240.9	245.0	2.81	0.13	16.3	2.58	1.58
244.4	152.1	3.02	0.14	16.7	2.57	1.60
248.7	92.2	3.24	0.14	17.2	2.57	1.60
254.3	30.4	3.72	0.13	17.8	2.55	1.72
259.1	13.7	4.07	0.13	18.3	2.53	1.77
264.2	8.32	4.28	0.16	19.3	2.55	1.65
		0.51M Ethyl-p-cyanobenzoate				
276.0	418.7	2.58	0.23	39.3	2.54	2.03
280.3	250.7	2.80	0.23	40.5	2.54	2.08
287.8	111.6	3.15	0.22	42.7	2.52	2.20
294.0	54.1	3.47	0.21	44.3	2.50	2.31
299.8	27.0	3.77	0.21	46.2	2.48	2.40
302.7	18.3	3.94	0.21	47.5	2.47	2.44
		0.53M Ethyl-p-fluorobenzoate				
210.0	103.0	3.19	0.11	7.9	2.55	1.15
215.9	63.8	3.40	0.11	8.3	2.54	1.17
219.7	50.5	3.50	0.13	8.6	2.55	1.14
224.5	27.1	3.77	0.10	8.8	2.52	1.31
229.5	11.9	4.13	0.09	9.2	2.50	1.47
239.3	4.04	4.60	0.11	10.0	2.50	1.41
249.4	2.59	4.79	0.12	10.8	2.50	1.38

TABLE V-1 continued...

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
0.49M Ethyl-p-chlorobenzoate						
152.8	297.4	2.73	0.19	3.4	2.60	0.508
156.0	280.4	2.75	0.18	3.6	2.60	0.540
159.3	197.1	2.91	0.17	3.7	2.60	0.565
163.0	174.3	2.96	0.16	3.9	2.59	0.603
169.5	127.5	3.10	0.15	4.0	2.57	0.649
173.7	91.9	3.24	0.14	4.1	2.56	0.687
179.0	40.9	3.59	0.14	4.4	2.56	0.739
183.7	19.4	3.91	0.11	4.6	2.55	0.836
188.4	10.7	4.17	0.11	4.8	2.55	0.872
193.7	5.90	4.43	0.17	5.2	2.56	0.745
198.9	2.38	4.82	0.13	5.4	2.54	0.892
213.4	0.811	5.29	0.25	5.8	-	-
223.1	0.585	5.43	0.19	5.9	-	-
229.2	0.274	5.76	0.24	6.2	-	-
234.0	0.195	5.91	0.19	6.5	-	-
237.7	0.130	6.09	0.22	7.0	-	-
241.4	0.102	6.19	0.20	7.1	-	-
246.4	0.071	6.35	0.20	7.5	-	-
Polymethyl methacrylate						
93.7	21.4	3.87	0.28	2.5	2.58	-
96.9	13.5	4.07	0.31	2.7	2.58	-
105.8	6.36	4.40	0.28	2.6	2.58	-
110.9	5.65	4.45	0.29	2.6	2.58	-
115.5	5.57	4.46	0.29	2.5	2.59	-
120.6	4.48	4.51	0.31	2.5	2.59	-
0.54M Ethyl-5-norbornene-2-carboxylate						
89.5	303.0	2.72	0.19	6.6	2.59	0.515
94.7	101.9	3.19	0.17	7.0	2.59	0.566
99.4	37.0	3.63	0.18	7.3	2.59	0.583
105.0	12.0	4.12	0.19	7.8	2.59	0.596
107.2	9.14	4.24	0.21	7.8	2.59	0.588
114.5	3.52	4.65	0.25	8.5	2.59	0.580

TABLE V-1 continued...

T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
		0.45M Ethyl indole-2-carboxylate				
273.0	63.2	3.40	0.21	6.8	2.52	0.968
278.2	40.2	3.60	0.20	7.1	2.51	1.03
282.8	26.2	3.78	0.20	7.4	2.51	1.06
292.7	10.0	4.20	0.20	8.1	2.50	1.12
298.0	5.89	4.43	0.19	8.5	2.49	1.18
303.6	3.91	4.61	0.20	8.9	2.48	1.19
		0.57M Ethyl-2-furoate				
210.7	103.5	3.19	0.26	19.3	2.71	1.09
215.8	56.5	3.45	0.25	19.6	2.71	1.12
220.8	30.9	3.71	0.26	19.9	2.71	1.13
225.6	18.5	3.93	0.26	20.3	2.71	1.15
230.5	10.9	4.17	0.26	20.4	2.71	1.16
236.0	5.62	4.45	0.25	20.6	2.70	1.22
245.5	2.62	4.78	0.28	20.8	2.71	1.17

NOTE:

A blank space (-) indicates that the information was not available

TABLE V-2: EYRING ANALYSIS RESULTS FOR AROMATIC ESTERS AND SOME RELATED COMPOUNDS IN POLYSTYRENE MATRICES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		150 K	200 K	300 K	150 K	200 K	300 K		
Dimethyl terephthalate	163-202	2.0×10^{-3}	2.4×10^{-6}	2.5×10^{-9}	28	27	24	32	27
Dimethyl 2,6-naphthalene dicarboxylate	170-213	5.0×10^{-3}	3.6×10^{-6}	2.3×10^{-9}	29	27	24	35	36
Methyl benzoate	165-205	2.2×10^{-3}	3.3×10^{-6}	4.4×10^{-9}	28	27	25	31	18
Ethyl benzoate	171-203	3.3×10^{-3}	3.6×10^{-6}	3.4×10^{-9}	29	27	25	33	26
Ethyl Cinnamate	159-188 286-311	8.9×10^{-4} 5.9×10^{11}	1.5×10^{-6} 5.1×10^{3}	2.3×10^{-9} 3.9×10^{-5}	27 70	26 63	24 48	30 91	22 143
Ethyl-p-nitro cinnamate	161-197 319-333	6.9×10^{-4} 1.4×10^{16}	1.9×10^{-6} 7.1×10^{6}	4.4×10^{-9} 3.2×10^{-3}	27 82	26 75	25 59	28 105	9 154
Ethyl-p-(N,N-dimethylamino)-benzoate	203-240 290-322	1.3×10^{-1} 2.3×10^{13}	2.6×10^{-4} 6.4×10^{4}	4.5×10^{-7} 1.5×10^{-4}	33 74	35 67	37 52	30 97	-25 152
Ethyl-p-amino benzoate	269-301	2.1×10^{8}	3.6×10^{1}	5.4×10^{-6}	60	54	43	76	110
Ethyl-p-nitro benzoate	271-306	1.2×10^{8}	3.7×10^{1}	1.0×10^{-5}	59	54	45	73	95
Ethyl-m-amino benzoate	241-264	8.6×10^{6}	9.6×10^{-1}	9.6×10^{-8}	56	48	33	78	151

TABLE V-2: continued....

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E	ΔS_E
		150K	200K	300K	150 K	200K	300K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Ethyl-p-cyano benzoate	276-307	$2.2x10^9$	$2.5x10^2$	$2.6x10^{-5}$	63	58	47	78	103
Ethyl-p-fluoro benzoate	210-249	2.9	$4.3x10^{-4}$	$5.7x10^{-8}$	37	35	32	43	36
Ethyl-p-chloro benzoate	153-199	$7.7x10^{-4}$	$4.4x10^{-6}$	$2.2x10^{-8}$	27	28	29	24	- 17
	213-246 (Q-meter)	$2.2x10^{-2}$	$6.8x10^{-6}$	$1.8x10^{-9}$	31	29	23	39	52
Polymethyl-methacrylate	93-121	$1.5x10^{-6}$	$4.7x10^{-7}$	$1.4x10^{-7}$	19	24	34	4	-100
Ethyl-5-norbornene-2-carboxylate	90-115	$6.2x10^{-8}$	$2.4x10^{-9}$	$8.6x10^{-11}$	15	15	16	15	- 3
Ethyl indole-2-carboxylate	273-304	$5.8x10^5$	1.9	$5.3x10^{-6}$	52	49	53	62	62
Ethyl-2-furoate	210-246	4.0	$4.2x10^{-4}$	$3.9x10^{-8}$	38	35	31	44	44
2,6-Dimethoxy-naphthalene**	91-108	$1.0x10^{-7}$	$7.8x10^{-9}$	$5.3x10^{-10}$	16	17	20	11	-30

** Data provided through the courtesy of J. P. Shukla, this laboratory.

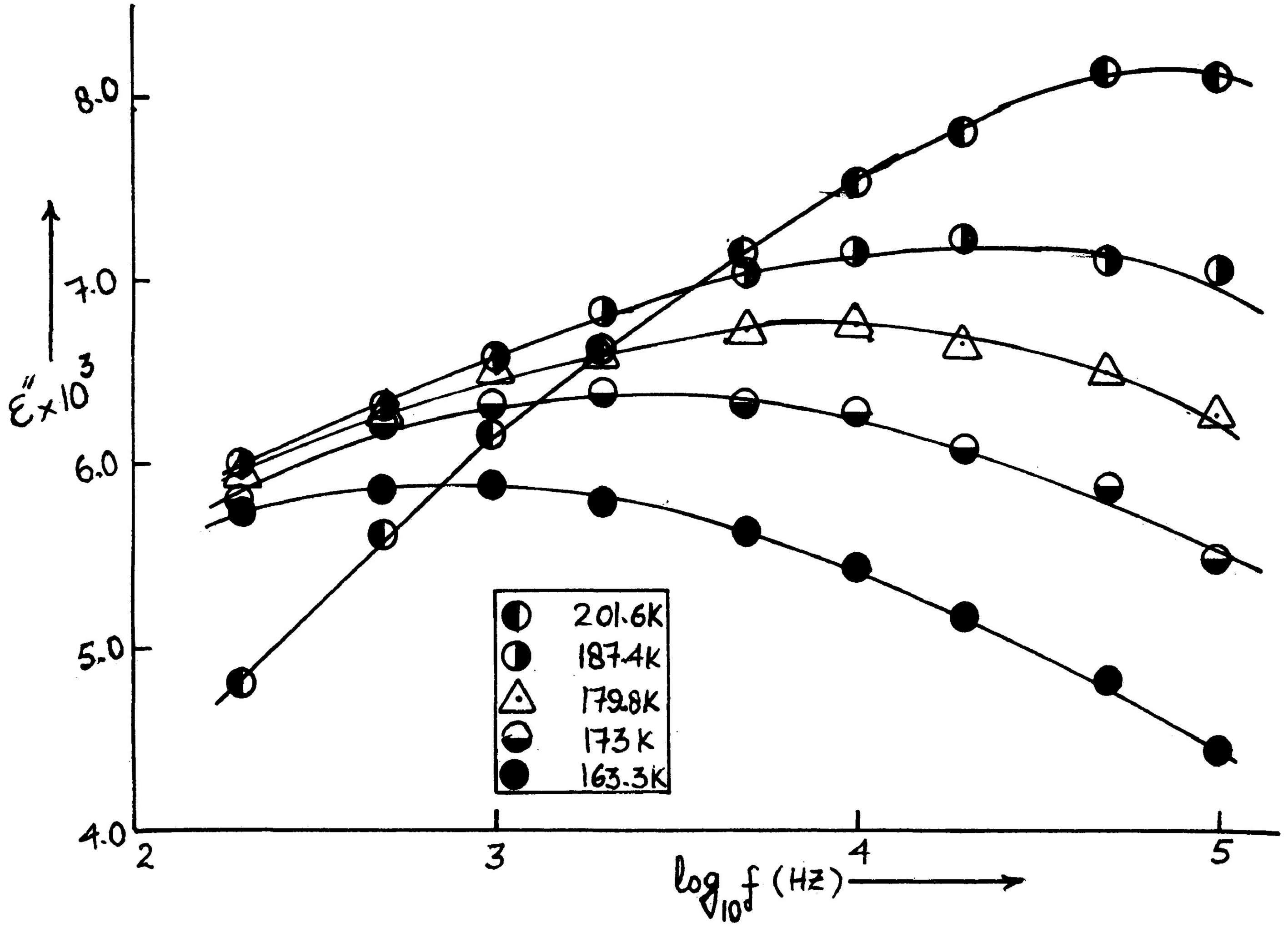

FIG V-1 Plot of Dielectric loss factor vs $\log_{10} f$ for Dimethyl terephthalate in polystyrene

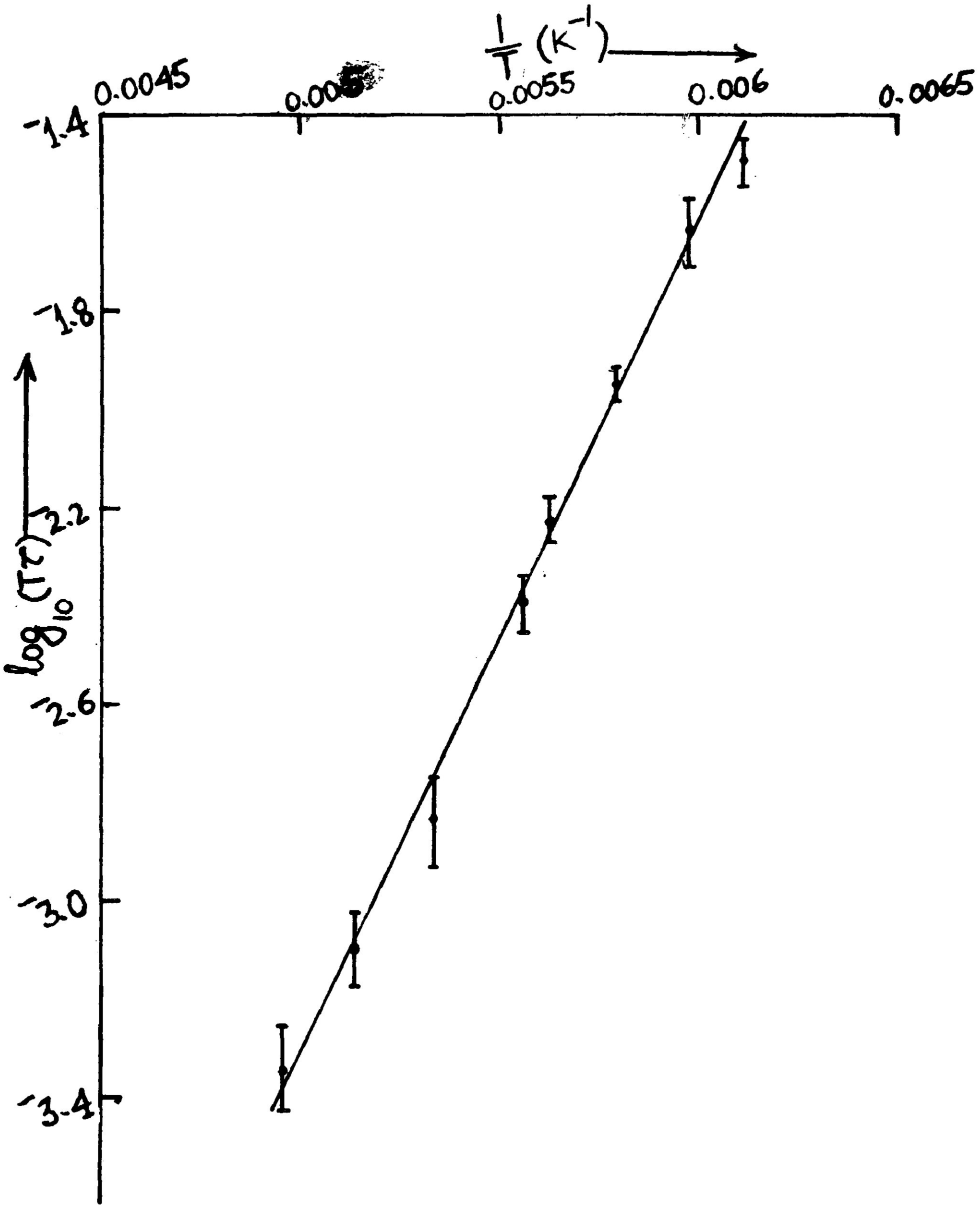

FIG V-2

Eyring plot of $\log_{10}$ (Tτ) vs $\frac{1}{T}$ for **dimethyl terephthalate in a polystyrene** matrix. The vertical bars represent 95% confidence intervals on log (Tτ) values.

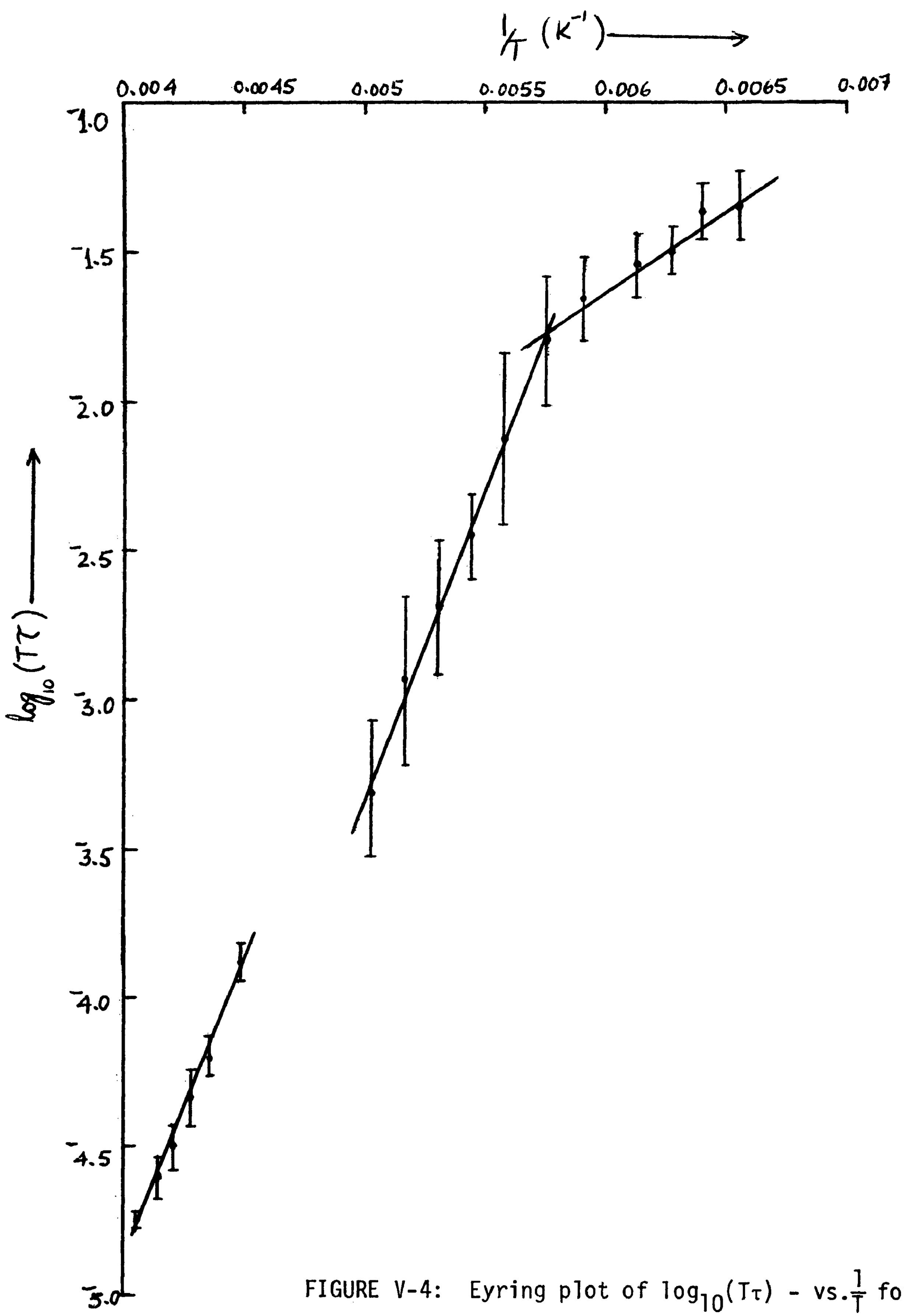

FIGURE V-4: Eyring plot of $\log_{10}(T\tau)$ - vs. $\frac{1}{T}$ for ethyl-p-chlorobenzoate in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values.

CHAPTER VI

RELAXATION PROCESS OF SOME HETEROCYCLIC ALDEHYDES

INTRODUCTION

Considerable attention has been given to the evaluation of the energy barrier to aldehyde group rotation around a C-C single bond between sp^2 type hybridized carbon atoms ().

An ultrasonic relaxation study has been reported by de Groot and Lamb[1,2] for unsymmetrical rotational barriers in acrolein and a few related unsaturated aldehydes.

N. m.r. techniques have been used by Anet and Ahmad to estimate the free energy of activation for the symmetrical rotational barriers in benzaldehyde and two para-substituted benzaldehyde derivatives[3] in solution.

The five-membered heteroaromatic aldehydes have also received some attention in the literature. In five-membered heterocyclic aldehydes, a resonance structure of the kind (Fig. VI-1) has often been invoked to explain their chemical properties. From

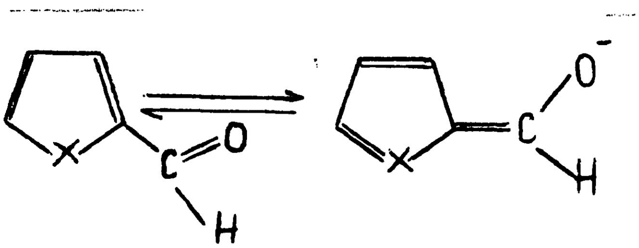

FIG VI-1

a resonance energy point of view a planar form of the molecule would be favoured and this would lead to two rotational isomers (Fig. VI-2).

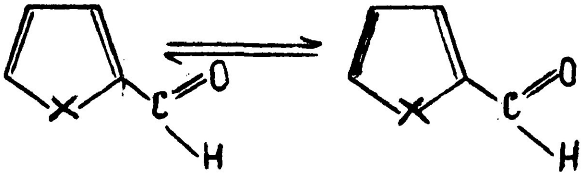

FIG VI-2

isomer I (XO-trans)

isomer II (XO-cis)

Of particular interest was furan-2-carbaldehyde which has been studied by different workers using different techniques.

In an earlier investigation by de Groot and Lamb,[1,4] it has been shown that an ultrasonic relaxation in liquid furan- and thiophen-2-carbaldehydes can be attributed to a perturbation of the equilibrium between the rotational isomers. Later, the technique of ultrasonic relaxation was used by Pethrick and Wyn-Jones[5] to study the rotational barriers in furan- and thiophen-2-carbaldehydes. They reported the values of 46 kJ mol^{-1} and 43 kJ mol^{-1}, respectively for the energy barrier for the cis to trans isomerization in these two molecules.

Karabatsos and Vane's n.m.r. study[6] in solution led to the result that the furan-2-carbaldehyde exists completely in the

00 - cis form.

The n.m.r. study of the internal rotation in furan-2-carbaldehyde has been reported by Dahlqvist and Forsen.[7] Their work has yielded an activation enthalpy, ΔH^{*}_{II}, of 44.7 kJ mol^{-1} for aldehyde group rotation around the C - C bond that is adjacent to the carbonyl bond. They also suggested that conjugative interaction between the furan ring and the 2-substituent aldehyde group is expected to favour the planar form of furan-2-carbaldehyde.

In addition to the above kinetic studies, the barrier to internal rotation in gaseous furan-2-carbaldehyde has also been derived from microwave spectroscopy[8] and far infrared spectroscopy[9]. These barriers were calculated from torsional frequencies and their respective values are, $V_2 = 36.2$,[8] and $V_2 = 29.6$[9] kJ mol^{-1}.

Nuclear magnetic resonance spectroscopy has been applied by Arlinger _et al_.[10] to determine the barrier to internal rotation in N-methyl pyrrole-2-carbaldehyde. These workers have reported the enthalpy of activation as 49.7 kJ mol^{-1} for aldehyde group rotation in this molecule. It is assumed in this study that the molecule exists in two essentially planar isomeric forms, since the conjugative interaction between the ring and the aldehyde group will favour a planar structure. They also suggested that the steric interactions between the CHO- group and the ring are small, but there may be some deviation from exact planarity.

In addition, despite several attempts, these workers were unable to observe any sign of intramolecular motion in the spectra of thiophen-2-carbaldehyde at temperatures down to -115°C. Their interpretation suggested that either the rotational barrier is very low (less than about 33.4 kJ mol^{-1}) or the two rotational isomers in this molecule have very unequal populations.

However, for the pyrrole series, the influence of the nature of an alkyl substituent on the nitrogen atom has been reported[11] by a study of the rotational barriers of the corresponding 2-aldehydes. A rotational barrier for N-t-butyl pyrrole-3-carbaldehyde has also been reported[12] recently.

Farnier and Drakenberg[13] studied ethyl-5-formyl-pyrrole-2-carboxylate and pyrrole 2,5-dicarbaldehyde, by using the n.m.r. technique, to examine the effect of substituents on the aldehyde torsional barrier. They reported the enthalpy of activation as $\Delta H^*_I = 41.8$ kJ mol^{-1} and the free energy of activation as $\Delta F^*_I = 39.9$ kJ mol^{-1} for the former molecule, while for the latter molecule only the free energy of activation as 38.5 kJ mol^{-1} has been reported.

However, taking into consideration the statement of Arlinger et al.[10] that, pyrrole-2-carbaldehyde behaves analogously to its N-methyl derivative, and that N-substitution has little effect on the free energy. These workers(11) assumed that the free energy of activation, ΔF^*_1, for pyrrole-2-carbaldehyde is ca. 46.0 kJ mol^{-1}.

It seems from the preceding literature references that these studies have been performed on a restricted number of carbonyl derivatives and no five-membered heterocyclic aldehyde has to our knowledge been investigated so far by using the dielectric absorption technique. Moreover, it is evident that the conjugation has a great deal of effect on the energy barrier for internal rotation in conjugated systems. The purpose of the present investigation is two-fold. In the first place, to elucidate the role of heteroaromatic nuclei by examining some heterocyclic aldehydes at low concentrations in a polystyrene matrix, using the dielectric absorption technique, where the means existed of determining the energy barriers to intramolecular and/or molecular rotation of aldehyde derivatives of five-membered heterocycles. In the second place, to examine qualitatively the effect of conjugation on the barriers to internal rotation in these heterocyclic aldehydes. Thus, the present investigation includes the dielectric absorption study of the following carbaldehydes of thiophen-, N-methyl pyrrole-, 5-bromo thiophen-, 5-methyl thiophen-, and 5-methyl furan-2- in a polystyrene matrix.

EXPERIMENTAL RESULTS

The samples of heterocyclic aldehyde used in this work were obtained from Aldrich Chemical Company. They were of high purity and were distilled prior to use.

A sample plot of loss factor {$\varepsilon'' = \varepsilon''(\text{obs}) - \varepsilon''$ (polystyrene)} against logarithm (frequency) for thiophen-2-carbaldehyde is shown in Fig. VI-3.

Table VI-1 lists the Fuoss-Kirkwood parameters and the effective dipole moments at various temperatures for some heterocyclic aldehydes. Table VI-2 collects the activation energy parameters, and the extrapolated relaxation time at 150K, 200K, and 300K for the systems listed in Table VI-1.

DISCUSSION

The present investigation of heterocyclic aldehydes did not include a study of furan-2-carbaldehyde, as it has recently been measured by a co-worker.[14]

At the beginning of the discussion it seems necessary to point out that our dielectric absorption technique determines the values of ΔG_E and ΔH_E for the activation process from the less stable form to the more stable form. In addition, recently Walker et al.[14] has shown a close agreement among dielectric, ultrasonic, and n.m.r. techniques in the evaluation of the enthalpy of activation value for an intramolecular motion corresponding to the switch from the isomer with the higher energy to that of the lower.

The first molecule studied in this series, for which data are given in Tables VI-1 and VI-2, is thiophen-2-carbaldehyde, showing two regions of absorption. The high temperature absorption yielded an activation enthalpy of 44 kJ mol^{-1} and an activation entropy of -7 J K^{-1} mol^{-1}. Previous ultrasonic study[5] assumed that the trans-isomer is the more stable isomer in thiophen-2-carbaldehyde. It yielded an activation enthalpy of 43 kJ mol^{-1} (SO - cis $\longrightarrow$ SO- trans isomerization) to internal rotation of the aldehyde group around the C - C bond adjacent to the carbonyl bond. Thus, the present value of activation enthalpy of 44 kJ mol^{-1} for the high temperature process of thiophen-2-carbaldehyde is in excellent agreement with the corresponding value of 43 kJ mol^{-1} obtained from the ultrasonic data.[5] This reveals that the aldehyde group relaxation contributes to the high temperature process of thiophen-2-carbaldehyde.

It is to be noted (Table VI-1) that for this process the observed value of the dipole moment decreases with the rise of temperature. Also an appreciable difference is found between the extrapolated value of observed dipole moment at 300K (μ_{extpd} = 1.17 D) and the observed value in benzene solution (μ_{LIT} = 3.55 D at 303K).[17] This observation of dipole moment values also supports the interpretation of aldehyde group relaxation.

A low temperature dielectric absorption measured in the range of 127 - 162K was found. This yielded an activation enthalpy of 20 kJ mol^{-1} and an activation entropy of -14 J K^{-1} mol^{-1}, which may be attributed to a molecular relaxation process in comparison with the corresponding values of 16 kJ mol^{-1} and 1 J K^{-1} mol^{-1} for a rigid molecule of fairly similar shape and about the same size, o-dichloro benzene in a polystyrene matrix,[15] where the process is only molecular relaxation.

5-Methyl-2-furan carbaldehyde shows two sets of dielectric absorption. The values of enthalpy of activation, 50 kJ mol^{-1}, and entropy of activation 25, J K^{-1} mol^{-1}, for the high temperature process of 5-methyl-2-furan carbaldehyde are found to be larger than that of the corresponding values of 45.6 kJ mol^{-1} and 11.0 JK^{-1} mol^{-1}, obtained for aldehyde group relaxation in furan-2-carbaldehyde in a polystyrene matrix.[14] In addition, the free energy of activation, ΔG_E (200K) = 45 kJ mol^{-1}, for the former also seems to be larger than the corresponding value of 43 kJ mol^{-1} for the latter. The higher value of activation enthalpy for the former molecule than that of the latter may be accounted as due to the presence of methyl group at C-5. This exerts a small +M and +I effect that donates electrons to the conjugated system, thus increasing the double bond character of the C - C bond that is adjacent to the carbonyl bond. Hence, as a result of increased conjugation, a slightly higher value of enthalpy of activation for aldehyde group relaxation for 5-methyl-2-furan carbaldehyde would be expected. This is also in agreement with some results that have been obtained for the benzene series[3] that "para substitution by a group with an electron donating mesomeric effect results in an increase in the rotational barrier". The 5-substituted furan-2-carbaldehydes are seen to be structural analogues of para-substituted benzaldehydes.

Thus, the presence of an electron-donating substituent would be expected to enhance the rotational barrier, as appears in 5-methyl-2-furan carbaldehyde. The assignment of an activation enthalpy of 50 kJ mol^{-1} to the aldehyde group relaxation in this high temperature absorption appears to be consistent with the observation of a decrease in dipole moment values with the rise of temperature.

A low temperature dielectric absorption measured from 181 - 208K was found, producing ΔH_E = 36 kJ mol^{-1} and ΔS_E = 27 J K^{-1} mol^{-1}. The low value of distribution parameter (β = ∿0.2) was found for this low temperature absorption. This is similar to that observed by Davies and Swain[15] for a molecular relaxation process. Comparison of the enthalpy of activation, ΔH_E = 36 kJ mol^{-1}, and the free energy of activation, ΔG_E (200K) = 30 kJ mol^{-1}, for the low temperature process of 5-methyl-2-furan carbaldehyde would seem reasonable with the corresponding values of 29 kJ mol^{-1} and 30 kJ mol^{-1}, respectively, for a rigid molecule fairly similar in shape and a little larger in size, m-diiodobenzene.[16] Here the process can only be that of molecular relaxation. Therefore, it seems most likely that the low temperature dielectric absorption of 5-methyl-2-furan carbaldehyde is a molecular relaxation process.

It appears in 5-methyl-2-furan carbaldehyde that the substitution of methyl group at C - 5 results in a higher value of enthalpy of activation for aldehyde group relaxation in comparison with the corresponding value for aldehyde group relaxation in the unsubstituted molecule, furan-2-carbaldehyde. Similarly, one might also expect a relatively higher energy barrier for aldehyde group relaxation in 5-methyl-2-thiophen carbaldehyde than that of the corresponding value in thiophen-2-carbaldehyde. However, 5-methyl-2-thiophen carbaldehyde shows a single dielectric absorption. It yielded a considerably smaller value of activation enthalpy, $\Delta H_E = 32$ kJ mol^{-1}, than that of $\Delta H_E = 44$ kJ mol^{-1} obtained for the aldehyde group relaxation in thiophen-2-carbaldehyde, This would not seem reasonable to be coupled with an aldehyde group relaxation in the former molecule. Nevertheless, it is to be noted that the temperature range of absorption, the β value, the τ and ΔG_E values at 200K, and the ΔH_E value for 5-methyl-2-thiophen carbaldehyde are all close to the corresponding values for the low temperature absorption of 5-methyl-2-furan carbaldehyde, where the process is most likely one of molecular relaxation.

A single dielectric absorption measured over the temperature range of 186 - 218K was found in 5-bromo-2-thiophen carbaldehyde, having a value of enthalpy of activation of $\Delta H_E = 38$ kJ mol^{-1}. It is not clear from the value of activation enthalpy alone for this molecule whether the relaxation process is group or molecular or an overlap of both group and molecular.

The increasing sequence of the free energy of activation, ΔG_E, (200K) of 23, 30, and 32 kJ mol^{-1} and relaxation time, τ, (200K) of 2.3×10^{-7}, 2.1×10^{-5}, and 5.6×10^{-5} s for the thiophen-2-carbaldehyde, 5-methyl-2-furan carbaldehyde, and 5-bromo-2-thiophen carbaldehyde could be explained by a molecular relaxation process. The larger molecule would be needed to sweep out a larger volume which could in turn lead to its experiencing a greater resistance from the surrounding polystyrene medium. However, it is not feasible from the data to establish whether there is also a contribution from the intramolecular process as well.

The last molecule studied in the heterocyclic aldehyde series was N-methyl pyrrole-2-carbaldehyde, which has shown two regions of absorption. For the high temperature absorption, an activation enthalpy of 53 kJ mol^{-1} was obtained. It is in good agreement with the corresponding value of 49.7 kJ mol^{-1} found for aldehyde group relaxation in N-methyl pyrrole-2-carbaldehyde, using the n.m.r. technique.[10] It may be noted that the enthalpy of activation, ΔH_E = 53 kJ mol^{-1}, for a high temperature process in N-methyl pyrrole-2-carbaldehyde is comparatively higher than those of ΔH_E = 44 kJ mol^{-1} and ΔH_E = 45.6 kJ mol^{-1},[14] found for aldehyde group relaxation in thiophen- and furan-2-carbaldehydes. This difference in ΔH_E values may be attributed to increased electronic interaction in the former molecule between the CHO group and the ring. As in the former molecule, the methyl group is expected to direct electrons to the aromatic pyrrole ring. Thus, it would increase the electron density of the ring, which would in turn facilitate the carbonyl group to attract electrons from the ring. This would lead to an increased conjugation in the bond connecting the ring and the aldehyde group in N-methyl pyrrole-2-carbaldehyde in comparison with the unsubstituted heterocyclic aldehydes, such as thiophen- and furan-2-carbaldehydes. Hence, a higher value of ΔH_E for aldehyde group relaxation in the former molecule than that of the latter molecules results.

It is apparent from Table VI-2 that the temperature range, the 'τ' and 'ΔG_E' values at 200K, and the 'ΔH_E' value for a high temperature process of N-methyl pyrrole-2-carbaldehyde are in good agreement with the corresponding values for a high temperature process of 5-methyl-2-furan carbaldehyde. It is also to be noted that for both molecules, the observed dipole moment values decrease with the rise of temperature. Thus, the most reasonable interpretation of our data is that aldehyde group relaxation occurs for the high temperature process of N-methyl pyrrole-2-carbaldehyde.

A low temperature dielectric absorption was found in the temperature range of 124-146K, having an activation enthalpy of 19 kJ mol^{-1} and an activation entropy of -9 J K^{-1} mol^{-1}, and may be attributed to a molecular relaxation process. It can be seen (Table VI-2), that the values of relaxation time and free energy of activation at

150K for the low temperature absorption of N-methyl pyrrole-2-carbaldehyde are in agreement with the corresponding values for the low temperature absorption of thiophen-2-carbaldehyde, where the process is molecular relaxation. Hence, this close similarity to the results seems to give support for the molecular relaxation process in N-methyl pyrrole-2-carbaldehyde. Furthermore, for the low temperature process, the observed dipole moment values increase with the rise of temperature. The extrapolated value of observed dipole moment at 300K (μ_{extpd} = 2.2 D) tends to the value observed in benzene solution at 298K (μ_{LIT} = 2.77 D),[17] as opposed to the behaviour of the high temperature process. Thus, this consideration of dipole moment values for a low temperature process also adds support to the above interpretation of molecular relaxation in N-methyl-pyrrole-2-carbaldehyde.

Altogether, the relaxation time and enthalpy data **favour** an aldehyde group relaxation in thiophen-2-carbaldehyde, 5-methyl-2-furan carbaldehye, and N-methyl pyrrole -2-carbaldehyde for the higher temperature process. Further, molecular relaxation also appears to have been observed in these molecules completely separated from the group process.

For the case of 5-methyl-2-thiophen carbaldehyde it is probable that molecular process contributes to the absorption of this molecule. The more likely interpretation from the experimental result of 5-bromo-2-thiophen carbaldehyde is that both the group and molecular processes overlap.

The activation enthalpy of 50 kJ mol^{-1} for 5-methyl-2-furan carbaldehyde is found to be higher than that of the corresponding value of 45.6 kJ mol^{-1},[14] for aldehyde group relaxation in furan-2-carbaldehyde. The increased ΔH_E can be explained by the increased conjugation in the heterocyclic ring due to the presence of methyl group at C-5 in the former molecule. Similarly it is probable that the increased conjugation in N-methyl pyrrole-2-carbaldehyde has yielded a relatively higher enthalpy of activation, ΔH_E = 53 kJ mol^{-1} for the aldehyde group relaxation in comparison with the corresponding values of 44 kJ mol^{-1} and 45.6 kJ mol^{-1},[14] for aldehyde group relaxation in thiophen- and furan-2-carbaldehydes.

The present value of activation enthalpy of 44 kJ mol^{-1} agrees well with the ultrasonic value[5] of 43 kJ mol^{-1} for aldehyde group relaxation in thiophen-2-carbaldehyde. In addition, our value of ΔH_E = 53 kJ mol^{-1} is within experimental error in agreement with the n.m.r. value[10] of 49.7 kJ mol^{-1} for the barrier to aldehyde group rotation in N-methyl pyrrole-2-carbaldehyde.

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TABLE VI-1 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS FOR SOME HETEROCYCLIC ALDEHYDES IN POLYSTYRENE MATRICES.

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.77M Thiophen-2-carbaldehyde High Temperature Absorption				
284.8	52.7	3.480	0.12	15.8	2.95	1.35
290.2	33.9	3.671	0.13	15.3	2.95	1.31
299.7	18.5	3.935	0.17	14.6	2.97	1.13
304.3	15.0	4.025	0.18	14.4	2.98	1.09
307.6	11.5	4.142	0.18	14.2	2.97	1.09
310.4	9.81	4.209	0.19	14.0	2.98	1.08
312.7	8.89	4.252	0.19	13.9	2.98	1.07
		Low Temperature Absorption				
126.9	355.8	2.650	0.18	26.9	2.68	1.02
130.8	235.3	2.830	0.18	28.2	2.67	1.07
136.3	98.4	3.208	0.19	30.1	2.67	1.10
141.9	46.1	3.538	0.19	31.8	2.68	1.12
146.7	26.5	3.779	0.20	33.1	2.67	1.16
152.1	14.2	4.049	0.20	34.3	2.67	1.19
156.7	8.30	4.282	0.20	35.5	2.67	1.23
162.2	4.68	4.530	0.20	36.7	2.67	1.26
		0.75M 5-Methyl-2-furan carbaldehyde High Temperature Absorption				
263.3	67.5	3.372	0.35	57.2	3.02	1.44
268.3	51.6	3.489	0.39	55.5	3.05	1.36
273.0	31.2	3.707	0.37	53.6	3.04	1.39
277.9	20.5	3.891	0.38	52.4	3.05	1.36
295.1	5.61	4.452	0.38	46.8	3.06	1.33
302.6	3.23	4.692	0.38	43.5	3.06	1.31
		Low Temperature Absorption				
180.6	200.7	2.899	0.19	31.0	2.67	1.28
183.3	156.8	3.006	0.18	32.4	2.67	1.34
187.8	104.1	3.184	0.18	34.3	2.66	1.40
192.7	55.3	3.459	0.18	36.8	2.64	1.50
197.5	28.9	3.741	0.17	39.2	2.62	1.60
202.3	16.1	3.994	0.16	41.7	2.61	1.69
207.5	8.19	4.288	0.15	44.3	2.58	1.82

TABLE VI-1 continued....

T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
0.60M 5-Methyl-2-thiophen carbaldehyde						
169.4	252.4	2.799	0.19	41.7	2.67	1.58
175.7	120.9	3.119	0.19	43.9	2.66	1.67
179.6	76.4	3.318	0.19	45.4	2.65	1.71
185.2	37.4	3.628	0.20	47.7	2.65	1.76
189.5	22.6	3.848	0.19	49.3	2.63	1.82
194.8	13.2	4.082	0.19	51.3	2.63	1.88
199.5	7.77	4.311	0.19	52.8	2.61	1.94
204.8	4.32	4.566	0.19	54.5	2.60	2.03
0.44M 5-Bromo-2-thiophen carbaldehyde						
186.4	285.8	2.745	0.15	21.4	2.67	1.63
190.1	207.5	2.884	0.14	21.9	2.67	1.67
198.5	75.5	3.324	0.14	23.2	2.65	1.81
204.4	32.2	3.693	0.14	24.5	2.65	1.86
213.8	11.4	4.145	0.17	26.0	2.67	1.80
217.9	7.83	4.308	0.17	26.5	2.67	1.79
0.73M N-Methylpyrrole-2-carbaldehyde High Temperature Absorption						
260.3	105.0	3.180	0.21	18.2	2.89	1.11
265.4	55.9	3.454	0.21	17.9	2.89	1.12
269.9	38.3	3.618	0.21	17.4	2.89	1.10
279.3	15.4	4.014	0.23	16.8	2.89	1.06
284.5	9.84	4.208	0.23	16.6	2.89	1.05
289.2	6.74	4.373	0.24	16.0	2.87	1.04
300.0	3.73	4.630	0.24	15.1	2.87	1.02
Low Temperature Absorption						
123.7	179.3	2.948	0.16	14.0	2.69	0.807
128.2	85.6	3.269	0.15	14.7	2.68	0.846
132.4	45.9	3.539	0.16	15.4	2.68	0.872
137.6	23.6	3.828	0.16	16.5	2.68	0.908
142.3	12.5	4.105	0.16	17.2	2.68	0.956
146.3	8.23	4.286	0.16	17.9	2.68	0.980

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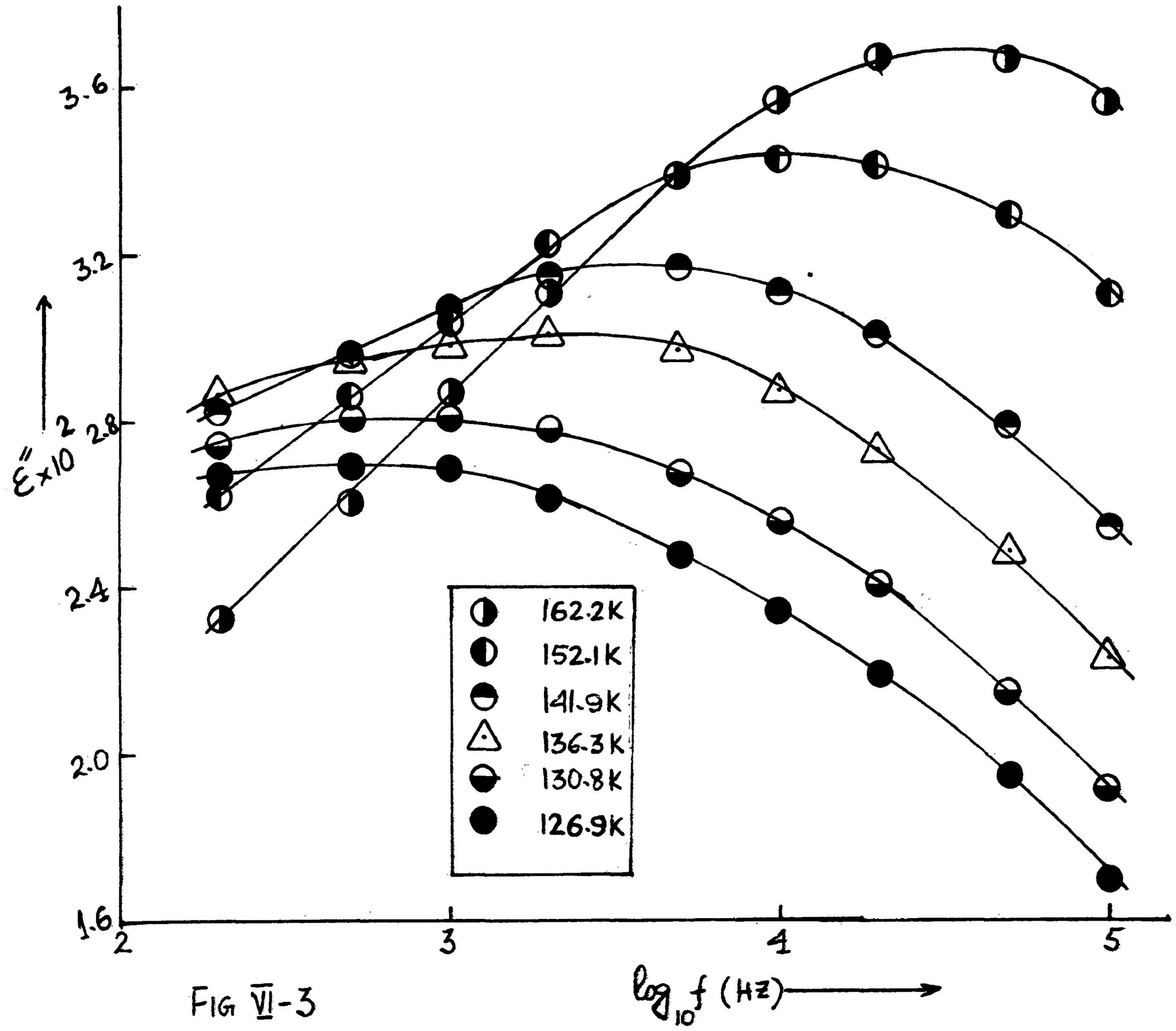


FIG VI-3

Plot of Dielectric loss factor vs $\log_{10}$f for Thiophen-2-carbaldehyde (molecular) in polystyrene

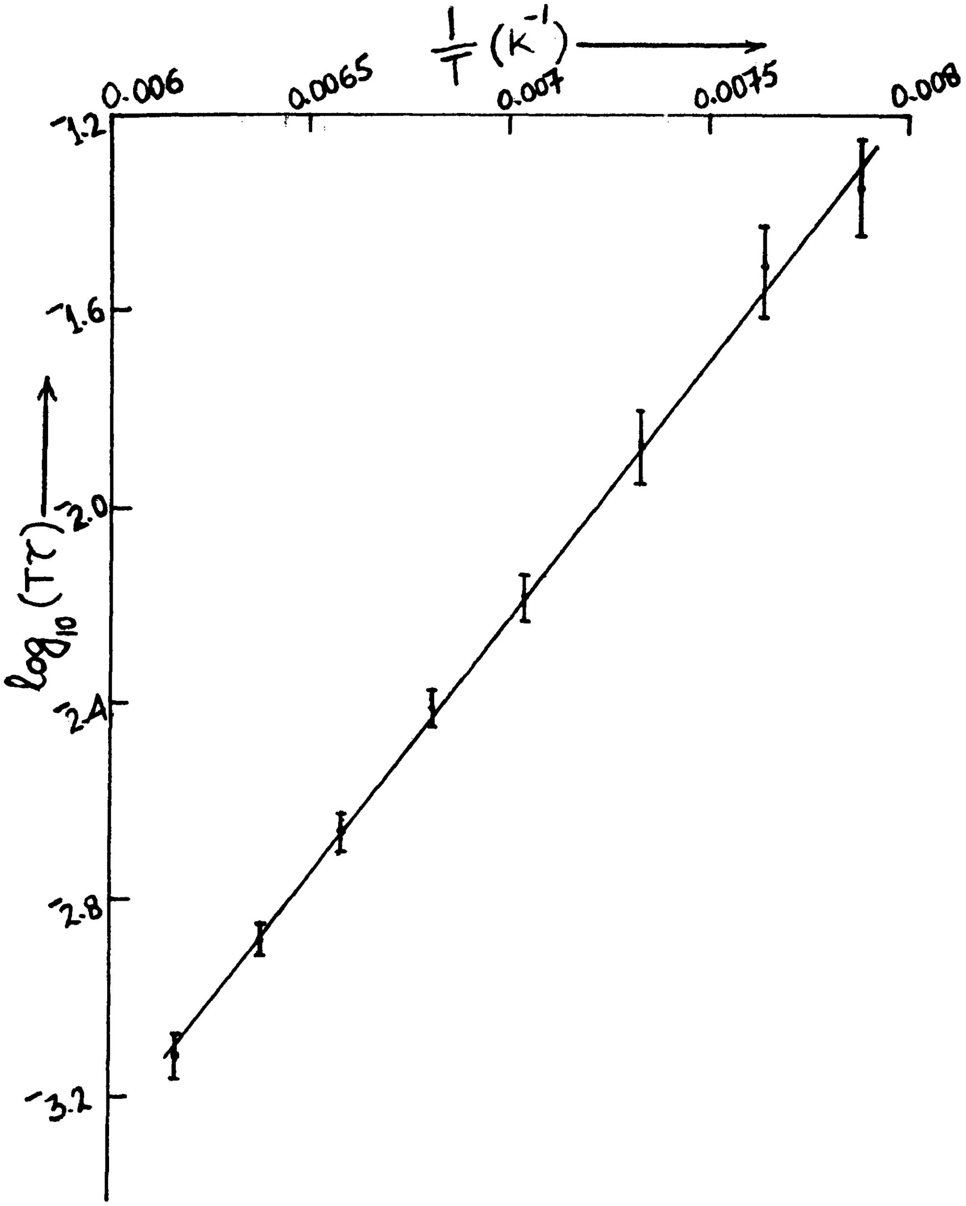


FIG VI–4. Eyring plot of $\log_{10}(T\tau)$ vs $\frac{1}{T}$ for Thiophen-2-carbaldehyde in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values.

CHAPTER VII

DIELECTRIC RELAXATION OF SOME UNSATURATED AND SATURATED ALDEHYDES

INTRODUCTION

The present investigation is part of a continuation of our programme (cf: Chapter VI) which studies the barriers due to hindered rotation around carbon — carbon single bonds in molecules containing the $= \overset{|}{C} - \overset{|}{C} =$ system. There are comparatively few investigations reported in the literature for systems of this nature: some of the literature references have already been given in Chapter VI.

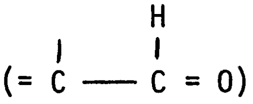
A preliminary investigation to study the unsymmetrical rotational barriers in acrolein and a few related unsaturated aldehydes has been made by de Groot and Lamb[1] who used ultrasonic relaxation technique. These workers demonstrated the effect of conjugation on the barrier for internal rotation of the formyl groups in the series: acrylaldehyde, crotonaldehyde, and cinnamaldehyde. The successive increase in the barrier for this series (acrylaldehyde, $\Delta H^*_{21} = 20.7$ kJ mol^{-1}, crotonaldehyde, $\Delta H^*_{21} = 23.0$ kJ mol^{-1}, and cinnamaldehyde, $\Delta H^*_{21} = 23.5$ kJ mol^{-1}, respectively) was attributed to the increase in bond order of the C — C bond around which rotation occurs. This increase in conjugation was thought to be mainly because of the increased electron-donating properties of the substituent in the <u>trans</u> position of the β carbon atom ($C_6H_6 > CH_3 > H$).

Later, the technique of ultrasonic relaxation was used by Pethrick and Wyn-Jones[2] to study the barriers to internal rotation of the aldehyde group in several unsaturated aldehydes. These workers suggested that the trend of increasing barrier with conjugation does not occur in the corresponding series, α-methyl acrolein, α,β-dimethyl acrolein, and α-methyl cinnamaldehyde, and the methyl group in the α-position has some additional effect on the barrier in this series. However, it seems that the degree of double bond character in the C — C bond adjacent to the carbonyl group plays an important role in determining the rotational barriers in systems of this nature. This can also be qualitatively illustrated if we compare the rotational barriers for aldehyde group relaxation in the above molecules with those obtained in furan-2-carbaldehyde[3] and thiophen-2-carbaldehyde(cf: Chapter VI) of ∿45 kJ mol^{-1}. This difference in rotational barriers may be attributed to the increased double bond character of the C—C bond in the -C—C—CHO group of the latter molecules as a result of the increased conjugation of the group with the heterocyclic rings.

The rotational barriers in butadiene and styrene have been calculated from infrared spectroscopic and thermodynamic data.[4,5] Nuclear magnetic resonance has been applied by Anet and Ahmad[6] to estimate the free energy of activation for the symmetrical rotational barriers in benzaldehyde and its two para-substituted derivatives in solution. Their work yielded an estimate of 33 kJ mol^{-1} for the free energy of activation for benzaldehyde at 150K.

The technique of far infrared has been used by Miller et al.[7] to study the C — C torsion vibration in conjugated molecules $(=\overset{|}{C}-\overset{|}{C}=)$, which were twelve derivatives of butadiene and glyoxal, plus benzaldehyde and styrene in the gas phase. Further,[8] these workers have studied the C — C torsion vibration in some conjugated aromatic compounds, such as benzaldehyde, p-fluoro-, p-chloro-, and p-bromo-benzaldehydes in the vapor and liquid phases, by using far infrared techniques. Their work yielded the energy barrier, V_2, for the vapors as 19.5, 15.0, 11.8, and 9.8 kJ mol^{-1}, while for the pure liquids they are 28.0, 21.9, 19.2, and 15.6 kJ mol^{-1}, respectively. These results indicate a fall in the energy barrier in passing from benzaldehyde to the p-halogenated aldehyde.

Dielectric measurements at microwave frequencies on propionaldehyde, crotonaldehyde, cinnamaldehyde and a few related unsaturated aldehydes in benzene have been carried out by Deshpande and Rao.[9] The relaxation times, dipole moments, and the activation energies for dipole orientation for these molecules have been reported in this study. A theoretical calculation based on molecular orbital theory by Hehre et al.[10] reported 27.7 kJ mol^{-1} for the activation enthalpy barrier (ΔH_E from Eyring theory) which the aldehyde group encounters as it rotates in benzaldehyde. The far infrared and Raman spectra of crotonaldehyde have been examined by Durig et al.[11] They reported a value of 68.6 kJ mol^{-1} for V* barrier for the aldehyde group in crotonaldehyde in the solid state.

In the literature, relatively few dielectric measurements on systems of type  $(=\overset{|}{C}-\overset{\overset{H}{|}}{C}=O)$ seem to have been carried out so far in comparison with other techniques. Thus, at the beginning of this work, it seemed of interest to examine the energy barriers to internal rotation in systems of this type with the help of the dielectric relaxation technique by trapping the solute molecules in polystyrene matrices, which might throw some light onto the effect of π-electron delocalization in conjugated molecules on the energy barrier to group relaxation. Hence, a part of this attempt to study the effect of conjugation on the barriers in conjugated systems has already been given in Chapter VI.

We have studied in the present investigation the dielectric absorption of nine aldehydes, two of which are aromatic and the rest saturated and unsaturated aliphatic ones, namely, 5,6-dihydro-2H-pyran-3-carboxaldehyde, 2-fluorenecarboxaldehyde, cyclohexanecarboxaldehyde, crotonaldehyde, trans-cinnamaldehyde, α-methylcinnamaldehyde, phenylpropargylaldehyde, α-n-hexylcinnamaldehyde, and hydrocinnamaldehyde in polystyrene matrices.

The Fuoss-Kirkwood analysis parameters for the molecules examined are listed in Table VII-1. The Eyring analysis parameters, along with the relaxation times calculated from these analyses at 150K, 200K, and 300K, are given in Table VII-2.

DISCUSSION

5,6-Dihydro-2H-pyran-3-carboxaldehyde in polystyrene exhibited two sets of dielectric absorption, one in the temperature range of 142 - 176K and the other in the temperature range of 288 - 312K. An activation enthalpy of 26 kJ mol^{-1} and an activation entropy of 10 J K^{-1} mol^{-1} have been obtained for the low temperature absorption, whereas the corresponding parameters for the high temperature absorption were 68 kJ mol^{-1} and 63 J K^{-1} mol^{-1}, respectively. The low temperature absorption has significantly higher values of about 0.3 for the distribution parameter than the high temperature absorption ($\beta = \sim 0.15$). The latter is similar to that observed by Davies and Swain[12] for a molecular relaxation process. The temperature range, the β values, and the τ and ΔG_E values at 200K for the low temperature absorption in the 5,6-Dihydro-2H-pyran-3-carboxaldehyde in polystyrene are all close to the corresponding values for the aldehyde group relaxation in terephthaldehyde[13] in polystyrene. In addition, the activation enthalpy of $\sim$26 kJ mol^{-1} and the activation entropy of 10 J K^{-1} mol^{-1} obtained for the low temperature absorption of 5,6-Dihydro-2H-pyran-3-carboxaldehyde agree well with the corresponding values of $\sim$29 kJ mol^{-1} and 15 J K^{-1} mol^{-1}, respectively, for the aldehyde group relaxation in terephthaldehyde.[13] Hence, these considerations favour the aldehyde group relaxation for the low temperature absorption of the former molecule.

The high temperature absorption of 5,6-dihydro-2H-pyran-3-carboxaldehyde has yielded an activation enthalpy of $\Delta H_E = 68$ kJ mol^{-1} and an activation entropy of $\Delta S_E = 63$ J K^{-1} mol^{-1}. These values seem to be considerably higher than those of $\Delta H_E = 16$ kJ mol^{-1} and $\Delta S_E = -43$ J K^{-1} mol^{-1} for a fairly similar-sized rigid molecule, iodobenzene (cf: Chapter III), where the process can only be one of molecular relaxation. However, the former may be attributed to the co-operative motion of the solute in polymer. Similar behaviour has been observed in a number of systems, for which a relation has been given earlier (cf: Chapter IV). The values of ΔH_E and ΔS_E fit precisely in this relation, thus giving support to the above interpretation of a co-operative molecular process in polystyrene for the high temperature absorption of 5,6-dihydro-2H-pyran-3-carboxaldehyde.

2-Fluorenecarboxaldehyde also exhibited two distinctly separate absorptions. The low temperature absorption was found in the temperature range of 195 - 234K covering a $\log_{10} f_{max}$ range of 2.7 - 4.0, having an activation enthalpy of 28 kJ mol^{-1} and an activation entropy of -31 J K^{-1} mol^{-1}. The present value of $\Delta H_E = 28$ kJ mol^{-1} for the low temperature absorption in 2-Fluorenecarboxaldehyde agrees very well with the reported value[10] of 27.7 kJ mol^{-1} for the activation enthalpy barrier (ΔH_E) to aldehyde group rotation in benzaldehyde. Further, the activation enthalpy of 28 kJ mol^{-1} and activation entropy of

-31 J K^{-1} mol^{-1} for the low temperature absorption in 2-fluorenecarboxaldehyde in the matrix show a good agreement with the corresponding values of 27 kJ mol^{-1} and -34 J K^{-1} mol^{-1}, respectively, obtained by Walker et al.[13] for aldehyde group relaxation in 2-fluorenecarboxaldehyde in the same matrix medium. Hence, this close similarity to the results favours an aldehyde group relaxation for the low temperature absorption of this molecule. The low temperature process has a significantly larger Fuoss-Kirkwood distribution parameter ($\beta = 0.3 - 0.4$) and a shorter relaxation time τ(300K) of 5×10^{-7} s relative to the corresponding parameters (Table VII-2) for the high temperature process. These observations also add support to the above interpretation of aldehyde group relaxation for the former process.

The high temperature absorption of 2-fluorenecarboxaldehyde was measured in the temperature range of 292 - 320K, covering a $\log_{10}f_{max}$ range of 2.9 - 4.2, and yielding an activation enthalpy of 98 kJ mol^{-1} and an activation entropy of 159 J K^{-1} mol^{-1}, respectively.

The ΔH_E of 98 kJ mol^{-1} of 2-fluorenecarboxaldehyde appears to be due to a molecular relaxation process, as this value is in agreement with that of ΔH_E = 89 kJ mol^{-1} for molecular relaxation of a similar-sized molecule, 2-acetylfluorene[16] in polystyrene. Moreover, the observed activation entropy of ΔS_{obsd} = 159 J K^{-1} mol^{-1} agrees well within experimental error with that of ΔS_{calcd} = 144 J K^{-1} mol^{-1}, calculated from the relation as given earlier (cf: Chapter III) corresponding to a molecular relaxation process.

It may be noted that the observed dipole moments for the low temperature absorption of this molecule are 0.9 - 1.3 D in the temperature range of 195 - 234 K. A linear extrapolation of the low temperature process values leads to μ = 2.01 D at 300K, while the interpolated value at 300K from the high temperature process is μ = 2.55 D. Thus, from the equation, $\mu^2 = \mu_{\parallel}{}^2 + \mu_{\perp}{}^2$, the molecular dipole moment μ = 3.24 D and is of the order to be expected for an aromatic aldehyde, benzaldehyde (μ_{LIT} = 3.02 D in benzene solution at 298K).[17] Such agreement suggests that the component moments so obtained are reasonably reliable. Therefore, it would appear more likely that aldehyde group and molecular relaxations contribute to the dielectric absorption of 2-fluorenecarboxaldehyde.

A six-membered saturated, aliphatic aldehyde, cyclohexanecarboxaldehyde in polystyrene showed two sets of dielectric absorption. The high temperature absorption, which was measured over the temperature range of 240 - 273K, yielded ΔH_E = 41 kJ mol^{-1} and ΔS_E = 3 J K^{-1} mol^{-1}. The high temperature absorption of this molecule has significantly high values for the distribution parameter (β = 0.5), which is similar to that observed by Davies and Swain[12] for an intramolecular relaxation process. However, it is to be noted that the absorption region at a given frequency range, the β values, and the trend of decreasing ε''_{max} with the rise of temperature for the high temperature process in cyclohexanecarboxaldehyde are all the same as observed for the high temperature process (ring inversion) in cyclohexyl chloride.[12] Further, it is seen that the value of enthalpy of activation, $\Delta H_E = 41$ kJ mol^{-1} for cyclohexanecarboxaldehyde, obtained for a high temperature absorption, is in good agreement with the corresponding value of 42.2 kJ mol^{-1} [12] for the ring inversion in cyclohexyl chloride. It may also be noted that the values of ΔH_E and ΔS_E for this molecule fit precisely in the relation: ΔS_E (J K^{-1} mol^{-1}) = $-17 + 4.2\ \Delta H_E$ (kJ mol^{-1}), given by Davies *et al.*[12] for an intramolecular motion. Thus, all the above evidence seems in favour of a ring inversion process for the high temperature absorption of cyclohexanecarboxaldehyde.

The low temperature absorption was measured in the temperature range of 109 - 134K covering a $\log_{10} f_{max}$ range of 2.5 - 4.6, having $\beta = 0.17$ to 0.24, $\Delta H_E = 21$ kJ mol^{-1}, and $\Delta S_E = 20$ J K^{-1} mol^{-1}. If one takes into consideration the enthalpy of activation for aldehyde group relaxation ($\sim$14 kJ mol^{-1}) in saturated aliphatic aldehyde (cf: Chapter VIII), it would seem reasonable to assign the activation enthalpy of $\Delta H_E = 21$ kJ mol^{-1} for the aldehyde group relaxation in saturated six membered ring aldehyde, i.e., cyclohexanecarboxaldehyde. As a higher enthalpy of activation for aldehyde group relaxation would be expected for this molecule owing to the possible steric hindrance to aldehyde group rotation due to the presence of hydrogen atom at C_1 and the possible steric interaction in the ring. On the other hand, it is noteworthy that the activation enthalpy of, ΔH_E = 21 kJ mol^{-1} for cyclohexanecarboxaldehyde agrees well within the experimental accuracy with the corresponding value of 16.4 kJ mol^{-1} for a molecular relaxation of an analogous molecule, cyclohexyl chloride in a polystyrene matrix.[12] In addition, the temperature range of absorption and the distribution parameter, β, values for the former molecule are all close to the corresponding values associated with the latter molecule. Therefore, the evidence seems more in favour of a molecular relaxation process for the low temperature absorption of cyclohexanecarboxaldehyde, although there exists a possibility of aldehyde group relaxation at such temperature range (109-134K) of this molecule.

Only one dielectric absorption in the temperature range of 282 - 317K was detected for crotonaldehyde, with ΔH_E = 61 kJ mol^{-1} and ΔS_E = 48 J K^{-1} mol^{-1}. The values of ΔH_E and ΔS_E for this molecule are seen to be much larger for a molecular relaxation in comparison with that of a rigid molecule of analogous size, for example, chlorobenzene (cf: Chapter III) which has identical length along the principal axis but slightly greater volume as examined through the Courtauld model and which in polystyrene gives a ΔH_E of 9 kJ mol^{-1} and ΔS_E of -60 J K^{-1} mol^{-1}. The τ and ΔG_E values at 200K for chlorobenzene are 5.7 x 10^{-8} s and 21 kJ mol^{-1}, respectively, whereas crotonaldehyde has yielded a much longer relaxation time (τ_{200K}=8.2 s) and a larger free energy of activation ($\Delta G_{E(200K)}$ = 52 kJ mol^{-1}). Thus, the possibility of a molecular relaxation process may be ruled out here for crotonaldehyde, as the activation parameters for this molecule differ vastly from that of a rigid chlorobenzene molecule. Therefore, the aldehyde group relaxation would be a possible relaxation candidate for the absorption of crotonaldehyde. It is, however, noteworthy that the activation enthalpy of 61 kJ mol^{-1}, free energy of activation at 200K of 52 kJ mol^{-1}, and relaxation time at 200K of 8.2 s for crotonaldehyde are considerably larger than those of ΔH_E = 28 kJ mol^{-1}, $\Delta G_{E(200K)}$ = 34 kJ mol^{-1} and τ_{200K} = 2 x 10^{-4} s, respectively, for aldehyde group rotation in 2-fluorenecarboxaldehyde. This difference in relaxation parameters may be attributed to the enhanced conjugation across the C — C bond in the former case, which does not seem to be in the latter case as reflected in the much lower stretching frequency of the carbonyl group ($\bar{\nu}_{C=O}$ = 1685 cm^{-1} in solution)[18] for crotonaldehyde compared to that of $\bar{\nu}_{C=O}$ = 1703 cm^{-1} in $\mathrm{CC\ell_4}$ for 2-fluorenecarboxaldehyde.

In addition, it is important to note that there is a regular increase in the free energy of activation for aldehyde group rotation on going from a saturated aldehyde such as butanal ($\Delta G_{E(200K)}$ = 15 kJ mol^{-1})(cf: Chapter VIII)to 2-fluorenecarboxaldehyde ($\Delta G_{E(200K}$ = 34 kJ mol^{-1}) and further to crotonaldehyde ($\Delta G_{E(200K)}$ = 52 kJ mol^{-1}).

This sequence is reflected in the stretching frequencies of the carbonyl group ($\bar{\nu}_{C=O}$) as can be seen in Table VII-3 for these compounds, these being 1730, 1703, and 1685 cm^{-1}, respectively. A decrease in the $\bar{\nu}_{C=O}$ value is in harmony with greater conjugation across the C — C bond adjacent to the carbonyl bond. Thus, both the $\Delta G_{E(200K)}$ and $\bar{\nu}_{C=O}$ suggest appreciably enhanced conjugation of the c=o group in crontonaldehyde in comparison with 2-fluorenecarboxaldehyde.

Hence, from the above considerations it would seem likely that aldehyde group relaxation contributes to the dielectric absorption of crotonaldehdye, and that the increased conjugation may have yielded the larger activation enthalpy owing to aldehyde group rotation in this molecule.

For trans-cinnamaldehyde and α-methylcinnamaldehyde only a single dielectric absorption was observed. This yielded values of activation enthalpy and entropy of 47 kJ mol^{-1} and 34 J K^{-1} mol^{-1} and 46 kJ mol^{-1} and 31 J K^{-1} mol^{-1}, respectively.

The enthalpies of activation (Table VII-2) for trans-cinnamaldehyde and α-methylcinnamaldehyde from the present dielectric absorption technique seem to be higher than the corresponding values of 23.5 kJ mol^{-1} and 21.5 kJ mol^{-1}, respectively, found for the internal rotation of the aldehyde group in these molecules by use of the ultrasonic absorption technique.[1] This difference in activation enthalpies would not be expected if the process were also aldehyde group relaxation in the former case, as Walker et al.[3] have shown that three techniques (dielectric, ultrasonics, and n.m.r.) give a close agreement for the enthalpy of activation value for the intramolecular motion in particular.

It may be noted that the effective dipole moments of trans-cinnamaldehyde and α-methylcinnamaldehyde are 1.7 - 2.0 D and 1.6 - 2.1 D in the temperature ranges of 226 - 255K and 224 - 260K, respectively. A linear extrapolation of these effective dipole moments yielded values of 2.5 D and 2.6 D, respectively, at 300K. These values are appreciably higher than the component of the dipole moment to be associated with typical aldehyde group relaxation, e.g., in 2-fluorenecarboxaldehyde, showing an extrapolated value of 2.0 D at 300K. This difference in dipole moment values suggests that molecular relaxation has contributed to some extent to the absorption of trans-cinnamaldehyde and α-methylcinnamaldehyde.

It may be seen that the activation enthalpies of trans-cinnamaldehyde (ΔH_E = 47 kJ mol^{-1}) and of α-methylcinnamaldehyde (ΔH_E = 46 kJ mol^{-1}) are lower than that for a rigid molecule of about the same size, p-fluorobiphenyl (cf:Chapter III) whose ΔH_E is 59 kJ mol^{-1}, which may be regarded as an upper limit for the ΔH_E for a molecular relaxation process. However, the values of ΔH_E and ΔS_E for the former molecules fit in the relation as described earlier (cf: Chapter III), within the experimental accuracy, corresponding to a molecular relaxation process. Thus, all the above evidences seem to favour an overlap of group and molecular processes for trans-cinnamaldehyde and α-methylcinnamaldehyde with the latter process predominating.

For α,n-hexylcinnamaldehyde, a single dielectric absorption was observed with an activation enthalpy of 63 kJ mol^{-1} and an activation entropy of 79 J K^{-1} mol^{-1}. Previous study of this molecule by ultrasonic absorption technique[2] has yielded an activation enthalpy of 19.7 kJ mol^{-1} to internal rotation of the aldehyde group, which is considerably lower than the present activation enthalpy of 63 kJ mol^{-1} for α,n-hexylcinnamaldehyde. This would not seem reasonable if the process were also aldehyde group relaxation in the latter case. However, it may be noted that the enthalpy of activation has been jacked up from 46 kJ mol^{-1} to 63 kJ mol^{-1} on going from α-methylcinnamaldehyde to α,n-hexylcinnamaldehyde, which could best be explained by increased size in the latter molecule due to n-hexyl substituent. This seems reasonable for a molecualr relaxation process, as it is sensitive to the size of the substituent group (cf: Chapter III). Moreover, the observed activation entropy, ΔS_{obsd}=79 J K^{-1} mol^{-1} agrees well within experimental error with that of $\Delta S_{calcd} = 67\ J\ K^{-1}\ mol^{-1}$, calculated from the relation (cf: Chapter III) for a molecular relaxation process. Therefore, it seems likely that molecular relaxation with little or no contribution from aldehyde group relaxation contributes to the dielectric absorption of α,n-hexylcinnamaldehyde.

For phenylpropargyl aldehyde only one absorption measured from 225-256K was found, having $\Delta H_E = 44\ kJ\ mol^{-1}$ and $\Delta S_E = 22\ J\ K^{-1}\ mol^{-1}$. The enthalpy of activation for this molecule may be compared with the corresponding value of 37 $kJ\ mol^{-1}$ for a rigid molecule, p-tolunitrile[14] in a polystyrene matrix, having identical length along the principal axis as examined through the Courtauld model. However, it is notable (Table VII-2) that the temperature range of absorption, the relaxation time, and the free energy of activation at 200K for this molecule are all found to be in close agreement with the corresponding parameters for trans-cinnamaldehyde and α-methylcinnamaldehyde. It may also be noted that the extrapolated value of the observed dipole moment of phenylpropargyl aldehyde is $\mu_{extpd} = 2.3$ D at 300K, which is somewhat higher than the value of $\mu = 2.0$ D at 300K for aldehyde group relaxation in 2-fluorenecarboxaldehyde. Therefore, it would appear that the observed relaxation process may be due to an overlap of both group and molecular relaxation, similar to that of trans-cinnamaldehyde and α-methylcinnamaldehyde.

The hydrocinnamaldehyde exhibited two sets of dielectric absorption. The low temperature absorption yielded an activation entahlpy of 21 kJ mol^{-1} and an activation entropy of -44 J K^{-1} mol^{-1}. It is to be noted (Table VII-1) that the effective dipole moment values decrease slightly with the rise of temperature. Further, the effective dipole moment value at 200K is 0.77 D, which agrees well with the corresponding value of 0.87 D at 200K, typical for aldehyde group relaxation in an aliphatic system (cf: Butyraldehyde, Chapter VIII). The enthalpy of activation of 29 kJ mol^{-1} for aldehyde group relaxation in terephthaldehyde[13] in a polystyrene matrix is to be compared with the present value of 21 kJ mol^{-1} for hydrocinnamaldehyde. This difference in activation enthalpy between terephthaldehyde and hydrocinnamaldehyde could be explained, as in the former molecule the aldehyde group is directly attached to an aromatic ring, in which there exists a possibility of increased double bond character of the bond connecting the aromatic ring and the aldehyde group because of the enhanced conjugation in the ring. This would lead in turn to a higher enthalpy of activation for aldehyde group relaxation. Whereas in the latter molecule, the aldehyde group is not directly attached with an aromatic system and there exists a possibility of less inductive effect. As a result a relatively lower enthalpy of activation for aldehyde group relaxation would be expected in this molecule than in the former molecule. However, it is seen that the enthalpy of activation value of 21 kJ mol^{-1} for hydrocinnamaldehyde is relatively higher than the corresponding value of 14 kJ mol^{-1} for aldehyde group relaxation in a long chain aliphatic system, butyraldehyde (cf: Chapter VIII). Thus, in view of the above considerations, the most reasonable interpretation of the data is that aldehyde group relaxation with a contribution from alkyl unit occurs in hydrocinnamaldehyde.

The high temperature absorption which was measured in the temperature range of 312-329K, yielded ΔH_E = 142 kJ mol^{-1} and ΔS_E = 279 J K^{-1} mol^{-1}. Since the ΔH_E for molecular relaxation is of the order of 38 kJ mol^{-1} in p-bromoethylbenzene (cf: Chapter III), a rigid molecule analogous in size to hydrocinnamaldehyde, then the only likely explanation for this large value of ΔH_E is that it is due to some form of co-operative motion involving the polymer chains. It would seem that the values of ΔH_E and ΔS_E for this high temperature absorption fit precisely in the relation as described earlier (cf: Chapter IV), corresponding to a co-operative molecular process in polystyrene, thus giving further support to the above interpretation for the high temperature absorption of hydrocinnamaldehyde.

From the foregoing discussion it may be concluded that, the enhanced conjugation seems to have caused an increase in the activation enthalpy of crotonaldehyde. The ΔG_E values at 200K for aldehyde group relaxation follow the sequence: butanal < 2-fluorenecarboxaldehyde < crotonaldehyde, and this is the order of increased conjugation as assessed by the carbonyl stretching frequency.

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TABLE VII-1 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS FOR SOME UNSATURATED AND SATURATED ALDEHYDES IN POLYSTYRENE MATRICES AT A VARIETY OF TEMPERATURES.

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.75M 5,6-Dihydro-2H-pyran-3-carboxaldehyde High Temperature Absorption				
287.7	204.2	2.89	0.12	16.2	3.21	1.33
292.3	157.1	3.01	0.12	15.6	3.20	1.34
297.6	53.5	3.47	0.13	15.6	3.22	1.28
302.5	41.0	3.59	0.14	15.4	3.22	1.22
305.9	30.3	3.72	0.14	15.3	3.22	1.25
309.6	25.4	3.80	0.15	15.2	3.23	1.19
311.9	24.0	3.82	0.16	15.1	3.23	1.16
		Low Temperature Absorption				
142.3	236.7	2.83	0.33	59.0	2.76	1.18
146.2	140.5	3.05	0.32	60.5	2.75	1.21
150.3	77.5	3.31	0.32	62.3	2.75	1.25
155.6	39.3	3.61	0.33	64.6	2.75	1.29
161.2	19.4	3.91	0.33	67.1	2.75	1.33
165.5	11.2	4.15	0.32	68.5	2.74	1.37
171.2	5.54	4.46	0.32	70.1	2.74	1.42
175.9	2.95	4.73	0.31	71.8	2.73	1.48
		0.41M 2-Fluorenecarboxaldehyde High Temperature Absorption				
292.3	246.8	2.81	0.17	34.9	2.64	2.48
296.2	179.5	2.95	0.17	35.0	2.62	2.54
299.0	135.1	3.07	0.16	35.3	2.62	2.58
304.2	65.6	3.38	0.17	35.9	2.62	2.55
308.8	35.0	3.66	0.18	36.6	2.61	2.56
313.2	20.7	3.89	0.18	37.4	2.61	2.57
316.4	13.8	4.06	0.19	38.0	2.61	2.59
319.5	9.37	4.23	0.19	38.7	2.60	2.61
		Low Temperature Absorption				
195.0	304.7	2.72	0.40	13.3	2.63	0.85
204.4	136.1	3.07	0.37	14.2	2.63	0.94
209.0	95.3	3.22	0.35	14.6	2.62	0.98
219.1	42.3	3.58	0.33	15.8	2.62	1.08
224.4	28.4	3.75	0.29	16.0	2.61	1.17
233.6	14.98	4.03	0.27	17.5	2.60	1.28

TABLE VII-1 continued...

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.92M Cyclohexanecarboxaldehyde High Temperature Absorption				
240.4	109.2	3.16	0.49	10.5	3.10	0.458
243.8	79.5	3.30	0.49	10.4	3.10	0.460
248.3	52.5	3.48	0.45	9.9	3.10	0.474
254.0	33.6	3.68	0.44	9.8	3.10	0.480
258.5	23.3	3.83	0.47	9.4	3.09	0.460
263.2	15.9	4.00	0.50	9.2	3.09	0.443
268.5	11.7	4.13	0.49	8.8	3.09	0.445
273.0	8.33	4.28	0.54	8.5	3.09	0.421
		Low Temperature Absorption				
108.7	451.5	2.55	0.17	34.0	2.69	0.98
110.4	224.4	2.85	0.18	34.3	2.70	0.96
113.7	103.9	3.18	0.20	35.4	2.70	0.95
117.4	50.4	3.50	0.21	36.5	2.69	0.97
120.8	28.4	3.75	0.20	37.8	2.70	1.00
126.6	11.5	4.14	0.22	39.7	2.71	1.01
134.4	4.0	4.60	0.24	41.7	2.73	1.01
		1.03M Crotonaldehyde				
281.9	180.0	2.95	0.18	9.4	2.67	0.808
287.4	63.6	3.40	0.18	9.2	2.67	0.791
293.7	52.0	3.49	0.19	9.4	2.67	0.799
300.1	26.1	3.78	0.17	9.2	2.66	0.835
306.7	14.0	4.05	0.18	9.2	2.66	0.820
311.8	10.3	4.19	0.20	9.1	2.66	0.790
316.8	5.58	4.45	0.20	9.1	2.66	0.787
		0.65M Trans-Cinnamaldehyde				
225.9	235.8	2.83	0.19	34.3	2.59	1.66
230.1	172.3	2.97	0.18	35.5	2.58	1.73
234.1	108.4	3.17	0.18	36.8	2.58	1.76
239.7	62.0	3.41	0.18	38.5	2.56	1.84
244.7	36.4	3.64	0.18	40.0	2.55	1.89
249.7	21.0	3.88	0.18	41.8	2.54	1.94
255.0	12.8	4.09	0.18	43.2	2.53	1.99

TABLE VII-1 continued...

T(K)	$10^6\tau(s)$	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
0.55M Alpha-methylcinnamaldehyde						
223.9	266.5	2.78	0.21	32.8	2.69	1.64
229.0	162.0	2.99	0.20	34.1	2.68	1.71
233.5	114.0	3.15	0.19	35.0	2.67	1.79
236.9	75.0	3.33	0.19	35.9	2.66	1.85
244.3	35.2	3.66	0.18	37.9	2.65	1.95
252.6	15.4	4.02	0.19	40.0	2.64	2.01
260.3	7.46	4.33	0.19	42.0	2.63	2.09
0.36M Alpha-hexlycinnamaldehyde						
250.0	203.9	2.89	0.24	19.0	2.63	1.56
255.2	130.9	3.08	0.24	19.9	2.63	1.60
259.9	81.6	3.29	0.22	20.4	2.62	1.71
265.1	39.4	3.61	0.21	21.5	2.61	1.81
269.5	23.9	3.82	0.21	22.2	2.60	1.88
273.8	15.1	4.02	0.21	23.0	2.60	1.91
279.0	9.58	4.22	0.22	23.7	2.60	1.93
283.8	5.02	4.50	0.21	24.6	2.58	2.03
0.65M Phenylpropargylaldehyde						
224.6	231.3	2.84	0.21	28.1	2.61	1.43
229.5	115.8	3.14	0.21	29.3	2.60	1.46
234.5	77.1	3.32	0.21	30.6	2.59	1.54
242.5	37.4	3.63	0.20	32.6	2.58	1.63
248.4	20.9	3.88	0.20	34.0	2.57	1.71
255.5	11.2	4.15	0.20	35.5	2.56	1.77
0.60M Hydrocinnamaldehyde High Temperature Absorption						
312.4	296.4	2.73	0.10	6.3	2.61	1.23
316.5	119.1	3.13	0.10	6.4	2.61	1.22
322.5	44.2	3.56	0.10	6.7	2.61	1.26
324.1	30.8	3.71	0.11	6.9	2.64	1.23
326.5	20.6	3.89	0.11	7.0	2.63	1.25
328.9	20.5	3.89	0.12	7.2	2.64	1.23

TABLE VII-1 continued...

T(K)	$10^6\tau(s)$	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
			Low Temperature Absorption			
175.6	86.2	3.27	0.09	4.3	2.67	0.791
184.7	51.9	3.49	0.10	4.6	2.67	0.795
193.9	27.4	3.76	0.12	4.9	2.67	0.775
203.1	15.1	4.02	0.14	5.2	2.67	0.742
213.1	5.47	4.46	0.15	5.6	2.67	0.758
222.5	3.28	4.69	0.17	5.8	2.67	0.755
232.0	2.46	4.81	0.19	6.1	2.67	0.754

TABLE VII-2: EYRING ANALYSIS RESULTS FOR SOME UNSATURATED AND SATURATED ALDEHYDES IN POLYSTYRENE MATRICES

Molecule	T(K)	τ(s) 150 K	200 K	300 K	ΔG_E(kJ mol^{-1}) 150 K	200 K	300 K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
5,6-Dihydro-2H-pyran-3-carboxaldehyde	288-312	8.3×10^{7}	7.4×10^{1}	5.8×10^{-5}	59	55	49	68	63
	142-176	8.0×10^{-7}	3.5×10^{-5}	1.4×10^{-9}	24	24	23	26	10
2-Fluorene-carboxaldehyde	292-320	3.0×10^{13}	6.2×10^{4}	1.1×10^{-4}	75	67	51	98	159
	195-234	7.1×10^{-2}	2.0×10^{-4}	5.0×10^{-7}	33	34	37	28	- 31
Cyclohexane-carboxaldehyde	240-273	3.7×10^{1}	7.9×10^{-3}	1.5×10^{-6}	40	40	40	41	3
	109-134	4.5×10^{-7}	5.4×10^{-9}	5.7×10^{-11}	18	17	15	21	20
Crotonaldehyde	282-317	2.4×10^{6}	8.2	2.5×10^{-5}	54	52	47	61	48
trans-Cinnam-aldehyde	226-255	1.2×10^{2}	7.5×10^{-3}	4.1×10^{-7}	42	40	37	47	34
α-Methyl-Cinnamaldehyde	224-260	8.9×10^{1}	6.4×10^{-3}	4.1×10^{-7}	41	40	37	46	31
Alpha-Hexylcinnam-aldehyde	250-284	2.4×10^{5}	5.8×10^{-1}	1.2×10^{-6}	51	47	40	63	79
Phenylpropargyl-aldehyde	225-256	3.5×10^{1}	4.3×10^{-3}	4.6×10^{-7}	40	39	37	44	22
Hydrocinnam-aldehyde	312-329	3.2×10^{22}	9.8×10^{9}	2.6×10^{-3}	101	87	59	142	279
	176-232	1.4×10^{-3}	1.5×10^{-5}	1.5×10^{-7}	28	30	34	21	- 44

TABLE VII-3: INFRARED CABRONYL STRETCHING FREQUENCIES

Compound	$\bar{\nu}_{c=o}$ (cm^{-1})	Solvent
Butanal*	1730	$CC\ell_4$
2-Fluorenecarboxaldehyde	1703	$CC\ell_4$
Crotonaldehyde*	1685	$CC\ell_4$

*Reference 18

CHAPTER VIII

DIELECTRIC RELAXATION OF SOME LONG-CHAIN ALIPHATIC ALDEHYDES

INTRODUCTION

The dipole reorientation by intramolecular rotation of polar groups substituted in an aromatic system has received considerable attention.[1]

In aliphatic molecules, which in general are far more flexible, there exists a possibility of the rotation of substituent groups as well as that of the segmental rotation of different molecular units. The dielectric properties of several aliphatic long-chain molecules, containing different dipole-bearing groups, have been extensively investigated. Investigations on some aliphatic molecules, RX, with varying size of 'R' group and with varying positions of 'X' groups have been made, and in some cases, the effect of solvent viscosity has been studied. Thorough and systematic investigations of the n-bromoalkanes both as pure liquids and in solution have been made at microwave frequencies,[2] and the distribution parameter, which increases with increasing chain length, has been discussed in terms of a distribution of relaxation times due to segmental rotations. The limits are given by two extreme values corresponding to -CH_2Br group relaxation and molecular end-over-end rotations.

Tay and Crossley[6] considered the relaxation data for 1-bromoalkanes in cyclohexane solution and suggested that the dipole reorientation about the long axis in these molecules involves a variety of molecular segments containing the CH_2Br group. Further, these workers reported the dielectric absorption study of solutions of 1-amino alkanes ($R - NH_2$),[7] and 2-alkanones ($R - COCH_3$),[8] and it was inferred that in these molecules dipole reorientation occurs primarily by rotation of the polar end group and that the mean relaxation times are almost independent of the length of the alkyl group 'R'. In a separate study[3] on alkyl amine, alkanone, and alkyl bromide, the potential barriers to rotation of the polar groups have been found to be 8.1, 3.3, and 14.9 kJ mol^{-1}, respectively, for the three systems.

In a recent paper, Madan[11,12] has examined the dielectric behaviour of solutions of aliphatic ketones in different non-polar solvents, and the results have been discussed in terms of dipole reorientation by overall molecular rotation and/or by intramolecular rotation around R - C or R' - C bonds. However, he reported the enthalpy of activation, (ΔH_E), for dipole relaxation in cyclohexane solutions of 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, and 2-decanone as 4.2, 10.0, 4.2, 10.0, and 10.0 kJ mol^{-1}, respectively.

The dielectric properties of alcohols have also been investigated extensively.[4,5,9] Gemert and coworkers[9] examined methanol, ethanol, propanol, and butanol in different non-polar solvents and reported the activation energies of these alcohols in benzene solution as 15.5, 23.0, 25.9, and 29.3 kJ mol^{-1}, respectively. These high values of activation energy were discussed in terms of the co-operative motion of a single molecule (after H-bond rapture) with its surroundings, or of a cyclic multimer with its surroundings. However, these mechanisms are in contrast with the findings of Imanov et al.,[4] where the rotation of the CH_2OH group near the C-C bond was suggested from studies on pure propanol, iso-propanol, butanol, and iso-butanol, and their solutions in hexane. The activation energies for these systems were only $\leq$ 10.5 kJ mol^{-1}.

A systematic study of the dielectric behaviour of ten alkyl acetates (i.e., $R_1 = CH_3$ and $R_2 = C_nH_{2n+1}$, n = 1, 2 --- 8) in solution has been undertaken by Higasi and coworkers.[10] The enthalpy of activation is found to increase from 5.1 kJ mol^{-1} for methyl acetate to 6.0 kJ mol^{-1} for n-octyl acetate. From the non-zero distribution parameters, these workers suggested that the dipole re-orientation in these molecules occurs by the internal rotation of various segments.

However, in contrast to the foregoing extensive investigations of long-chain aliphatic molecules, containing different rotatable polar groups, by using dielectric absorption technique, only a limited number of literature references is available for long-chain aliphatic aldehydes. Verdier and Wilson[13a] examined acetaldehyde and reported a barrier height (V_3) of 4.8 kJ mol^{-1} from the microwave technique. A hindered rotation leading to the different rotameric forms has been suggested for propionaldehyde[13b] and n-butyraldehyde,[13c] by using microwave spectroscopy. Dielectric measurements[13d] on propionaldehyde and some other aldehydes in benzene solution, have been carried out by Deshpande and Rao, who reported an activation energy of 6.8 kJ mol^{-1} for dipole orientation in propionaldehyde. Smyth and coworkers[13e] examined the dielectric behaviour of n-octyl aldehyde and some long-chain aliphatic molecules in n-heptane solution at 298K. They suggested that the molecules have two dispersion regions and the results are consistent with contributions from an intramolecular and a molecular relaxation time.

Hence, the above information available in the literature reveals the lack of adequate and systematic dielectric relaxation data and the energy barriers for intramolecular and/or molecular processes for long-chain aliphatic aldehydes. It thus seemed of interest to examine long-chain aliphatic aldehydes in polystyrene matrices by using the dielectric absorption technique, as in the past few years this approach has proved quite fruitful in the study of suitable intramolecular motions and has been successful in the determination of the energy barrier for an intramolecular and/or molecular relaxation process separately. Thus, the present work was undertaken in order to make a systematic dielectric relaxation study of long-chain aliphatic aldehydes in a polystyrene matrix and also with a view to gain information about the energy barrier of intramolecular and/or molecular motions in this area.

EXPERIMENTAL RESULTS

The molecules examined in this study are seven aliphatic long-chain aldehydes (i.e., $R(CH_2)_nCHO$, where $R = CH_3$ and $n = 2$, 3, 4, 5, 7, 8, 10) in a polystyrene matrix. The n-nonanal molecule has also been examined in another medium (polypropylene). A study of n-hexyl bromide has also been made in a polystyrene matrix. The sample plots of loss factor ($\varepsilon'' = \varepsilon''(\text{obs}) - \varepsilon''(\text{polystyrene})$) against logarithm (frequency) and $\log T\tau$ against T^{-1} are shown in Figures VIII-1 and VIII-2 for n-butanal. The Fuoss-Kirkwood analyses parameters for the molecules examined are presented in Table VIII-1. The results of Eyring equation analyses of these data, along with the relaxation times calculated from these analyses at temperatures 100K, 200K, and 300K, are given in Table VIII-2.

DISCUSSION

All the long-chain aliphatic aldehydes studied in this investigation show two distinctly separate regions of absorption.

However, the second and third members of the homologous series of aliphatic aldehydes ($R(CH_2)_nCHO$, $R = CH_3$, $n = 2$ and 3), viz., butanal and pentanal, exhibited the low temperature dielectric absorption in a similar range of temperatures (around 100K) and have yielded similar values for the enthalpy of activation ($\Delta H_E =$ 14 kJ mol^{-1}) and entropy of activation ($\Delta S_E = \sim -7$ J K^{-1} mol^{-1}).

It is seen for aliphatic molecules in n-heptane solutions,[13e] acetophenone in cyclohexane,[18] and 2-acetonaphthone and 4-acetyl-o-terphenyl in benzene,[19] that the relaxation times for molecular rotation are rather long compared to the relatively short relaxation times associated with the intramolecular process.

It is to be noted (Table VIII-2) that the relaxation times at 300K for the low temperature absorption of butanal and pentanal are considerably shorter than the corresponding values obtained for the high temperature dielectric absorption of these molecules, which suggests a possibility of an intramolecular process in the low temperature region for these molecules. Further, relaxation times for the low temperature absorption of butanal and pentanal at 300K (Table VIII-2) appear to be similar to the short relaxation times associated with the intramolecular process of, for example, ethyl ether[15] in heptane, and ethyl hexnoate[16] in benzene solution.

The values of the relaxation time for butanal and pentanal ($\sim 1.8 \times 10^{-9}$ s at 200K) in the polystyrene matrix are found to be $\sim 10^{3}$ times shorter than the relaxation time for aldehyde group rotation in an aromatic molecule, terephthaldehyde[14] (1.8×10^{-6} s at 200K) in the same medium. Such a difference in relaxation time between an aliphatic and an aromatic system could be related, owing to the conjugation of π electrons in the latter case, to the carbonyl group of aldehyde substituent and the bond connecting the aldehyde group with the ring ($C_{aldehyde}$ — $C_{aromatic}$). Furthermore, the relaxation times (300K) for butanal and pentanal in the polystyrene matrix (Table VIII-2) seem to be of the same order of magnitude as the relaxation times (298K) attributed to the rotation of the polar end group in n-butyl amine[7] and 2-hexanone[8] in cyclohexane solution.

It should be recognized that the 'τ' and 'ΔG_E' values in the middle of the temperature range of absorption are most reliable parameters as these are the measured values and can be deduced directly from the frequency maximum values. However, in the middle of the temperature range of absorption (100K), butanal and pentanal yield 'τ' and 'ΔG_E' values as 1.5×10^{-5} s and 14 kJ mol^{-1}, and 1.0×10^{-5} s and 14 kJ mol^{-1}, respectively. This indicates that there is no significant variation in these two parameters when the number of carbon atoms in the chain length is increased (i.e., in going from butanal to pentanal). This observation is in contrast to the molecular relaxation process in which one would expect a progression in 'τ' and 'ΔG_E' with increasing size of the molecule.

Tay and Crossley[6] suggested that as the potential barriers to rotation of the terminal NH_2, $COCH_3$ groups in amino alkanes and alkanones are significantly smaller than the potential barrier to rotation about the C—C bond in saturated aliphatic hydrocarbons.[3] As a result the rotation of the polar end group would be faster than any segmental rotations within their hydrocarbon chain, and the dipole reorientation in these compounds would occur primarily by rotation of the polar group. In view of this suggestion it should be noted that our value of activation enthalpy for butanal and pentanal (14 kJ mol^{-1}) is significantly smaller than the barrier height in saturated aliphatic hydrocarbons[3] (for example, for butane it is ca: 15 kJ mol^{-1}). In addition, the enthalpy of activation, ΔH_E = 14 kJ mol^{-1}, obtained for butanal and pentanal in the polystyrene matrix, is comparable to the corresponding value of 10.0 kJ mol^{-1},[12] found for an intramolecular relaxation process in 2-pentanone in cyclohexane solution. Thus, all the above considerations for butanal and pentanal suggest that the dipole reorientation by intramolecular rotation is dominated by the terminal aldehyde group with little or no contribution from the $-CH_2$ unit of the aliphatic chain.

It may be seen from Table VIII-2 that the enthalpy of activation for butanal is slightly smaller than its free energy of activation (100K), so that the entropy of activation is negative, which according to Branin and Smyth[17] shows that there are fewer configurations possible in the activated state, and for these configurations the activated state is more ordered than the normal state.

The higher members of the homologous series of aliphatic aldehydes, hexanal, heptanal, and nonanal in polystyrene matrices, showed two sets of dielectric absorption. The low temperature absorption of these molecules yielded the enthalpy and entropy values of activation: 16 kJ mol^{-1} and 13 J K^{-1}mol^{-1}, 16 kJ mol^{-1} and 8 J K^{-1}mol^{-1}, and 17 kJ mol^{-1} and -4 J K^{-1}mol^{-1}, respectively. Again the magnitude of 'τ' (300K) for the low temperature absorption of these molecules is considerably shorter than the respective values obtained for their high temperature absorption. In addition, the short relaxation times associated with these molecules are of about the same order of magnitude as those found for the low temperature absorption of butanal and pentanal, thus suggesting the possibility of an intramolecular relaxation process in these molecules. However, it is notable from Table VIII-2 that there is a slight progression in the values of the relaxation time (τ at 100K) with an increasing number of carbon atoms in the chain, i.e., in going from hexanal to heptanal and nonanal. The free energies of activation at 100K for hexanal, heptanal, and nananal are 15 kJ mol^{-1}, 15 kJ mol^{-1}, and 17 kJ mol^{-1}, respectively, showing a similar trend as that noticed for the relaxation times of these molecules. It is, however, noteworthy (Table VIII-2) that the enthalpies of activation (ΔH_E) for hexanal, heptanal, and nonanal in the polystyrene matrices are comparatively higher ($\sim$2 kJ mol^{-1}) than the respective values for butanal and pentanal in the same medium. In addition, the activation enthalpies for these molecules seem to be slightly greater than that of the barrier height to rotation about the C — C bonds in saturated aliphatic hydrocarbons.[3] This observation suggests that the rotation of the terminal aldehyde group in hexanal, heptanal, and nonanal may be slightly slower than any segmental rotations within the aliphatic chain, and thus the dipole reorientation of these molecules is likely to involve a contribution from smaller segments which contain the terminal aldehyde group. This explanation seems to be reasonable, since an increase in chain length (i.e., hexanal, heptanal, and nonanal) gives rise to an increase in the flexibility of the molecule which in turn increases the number of degrees of freedom within the molecule. As a result, the smaller segments which contain the terminal aldehyde group would be expected to contribute to the dielectric absorption of these molecules. It seems, therefore, reasonable to assume that the terminal end group rotation with a contribution from smaller segments is a predominant process of dipole reorientation for hexanal, heptanal, and nonanal in polystyrene matrices.

An experiment was carried out to examine whether the change in a local environment does affect on the intramolecular process or not. Such influences for molecular process may be expected to exhibit considerable variation in enthalpy of activation by such changes in surrounding medium, whereas an intramolecular process may be expected to be reasonably independent of such a change in a local environment. Therefore, nonanal was examined in a polypropylene matrix which showed two regions of dielectric absorption similar to that observed in a polystyrene medium. The low temperature absorption of nonanal was measured from 94 - 115K, having larger β values ($\sim$0.3) and ΔH_E = 17 kJ mol^{-1}. It may be seen (Table VIII-2) that the activation enthalpy of ΔH_E = 17 kJ mol^{-1} for nonanal in a polypropylene medium is in excellent agreement with the value of ΔH_E = 17 kJ mol^{-1} for this molecule in a polystyrene medium. In addition, the temperature range, the β values, ΔG_E and τ values at 100K for nonanal in a polypropylene medium are all close to the corresponding values of this molecule in a polystyrene medium. Hence this close similarity in the results of this molecule in two different media, (polypropylene and polystyrene strongly suggests that the intramolecular process is independent of such a change in the surrounding medium. This observation is also supported by the study of Walker _et al._,[20] in which a similar enthalpy of activation of $\sim$35 kJ mol^{-1} is found for hydroxyl group relaxation in 2,6-dinitro-4-methyl phenol in polystyrene and polyethylene matrices. However, in contrast to the low temperature absorption of nonanal in polypropylene, the activation enthalpy and entropy for the high temperature absorption of this molecule were very large, being 80 kJ mol^{-1} and 297 J K^{-1} mol^{-1}, respectively, in comparison with the respective values of 38 kJ mol^{-1} and 5 J K^{-1} mol^{-1} for nonanal in a polystyrene medium. Such differences in ΔH_E and ΔS_E may be accounted for by the change in local environment provided by polypropylene and polystyrene, as molecular relaxation is expected to be dependent of the medium.

For higher members of the long-chain aliphatic aldehyde series $\{R(CH_2)_nCHO$, $R = CH_3$, and $n = 8$ and $10\}$, viz., decanal and lauraldehyde, again two sets of dielectric absorptions were found. The low temperature absorptions of these molecules have yielded the enthalpies and entropies of activation as 25 kJ mol^{-1} and 48 J K^{-1} mol^{-1}, and 27 kJ mol^{-1} and 46 J K^{-1} mol^{-1}, respectively. The low temperature absorptions of these molecules have significantly higher distribution parameters ($\beta = 0.3 - 0.4$) and shorter relaxation times (300K) relative to those associated with their high temperature absorption. It is apparent from Table VIII-2 that the relaxation time, τ, and the free energy of activation, ΔG_E, at 100K, show a significant increase with the increased number of carbon atoms in the chain. That is the τ and ΔG_E values (100K) for decanal (ten carbon atoms in the chain) are 1.3 x 10^{-2} s and 20 kJ mol^{-1}, respectively, whereas the corresponding parameters for lauraldehyde (twelve carbon atoms in the chain) are 1.9 x 10^{-1} s and 22 kJ mol^{-1}, respectively. Furthermore, the τ and ΔG_E values at 100K (Table VIII-2) for these molecules are considerably larger in comparison with the corresponding parameters obtained for the low temperature absorption of butanal and pentanal where more likely a terminal aldehyde group rotation contributes to the dielectric absorption. Taking into consideration the much greater flexibility in the aliphatic chain of decanal and lauraldehyde compared with that of butanal and pentanal, this would tend to increase the possibility of rotation for a variety of segments which contain the terminal aldehyde group. Thus as the rotation of larger alkyl unit together with the terminal aldehyde group would be expected to involve a greater resistance from the surrounding medium (polystyrene matrix) and owing to the possible steric interactions with a spiral chain, one would expect a higher activation enthalpy for an intramolecular rotation in long chain aliphatic molecules (i.e., decanal and lauraldehyde) than short chain aliphatic molecules (i.e., butanal and pentanal). Hence, in view of the above considerations it is probable that for the low temperature absorption of decanal and lauraldehyde, dipole reorientation by intramolecular rotation occurs by terminal aldehyde group rotation with a contribution from a longer alkyl unit, which in turn leads to the higher values of ΔH_E for these molecules than those for butanal and pentanal.

In general, it would be expected that the relaxation time, τ, and the free energy of activation, ΔG_E, at a given temperature (say 300K) would increase with the number of carbon atoms in the chain, if the overall molecular rotation were a dominant contributing factor in the relaxation process. This indicates that the increase in molecular chain length would increase the amount of energy required for the molecular dipole orientation. In contrast to this expectation, the high temperature absorption of butanal, pentanal, hexanal, heptanal, nonanal, decanal, and lauraldehyde did not show a regular increase in the values of 'τ' and 'ΔG_E' (300K) with the increasing number of carbon atoms in the chain. As seen from Table VIII-2, the relaxation time 'τ' and free energy of activation 'ΔG_E' at 300K for butanal, pentanal, and hexanal are 6.8×10^{-6} s and 44 kJ mol^{-1}, 1.3×10^{-5} s and 45 kJ mol^{-1}, and 1.4×10^{-5} s and 46 kJ mol^{-1}, respectively, showing a slight lengthening in 'τ' and an increase in 'ΔG_E' values as the number of carbon atoms in the chain is increased from C_4 to C_6. However, heptanal (C_7) yields an appreciably lower value of relaxation time, $\tau = 1.3 \times 10^{-8}$ s, and free energy of activation,

ΔG_E = 28 kJ mol^{-1}, whereas nonanal (τ = 4.1 x 10^{-7} s, ΔG_E = 37 kJ mol^{-1}), decanal (τ = 3.1 x 10^{-6} s, ΔG_E = 42 kJ mol^{-1}), and lauraldehyde (τ = 1.6 x 10^{-4} s, ΔG_E = 52 kJ mol^{-1}) all show a significant increase in these parameters with increasing chain length, i.e., from C_9 to C_{12}. Thus lack of consistency in 'τ' and 'ΔG_E' values with increasing chain length suggests that the absorption is not solely due to overall molecular relaxation. It is, however, more likely that the variety of molecular segments are making an appreciable contribution to the high temperature dielectric absorption. In particular for the molecules having a long chain, where because of the larger freedom in the chain there exists a much greater possibility from segmental reorientation, of contributing to the absorption rather than in the case of molecules having a short chain. Further, it is notable (TableVIII-2) that the enthalpy of activation for the high temperature absorption of these molecules is considerably higher than those associated with the low temperature absorption of these systems. This observation can be explained as in the former case dipole orientation may occur either by overall molecular oreintation or by longer segmental reorientation. This would in turn encounter a greater resistance from the surrounding polystyrene medium than that of the rotation of small polar end group (i.e., aldehyde group) with little or no contribution from smaller segments, which is more likely a mechanism in the low temperature absorption of these systems. As a result, the activation enthalpies, ΔH_E, for the high temperature absorption of these molecules are higher compared to the values associated for their low temperature absorption.

It is to be noted (Table VIII-2) that the activation entropies and enthalpies for the high temperature absorption of hexanal, decanal, and lauraldehyde are enormously larger than the corresponding values obtained for the other members of this series. The higher values of ΔH_E and ΔS_E for these molecules do not seem reasonable for a molecular relaxation. It appears that the absorption might have reached the glass-rubber transition temperature, and therefore, the absorption might be associated with the co-operative motion of polymer segments with that of solute molecules. As a result, it would produce a large local disorderliness in the medium, thus giving rise to a large positive entropy of activation for these molecules. The entropies of activation were further estimated from the relation (cf: Chapter IV), corresponding to a co-operative molecular motion in polymers. The observed activation entropies of hexanal, ΔS_{obsd} = 165 J K^{-1} mol^{-1}, decanal, ΔS_{obsd} = 135 J K^{-1} mol^{-1}, and lauraldehyde, ΔS_{obsd} = 285 J K^{-1} mol^{-1} are found to be in good correspondence with the calculated values of 158 J K^{-1} mol^{-1}, 119 J K^{-1} mol^{-1}, and 294 J K^{-1} mol^{-1}, respectively, give further support to the co-operative motion of these molecules in a polymer.

In general, it may be seen that for various aliphatic aldehydes the effective dipole moments observed from the low temperature absorption are of the order of 0.4 - 0.6 D in the temperature range of absorption of 90 - 150K. The values of the observed dipole moment are considerably lower than the literature values[21] of 2.6 D at ∿293K for butanal and pentanal. Further, it is to be noted that the observed values of the dipole moment for the low temperature absorption of hexanal are 0.4 - 0.5 D in the temperature range of 91 - 114K. Extrapolation to 300K yielded a value of ∿1.73 D. This indicates that at lower temperatures the polymer matrix does not allow a complete relaxation of the full dipole moment. It would seem likely that there should be another absorption for the various aldehydes at higher temperatures. In fact, this higher temperature absorption for various aldehydes has been observed.

A rough estimate of the total intensity of the two dielectric absorptions may be made from the relation $\mu_1^2 + \mu_2^2 = \mu_{total}^2$, where μ_2 is the extrapolated value of the dipole moment at 300K from the low temperature intramolecular process, and μ_1 is the interpolated value from the high temperature process. Therefore, the estimated value of total moment at 300K for hexanal is $\sqrt{(0.89)^2 + (1.73)^2} \sim 2$ D, which is somewhat less than the literature value of 2.6 D at 293K for pentanal. The divergence in the observed values of the dipole moment with the literature data may possibly be attributed to the fact that the extrapolation has been made in a wider temperature interval, thus giving rise to the apparent discrepancies between the two values. Moreover, it may be apparent that "only some of the molecules reorient and/or their range of reorientation is well below ±π", as was suggested by Davies and Swain.[22]

Although the last molecule, for which the data are given in Table VIII-2, does not belong to long-chain aliphatic aldehyde series, it was examined in order to obtain the information about relaxation parameters in long-chain alkyl bromides. As given in Table VIII-2, 1-bromohexane in polystyrene shows two distinctly separate regions of absorption. The low temperature absorption yields an activation enthalpy and entropy of 17 kJ mol^{-1} and 3 J K^{-1} mol^{-1}, respectively, while the high temperature absorption yields the corresponding parameters of 39 kJ mol^{-1} and 31 J K^{-1} mol^{-1}, respectively. It is seen (Table VIII-2) that the low temperature absorption has significantly higher 'β' values and short relaxation times (100K) than the corresponding parameters obtained in the high temperature absorption region. The enthalpy of activation 17 kJ mol^{-1} for the low temperature absorption is in good agreement with the barrier height of 14.9 kJ mol^{-1},[3] obtained for the rotation of $-CH_2Br$ group in CH_3-CH_2Br. Hence, it suggests that more likely a polar end group rotation is occurring for the low temperature absorption of 1-bromohexane. The high temperature absorption in this molecule may be attributed to intramolecular rotation by segmental reorientation.

All that can be concluded, from the present experimental data of long-chain aliphatic aldehydes, therefore, is that for the low temperature absorption of butanal and pentanal, dipole reorientation involve the rotation of the -CHO group with little or no contribution from the smaller $-CH_2$ unit of the aliphatic chain. For higher members of this series, i.e., hexanal, heptanal, nonanal, decanal, and lauraldehyde, it is probable that in addition to terminal aldehyde group rotation, segmental reorientation also makes a significant contribution to their dielectric absorption. The high temperature dielectric absorption of these molecules may be attributed to either overall molecular rotation or to the intramolecular rotation of molecular segments.

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TABLE VIII - 1 TABULATED SUMMARY OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS FOR SOME ALIPHATIC LONG-CHAIN ALDEHYDES AT A VARIETY OF TEMPERATURES.

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		1.0 M Butanal in polystyrene High temperature absorption				
273.2	86.2	3.27	0.17	8.1	2.85	0.715
279.3	43.8	3.56	0.18	8.0	2.84	0.703
282.8	27.9	3.76	0.18	7.8	2.84	0.693
287.3	19.1	3.92	0.20	7.7	2.84	0.670
293.3	10.6	4.18	0.21	7.7	2.84	0.651
299.2	8.67	4.26	0.23	7.4	2.84	0.620
		Low temperature absorption				
91.1	92.3	3.24	0.18	15.7	2.67	0.576
92.6	58.1	3.44	0.19	15.9	2.68	0.572
98.3	19.2	3.92	0.19	17.0	2.68	0.596
102.4	8.90	4.25	0.20	17.6	2.67	0.618
106.2	5.63	4.45	0.21	18.0	2.68	0.615
110.9	3.10	4.71	0.22	18.4	2.69	0.621
		1.0 M Pentanal in Polystyrene High temperature absorption				
266.6	237.9	2.83	0.13	5.7	2.80	0.691
270.7	146.3	3.04	0.18	5.6	2.80	0.595
275.0	84.2	3.28	0.17	5.4	2.80	0.610
280.2	57.0	3.45	0.20	5.2	2.80	0.556
304.3	9.26	4.24	0.25	4.4	2.78	0.474
309.0	7.22	4.34	0.26	4.2	2.77	0.461
		Low temperature absorption				
90.4	61.2	3.41	0.16	9.7	2.60	0.491
91.9	44.1	3.56	0.18	9.9	2.61	0.481
95.5	24.5	3.81	0.15	10.2	2.60	0.534
97.3	16.5	3.98	0.15	10.4	2.59	0.556
99.2	12.1	4.12	0.14	10.6	2.59	0.576
102.7	6.16	4.41	0.13	10.9	2.58	0.617
105.9	3.75	4.63	0.13	11.2	2.58	0.646

TABLE VIII - 1 continued....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.80 M Hexanal in polystyrene High temperature absorption				
284.8	116.4	3.14	0.12	7.5	2.70	1.00
288.6	94.3	3.23	0.15	7.3	2.71	0.881
292.4	41.7	3.58	0.13	7.3	2.70	0.950
295.4	22.9	3.84	0.15	7.2	2.70	0.877
298.8	11.0	4.16	0.14	7.2	2.69	0.912
304.4	6.18	4.41	0.17	7.4	2.70	0.847
309.1	4.92	4.51	0.19	7.4	2.70	0.821
314.3	3.21	4.69	0.20	7.5	2.71	0.794
		Low temperature absorption				
90.5	217.5	2.86	0.21	6.5	2.63	0.397
92.5	129.8	3.09	0.20	6.6	2.63	0.412
96.5	57.8	3.44	0.20	7.0	2.63	0.436
99.7	32.5	3.69	0.20	7.2	2.63	0.451
100.8	21.2	3.87	0.20	7.3	2.62	0.461
107.1	5.28	4.48	0.19	7.8	2.62	0.499
109.7	3.76	4.63	0.20	8.1	2.62	0.501
113.6	2.86	4.74	0.21	8.3	2.62	0.506
		0.67 M Heptanal in polystyrene High temperature absorption				
197.2	193.9	2.91	0.21	11.1	2.74	0.821
208.8	26.9	3.77	0.20	12.0	2.72	0.900
213.7	14.8	4.03	0.20	12.2	2.72	0.914
218.3	9.43	4.23	0.19	12.2	2.72	0.940
223.1	5.30	4.48	0.18	12.3	2.71	0.988
227.6	3.41	4.67	0.18	12.4	2.71	1.00
		Low temperature absorption				
92.1	307.7	2.71	0.21	9.1	2.62	0.517
96.2	119.6	3.12	0.22	9.5	2.62	0.531
98.6	69.0	3.36	0.22	9.8	2.62	0.538
101.7	37.4	3.63	0.23	10.0	2.62	0.548
106.6	14.7	4.04	0.25	10.6	2.62	0.553
111.1	6.58	4.38	0.25	10.9	2.62	0.568
112.7	4.89	4.51	0.26	11.1	2.62	0.573
115.9	3.44	4.66	0.27	11.3	2.62	0.567

TABLE VIII - 1 continued....

$T(K)$	$10^6\tau(s)$	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
0.59 M Nonanal in polystyrene High temperature absorption						
219.4	130.4	3.09	0.19	7.5	2.70	0.802
223.3	113.9	3.15	0.17	7.7	2.70	0.874
228.5	87.1	3.26	0.15	7.8	2.69	0.942
232.4	51.5	3.49	0.15	8.0	2.69	0.958
243.2	15.2	4.02	0.11	8.2	2.67	1.18
253.4	6.07	4.42	0.11	8.5	2.67	1.19
263.0	4.69	4.53	0.13	8.7	2.68	1.14
273.2	2.19	4.86	0.13	8.5	2.67	1.17
Low temperature absorption						
108.2	120.5	3.12	0.26	6.2	2.63	0.443
112.8	43.8	3.56	0.28	6.5	2.64	0.447
115.3	27.1	3.77	0.28	6.6	2.64	0.456
120.1	12.6	4.10	0.30	6.9	2.64	0.456
123.1	8.47	4.27	0.32	7.0	2.64	0.460
132.4	3.17	4.70	0.35	7.1	2.65	0.455
0.58 M Nonanal in polypropylene High temperature absorption						
171.3	159.0	3.00	0.15	6.1	1.92	0.862
173.5	74.1	3.33	0.14	6.1	1.92	0.890
175.6	30.9	3.71	0.14	6.1	1.92	0.924
177.0	20.3	3.89	0.14	6.1	1.92	0.926
180.1	8.21	4.29	0.14	6.0	1.92	0.930
182.4	5.34	4.47	0.15	6.1	1.93	0.885
Low temperature absorption						
93.8	300.6	2.72	0.23	2.9	1.87	0.365
97.6	116.5	3.14	0.24	3.0	1.87	0.373
100.2	64.1	3.40	0.25	3.1	1.87	0.375
107.5	12.5	4.11	0.28	3.3	1.87	0.381
111.9	5.73	4.44	0.29	3.4	1.87	0.385
115.0	4.65	4.53	0.33	3.5	1.88	0.369

TABLE VIII - 1 continued....

0.34 M Decanal in polystyrene
High temperture absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
267.0	211.1	2.88	0.14	4.2	2.67	1.05
274.0	99.8	3.20	0.14	4.2	2.67	1.03
279.6	35.1	3.66	0.14	4.2	2.67	1.05
289.8	5.81	4.44	0.14	4.3	2.66	1.08
295.7	5.63	4.45	0.16	4.3	2.66	1.03
300.3	4.06	4.59	0.18	4.4	2.66	0.988

Low temperature absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
117.3	140.7	3.05	0.27	5.8	2.69	0.573
120.3	66.3	3.38	0.27	5.9	2.69	0.583
123.7	37.3	3.63	0.30	6.0	2.68	0.574
125.9	22.2	3.85	0.31	6.1	2.68	0.571
129.2	10.8	4.17	0.32	6.3	2.68	0.575
134.0	5.35	4.47	0.35	6.5	2.68	0.568

0.44 M Lauraldehyde in polystyrene
High temperature absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
298.3	189.0	2.93	0.16	6.5	2.63	1.10
304.3	82.9	3.28	0.16	6.6	2.63	1.14
308.1	41.9	3.58	0.17	6.6	2.63	1.13
313.7	15.3	4.02	0.17	6.8	2.62	1.16
318.3	5.07	4.50	0.16	7.0	2.61	1.20
323.3	2.99	4.73	0.17	7.1	2.61	1.20

Low temperature absorption

T(K)	$10^6\tau(s)$	$\log_{10}f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	$\mu(D)$
123.8	310.2	2.71	0.26	6.5	2.66	0.557
125.7	211.3	2.88	0.26	6.6	2.66	0.568
129.6	90.3	3.25	0.27	6.8	2.66	0.579
133.9	36.8	3.64	0.27	6.9	2.66	0.596
142.0	9.92	4.21	0.31	7.2	2.66	0.587
146.3	4.75	4.52	0.33	7.4	2.65	0.585

TABLE VIII - 1 continued...

0.55 M 1-bromohexane in polystyrene

High temperature absorption

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
199.2	106.4	3.17	0.18	11.2	2.62	1.01
204.1	62.2	3.41	0.17	11.3	2.62	1.04
209.1	35.1	3.66	0.17	11.4	2.61	1.07
214.3	20.6	3.89	0.18	11.6	2.61	1.07
218.9	12.7	4.10	0.17	11.7	2.61	1.10
224.4	6.37	4.40	0.17	11.7	2.60	1.14
229.5	3.50	4.66	0.17	11.8	2.60	1.16
239.8	1.91	4.92	0.19	12.0	2.60	1.11

Low temperature absorption

T(K)	$10^6\tau$(s)	$\log_{10} f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
97.1	366.6	2.64	0.25	5.4	2.61	0.416
100.6	209.1	2.88	0.24	5.6	2.61	0.449
105.7	68.9	3.36	0.25	6.0	2.61	0.456
110.3	27.8	3.76	0.25	6.2	2.61	0.484
113.5	17.4	3.96	0.26	6.5	2.61	0.486
116.6	9.93	4.20	0.26	6.7	2.61	0.502
121.5	4.59	4.54	0.26	7.0	2.61	0.522
126.6	2.41	4.82	0.27	7.2	2.60	0.533

TABLE VIII-2: EYRING ANALYSIS RESULTS FOR SOME ALIPHATIC LONG-CHAIN ALDEHYDES

		τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E	ΔS_E
Molecule	T(K)	100 K	200 K	300 K	100 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Butanal	273-299	$1.1\text{x}10^{16}$	1.6	$6.8\text{x}10^{-6}$	54	49	44	60	52
	91-111	$1.5\text{x}10^{-5}$	$2.3\text{x}10^{-9}$	$1.0\text{x}10^{-10}$	14	15	16	14	- 9
Pentanal	267-309	$1.1\text{x}10^{14}$	$7.9\text{x}10^{-1}$	$1.3\text{x}10^{-5}$	50	48	45	53	25
	90-106	$1.0\text{x}10^{-5}$	$1.5\text{x}10^{-9}$	$6.5\text{x}10^{-11}$	14	15	15	14	- 5
Hexanal	285-314	$5.6\text{x}10^{28}$	$4.1\text{x}10^{3}$	$1.4\text{x}10^{-5}$	79	62	46	95	165
	90-114	$2.6\text{x}10^{-5}$	$8.3\text{x}10^{-10}$	$2.2\text{x}10^{-11}$	15	14	12	16	13
Heptanal	197-228	$1.1\text{x}10^{7}$	$8.0\text{x}10^{-5}$	$1.3\text{x}10^{-8}$	37	33	28	42	45
	92-116	$5.3\text{x}10^{-5}$	$1.6\text{x}10^{-9}$	$4.1\text{x}10^{-11}$	15	15	14	16	8
Nonanal	219-273	$2.7\text{x}10^{7}$	$1.3\text{x}10^{-3}$	$4.1\text{x}10^{-7}$	38	37	37	38	5
	108-132	$5.1\text{x}10^{-4}$	$1.0\text{x}10^{-8}$	$2.3\text{x}10^{-10}$	17	18	18	17	- 4
Nonanal in polypropylene	171-182	$4.6\text{x}10^{13}$	$4.1\text{x}10^{-8}$	$3.3\text{x}10^{-15}$	50	20	1.0	80	297
	94-115	$6.7\text{x}10^{-5}$	$9.5\text{x}10^{-10}$	$1.9\text{x}10^{-11}$	16	14	12	17	18

TABLE VIII-2: Continued....

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
		100K	200 K	300 K	100 K	200K	300K		
Decanal	267-300	4.8×10^{23}	7.1	3.1×10^{-6}	69	55	42	83	135
	117-134	1.3×10^{-2}	2.2×10^{-9}	1.0×10^{-11}	20	15	10	25	48
Lauraldehyde	298-323	2.6×10^{44}	2.1×10^{8}	1.6×10^{-4}	109	80	52	137	285
	124-146	1.9×10^{-1}	9.3×10^{-9}	2.9×10^{-11}	22	18	13	27	46
1-Bromohexane	199-240	3.3×10^{6}	9.9×10^{-5}	2.6×10^{-8}	36	33	30	39	31
	97-127	2.1×10^{-4}	4.1×10^{-9}	9.3×10^{-11}	17	16	16	17	3

* NOTE: All solute molecules were studied in polystyrene matrices unless stated otherwise.

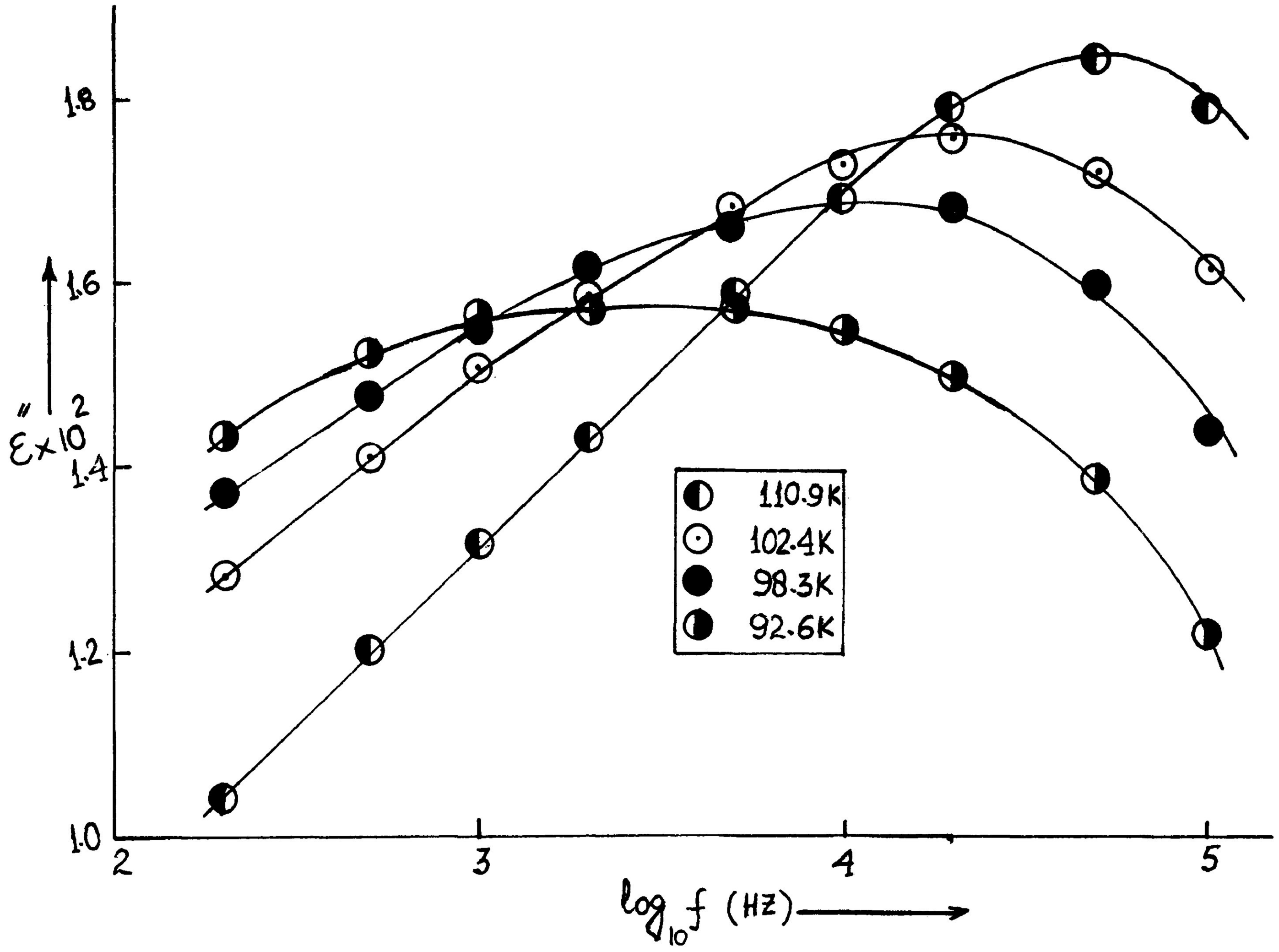


FIG. VIII-1

Plot of Dielectric loss factor vs $\log_{10}f$ for n-butanal in Polystyrene

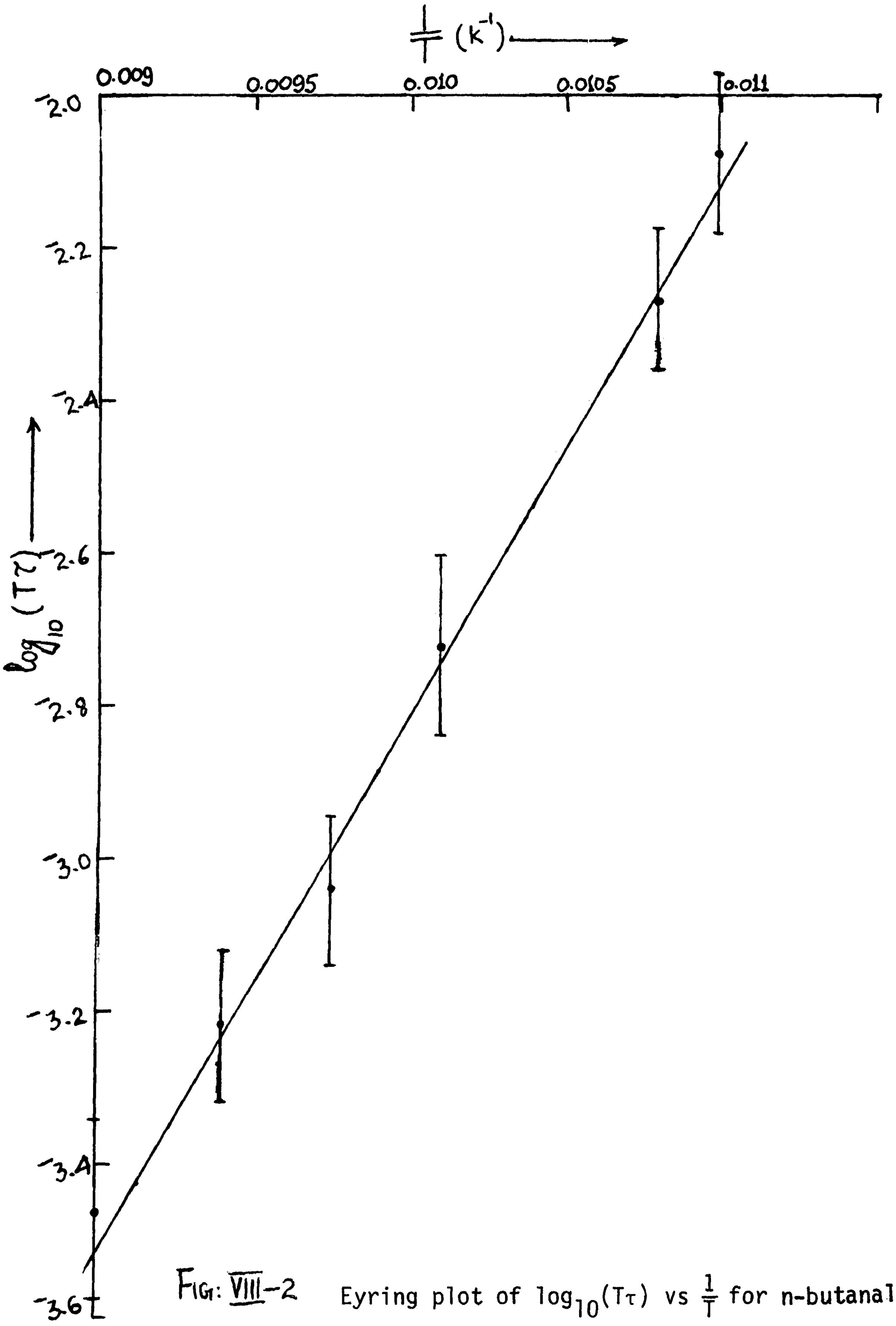
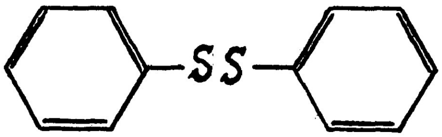


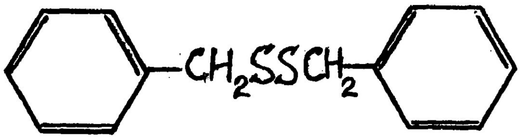
FIG: VIII-2 Eyring plot of $\log_{10}(T\tau)$ vs $\frac{1}{T}$ for n-butanal in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values

APPENDIX 1

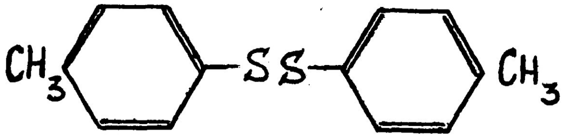
APPENDIX -1



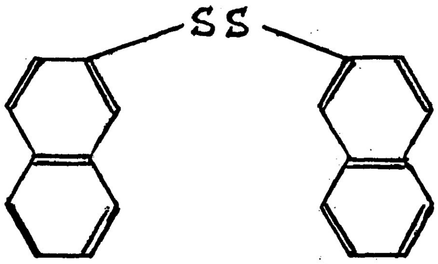
DIPHENYL DISULFIDE



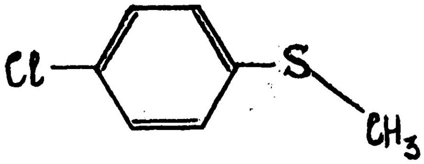
DIBENZYL DISULFIDE



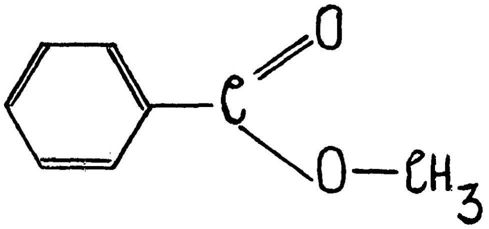
P-TOLYL DISULFIDE



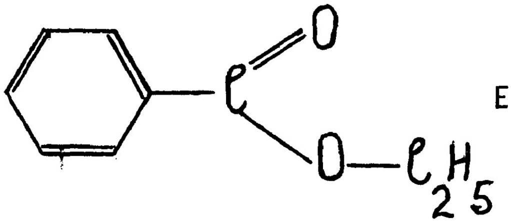
DI-β-NAPHTHYL DISULFIDE



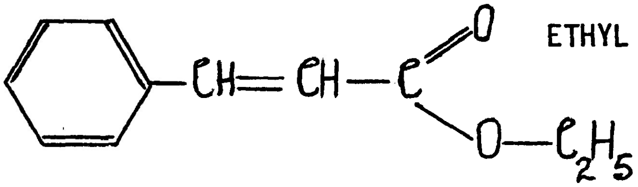
P-CHLOROTHIOANISOLE



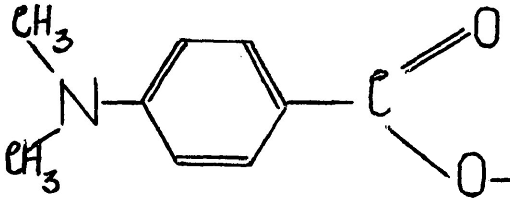
METHYL BENZOATE



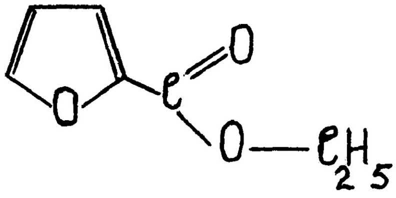
ETHYL BENZOATE



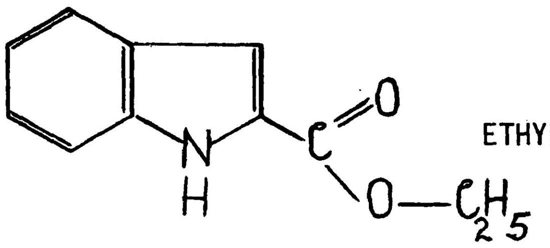
ETHYL CINNAMATE



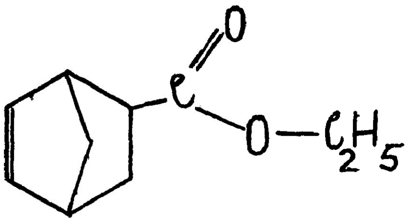
ETHY-P-(N,N-DIMETHYLAMINO)
--BENZOATE



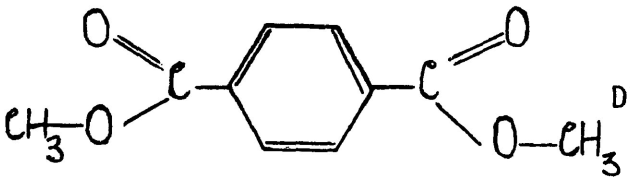
ETHYL FUROATE



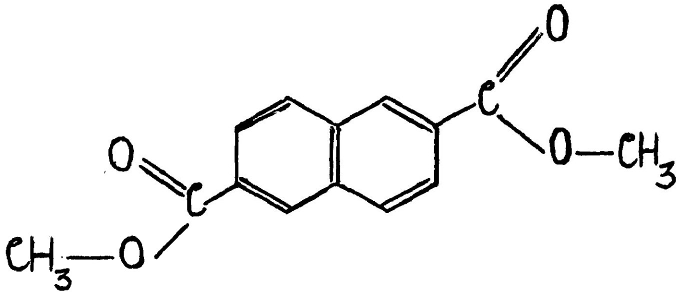
ETHYL INDOLE-2-CARBOXYLATE



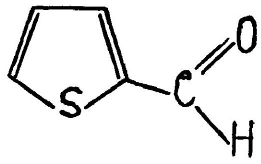
ETHYL-5-NONBORNENE-2-
CARBOXYLATE



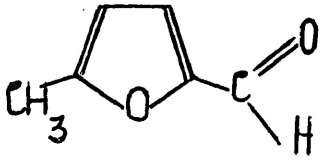
DIMETHYL TEREPHTHALATE



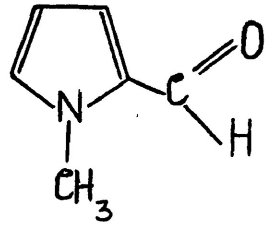
DIMETHYL-2,6-
NAPHTHALENE DICARBOXYLATE



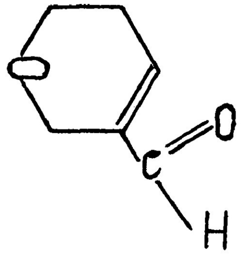
THIOPHEN-2-CARBALDEHYDE



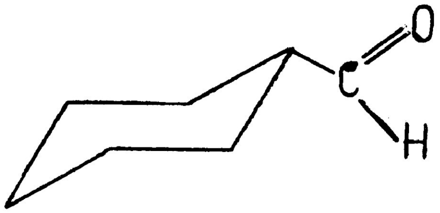
5, METHYL FURAN-2- CARBALDEHYDE



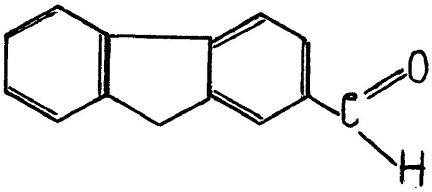
N-METHYLPYRROLE-2-CARBALDEHYDE



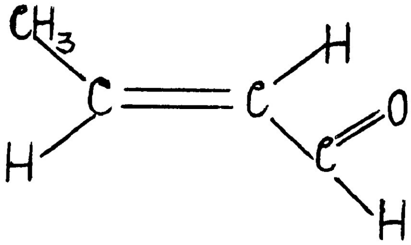
5,6 DIHYDRO-2H-PYRAN-3-CARBOXALDEHYDE



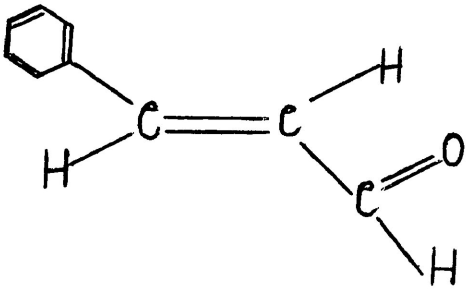
CYCLOHEXANECARBOXALDEHYDE



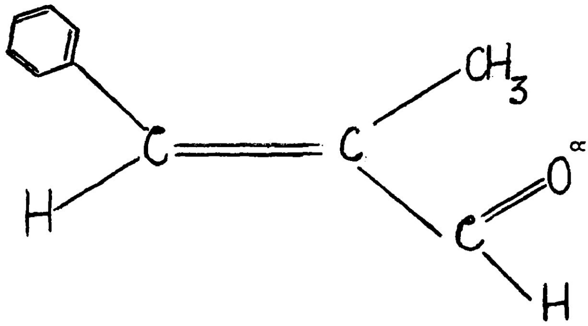
2-FLUORENECARBOXALDEHYDE



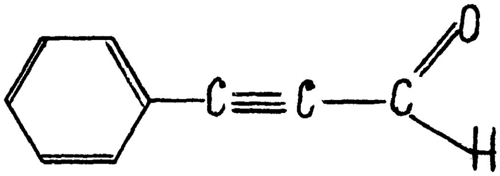
CROTONALDEHYDE



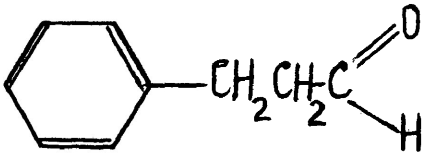
TRANS-CINNAMALDEHYDE



α- METHYLCINNAMALDEHYDE



PHENYLPROPARGYL ALDEHYDE



HYDRO CINNAMALDEHYDE