DIELECTRIC STUDIES OF MOLECULAR AND INTRAMOLECULAR MOTIONS IN POLYSTYRENE MATRICES

A THESIS SUBMITTED BY

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ABSTRACT

Dielectric absorption studies of a variety of polar solutes containing rotatable groups and of some analogous rigid molecules dispersed in atactic polystyrene have been carried out. Preparation of the 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 have been described. The experimental data as a function of frequency at different temperatures were subjected to analysis by a series of computer programmes written in the APL language. The activation energy barriers opposing the dielectric relaxation processes were obtained by the application of the Eyring rate equation.

Different types of polar rigid molecules have been studied mainly to provide sources of relaxation data and activation parameters for comparisons with those of flexible molecules of analogous size. Attempts have also been made to correlate the activation parameters with size, shape, and rotating volume of the rigid molecules. Studies of some nitrogen-containing heterocyclic rigid molecules and the comparison of their Eyring analysis results with those of the analogous non-heterocycles showed no

significant molecular interaction with the polymer matrix.

Of the flexible molecules, a wide variety of compounds containing the carbonyl group have been studied. Intramolecular processes involving the rotation of the polar carbonyl group with one or more segments from the alkyl substituents have been observed for phenyl alkyl (aryl-alkyl) and dialkyl ketones. Significantly higher energy barriers to acetyl group rotation around the C — N bond have been found in N-acetylimidazole in which the N atom is involved in ring conjugation. However, this barrier appeared to have been reduced considerably due to the effect of saturation as in N-acetyl-4-piperidone.

Cyclohexyl derivatives showed two different absorptions, one corresponding to the intramolecular ring inversion at higher temperatures while, in some cases, the low temperature absorption could not be assigned properly due to the possibility of both molecular and group relaxation. In the cases of larger fused-ring systems, viz., 2- and 3-acetylphenanthrenes, the group relaxation was completely separated from the molecular process while the dielectric absorption of 2-acetylnaphthalene was complicated by overlapping absorptions. The question of an enhanced resonance, particularly at the 2-position of the naphthalene nucleus as suggested

by Fong and Smyth, and the weight factor anomalies observed from solution studies of these molecules have been discussed.

A series of halophenols and other substituted phenols have been studied. Hydroxyl group relaxation of halophenols occurred at temperatures around 100K. Molecular relaxations of substituted phenols were also observed, and, in a number of cases, these showed considerable dependence on intermolecular hydrogen bonding.

Finally, several substituted anisoles were studied to characterize the methoxy group rotation.

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I am indebted to my research colleagues, expecially to C. K. McLellan and S. P. Tay, for many helpful discussions. Thanks are also due to Mr. B. K. Morgan for his indispensable technical assistance, and to Mrs. J. Parnell for typing the thesis. Financial support for this work was provided by the Lakehead University, which assistance is gratefully acknowledged.

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ADDENDUM

Three papers involving parts of the work described in this thesis have been accepted for publications, and one manuscript is under preparation as listed below.

1. Dielectric Relaxation in 2-Acetylnaphthalene and Related Compounds, J. Crossley, M. A. Mazid, C. K. McLellan, P. F. Mountain, and S. Walker, Can. J. Chem. (accepted for publication).

2. Sterically Hindered Acetyl Group Relaxation in Four Aromatic Compounds, J. Crossley, M. A. Mazid, C. K. McLellan, P. F. Mountain, and S. Walker. Adv. Mol. Relax. Inter. Proc. (accepted for publication).

3. Activation Energy for Methoxy Group Relaxation, M. A. Mazid, J. P. Shukla, and S. Walker. Can. J. Chem. (accepted for publication).

4. Intramolecular Relaxation of Phenyl-Alkyl and Two Dialkyl Ketones in Polystyrene Matrices, M. A. Mazid, S. Walker, and N. A. Weir. (Manuscript in preparation).

Manuscripts for some more papers from the remainder of the thesis will be ready shortly.

CHAPTER I

INTRODUCTION

Dielectric absorption techniques have been widely employed in physico-chemical studies,[1] principally of structure and molecular forces in different types of systems. Measurements at microwave frequencies have provided an effective means of studying molecular structure in liquids and solutions.[2,3] Aromatic molecules, especially those containing rotatable polar groups, have been extensively investigated.[4] The role of dielectric studies is also well known for the investigation of biological solutions.[5] Dielectric measurements are frequently made on various solids[6] including the commercial dielectric materials. During recent years there has been considerable interest in dielectric studies of polar solutes dispersed in polymer matrices. This method has been considered[7] to be the most promising procedure for determining an intramolecular energy barrier which can also be obtained from other relaxation techniques.[8] One of the great advantages of the polymer-matrix technique is that for a system with a flexible polar molecule, where both molecular and intramolecular processes can occur simultaneously, the former can be considerably slowed down or may even be eliminated[9] without affecting the other significantly so that either or both the processes may be studied independently. This is particularly valuable in view of the complications frequently observed in solution studies due to the possible overlap of the different types of processes

requiring Budó analysis which in a number of cases, is now known to be unsatisfactory.[10] Moreover, the frequency and temperature ranges accessible to the solution studies are fairly limited, and hence the energy barriers cannot be obtained with reasonable accuracy. These limitations may be overcome in polymer-matrix studies since different instruments can be used to cover a wide frequency range of investigations over a broad temperature range from liquid nitrogen temperature to around the glass-transition temperature of the matrix system. Therefore, the technique can be used more reliably to evaluate the energy barrier data which can be compared with the results obtained from other direct relaxation methods.

The fundamental theories and basic equations for dealing with dielectric absorptions are well established. This area of chemical physics or physical chemistry is concerned mainly with the polarization and dielectric absorption due to dipole orientation.[6] The phenomenon arises from the dispersion of the so-called dielectric constant as a result of the inability of the dipoles to follow the changing polarity of the measuring field. The dielectric constant or permittivity of a material may be expressed in terms of its polarizability which is a function of the frequency of the applied field. For most simple polar molecules in non-polar solvents, all types of polarization can reach their equilibrium value when the

field is of the order of 10^8 Hz. But at higher frequencies, the dipoles lag behind the field and polarization falls off so that it contributes less and less to the total permittivity. It is this fall of polarizability with its associated fall of permittivity accompanied by the absorption of energy which constitutes dielectric dispersion.

In the frequency region, where the dispersion occurs, the dielectric constant becomes a complex quantity, ε^*, which is related to the real part, ε', commonly called the dielectric constant (even though it is not a constant), and the imaginary part, ε'', known as the dielectric loss factor, by the equation:

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

where $i = \sqrt{-1}$. For simple systems, the frequency dependence of the complex permittivity is given by:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{1+i\omega\tau} \qquad \text{I-2}$$

where ε_o and ε_∞ are the low and high-frequency limiting values of ε^*, respectively, ω is the angular frequency in rad s^{-1}, and τ is

the characteristic relaxation time in seconds which may be defined[2] as the time required for the polarization to decay to $\frac{1}{e}$ of its initial value when 'e' is the natural logarithmic base.

A combination of Eqns. I-1 and I-2 and a separation into real and imaginary parts, the following equations due to Debye and Pellat are obtained:

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

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

Eqn. I-4 shows that ε'' becomes maximum when $\omega\tau = 1$, and this permits the evaluation of the relaxation time from the known frequency of maximum absorption. By the elimination of $\omega\tau$ between Eqns. I-3 and I-4, it is possible to obtain the following equation, which is the basis of Cole-Cole plot:

$$\left[\varepsilon' - \frac{\varepsilon_o + \varepsilon_\infty}{2}\right]^2 + (\varepsilon'')^2 = \left[\frac{\varepsilon_o - \varepsilon_\infty}{2}\right]^2 \qquad \text{I-5}$$

Thus, the plot of ε'' against ε' gives a semicircle yielding the

values of ε_o and ε_∞ from its intersection with the ε' axis.

The foregoing equations apply[6] to both liquids and solids although different models have been used in their derivation and are valid for systems with a single relaxation process characteristic of the Debye behaviour. But many solids show dielectric absorption wider than a normal Debye curve, owing to the presence of a range of relaxation times, and these have frequently been represented by the Fuoss-Kirkwood equation:[11]

$$\varepsilon''_{obs} = \varepsilon''_{max} \operatorname{sech} \left[\beta \ln \left(\frac{f_{obs}}{f_{max}}\right)\right] \qquad \text{I-6}$$

where f_{obs} is the frequency in Hz, f_{max} is the frequency, at which maximum absorption occurs, and β is an empirical constant known as the distribution parameter, which measures the width of the absorption and may have values between unity for a single relaxation and zero for an infinite range.

Assuming a continuous distribution of relaxation times about a most probable value, τ_o, Cole and Cole[12] also gave a general dispersion equation as follows:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{1+(i\omega\tau_o)^{1-\alpha}} \qquad \text{I-7}$$

where α is the distribution parameter and again varies between zero and unity. Eqn. I-7 can be rationalized to yield:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1+(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)}{1+2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_o)^{2(1-\alpha)}} \qquad \text{I-8}$$

and

$$\frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{(\omega\tau_o)^{1-\alpha}\cos(\alpha\pi/2)}{1+2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)+(\omega\tau_o)^{2(1-\alpha)}} \qquad \text{I-9}$$

For α = o, the Eqns. I-7 to I-9 reduce to the Debye-Pellat Eqns. I-2 to I-4, but the mean relaxation time τ_o can be obtained from a plot of log(v/u) versus log(ω) according to the relation,[2]

$$\frac{v}{u} = (\omega\tau_o)^{1-\alpha} \qquad \text{I-10}$$

when v is the distance between the experimental point and ε_o in the Cole-Cole arc plot and u is that between ε_∞ and the same experimental point. Davidson and Cole[13] further modified the expression for the

frequency dependence of the complex permittivity to represent the behaviour of some systems for which the shape of the complex plane plot is not symmetrically semicircular, i.e., a skewed arc, in terms of the equation:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{(1+i\omega\tau_o)^h} \qquad \text{I-11}$$

where h is again a constant having values $0<h\leq 1$, with h=1 corresponding to the Debye-Pellat Eqn. I-2. Eqn. I-11 can also be rationalized to obtain:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \cos^h(\phi)\ \cos(h\phi) \qquad \text{I-12}$$

and

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

where ϕ = arc tan($\omega\tau$). The skewed arc behaviour as described by Eqns. I-11 to I-13 is often used to interpret the dielectric absorption, which arises from a relaxation mechanism involving cooperative motion of the surroundings as the dipolar molecule relaxes.

All the modified equations mentioned so far have been used to account for a distribution of a range of relaxation times in terms of Debye processes. In many cases, however, dielectric absorptions are characterized by more than one discrete relaxation process, each of which shows Debye behaviour and may have contributed independently to the total dispersion. For such systems, Budó[14] has shown that the overall absorption can be represented as the sum of the Debye terms according to the general expression:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \sum_{k=1}^{n} \frac{C_k}{1+i\omega\tau_k} \qquad \text{I-14}$$

where τ_k is the relaxation time characteristic of the kth mode of relaxation, and C_k is a factor representing the proportion by which the kth mode contributes to the total dispersion so that $\sum_{k=1}^{n} C_k = 1$. Thus, for two different processes with relaxation times τ_1 and τ_2, the following equations can easily be derived:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \qquad \text{I-15}$$

$$\frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \qquad \text{I-16}$$

where C_1 and C_2 are commonly known as weight factors, and $C_1 + C_2 = 1$. The relaxation times can be obtained from the complex plane plot. This plot depends on the relative magnitudes of τ_1, τ_2, and the weight factors but may often be approximated by a sector of a semicircle.[15]

It may be noted that the common practice in dielectrics work is to employ any of the several empirical relationships for the analysis of experimental data. Those most often used are the Cole-Cole equation, the Cole-Davidson equation, and the Fuoss-Kirkwood equation. Each of these has been found adequate for data from certain types of systems but not for others, so that one chooses whichever emperical relationship is most useful for one's particular study.

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CHAPTER II

APPARATUS AND PROCEDURE

INTRODUCTION:

Dielectric properties of a material can be conveniently discussed by considering it to be situated between the plates of a condenser, and the dielectric constant of the material may be defined as the ratio of the capacitance C of the condenser with the dielectric to the capacitance C_0 with vacuum such that:

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

where ε is the dielectric constant which, in fact, is a frequency-dependent complex quantity as was given by Eqn. I-1. If a sinusoidal potential of amplitude E and frequency ω rad s^{-1} is applied to the capacitor, then the current I flowing through the circuit can be expressed by:

$$I = E\omega C = E\omega C_0(\varepsilon' - i\varepsilon'') \qquad \text{II-2}$$

in which the substitution for C and ε follows from Eqns. II-1 and I-1, respectively. The real component, $E\omega C_0\varepsilon'$, known as the charging current is 90° out of phase with the applied potential and therefore does not need any electrical work to be done. If, however,

the dielectric is of polar substance then the displacement current acquires an imaginary component, $E\omega C_o\varepsilon''$, in phase with the applied potential. This is known as the loss current, which is related to the energy dissipated as heat since it causes some electrical work to be done as given by the dot product, $EI = E^2\omega C_o\varepsilon''$. Now, if we define δ as the angle between the total current and the charging current axis, i.e., the angle by which the charging current fails to become 90^o out of phase with the potential, then:

$$\tan\delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'} \qquad \text{II-3}$$

where ε' is the observed dielectric constant according to Eqn. II-1, and ε'' is known as the loss factor, which is directly proportional to the concentration of the polar material in the dielectric. These principles are the basis of all dielectric measurements, and for the purpose of this thesis the General Radio 1615-A Capacitance bridge and the Hewlett-Packard 4342A Q-meter have been used.

THE GR BRIDGE

This measures the capacitance and conductivity of the capacitor, which can be related to the components of the complex permittivity by the following equations[1]:

$$\varepsilon' = \frac{C}{C_o} \qquad \text{II-4}$$

and

$$\varepsilon'' = \frac{G}{\omega C_o} \qquad \text{II-5}$$

where G is the conductivity of the system and the other terms have their usual meaning, mentioned previously. The capacitor consists of the sample between the high and the low electrodes. Since it is difficult to measure C_o, which would require the electrodes to be arranged exactly as they were when containing the sample, this has been calculated from the relation,[2]

$$C_o = \frac{0.2244\ A_1}{d_1} \qquad \text{II-6}$$

where A_1 is the effective area of the plates in $in.^2$, d is the spacing of the plates in in., and C is the capacitance in units of picofarads. For the convenience of handling the experimental data, therefore, the Eqns. II-4 through II-6 can be combined as follows:

$$\varepsilon' = \frac{Cd_1}{0.2244\ A_1} \qquad \text{II-7}$$

and $$\varepsilon'' = \frac{\varepsilon' G}{\omega C} \qquad \text{II-8}$$

where G is in picomhos. The GR bridge also allows the measurement of tanδ directly so that the loss factor can be obtained alternatively from Eqn. II-3. The effective area of the electrode plates, A_1, has been determined by measuring the capacitance of the cell containing a standard quartz disk of diameter 2.0 in. and thickness 0.0538 in. (supplied by the Rutherford Research Products Co., New Jersey, USA) with a dielectric constant of 3.819.

The capacitor measured by the GR bridge consists of polystyrene matrix disk clamped between electrodes. The electrode assembly as shown in Fig. II-1 (reproduced by the courtesy of C. K. McLellan[3] of this laboratory) is of the three-terminal type with an outer diameter of 2.0 inches. The low electrode has a diameter of about 1.5 in. and is surrounded by a guard ring, which would reduce any error due to fringing of the electric field at the edges so that the measured capacitance is solely that between the high and the low electrodes. Late in the experimental programme, a somewhat modified cell was designed by Mr. B. K. Morgan for more convenient handling of the sample inside the cell, allowing it to achieve temperature equilibrium more quickly.

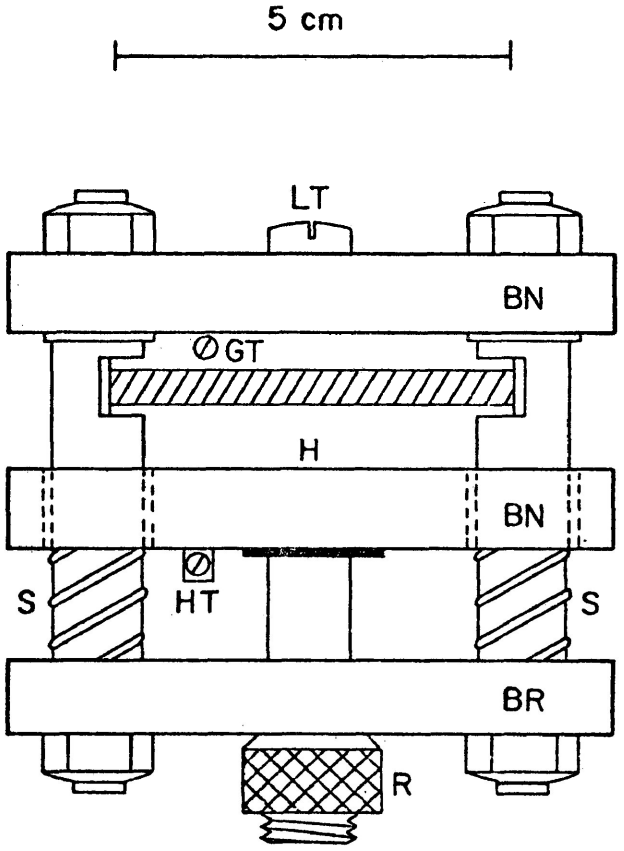

Figure II-1: Three-terminal electrode assembly for dielectric measurements on solid disks.

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

The electrode assembly was encased in an air-tight aluminium chamber with sealed outlets to provide connections to the electrodes and for purging the chamber with dry nitrogen gas, which was maintained at a slight positive pressure to prevent the entry of atmospheric moisture during measurements at low temperatures. The exterior of the chamber was wrapped with a heating coil of nichrome wire, to which power was supplied through a Beckmann/RIIC model TEM-1, indicating a proportional controller which detected the chamber temperature via a small thermocouple placed well inside the chamber wall. A container of liquid nitrogen placed on the flat top of the chamber was used for cooling, and a particular temperature was maintained by inserting an appropriate number of sheets of paper in between so that the heater current was about 2 amps corresponding to a power of about 8 watts. The sample inside the cell was measured only after it had reached thermal equilibrium with the chamber case, as could be judged by the stability of the conductivity and capacitance readings. The temperature was set initially, according to the controller dial, but the exact temperature was recorded to an accuracy of $\pm 0.1^{o}C$ with the help of a Hewlett-Packard 2802A platinum resistance thermometer via a probe inserted near the sample area through a hole in the chamber wall.

The General Radio bridge allowed dielectric measurements

at frequencies ranging from 50 to 10^5Hz when 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 split and was partly allowed to go to the input terminals of the bridge. The other part was used to supply the horizontal deflection signal of an oscilloscope connected to facilitate the measurements, the vertical deflection signal being provided by the amplified bridge unbalance signal from the output terminals of the detector. The detector, in turn, was connected to the oscilloscope ground lead through a small capacitor to avoid any possibility of error due to ground loop currents. The average value of the signal was seen from the oscilloscope pattern, and any unbalance of bridge controls could be corrected easily to achieve the desired null condition. This was particularly very useful at low frequencies, where environmental noise makes a contribution to the total signal displayed by the null detector. At low frequencies the transformer core in the bridge may also become saturated especially if the generator supplies a high signal power. This was indicated by a severe distortion on the oscilloscope pattern, but the situation could be avoided by reducing the signal generator output. Furthermore, the oscilloscope was used for the calibration of the frequency scale of the signal generator against the power line frequency of 60 Hz.

THE Q-METER

Additional dielectric measurements in the range of 2.2×10^4 Hz to 5×10^7 Hz have been made on a Hewlett-Packard Q-meter type HP4342A connected to a cell (designed by Mr. B. K. Morgan of this laboratory) via a low inductance gold plated jig (supplied by the Rutherford Research Products Co.) which eliminates most of the measurement errors that would occur if the cell were connected by parallel conductors. The cell diagram[3] is shown in Fig. II-2, and it is essentially a shielded two terminal type in which the low terminal connection is provided through the inductance plate while that of the high terminal is made via a gold plated flexible metal strip. Basically, 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, which serves as the reference capacitor, the sample and the reference capacitors being placed inside the low (ground) and high electrodes, respectively. A switch arm mounted on the common central plate allows the plate to be connected either to the low or high side so that the sample or the reference capacitor can be examined separately. The whole assembly is clamped together by a spring bellows bearing upon the low electrode of the sample capacitor and is enclosed in a chamber similar to that of the cell used with

Key to Figure II-2 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

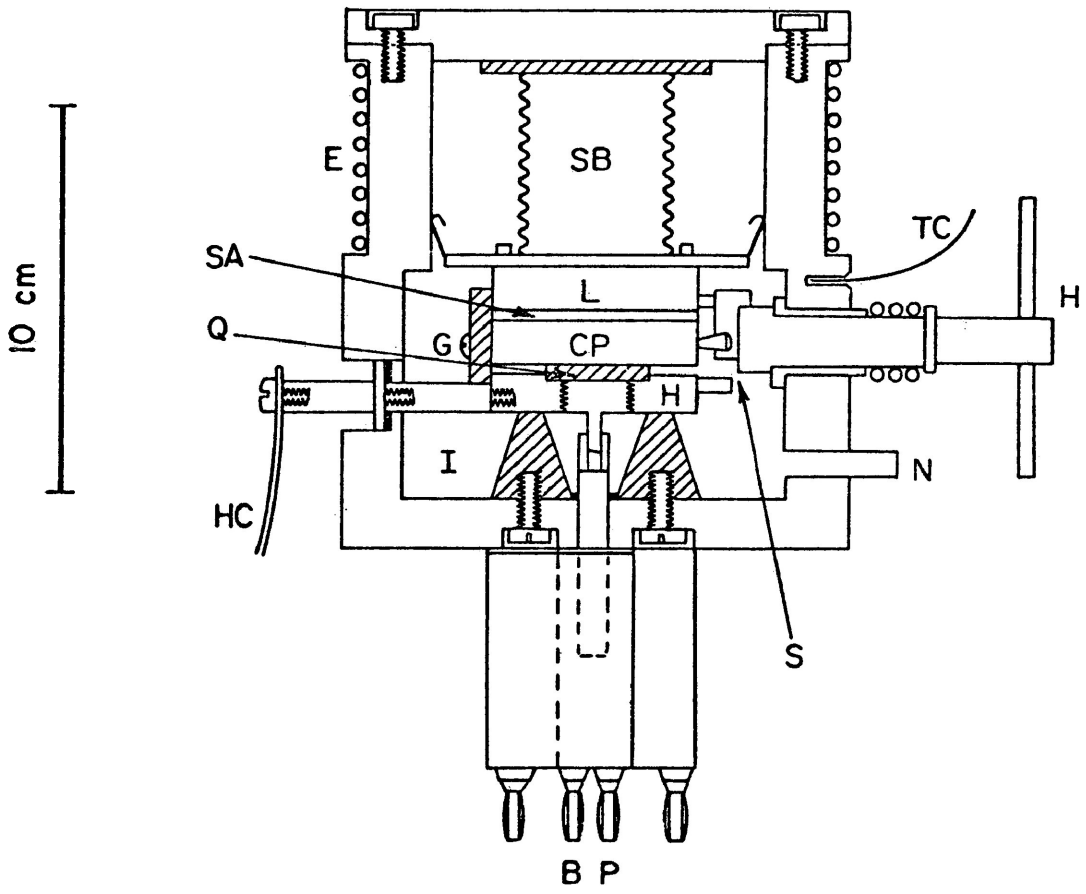

Figure II-2: The Morgan tri-electrode cell for Q-meter.
(key on facing page)

the GR bridge. The heater windings, cooling arrangements and the temperature control of the cell have also been accomplished similarly.

At the beginning of a set of measurements, the sample was placed in the appropriate position and the air spacing between the reference capacitor plates was adjusted so that the two capacitors had almost the same capacitance value as was judged by the ability to achieve resonance of the Q-meter circuits at the same settings of the meter's capacitance controls for both capacitors. The difference in capacitance between the two capacitors, in principle, could be related to the dielectric constant of the sample if this parameter was known for at least one frequency, but this information gave no consistent value for the dielectric constant, and, therefore, only the dielectric loss factor, ε'', as a function of frequency was evaluated. This was based on the assumption that the conductivity, G, of the system is comprised of the two additive components, one each for the sample and the measurement system alone. Hence, by the use of Eqns. II-4 and II-5, and with the definitions of loss tangent and of Q in mind, it is possible to obtain:

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

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

$$= \frac{\Delta Q}{Q_x} \times \frac{\Delta C_r}{2C_r} \qquad \text{II-9}$$

where $(\tan\delta)_s$ = tanδ for the sample only, Q is the Q value for the capacitor being examined, ΔQ is the difference in Q readings for sample and reference, C_r is the capacitance of the reference capcitor, 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 was not known, but it had been adjusted to be equal to the value of the sample capacitor. Therefore, the application of Eqns. II-4 and II-6 and then Eqn. II-3 yields:

$$\varepsilon''_s = \frac{(\Delta Q)(\Delta C_r)(d_1)}{(Q_x)(2)(0.2244A_1)} \qquad \text{II-10}$$

where ε''_s is the dielectric loss factor of the sample, d_1 is the

sample thickness in inches, A_1 is the effective area of the cell electrodes in one of the capacitors, and the remaining quantities are defined as in Eqn. II-9.

POLYSTYRENE MATRIX SAMPLE PREPARATIONS

The capacitors measured by the GR bridge and by the Q-meter were solid disks consisting of the polar solutes dispersed in polystyrene (atactic) matrices. The disks were prepared by employing the procedure similar to that described by Davies and Swain.[4] The desired amount of the solute ($\sim$0.2 to 0.4 g) and polystyrene pellets (nearly 4 g as required to make about 5 mole % of the former) was dissolved in $\sim$10 ml of a non-polar solvent, usually trans-1,2-dichloroethylene (b.p. 320.7K), in a porcelain crucible. The actual weight of the solute was determined roughly from the knowledge of its dipole moment, solubility in the solvent used and taking into account its effect on the glass transition temperature of the polymer. The mixture was stirred thoroughly, until it dissolved well, followed by evaporation in a drying oven at 100°C. After sufficient evaporation of the solvent, when the mixture appeared to be extremely thick, the crucible was removed from the oven and allowed to cool so that the solid mass could be gently pried away from the crucible walls with the help of a stainless steel spatula.

This was rolled into a flat disk and then placed on a teflon sheet in a vacuum oven at 85°C, the pressure being reduced by a single-stage rotary pump, and finally dried to a constant weight which was almost the same as the initial weight of the solute and polystyrene together. In case of a few low boiling liquids, the method was modified in that the solute itself was used as the solvent, and the mixture was dried similarly until the desired amount of the solvent was left unevaporated.

The matrix material was placed in a stainless steel die equipped with polished tungsten carbide faces of 2 in. diameter. A heating sleeve was placed around the die and was heated to a temperature of 115°C, depending on the amount of solute taken, for about 20 mins. to melt the material. The sample was then pressed by applying a pressure of 5 tons to the moving element of the die followed by disassembling and pressing out of the disk after cooling down to room temperature by using a fan for about 30 mins. The glass-like circular disk was trimmed around its edges with a sharp knife blade, and its average thickness was measured. The weight of the disk was also noted, and the concentration of the solute (in moles/liter) in the matrix was calculated according to the formula given by Tay and Walker[5] as:

$$\text{Concentration} = \frac{\text{wt. of solute used}}{\text{M. wt. of solute}} \times \frac{\text{wt. of disk}}{\text{Wt. of p.s. \& solute}} \times \frac{1000}{\text{Vol. of disk}}$$

The polystyrene used in the preparation of the matrix samples was obtained from the Monomer-Polymer Laboratory, Philadelphia, USA (Lot #700,215-8) and had a nominal molecular weight of 230,000 (M_w). The solutes were procured from various manufacturers and were purified appropriately prior to use, wherever it was considered necessary.

It can be emphasized that the solutes were of low concentration in the matrices such that they could be monomolecularly dispersed[4]; and, hence, any strong internal electric field, for example, in the crystalline solid, would be largely eliminated. Moreover, such a low concentration would not affect the relaxation process appreciably, for Borisova and Chirkov[6] showed that the energy barrier for relaxation of small molecules in a polystyrene matrix are independent of concentration less than 5 - 7 mole per cent.

EVALUATION OF RESULTS

The experimental data as functions of frequency and

temperature were subjected to analysis by a series of computer programmes written in the APL language. Fig II-3 shows a dielectric absorption curve as a sample plot of dielectric loss against log(frequency). The loss due to solute itself, $\varepsilon''_{solute} = \varepsilon''_{matrix} - \varepsilon''_{p.s.}$, was calculated by substracting the values for pure polystyrene at each frequency, obtained through similar measurements, from those observed for the matrix. For each temperature, the loss data as a function of frequency was analysed in the computer according to the Fuoss-Kirkwood Eqn. I-6, which has been employed [4], when a continuous range of relaxation times due to much broader Debye curves exists. The computer programme finds that the value of ε''_{max}, by iteration provides the best linear fit to the plot of $\cosh^{-1}$ ($\varepsilon''_{max}/\varepsilon''$) against $\log(f_{obs})$. The slope of this straight line gives the value of the distribution parameters, β, and the frequency of maximum absorption, f_{max}, is obtained from the slope and the intercept of the line on the $\cosh^{-1}$ axis.

The Fuoss-Kirkwood equation does not consider the real part of the complex permittivity nor does it deal with the limiting values at low and high frequencies, ε_o, and ε_∞, respectively, except that the total dispersion is given by the expression:

$$\Delta\varepsilon' = \varepsilon_o - \varepsilon_\infty = 2\varepsilon''_{max}/\beta \qquad \text{II-11}$$

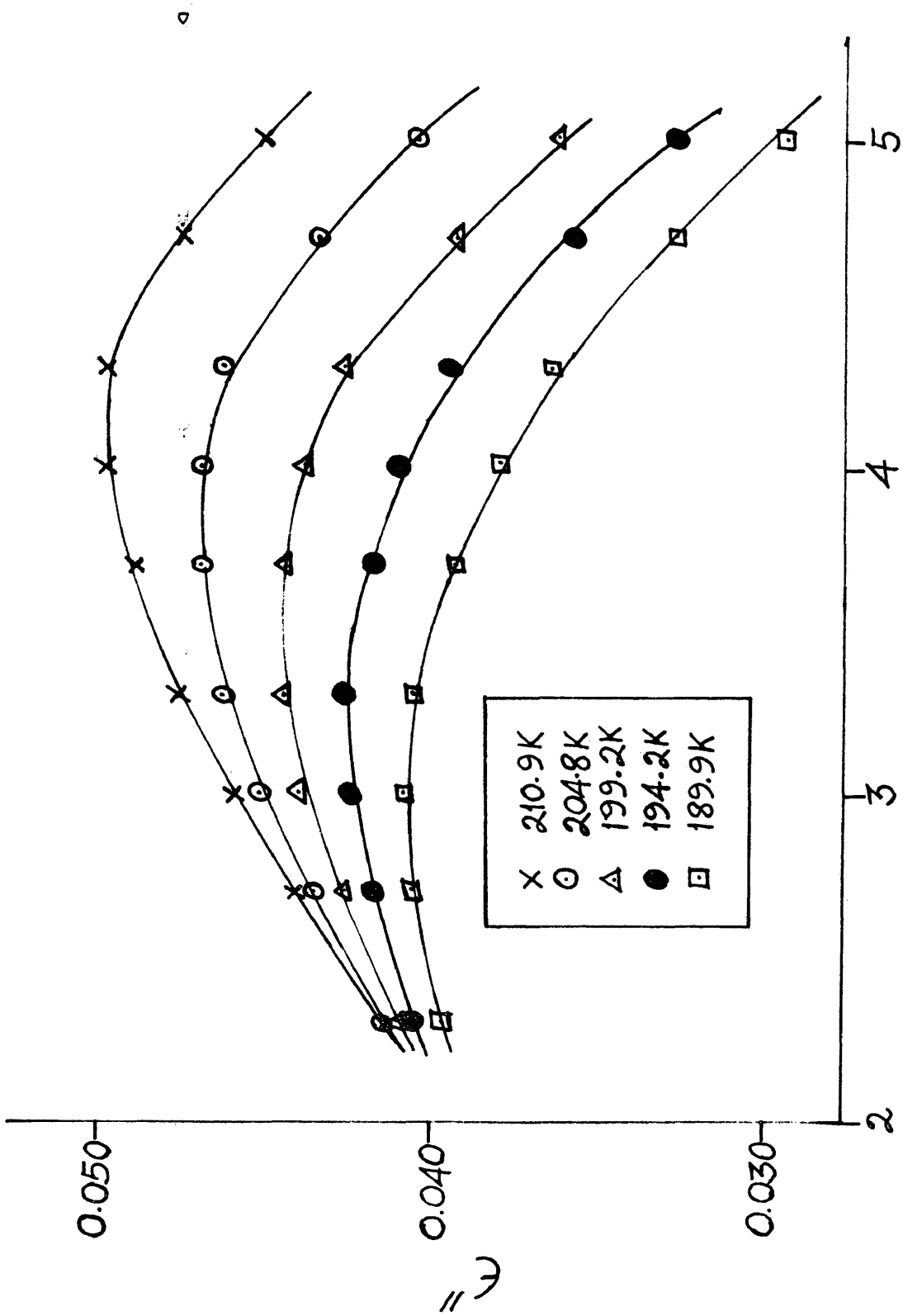

Fig. II-3: Dielectric loss factor (ε'') vs. logarithmic frequency for 0.576M p-nitrotoluene in a polystyrene matrix at temperatures as indicated.

Therefore, the analysis was supplemented with the Cole-Cole Eqn. I-8 to obtain ε_∞ in conjunction with the following relation[7] for the value of α, the Cole-Cole distribution parameter:

$$\beta = \frac{1 - \alpha}{\sqrt{2}\cos\left[\pi\frac{(1-\alpha)}{4}\right]} \qquad \text{II-12}$$

Several estimates of ε_∞ were obtained from the Cole-Cole equation given the experimental values of ε' at various frequencies. The average of these estimates was calculated, along with a value for ε' at the frequency of maximum loss.

The results from the foregoing analysis were used for the calculation of the effective dipole moments involved in the relaxation process from both the Debye[8] equation II-13 and the Onsager[9] equation II-14:

$$\mu^2 = \frac{27000\,kT\,(\varepsilon_o - \varepsilon_\infty)}{4\pi Nc(\varepsilon' + 2)^2} \qquad \text{II-13}$$

$$\mu^2 = \frac{9000\,kT\,(2\varepsilon_o + \varepsilon_\infty)(\varepsilon_o - \varepsilon_\infty)}{4\pi Nc\varepsilon_o(\varepsilon_\infty + 2)^2} \qquad \text{II-14}$$

where the value of $\varepsilon_o - \varepsilon_\infty$ is given by Eqn. II-11, ε' is the value of ε' at $\omega_{max} = \frac{1}{\tau_o} = 2\pi f_{max}$, ε_o is the static dielectric constant derived from the estimated average of ε_∞ and Eqn. II-11, c is the concentration in moles/liter, T is the temperature in K, and N and k are the Avogadro's number and Boltzmann constant, respectively. Eqns. II-13 and II-14 give dipole moments in units of e.s.u. - cm., but these were converted to the more common Debye units ($1D = 10^{-18}$ e.s.u. - cm.), and the values from the Debye equation have been noted for the purpose of comparison. It should be mentioned that the values of ε_∞ and μ were not calculated from the Q-meter data since ε' from these measurements was not reliable.

Next, the observed dipole moments at different temperatures were used in a separate programme to estimate the extrapolated values at different temperatures. This was based on the assumption that the dipole moment is a linear function of temperature, as employed by Davies and Swain,[4] although there is no theoretical basis for such a procedure. It is, however, well established that in many cases the variation of ε_o and ε_∞ with temperature may be described by an equation of the form[10] $\log(\varepsilon) = aT + b$. Extrapolated values of ε_o and ε_∞ derived in this manner have been used in conjunction with Eqn. II-13 to calculate dipole moments at warmer temperatures, as well as from Davies and Swain's technique. It must be noted that these values were, in most cases, less than the true dipole

moments, probably because as Davies and Swain[4] suggest, "only some of the molecules reorient at these temperatures and/or their range of reorientation is well below ±Π." In addition, the dipole moments at various experimental temperatures should be regarded more appropriately as only the effective or the apparent dipole moments.

Dipole reorientations have been considered as a rate phenomenon,[11] and the Eyring rate equation was utilized to evaluate the energy barriers opposing the dielectric relaxation process, a commonly used procedure in dielectrics work[4,5,7] although limitations[12,13] are not unknown. The rate constant is obtained from the equation:

$$\tau = \frac{1}{\text{rate constant}} = \frac{h}{kT} \exp\left(\frac{\Delta G_E}{RT}\right) \qquad \text{II-15}$$

which can be rearranged to the following linear form:

$$\ln(T\tau) = \frac{\Delta H_E}{RT} - \left[\frac{\Delta S_E}{R} - \ln(h/k)\right] \qquad \text{II-16}$$

where the terms have their usual significance. Accordingly, plots of $\log(T\tau)$ against $\frac{1}{T}$ yielded straight lines (Fig. II-4) and the values of the enthalpies of activation, ΔH_E, and the entropies of

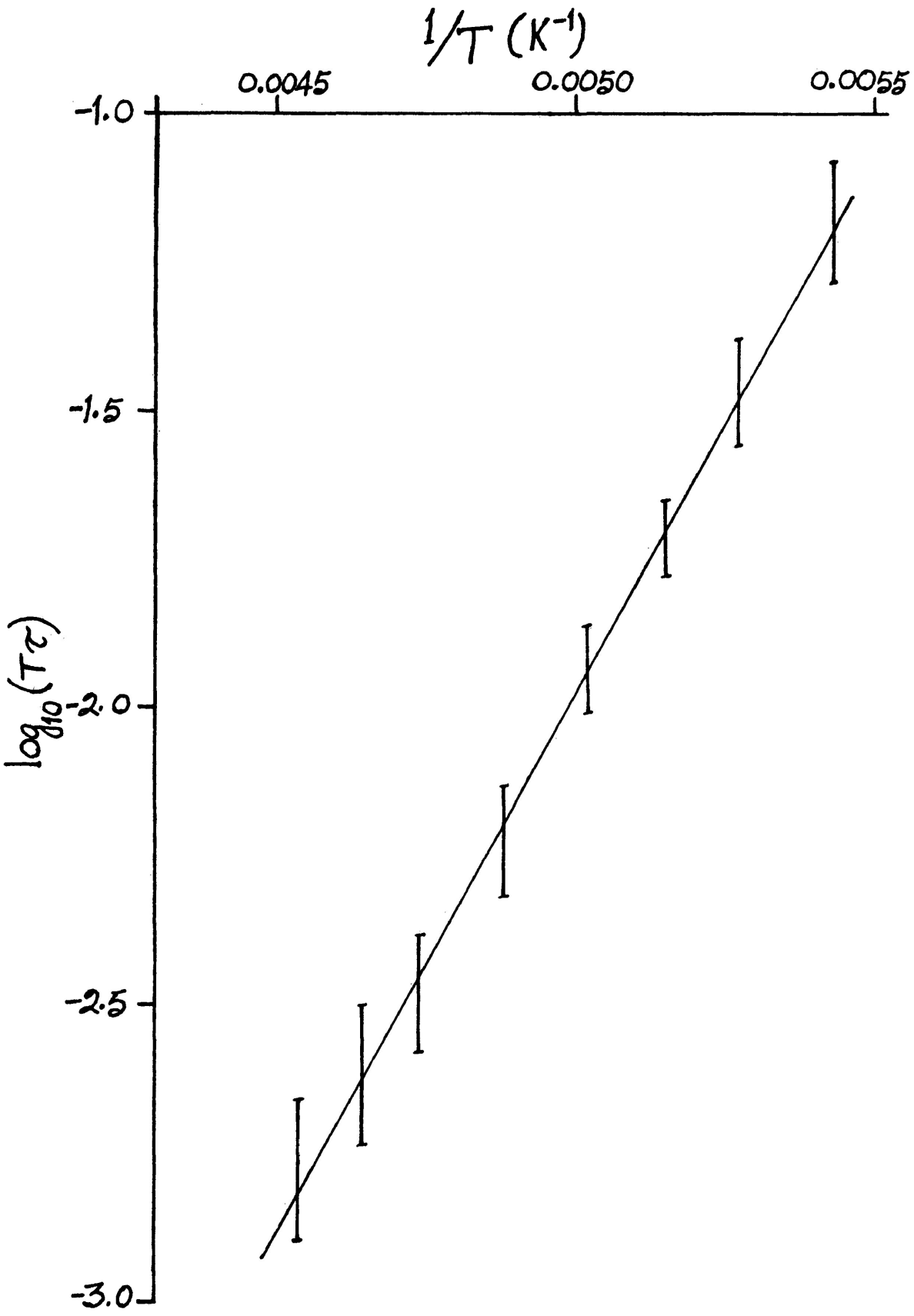

Fig. II-4: Eyring plot of $\log_{10}(T\tau)$ vs. $1/T$ for 0.576 M p-nitrotoluene in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values.

activation, ΔS_E , were obtained from the slope and intercept, respectively, of the line with the help of a computer programme. The programme also calculated the relaxation times, τ, and the free energies of activation, ΔG_E , at different temperatures according to the equation, $\Delta G_E = \Delta H_E - T\Delta S_E$.

Finally, the energy difference, V, between the two sides of the activation energy barrier was obtained from the plot of $\ln(\varepsilon''_{max}T)$ against $\frac{1}{T}$ according to the following equation, as employed by Meakins[14]:

$$\varepsilon''_{max} = \frac{B}{kT} \exp(-V/RT) \qquad \text{II-17}$$

where B is a simple proportionality constant. In most cases, the V values calculated by a computer programme were less than the mean thermal energy, and, therefore, according to Meakins could not be considered reliably to be different from zero.

The important results from the computer analyses to obtain the Fuoss-Kirkwood parameters $\log(f_{max})$, ε''_{max}, and β, the limiting high frequency dielectric constant, ε_∞, and the effective dipole moments, μ, are given in Appendix A while the Eyring analyses results of these data have been presented separately in

each of the following chapters. Structural diagrams of some of the molecules investigated are given in Appendix B.

It is to be noted that standard statistical techniques[15] have been employed in the fitting and analyses of the data with the various computer programmes, and the important parameters, viz., $\log(f_{max})$ and β values from the Fuoss-Kirkwood analyses, as well as the enthalpies and the entropies of activation from the Eyring analyses, were obtained with different confidence interval widths. For the present purpose, however, the 95% confidence interval was chosen as a good representation of experimental error, and the net result of the consideration of errors has led to the conclusion that the error in ΔH_E is at worst $\pm 10\%$, and that of ΔS_E may be as high as $\pm 50\%$. The values of activation enthalpies and entropies have been quoted in this work to round figures for comparative purposes only.

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CHAPTER III

MOLECULAR RELAXATION PROCESSES OF RIGID MOLECULES

INTRODUCTION:

Dielectric relaxation is a strongly temperature dependent phenomenon. This permits the evaluation of activation parameters which are very useful for the understanding of the nature of the process involved. The dielectric material itself is responsible in determining the energy barriers in that the geometry of the dipolar molecule has a great influence even when the same process is occurring in a series of similar molecules. It would, therefore, seem necessary to gain a wider background knowledge of what influences the energy barriers and relaxation times for molecular relaxation processes of rigid molecules, and of the extent to which concepts developed for dilute solutions can be applied to matrix systems. Detailed knowledge of the molecular relaxation parameters and the associated activation energy barriers are essential for the assignment of a particular process in a similarly sized flexible molecule as will be seen in the following chapters. It is mainly for this second reason that different types of polar rigid molecules have been studied which could also provide, at least, a qualitative interpretation of the activation parameters in terms of size, shape, and volume of the dipole units. However, an extensive quantitative treatment of the latter aspect, which would be more pertinent to appreciating the chemical physics of the system, has not been made.

It should be mentioned that the activation parameters were evaluated by using the Eyring rate expression, because of its simplicity and considerable flexibility in the interpretation of experimental observations.

DISCUSSION:

The Eyring analysis results for the variety of rigid molecules have been presented under separate headings in Tables III-1 to III-4 throughout the Chapter. The relaxation times and the free energies of activation have been shown at temperatures which are closer to the individual absorptions but yet covering the wide range for all the molecules of a particular type classified in different Tables for the convenience of discussions. For some molecules, the parameters may not be meaningful at all temperatures, but a more reasonable comparison can easily be made by choosing the ones within or closest to the experimental observations. Similar reasoning applies equally to all other Tables for Eyring analysis results given in other chapters of the thesis.

It is notable that in systems of similar character, there has been frequently a correlation between the activation enthalpies, ΔH_E, and entropies, ΔS_E, as was illustrated for dipole relaxations[1]

by Levi's data.[2] A linear relationship was indicated for dipole relaxation processes in polymers[3] which corresponded to the cooperative reorientation of polar groups in polymer or other media whereby the neighbouring molecules or segments of polymer chains essentially moved with the dipole reorientation. Davies et al.[4,5] obtained linear ΔH_E - ΔS_E plots for various solutes dispersed in polystyrene matrices. From the available literature data for pure liquids, Higasi[6] also showed a similar relationship. Figure III-1 shows the plot of ΔS_E against ΔH_E obtained from the present studies in polystyrene matrices of different mono- and para-substituted rigid molecules listed in Table III-1, indicating clearly that the entropy of activation increases linearly with enthalpy of activation as the size of the molecule increases. According to Davies and Edwards,[4] such behaviour can be understood qualitatively if the activation energy is needed primarily to displace the adjacent solvent media so that the larger the energy required for ΔH_E the larger the local disorder, ΔS_E. However, it was not possible to fit into the same plot the data for the other types of rigid molecules presented in Tables III-2 to III-4 which could, at best, be represented by different straight lines. But a sufficient number of molecules of each of the latter classes has not been studied to establish such a correlation. It appears that the linear ΔH_E - ΔS_E relationship would be more reasonable for any series of molecules

TABLE III-1 EYRING ANALYSIS RESULTS FOR MONO- AND PARA-SUBSTITUTED BENZENES

Molecule	T(K)	τ(s) 100 K	τ(s) 150 K	τ(s) 200 K	ΔG_E(kJ mol^{-1}) 100 K	ΔG_E(kJ mol^{-1}) 150 K	ΔG_E(kJ mol^{-1}) 200 K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
Chlorobenzene	81 - 111	2.3×10^{-5}	2.1×10^{-7}	1.8×10^{-8}	14.7	16.7	18.7	11	-40
Bromobenzene	101 - 136	5.5×10^{-4}	6.9×10^{-7}	2.2×10^{-8}	17.3	18.2	19.0	16	-17
Iodobenzene[1]	134 - 161	5.5×10^{-2}	2.1×10^{-5}	3.6×10^{-7}	21.2	22.4	23.7	19	-25
α,α,α-Trichloro-toluene[2]	147 - 173	5.0×10^{-1}	9.2×10^{-5}	1.2×10^{-6}	23.0	24.3	25.6	20	-26
1-Adamantane-carbonitrile	106 - 158	3.7×10^{-3}	5.1×10^{-6}	1.7×10^{-7}	18.9	20.7	22.4	16	-35
Benzonitrile	133 - 175	6.5×10^{-1}	7.3×10^{-5}	7.1×10^{-7}	23.2	24.0	24.8	22	-16
p-Tolunitrile	196 - 244	3.6×10^{6}	9.3×10^{-1}	4.3×10^{-4}	36.1	35.8	35.4	37	7
p-Nitrotoluene	184 - 220	1.5×10^{5}	7.9×10^{-2}	5.3×10^{-5}	33.5	32.7	31.9	35	16
p-Chloro-toluene[1]	163 - 196	9.5×10^{1}	1.6×10^{-3}	5.8×10^{-6}	27.3	27.8	28.2	26	- 9
p-Bromotoluene[3]	174 - 264	1.7×10^{3}	7.6×10^{-3}	1.5×10^{-5}	30.1	30.2	30.2	30	- 1
p-Iodotolune[1]	199 - 241	4.3×10^{7}	1.7×10^{0}	3.1×10^{-4}	38.2	36.5	34.9	42	33
p-Bromonitro-benzene	204 - 252	8.0×10^{7}	3.8×10^{0}	7.7×10^{-4}	38.7	37.6	36.4	41	23

NOTE: Data provided through the courtesy of H.A.Khwaja,[1] J. P. Shukla,[2] and B. K. Morgan[3] of this laboratory.

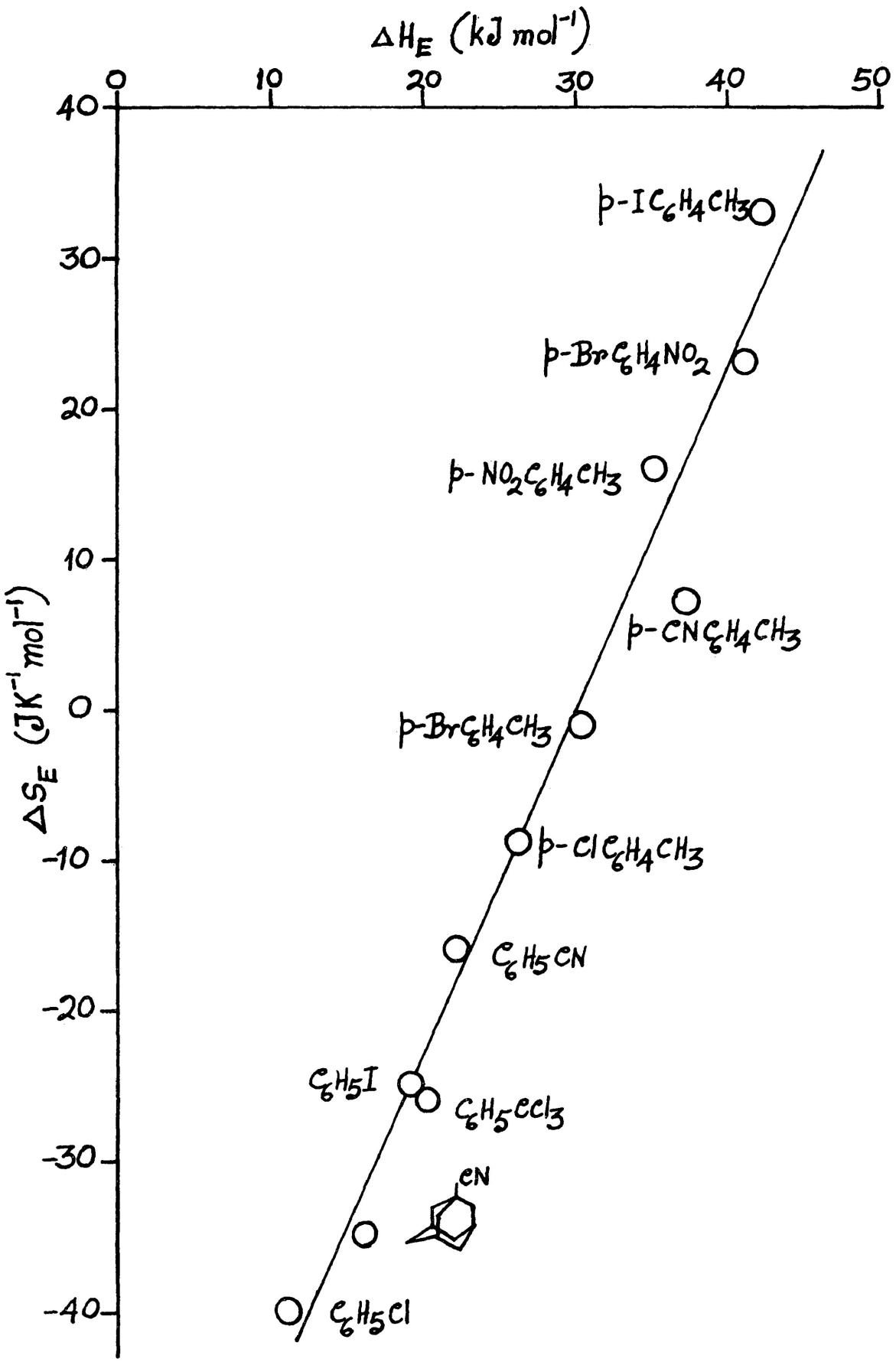

Fig. III-1: Plot of activation enthalpy, ΔH_E, vs. activation entropy, ΔS_E, for different mono- and para-substituted benzenes.

when the shape is quite similar and the inclination of the dipole to the principal axis is about the same. It is also necessary to point out that there is no absolute significance of the activation entropy determined by the Eyring expression since the pre-exponential factor cannot be fully justified. As Davies and Edwards[4] say, "the Eyring entropy terms ΔS_E^* are best regarded as emperical corrections (exp $(\Delta S_E^*/R)$) to a predetermined frequency value (kT/h) in the rate equation". Therefore, the breakdown of a single linear ΔS_E - ΔH_E relationship would not be surprising for a wide variety of dipolar molecules.

It was assumed by Cooke[7] that the barrier to rotation of a rigid dipolar molecule in solution is due to the resistance produced by the neighbouring molecules of its environment. In order to reorient, then, the dipolar molecule displaces the molecules surrounding it and does work against the attractive forces of the liquid in going from an equilibrium position of orientation to the activated state. The activated state was regarded as a process which involves a volume expansion within the liquid due to the displacement of neighbours by the reorienting molecule. The work done in creating the volume change, i.e., the activation energy, ΔH_E, was calculated from the product of the thermodynamic quantity, P_i, known as the internal pressure or cohesion energy density and the

activation volume, $\Delta V_{\varepsilon}^{\ddagger}$ i.e., the volume swept out in going from the initial to the activated state. The activation volume was obtained from the slope of the plot of $\log\tau$ against P_i for a particular solute in a number of solvents of differing internal pressure. From the linearity of these plots, it was suggested that the activation volume for solute reorientation does not change with the change of solvent and, indeed, the activation volumes for some solutes were found to be identical in different solvents. The activation volumes cannot be obtained directly, but these may be assumed to be similar in matrices to those in solutions although the reorientation angle may be different, as it was shown to vary from comparison with the ratio of activation volume to molar volume or to volume swept out in solutions. Cooke evaluated the activation volumes for a number of rigid polar molecules from the data obtained by Sinha et al.[8] in solutions of hexane, benzene, and carbon tetrachloride, and also from those obtained by Hassel[9] and by Mountain[10] in solutions of p-xylene.

Figure III-2 shows the plot of activation enthalpy obtained from the present studies against the activation volumes as derived from Hassell's and Mountain's data which also include the ortho- and meta-diiodobenzenes (Table III-2). It can be seen that ΔH_E and $\Delta V_{\varepsilon}^{\ddagger}$ increase as the size of the molecule increases, but

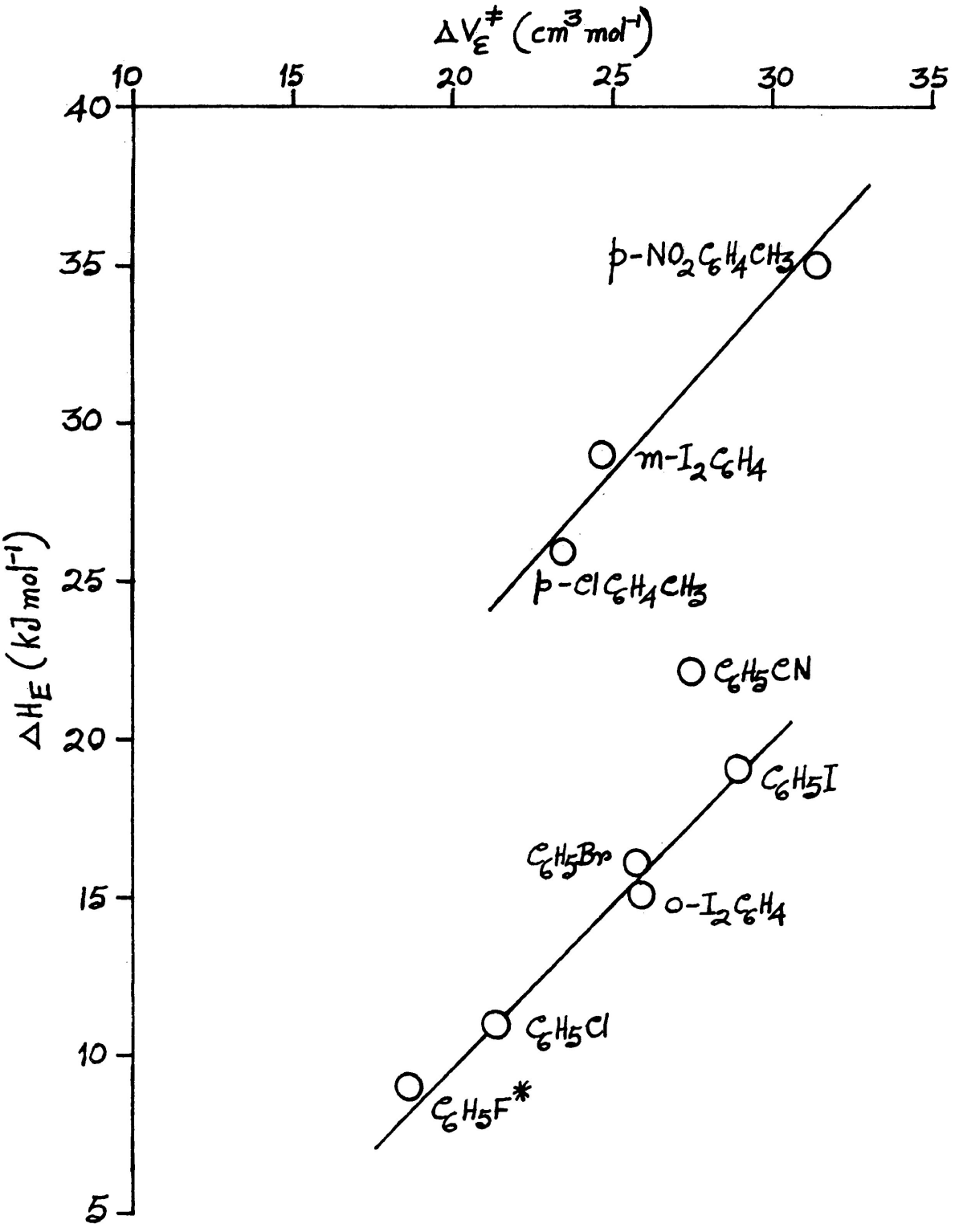

Fig. III-2: Plot of activation volume, $\Delta V_E^{\neq}$, against activation enthalpy, ΔH_E, for some mono- and disubstituted benzenes.

(* Activation enthalpy provided through the courtesy of H. A. Khwaja of this laboratory).

while the monohalobenzenes and the o-diiodobenzene fall on the same straight line, the p-substituted toluenes and the m-diiodobenzene fall on a different straight line whereas the benzonitrile does not fit anywhere. The apparent increase of activation energy with respect to activation volume is relatively higher for the latter molecules, and the case of benzonitrile is somewhat in between the two series of molecules. It would seem that the monohalobenzenes, because of their smaller sizes, rotate through relatively large angles compared to the other molecules so that the activation volumes are correspondingly larger, and so also for o-diiodobenzene which is similar in size and shape to those of the monohalobenzenes. In contrast to o-diiodobenzene, the reorientation of m-diiodobenzene could be very much restricted owing to the bulky iodine atoms which also make the molecule altogether quite large in size and different in shape. Benzonitrile, however, has the additional π-electron clouds, which might be responsible for the deviation from the behaviour of the monohalobenzenes owing to any interaction, if possible, with the surrounding medium (to be discussed later in this Chapter). Alternatively, these would also appear to indicate that the activation volume and, hence, the activation energy depend on the size of the 'cavity or hole' inside the matrix determined by the geometry of the molecule. However, a very detailed investigation is necessary to visualize the exact behaviour of the polystyrene-matrix system.

It was desirable to see how the swept volumes influence the energy barriers. The swept out volumes due to the rotation of the dipoles were calculated by using either the dimensions from Courtauld molecular models or from scale drawings constructed from known bond lengths and van der Waals radii.[11] The dipoles were assumed to be cylinders, and their rotation was arbitrarily considered through 180^{o} about the two axes perpendicular to the molecular moment corresponding to the in-plane and out-of-plane motions. The swept volumes were calculated for dipole rotations around the centre of mass, centre of symmetry, and the centre of aromatic rings of the molecules since the point about which the molecule rotates is not known. For calculations around the centre of mass and of the ring, the volumes were assumed to be composed of two half-cylinders, for which the maximum lengths of the molecules in each direction from the point of rotation were taken as the radii, and the length of the molecule in the direction parallel to the axis of rotation corresponded to the length of the cylinders. The rotational volumes about the Y-axis, V_y, the Z-axis, V_z, and the mean volumes, $V_{mean} = (V_y + V_z)/2$ for rotations about the different centres were calculated, and these were plotted against the activation energies. It was found that within the limits of experimental error estimates, there is some linear relationship between the swept volumes and the activation energies, the best linear fit being obtained for the plot

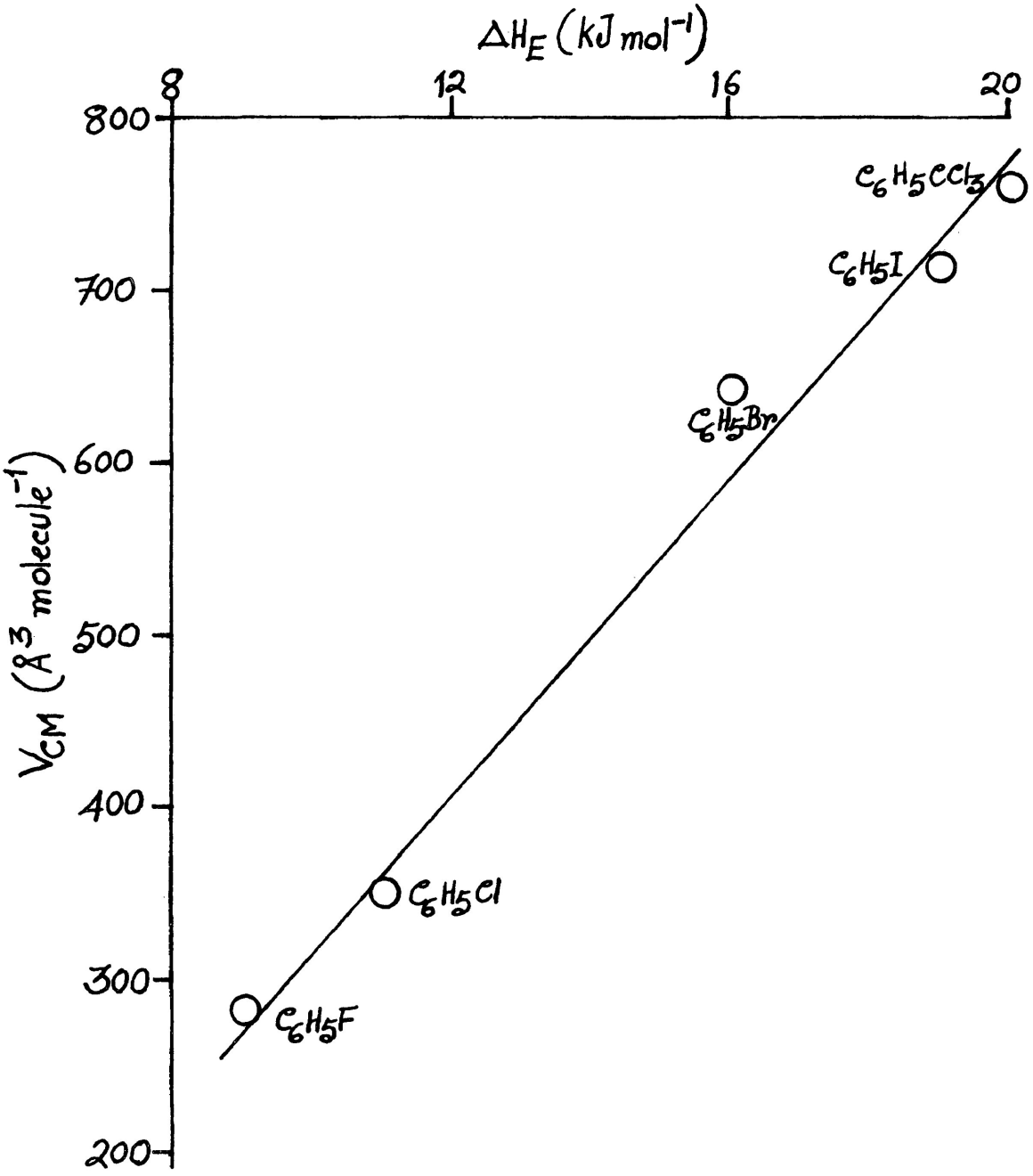

Fig. III-3: Plot of activation enthalpy, ΔH_E, against the mean swept volume around the centre of mass, V_{CM}, for some mono-substituted benzenes.

of mean swept volume around the centre of mass against the enthalpy of activation as shown in Figure III-3. It must be noted that for such correlations, only the monosubstituted benzenes have been considered among the many rigid molecules studied for the purpose of this thesis but this attempt, at least, does indicate that the activation energy increases with the mean rotational volume and that the dipole rotates, most probably, around the centre of its mass.

A more extensive study of the effect of size, shape, and inclination of the dipole to the principal axis of rotation would seem worthwhile. The data provided in Table III-2 for the Eyring analysis results of ortho- and meta-disubstituted benzenes accomplishes this to a further extent. It can be seen that in the case of m-dihalobenzenes there is almost a regular increase in the enthalpy of activation but for the o-dihalobenzenes the values are about the same while the entropies of activation are generally negative. The increase of activation enthalpy from 16 kJ mol^{-1} for m-dichlorobenzene to 29 kJ mol^{-1} for m-diiodobenzene appears to be in accord with the increasing size of the molecules along the series. The free energies of activation and the relaxation times also increase consistently at 150K, a more or less common temperature, but there is an apparent anomaly for the m-dibromobenzene. The enthalpy of activation of 23 kJ mol^{-1} for this molecule is higher

TABLE III-2 EYRING ANALYSIS RESULTS FOR ORTHO- AND META-DIHALOBENZENES

Molecule	T(K)	τ(s) 100K	τ(s) 150K	τ(s) 200K	ΔG_E(kJ mol^{-1}) 100 K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
o-Flucrochloro-benzene	81 - 106	1.6×10^{-5}	9.1×10^{-8}	6.3×10^{-9}	14.4	15.7	16.9	12	-24
o-Bromochloro-benzene	88 - 120	3.6×10^{-5}	4.1×10^{-8}	1.3×10^{-9}	15.1	14.7	14.3	16	8
o-Chloroiodo-benzene	108 - 138	1.4×10^{-3}	1.6×10^{-6}	4.8×10^{-8}	18.1	19.2	20.3	16	-22
o-Bromoiodo-benzene	103 - 139	8.4×10^{-4}	1.2×10^{-6}	4.1×10^{-8}	17.7	18.9	20.0	15	-23
o-Diiodo-benzene	109 - 147	2.1×10^{-3}	3.0×10^{-3}	1.1×10^{-7}	18.5	20.0	21.6	15	-31
m-Dichloro-benzene	115 - 146	4.7×10^{-3}	4.9×10^{-6}	1.5×10^{-7}	19.1	20.6	22.2	16	-30
m-Chlorobromo-benzene	128 - 176	1.9×10^{-2}	2.0×10^{-5}	6.1×10^{-7}	20.3	22.4	24.5	16	-43
m-Chloroiodo-benzene	154 - 215	4.1×10^{0}	6.4×10^{-4}	7.4×10^{-6}	24.8	26.7	28.7	21	-39
m-Dibromo-benzene	140 - 174	1.3×10^{0}	1.0×10^{-4}	8.4×10^{-7}	23.8	24.4	25.1	23	-12
m-Bromoiodo-benzene	166 - 215	1.1×10^{2}	2.6×10^{-3}	1.2×10^{-5}	27.5	28.5	29.5	26	-20
m-Diiodo-benzene	166 - 223	1.5×10^{3}	9.0×10^{-3}	2.0×10^{-5}	29.7	30.0	30.3	29	- 6

than that of 14.6 kJ mol^{-1} as reported by Tay and Walker,[12] but the present value seems to be more reasonable particularly in view of the activation enthalpies of 16 and 26 kJ mol^{-1} for m-bromochlorobenzene and m-bromoiodobenzene, respectively, which can be regarded as the lower and upper limits in terms of their sizes. Moreover, the free energy of activation (24.4 kJ mol^{-1}) and relaxation time at 150K (1.0×10^{-4} s) for m-dibromobenzene are well within those of the two limiting molecules. The apparent anomalies in the values of these two parameters at higher temperatures essentially reflects the contribution of the entropy term for which it is difficult to assign any absolute significance. It is to be noted that m-dichlorobenzene and m-bromochlorobenzene have similar enthalpies of activation, i.e., of 16 kJ mol^{-1} for each of them, but the relaxation times and so also the free energies of activation at different temperatures are greater for the larger molecule. Therefore, it can reasonably be said that the activation energy barriers and the relaxation times for the m-dihalobenzenes increase with the size of the molecules, and this is possibly due to the larger volumes swept out by the rotating molecules.

The results obtained for the o-dihalobenzenes are interesting especially since their activation enthalpies are similar, except that for the o-fluorochlorobenzene ΔH_E is about 3.5 kJ mol^{-1} less than

the average value of 15.5 kJ mol^{-1} obtained for the other molecules in the series. However, an enthalpy of activation of 12 kJ mol^{-1} for o-fluorochlorobenzene would not be unjustifiable when chlorobenzene, a molecule of similar size, has a value of 11 kJ mol^{-1} (Table III-1). The activation free energies of 15.7 and 14.7 kJ mol^{-1} for o-fluorochlorobenzene and o-bromochlorobenzene, respectively, at 150K are indistinguishable. The corresponding values for o-chloroiodobenzene, o-bromoiodobenzene, and o-diiodobenzene are relatively higher and are all about 19 - 20 kJ mol^{-1}. Relaxation times are also different by a factor of 10 - 100 among the smaller and the larger members of the series, i.e., among the o-chloro and the o-iodobenzenes. For example, o-fluorochlorobenzene and o-diiodobenzene have values of 1.6×10^{-5} s and 2.1×10^{-3} s, respectively, at 100K, the absorptions having been observed between ~80 - 150K. Similar differences in relaxation times have been noted from solution studies although the absolute values are much less in solutions than in matrices. Thus, o-dichlorobenzene[13] showed a relaxation time of 9.4 ps at 25°C while that of o-diiodobenzene[10] was 14.6 ps at 60°C and 27 ps at 15°C, the extrapolated values at 300K in polystyrene matrices being of the order of 10^{-9} s for the latter. It appears, therefore, that within the series of o-dihalobenzenes the very bulky iodine atoms are, at least, partially responsible for the much longer relaxation times and for the relatively higher free energies of activation of the o-

iodobenzenes compared to those of the o-chlorobenzenes. However, the enthalpies of activation are virtually the same, possibly because the size and shape of the dipoles and hence the swept out volumes do not differ appreciably.

The relaxation data for the o-dihalobenzenes merit comparison with those of the m-dihalobenzenes particularly in the light of solution results. Table III-2 shows that for any particular m-dihalobenzene the relaxation times are longer, and so also the free energies of activation are higher than the corresponding values for the o-disubstituted ones. This is consistent with the suggestion that the relaxation time is proportional to the molecular volume since the volume of an m-disubstituted compound is greater than that of the corresponding o-disubstituted one. In contrast, Walker *et al.*[13] found that the relaxation times of o- and m-dichlorobenzenes in p-xylene at 25°C differ very little and are only slightly longer than those of the mono-substituted compounds. Crossley[14] had accounted for this discrepancy by the suggestion that the mean relaxation time is more related to the length of the molecule than to its volume. This might also be coupled with the different directions of the dipole rotations. Mountain[10] expanded the work to o- and m-diiodobenzenes in p-xylene in order to discern if the large volume of the iodine atom could emphasize any significant

difference between the two types of compounds. He compared the relaxation time of iodobenzene (9.2 ps) with that of o-diiodobenzene (14.6 ps) both at 60°C and stated that "the relaxation time of m-diiodobenzene is to fall in between that of the ortho- and mono-substituted derivatives, being 12.6 x 10^{-12} s at 60°C". This is to be contrasted with the relaxation times of 11.1, 11.7, and 9.4 ps for chlorobenzene, o-dichlorobenzene, and m-dichlorobenzene, respectively, in solutions of benzene at ~23°C as reported by Sinha and his coworkers.[8] It was concluded by Mountain that "within the experimental error the relaxation times of the m-compounds may be said to be the same as those of the ortho-derivative," and, "similarly the enthalpies of activation are also equivalent and show no suggestion of increasing ΔH_E with larger molecular volume as was obtained by Hassell with the mono-substituted halobenzenes". However, from the present studies in matrices, the differences in activation parameters and in relaxation times between the ortho- and the meta-dihalobenzenes are beyond the estimated experimental errors and are most likely due to the varying size and volume of the dipoles.

Some other rigid molecules with greater numbers of substituents in the benzene ring have been studied only to provide sources of relaxation data and activation parameters for comparisons with those of flexible molecules of analogous size. These rigid

molecules may be grouped as polysubstituted benzenes for which the Eyring analysis results are given in Table III-3. The large variation of activation enthalpy (9- 64 kJ mol^{-1}) with size of the molecules is clearly evident for the pentasubstituted toluenes. The most remarkable features of these molecular relaxations are the values of β, the distribution parameter (see Appendix A, Table 3). Pentachloro- and pentabromotoluenes have β values of 0.74 - 0.90 and 0.55 - 0.78, respectively, indicating very narrow distributions of relaxation times. These values are even higher than those observed by Davies and Swain[5] for the intramolecular ring inversion of cyclohexyl derivatives. These workers commented that "the increase in β would be expected for an intramolecular dipolar motion as this would be appreciably less dependent upon the cooperative movement of the adjacent polystyrene units than is the whole molecule rotation". A wide range of local environments are generally encountered by the polar solutes dispersed in polymer matrices as is reflected in typically low β values. Since this parameter is a measure of the width of the absorption relative to the simplest Debye process for which β equals unity, the high values obtained for pentachloro and pentabromotoluene appear to indicate that the dielectric relaxations of these molecules in polystyrene matrices occur by a similar mechanism. The shape of the molecules is such that a wide variety of local environments could, perhaps, be avoided easily. It is possible also that the size is large enough to restrict their accommo-

TABLE III - 3 EYRING ANALYSIS RESULTS FOR SOME POLYSUBSTITUTED BENZENES

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 (JK^{-1} mol^{-1})
3,5-Dichlorobenzonitrile	207 - 250	8.4×10^{6}	5.3×10^{-4}	1.8×10^{-7}	36.8	35.8	34.7	38	11
3,5-Dinitrobenzonitrile	195 - 234	6.9×10^{4}	2.2×10^{-4}	2.7×10^{-7}	32.9	34.3	35.8	31	-15
2,4-Dinitrochlorobenzene	186 - 234	8.5×10^{6}	2.3×10^{-4}	5.7×10^{-8}	36.9	34.4	31.9	39	25
2,4,6-Trichloropyrimidine	172 - 219	2.8×10^{5}	2.3×10^{-5}	8.3×10^{-9}	34.0	30.5	27.1	38	35
2,4,6-Trimethylbenzonitrile	160 - 193	4.0×10^{2}	4.7×10^{-6}	9.1×10^{-9}	28.6	27.9	27.3	29	6
2,4,6-Trichloronitrobenzene	166 - 200	8.3×10^{2}	9.2×10^{-6}	1.7×10^{-8}	29.2	29.0	28.9	29	
Pentafluorotoluene	81 - 102	5.8×10^{-6}	1.7×10^{-8}	2.0×10^{-9}	13.6	18.6	23.6	9	-50
Pentachlorotoluene	215 - 274	3.1×10^{10}	7.5×10^{-3}	4.0×10^{-7}	43.7	40.2	36.7	47	35
Pentabromotoluene	284 - 344	1.2×10^{19}	1.1×10^{2}	1.8×10^{-4}	60.1	56.1	52.1	64	40

dation in any intramolecular spaces along the polymer chains. Therefore, the dipoles are almost invariably surrounded by similar environments created by folding of the polymer chains in course of which they occupy some sort of holes within the matrix. In other words, these are the cases of suitably-sized molecules relaxing in something approaching a spherical hole or, at least, the former is true so that similar behaviour might be expected even in different systems. This is borne out by the fact that Turney[15] observed almost perfect Debye curves for pentchlorotoluene and 1,2,4-trimethyl-3,5,6-trichlorobenzene in pure solids. The activation energy, entropy of activation and free energy of activation at 20°C obtained for the former being 49 kJ mol^{-1}, 39 JK^{-1} mol^{-1} and 37 kJ mol^{-1}, respectively, are in excellent agreement with the corresponding values of 47 kJ mol^{-1}, 35 JK^{-1} mol^{-1}, and 37 kJ mol^{-1} at 27°C found from the present studies. The results for pentabromotoluene can be interpreted similarly, the difference in activation parameters and relaxation times being essentially due to the greater size and, hence, larger volume of the molecule. Much lower energy barriers and shorter relaxation times have been obtained for pentafluorotoluene which is of significantly smaller size. This molecule may also be expected to show Debye curves, but the very low temperatures (81 - 102K) at which the absorptions occur are probably responsible for the low β values of 0.20 - 0.26.

Other rigid molecules listed in Table III-3 show significantly high energy barriers, except 2,4,6-trimethylbenzonitrile and 2,4,6-trichloronitrobenzene, and are all associated with positive entropies, except 3,5-dinitrobenzonitrile. The activation parameters for this latter molecule are not very accurate as was evident from larger error estimates on enthalpy and entropy of activation. This resulted from the fact that the frequencies at which maximum absorption occurred could not be estimated accurately on account of the extremely low loss (ε''_{max} = 1.2 - 1.3 x 10^{-3}) consistent with the low dipole moment of the solute (μ_{eff} = 0.37 D at 300K) and thereby making the absorption peak poorly defined. However, the mean values of the activation enthalpy and of the entropy, i.e., 31 kJ mol^{-1} and -15 $JK^{-1}mol^{-1}$ respectively, are of the orders expected when compared to the corresponding values of 25 kJ mol^{-1} and -3 JK^{-1} mol^{-1} obtained for m-dinitrobenzene studied by Walker et al.[16] It is surprising that 2,4,6-trimethylbenzonitrile has an enthalpy of activation of 29 kJ mol^{-1}, which is about 8 kJ mol^{-1} less than that of p-tolunitrile (Table III-1), while both have similarly small positive entropies of activation of 6 - 7 JK^{-1} mol^{-1}. Consequently, the free energies of activation at various temperatures also differ by about 7 KJ mol^{-1}. The former solute was well purified by recrystallization and the latter by redistillation, and for both of them the dielectric measurements were repeated, but almost the same results have been obtained. This was further confirmed by the activation enthalpy and entropy

of 29 kJ mol^{-1} and 1 JK^{-1} mol^{-1}, respectively, for 2,4,6-trichloronitrobenzene which differ similarly from the corresponding values of 35 kJ mol^{-1} and 16 JK^{-1} mol^{-1} for p-nitrotoluene obtained through the same procedure. 2,4,6-Trimethylbenzonitrile and 2,4,6-trichloronitrobenzene are equivalent in size, and so also p-tolunitrile and p-nitrotoluene. The results for the two polysubstituted benzenes are also consistent with ΔH_E = 33 kJ mol^{-1} and ΔS_E = 12 JK^{-1} mol^{-1} for the molecular relaxation of 2,4,6-tribromoanisole (see Chapter VIII), but it is difficult to account for the anomaly with the results of p-tolunitrile and p-nitrotoluene, molecules of smaller size although having identical length along the long axis. There is an important difference between the distribution parameters, β, of the two pairs of molecules concerned. For example, 2,4,6-trimethylbenzonitrile has values of 0.16 - 0.23 between 160 - 193K while that of p-tolunitrile is 0.18 - 0.19 between 196 - 244K. Evidently, the β values for the latter would not be considerably different even at room temperatures but for the other a much larger value would seem likely. It suggests that 2,4,6-trimethylbenzonitrile would tend more to Debye behaviour on account of its more uniform environment determined by the size and shape of the molecule, similar to those of pentahalotoluenes discussed previously. On the other hand, p-tolunitrile might occupy positions in the intramolecular spaces along the polymer chain or in between the two adjacent phenyl substituents of the polymer, and, therefore, its reorientation would be more hindered than that of the

other. But it is still hard to reconcile this further with the results of 3,5-dichlorobenzonitrile, 2,4-dinitrochlorobenzene and 2,4,6-trichloropyrimidine having activation enthalpies of 38-39 kJ mol^{-1}. Certainly, a more detailed knowledge of the intermolecular architecture in the system is necessary at this stage, and this would seem feasible by studying a wider variety and a sufficient number of solute molecules.

Nitrogen-containing heterocyclic rigid molecules received special consideration since these would also provide some information concerning molecular interaction with the matrix due to the hybridized lone pair electron of the hetero atom. The Eyring analysis results for such molecules are given in Table III-4 which can be compared with those of the analogous non-heterocyclic rigid molecules listed in Tables III-1 and III-2. It is apparent that there is small difference between the results for 4-methylpyridine and chlorobenzene, the activation enthalpy of the former (14 kJ mol^{-1}) being 3 kJ mol^{-1} higher than that of the latter. In the case of 3-bromopyridine, the activation enthalpy (21 kJ mol^{-1}) differs a little more from that of bromobenzene (16 kJ mol^{-1}) but the free energies of activation, say, at 150K of 21.1 and 18.2 kJ mol^{-1}, respectively, are still similar within the experimental accuracy. The relaxation time of 5.7×10^{-2} s at 100K for 3-bromopyridine is considerably longer than the corresponding value of 5.5×10^{-4} s

TABLE III-4 EYRING ANALYSIS RESULTS FOR HETEROCYCLIC RIGID MOLECULES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E	ΔS_E
		100K	150 K	200 K	100 K	150 K	200 K	(kJ mol^{-1})	(JK^{-1} mol^{-1})
4-Methylpyridine	88 - 124	8.5×10^{-5}	2.1×10^{-7}	9.8×10^{-9}	15.8	16.7	17.7	14	-19
3-Bromopyridine	117 - 155	5.7×10^{-2}	7.3×10^{-6}	7.5×10^{-8}	21.2	21.1	21.0	21	2
o-t-Butyl-pyridine	119 - 162	9.0×10^{-3}	7.4×10^{-6}	2.0×10^{-7}	19.7	21.2	22.6	17	-30
p-t-Butyl-pyridine[1]	146 - 175	3.0×10^{0}	8.1×10^{-5}	3.8×10^{-7}	24.5	24.1	23.7	25	8
2,6-Dibromo-pyridine	126 - 163	5.4×10^{-1}	1.5×10^{-5}	7.0×10^{-8}	23.1	22.0	20.9	25	22
3,5-Dibromo-pyridine	142 - 193	2.3×10^{0}	2.5×10^{-4}	2.3×10^{-6}	24.3	25.5	26.8	22	-25
Quinoline[2]	139 - 174	1.2×10^{0}	4.8×10^{-5}	2.7×10^{-7}	23.8	23.5	23.2	24	6
8-Hydroxy-quinoline	110 - 143	4.5×10^{-3}	2.5×10^{-6}	5.5×10^{-8}	19.1	19.8	20.5	18	-14
8-Chloro-quinoline	121 - 158	8.4×10^{-2}	5.8×10^{-6}	4.4×10^{-8}	21.5	20.8	20.2	23	14
3-Bromo-quinoline	205 - 256	2.7×10^{7}	2.8×10^{0}	8.2×10^{-4}	37.8	37.2	36.5	39	13

NOTE: Data provided through the courtesy of H. A.Khwaja[1] and J. P. Shukla[2] of this laboratory.

for bromobenzene, but the difference becomes smaller at higher temperatures. Similar results have been obtained for ortho- and p-t-butylpyridines, the activation enthalpies being 17 and 25 kJ mol^{-1}, respectively, where the lone-pair electrons in the nitrogen p-orbital of the latter is more exposed to the surrounding medium. The same is true for 3,5-dibromopyridine compared to 2,6-dibromopyridine, but the activation enthalpies of 22 and 25 kJ mol^{-1}, respectively, are about the same although the relaxation times are longer and the free energies of activation at different temperatures are higher for 3,5-dibromopyridine. The results for m-dibromobenzene (Table III-2), which is not expected to interact at all, however, are somewhat in between those of the two analogous heterocycles. 8-Hydroxyquinoline and 8-chloroquinoline results are remarkable compared to those of quinoline.[17] The two derivatives are equivalent in size and would have very little chance of interaction due to the hybridized lone-pair electrons because the former is restricted by intramolecular O - H ··· N bonding which prevents the lone-pair nitrogen electrons from being exposed to the surrounding medium while there is appreciable steric blocking in the latter. The enthalpies of activation obtained for these two molecules are 18 and 23 kJ mol^{-1}, respectively, but there is little difference in the free energies of activation, for example, of 19.8 and 20.8 kJ mol^{-1} at 150K, and so also in relaxation times particularly at higher temperatures. On the other hand, quinoline would be least restricted

in any interaction with the surrounding medium, but its activation enthalpy of 24 kJ mol^{-1} is virtually identical to that of 23 kJ mol^{-1} obtained for 8-chloroquinoline while the activation free energy of 23.5 kJ mol^{-1} at 150K for the former molecule is still higher than that of 20.8 kJ mol^{-1} for the latter. A similar difference has been observed for 3-bromoquinoline with an activation enthalpy of 39 kJ mol^{-1} compared to that of 35 kJ mol^{-1} for 2-bromonaphthalene as studied by Tay and Walker.[12] However, the free energy of activation of 36.5 kJ mol^{-1} at 200K for 3-bromoquinoline is about the same as that of 34.6 kJ mol^{-1} for the naphthalene derivative at the same temperature. This would seem more justifiable when 3-bromopyridine, which is expected to be a stronger interactor than 3-bromoquinoline, does not show marked difference with the results of bromobenzene. It is evident from the findings of Crossley and Walker[18] that quinoline and, presumably, its derivatives are much weaker interactors than γ-picoline (4-methylpyridine), and, in fact, no interaction was detected for the quinoline type of molecules studied in solutions. However, the results from the present studies show considerably higher activation enthalpies, at least for p-t-butylpyridine and quinoline compared to those of o-t-butylpyridine and the bigger 8-hydroxyquinoline, respectively. In the cases of other heterocyclic molecules, although the activation enthalpies are somewhat higher than those of the corresponding non-heterocycles of similar size and shape, the

differences may be well within the experimental error of, say, ± 3 kJ mol^{-1}. If the comparisons are being made on the basis of the free energies of activation in the middle of the experimental temperature range, which should be most reliable for the assessment of any molecular interaction since the errors would be smaller, then the present data may not indicate any significant interaction even for the p-t-butylpyridine or quinoline. It seems, however, that a detailed study of a wider range of molecules is necessary to determine whether such interaction definitely takes place. For this thesis involving these compounds such weak interaction, if it occurs, does not substantially influence the arguments.

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CHAPTER IV

INTRAMOLECULAR MOTION OF ARYL-ALKYL AND TWO DIALKYL KETONES

INTRODUCTION:

The carbonyl group containing compounds have received much attention from dielectric studies. Both aliphatic and aromatic ketones have been widely investigated but there is hardly any dielectric data available in the literature for the mixed aryl-alkyl ketones. Also, very little is known about the energy barriers for the relaxation processes of the various types of ketones. Acetophenones have been of particular interest and were studied extensively by different workers using various techniques. There are, however, very serious disagreements between the energy barriers obtained from the different techniques. Thus, Fateley and his coworkers[1] reported a barrier, V_2, of 13.0 kJ mol^{-1} from a far-infrared study of acetophenone in the gas phase while Fong and Smyth[2,3] obtained enthalpies of activation values of 4.2 to 6.3 kJ mol^{-1} for the acetyl group rotation in benzene solutions of 1- and 2-acetyl-naphthalenes, 4-acetyl-o-terphenyl, 4-phenylacetophenone, and 1,4-diacetylbenzene. Similarly low activation enthalpies of 4.2 - 12.1 kJ mol^{-1} have been observed by Madan[4,5] for a number of aliphatic ketones in solutions of different non-polar solvents. From the energy barriers and relaxation times data, Madan has suggested a dominant intramolecular process where the dipole relaxes by the rotation of the terminal carbonyl group. This is consistent with

the behaviour of some of the other aliphatic ketones as studied by Crossley[6,7] and Smyth et al.[8]. These workers, however, considered only the relaxation times and distribution parameters which they compared with those of other similar molecules. Crossley[9] also proposed molecular rotations for symmetrical ketones, where the carbonyl group is well removed from either end, and concluded for hexanophenone "that the steric effect of the alkyl group together with the resonance effect of the aromatic group gives rise to a high barrier to intramolecular rotation and dipole reorientation is dominated by rotation of the whole molecule".

Katritzky and his coworkers[10] estimated a rotational barrier of 26.0 kJ mol^{-1} for acetophenone itself from n.m.r. data on p-substituted acetophenone whereas theoretical calculations by Hehre et al.[11] yielded 18.4 kJ mol^{-1}. Recently, McLellan and Walker[12] have shown for the acetyl group rotation an enthalpy of activation of $\sim$30 kJ mol^{-1} with different ketones in polystyrene matrices. In view of the above disagreements found in the literature for the energy barrier to acetyl group rotation and also owing to the unavailability of detailed energy barrier data for any series of ketones, it was desirable to investigate acetophenone further and to extend the study to a series of aryl-alkyl ketones in which the number of carbon atoms in the alkyl group was increased from one to eleven. Some purely aliphatic ketones were also studied for the purpose of comparison,

and all measurements were carried out in dilute solutions of ordinary atactic polystyrene, an amorphous polymer with no rigidly-defined crystalline lattice structure, so that there would be little possibility of the effect of any internal electric field. Such studies already indicated that the solutes behave as if they were in a medium of very high viscosity,[13,14] the effect of which would be more pronounced for molecular rotation involving the motion of a species of larger volume than for the rotation of smaller substituent groups within the molecule. Therefore, the results would appear to be more straightforward than those from similar studies in dilute liquid-phase solutions since the latter have often been complicated by overlapping absorptions due to different processes.

DISCUSSION:

The relaxation times and the activation parameters for the series of carbonyl compounds of type PhCOR, where the rotatable polar group is directly attached to the benzene ring at one end while the other side has varying alkyl groups with differing chain lengths, are presented in Table IV-1. The simplest of these ketones is acetophenone in which the dipole relaxation may occur by either or both the rotation of the group and the molecule

TABLE IV-1 EYRING ANALYSIS RESULTS FOR ARALKYL AND TWO DIALKYL KETONES

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
Acetophenone	162 - 181	6.8×10^{-4}	1.2×10^{-6}	1.9×10^{-9}	26.8	25.6	23.3	30	23
n-Butyrophenone	149 - 174	9.6×10^{-5}	2.6×10^{-7}	6.3×10^{-10}	24.4	23.1	20.6	28	25
i-Butyrophenone	158 - 185	3.2×10^{-4}	5.6×10^{-7}	8.6×10^{-10}	25.9	24.4	21.4	30	30
n-Valerophenone	140 - 213	4.5×10^{-5}	2.4×10^{-7}	1.1×10^{-9}	23.4	23.0	22.1	25	9
i-Valerophenone	147 - 173	8.7×10^{-5}	3.4×10^{-7}	1.2×10^{-9}	24.4	23.6	22.3	26	13
Hexanophenone	140 - 170	6.5×10^{-5}	1.9×10^{-7}	4.7×10^{-10}	23.9	22.5	19.9	28	26
Octanophenone	157 - 184	4.4×10^{-4}	1.1×10^{-6}	2.5×10^{-9}	26.2	25.5	24.1	28	14
Undecanophenone	149 - 171	2.6×10^{-4}	5.9×10^{-7}	1.2×10^{-9}	25.6	24.5	22.3	29	22
"	294 -317	3.5×10^{21}	5.4×10^{8}	7.5×10^{-5}	97.7	81.8	49.8	146	320
3-Nonanone	108 - 128	1.4×10^{-7}	1.2×10^{-9}	8.5×10^{-12}	16.2	14.1	9.9	23	42
8-Pentadecanone	124 - 149	3.5×10^{-6}	1.5×10^{-8}	5.9×10^{-11}	20.2	18.4	14.8	26	36

as a whole. The enthalpy and entropy of activation for this molecule have been found to be 30 kJ mol^{-1} and 23 JK^{-1} mol^{-1}, respectively. These values are in excellent agreement with those of 29.6 kJ mol^{-1} and 26 JK^{-1} mol^{-1}, respectively, as obtained by McLellan and Walker.[12] These workers established the activation energy barriers for the acetyl group rotation by studying several substituted aromatic molecules of different size in polystyrene matrices and also in some pure solid disks. In all cases, they observed a common absorption process within similar temperature ranges and with almost the same activation parameters. For example, a low temperature absorption near 150K, similar to that for acetophenone, was observed for 1,4-diacetylbenzene in both polystyrene matrix and crystalline samples, which yielded activation enthalpies of 29 and 27 kJ mol^{-1}, respectively. For this molecule, the parallel component of the substituent group moments along the long axis of the molecule cancel out one another leaving the perpendicular ones to be responsible for the group rotation. On the other hand, the group and the molecular relaxation processes were completely separated for 4-acetylbiphenyl in a polystyrene matrix, showing activation enthalpies of 30 and 68 kJ mol^{-1}, respectively, the high energy process corresponding to the molecular absorption being observed around 320K. This substance also showed a low temperature process with an activation enthalpy of 33 kJ mol^{-1} in the pure solid state,

where it is expected that molecular relaxation would be eliminated while group relaxation may still occur.

The results from the presently observed dielectric absorption between 162 - 181K for acetophenone are consistent with those from the low temperature absorption for the acetyl group relaxation observed by McLellan and Walker.[12] There is also a very good correspondence of ΔG_E = 25.6 kJ mol^{-1} at 200 K with that of 26 kJ mol^{-1} from the estimated[10] n.m.r. value in liquid solution. However, the energy barriers obtained by other workers[1-5,11] from various studies are much too low compared to those observed in polystyrene matrices. Nevertheless, the experimental dipole moments of 1.24 - 1.36 D (see Appendix A, Table 5) further support the view that the group relaxation has been observed in the matrix. This is evident from the extrapolated dipole moment at 300K of $\sim$2.0 D which is to be compared with the perpendicular component of $\sim$2.4 D of the acetyl group moment[21] of 2.89 D. There was also no indication of any other absorption throughout the entire temperature range of 80 - 350K. This is surprising when the molecular relaxation is also possible.

A more detailed and careful analysis of the data for acetophenone over a wider temperature range (143 - 213K) of the absorption, as obtained by McLellan and Walker[12] from two different instruments (the GR bridge and the Q-meter), was carried out. This

was performed by the Eyring programme in the computer by deleting a point each time from either or both the low and high temperature side of the full range, but similar activation parameters have always been obtained although the error estimates varied considerably owing to decreasing numbers of degrees of freedom. In addition, there was no observable curvature in the Eyring plot, which might be described by two straight lines of limiting slopes, to account for any overlapping absorption. This means that either the molecular absorption occurred exactly at the same temperature range as the group process with similar energy barriers so that they are both perfectly overlapped, or else the magnitude of the weight factor for the group process:

$$C_2 = \frac{\mu_\perp^2}{\mu_\parallel^2+\mu_\perp^2} \simeq 0.70$$

(calculated on the basis of the acetyl group moment[21] μ of 2.89 D and assuming an angle of inclination[21] θ of 57°, which the group makes with the axis of rotation along the carbonyl carbon to the aromatic carbon bond, whereby $\mu_\perp = \mu\sin\theta$ and $\mu_\parallel = \mu\cos\theta$), is large enough to obscure the other and hence to make it insignificant. However, the former possibility can be ruled out by considering the results for iodobenzene (Table III-1), a molecule of similar size, which absorbs at a lower temperature range of 134 - 161K and has an

activation enthalpy of 19 kJ mol^{-1} only. Therefore, it appears that the most likely source of dielectric absorption for acetophenone in a polystyrene matrix is the rotation of the acetyl group.

The enthalpies and entropies of activation obtained for the low temperature absorption around 150K for all other aryl-alkyl ketones are in the range of 28 ±3 kJ mol^{-1} and 20 ±11 JK^{-1} mol^{-1}, respectively, in good agreement with those of acetophenone within the error limits. Also, the free energies of activation at 150K (25 ±2 kJ mol^{-1}) and at 200K (24 ±1.5 kJ mol^{-1}) as well as the relaxation times at different temperatures are similar to the corresponding values for each other, the difference being much less pronounced at a more common temperature, say, 170K. However, the relaxation times are found to be much longer (about 100 times at ~300K) relative to the values obtained from microwave studies in solutions by different workers.[2,4,7] Crossley[6,7] obtained relaxation times of 4 - 22 ps at 25°C, whereas Madan[4,5] reported values of 2 - 13 ps between 10 - 60°C for a number of aliphatic ketones, while Fong and Smyth[2] found 6 - 35 ps for several acetyl substituted aromatic molecules within 20 - 60°C. Smyth and his co-workers[15,20] also measured some ketones as pure liquids and found that the mean relaxation time, τ_0, lengthens with increased molecular weight. This was interpreted in terms of dipole reorientation by whole molecule rotation and an intramolecular process involving

rotation around the R - C and R' - C bonds of the ketones ($R - \overset{O}{\overset{\|}{C}} - R'$). Crossley[6,7] studied some aliphatic ketones in cyclohexane solutions at 25°C. He found that the τ_o values for the 2-alkanones and all the nonanones, as well as 4-decanone, were shorter than anticipated for molecular rotation and were of a similar order of magnitude (4 - 8.3 ps) to the relaxation time for acetyl group rotation in aromatic molecules[2,15,16] ($\sim$7 ps) and for acetone[17,18] (3.2 ps) in dilute solutions. Moreover, for the 2-alkanones τ_o lengthened only slightly as the alkyl group was increased from C_4 to C_{17}, a typical value for 2-octanone[8] being 4 ps in n-heptane at 25°C. It was considered probable that the dipole reorientation occurred primarily by the intramolecular rotation of the terminal acetyl group. Similar conclusions were drawn by Madan,[5] who also evaluated activation enthalpies and free energies of 4 - 10 and 7 - 10 kJ mol^{-1}, respectively. Crossley further showed that the location of the carbonyl group on the hydrocarbon backbone had relatively little effect on the relaxation time for the nonanones and decanones, in which the dipole reorientation might occur either by overall molecular orientation or by rotation around the R - C and R' - C bonds. In the case of long chain symmetrical ketones, the relaxation times were significantly longer than those for the 2-alkanones and appreciably lengthened with increased molecular size. Thus, the relaxation times, τ_o, for 7-tridecanone, 8-pentadecanone,

10-nonadecanone and 11-hexacosanone were found to to be 13.8, 17.1, 22.0, and 22.2 ps, respectively, in cyclohexane solutions at 25°C. For hexanophenone the relaxation time of 18.8 ps was comparable with that of 19 ps for benzophenone,[19] both in cyclohexane solutions at 25°C. Therefore, it appeared that when both R and R' were sufficiently long the intramolecular process was restricted, and the contribution from the whole molecule rotation increased with increased length of the alkyl groups.

The relaxation times obtained from the solution studies, whether for the molecular or intramolecular processes, are to be contrasted with those of the typical values of the order of 10^{-9} to 10^{-10} s, observed in polystyrene matrices at 300K, and more specifically with one of the lowest value of 4.7×10^{-10} s for hexanophenone. It would not be unexpected to observe much longer relaxation times in polymer matrices since the solutes are dissolved in a medium of extremely high viscosity so that the frequencies, at which maximum absorptions occur, are considerably lower than those for the case of a liquid solution. Furthermore, the influence of the medium would be much greater on molecular relaxation processes than for the relaxation of smaller substituent groups within the molecule. Although there are certain variations of results within the series of molecules, the difference

in relaxation times, e.g., of 1.9×10^{-9} and 1.2×10^{-9} s at 300K between the smallest acetophenone and the largest undecanophenone, respectively, would appear to be more consistent with some intra-molecular motion involving the polar carbonyl group as was also observed by Crossley[6,7] and by Madan[4,5] for alkanones in solutions. Moreover, the activation parameters observed for the series of aryl-alkyl ketones of widely varying size and showing absorptions at similar temperature ranges are so close to the corresponding values for each other that molecular relaxation processes would seem unlikely. Moreover, there is no evidence that any substantial contribution to the dielectric absorption due to molecular process has been detected. This is apparent from the low effective dipole moments of (0.86 - 1.39 D), which are even smaller than those observed with acetophenone, and is further borne out by the appearance of a second absorption for only undecanopheonone above room temperatures. The dielectric measurements for this absorption could not be performed over a wider temperature range owing to the onset of the glass-transition process in the polymer for which the capitance values were not steady during the measurements, but the Eyring analysis results gave values of activation enthalpy and entropy of 146 kJ mol^{-1} and 320 JK^{-1} mol^{-1}, respectively. Such values are too high even for the simple molecular relaxation of undecanophenone but may be accounted for by the molecular process involving probably some sort of

cooperative motion with the polymer chain. A number of other systems exhibiting similar behaviour in polystyrene matrices has been carefully examined by Walker et al.[22] in this laboratory, and a relation of the form, ΔS_E (JK^{-1} mol^{-1}) = -150 + 3.24 ΔH_E (kJ mol^{-1}), has been derived. According to this equation, the calculated ΔS_E value of 323 JK^{-1} mol^{-1} is in good agreement with that obtained from the Eyring analysis.

It is important to note that the distribution parameters, β values, for the low temperature absorption of undecanophenone, 0.24 - 0.26 (see Appendix A, Table 5), are markedly higher than those of 0.11 - 0.12 for the higher temperature process, the typical values for the other ketones being 0.20 ±0.05. Although these values are low, the relatively higher values even at lower temperatures (∿140 - 200K) would be more reasonable for intramolecular processes.

Most of the above considerations favour the suggestion that the dielectric absorption of the aryl-alkyl ketones in polystyrene matrices is due to intramolecular motion, probably involving the rotation of the carbonyl group with one or more segments from the alkyl substituents. It is possible that a different number of carbon atoms up to the maximum number for a particular substituent is involved in the relaxation, and that the observed process is probably the average of

all the different absorptions. This is possibly the reason that a certain degree of variation in relaxation times and activation parameters among the different members of the series has been observed. It is also notable that the energy barriers have been somewhat less than those for acetyl group rotation in acetophenone, which may suggest that the intramolecular motion of a segment is relatively free, probably, on account of the lack of any entanglement of the alkyl part with the polymer chain. This would effectively shield the dipole reorientation from the influence of the surrounding medium without which a rotating unit may have to overcome greater resistance owing to the viscosity of the medium.

Two other ketones, viz. 3-nonanone ($C_6H_{13}COC_2H_5$) and 8-pentadecanone ($C_7H_{15}COC_7H_{15}$), in which both sides of the polar carbonyl group are attached to the alkyl substituents, have been studied in polystyrene matrices. The latter molecule is comparable in size to that of octanophenone, but its shape may be significantly different owing to the greater flexibility of the alkyl substituents on either side. The relaxation times and the activation parameters for a single absorption of each of these solutes are also given in Table IV-1. It can be seen that the free energies of activation as well as the relaxation times at different temperatures are, in general, significantly lower than the corresponding values of the phenylalkyl ketones. For 3-nonanone, the enthalpy of activation (23 kJ mol^{-1})

is slightly lower, and the entropy of activation (42 JK^{-1} mol^{-1}) is a little higher, while the free energies of activation (16.2 kJ mol^{-1} at 150K) are considerably lower than those of the other systems. The relaxation time of 8.5 ps at 300K is remarkably comparable to those of 6.5 ps obtained by Crossley[6] in cyclohexane solution at 25°C and of 6.8 - 10.2 ps obtained by Madan[5] in solutions of different solvents at 20°C. These workers suggested that the dipole reorientation occurred to a significant degree by intramolecular rotation of the terminal carbonyl group although the possibility of an overall molecular orientation or of an overlap of the molecular and the intramolecular rotation was pointed out. A similar situation probably exists in the polymer matrix, but it appears that the intramolecular process is more likely to have been observed, for which the energy barriers would be expected to be lower, since there is no extra conjugation of the carbonyl p-electron with any aromatic π-system as in the phenylalkyl ketones.

It is again difficult to distinguish clearly the mechanism of the dielectric absorption for 8-pentadecanone in a polystyrene matrix. For this system, the enthalpy of activation (26 kJ mol^{-1}) and the free energies of activation (20.2 kJ mol^{-1} at 150K) are relatively higher than those for 3-nonanone but still lower than the corresponding values of 28 and 26.2 kJ mol^{-1}, respectively, for octanophenone. The relaxation time of 5.9×10^{-11} s at 300K is only

about three and a half times longer than the solution value of 17.1×10^{-12} s at $20^{o}C$, but it would have been expected to be much longer for a molecular process in the matrix. Moreover, the significantly lower free energies of activation compared to those of octanophenone would appear to indicate that similar intramolecular relaxations have been observed, while the higher barriers compared to those of 3-nonanone are probably due to the involvement of larger segments from either side of the polar group. In addition, the inductive and steric effects of the long alkyl substituents may be responsible for increasing the energy barriers for 8-pentadecanone. Further it should be mentioned that the effective dipole moments of 1.13 - 1.23 D are comparable to those obtained for the aryl-alkyl ketones, while the β values of 0.29 - 0.36 at relatively lower temperatures (124 - 149K) are even greater than those observed for any other ketones, suggesting further the intramolecular nature of the dielectric relaxation of this symmetrical ketone. However, it may be summarized that, in general, intramolecular processes have been observed for all the ketones studied in polystyrene matrices and that except for undecanophenone above room temperatures there has been no other absorption, indicating that the dipoles relax solely by a single process.

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CHAPTER V

DIELECTRIC RELAXATION OF SOME ACETYL SUBSTITUTED HETEROCYCLIC MOLECULES

INTRODUCTION:

Heterocyclic molecules containing rotatable polar groups have received little attention in dielectric studies while n.m.r. spectroscopy has proved to be a valuable tool for studying intramolecular motions in such systems. In several cases, σ-bonds attached to carbonyl groups have some π-character. Energy barriers to rotation about such bonds have often been estimated by proton spectroscopy.[1,2,3] Comparatively high values for the barrier to internal rotation about single bonds have been observed in a number of molecules including acetyl substituted aromatic ones. In many cases, the main contributor to the barrier has been assumed to be conjugative interaction between π-electrons on both sides of the single bond that exhibits restricted rotation. Restricted rotation about the C — N bond in N,N-dimethylformamide and its analogues[4] is among the most extensively investigated by n.m.r. spectroscopy. The barrier to internal rotation of this type has generally been ascribed to the partial double bond character of the C — N bond of the amide group. The C — N bond of 1-acetylpyrroles is also known to possess similar double bond character. Consequently, the barrier to acetyl group rotation in such compounds has been found[5] to be as high as 55 - 59 kJ mol^{-1}, estimated for the free energies of

activation at coalescence temperatures. On the other hand, significant reduction of the barrier to rotation about the C — N bond is also known to occur in a variety of systems as has been explained by Bushweller et al.[6] The polymer matrix technique has already been shown[7] to yield energy barriers comparable to those from n.m.r. studies. Therefore, it seemed desirable to examine dielectrically in polystyrene matrices some heterocyclic molecules with acetyl substituents. Of particular interest would be the energy barriers to group relaxation since Fong and Smyth[8] pointed out that ΔH_E is related to the resonance energy which governs the group rotation. Thus, any appreciable enhanced conjugation of the acetyl group with the ring should be reflected in enhanced energy barriers over those found in acetophenone and like molecules.

DISCUSSION:

Several pyridines and other simple heterocycles containing acetyl groups have been studied. The former molecules are analogous to the aromatic acetophenone, in which the effect of conjugation at different positions with respect to the heteroatom in the ring may also be observed. The Eyring analysis results of the various substituted heterocyclic molecules

TABLE V-1 EYRING ANALYSIS RESULTS FOR ACETYL SUBSTITUTED HETEROCYCLIC MOLECULES

Molecule	T(K)	τ(s)			ΔG_E(kJ mol^{-1})			ΔH_E	ΔS_E
		150K	200K	300K	150K	200K	300K	(kJ mol^{-1})	(JK^{-1} mol^{-1})
2-Acetylpyridine	171 - 203	8.1×10^{-3}	1.0×10^{-5}	1.1×10^{-8}	29.9	29.2	27.8	32	14
3-Acetylpyridine	165 - 196	6.7×10^{-3}	4.6×10^{-6}	2.8×10^{-9}	29.6	27.9	24.4	35	35
4-Acetylpyridine	154 - 177	5.8×10^{-4}	6.5×10^{-7}	6.6×10^{-10}	26.6	24.6	20.8	32	39
2,6-Diacetyl-pyridine	165 - 209	3.7×10^{-3}	1.2×10^{-5}	3.6×10^{-8}	28.9	29.5	30.8	27	-13
N-Acetyl-imidazole	126 - 158	2.5×10^{-5}	1.6×10^{-7}	9.2×10^{-10}	22.7	22.3	21.6	24	-7
"	240 - 297	3.9×10^{3}	1.2×10^{-1}	3.5×10^{-6}	46.2	44.9	42.2	50	27
N-Acetyl-pyrrolidine	141 - 182	2.4×10^{-4}	1.1×10^{-6}	4.6×10^{-9}	25.5	25.6	25.6	25	- 1
N-Acetyl-4-piperidone	179 - 212	2.7×10^{-1}	3.2×10^{-5}	3.4×10^{-9}	34.2	31.1	24.9	44	62
"	307 - 333	1.1×10^{14}	2.9×10^{5}	6.9×10^{-4}	76.2	69.2	55.3	97	139

are shown in Table V-1 from which it is evident that a wide range of energy barriers has been obtained.

Before a detailed discussion of the results is given, it would appear necessary to consider the theoretical weight factor calculations since these parameters sometimes throw considerable light on the nature of the process causing the dielectric absorption and may help to distinguish group from molecular processes or from an overlap of the two. This has been attempted only for the 2-, 3-, and 4-acetylpyridines, each of which shows a single absorption although both molecular and group processes may seem probable. With acetophenone as the parent molecule and the assumption that the group is free to rotate, the dipole moment for this type of molecule can be resolved into two components, one along the major symmetry axis and the other perpendicular to it. The latter component is free to rotate intramolecularly while relaxation of the other involves the rotation of the whole molecule. Acetylpyridines may be regarded as substituted acetophenones, in which the substituent nitrogen atom is placed at different positions in the ring. For the 4-acetylpyridine, the treatment is similar to that mentioned for acetophenone in the previous chapter, except that the molecular component ($\mu_{\parallel}$) will be reduced owing to the moment of N acting

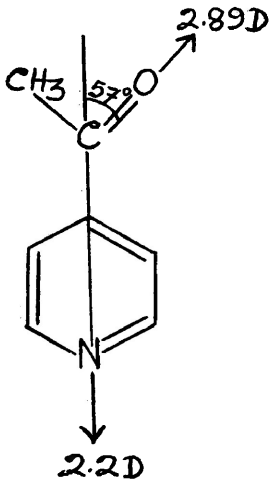
in the opposite direction, while the component associated with the group rotation ($\mu_{\perp}$) will remain unchanged since the resultant dipole of the substituent is along the same major axis. In the case of 2- and 3-acetylpyridines, the molecular component of the moment no longer lies along the axis of group rotation. The contributing moments are now resolved into three components, a molecular moment (μ_1) along the major symmetry axis, another rigid moment (μ_3) at right angles to this, and the rotating group moment (μ_2) again at right angles to the main symmetry axis. The dipole moment corresponding to the overall molecular rotation is now the resultant of the two rigid moments. The molecular weighting factor is, therefore, given by:

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2}$$

The details of the calculation of the weight factors for the molecular (C_1) and group rotations (C_2) are shown in Figure V-1. This is based on the group moment[14] of μ_{COCH_3} = 2.89 D and the angle of inclination[14] of the group to the principal axis as 57^o while the moment due to nitrogen has been taken as 2.2 D for pyridine[15] itself. The calculations show that the contribution to the dielectric absorptions from group process (C_2) follows the

FIG. V-1 Calculation of weight factors for mono-acetyl-pyridines

(a) 4-Acetylpyridine



$\mu_{\parallel}$ = 2.2 - 2.89 cos 57

= 0.626 D

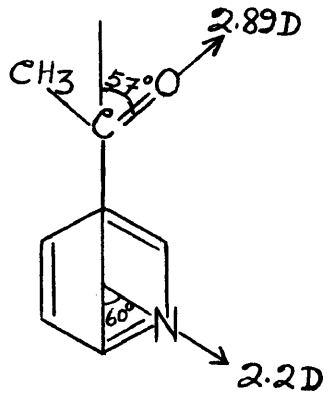
$\mu_{\perp}$ = 2.89 sin 57

= 2.424 D

$$C_2 = \frac{\mu_{\perp}^2}{\mu_{\parallel}^2 + \mu_{\perp}^2} = 0.94$$

$C_1 = 1 - C_2 = 0.06$

(b) 3-Acetylpyridine



μ_1 = 2.89 cos 57 - 2.2 cos 60

= 0.474 D

μ_2 = 2.89 sin 57

= 2.424 D (mobile)

μ_3 = 2.2 sin 60

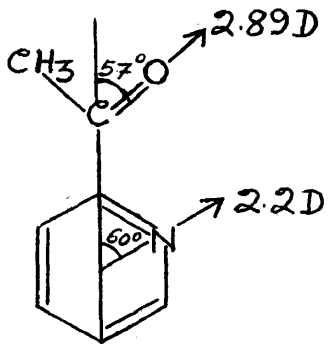
= 1.905 D (fixed)

FIG. V-1 cont'd...

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.40$$

$$C_2 = \frac{\mu_2^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.60$$

(c) <u>2-Acetylpyridine</u>



μ_1 = 2.2 cos 60 + 2.89 cos 57

= 2.674 D

μ_2 = 2.89 sin 57

= 2.424 D (mobile)

μ_3 = 2.2 sin 60

= 1.905 D (fixed)

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.65$$

$$C_2 = \frac{\mu_2^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.35$$

order 4- > 3- > 2-acetylpyridine, and conversely the molecular weight factor (C_1) decreases from 2-acetylpyridine to 4-acetylpyridine. The high C_2 value of 0.94 for 4-acetylpyridine suggests that there should be little contribution from the molecular process to the overall absorption. 2-Acetylpyridine shows a C_2 value of only 0.35, and, therefore, the molecular process should be predominant. In the case of 3-acetylpyridine, the molecular and the group weight factors of C_1 = 0.40 and C_2 = 0.60, respectively, are more comparable to each other so that the dielectric absorptions associated with the two relaxation processes should have approximately equal intensities.

The results obtained for the mono-substituted acetylpyridines may be examined with respect to theoretical predictions. In systems where there is no enhanced conjugation, e.g., in acetophenone, 1,4-diacetylbenzene and 4-acetylbiphenyl, McLellan and Walker[9] have reported that the acetyl group relaxation was characterized by enthalpies of activation in the range of 27 - 30 kJ mol^{-1} and entropies of activation in the range of 26 - 36 JK^{-1} mol^{-1} while ΔG_E at 200K ranged from 21.5 to 24.4 kJ mol^{-1}. Similar results were obtained for the intramolecular rotation involving the carbonyl group of aryl-alkyl ketones discussed in the previous chapter. In the case of 4-acetylpyridine, the free energy of activation at 200K of 24.6 kJ mol^{-1} is similar to those of the acetyl group

relaxation in acetophenone and the related molecules. The activation enthalpy and entropy of 32 kJ mol^{-1} and 39 JK^{-1} mol^{-1}, respectively, are slightly higher but still may be considered similar within the experimental accuracy. Moreover, the upper limits of such parameters for the molecular process would be considerably lower. For example, values of ΔH_E = 25 kJ mol^{-1} and ΔS_E = 8 JK^{-1} mol^{-1} were obtained for p-t-butylpyridine (Table III-4). It is to be noted that the relaxation times and the ΔG_E values are the most reliable parameters, particularly in the middle of the experimental temperature range, since they are the measured values and can be deduced directly from the frequencies at which maximum abosrption occur. The absorptions of 4-acetylpyridine and p-t-butylpyridine were measured in the temperature range of 154 - 177K and 146 - 175K, respectively. For the purpose of comparison, the activation free energy of 26.6 kJ mol^{-1} at 150K for the former is found to be higher than the corresponding value of 24.1 kJ mol^{-1} for the rigid molecule. Similarly the relaxation time of 5.8 x 10^{-4} s at 150K of 4-acetylpyridine is longer than the corresponding value of 8.1 x 10^{-5} s for p-t-butylpyridine which is, in fact, a larger molecule. Therefore, the data for 4-acetylpyridine would seem to characterize the group rotation. But the temperature range of absorption for the rigid molecule is practically the same as that for the 4-acetylpyridine so that some overlap of the group and

molecular processes for the latter may be anticipated. However, since $\mu_{\perp} >> \mu_{\parallel}$, the acetyl group relaxation would be expected to predominate as reflected in the high C_2 value of 0.94. This is further borne out by the observed dipole moments of 0.97 - 1.08 D (see Appendix A, Table 6) which on extrapolation at 300K gave ∿1.9 D. This value is smaller than the literature[16] value of 2.41 D but is too large for the molecular component ($\mu_{\parallel}$) of 0.63 D as shown in Figure V-1. The dielectric absorption of 4-acetylpyridine may therefore be attributed reasonably to the group relaxation.

In the case of 2- and 3-acetylpyridines, the enthalpies of activation were found to be 32 and 35 kJ mol^{-1}, respectively. The activation entropy of 14 JK^{-1} mol^{-1} for 2-acetylpyridine is lower than that of 35 JK^{-1} mol^{-1} for 3-acetylpyridine. The free energies of activation at 200K of 29.2 and 27.9 kJ mol^{-1}, respectively, are higher than the corresponding value of 24.6 kJ mol^{-1} for 4-acetylpyridine. In addition, the relaxation times of 1.0×10^{-5} s and 4.6×10^{-6} s for 2- and 3-acetylpyridine, respectively, at 200K are longer than that of 6.5×10^{-7} s for 4-acetylpyridine at the same temperature. On the other hand, the upper limits of the activation parameters for the molecular process, as given by ΔH_E = 17 kJ mol^{-1} and ΔS_E = -30 JK^{-1} mol^{-1} for o-t-butylpyridine

(Table III-4), are significantly lower than the corresponding values for 2-acetylpyridine. The free energy of activation at 200K of 22.6 kJ mol^{-1} for the former is also lower by about 7 kJ mol^{-1} than that of the latter, the absorptions being measured at 119 - 162K and 171 - 203K, respectively. Likewise, the activation parameters for 3-acetylpyridine differ from those of ΔH_E = 21 kJ mol^{-1}, ΔS_E = 2 JK^{-1} mol^{-1}, and ΔG_E = 21 kJ mol^{-1} at 200K for 3-bromopyridine (Table III-4). The absorption of 3-acetylpyridine was also observed at a considerably higher temperature range (165 - 196K) than that of 3-bromopyridine (117 - 155K), and the relaxation time of 6.7 x 10^{-3} s for the former is much longer than the value of 7.3 x 10^{-6} s for the latter, both values being taken at 150K. Evidently, the results for the two rigid molecules, i.e., of o-t-butylpyridine and 3-bromopyridine are not in agreement with those of the analogous 2- and 3- acetylpyridines, respectively. Therefore, it would appear that the dielectric absorptions of the two latter molecules were not, at least, due solely to molecular processes. However, it is also difficult to justify only group relaxation, particularly for 2-acetylpyridine with a C_2 value of 0.35, which suggests a predominant molecular process. Alternatively, the most likely interpretation of the results especially for 2-acetylpyridine would

be that its data contain significant contributions from both molecular and group processes. In the case of 3-acetylpyridine, however, the larger C_2 value of 0.60 would lead one to expect that the group rotation was predominant. It should be mentioned that the extrapolated dipole moments for 2- and 3-acetylpyridines at 300K were found to be 2.1 D and 2.2 D, respectively, while the corresponding literature[16] values are 2.85 D and 2.53 D. The difference between the literature value and the extrapolated value for 2-acetylpyridine is quite appreciable and is probably due to a decreased contribution from the group relaxation.

It can further be noted that the relaxation times of 1.0×10^{-5} s, 4.6×10^{-6} s, and 6.5×10^{-7} s, all at 200K, of 2-, 3-, and 4-acetylpyridine, respectively, are consistent with the sequence of increasing molecular weight factor in the order 2- > 3- > 4-acetylpyridine. A similar trend is also found in the free energies of activations at 200K of 29.2, 27.9, and 24.6 kJ mol^{-1}, respectively. In terms of ΔH_E values, however, the relatively higher activation enthalpy of 35 kJ mol^{-1} for the 3-acetylpyridine may reflect some enhanced conjugation at the 3-position leading to an increased barrier to group rotation. This may also be supported by the carbonyl stretching frequencies of 1710, 1700, and 1708 cm^{-1} observed for 2-, 3-, and 4-acetylpyridines, respectively. It can be noted that the literature[10] value of

1706 cm^{-1} for 4-acetylpyridine is in reasonable agreement with the present value of 1708 cm^{-1}, both in the $CC\ell_4$ solutions. The variation of carbonyl stretching frequency reflects, at least qualitatively, the extent of conjugation between the carbonyl carbon and the ring carbon since it is well known[11] that conjugation has an effect upon the force constant of a group with π-electrons. It must, however, be recognized that the activation energy barriers obtained from an overlapping absorption may not be very meaningful. Therefore, the question of an enhanced conjugation in the mono-acetylpyridines may not be settled conclusively by the present work.

The single absorption of 2,6-diacetylpyridine showed an activation enthalpy of 27 kJ mol^{-1}, which would not be unreasonable for the group relaxation, while the free energy of acivation of 29.5 at 200K is higher and the entropy of activation of -13 JK^{-1} mol^{-1} is much lower than those for the acetyl group rotation as characterized by McLellan and Walker.[9] On the other hand, these results for 2,6-diacetylpyridine are comparable to the corresponding values of ΔH_E = 29 kJ mol^{-1}, ΔG_E = 30.3 kJ mol^{-1} at 200K, and ΔS_E = -6 JK^{-1} mol^{-1} obtained for m-diiodobenzene (Table III-2) which may be considered to be of similar size. Both 2,6-diacetylpryidine and m-diiodobenzene showed absorption in

similar temperatures (165 - 223K), and frequency ranges and their relaxation times, e.g., of 1.2×10^{-5} s and 2×10^{-5} s at 200K, respectively, were very similar within this range. It may also be mentioned that acetyl group relaxation in 2- and 3-acetylphenanthrenes (Chapter VI) has been observed with similar ΔH_E values of 28 - 30 kJ mol^{-1}, but ΔS_E values are noticeably lower (almost zero), with the result that ΔG_E values are appreciably greater (27 - 29 kJ mol^{-1} at 200K) than in the cases of acetophenone, 1,4-diacetylbenzene and 4-acetylbiphenyl as studied by McLellan and Walker.[9] Therefore, it is difficult to decide which of the processes, viz., molecular or group rotation contributes most to the dielectric absorption of 2,6-diacetylpyridine. The effective dipole moments of 0.31 - 0.35 D obtained from this absorption in the temperature range of 165 - 209K were very low and decreased with increasing temperature (see Appendix A, Table 6) so that the extrapolation was not feasible while the β values of 0.15 - 0.28 showed considerable dependence on temperature as would be more reasonable for a molecular processes. However, the weight factor (C_2) for the group rotation would be expected to be larger than 0.35 as calculated for 2-acetylpyridine since there would be contributions from another group at the 6-position of 2,6-diacetylpyridine. This, in turn, would reduce the molecular weight

factor (C_1), and, hence, the two might be comparable to each other so that the contribution from both the processes to the overall absorption is equally likely.

Several heterocyclic molecules were chosen in which the substituent acetyl group is directly attached to the heteroatom. The Eyring analysis results obtained for the dielectric absorptions of such systems, viz., N-acetylimidazole, N-acetylpyrrolidine, and N-acetyl-4-piperidone in polystyrene matrices are also given in Table V-1. Only one absorption was observed for N-acetylpyrrolidine while the other two molecules showed two separate absorptions. It can be seen from Table V-1 that the relaxation times and activation energies are widely different between the two absorptions in either N-acetylimidazole or N-acetyl-4-piperidone. The higher temperature process observed for the former molecule occurred between 240 - 297K, showing activation enthalpy and entropy of 50 kJ mol^{-1} and 27 JK^{-1} mol^{-1}, respectively. The enthalpy of activation is in good agreement with that of 48 kJ mol^{-1} obtained by McLellan[12] for the acetyl group rotation in N-acetylindole studied in a polystyrene matrix. The free energies of activation of 44.9 and 42.2 kJ mol^{-1} at 200K and 300K, respectively, are significantly higher, and the corresponding relaxation times at these temperatures are much longer than those obtained for the

intramolcular processes involving the carbonyl group as discussed in Chapter IV. It is not surprising that a higher energy barrier to group rotation has been found in the imidazole system since the presence of a non-bonding electron pair from the nitrogen atom would increase the π-electron density at the bond between the acetyl substituent group and the ring. Similarly high activation energy barriers of ∿50 kJ mol^{-1} have also been observed for the acetyl group rotation in N-acetylpyrrole from n.m.r. studies by Dahlqvist and Forsen.[13]

The lower temperature absorption of N-acetylimidazole yielded activation enthalpy and entropy of 24 kJ mol^{-1} and 7 JK^{-1} mol^{-1}, respectively. These results may be compared with the corresponding values of 19 kJ mol^{-1} and -25 JK^{-1} mol^{-1} for iodobenzene (Table III-1) which is, in fact, slightly larger in size. Although the values of ΔH_E and ΔS_E for N-acetylimidazole are higher than those of iodobenzene, the free energy of activation of 22.7 kJ mol^{-1} at 150K of the former is in good agreement with that of 22.4 kJ mol^{-1} for the latter at the same temperature, the absorptions having been observed at the similar temperature ranges of 126 - 158K and 134 - 161K, respectively. Therefore, it is reasonable that the lower temperature absorption of N-acetylimidazole be assigned to the molecular process while the higher temperature one is due to the acetyl group rotation around

C — N bond, showing much higher activation energies and longer relaxation times than those observed in systems where there is no enhanced conjugation, e.g., in acetophenone, 1,4-diacetylbenzene, and 4-acetylbiphenyl.[9]

The single absorption of N-acetylpyrrolidine showed activation enthalpy of 25 kJ mol^{-1} with almost zero entropy of activation. The molecule is similar in shape and size to 1-acetylimidazole and may also be compared with iodobenzene for the relaxation parameters to be expected for a molecular process. The absorption of N-acetylpyrrolidine was measured at a higher temperature range of 141 - 182K than that of 126 - 158K for the molecular relaxation (low temperature absorption) of N-acetylimidazole. The activation enthalpy of the former agrees very well with that of 24 kJ mol^{-1} for the latter while the activation free energies of 25.5 kJ mol^{-1} and 22.7 kJ mol^{-1}, respectively, at 150K differ to some extent.

The relaxation time of 2.4×10^{-4} s at 150K for N-acetylpyrrolidine is appreciably longer than the corresponding value of 2.5×10^{-5} s for N-acetylimidazole and longer also than that of 2.1×10^{-5} s for iodobenzene, for which the activation

enthalpy (19 kJ mol^{-1}) is considerably lower. Therefore, it might be inferred that the absorption of N-acetylpyrrolidine was not solely due to a molecular process, especially when no other absorption was found over the temperature range of 80 - 350K. In contrast, the activation energies obtained for N-acetylpyrrolidine (25 - 26 kJ mol^{-1}) are much lower than those of $\sim$50 kJ mol^{-1} for the acetyl group rotation in N-acetylpyrrole as observed from n.m.r. studies[13] while the entropies of activation are similar, being nearly zero in either case. The difference in activation energies may, however, be due to the effect of saturation in the former molecule. Similar behaviour in a number of other systems was explained by Bushweller and his co-workers.[6] It seems possible that the significant lowering of energy barriers to acetyl group rotation is the result of the effective delocalization of the nitrogen lone pair into the pyrrole ring with consequent lowering of π-bonding across the carbonyl carbon to nitrogen bond. Hence, it would appear that the acetyl group rotation in N-acetylpyrrolidine is faster than that in the strongly conjugated N-acetylpyrrole or N-acetylimidazole. This and the observed low β values of 0.15 - 0.17 (see Appendix A, Table 6) suggest the possibility of some overlap with the molecular process in N-acetylpyrrolidine. This is probably more evident from the effective dipole moments of 1.05 - 1.47 D observed between 141 - 182K, which are, in fact, typical values for

the acetyl group relaxation, but the extrapolated value of 2.73 D at 300K exceeds the value that would be expected for the group component while the literature value[15] of 4.3 D is still higher.

N-acetyl-4-piperidone showed different results compared to those of N-acetylimidazole and N-acetylpyrrolidine although two absorptions were noted for the former. The lower temperature absorption was measured in the range of 179 - 212K, and it yielded an activation enthalpy of 44 kJ mol^{-1}. This value is 6 kJ mol^{-1} lower than that observed for the acetyl group rotation in N-acetylimidazole while the free energy of activation of 31.1 kJ mol^{-1} at 200K is about 14 kJ mol^{-1} lower than the corresponding value for the imidazole derivative. The reduction of barriers would not be unexpected for the group rotation since the system is more or less saturated. But compared to N-acetylpyrrolidine (ΔH_E = 25 kJ mol^{-1}) the activation enthalpy of 44 kJ mol^{-1} obtained for the lower temperature absorption of N-acetyl-4-piperidone is considerably higher. The former shows almost constant activation free energies of $\sim$26 kJ mol^{-1} at different temperatures as the entropy is about zero (-1 JK^{-1} mol^{-1}) while the latter being associated with much higher activation entropy of 62 JK^{-1} mol^{-1} shows a decrease of activation free energy from 34.2 kJ mol^{-1} at 150K to 24.9 kJ mol^{-1} at 300K. However, because the absorption of

N-acetylpyrrolidine may be due to some overlap of both molecular and group relaxations, its data cannot be considered as the standards for acetyl group rotation around the C — N bond in a saturated system. On the other hand, the activation energy barriers, particularly the enthalpy of activation of 44 kJ mol^{-1} obtained from the lower temperature absorption of N-acetyl-4-piperidone, appear to be too high compared to the value of ΔH_E = 25 kJ mol^{-1} for the molecular relaxation of the rigid molecule, p-t-butylpyridine (Table III-4). The free energy of activation of 34.2 kJ mol^{-1} at 150K for the former is also considerably higher than the corresponding value of 24.1 kJ mol^{-1} for the latter while the absorptions were observed in different temperature ranges of 179 - 212K and 146 - 175K, respectively. Therefore, it seems likely that the acetyl group relaxation has been observed in N-acetyl-4-piperidone with somewhat lower energy barriers than those observed for the group rotation in N-acetylimidazole. It should further be noted that the effective dipole moments obtained from the lower temperature absorption of the former molecule showed little variation with temperature and did not increase consistently, but the observed values of $\sim$1.4 D (see Appendix A, Table 6) appear to be reasonable for the group relaxation.

The higher temperature absorption of N-acetyl-4-

piperidone was measured in the range of 307 - 333K, and it tended to overlap with the lower temperature process. In each case, the Fuoss-Kirkwood analysis was carried out by deleting the points which did not fit into a symmetric loss curve (cf: Figure II-3). In spite of this approximation, the frequencies at which maximum absorption occurred might not have been estimated accurately so that the activation parameters from the subsequent Eyring analysis for either of the absorptions may not be as accurate as in simpler cases. However, the higher temperature process yielded activation enthalpy and entropy of 97 kJ mol^{-1} and 139 JK^{-1} mol^{-1}, respectively. These values would seem to be too high either for a molecular or group process but may be accounted for by the cooperative motion of the molecule with the polymer chain. Similar behaviour has been observed in a number of other cases, and these have been described by an equation relating the activation enthalpy and entropy, as was given for undecanophenone in the previous chapter.

To summarize, then, it would appear that acetyl group relaxation has been characterized in 4-acetylpyridine while the results for 2- and 3-acetylpyridine and for 2,6-diacetylpyridine are not straightforward. Significantly higher energy barriers to acetyl group rotation around the C — N bond have been observed

in N-acetylimidazole. In the case of N-acetyl-4-piperidone, this barrier appears to have been reduced considerably owing to the effect of saturation, but such behaviour could not be resolved properly for N-acetylpyrrolidine since the single absorption of the latter may have contributions from both molecular and group relaxations.

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CHAPTER VI

INTRAMOLECULAR AND MOLECULAR RELAXATION OF VARIOUS ACETYL/CARBONYL COMPOUNDS

INTRODUCTION:

In the preceeding two chapters, dielectric absorption in polystyrene matrices of two different types of simple flexible molecules have been considered. It was indicated that the barriers to intramolecular rotations involving carbonyl groups, in general, and of acetyl groups, in particular, depend to some extent on the conjugation of carbonyl p-electrons with the aromatic or ring π-electron system. It is also of interest to investigate such processes in some systems where the barrier would be free from the effect of any conjugation. Various other factors are also known to affect the energy barriers and the associated dielectric absorptions. The effect of the size of the polar substituent group and of the substituted nucleus may be observed in the polystyrene matrix systems. However, the former is limited by the unwanted flexibility of a larger rotating group while the latter may be facilitated by the separation of the absorptions into group and molecular processes. Recent works in this laboratory[1-3] have indicated that the relaxation of a substituent group may well be separated from that of the molecule if the solute is examined in a polystyrene matrix at low temperatures. Moreover, the technique was found particularly suitable for the study of fused ring systems, e.g., naphthalenes, phenanthrenes, and anthracenes with a flexible

substituent.[2,3]

Acetyl substituted fused ring molecules have been closely considered for solution studies in the microwave region, but in a number of cases the relaxation mechanisms are not clearly understood. For example, Fong and Smyth[4-6] studied the dielectric relaxation of 2-acetylnaphthalene in benzene solutions. The analysis of their data in terms of two relaxation times consistently yielded a weight factor $C_2 \simeq 0.14$ for the acetyl group relaxation which is markedly less than that of 0.6 ±0.1 reported by Farmer et al.[7] for acetophenone. Theoretical calculations for acetophenone based on group or bond moments yielded[7] expected C_2 values of 0.67 and 0.49, respectively. It was suggested by Fong and Symth that the reduced contribution, i.e., smaller C_2 value, from acetyl group rotation might be due particularly to enhanced resonance at the 2-position of the naphthalene nucleus, and that it would be linked to an increased energy barrier to such a motion in 2-acetylnaphthalene as compared to acetophenone. Since the molecules which can further be increased to those of phenanthrenes, differ considerably in size, it seems possible to characterize acetyl group relaxation in such compounds dispersed in polystyrene matrices and possibly to correlate the activation parameters with the findings from solution studies.

DISCUSSION:

With the above considerations in mind, several different carbonyl/acetyl substituted molecules from the simple cyclohexane derivatives to the large fused ring phenanthrenes have been studied. The Eyring analysis results for all such systems are presented in Table VI-1. Acetyl groups attached to the saturated ring systems, viz., cyclohexane, norbornene and adamantane, and the $-CH_2COCH_3$ substituent attached to a cyclohexane ring were considered to provide the basis for group rotation barriers in systems which are somewhat similar to the aliphatic ones. The size of the molecules are appreciably different, but 1-adamantyl methyl ketone and 2-acetyl-5-norbornene yielded the same activation enthalpy of 23 kJ mol^{-1} for acetyl group relaxation. The entropies of activation are quite similar to that of acetyl group rotation in acetophenone, but the relaxation times and the free energies of activation at experimental temperatures are considerably lower as could be expected in accordance with lower energy barriers to rotation of groups in systems which are not attached to a conjugated one. These results coupled with those for the rigid molecule 1-adamantanecarbonitrile, analogous to the larger of the two, with activation enthalpy of

TABLE VI-1 EYRING ANALYSIS RESULTS FOR VARIOUS ACETYL/CARBONYL COMPOUNDS

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300 K	ΔG_E(kJ mol^{-1}) 150 K	ΔG_E(kJ mol^{-1}) 200 K	ΔG_E(kJ mol^{-1}) 300 K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
Cyclohexyl-methyl ketone	109 - 144	1.5×10^{-6}	1.8×10^{-8}	1.9×10^{-10}	19.2	18.7	17.6	21	10
"	231 - 265	5.2×10^{2}	1.7×10^{-2}	5.0×10^{-7}	43.7	41.6	37.3	50	43
Cyclohexyl iodide	115 - 145	1.2×10^{-6}	1.2×10^{-8}	9.7×10^{-11}	18.9	17.9	16.0	22	19
"	271 - 303	2.3×10^{3}	1.2×10^{-1}	5.1×10^{-6}	45.6	44.7	43.1	48	17
Cyclohexyl-acetone	113 - 136	5.3×10^{-7}	1.8×10^{-9}	5.4×10^{-12}	17.9	14.8	8.8	27	61
"	188 - 213	1.3×10^{1}	7.0×10^{-5}	3.4×10^{-10}	39.1	32.4	19.1	59	133
Cyclohexyl-methyl bromide	138 - 169	7.4×10^{-5}	4.4×10^{-7}	2.3×10^{-9}	24.0	24.0	23.9	24	?
2-Acetyl-5-norbornene	116 - 141	1.2×10^{-6}	8.7×10^{-9}	5.6×10^{-11}	18.9	17.4	14.6	23	29
1-Adamantyl-methyl ketone	130 - 150	3.4×10^{-6}	2.5×10^{-8}	1.6×10^{-10}	20.2	19.2	17.3	23	20
Cyclopropyl-phenyl ketone	141 - 175	1.5×10^{-4}	1.0×10^{-6}	6.1×10^{-9}	24.9	25.4	26.3	24	- 9
1,1-Diphenyl-acetone	238 - 271	2.9×10^{5}	1.9×10^{-1}	1.1×10^{-7}	51.6	45.6	33.6	70	120
1,3-Diphenyl-acetone	113 - 133	2.1×10^{-7}	1.3×10^{-9}	6.8×10^{-12}	16.7	14.3	9.4	24	49
"	290 - 309	3.6×10^{21}	1.9×10^{8}	9.0×10^{-6}	97.8	80.0	44.5	151	355

TABLE VI-1 EYRING ANALYSIS RESULTS FOR VARIOUS ACETYL/CARBONYL COMPOUNDS continued...

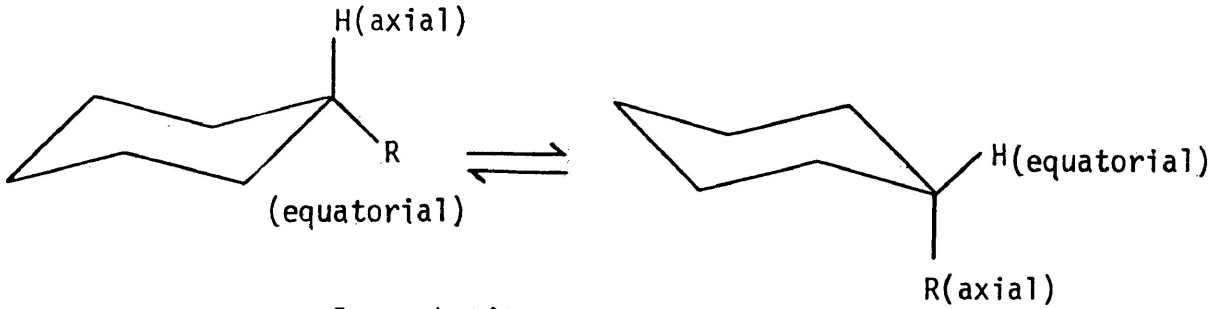
Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150 K	ΔG_E(kJ mol^{-1}) 200 K	ΔG_E(kJ mol^{-1}) 300 K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
Mesityl oxide	144 - 169	1.5×10^{-4}	2.1×10^{-7}	2.7×10^{-10}	24.9	22.8	18.5	31	43
1-Acetylcyclo-hexene	154 - 209	3.6×10^{-4}	7.7×10^{-7}	1.4×10^{-9}	26.0	24.9	22.7	29	22
p-N,N-Dimethyl-aminoacetophenone	244 - 301	3.6×10^{3}	1.3×10^{-1}	4.1×10^{-6}	46.1	44.9	42.6	50	24
2-Acetyl-1-tetralone	244 - 275	5.2×10^{4}	2.1×10^{-1}	7.6×10^{-7}	49.4	45.7	38.3	61	74
2-Acetyl-naphthalene	202 - 232	2.6×10^{0}	2.4×10^{-3}	1.9×10^{-6}	37.1	38.3	40.6	34	-24
	242 - 277	4.0×10^{6}	2.3×10^{-1}	1.2×10^{-8}	54.8	45.9	28.0	82	179
2-Acetyl-phenanthrene	157 - 187	1.3×10^{-3}	3.5×10^{-6}	8.0×10^{-9}	27.6	27.4	27.0	28	4
"	304 - 333	1.7×10^{12}	4.6×10^{4}	1.1×10^{-3}	71.0	66.2	56.5	86	97
3-Acetyl-phenanthrene	165 - 206	5.4×10^{-3}	1.0×10^{-5}	1.7×10^{-8}	29.4	29.2	28.9	30	3
"	294 - 323	1.4×10^{12}	3.1×10^{-4}	5.9×10^{-4}	70.8	65.5	55.0	87	106

16 kJ mol^{-1} and activation entropy of -35 JK^{-1} mol^{-1} (Table III-1) suggest that acetyl group rotation has been observed in 1-adamantyl methyl ketone and in 2-acetyl-5-norbornene although molecular relaxation and/or overlap with the group one is not improbable.

Cyclohexylmethyl ketone, cyclohexylacetone, as well as cyclohexyl iodide have shown two absorptions clearly, while for cyclohexylmethyl bromide only one absorption has been measured in the range of 138 - 169K. The lower temperature absorption of cyclohexylmethyl ketone gives activation enthalpy and entropy of 21 kJ mol^{-1} and 10 JK^{-1} mol^{-1}, respectively. These as well as the free energies of activation and the relaxation times are correspondingly similar to those for the molecular relaxation process observed for cyclohexyl iodide at the same temperature ranges. The low β values of 0.10 - 0.13 (see Appendix A, Table 7) for cyclohexylmethyl ketone are comparable to those of 0.13 - 0.16 for cyclohexyl iodide. This suggests a molecular relaxation process for the former case. Moreover, the relaxation time of 1.5×10^{-6} s at 150K is much shorter than the corresponding value of 6.8×10^{-4} s for acetophenone. On the other hand, the results are in reasonable agreement with those of 1-adamantyl methyl ketone and of 2-acetyl-5-norbornene with ΔH_E = 23 kJ mol^{-1} and ΔG_E = 19 - 20 kJ mol^{-1} at 150K. It is notable that the acetyl group rotation in cyclohexylmethyl ketone would experience some steric hindrance due to its

C(1) - H. Therefore, it would appear that the lower temperature absorption of cyclohexylmethyl ketone is more likely to be due to a molecular process while the possibility of a group rotation or of an overlap between the two cannot be ruled out.

The higher temperature absorption of cyclohexylmethyl ketone (231 - 265K) is clearly due to intramolecular ring inversion for which results are in good agreement with those observed by Davies and Swain[8] for cyclohexyl chloride and cyclohexyl bromide with activation enthalpies of 42 and 43 kJ mol^{-1}, respectively. Present studies of cyclohexyl iodide and cyclohexylmethyl ketone give activation enthalpies of 48 and 50 kJ mol^{-1}, respectively. The ring inversion of the cyclohexyl derivatives can be represented by the following diagram showing the two low energy chair conformations in equilibrium which, of course, involve a number of possible intermediates. It may be noted that a little



R = substituent

higher energy barrier to ring inversion of the two latter molecules is probably due to the larger size of the substituents. There are evidences[9] from n.m.r. studies that the substitutent effects upon the energy barriers to ring inversion depend directly on the effective size of the substituents. This is consistent with the activation enthalpy of 59 kJ mol^{-1} observed presently for cyclohexylacetone where the substituent group ($-CH_2COCH_3$) is larger than in any of those mentioned above. In the case of cyclohexylmethyl bromide, the higher temperature absorption, presumably due to ring inversion, was not measured since it showed complications in changing capacitance at a particular temperature. Furthermore, it was evident from the extrapolated dipole moment of $\sim$1.8 D at 300K, obtained from the low temperature absorption, that most of the dipole relaxation would occur by this process around room temperatures. Therefore, some accentuation of the amplitude of the low temperature process would diminish the intensity of the intramoleular absorption appreciably. Similar arguments were advanced by Davies and Swain[8] as to why they did not observe the intramolecular ring inversion of 1,1-dichlorocyclohexane, or of cyclohexanone which indicated only a small but not well defined absorption.

The low temperature absorption of cyclohexylmethyl

bromide showed activation enthalpy of 24 kJ mol^{-1} with almost zero entropy of activation. The β values (0.25 - 0.27) are relatively larger which would be more reasonable for an intramolecular $-CH_2Br$ group rotation. But the relaxation time of 2.3×10^{-9} s at 300K is much longer than would be expected, due only to the viscosity effect of the medium in contrast to those of the order of picoseconds observed for 1-bromoalkanes in solutions.[10] Moreover, the relaxation times at 150K and 200K are shorter than those of acetophenone (Chapter IV), but the steric effect of C(1) - H in cyclohexylmethyl bromide, combined with the fact that $-CH_2Br$ group is bigger than $-COCH_3$ could have compensated for the conjugative effect in acetophenone. In addition, the possibility exists that the steric effect would eliminate the intramolecular rotation as might be the case in cyclohexylmethyl ketone. A similar situation is apparent for the lower temperature absorption of cyclohexylacetone, but now the activation parameters are significantly different. Although the enthalpy of activation (27 kJ mol^{-1}) is slightly higher than that of cyclohexylmethyl bromide as could be expected owing to the greater size of the former, the entropies of activation are very much different and so also the free energies of activation and the relaxation times at various temperatures. Almost zero activation entropy for cyclohexylmethyl bromide is a candidate for molecular process, while the very high entropy of activation (61 JK^{-1} mol^{-1})

and the associated low activation free energies of 17.9 and 14.8 kJ mol^{-1} at 150K and 200K, respectively, for cyclohexylacetone may indicate the possibility of a predominantly different process, viz., the rotation of the $-CH_2COCH_3$ group as a whole. It is, however, difficult to assign one absorption process with any degree of certainty when there are several possibilities.

It should be noted that the effective dipole moments observed from the low temperature absorption of the various cyclohexyl derivatives fall in the range of 0.8 - 1.0 D (see Appendix A, Table 7). These values are significantly lower than those expected for the total moments, but their extrapolation yields values of the order of 2 D at 300K. For example, the low temperature values of 0.80 - 0.96 D between 115 - 145K for cyclohexyl iodide, when extrapolated to 300K, give 1.9 D, which is in good agreement with the literature[23] value of 2 D. This shows that the solute molecule would be able to reorient more completely and so exhibit its total polar moment if the absorption were pursued at higher temperatures. Further, the discrepancy between the effective molecular moment and the literature value points to the fact that the polystyrene matrix probably does not allow a complete relaxation of the dipole by the whole molecule motion. Therefore, some other absorption should be present for the cyclohexyl derivatives at frequencies

higher than those of the low temperature measurements. In fact, this was observed for the same frequency range but at higher temperatures corresponding to the ring inversion processes. For cyclohexyl iodide, this absorption was noted between 271 - 303K and the apparent dipole moment at the highest temperature was 0.57 D. An estimate of the total intensity of the two absorptions around 300K may be taken as Σ(effective dipole moment)^2, i.e., $(1.90)^2 + (0.57)^2 = 3.94$, which is in good agreement with the value $(2.0)^2 = 4.0$ for the free molecule. Similar considerations may apply for the other derivatives.

Several molecules with carbonyl substituents in other conjugated systems, viz., cyclopropylphenyl ketone, 1,3- and 1,1-diphenylacetone, have also been studied in polystyrene matrices. Only 1,3-diphenylacetone have shown two distinct absorptions while each of the others has a single absorption occurring at different temperature ranges. The higher temperature absorption of 1,3-diphenylacetone was measured in the temperature range of 290 - 309K and yielded very high energy barriers. However, the results for this absorption are not reasonably accurate which has been largely due to the onset of a glass-transition process evidenced from the changing capacitance values during measurements, thereby limiting

the temperature range. This molecule is fairly comparable in size to diphenylcyclopropanone, for which activation enthalpy of 102 kJ mol^{-1} and free energy of 49.7 kJ mol^{-1} at 200K have been obtained by one of the co-workers.[11] But the corresponding values of 151 kJ mol^{-1} and 80 kJ mol^{-1} for 1,3-diphenylacetone seem to be too high for a molecular process compared to that of diphenylcyclopropanone. It would appear likely that the higher temperature absorption for 1,3-diphenylacetone has been associated with a cooperative molecular motion with the surrounding polymer medium. Such a process would produce a large local disorder in the system as is evident from the very high activation entropy of 355 JK^{-1} mol^{-1}. It may again be noted that this and similar other systems have been tested by an equation derived recently in this laboratory. According to this equation, ΔS_E (JK^{-1} mol^{-1}) = -150 + 3.24 ΔH_E (kJ mol^{-1}), introduced in Chapter IV, the calculated activation entropy of 339 JK^{-1} mol^{-1} is in reasonable agreement with the observed value of 355 JK^{-1} mol^{-1} within experimental accuracy. The other absorption of 1,3-diphenylacetone occurred at much lower temperatures (113 - 133K) and showed an activation enthalpy of 24 kJ mol^{-1}. The free energies of activation (16.7 kJ mol^{-1} at 150K) are significantly lower, and the relaxation times are shorter than those observed for the intramolecular motion of the phenyl-alkyl ketones but somewhat similar to those of the two dialkyl ketones, viz., 3-nonanone and 8-pentadecanone, discussed in Chapter IV.

Since these parameters are too low for a molecular process, it may be postulated that the absorption is either due to the rotation of the carbonyl group, probably involving the adjacent $-CH_2-$ units in between the benzene rings, or else due to the rotation of the carbonyl group with the adjacent benzyl unit ($-CH_2$ Ph) on either side of the dipole. The former mechanism, however, seems to be unlikely because of considerable steric restriction imposed by the geometry of the molecule.

In contrast to 1,3-diphenylacetone, the results obtained for the single absorption of 1,1-diphenylacetone are significantly different. The absorption was noted in the temperature range of 238 - 271K yielding activation enthalpy of 70 kJ mol^{-1} which was higher than those of 60 and 58 kJ mol^{-1} obtained by a co-worker.[11] for the molecular relaxations of somewhat similarly sized diphenylsulphoxide and o-hydroxybenzophenone, respectively. But the activation free energy of 45.6 kJ mol^{-1} at 200K for the former molecule is in better agreement with the corresponding values of 48 and 46.6 kJ mol^{-1} for the latter two molecules, respectively, which shows absorptions within similar temperature ranges (250 - 300K) as in the case of 1,1-diphenylacetone. The effective dipole moments of 1.46 - 1.56 D observed within 238 - 271K for this ketone appears to be higher than those of 1.24 - 1.36 D for the acetyl group

rotation in acetophenone (Chapter IV). It therefore seems reasonable that overall molecular relaxation has been observed for 1,1-diphenylacetone.

Cyclopropylphenyl ketone has a larger carbonyl substituent, and again there is a single absorption although both molecular and intramolecular relaxations are possible. It would not be unexpected to have a little higher energy barrier to the substituent group rotation due to the larger cyclopropyl unit than that of the acetyl group relaxation in acetophenone, while there is no way that the effective conjugation between the benzene ring and the carbonyl group may be less so that the barrier could be reduced. However, the activation free energies of 25.4 and 25.6 kJ mol^{-1} at 200K obtained for cyclopropylphenyl ketone and acetophenone, respectively, are identical and so also the relaxation times, but the activation enthalpy and entropy of 24 kJ mol^{-1} and -9 JK^{-1} mol^{-1}, respectively, for the former molecule are considerably lower than those of acetophenone. On the other hand, α,α,α-trichlorotoluene (Table III-1), a comparably sized, rigid molecule showed absorptions in the temperature range of 147 - 173K, which is very similar to that in the case of cyclopropylphenyl ketone. But now the activation enthalpy and entropy of 20 kJ mol^{-1} are -26 JK^{-1} mol^{-1}, respectively, are relatively lower than those observed for the ketone whereas the free energies of activation

are still identical, at least, within experimental temperature ranges. Therefore, it seems possible that the activation parameters obtained for cyclopropylphenyl ketone are those due to its molecular relaxation, but an overlap with the intramolecular process or some contribution from the latter is not unlikely. However, the observed dipole moments of 0.87 - 1.24 D (see Appendix A, Table 7) between 141 - 175K, in comparison with those for the acetyl group rotation in acetophenone, apparently indicate that the contribution from overall molecular relaxation is not very significant.

Some of the other acetyl substituted molecules studied in polystyrene matrices include mesityl oxide, 1-acetylcyclohexene, and p-N,N-dimethylaminoacetophenone. The substitutent groups in these molecules are relatively under different environments. The former two molecules are essentially different from each other in that mesityl oxide is aliphatic while 1-acetyleyclohexene is non-aromatic but there is a common aspect for the acetyl groups, in which the carbonyl carbons are attached by a formal single bond to a double bonded carbon on the other side. As a result, significantly higher barriers to group rotation would be expected, owing to increased conjugation along the C - C single bonds, around which the group can rotate. Each of the two molecules showed only one absorption around 150K. The results for 1-acetylcyclohexene can be compared with those of acetophenone (Chapter IV), the two molecules being similar

in size. The activation enthalpy, entropy and free energy at 150K for 1-acetylcyclohexene are found to be 29 kJ mol^{-1}, 22 JK^{-1} mol^{-1}, and 26 kJ mol^{-1}, respectively. These are virtually identical to those of the corresponding values of ΔH_E = 30 kJ mol^{-1}, ΔS_E = 23 JK^{-1} mol^{-1} and ΔG_E = 26.8 kJ mol^{-1} at 150K for acetyl group relaxation in acetophenone. Relaxation times of 3.6×10^{-4} s and 6.8×10^{-4} s at 150K for 1-acetylcyclohexene and acetophenone, respectively, are also of similar orders of magnitude. In contrast, a low temperature absorption in the range of 109 - 144K and due to the acetyl group or molecular relaxation of cyclohexylmethyl ketone (discussed previously) yielded ΔH_E = 21 kJ mol^{-1} and ΔG_E = 19.2 kJ mol^{-1} at 150K. These values are significantly lower, and also the relaxation times (1.5×10^{-6} s at 150K) are much shorter than the corresponding ones for 1-acetylcyclohexene, which, of course, showed absorption at a higher temperature range of 154 - 209K. Therefore, by analogy with acetophenone it may be inferred that the group relaxation has been observed in 1-acetylcyclohexene and that the energy barriers have been comparable because of a similar effect of conjugation, which is absent in cyclohexylmethyl ketone which is a saturated system. It is not, however, understood why the barrier to group rotation would not be higher in 1-acetylcyclohexene since its carbonyl stretching frequency[12] of 1670 cm^{-1} is considerably lower than that of 1691 cm^{-1} in acetophenone, suggesting a much more highly conjugated CO group in the former.

In a similar way, the results obtained for mesityl oxide can be interpreted in terms of acetyl group relaxation. In this case, the enthalpy of activation (31 kJ mol^{-1}) and free energy of activation at 150K (24.9 kJ mol^{-1}) are also comparable to the corresponding ones for 1-acetylcyclohexene or acetophenone while the activation entropy (43 JK^{-1} mol^{-1}) is slightly higher. The relaxation times (1.5×10^{-4} s at 150K) are relatively shorter than those observed for the 1-acetylcyclohexene but still much longer than those would be expected for a rigid molecule of similar size. For example, bromobenzene, having identical length along the principal axis but with a greater volume as examined through Courtauld models, shows a relaxation time of 6.9×10^{-7} s compared to the value of 1.5×10^{-4} s observed for mesityl oxide at the same temperature of 150K. The dielectric absorption of bromobenzene also (Table III-1) occurred at much lower temperatures (101 - 136K), and the energy barriers for this molecular relaxation are much lower than those observed for mesityl oxide. Therefore, the most reasonable candidate for the absorption of the latter molecule would appear to be acetyl group rotation in conformity with that in 1-acetylcyclohexene. This is also consistent with the effective dipole moments of 1.31 - 1.43 D observed between 144 - 169K which are, in fact, typical values for the acetyl group relaxation as in acetophenone.

Of all the molecules containing the acetyl group, p-N,N-dimethylaminoacetophenone received special consideration because of the presence of the $-NMe_2$ group which exerts a strong +M effect, i.e., donates electron density to the ring by a conjugative effect. The compound exists in two equivalent planar forms which are stabilized by resonance interaction. Moreover, since $-NMe_2$ group is electron donating, the barrier to rotation about the aromatic carbon to carbonyl carbon bond would be appreciably higher. This has possibly been observed in the single absorption (244 - 301K) showing activation enthalpy and entropy of 50 kJ mol^{-1} and 24 JK^{-1} mol^{-1}, respectively. The activation free energy of 42.6 kJ mol^{-1} at 300K is in reasonable agreement with that of 38 kJ mol^{-1} obtained from n.m.r. studies by Klinck et al.[13] On the other hand, for the $-NMe_2$ group rotation the free energies of activation at coalescence temperatures around 135K have been reported[14] to be 29 - 30 kJ mol^{-1}. This process may not have been significant from the present studies since it is associated with a smaller component moment of 1.58 sin 34 = 0.88 D compared to that of 2.89 sin 57 = 2.42 D for the acetyl group, the components being obtained from the group moments[21,22] of μ_{NMe_2} = 1.58 D and μ_{COCH_3} = 2.89 D and their angles of inclination θ of 34^o and 57^o, respectively, to the principal axis of rotation. However, the component of 2.89 cos 57 + 1.58 cos 34 = 2.88 D parallel to the

long axis is even higher than those due to the groups and would suggest that the dielectric absorption of p-N,N-dimethylaminoacetophenone may be molecular, or, at least, it will contribute greatly to the acetyl group relaxation. This is apparent from the effective dipole moments of 2.5 - 3.2 D (see Appendix A, Table 7), observed within the experimental temperatures of 244 - 301K, which exceed the perpendicular component of the acetyl group moment. A reasonable estimate of the energy barriers for the molecular relaxation process of this molecule may be provided by those of p-bromoethylbenzene, which, in fact, is slightly smaller in size. This rigid molecule was studied by one of the co-workers[15], and an activation enthalpy of 38 kJ mol^{-1} was obtained for the absorption measured in the temperature range of 206 - 253K. The free energies of activation at 200K and 300K are 36.2 and 35.3 kJ mol^{-1}, respectively. Thus, the higher energy barriers for p-N,N-dimethylaminoacetophenone may not be inconsistent with those of a molecular process, and, therefore, it would seem justified that there is significant possibility of an overlap with the acetyl group rotation but with the molecular process predominating.

Finally, the fused ring systems, which have been of particular interest are the 2-acetyl-1-tetralone, 2-acetylnaphthalene, 2- and 3-acetylphenanthrenes. The larger phenanthrenes have clearly

shown two absorptions each at widely separated temperature ranges. The higher temperature absorption for 2- and 3-acetylphenanthrenes occurred around 300K and yielded activation enthalpies of 86 - 87 kJ mol^{-1}, which are well within those of 90 and 72 kJ mol^{-1} obtained by some co-workers for the molecular relaxation of 4-bromobiphenyl[15] and 3-nitrobiphenyl,[17] respectively. The latter two molecules are essentially different from the substituted phenanthrenes in that there is an additional fused ring in between the two benzene rings of the biphenyls, which is projected outwards in the phenanthrenes. As a result, the size of the two types of molecules may be appreciably different so that it would not be unexpected to have different energy barriers for molecular relaxation processes of these molecules. Moreover, the size of the substituent groups is not exactly equivalent. However, considering the possible error limits of ±10% on activation enthalpies, the higher temperature process of the acetylphenanthrenes may well be assigned to molecular relaxations in comparison with those of the substituted biphenyls.

The lower temperature process (∿160 - 210K) for 2- and 3-acetylphenanthrenes yielded activation enthalpies of 28-30 kJ mol^{-1}, comparable to that of acetyl group relaxation in acetophenone (Chapter IV). In fact, these are the typical values

for acetyl group relaxation in aromatic ketones as shown by McLellan and Walker.[1] But now the activation entropies are noticeably lower, being close to zero, resulting into higher free energies of activation ($\sim$27 - 29 kJ mol^{-1} at 200K) at different temperatures. However, these values could not be ascribed to the molecular relaxation processes, and it is more reasonable to assign them for group rotation which is further supported by the β values of 0.13 - 0.21 compared to those of 0.14 - 0.19 observed for the much higher temperature absorptions. Moreover, the lower temperature absorptions occurred at temperature ranges similar to those for the typical acetyl group relaxations mentioned previously. It may also be emphasized that the two absorptions, i.e., those due to group and the molecular processes, have been completely separated for both 2- and 3-acetylphenanthrenes in polystyrene matrices.

In contrast to phenanthrenes, the dielectric absorption of 2-acetylnaphthalene was complicated by overlapping absorptions. This was clearly indicated at the higher temperature side in that each dielectric loss curve composed of two peaks was located rather close to each other in terms of frequency. This is shown in Figure VI-1 for which the data at each temperature have been analyzed in terms of a single absorption of the Fuoss-Kirkwood type since preliminary attempts to analyse them as two absorptions have proved unsatisfactory. However,

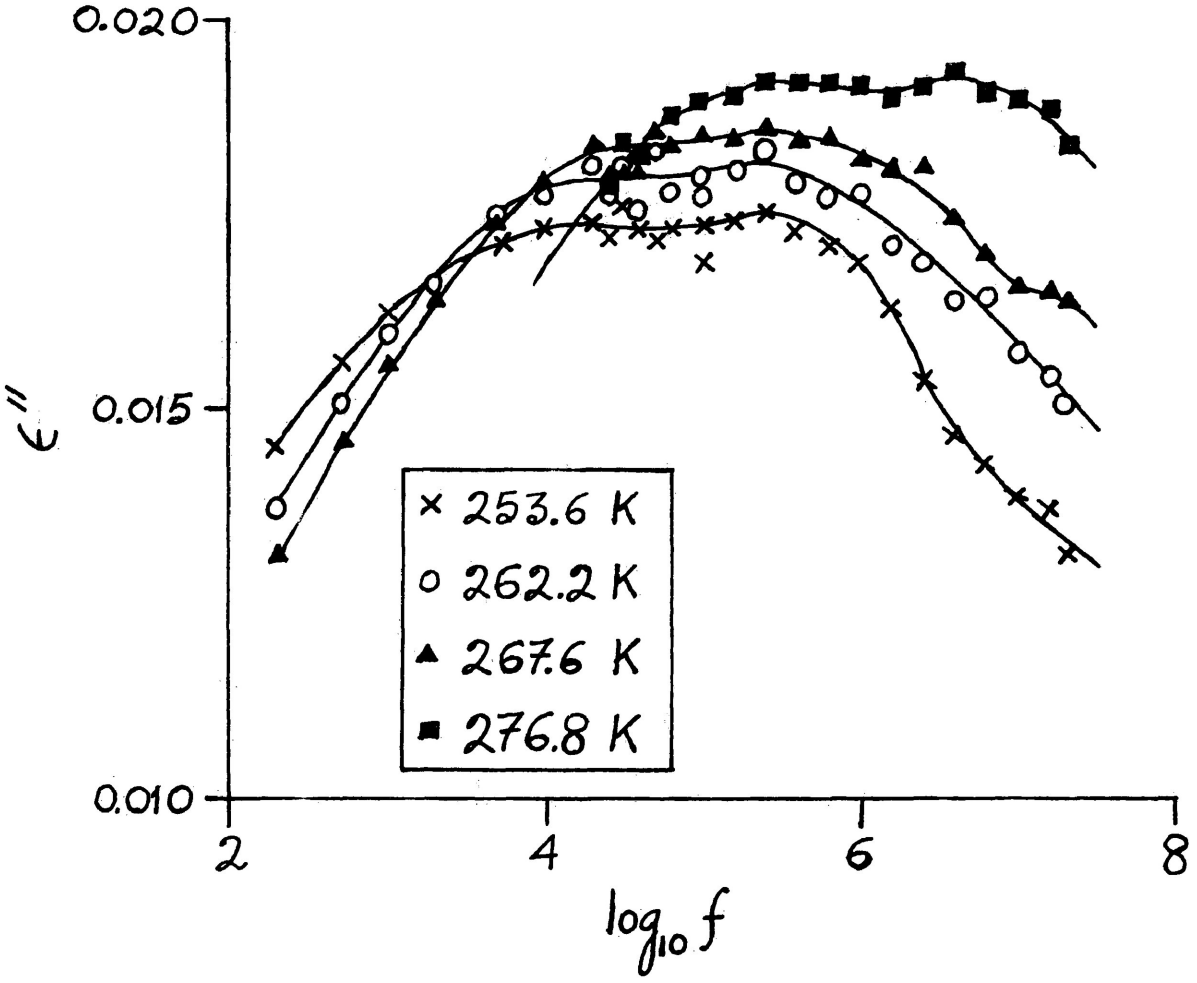


Fig. VI-1: Dielectric loss factor (ϵ'') vs. logarithmic frequency for 0.375M 2-acetylnaphthalene in a polystyrene matrix at temperatures as indicated.

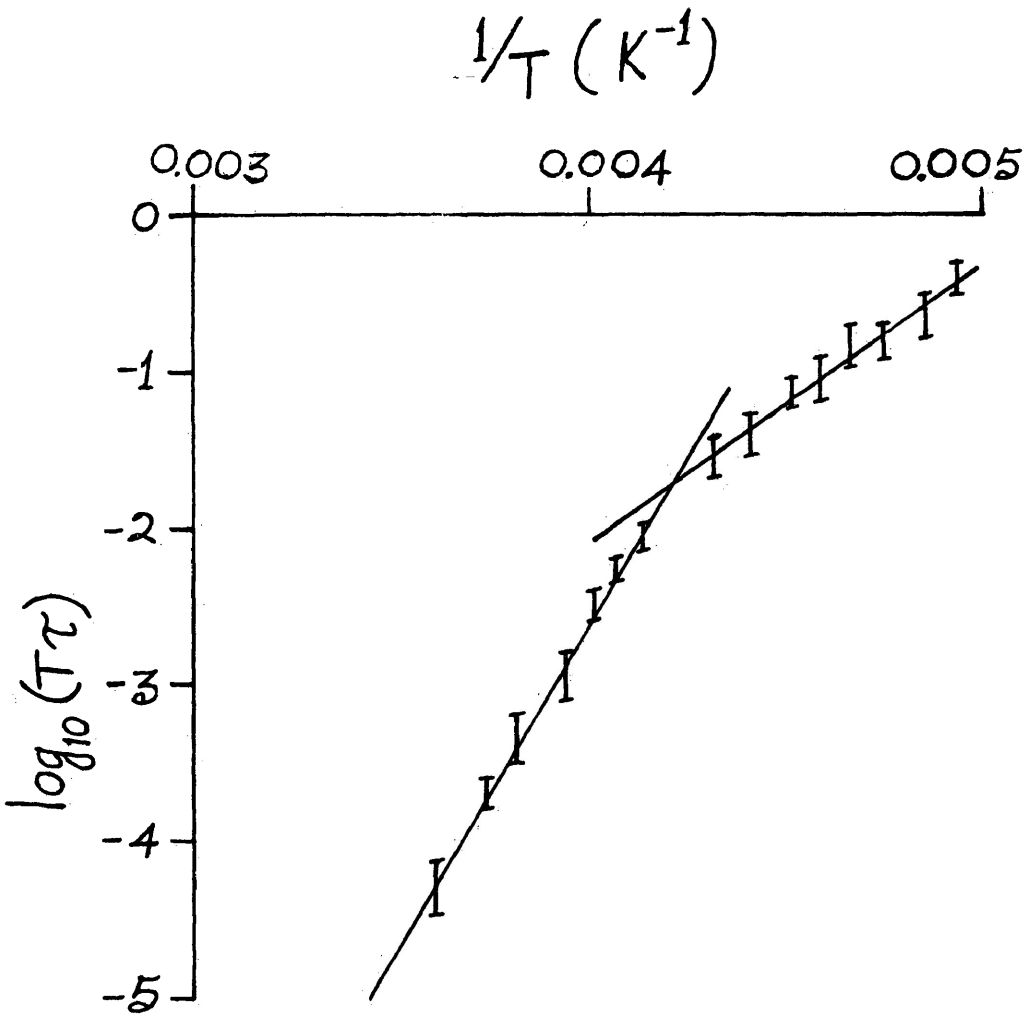


Fig. VI-2: Eyring plot of $\log_{10}(T\tau)$ vs. $1/T$ for 0.375 M 2-acetylnaphthalene in a polystyrene matrix. The vertical bars represent 95% confidence intervals on $\log(T\tau)$ values.

the resulting data from the Fuoss-Kirkwood analysis sucessfully fitted the Eyring plot of $\log(T\tau)$ against $\frac{1}{T}$, Figure VI-2, into two straight lines in adjacent temperature regions. The lower temperature (202 - 232K) data yielded ΔH_E = 34 kJ mol^{-1} and ΔS_E = -24 JK^{-1} mol^{-1}, while those at higher temperatures (242 - 277K) showed ΔH_E = 82 kJ mol^{-1} and ΔS_E = 179 JK^{-1} mol^{-1}. These results suggest more clearly that the overall absorption is composed of two different processes in the limits of lower and higher temperature regions.

Only one relaxation process was observed with 2-acetyl-1-tetralone for which ΔH_E = 61 kJ mol^{-1} and ΔG_E = 45.7 kJ mol^{-1} at 200K correspond closely with those of 54 kJ mol^{-1} and 45 kJ mol^{-1}, respectively, for the molecular relaxation of 2-cyanonaphthalene, a molecule of fairly similar shape and size, studied by another co-worker.[18] It should be noted that the temperature range of (244 - 275K) observation for 2-acetyl-1-tetralone is higher than those found for the other acetyl group relaxation processes but is very similar to that (247 - 267K) for 2-cyanonaphthalene. Therefore, in the absence of a second absorption for the former molecule, it would appear that either the process is totally molecular or is a mixture of group and molecular with the latter predominating. However, the activation enthalpy of 82 kJ mol^{-1} obtained from the higher temperature side of the absorption for 2-acetylnaphthalene exceeds

that for the comparably sized 2-acetyl-1-tetralone, but excellent agreement is observed between the free energies of activation at 200K. In view of the differences between the inclinations of the molecular dipole moments to the long axes of the molecules in 2-acetyl-1-tetralone and 2-acetylnaphthalnene, it is expected that the latter would yield higher values for activation enthalpy and entropy, and indeed these have been obtained. Such an expectation is supported by the relaxation times for acetylnaphthalenes in dilute liquid solutions[4] and by polystyrene matrix studies of rigid halonaphthalenes.[19] The higher activation enthalpy for 2-acetylnaphthalene may be too large for its molecular process, but it should not be ignored that the former was obtained from the analyses of data which contain interfering overlapping absorptions. Therefore, the possibility exists that the activation parameters from either the lower and/or higher temperature part of the absorption are in significant error. However, there would appear to be little doubt that the higher values are assigned to the molecular motion and that the lower temperature ones are associated with the acetyl group relaxation.

Another important observation is that the estimated effective dipole moments for the group relaxations in acetylphenanthrenes are less than 1 D, while those in acetophenone fall into the range of

1.2 - 1.4 D and in 2-acetylnaphthalene the values are even higher. The decrease in the former cases are consistent with a contribution from group relaxation which is less than that in acetophenone whereas the higher values for the latter could probably have resulted from the fact that the data contains appreciable contribution from both group and molecular processes. It may be recalled that the Debye and the Fuoss-Kirkwood relationships have been employed to estimate the effective dipole moments, μ, associated with the relaxation processes observed. Davies and Swain[8] also obtained low values from their polystyrene matrix data at the measurement temperatures, but they found that a linear extrapolation of μ versus temperature yielded, on the whole, values comparable to liquid solution results at temperatures between 300 to 320K. The same procedure has been followed for the purpose of this thesis, and the data for 2- and 3-acetylphenanthrenes may be considered in some detail since in each of these cases molecular and group relaxations are observed to be well separated. An estimate of the dipole moment of a molecule exhibiting both molecular and group rotations may be made roughly from the relationship, $\mu_{total}^2 = \mu_{\parallel}^2 + \mu_{\perp}^2$ where $\mu_{\parallel}$ is an interpolated value for the molecular process, and $\mu_{\perp}$ is the value of the dipole moment for the group relaxation extrapolated to around room temperatures. Evaluation of the two dipole moments separately at 320K for 2-acetylphenanthrene give $\mu_{\parallel}$ = 2.02 D

and $\mu_{\perp}$ = 1.91 D yielding a μ_{total} of 2.78 D, which is of the correct order of the dipole moment for an aromatic ketone. In the case of 3-acetylphenanthrene, the $\mu_{||}$ is 2.20 D at 320K, but $\mu_{\perp}$ at the same temperature appears to be much lower based on the present data (see Appendix A, Table 7). More recently, a co-worker[20] has made some additional measurements, and a $\mu_{\perp}$ = 1.70 D at 320K has been obtained from the combined data for the low temperature absorption of 3-acetylphenanthrene. This value of $\mu_{\perp}$ together with $\mu_{||}$ = 2.20 D again gives a μ_{total} = 2.78 D, and therefore, would suggest that the component dipole moments so obtained are reasonably reliable.

Now, it seems worthwhile to consider the question of an enhanced resonance effect in naphthalenes as suggested by Fong and Smyth.[4] Several parameters may be discussed for this purpose, but the consideration of activation enthalpies would appear to be of lesser importance since the higher value of ΔH_E = 34 kJ mol^{-1} for acetyl group relaxation in 2-acetylnaphthalene is prone to error owing to its being acquisitioned from overlapping absorptions. However, the sequence of increasing ΔG_E values at 200K for acetyl group relaxation in acetophenone, 2- and 3-acetylphenanthrenes and 2-acetylnaphthalene 25.6, 27.4, 29.2, and 38.3 kJ mol^{-1}, respectively offers a promising lead in this regard. This sequence

is also reflected in the carbonyl stretching frequencies[20] of 1691, 1689, 1688, and 1678 cm^{-1}, respectively, in $CC\ell_4$ solutions. Such a trend is in harmony with greater conjugation of the carbonyl group with the ring and is further consistent with lengthened τ_2 values as obtained from solution studies.[12] However, this enhanced conjugation alone does not account for the low weight factor (C_2) for group relaxation in 2-acetylnaphthalene since 2- and 3-acetylphenanthrenes have also similar weight factors ($\sim$0.2) but exhibit no sign of an enhanced enthalpy of activation for group relaxation, although the sequence of ΔG_E values at 200K, carbonyl stretching frequencies, and the lengthened τ_2 values would tend to support the theory that there is enhanced conjugation of the acetyl group in 2-acetylnaphthalene compared to that in acetophenone as was suggested by Fong and Smyth.[4]

The weight factor anomalies for the 2- and 3-acetylphenanthrenes can be examined with the help of the $\mu_{//}$ and $\mu_{\perp}$ values as discussed before. These are related to the weight factors for the molecular (C_1) and group (C_2) processes by the expression, $C_1/C_2 = (\mu_{//}/\mu_{\perp})^2$ where $C_1 + C_2 = 1$. The C_1 values derived in this manner for 2- and 3-acetylphenanthrenes are 0.53 and 0.63, respectively. These are significantly greater than that of $\sim$0.33 for acetophenone,[7] while 4-acetylbiphenyl, which has more structural

similarity with acetophenone, has been found[20] to give a C_1 value of 0.38. These results bear out the solution studies[12] in the microwave region, and, therefore, it appears that some factor is at play which diminishes the value of C_2 in the two phenanthrenes containing the 2-acetylnaphthalene unit. However, the actual value of C_2 obtained from either of the approaches, viz., the matrix and the solution studies, is prone to considerable error, but when both are taken into account, it would seem that the C_2 value for 2- and 3-acetylphenanthrene as well as for 2-acetylnaphthalene is something of the order of 0.3 ±0.15. In conclusion, therefore, it may be noted that the results obtained for the acetyl substituted fused-ring aromatic systems have shown the considerable usefulness of the present technique.

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CHAPTER VII

HYDROXYL GROUP AND MOLECULAR RELAXATION OF SUBSTITUTED PHENOLS

INTRODUCTION:

Hydroxyl group-containing compounds, especially, the aliphatic alcohols and their solutions, have been studied by many physical methods.[1,2] The nature and concentration of the various hydrogen bonded species including monomers and a variety of linear and cyclic multimers are by no means established.[3] Aromatic phenols have also been studied by dielectric techniques, and their relaxation data from solutions have often been analyzed in terms of two relaxation times with respect to molecular and group relaxation processes. Thus, very short relaxation times, almost certainly corresponding to the rotational orientation of OH around the C—O bond, have been observed for 1-naphthol, 4-hydroxybiphenyl, and 2,6-dimethylphenol.[4] For 2,6-dimethylphenol, the overall absorption was dominated by the contribution from the group rotation, and, therefore, Fong and Smyth[4] suggested that the OH group is prevented from intermolecular interaction by the methyl groups. In a later study by dielectric relaxation, proton magnetic resonance, and infrared spectroscopy, Fong et al.[5] confirmed that the presence of 2,6-dialkyl groups provide effective screening of the OH group from interaction with the surrounding solvent molecules, and that substitution of alkyl groups (particularly

the bulky t-butyl group) on the 2- and 6- positions does not hinder rotation of such a group.

Further useful results were obtained with 2,4,6-tri-t-butylphenol and the tricyclohexylcarbinol studied in pure solids[6] and also in solutions of decalin.[7] In each case, two distinct dielectric absorptions were obtained at frequencies up to 2.4×10^{10} Hz, the higher-frequency one being due to the hydroxyl group relaxation. For the 2,4,6-tri-t-butylphenol in solution in decalin, the mechanism of the molecular rotation and hydroxyl relaxation showed little difference in activation energy and the separation of the two absorptions was considered to be due mainly to an appreciable difference in frequency factors.[7] Moreover, the activation energy for the hydroxyl relaxation in solution (11.7 kJ mol^{-1}) was found to be similar to that in the solid (9.2 kJ mol^{-1}). The energy barriers of 9.2 and 18.4 kJ mol^{-1} obtained for tri-t-butylphenol and tricyclohexylcarbinol, respectively, in solids[6] appeared to be relatively large for the small hydroxyl group relaxation but were suggested to reflect considerable hindrance to the rotation of the dipole, especially in the latter compound.

Th C — O bond of phenols is known to possess some double bond character which causes the hydrogen atom to lie in

the plane of the ring. Various spectroscopic studies[8-11] indicate a barrier of 14 - 15 kJ mol^{-1} for the rotation of the OH group in phenol. Davies and Edwards[12] studied β-naphthol in a polystyrene matrix. Their high-frequency absorption data yielded an activation enthalpy of 2.1 ±1.3 kJ mol^{-1} for the hydroxyl group relaxation, which did not appear to be consistent with appreciable double bond character in the C — O link. In the case of appropriately o-substituted phenols, the hydroxyl rotational barrier would be modified by intramolecular hydrogen bonding. As a consequence, much higher activation enthalpies of ∿35 kJ mol^{-1} have been obtained by Walker et al.[13] for the OH group relaxation in 2,6-dinitrophenol and in 2,6-dinitro-4-methylphenol. It was concluded that the transition of the hydroxyl group from one planar hydrogen bonded position to the other takes place over an energy barrier which is strongly dependent on the energy required to break the intramolecular hydrogen bond.

From the above discussion, it would appear that the barrier to hydroxyl group relaxation in substituted phenols depends upon the steric and probably on the inductive effects of the substituents as well as on the strength of intramolecular hydrogen bond. Similarly, intermolecular hydrogen bonding would also be expected to influence the barriers to molecular rotations of such

systems. Therefore, it seemed desirable to investigate systematically a series of substituted phenols in polystyrene matrices since, in priciple at least, it ought to be possible to separate the two processes. The work was particularly aimed at a study of the energy barrier to hydroxyl group relaxation in such intramolecularly hydrogen bonded systems as 2,6-disubstituted phenols, and in related compounds bearing additional substituents such as 2,4,6-trisubstituted and pentahalophenols, so that the effect of the various factors might be deduced. Moreover, it may be possible to gain information about the strength of intermolecular hydrogen bonds, at least, roughly from the energy barrier data for the molecular relaxation of any associated species in comparison with those for the analogous rigid molecules.

DISCUSSION:

The Eyring analysis results for the different substituted phenols are presented in Table VII-1. The relaxation times and the free energies of activation are given at wider temperature intervals, i.e., at 100K, 200K, and 300K, since many of the molecules have shown two absorptions covering such a range. The simplest situation is probably that due to the

TABLE VII-1 EYRING ANALYSIS RESULTS FOR SUBSTITUTED PHENOLS

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 (JK^{-1} mol^{-1})
p-Nitrophenol	128 - 153	2.9×10^{-2}	5.5×10^{-7}	1.2×10^{-8}	20.7	24.4	28.1	17	- 37
"	234 - 267	3.2×10^{12}	2.8×10^{-2}	4.9×10^{-7}	47.5	42.4	37.3	53	51
3,5-Dichloro-phenol	226 - 251	3.3×10^{10}	2.2×10^{-3}	7.6×10^{-8}	43.7	38.2	32.6	49	56
2,4-Dinitro-phenol	164 - 206	2.5×10^{-4}	4.1×10^{-6}	1.9×10^{-9}	32.0	27.7	23.4	36	43
2,4,6-Trimethyl-phenol	204 - 234	3.6×10^{11}	5.2×10^{-4}	5.0×10^{-9}	45.7	35.8	25.8	56	100
2,4,6-Tri-t-butylphenol	294 - 324	2.5×10^{23}	7.1×10^{2}	8.5×10^{-5}	68.4	59.2	50.1	78	91
2,4,6-Tri-chlorophenol	92 - 111	6.7×10^{-5}	3.7×10^{-9}	1.2×10^{-10}	15.6	16.1	16.5	15	- 5
"	210 - 246	5.9×10^{8}	5.1×10^{-4}	4.1×10^{-8}	40.4	35.7	31.1	45	47
2,4,6-Tri-bromophenol	108 - 138	2.7×10^{-4}	3.8×10^{-8}	1.6×10^{-9}	16.8	19.9	23.0	14	- 31
"	220 - 249	2.3×10^{9}	1.7×10^{-3}	1.3×10^{-7}	41.5	37.8	34.0	45	38
2,4,6-Tri-iodophenol	84 - 116	2.3×10^{-5}	3.0×10^{-8}	4.0×10^{-9}	14.7	20.0	25.3	10	- 53
"	275 - 306	2.4×10^{12}	2.7×10^{-1}	1.1×10^{-5}	47.3	46.2	45.0	48	11

TABLE VII-1 EYRING ANALYSIS RESULTS FOR SUBSTITUTED PHENOLS 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 (JK^{-1} mol^{-1})
Pentachloro-phenol	122 - 149	2.2×10^{-1}	2.0×10^{-8}	7.3×10^{-11}	22.3	18.8	15.3	26	35
"	210 - 238	2.9×10^{9}	5.1×10^{-4}	2.4×10^{-8}	41.7	35.7	29.7	48	60
Pentachloro-benzenethiol	93 - 132	1.6×10^{-4}	2.0×10^{-8}	8.5×10^{-10}	16.3	18.8	21.4	14	-26
"	218 - 269	1.8×10^{10}	6.5×10^{-3}	3.9×10^{-7}	43.2	40.0	36.7	47	33
Pentabromo-phenol*	114 - 145	8.1×10^{-3}	2.2×10^{-8}	2.5×10^{-10}	19.6	19.0	18.4	20	6

*The higher temperature process is not shown in the Table for reasons given in the text.

single absorption noted for 2,4-dinitrophenol, in which the hydroxyl group is strongly hydrogen bonded intramolecularly. The absorption was measured in the temperature range of 164 - 206K yielding activation enthalpy and free energy at 200K of 36 and 27.7 kJ mol^{-1}, respectively. These values may be compared with those of 39 kJ mol^{-1} and 34.4 kJ mol^{-1}, respectively, observed for 2,4-dinitrochlorobenzene (Table III-3), a similarly sized rigid molecule, which also showed absorption around 200K. Therefore, it would appear that a molecular relaxation process has been observed for the former molecule, as can further be supported by its low β values of 0.12 - 0.15 (see Appendix A, Table 8). The behaviour of this molecule is also consistent with that of o-nitrophenol studied by Walker et al.[13] in a polystyrene matrix, where they observed only the molecular process, and, moreover, Meakins[14] found no dielectric loss in the pure solid state, indicating that the group relaxation does not occur in this compound.

In contrast to 2,4-dinitrophenol, the results obtained for p-nitrophenol present a complicated problem although two different absorptions were observed. The latter molecule is similar in size and shape to p-nitrotoluene (Table III-1), but neither the low nor the high temperature absorption of p-nitrophenol

corresponds with the molecular relaxation parameters of the rigid molecule. The lower temperature (128 - 153K) absorption yielded an activation enthalpy of 17 kJ mol^{-1}, comparable to the barrier (V) of 14 - 15 kJ mol^{-1} for the OH group rotation in phenol as obtained from spectroscopic studies.[8-11] However, p-nitrophenol has a greater acidity (pK_a=7.15)[15] than that of phenol (pK_a=9.89) itself. This can be ascribed to the strong electron-withdrawing effect of the nitro group at the para position enhancing the quinoniod structure. As a result, the hydroxyl group rotational barrier in p-nitrophenol is expected to be higher than that in phenol, and this should be reflected in an enhanced enthalpy of activation.

Fateley and his co-workers[11] studied the effect of 4-substituents on the barrier to internal rotation about the C — O bond in phenol as determined by far-infrared studies of the torsional frequencies. Their work showed clearly that substituents, which are π-electron donors, lower the observed barrier, while π-electron acceptors raise the barrier. Moreover, the experimental results were found to be in excellent agreement with those obtained by ab initio molecular orbital calculations. These were rationalized in terms of the opposition to or reinforcement of delocalization of the oxygen lone pair electrons by the π-donating

or π-accepting substituents, respectively. Thus, when the substituent is a π-donor, π-electron donation by OH decreases, the double bond character in the C — O bond decreases and the barrier decreases. Conversely, when the substituent is a π-acceptor, electron donation by OH increases, the double bond character in the C — O bond increases and the barrier increases. Fateley and his co-workers[11] obtained for p-nitrophenol a ΔV_2, i.e., the change in the twofold barrier, of ∿4 kJ mol^{-1} over the V_2 value of ∿14 kJ mol^{-1} for phenol. Therefore, the activation enthalpy of 17 kJ mol^{-1} obtained from the low temperature dielectric absorption of p-nitrophenol in a polystyrene matrix would not be unreasonable for the hydroxyl group relaxation. It is more evident from the activation free energies of 20.7 and 24.4 kJ mol^{-1} at 100K and 200K, respectively, that the barrier has been enhanced, but it must be pointed out that V_2 values from spectroscopic studies should not be considered equivalent to either the ΔH_E or ΔG_E values obtained from the present studies. Another point to note is that the dielectric loss curves for the said absorption are not symmetrical, although the β values of 0.18 - 0.20 are not too low to be associated with broad absorptions at 128 - 153K. But this would probably suggest that the absorption is a composite of relaxation processes for free and hindered hydroxyl groups, the latter being due to the presence of associated species (to be

discussed in the next paragraph). It may also be mentioned that the behaviour of p-nitrophenol is different from that of p-nitroanisole since the group relaxation does not appear to have been observed separately for the latter (see next chapter).

The higher temperature process (234 - 267K) observed for p-nitrophenol may not also be free from complication because of a number of possibilities for molecular relaxations. The association constant for the dimerization of the molecule is found[2] to be 5.2 ℓ/m in benzene at 278K and is much higher than that of 0.57 ℓ/m for phenol itself at 298K. It would, therefore, appear that at lower temperatures of the absorption p-nitrophenol exists significantly in the associated form. There is also the possibility of a monomer to dimer equilibrium or even with higher polymers, which would all contribute to the absorption and produce some form of overlap. But the absorption curves were highly symmetrical showing β values of 0.24 - 0.27, inferring that a wide variety of processes might not have occurred, probably owing to the restriction imposed by the geometry of the associated species. However, the activation enthalpy was found to be 53 kJ mol^{-1} which is significantly higher than that of 35 kJ mol^{-1}, obtained for p-nitrotoluene (Table III-1), a rigid molecule of almost the same size. The activation free energy of 31.9 kJ mol^{-1} at 200K for

the rigid molecule is about 10 kJ mol^{-1} lower, and also the relaxation time of 5.3 x 10^{-5} s at 200K is much shorter than the corresponding value of 2.8 x 10^{-2} s observed from the higher temperature absorption of p-nitrophenol. Moreover, the absorption of p-nitrotoluene occurred at considerably lower temperatures of 184 - 220K. In view of these results, it is very unlikely that a simple molecular relaxation process has been observed for p-nitrophenol at higher temperatures (234 - 267K) although the possibility of contribution from unassociated molecules may not be overlooked. Alternatively, the relaxation of a monomer could have been restricted by intermolecular hydrogen bonding so that the process would require additional energy, as reflected in the higher activation energy barriers, and/or the absorption may be due to the relaxation of dimers, if not multimers, while the possibility of some sort of overlap still exists. The latter situations are difficult to recognize from the present studies especially when the relaxation and activation parameters of suitable rigid molecules corresponding to the different shapes and sizes of the various species of p-nitrophenol are not available. However, for the molecular relaxation of 4,4'-dibromobenzophenone, which would probably approximate a dimer of p-nitrophenol, a co-worker[16] obtained the activation enthalpy and free energy at 200K to be 63 and 37 kJ mol^{-1}, respectively. The corresponding values of 53 and 42.4

kJ mol^{-1}, respectively, shown by the higher temperature (234 - 267K) absorption of p-nitrophenol were well within those of 4,4'-dibromobenzophenone, and also the absorption for the latter molecule was measured at somewhat similar temperatures (204 - 233K). Therefore, it would appear that the dimers may make some contribution to the higher temperature absorption of p-nitrophenol, and that any contribution from higher multimers is not apparent since the latter would involve much higher energy barriers.

In the case of 3,5-dichlorophenol, only one absorption was measured above 200K although at lower temperatures hydroxyl group relaxation should have been observed, but it was not possible to characterize the process since the measurements were associated with very low loss. This is contrary to the behaviour of 3,5-dimethylanisole (see next chapter), where both the molecular and the group relaxations have been well characterized. Again, the single absorption measured at 226 - 251K does not appear to be due to simple molecular relaxation process since the results are significantly different, as in the case of p-nitrophenol, from those of similarly sized rigid molecules. Thus, the activation enthalpy of 49 kJ mol^{-1} obtained for 3,5-dichlorophenol is considerably higher than that of 38 kJ mol^{-1} for 3,5-dichlorobenzonitrile (Table III-3), which is even larger in size. 2,4,6-

Trichloropyrimidine, another rigid molecule of similar size, and also the molecular relaxation of 3,5-dimethylanisole showed activation enthalpies of 38 and 37 kJ mol^{-1}, respectively. The corresponding free energies of 30.5 and 28.4 kJ mol^{-1}, respectively, at 200K of the latter two cases are similarly lower than that of 38.2 kJ mol^{-1} observed for 3,5-dichlorophenol at the same temperature. Furthermore, the relaxation times at different temperatures of the dichlorophenol are much longer than the corresponding values for the other comparably-sized molecules. For example, the former shows a value of 2.2×10^{-3} s while those of 2,4,6-trichloropyrimidine and 3,5-dichlorobenzonitrile are 2.3×10^{-5} s and 5.3×10^{-4} s, respectively, all at 200K. Further, the molecular relaxation of the two rigid molecules, particularly of 2,4,6-trichloropyrimidine and of 3,5-dimethylanisole, occurred at lower temperatures. All the above evidence suggests that the absorption noted for 3,5-dichlorophenol is not solely due to molecular relaxation. The situation is probably similar to that for the higher temperature absorption of p-nitrophenol, but now the differences in activation energies from those of the rigid molecules are only of the order of 10 kJ mol^{-1} or less, so that any contribution from the relaxation of some dimer would appear to be unlikely. Therefore, the most plausible mechanism is that the molecular relaxation has been hindered by intermolecular association. An interesting feature of this aspect was revealed by

the effective dipole moments which decreased from 1.41 D to 1.23 D as the experimental temperature was increased (see Appendix A, Table 8), so that the extrapolation to higher temperatures was not possible. This sort of behaviour has also been observed for the higher temperature absorption of other similar systems, viz., the tri- and pentahalophenols, to be discussed later, and perhaps this can be understood from the fact that the concentration of the associated species is expected to decrease with increasing temperatures.

2,4,6-Trimethylphenol and 2,4,6-tri-t-butylphenol were of particular interest in view of the results obtained by previous workers.[4-7] Each of the molecules showed a single absorption at 204 - 234K and 294 - 324K temperature ranges, respectively, in polystyrene matrices although both molecular and group processes would be expected to occur. The very bulky t-butyl groups at the 2,6-positions of the latter molecule prevent the hydroxyl group from any intermolecular hydrogen bonding as is evident from the single OH stretching peak at 3684 cm^{-1} obtained by Davies and Meakins.[7] The alkyl substituents are also non-interacting with the hydroxyl group, but these could possibly exert some steric hindrance to the rotation of the group so that the barrier may be increased to some extent. However, the results obtained from the present studies

indicate that only the molecular process has been observed for 2,4,6-tri-t-butylphenol with activation enthalpy and entropy of 78 kJ mol^{-1} and 91 JK^{-1} mol^{-1}, respectively. These values appear to be very high compared to those for the molecular process observed by Davies and Meakins[7] in solution in decalin, but are not unusual for the relaxation of large molecules in polystyrene matrices. Thus, pentabromotoluene (Table III-3) showed an activation enthalpy of 64 kJ mol^{-1}, while its activation free energy of 52.1 kJ mol^{-1} at 300K is in better agreement with that of 50.1 kJ mol^{-1} obtained for the tri-t-butylphenol. It should be noted that attempts have been made to detect the group relaxation of the latter molecule in the polystyrene matrix and also in a pure solid disk, but even at the highest frequencies, up to 5 x 10^7 Hz, of the Q-meter only the tail-end of the absorption was observed where ε'' increased with increasing frequency. This would simply mean that the process was not slowed down enough to be observable within the frequency and temperature range used in the present technique.

The behaviour observed for 2,4,6-trimethylphenol at lower temperatures was similar to that of 2,4,6-tri-t-butylphenol. Fong *et al.*[4,5] demonstrated from their solution studies and other spectroscopic evidence that the methyl groups in 2,6-dimethylphenol provide steric hindrance to intermolecular hydrogen bonding. This

is contrary to the present observation of a broad and strong absorption around 3400 cm^{-1} in the infrared spectra of 2,4,6-trimethylphenol in the polystyrene matrix. Further, the dielectric results for this molecule do not appear to indicate appreciable steric hindrance to hydrogen bonding since the activation energy barriers are significantly higher than would be expected for the relaxation of simple unassociated monomers. Moreover, the relaxation times are much longer than those for a similarly sized, rigid molecule. Thus, 2,4,6-trimethylbenzonitrile and 2,4,6-trichloronitrobenzene (Table III-3) showed relaxation times of 4.7×10^{-6} s and 9.2×10^{-6} s, respectively, at 200K compared to that of 5.2×10^{-4} s for the trimethylphenol at the same temperature. The activation enthalpy of 56 kJ mol^{-1} and free energy of activation at 200K of 35.8 kJ mol^{-1} obtained for 2,4,6-trimethylphenol can be contrasted with the corresponding values of 29 and 27.9 kJ mol^{-1} for the substituted benzonitrile. Similar differences may be noted with the results obtained for 2,4,6-trichloronitrobenzene, and also with those for the molecular relaxation of 2,4,6-tribromoanisole (Table VIII-1). The latter molecule is considerably larger in size and shows activation enthalpy and free energy at 200K of 33 and 30.2 kJ mol^{-1}, respectively. Hence, there can be little doubt that a simple molecular process was not observed for 2,4,6-trimethylphenol. It would appear likely that the molecular

relaxation was restricted by intermolecular hydrogen bonding, thus requiring additional energy to break the hydrogen bond before the molecule relaxed.

It may be noted that the effective dipole moments ($\sim$0.5 D) observed from the dielectric absorption of 2,4,6-trimethylphenol were virtually constant (see Appendix A, Table 8), and, therefore, the extrapolation did not seem feasible, the literature value[20] being 1.4D. In the case of 2,4,6-tri-t-butylphenol, the observed values were also more or less the same ($\sim$0.55D) and were considerably lower than the literature value of 1.6D.

Table VII-1 shows two different absorptions for each of the halophenols, except for pentabromophenol, one around 100K and the other above 200K. Such a wide separation in the experimental temperature range enabled the dielectric measurements to be made free from any appreciable contribution from one to the other absorption. The higher temperature process observed for the various halophenols yielded similar activation enthalpies. This is unusual since the barriers to molecular relaxation processes are known to increase with the size of the molecules (Chapter III). The enthalpies of activation and the free energies of activation at 200K are remarkably similar for 2,4,6-trichlorophenol and 2,4,6-tribromophenol, the

former values being 45 kJ mol^{-1} for each of them, while the latter values are 35.7 and 37.8 kJ mol^{-1}, respectively. However, the relaxation time of 1.7×10^{-3} s for the tribromophenol is longer than that of 5.1×10^{-4} s for the trichlorophenol, both at 200K, the absorptions having been observed in the same temperature range of ∿210 - 250K. On the other hand, the relaxation times for the latter molecule are also longer and its activation energies are higher than the corresponding values obtained for the molecular relaxations of 2,4,6-trimethylbenzonitrile (ΔH_E = 29 kJ mol^{-1}, $\Delta G_{E(200)}$ = 27.9 kJ mol^{-1}, $\tau_{200} = 4.7 \times 10^{-6}$ s); 2,4,6-trichloronitrobenzene (ΔH_E = 29 kJ mol^{-1}, $\Delta G_{E(200)}$ = 29 kJ mol^{-1}, $\tau_{200} = 9.2 \times 10^{-6}$ s); and 2,4,6-trichloropyrimidine (ΔH_E = 38 kJ mol^{-1}, $\Delta G_{E(200)}$ = 30.5 kJ mol^{-1}, $\tau_{200} = 2.3 \times 10^{-5}$ s), all the rigid molecules being fairly comparable to 2,4,6-trichlorophenol in size and shape. Likewise, the enthalpy of activation of 33 kJ mol^{-1} and the free energy of activation at 200K of 30.2 kJ mol^{-1} observed for the molecular relaxation of 2,4,6-tribromoanisole (Table VIII-1) are significantly lower than the corresponding values for 2,4,6-tribromophenol. Again the relaxation times of 1.9×10^{-5} s and 1.7×10^{-3} s, respectively, at 200K are quite different. Therefore, it appears that the molecular relaxations of the trihalophenols have been restricted by intermolecular hydrogen bonding. This would account for similar activation enthalpies since the contribution

from breaking the hydrogen bonds would decrease in the order iodo < bromo < chlorophenols. This sequence is in agreement with that given by Baker and Shulgin,[17] and is according to the reverse order of the intermolecular halogen-hydroxyl bond strength which would be weakened as the size of the ortho-substituent was increased. Consequently, the energy barriers observed for the higher temperature process of 2,4,6-triiodophenol, e.g., ΔH_E = 48 kJ mol^{-1} and $\Delta G_{E(200K)}$ = 46.2 kJ mol^{-1}, may be entirely due to simple molecular relaxation since hydrogen bonding would be negligible and very weak owing particularly to the steric hindrance of the iodine atoms at the ortho positions. In a similar manner, the molecular relaxation barriers of 2,4,6-tribromophenol probably involve less contribution for hydrogen bond breaking than that with 2,4,6-trichlorophenol, but the larger size of the former could compensate for this effect. It can be noted that although the activation enthalpies obtained from the high temperature absorption of the trihalophenols are similar, the free energies of activation increase from 35.7 to 46.2 kJ mol^{-1} at 200K and so also the corresponding relaxation times are lengthened from 5.1 x 10^{-4} s to 2.7 x 10^{-1} s as the size of the molecule increases from that of trichloro to triiodophenol. This is further consistent with the concept that molecular relaxations which, of course, were restricted by intermolecular hydrogen bonding to some extent, were the primary feature.

In the cases of pentachlorophenol and pentachlorobenzenethiol, the influence of intermolecular hydrogen bonding on the molecular relaxation energy barriers and on the associated relaxation times is not apparent although the steric effect of the chlorine atoms would not be expected to restrict the association. The enthalpies of activation for the higher temperature absorption of the two molecules were found to be 48 and 47 kJ mol^{-1}, respectively, which are in excellent agreement with that of 47 kJ mol^{-1} obtained for pentachlorotoluene (Table III-3) and are also comparable to those of 45 - 48 kJ mol^{-1} observed from the higher temperature absorption of the trihalophenols. The activation free energy of 35.7 kJ mol^{-1} at 200K of pentachlorophenol is even lower than that of 40.2 kJ mol^{-1} for the pentachlorotoluene. The corresponding relaxation time of 5.1×10^{-4} s for the former at 200K is also shorter than that of 7.5×10^{-3} s for the rigid molecule at the same temperature. On the other hand, the activation energy barriers for the higher temperature absorptions of 2,4,6-trichlorophenol and pentachlorophenol are remarkably similar, and their relaxation times are identical at 200K (5.1×10^{-4} s). However, since the latter does not show any increased barrier or longer relaxation time over those of pentachlorotoluene, it would appear that the molecular relaxation of pentachlorophenol has not been restricted, in contrast to that of the trichlorophenol. A similar situation is apparent for the higher temperature absorption of pentachlorobenzene-

thiol showing ΔH_E = 47 kJ mol^{-1}, $\Delta G_{E(200K)}$ = 40.0 kJ mol^{-1}, and $\tau_{200K} = 6.5 \times 10^{-3}$ s which correspond very well with the values of 47 kJ mol^{-1}, 40.2 kJ mol^{-1}, and 7.5 x 10^{-3} s, respectively, for pentachlorotoluene. Nevertheless, the free energies of activation are higher and the relaxation times are longer for pentachlorobenzenethiol compared to those of pentachlorophenol, in accord with their relative sizes.

It should be mentioned that a high temperature absorption was also observed for pentabromophenol above 300K, but the dielectric measurements could not be carried out reliably owing to the very low loss of the system and also to the onset of the glass-transition process at higher temperatures. However, an estimate of the free energy of activation of ∿50 kJ mol^{-1} at 310K was made, and this seemed to be reasonable for a molecular process compared to that of 52.1 kJ mol^{-1} at 300K of pentabromotoluene (Table III-3), a similarly-sized rigid molecule. A remarkable feature of the higher temperature absorptions of pentachlorophenol and pentachlorobenzenethiol is that they show high β values of 0.35 - 0.53 and 0.59 - 0.75, respectively, (see Appendix A, Table 8), similar to those observed for the pentachloro- and pentabromotoluenes in polystyrene matrices. This would appear to indicate that the geometry of the molecules allows the dielectric relaxations to approach Debye behaviour as the temperature is increased. In other words, the size and shape of the molecules

are such that the relaxation processes are very much less dependent on the medium, as has also been observed in the pure solids (discussed in Chapter III).

It is also notable that the higher temperature processes, where intermolecular hydrogen bonding has been found to be responsible for increased energy barriers and longer relaxation times of the molecular processes, are associated with higher entropies of activation than those of the corresponding rigid molecules. For example, 2,4,6-trimethylphenol shows ΔS_E = 100 JK^{-1} mol^{-1} compared to 6 JK^{-1} mol^{-1} obtained for 2,4,6-trimethylbenzonitrile (Table III-3). Similar comparisons can be made for the other systems, the differences being less marked where hydrogen bonding is not very important owing to steric and/or other factors. This would not be unreasonable since breaking of hydrogen bonds as a prerequisite to molecular relaxation introduces considerable disorder in the activation process.

In all the halophenols, where both ortho positions are substituted, the hydroxyl group can exist in two equilibrium positions, i.e., hydrogen bonded to one or the other of the two substituents. It can reverse its direction by breaking the hydrogen bond, rotating around the C — O bond and then hydrogen

bonding to the other substituent. Such a process would give rise to dielectric absorption, but the energy barrier would depend significantly on the strength of the intramolecular hydrogen bond. This is possibly the reason that a low temperature absorption around 100K, which is presumably due to OH group relaxation, has been observed for each of the halophenols in contrast to those in 2,4,6-trimethylphenol or in 2,4,6-tri-t-butylphenol, where the tail-end of the absorptions was noted only at low temperatures.

The enthalpies of activation for the low temperature processes observed for 2,4,6-trichlorophenol, 2,4,6-tribromophenol, and 2,4,6-triiodophenol were 15, 14, and 10 kJ mol^{-1}, while the free energies of activation at 100K were 15.6, 16.8, and 14.7 kJ mol^{-1}, respectively. These are almost the same except that the activation enthalpy in the case of 2,4,6-triiodophenol appears to be slightly lower than those of the other two cases. Similarly low activation energies of 9.2 and 11.7 kJ mol^{-1} for the hydroxyl group relaxation of 2,4,6-tri-t-butylphenol have been obtained in the pure solid studied by Meakins,[6] and in solution in decalin as studied by Davies and Meakins,[7] respectively. On the other hand, Walker _et al._[13] found much higher activation enthalpies of ~35 kJ mol^{-1} for hydroxyl relaxation of 2,6-dinitrophenols in polystyrene matrices, suggesting that "the intramolecular hydrogen bond in 2,6-dinitrophenol is much

closer to being a strong hydrogen bond than a weak one". It was also proposed that the transition of the hydroxyl group from one planar hydrogen bonded position to the other takes place over an energy barrier which is strongly dependent on the energy required to break the intramolecular hydrogen bond. Therefore, the low energy barriers observed for the trihalophenols would appear to indicate that the intramolecular hydrogen bonding of the hydroxyl group with the various halogens is of the weak type. The enthalpies of intramolecular halogen-hydroxyl interaction have been determined by different methods, and the most generally accepted order, as given by Baker and Shulgin,[17] for the three heavier halogens is $c\ell > Br > I$. These workers also found the magnitude of the enthalpies to be 6.0, 5.1, and 4.5 kJ mol^{-1}, respectively, from infrared studies, and such values are clearly consistent with the low energy barriers obtained for the hydroxyl group relaxations in the trihalophenols. Although the difference between the strength of intramolecular halogen-hydroxyl interaction in the trihalophenols is not apparent from the present observations, it is conceivable that the hydroxyl relaxation barrier depends on the energy required to break the hydrogen bond. With the increase of the size of the halogen atom the barriers might have been compensated to some extent by a small steric effect. It can be noted that the relaxation time of 2.7×10^{-4} s at 100K from the low temperature absorption

of 2,4,6-tribromophenol is appreciably longer than the corresponding value of 6.7×10^{-5} s for the OH group relaxation in 2,4,6-trichlorophenol, while the shortest relaxation time of 2.3×10^{-5} s at the same temperature is observed for 2,4,6-triiodophenol. This would appear to indicate that the strength of the halogen-hydroxyl interaction does not alone determine the energy barriers and the relaxation times for the OH group rotations observed in the trihalophenols.

The pentahalophenols showed larger variations in the energy barriers of their low temperature absorptions. In addition, these values are higher than those of the trihalophenols. The highest enthalpy of activation of 26 kJ mol^{-1} was obtained for pentachlorophenol, that of pentabromophenol being 20 kJ mol^{-1}. The corresponding free energies of activation at 100K are 22.3 and 19.6 kJ mol^{-1}, the relaxation times being 2.2×10^{-1} s and 8.1×10^{-3} s, respectively, at the same temperature. The relatively higher barriers and longer relaxation times compared to those of the trihalophenols may not be due solely to the strength of the intramolecular halogen-hydroxyl interaction.

It is important to note that the acidity of the tri- and pentahalophenols varies considerably as reflected in the pK_a values[18] of 4.8 for pentachlorophenol compared to those of 6.5

and 6.2 for 2,4,6-trichlorophenol and 2,4,6-tribromophenol, respectively. This would indicate that the double bond nature of the bond from the phenolic oxygen to the ring carbon is greater in pentachlorophenol so that the rotation of the hydroxyl group would involve higher energy barriers. The pK_a values for the two trihalophenols are almost the same and so also their energy barriers. In terms of the acidity of a substituted phenol, a much lower barrier for the OH group relaxation may be anticipated for 2,4,6-trimethylphenol, which has a pK_a value[18] of 10.9. These considerations also correlate well with the OH torsional frequencies obtained by Fateley and his co-workers.[19] They have clearly demonstrated that the phenolic-OH torsional frequency is a direct measure of the double bond character of the phenolic C — O bond. Thus, the sequence of activation enthalpy of 15, 14, 10, and 26 kJ mol^{-1} for 2,4,6-trichlorophenol, 2,4,6-tribromophenol, 2,4,6-triiodophenol, and pentachlorophenol, respectively, compares well with the sequence of the corresponding OH torsional frequencies of 393, 393, 382, and 407 cm^{-1} observed in cyclohexane solutions. 2,4,6-Trichloro and 2,4,6-tribromophenol show similar double bond character of the C — O bond as evidenced from the same OH torsional frequency. On the other hand, pentachlorophenol shows a higher OH torsional frequency while 2,4,6-trimethylphenol has a much lower value of 289 cm^{-1} in accordance with its pK_a of 10.9.

In contrast to pentachlorophenol, the absorption due to the SH group rotation in pentachlorobenzenethiol shows significantly lower energy barriers. The enthalpy of activation and free energy of activation at 100K are only 14 and 16.3 kJ mol^{-1}, respectively, and are comparable to those observed for the OH group rotation in trihalophenols. This is noteworthy since the size of the SH group is relatively bigger than that of the OH group so that, if there is any steric factor responsible for the energy barriers, then it would be more pronounced for the thiol group. Neither the pK_a nor the S — H torsional frequency is available at present for pentachlorobenzenethiol but there is evidence in the literature that thiols form only weak hydrogen bonds, if any at all. As Pimental and McClellan[2] stated, "the S - H group does show the specific H - bond association behaviour with strong bases, and it seems likely that the relative weakness of the S — H as a proton donor accounts for the absence of H - bonds in some systems". Therefore, the lower barrier to S — H group relaxation may be accounted for mainly by the strength of the intramolecular hydrogen bond in that the S — H bond is much less ionic (lower acidity and hence weaker proton donor) than the O — H bond and would form weaker hydrogen bonds with the chlorine atoms at the ortho positions. Relaxation times also follow the same pattern as the energy barriers for the OH group rotations in the various halophenols. Thus, at 100K,

pentachlorobenzenethiol shows a much shorter relaxation time of 1.6×10^{-4} s than those of 2.2×10^{-1} s and 8.1×10^{-3} s for pentachlorophenol and pentabromophenol, respectively. On the other hand, 2,4,6-tribromophenol shows a relaxation time of 2.7×10^{-4} s at 100K, comparable to the corresponding value of 1.6×10^{-4} s for pentachlorobenzenethiol, the absorptions being observed in the temperature ranges of 108 - 138K and 93 - 132K respectively.

It is important to note that the β values observed for the hydroxyl relaxations are significantly high even though the absorptions occurred at low temperatures. Of all the low temperature absorptions noted for the different substituted phenols, 2,4,6-triiodophenol showed the highest β values of 0.25 - 0.57 (see Appendix A, Table 8) in the temperature range of 84 - 116K. Walker et al.[13] also found high β values of 0.30 - 0.45 for the hydroxyl relaxation in 2,6-dinitrophenols, and this would appear reasonable since the relaxation of the small OH group between the two planar equilibrium positions would be little dependent on the surrounding medium. Concerning the dipole moments observed from the low temperature absorption of the various halophenols, it may be noted that the effective values range between ∿0.4 - 0.9 D, which are of the order of magnitude to be expected for OH group

relaxation at low temperatures. However, the observed moments for a particular halophenol were virtually constant, and, except for pentachlorophenol, their variations with temperature were anomalous so that the extrapolation was not fruitful.

In conclusion, it may be said that the energy barriers as well as the relaxation times obtained for the dielectric absorptions of the different substituted phenols showed considerable dependence upon the intermolecular and intramolecular hydrogen bonding. In addition, molecular relaxations were restricted in a number of cases by intermolecular hydrogen bonding and, at least for the trihalophenols, it would appear that the contribution to energy barriers from such association followed the order chloro > bromo > iodo, in accordance with the sequence given by Baker and Shulgin.[17]

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CHAPTER VIII

METHOXY GROUP AND MOLECULAR RELAXATION OF SUBSTITUTED ANISOLES

INTRODUCTION:

Many dielectric studies of anisole and its derivatives have been carried out in solutions, and there exists sufficient evidence to suggest that the methoxy group has a high degree of mobility. For example, Farmer and Walker[1] found that anisole, p-methylanisole, and p-dimethoxybenzene relax predominantly by methoxy group rotation, while the mean relaxation time, τ_0, of the latter compound has been shown by Grubb and Smyth[2] to vary little with increasing solvent viscosity. However, there are conflicting views on the mobility of the methoxy group in sterically hindered aromatic ethers. Maier's[3] work on 2-chloro, 2,6-dichloro, and 2,4,6-trichloroanisole in dilute benzene solutions at 20°C gave τ_0 values of 12.3, 19.9, and 12.0 ps, respectively. By comparing these values with a theoretical relaxation time, calculated on the basis of molecular dimensions and assuming the molecule to be rigid, Maier concluded that the methoxy group rotation was not hindered at all by the chlorine substituents. He explained the longer τ_0 for the disubstituted molecule by an increased molecular component of the dipole moment, leading to a greater contribution from molecular relaxation, while the C - Cl dipoles in trichloroanisole compensate one another.

Although Mountain[4] found that the relationship between relaxation time and molecular volume is only of approximate nature and should not be used for axially asymmetric molecules,[5] he stated that an intramolecular process would certainly appear to occur in these compounds, especially in 2,4,6-trichloroanisole. For this molecule, however, Le Fèvre and his co-workers[6] obtained a longer τ_0 of 20.9 ps in benzene solution at 18°C, suggesting that the methoxy group encountered a higher barrier to rotation. Klages and Zenteck[7] reported an approximate mean relaxation time of 15.9 ps for 2,4,6-trimethylanisole in benzene solution at 20°C with τ_1 = 22.7 and τ_2 = 0.8 ps. This result is in disagreement with that of Le Fèvre *et al.* since the two molecules are of equivalent size. In a later paper, however, Klages and Knoblich[8] showed that the relaxation time for the intramolecular process in the 2- and 2,5-substituted anisoles had lengthened in comparison with that of the parent compound, whereas substitution of the same groups in acetophenone appeared to increase the mobility of the acetyl group.

The different behaviour between the acetyl and the methoxy compounds was especially noticeable in the 1-substituted naphthalenes where the peri-hydrogen on the carbon at position 8 is a possible hindrance to group rotation. This is further

substantiated by the results of Grubb and Smyth[2], who also studied naphthalene ethers in viscous solutions. These workers observed longer τ_0 for 1-substituted naphthalenes than that of the 2-substituted ones and concluded that the ether group in the 1-position was being sterically hindered. Vaughan and his co-workers[9] disagreed with these conclusions and argued that internal rotation was not restricted in either 1- or 2-methoxynaphthalene, the τ_2 and C_2 values being comparable in both cases measured in the liquid state. But their analysis appeared to be doubtful since the extrapolated molecular relaxation times at 80°C were 14.9 and 30.6 ps for 2- and 1-methoxynaphthalene, respectively, whereas 2-substituted naphthalenes normally have the longer relaxation time.[10] Further evidence for an increased potential energy barrier to methoxy group rotation has been provided by the dielectric data of 2,6-dimethylanisole in benzene solution studied by Fong and Smyth.[11] The mean relaxation time, τ_0, of this molecule was found to be longer than that of the equivalently-sized 3,5-dimethylanisole, although the increase could partly be accounted for by a smaller molecular component moment in the latter. Similar behaviour was observed by Mehrotra and his co-workers[12], who studied 2,4-dinitro derivatives of phenol, anisole, and phenetole, concluding that the relaxation times increased with the size of the mobile group owing to greater steric hindrance.

It is evident that some controversy exists in the literature regarding the mobility of the ether groups when there is possible steric hindrance between the movable group and the neighbouring substituent. All these discussions, however, are based on comparisons of relaxation times obtained by different methods which are susceptible to varying errors depending on the number of frequencies and of measurement temperatures. Mountain[4] made a more rigorous approach for detecting such processes from comparison of the mean relaxation time of ortho substituted ethers with those of the analogous dihalobenzenes. He also studied some aromatic ethers including those containing the ethoxy group and came to the conclusion that, of the ortho substituted derivatives studied, an intramolecular relaxation mechanism was detected only in 2-fluoroanisole, the remaining molecules having τ_0 values similar to those of analogous rigid molecules. Mountain, however, did not rule out the possibility of methoxy group rotation when there is a larger ortho substituent to the group.

The current technique of studying molecular and intramolecular motions in polystyrene matrices has demonstrated its effectiveness particularly in the case of acetyl-substituted, fused ring systems as discussed in Chapter VI. The two processes

were completely separated for 2- and 3-acetylphenanthrenes while the absorption of 2-acetylnaphthalene was complicated by overlapping absorptions. The question of an enhanced conjugation in the latter compound has been discussed, and it would also seem desirable to investigate similar problems related to methoxynaphthalenes, but an appreciation of the relaxation behaviour of the methoxy group rotation in polystyrene matrices is essential beforehand. The work reported in this chapter was initiated mainly to characterize the methoxy group rotation in several molecules where it would be expected to occur, thus laying the ground work for further studies.

DISCUSSION:

The Eyring analysis results for the different methoxy substituted compounds are given in Table VIII-1. It can be seen that only 3,5-dimethylanisole and 2,4,6-tribromoanisole have shown two absorptions. The former molecule is expected to have the same component moments along the long axis as for p-methylanisole, and, therefore, Farmer[13] suggested that the molecular weight factor, C_1, would be virtually zero. The present observations do not seem to bear this out since the higher temperature absorption (170 - 199K) may be assigned to the molecular process by comparison with the results for the molecular relaxation of 3,5-dichlorobenzonitrile,

TABLE VIII-1 EYRING ANALYSIS RESULTS FOR SUBSTITUTED ANISOLES

Molecule	T(K)	τ(s) 150K	τ(s) 200K	τ(s) 300K	ΔG_E(kJ mol^{-1}) 150K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (JK^{-1} mol^{-1})
p-Nitro-anisole	212 - 250	6.4×10^{0}	1.2×10^{-3}	1.9×10^{-7}	38.2	37.1	34.9	42	22
3,5-Dinitro-anisole	188 - 249	2.7×10^{-1}	1.8×10^{-4}	1.1×10^{-7}	34.2	34.0	33.6	35	4
3,5-Dimethyl-anisole	81 - 109	1.2×10^{-7}	1.3×10^{-8}	1.2×10^{-9}	16.0	18.1	22.3	10	-42
"	170 - 199	1.5×10^{-2}	6.4×10^{-6}	2.4×10^{-9}	30.6	28.4	24.0	37	44
2,4,6-Tri-bromoanisole	115 - 150	4.2×10^{-6}	1.2×10^{-7}	3.2×10^{-9}	20.5	21.9	24.7	16	-28
"	178 - 217	1.7×10^{-2}	1.9×10^{-5}	1.8×10^{-8}	30.8	30.2	29.1	33	12
Pentafluoro-anisole	112 - 143	1.6×10^{-6}	3.6×10^{-8}	7.1×10^{-10}	19.3	19.8	20.9	18	-11
2,6,-Dimethoxy-naphthalene	278 - 301	4.3×10^{12}	6.3×10^{3}	8.3×10^{-6}	72.2	62.9	44.3	100	186

a similarly-sized rigid molecule. The activation enthalpy of 37 kJ mol^{-1} obtained for 3,5-dimethylanisole is in good agreement with that of 38 kJ mol^{-1} for 3,5-dichlorobenzonitrile (Table III-3) although the relaxation times and the free energies of activation, particularly at higher temperatures, are considerably lower for the anisole derivative since the latter exhibits a higher entropy of activation (44 JK^{-1} mol^{-1}) than that of the other (11 JK^{-1} mol^{-1}). The lower temperature (81 - 109K) process yielded activation enthalpy and entropy of 10 kJ mol^{-1} and -42 JK^{-1} mol^{-1}, respectively, presumably for the methoxy group rotation. The relaxation time of 1.2×10^{-7} s at 150K is about 10^5 times shorter than the corresponding value from the higher temperature absorption, suggesting further the intramolecular nature of the low temperature process. The extrapolated value of 1.2×10^{-9} s at 300K is much longer than the relaxation time of $\sim 7 \times 10^{-12}$ s at $25^{o}C$ observed in solutions for the methoxy group rotation in anisole.[13] Such a difference has been observed, in general, both for the molecular and intramolecular relaxations in polystyrene matrices compared to those in solutions (see Chapters III and IV) and is most likely due to the viscosity effect of the medium. Therefore, since there are two possible sources of dielectric absorption, i.e., by molecular or group relaxation processes, then either of the processes may be assignable to one

or the other, but it is more reasonable that the higher temperature process is the molecular one, while the other is due to the methoxy group rotation.

The results obtained for 3,5-dimethylanisole can be contrasted with those for 3,5-dichlorophenol (Chapter VII). The latter molecule showed only one absorption which corresponded to a restricted molecular motion due to association. This is possibly the reason that the OH group relaxation was too weak to be observed at low temperatures since intermolecular association would decrease the concentration of species capable of exhibiting the free intramolecular group rotation.

In the case of 2,4,6-tribromoanisole, the low energy absorption has been shifted to higher temperatures (115 - 150K). Correspondingly, the activation parameters are greater and the relaxation times are longer than those obtained for the lower temperature process of 3,5-dimethylanisole. Thus, the enthalpy and free energy of activation of 16 kJ mol^{-1} and 20.5 kJ mol^{-1} at 150K, respectively, appear to be greater for a methoxy group rotation. The relaxation time of 3.2×10^{-9} s at 300K is of an order of magnitude similar to that of the previous case but is longer than at lower temperatures. On the other hand, the hydroxyl group relaxation in 2,4,6-tribromophenol (Chapter VII) showed

ΔH_E = 14 kJ mol^{-1} and ΔG_E = 18.3 kJ mol^{-1} at 150K, which are comparable to those of the methoxy group rotation in the tribromoanisole. This is not surprising especially since the mesomeric moments would be fairly similar for phenols and anisoles. But the hydroxyl relaxation barrier in halophenols appeared to have been modified by intramolecular hydrogen bonding (as discussed in Chapter VII) while the methoxy group rotation in the corresponding anisole derivative would be more restricted by steric hindrance. However, the higher energy barriers for the methoxy group rotation in 2,4,6-tribromoanisole compared to that in 3,5-dimethylanisole would appear to indicate the latter effect, owing to the adjacent bromine atoms in positions 2 and 6, since any effects of substituent dipoles cancel each other. This is in more or less general agreement with various workers but differs from Mountain's finding[4] in that a substituent much larger than fluorine in size has not inhibited completely the methoxy group rotation by steric effect. Mountain also studied this molecule in solution, but he found no evidence of intramolecular relaxation.

Fong and Smyth[11] suggested that the methoxy group is forced out of coplanarity with the benzene ring by the two adjacent methyl groups in the 2,6-derivative. In the 2,4,6-tribromoanisole, the methoxy group is probably further out of the plane of the

benzene ring than in the dimethylanisole. It is possible that the most likely orientation of the methoxy group is between two non-planar equilibrium positions and that the group never passes through a planar position. Employing Kerr constants in studying the conformations of anisoles with methyl, chloro, or bromo substituents in both ortho positions, Le Fèvre and his co-workers[14] reported that the molecules existed preferentially in a conformation in which the C_{Ar}-O-C_{Me} plane is orthogonal to the benzene ring. As a result, there can be little release of charge from oxygen to the aromatic nucleus so that the energy barriers to group rotations may have been governed mainly by the steric effect of the ortho substituents in 2,4,6-tribromoanisole.

The difference in the activation parameters and relaxation times obtained for the other absorption of 2,4,6-tribromoanisole is also notable. The higher temperature (178 - 217K) process with ΔH_E = 33 kJ mol^{-1}, ΔS_E = 12 JK^{-1} mol^{-1} and ΔG_E = 30.2 kJ mol^{-1} at 200K can be attributed to the molecular relaxation by comparison with the corresponding values of 29 kJ mol^{-1}, 6 JK^{-1} mol^{-1}, and 27.9 kJ mol^{-1} for 2,4,6-trimethylbenzonitrile; and of 29 kJ mol^{-1}, 1 JK^{-1} mol^{-1}, and 29.0 kJ mol^{-1} for 2,4,6-trichloronitrobenzene, respectively (Table III-3). These two rigid molecules are smaller than the tribromoanisole in size, both showing absorptions at

similar temperature ranges of ∿160 - 200K, and therefore, the comparisons seem reasonable. It can be mentioned that significantly higher energy barriers, ΔH_E = 45 kJ mol^{-1} and ΔG_E = 37.8 kJ mol^{-1} at 200K, were obtained for the molecular relaxation of 2,4,6-tribromophenol, which appeared to have been restricted by intermolecular association.

There is another distinctive feature between the lower and the higher temperature absorptions of 2,4,6-tribromoanisole in that the β values of 0.22 - 0.32 for the lower temperature process are relatively higher than those of 0.14 - 0.22 (see Appendix A, Table 9) for the other process. This means that the former relaxation mechanism was less dependent on the medium even at much lower temperatures, which is generally true for the intramolcular process. Therefore, the two processes are clearly distinguished and it appears that the technique has been of value in separating the methoxy group absorption from the molecular one in, at least, a sterically hindered situation and also in the case of 3,5-dimethylanisole where no such factor is involved.

Pentafluoroanisole has been of particular interest since the size of the molecule is very close to that of the parent

anisole, the van der Waals radius of fluorine (1.4 Å) being nearly equivalent to that of hydrogen (1.2 Å). But fluorine has a strong electron-withdrawing effect and hence would enhance planarity of the methoxy group with the benzene ring. This, in turn, would give rise to increased double bond character of the aromatic carbon to methoxy oxygen bond so that the barrier to intramolecular group rotation could be increased. The fact that halophenols have lower pK_a values than phenol itself also substantiate the above statement. In addition, the substituents at the ortho positions may impart a little steric hindrance to rotation of the group in pentafluoroanisole. However, this molecule has shown a single absorption in the temperature range of 112 - 143K, nearly the same range as that of lower temperature absorption in 2,4,6-tribromoanisole but at a higher range than (81 - 102K) for the molecular relaxation of the similarly-sized rigid molecule pentafluorotoluene. Pentafluoroanisole shows an activation enthalpy of 18 kJ mol^{-1}, in agreement with that of 16 kJ mol^{-1} obtained from the low temperature absorption in tribromoanisole but markedly higher than that of only 9 kJ mol^{-1} for the pentafluorotoluene (Table III-3). The activation free energy of 19.3 kJ mol^{-1} at 150K for the former is similar to the corresponding value of 20.5 kJ mol^{-1} in tribromoanisole but is relatively higher than the value of 16.1 kJ mol^{-1}

for pentafluorotoluene. In contrast to pentafluorotoluene, there is remarkable agreement with the results for p-fluorotoluene, showing ΔH_E = 18 kJ mol^{-1} and ΔG_E = 18.4 kJ mol^{-1} at 150K. This rigid molecule was studied by a co-worker[16] and the absorption was measured in the same temperature (113 - 140K) and frequency range as those of pentafluoroanisole. Similarly, the results for bromobenzene (Table III-1) with ΔH_E = 16 kJ mol^{-1} and ΔG_E = 18.2 kJ mol^{-1} at 150K are also comparable with those of pentafluoroanisole, the bromo substituent being slightly smaller than the methoxy group and so also the benzene ring. It is, however, difficult to make an exact comparison for molecular relaxation of pentafluoroanisole since neither of the rigid molecules is equivalent in size. On the other hand, the energy barrier to methoxy group rotation in 2,4,6-tribromoanisole apparently is increased by the steric effect of the ortho substituents for which there is no extra moment, while in pentafluoroanisole the additional fluorine atoms in the meta positions with a resultant moment along the direction of the principal axis but acting away from the ring may increase the barrier to some extent.

Pentafluoroanisole may be expected to give a high C_2 value, analogous to the 4-haloacetophenones,[4] so that the molecular

process would seem less probable. But Walker et al.[15] calculated for this molecule a C_1 value of 0.71 although they analysed and interpreted their relaxation times data in cyclohexane solution at 25°C in terms of two relaxation processes, one corresponding to the molecular rotation and the other to the intramolecular group rotation. The same workers calculated a mesomeric moment of 0.6D which was very close to that of p-chloroanisole, indicating that the resonance effects in the two molecules are similar. This is in harmony with the analogous dipole moments[17] of 2.27D and 2.17D for p-chloroanisole and pentafluoroanisole, respectively. The high mesomeric moment would result in an appreciable double bond character of the aromatic carbon to methoxy oxygen bond so that the energy barrier to group rotation may be relatively high. p-Methylanisole also showed[15] a high mesomeric moment of 0.7D and this molecule was found[1] to relax predominantly by methoxy group rotation. In view of these evidences it would be unwise to assign the absorption of pentafluoroanisole to any particular process, and perhaps the most credible interpretation is an overlap of group and molecular processes. Nevertheless, the effective dipole moment of ~0.9D extrapolated at 300K does probably signify that the intramolecular process has been predominantly observed because such a low value is far from the component to be associated with the molecular process, while the literature[17] value is 2.17D.

Attempts have been made to characterize methoxy group rotation, which would be free from any complication caused by molecular relaxation, but owing to the very high degree of mobility of the group these were not successful. Such is probably the case with 2,6-dimethoxynaphthalene although there is some mesomeric moment along the long axis of the molecule to hinder the methoxy group rotation. A very weak absorption around room temperatures (278 - 301K) yielded activation enthalpy and entropy of 100 kJ mol^{-1} and 186 JK^{-1} mol^{-1}, respectively. These values fit precisely in the relation, ΔS_E (JK^{-1} mol^{-1}) = -150 + 3.24 ΔH_E (kJ mol^{-1}), given in Chapter IV, corresponding to the cooperative motion of solutes in polystyrene matrices. However, the results obtained for this process are not very reliable owing to inaccuracy of dielectric measurements associated with low loss, e.g., $\varepsilon''_{max} = 2.12 \times 10^{-3}$ at 301K. This molecule was also studied in pure solid disks where only the intramolecular process could be expected to occur, but again the loss was too low at liquid nitrogen temperatures. However, an activation free energy of 13 kJ mol^{-1} has been estimated for a very weak absorption at 80.4K, and a similar enthalpy of activation would also be expected. Very recently, another co-worker[18] in this laboratory succeeded in characterizing the methoxy group rotation in 4,4'-dimethoxybiphenyl for which the absorption measured in the temperature range of 85 - 103K resulted in comparable activation

parameters, such as ΔH_E = 13.8 kJ mol^{-1} and ΔG_E = 13.6 kJ mol^{-1} at 100K.

Some nitro derivatives of anisole, viz., p-nitroanisole and 3,5-dinitroanisole, have been studied to ascertain whether the stro electron-withdrawing effect of the nitro group on the energy barriers to methoxy group rotation and on its relaxation times could be observed. But each of these molecules has shown only one absorption, the relaxation parameters for which correspond well with those of the similarly-sized rigid molecules. Thus, p-nitroanisole yields ΔH_E = 42 kJ mol^{-1}, ΔS_E=22 JK^{-1} mol^{-1}, and ΔG_E = 37.1 kJ mol^{-1} at 200K, in excellent agreement with the corresponding values of 41 kJ mol^{-1}, 23 JK^{-1} mol^{-1}, and 36.4 kJ mol^{-1}, respectively, for p-bromonitrobenzene (Table III-1). The relaxation time of 1.2 x 10^{-3} s at 200K for p-nitroanisole may be compared with that of 7.7 x 10^{-4} s at the same temperature for the rigid molecule, the absorptions having been observed in the same temperature range of ∿200 - 250K. Similarly, 3,5-dinitroanisole gives an activation enthalpy of 35 kJ mol^{-1} which appears to be slightly higher than the value of ΔH_E = 31 kJ mol^{-1} obtained for 3,5-dinitrobenzonitrile (Table III-3), but the activation free energy of 34 kJ mol^{-1} at 200K is in good agreement with the corresponding value of 34.3 kJ mol^{-1}, respectively. The absorptions of these two latter molecules were also measured

in the similar temperature range of ∿190 - 250K, and their relaxation times of 1.8×10^{-4} s and 2.2×10^{-4} s, respectively, at 200K are also comparable. On the other hand, the above results for the two nitro derivatives of anisole are markedly different from those of the methoxy group rotations observed in 3,5-dimethylanisole and 2,4,6-tribromoanisole, discussed previously.

It is understandable that a nitro substituent at the para position would favour the quinonoid structure, thereby increasing the barrier to methoxy group rotation. The effect would be similar in the 3,5-dinitro derivative since the resultant moment of the two nitro substituents acts from the para position along the long axis but away from the ring. But it is not distinguishable whether the barriers increased so much as to cause any significant overlap with the molecular process, especially when the extrapolated dipole moments of the order of 3 D were found to be too high to be accountable for by only the intramolecular process in either case. It may also be possible that the substituents withdraw more electron density towards the ring than is retained in the aromatic carbon to methoxy oxygen bond so that the barrier to group rotation would, in essence, be decreased. However, from comparison of the results with those of the analogous rigid molecules

and from consideration of the high effective dipole moments of 1.7 - 2.3 D (see Appendix A, Table 9) even at the experimental temperatures around 200K, it would appear that, at least, group rotations have not been favoured or, in other words, molecular relaxation processes have been observed to predominate.

The behaviour of the two nitro derivatives, particularly of the p-nitroanisole, is to be contrasted with that of p-nitrophenol (Chapter VII) since the mesomeric moments would be similar. However, the dielectric absorptions of the latter molecule were not due to simple molecular and group relaxations, independently. Therefore, it is difficult to justify on that basis that two different absorptions would not be observed for p-nitroanisole although an overlap of both the molecular and group processes is possible.

In view of the above results, however, it may be concluded that some appreciation of the methoxy group relaxation behaviour in polystyrene matrices has been gained. The technique has been useful in some cases to separate the molecular and group relaxation processes in anisoles, as in other types of molecules discussed in the previous chapters, but further work should be carried out to handle complicated overlapping absorptions.

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APPENDIX A

TABLES OF FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS

TABLE 1 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR MONO- AND PARA- SUBSTITUTED BENZENES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.881M Chlorobenzene				
80.7	541	2.469	0.18	6.18	2.431	0.39
85.7	250	2.804	0.18	6.60	2.436	0.42
89.8	126	3.102	0.18	6.96	2.437	0.44
94.0	59.8	3.425	0.18	7.31	2.438	0.46
98.7	28.5	3.747	0.19	7.70	2.443	0.47
104.5	12.5	4.106	0.20	8.18	2.447	0.49
110.7	5.59	4.454	0.21	8.61	2.452	0.51
		0.641M Bromobenzene				
101.0	433	2.566	0.16	6.91	2.554	0.56
105.7	208	2.883	0.17	7.27	2.555	0.58
110.6	91.9	3.238	0.17	7.36	2.451	0.61
117.0	25.9	3.789	0.17	8.16	2.556	0.64
122.5	12.4	4.110	0.18	8.66	2.560	0.65
128.6	6.67	4.378	0.20	9.17	2.568	0.65
136.1	3.03	4.721	0.22	9.75	2.575	0.66
		0.331M 1-Adamantanecarbonitrile				
106.3	1093	2.163	0.17	23.71	2.716	1.37
113.7	459	2.540	0.16	25.51	2.704	1.51
121.3	117	3.136	0.17	27.42	2.704	1.57
130.7	28.4	3.748	0.18	29.43	2.700	1.64
140.5	10.2	4.195	0.20	31.51	2.704	1.68
149.5	5.77	4.441	0.23	33.12	2.728	1.65
157.5	3.14	4.705	0.25	34.58	2.736	1.67
		0.560M Benzonitrile				
132.5	838	2.279	0.16	16.35	2.586	1.03
140.6	216	2.867	0.17	17.68	2.585	1.07
146.8	118	3.132	0.17	18.80	2.582	1.14
154.1	50.1	3.502	0.17	20.19	2.575	1.21
159.9	23.9	3.823	0.17	21.03	2.567	1.27
164.7	12.9	4.090	0.17	22.19	2.565	1.30
174.6	5.39	4.470	0.19	23.98	2.570	1.33

TABLE 1 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			0.291M p-Tolunitrile			
196.2	686	2.365	0.19	32.02	2.572	2.23
203.9	268	2.773	0.19	34.16	2.565	2.34
209.1	146	3.038	0.19	35.74	2.560	2.41
214.3	93.8	3.230	0.19	37.43	2.550	2.52
223.7	41.4	3.585	0.18	40.12	2.525	2.75
234.1	13.8	4.061	0.18	43.36	2.505	2.93
244.3	6.21	4.409	0.19	46.29	2.496	3.04
			0.576M p-Nitrotoluene			
184.3	355	2.652	0.17	38.57	2.703	1.74
189.9	177	2.954	0.17	40.59	2.701	1.78
194.2	98.6	3.208	0.18	42.54	2.699	1.82
199.2	58.1	3.438	0.17	44.49	2.689	1.89
204.8	29.1	3.738	0.17	46.89	2.677	1.98
210.9	15.4	4.014	0.17	49.63	2.666	2.06
215.3	11.1	4.156	0.18	51.47	2.671	2.08
220.2	7.60	4.321	0.18	53.55	2.672	2.12
			0.414M p-Bromonitrobenzene			
204.1	393	2.608	0.19	17.32	2.529	1.46
213.5	164	2.987	0.18	18.33	2.518	1.56
221.3	73.3	3.337	0.17	19.05	2.508	1.65
228.8	33.2	3.681	0.17	19.77	2.493	1.74
236.4	14.3	4.045	0.17	20.60	2.483	1.81
245.0	6.32	4.401	0.17	21.50	2.470	1.85
251.6	3.70	4.633	0.18	22.17	2.467	1.88

TABLE 2 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR ORTHO- AND META- DIHALOBENZENES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.447M o-Fluorochlorobenzene				
80.7	582	2.437	0.18	7.96	2.488	0.63
85.1	214	2.872	0.18	8.43	2.489	0.66
89.7	96.3	3.218	0.17	9.01	2.486	0.71
92.7	55.2	3.460	0.18	9.38	2.489	0.72
96.5	26.9	3.772	0.18	9.87	2.487	0.74
101.6	10.7	4.173	0.19	10.65	2.489	0.77
106.2	6.97	4.358	0.21	11.08	2.494	0.77
		0.496M o-Bromochlorobenzene				
88.3	552	2.460	0.14	7.27	2.547	0.65
93.6	187	2.929	0.14	7.76	2.544	0.70
98.8	47.5	3.525	0.13	8.45	2.538	0.77
103.7	11.6	4.138	0.15	9.23	2.540	0.77
106.7	7.27	4.341	0.16	9.66	2.543	0.78
110.5	3.73	4.630	0.16	10.17	2.544	0.80
115.6	2.77	4.760	0.19	10.72	2.555	0.79
119.9	1.97	4.908	0.20	11.16	2.562	0.80
		0.364M o-Chloroiodobenzene				
108.2	264	2.781	0.20	5.57	2.531	0.63
112.4	173	2.963	0.19	5.85	2.531	0.67
118.8	58.6	3.434	0.19	6.32	2.529	0.71
122.1	41.4	3.585	0.21	6.59	2.532	0.71
128.9	13.8	4.063	0.20	7.04	2.530	0.77
134.4	7.34	4.336	0.20	7.41	2.529	0.80
138.0	5.26	4.481	0.21	7.63	2.533	0.80
		0.307M o-Bromoiodobenzene				
102.5	538	2.471	0.19	4.40	2.570	0.61
107.5	226	2.848	0.19	4.70	2.573	0.64
111.8	105	3.181	0.19	4.98	2.574	0.66
116.4	53.8	3.471	0.20	5.28	2.576	0.69
121.5	24.0	3.822	0.20	5.62	2.574	0.72
126.9	11.1	4.156	0.21	6.02	2.579	0.75
132.5	7.07	4.352	0.22	6.30	2.583	0.76
138.9	3.88	4.613	0.23	6.59	2.587	0.78

TABLE 2 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
			0.354M o-Diiodobenzene			
109.4	398	2.602	0.19	5.13	2.621	0.62
115.3	170	2.972	0.19	5.49	2.622	0.66
120.7	84.7	3.274	0.19	5.81	2.625	0.69
127.3	28.7	3.745	0.21	6.21	2.268	0.70
132.5	14.8	4.032	0.21	6.47	2.629	0.72
136.8	9.51	4.224	0.22	6.72	2.632	0.73
141.9	7.06	4.353	0.24	6.87	2.637	0.72
146.7	4.76	4.524	0.25	7.10	2.641	0.72
			0.589M m-Dichlorobenzene			
115.1	264	2.781	0.22	4.89	2.589	0.45
120.5	168	2.976	0.19	5.12	2.591	0.50
124.5	93.3	3.232	0.21	5.37	2.594	0.50
129.3	48.2	3.519	0.22	5.62	2.594	0.51
134.0	24.9	3.805	0.21	5.81	2.598	0.54
139.5	12.1	4.120	0.23	6.16	2.602	0.54
145.9	7.46	4.329	0.25	6.39	2.608	0.54
			0.362M m-Bromochlorobenzene			
128.8	233	2.835	0.18	3.28	2.589	0.56
138.8	56.4	3.451	0.23	3.64	2.597	0.54
148.2	21.7	3.866	0.25	3.96	2.603	0.55
156.7	9.89	4.207	0.24	4.22	2.603	0.59
166.4	5.00	4.503	0.25	4.48	2.611	0.62
176.2	3.09	4.712	0.28	4.74	2.618	0.61
			0.350M m-Chloroiodobenzene			
154.7	375	2.628	0.22	2.42	2.448	0.49
164.7	131	3.084	0.24	2.84	2.460	0.53
184.7	24.3	3.816	0.22	3.37	2.473	0.62
194.6	10.1	4.200	0.24	3.59	2.486	0.64
204.3	5.35	4.473	0.26	3.77	2.495	0.64
214.6	3.09	4.712	0.27	3.90	2.501	0.65

TABLE 2 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			0.722M m-Dibromobenzene			
140.3	396	2.604	0.22	4.82	2.491	0.46
144.7	204	2.892	0.22	5.05	2.499	0.47
149.8	107	3.172	0.22	5.31	2.506	0.49
155.4	51.5	3.490	0.21	5.65	2.507	0.52
160.5	29.0	3.739	0.22	5.98	2.515	0.54
165.0	18.8	3.297	0.22	6.29	2.518	0.56
169.8	11.5	4.142	0.23	6.55	2.522	0.57
173.6	7.35	4.336	0.23	6.77	2.523	0.59
			0.295M m-Bromoiodobenzene			
166.4	420	2.578	0.20	2.28	2.614	0.55
173.7	114	3.146	0.28	2.51	2.621	0.49
180.0	60.7	3.419	0.28	2.64	2.624	0.51
185.4	44.8	3.550	0.27	2.73	2.625	0.54
195.3	15.0	4.025	0.28	2.90	2.631	0.56
204.9	7.51	4.326	0.28	2.94	2.636	0.58
214.9	4.71	4.529	0.31	3.07	2.642	0.57
			0.534M m-Diiodobenzene			
165.6	925	2.236	0.20	2.23	2.606	0.40
175.7	234	2.832	0.27	2.51	2.613	0.38
184.9	101	3.196	0.23	2.71	2.618	0.43
189.7	53.7	3.472	0.24	2.83	2.622	0.43
195.1	29.5	3.731	0.25	3.02	2.624	0.45
204.7	12.8	4.095	0.25	3.20	2.631	0.48
214.2	6.16	4.413	0.25	3.35	2.635	0.50
222.7	2.95	4.732	0.26	3.73	2.638	0.52

TABLE 3 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR POLYSUBSTITUTED BENZENES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.466M 3,5-Dichlorobenzonitrile				
206.8	220	2.860	0.20	22.66	2.638	1.49
214.9	112	3.154	0.19	23.59	2.626	1.60
222.6	51.5	3.490	0.19	24.41	2.618	1.66
229.6	23.5	3.831	0.19	25.18	2.609	1.71
235.2	13.7	4.066	0.19	25.86	2.607	1.73
239.8	9.83	4.209	0.20	26.41	2.608	1.73
245.3	6.09	4.417	0.20	27.03	2.605	1.75
249.5	4.91	4.511	0.21	27.19	2.607	1.76
		0.426M 3,5-Dinitrobenzonitrile				
194.9	428	2.570	0.31	1.17	2.629	0.28
204.7	126	3.102	0.28	1.16	2.632	0.30
214.1	53.3	3.475	0.35	1.25	2.636	0.29
224.2	21.4	3.782	0.29	1.19	2.638	0.32
233.9	15.1	4.024	0.32	1.23	2.640	0.31
		0.401M 2,4-Dinitrochlorobenzene				
185.9	1209	2.120	0.17	15.08	2.622	1.36
199.8	263	2.782	0.16	16.40	2.623	1.49
204.9	148	3.032	0.16	17.46	2.621	1.58
209.8	82.5	3.286	0.16	17.65	2.619	1.62
215.0	43.1	3.567	0.17	18.33	2.617	1.67
219.8	20.6	3.887	0.15	19.05	2.613	1.72
224.5	10.4	4.185	0.16	20.01	2.612	1.77
229.3	8.25	4.286	0.17	20.66	2.627	1.72
234.4	6.30	4.402	0.19	21.37	2.638	1.71
		0.450M 2,4,6-Trichloropyrimidine				
172.1	898	2.249	0.17	10.75	2.652	1.03
178.2	410	2.589	0.17	11.27	2.646	1.08
185.9	149	3.028	0.17	11.98	2.638	1.13
192.7	62.9	3.403	0.17	12.52	2.631	1.19
202.4	16.5	3.984	0.17	13.37	2.621	1.25
212.0	5.68	4.448	0.18	14.25	2.614	1.29
218.7	2.95	4.732	0.19	14.95	2.610	1.30

TABLE 3 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.538M 2,4,6-Trimethylbenzonitrile				
160.2	497	2.505	0.16	29.52	2.622	1.51
165.6	197	2.907	0.18	31.03	2.623	1.52
169.9	127	3.099	0.17	32.39	2.617	1.59
174.5	70.3	3.355	0.18	33.95	2.612	1.64
179.5	41.0	3.589	0.17	35.29	2.601	1.71
184.0	23.9	3.823	0.19	36.99	2.609	1.70
188.0	15.4	4.016	0.21	38.35	2.621	1.67
193.2	9.05	4.245	0.23	40.35	2.635	1.64
		0.244M 2,4,6-Trichloronitrobenzene				
165.7	381	2.621	0.18	7.01	2.691	1.09
171.7	200	2.900	0.18	7.36	2.691	1.12
176.5	125	3.103	0.18	7.73	2.689	1.18
180.4	69.9	3.357	0.18	7.83	2.689	1.18
186.4	37.4	3.629	0.19	8.20	2.688	1.20
190.3	23.4	3.833	0.20	8.50	2.688	1.21
194.9	14.3	4.048	0.21	8.78	2.687	1.22
199.9	9.07	4.245	0.22	9.04	2.688	1.22
		0.425M Pentafluorotoluene				
80.7	90.9	3.243	0.20	4.88	2.587	0.46
85.4	41.7	3.582	0.23	5.24	2.591	0.46
87.7	25.5	3.796	0.22	5.33	2.591	0.48
89.2	22.2	3.856	0.24	5.47	2.592	0.48
93.2	12.2	4.116	0.24	5.69	2.591	0.49
97.1	8.33	4.281	0.25	5.84	2.594	0.50
101.8	5.15	4.490	0.26	6.01	2.596	0.50
		0.305M Pentachlorotoluene				
215.3	947	2.226	0.74	3.75	2.609	0.41
224.0	317	2.702	0.79	3.74	2.603	0.40
233.4	111	3.157	0.80	3.73	2.594	0.41
245.7	31.7	3.701	0.82	3.61	2.580	0.41
255.2	12.8	4.096	0.81	3.55	2.570	0.42
263.5	5.88	4.432	0.83	3.54	2.561	0.42
273.9	2.72	4.768	0.90	3.49	2.551	0.41

TABLE 3 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.233M Pentabromotoluene				
283.9	914	2.241	0.55	6.63	2.594	0.82
294.2	289	2.741	0.62	6.54	2.576	0.79
304.8	120	3.121	0.63	6.62	2.571	0.80
314.3	52.5	3.482	0.70	6.70	2.566	0.78
324.1	24.4	3.814	0.70	6.55	2.561	0.79
334.0	12.7	4.098	0.73	6.60	2.558	0.78
344.2	6.08	4.418	0.78	6.55	2.556	0.77

TABLE 4 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR HETEROCYCLIC RIGID MOLECULES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
			0.692M 4-Methylpyridine			
88.0	758	2.322	0.16	10.14	2.489	0.61
93.1	352	2.655	0.16	10.78	2.486	0.67
97.9	153	3.018	0.16	11.36	2.486	0.70
102.9	59.1	3.430	0.15	11.95	2.480	0.75
108.4	20.3	3.894	0.16	12.71	2.484	0.76
114.3	8.38	4.279	0.17	13.44	2.485	0.78
119.4	4.02	4.598	0.19	14.38	2.491	0.79
124.3	2.85	4.746	0.21	14.81	2.500	0.78
			0.469M 3-Bromopyridine			
117.2	1015	2.196	0.15	8.46	2.513	0.80
124.5	303	2.720	0.16	9.09	2.512	0.84
129.5	148	3.031	0.16	9.40	2.507	0.89
135.7	52.5	3.482	0.18	9.93	2.511	0.88
142.5	15.8	4.004	0.18	10.41	2.509	0.91
149.1	7.93	4.302	0.20	11.00	2.515	0.92
155.1	4.16	4.583	0.21	11.46	2.518	0.93
			0.540M o-t-Butylpyridine			
119.0	283	2.751	0.15	7.15	2.606	0.70
125.0	172	2.966	0.13	7.58	2.603	0.77
129.7	64.3	3.393	0.15	7.94	2.611	0.75
134.5	39.3	3.608	0.16	8.26	2.611	0.77
142.2	13.3	4.077	0.17	8.82	2.617	0.80
148.7	7.53	4.325	0.17	9.26	2.620	0.82
156.3	3.76	4.627	0.18	9.79	2.627	0.85
162.4	3.16	4.703	0.19	10.08	2.632	0.85
			0.227M 2,6-Dibromopyridine			
126.2	621	2.409	0.15	3.71	2.563	0.81
132.8	278	2.758	0.13	3.91	2.561	0.90
139.0	104	3.184	0.13	4.11	2.561	0.96
144.0	36.1	3.645	0.13	4.33	2.559	0.98
148.5	14.4	4.044	0.14	4.46	2.561	1.00
152.7	8.70	4.262	0.15	4.67	2.562	1.00
158.9	3.89	4.612	0.15	5.06	2.563	1.06
163.2	3.15	4.704	0.15	5.33	2.564	1.08

TABLE 4 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
			0.789M 3,5-Dibromopyridine			
141.8	613	2.415	0.20	2.28	2.478	0.31
148.7	299	2.727	0.19	2.48	2.485	0.34
155.9	129	3.091	0.23	2.71	2.491	0.34
162.8	66.4	3.380	0.22	3.03	2.491	0.38
172.4	24.4	3.815	0.22	3.32	2.495	0.40
182.6	7.57	5.323	0.23	3.71	2.493	0.43
192.9	3.80	4.622	0.23	4.01	2.490	0.46
			0.560M 8-Hydroxyquinoline			
110.4	487	2.514	0.16	9.46	2.635	0.72
115.7	229	2.841	0.15	10.04	2.636	0.78
120.3	118	3.132	0.16	10.59	2.637	0.80
124.5	57.1	3.445	0.17	11.09	2.641	0.80
129.1	28.1	3.753	0.18	11.63	2.639	0.82
133.8	13.8	4.063	0.18	12.28	2.641	0.86
139.2	8.21	4.287	0.19	12.95	2.645	0.88
143.0	5.38	4.471	0.19	13.21	2.645	0.90
			0.348M 8-Chloroquinoline			
121.0	475	2.525	0.15	7.84	2.590	0.90
127.0	243	2.816	0.14	8.33	2.588	0.98
132.2	120	3.125	0.13	8.75	2.581	1.07
139.0	29.6	3.730	0.14	9.36	2.577	1.13
143.2	13.2	4.081	0.13	9.79	2.574	1.19
147.2	8.61	4.267	0.15	10.28	2.577	1.17
153.0	3.39	4.672	0.14	10.98	2.567	1.25
158.2	2.27	4.845	0.15	11.68	2.572	1.27
			0.418M 3-Bromoquinoline			
205.3	410	2.589	0.19	11.58	2.574	1.18
210.5	236	2.829	0.19	11.79	2.570	1.21
215.0	146	3.037	0.19	12.04	2.566	1.24
223.2	72.2	3.343	0.18	12.41	2.559	1.30
232.3	28.1	3.754	0.18	12.86	2.552	1.36
241.0	13.1	4.084	0.18	13.26	2.542	1.41
248.7	6.40	4.396	0.17	13.57	2.532	1.48
255.8	3.55	4.651	0.17	13.97	2.525	1.51

TABLE 5 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR ARYL-ALKYL AND TWO DIALKYL KETONES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.479M Acetophenone				
162.0	106	3.178	0.21	22.08	2.697	1.24
166.1	44.3	3.555	0.21	22.95	2.689	1.29
173.2	23.7	3.828	0.22	24.07	2.692	1.29
177.0	14.2	4.050	0.23	24.62	2.690	1.31
181.1	8.73	4.261	0.23	25.54	2.683	1.36
		0.484M n-Butyrophenone				
149.1	104	3.187	0.16	12.76	2.706	1.02
153.9	50.7	3.497	0.16	13.34	2.701	1.06
158.3	29.5	3.733	0.16	13.95	2.692	1.11
163.7	17.1	3.968	0.14	14.71	2.672	1.22
168.5	6.71	4.375	0.13	15.52	2.658	1.33
173.5	3.58	4.648	0.13	16.36	2.647	1.39
		0.487M i-Butyrophenone				
157.5	92.7	3.235	0.19	15.17	2.656	1.07
162.0	50.6	3.498	0.19	15.90	2.653	1.10
168.0	23.3	3.834	0.18	16.74	2.645	1.18
172.7	11.2	4.152	0.17	17.44	2.631	1.27
179.4	4.48	4.551	0.17	18.52	2.621	1.35
184.7	2.93	4.735	0.18	19.52	2.625	1.35
		0.437M n-Valerophenone				
139.9	201	2.900	0.18	10.79	2.645	0.91
145.2	96.7	3.216	0.18	11.37	2.642	0.96
149.4	46.2	3.538	0.19	11.83	2.642	0.97
153.3	29.3	3.735	0.20	12.30	2.641	0.99
160.2	12.5	4.107	0.19	12.92	2.631	1.05
164.2	7.60	4.321	0.19	13.46	2.628	1.09
168.2	4.17	4.582	0.19	14.16	2.624	1.12
171.9	3.17	4.701	0.20	14.72	2.625	1.14
177.2	1.94	4.915	0.20	15.27	2.621	1.19
188.5	0.549	5.463	0.25	15.12		
193.1	0.457	5.542	0.25	15.44		
197.7	0.300	5.724	0.24	16.00		
202.4	0.227	5.846	0.24	16.63		
208.4	0.121	6.120	0.25	18.06		
213.3	0.079	6.302	0.23	18.45		

TABLE 5 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.471M i-Valerophenone				
147.4	126	3.103	0.20	10.71	2.653	0.86
151.9	62.5	3.406	0.21	11.17	2.652	0.88
156.8	35.5	3.651	0.20	11.75	2.650	0.94
160.9	20.2	3.897	0.20	12.29	2.646	0.98
166.9	9.39	4.229	0.19	12.97	2.642	1.04
173.0	4.41	4.558	0.19	13.84	2.639	1.09
		0.40M Hexanophenone				
139.9	353	2.654	0.18	10.41	2.650	0.94
143.9	166	2.983	0.19	10.83	2.650	0.95
148.8	82.0	3.288	0.19	11.25	2.646	1.00
152.6	45.1	3.547	0.20	11.69	2.648	0.99
158.5	18.4	3.937	0.20	12.48	2.642	1.05
165.3	7.81	4.309	0.20	13.33	2.636	1.12
169.5	4.25	4.574	0.19	13.87	2.630	1.17
		0.380M Octanophenone				
157.4	127	3.099	0.25	11.54	2.639	0.92
161.3	90.6	3.245	0.24	11.85	2.635	0.97
166.0	46.3	3.536	0.25	12.26	2.631	0.99
171.1	24.2	3.819	0.24	12.69	2.626	1.03
175.0	14.1	4.054	0.24	13.04	2.621	1.06
179.2	9.23	4.237	0.26	13.45	2.620	1.06
183.6	5.26	4.481	0.26	13.85	2.615	1.08
		0.331M Undecanophenone Low Temperature Absorption				
149.0	295	2.733	0.25	10.98	2.632	0.94
153.0	169	2.973	0.24	11.40	2.630	0.99
156.4	101	3.200	0.24	11.73	2.628	1.01
160.4	55.2	3.460	0.24	12.16	2.626	1.05
164.1	30.9	3.712	0.24	12.59	2.623	1.08
171.4	12.8	4.096	0.26	13.40	2.622	1.11

TABLE 5 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
			High Temperature Absorption			
294.0	180	2.948	0.11	9.30	2.672	1.84
299.0	113	3.149	0.11	9.26	2.668	1.87
303.9	39.7	3.603	0.11	9.27	2.667	1.84
310.6	14.8	4.031	0.12	9.39	2.670	1.79
317.4	1.95	4.913	0.10	9.83	2.647	2.00
			0.365M 3-Nonanone			
107.9	220	2.859	0.23	10.69	2.654	0.79
111.5	96.9	3.215	0.22	11.08	2.649	0.83
115.3	45.0	3.548	0.24	11.52	2.650	0.82
120.2	13.8	4.061	0.25	12.27	2.645	0.85
124.4	7.56	4.324	0.27	12.77	2.645	0.85
128.3	3.42	4.668	0.28	13.29	2.643	0.86
			0.234M 8-Pentadecanone			
123.6	351	2.657	0.29	15.43	2.617	1.13
127.0	166	2.981	0.29	15.85	2.613	1.16
131.0	77.0	3.315	0.29	16.28	2.609	1.20
136.8	25.8	3.790	0.31	17.18	2.604	1.22
143.5	9.40	4.229	0.34	17.97	2.602	1.22
148.5	4.37	4.562	0.36	18.69	2.600	1.23

TABLE 6 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR ACETYL SUBSTITUTED HETEROCYCLIC MOLECULES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
			0.666M 2-Acetylpyridine			
170.6	310	2.711	0.19	25.01	2.624	1.22
175.1	174	2.960	0.18	26.10	2.612	1.29
183.1	66.6	3.378	0.19	27.46	2.611	1.31
187.1	42.7	3.572	0.19	28.42	2.605	1.34
191.4	25.2	3.801	0.19	29.47	2.599	1.38
197.0	13.2	4.080	0.20	30.55	2.596	1.41
203.1	7.10	4.351	0.21	31.80	2.592	1.43
			0.564M 3-Acetylpyridine			
164.8	469	2.530	0.19	23.41	2.643	1.25
171.4	180	2.946	0.19	24.80	2.638	1.31
175.7	101	3.196	0.19	25.71	2.633	1.35
181.0	49.0	3.511	0.19	26.58	2.628	1.39
185.6	24.2	3.818	0.20	27.75	2.625	1.42
190.8	12.8	4.096	0.20	29.02	2.624	1.45
196.1	7.16	4.347	0.22	30.20	2.527	1.45
			0.658M 4-Acetylpyridine			
153.9	286	2.745	0.17	15.50	2.710	0.97
160.4	102	3.193	0.17	16.59	2.708	1.00
166.7	38.4	3.618	0.18	17.60	2.702	1.04
171.4	19.2	3.919	0.18	18.30	2.701	1.06
176.6	9.84	4.209	0.19	19.00	2.699	1.08
			0.820M 2,6-Diacetylpyridine			
165.2	619	2.410	0.15	2.02	2.628	0.35
170.4	218	2.863	0.18	2.07	2.629	0.32
175.1	113	3.148	0.21	2.13	2.629	0.32
179.9	64.0	3.396	0.22	2.18	2.629	0.32
185.0	44.1	3.557	0.22	2.23	2.628	0.33
193.9	20.2	3.879	0.23	2.27	2.626	0.33
202.2	11.0	4.160	0.28	2.37	2.625	0.31
208.6	6.62	4.381	0.28	2.38	2.625	0.31

TABLE 6 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.566M N-Acetylimidazole Low Temperature Absorption				
125.5	1198	2.123	0.17	29.07	2.683	1.28
130.7	472	2.528	0.18	30.05	2.684	1.30
137.9	136	3.068	0.19	31.66	2.685	1.33
144.9	53.4	3.474	0.20	32.98	2.687	1.35
151.5	19.2	3.918	0.22	34.73	2.695	1.34
157.5	9.59	4.220	0.24	36.32	2.709	1.33
		0.571M N-Acetylimidazole High Temperature Absorption				
239.5	719	2.345	0.26	24.23	2.629	1.32
249.1	243	2.817	0.25	24.74	2.629	1.38
259.2	101	3.196	0.23	25.12	2.624	1.48
269.2	40.9	3.591	0.22	25.11	2.619	1.55
278.8	17.5	3.959	0.23	25.14	2.623	1.54
288.3	8.34	4.281	0.25	24.95	2.631	1.49
296.8	4.28	4.570	0.24	24.17	2.625	1.53
		0.473M N-Acetylpyrrolidine				
141.4	757	2.323	0.17	13.67	2.616	1.05
149.5	256	2.794	0.16	14.62	2.611	1.12
157.3	110	3.159	0.16	15.67	2.602	1.22
164.1	50.8	3.496	0.15	16.59	2.594	1.30
169.0	23.7	3.828	0.15	17.21	2.586	1.36
174.1	11.4	4.144	0.16	18.21	2.582	1.39
181.8	5.07	4.497	0.15	19.27	2.575	1.47
		0.575M N-Acetyl-4-piperidone Low Temperature Absorption				
179.3	706	2.353	0.13	17.17	2.597	1.37
185.0	309	2.712	0.13	17.99	2.596	1.40
190.1	136	3.069	0.14	18.73	2.599	1.39
195.0	66.6	3.378	0.14	19.43	2.594	1.42
201.1	25.7	3.792	0.15	20.41	2.591	1.44
206.3	13.0	4.088	0.17	21.22	2.598	1.40
211.9	7.50	4.327	0.20	22.20	2.611	1.35

TABLE 7 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR VARIOUS TYPES OF MOLECULES CONTAINING ACETYL/CARBONYL SUBSTITUENTS

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.390M Cyclohexyl iodide				
		Low Temperature Absorption				
114.8	315	2.704	0.14	6.68	2.634	0.80
121.8	87.3	3.261	0.14	7.20	2.629	0.86
127.8	35.6	3.650	0.13	7.57	2.622	0.93
136.2	5.67	4.448	0.13	8.23	2.615	0.99
144.8	2.65	4.778	0.16	8.87	2.622	0.96
		High Temperature Absorption				
271.2	41.3	3.586	0.52	4.61	2.704	0.52
278.7	25.0	3.804	0.54	4.43	2.701	0.51
286.1	13.5	4.072	0.48	4.27	2.696	0.54
292.1	9.03	4.246	0.45	4.04	2.692	0.55
297.8	6.16	4.412	0.48	4.02	2.689	0.54
303.1	3.86	4.615	0.42	3.89	2.685	0.57
		0.652M Cyclohexylmethyl ketone				
		Low Temperature Absorption				
109.4	949	2.224	0.11	8.90	2.634	0.77
112.5	412	2.587	0.11	9.27	2.631	0.80
119.1	159	3.001	0.10	10.09	2.619	0.89
123.5	86.1	3.267	0.10	10.48	2.606	0.95
135.6	6.01	4.423	0.11	11.85	2.597	1.01
144.4	3.57	4.649	0.13	12.64	2.615	0.96
		High Temperature Absorption				
230.9	263	2.781	0.33	8.43	2.709	0.63
235.9	143	3.045	0.31	8.39	2.706	0.65
240.5	85.7	3.269	0.27	8.28	2.699	0.71
245.2	59.0	3.431	0.30	8.24	2.704	0.67
250.2	34.6	3.663	0.27	8.08	2.699	0.71
255.3	18.9	3.925	0.24	7.95	2.695	0.75
259.8	11.5	4.140	0.25	8.02	2.697	0.75
264.8	8.64	4.266	0.25	7.88	2.698	0.75

TABLE 7 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.576M Cyclohexylacetone				
		Low Temperature Absorption				
113.6	711	2.350	0.14	10.27	2.666	0.79
119.0	189	2.926	0.14	11.13	2.659	0.84
124.6	56.6	3.449	0.14	12.06	2.650	0.90
127.8	26.1	2.786	0.15	12.50	2.645	0.91
130.8	13.3	4.078	0.15	13.16	2.645	0.93
135.9	5.84	4.435	0.17	14.12	2.644	0.94
		High Temperature Absorption				
187.7	709	2.351	0.15	13.67	2.702	1.13
193.6	263	2.782	0.15	13.90	2.693	1.18
197.9	105	3.183	0.15	14.14	2.688	1.19
203.3	38.6	3.616	0.15	14.27	2.679	1.22
208.3	15.4	4.014	0.15	14.46	2.678	1.21
213.0	7.77	4.311	0.16	14.70	2.675	1.22
		0.446M Cyclohexylmethyl bromide				
138.2	426	2.572	0.26	11.31	2.542	0.80
143.4	185	2.934	0.27	11.91	2.549	0.82
147.6	101	3.196	0.27	12.07	2.549	0.83
151.9	56.2	3.452	0.27	12.47	2.554	0.86
159.5	22.0	3.859	0.27	13.18	2.556	0.91
164.9	11.7	4.134	0.26	13.63	2.556	0.95
169.3	7.25	4.341	0.25	13.90	2.558	0.99
		0.547M Cyclopropylphenyl ketone				
140.7	513	2.492	0.17	11.24	2.678	0.87
146.7	227	2.846	0.17	11.88	2.674	0.92
151.8	124	3.107	0.16	12.48	2.667	0.98
156.4	77.5	3.312	0.15	13.05	2.661	1.03
160.4	47.7	3.523	0.15	13.69	2.655	1.08
166.9	18.7	3.931	0.14	14.49	2.640	1.18
174.5	8.35	4.28	0.14	15.56	2.631	1.24

TABLE 7 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.623M 2-Acetyl-5-norbornene				
116.3	317	2.701	0.13	20.50	2.671	1.13
121.0	136	3.070	0.12	21.45	2.660	1.19
126.3	47.5	3.525	0.13	22.44	2.653	1.24
130.8	20.5	3.890	0.13	23.35	2.650	1.27
135.4	9.51	4.223	0.14	24.39	2.655	1.27
140.9	4.26	4.572	0.15	25.65	2.662	1.27
		0.439M 1-Adamantylmethyl ketone				
130.3	68.9	3.364	0.07	15.46	2.609	1.64
136.0	27.2	3.767	0.10	15.99	2.655	1.48
140.0	12.9	4.093	0.11	16.31	2.672	1.42
145.0	5.83	4.436	0.13	16.95	2.690	1.35
149.3	4.46	4.553	0.15	17.37	2.711	1.27
		0.352M 1,3-Diphenylacetone Low Temperature Absorption				
112.9	179	2.950	0.15	5.30	2.694	0.72
117.0	60.0	3.424	0.13	5.68	2.686	0.80
122.3	17.1	3.970	0.15	6.28	2.685	0.81
128.3	8.54	4.271	0.17	6.73	2.687	0.80
133.0	2.60	4.786	0.16	7.16	2.679	0.86
		High Temperature Absorption				
289.4	118	3.130	0.13	7.02	2.725	1.38
293.7	25.5	3.795	0.15	7.13	2.724	1.31
299.1	9.34	4.232	0.17	7.40	2.727	1.25
303.2	4.08	4.591	0.17	7.59	2.723	1.28
308.5	2.11	4.878	0.18	7.86	2.722	1.28

TABLE 7 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.379M 1,1-Diphenylacetone				
237.6	220	2.860	0.15	11.88	2.658	1.49
244.7	70.5	3.354	0.16	12.18	2.659	1.46
251.6	30.5	3.717	0.17	12.54	2.658	1.47
258.5	11.8	4.130	0.17	12.96	2.652	1.52
263.7	5.23	4.483	0.17	13.17	2.644	1.57
271.0	2.61	4.785	0.18	13.66	2.645	1.56
		0.745M Mesityl oxide				
144.4	425	2.574	0.18	38.14	2.698	1.31
149.1	174	2.960	0.18	39.59	2.695	1.34
154.3	66.2	3.381	0.19	41.21	2.695	1.36
159.3	30.8	3.713	0.20	42.94	2.696	1.38
164.9	14.8	4.031	0.22	45.20	2.709	1.38
169.2	7.70	4.316	0.21	46.33	2.699	1.43
		0.445M 1-Acetylcyclohexene				
153.7	176	2.958	0.16	14.77	2.646	1.18
158.0	128	3.095	0.14	15.12	2.633	1.29
162.4	56.0	3.454	0.15	15.86	2.630	1.32
167.2	29.1	3.738	0.14	16.48	2.622	1.38
172.5	14.9	4.029	0.15	17.27	2.620	1.41
190.0	1.82	4.942	0.22	17.52		
195.0	1.11	5.156	0.22	17.89		
199.1	0.91	5.244	0.22	18.21		
204.6	0.50	5.501	0.22	19.27		
208.9	0.37	5.629	0.18	19.25		
		0.322M p-N,N-Dimethylaminoacetophenone				
244.1	421	2.579	0.17	32.78	2.548	2.50
253.7	189	2.926	0.17	34.98	2.529	2.69
264.1	79.3	3.303	0.17	37.89	2.515	2.83
273.0	37.2	3.631	0.17	39.96	2.495	2.98
281.2	16.5	3.984	0.18	41.98	2.484	3.04
287.0	10.1	4.197	0.18	43.59	2.481	3.06
293.8	6.28	4.404	0.19	45.14	2.481	3.09
300.8	3.63	4.643	0.19	46.38	2.469	3.17

TABLE I continued....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			0.424M 2-Acetyl-1-tetralone			
244.4	221	2.858	0.17	22.75	2.589	1.84
250.0	116	3.139	0.17	23.65	2.581	1.90
255.0	67.7	3.372	0.17	24.38	2.576	1.95
260.1	38.3	3.619	0.17	25.11	2.569	2.01
265.1	20.6	3.888	0.17	25.91	2.562	2.05
270.3	11.6	4.138	0.19	27.00	2.565	2.03
275.4	7.15	4.348	0.19	27.90	2.563	2.06
			0.375M 2-Acetylnaphthalene			
202.4	1973	1.907	0.12	12.95	2.597	1.60
205.9	1112	2.156	0.13	13.23	2.606	1.60
210.3	760	2.321	0.12	13.68	2.600	1.66
214.3	688	2.365	0.12	14.07	2.607	1.72
217.7	431	2.567	0.12	14.37	2.597	1.77
221.3	339	2.671	0.12	14.68	2.601	1.80
226.5	182	2.941	0.11	15.05	2.592	1.90
231.7	125	3.105	0.12	15.60	2.605	1.92
241.8	35.5	3.652	0.12	16.36	2.599	1.98
245.5	21.3	3.873	0.13	16.64	2.607	1.93
249.5	13.2	4.083	0.13	17.17	2.614	1.96
253.6	4.48	4.551	0.12	17.59		
262.2	1.69	4.973	0.13	18.33		
267.6	0.78	5.309	0.12	18.62		
276.8	0.18	5.953	0.10	19.36		
			0.242M 2-Acetylphenanthrene Low Temperature Absorption			
156.8	402	2.598	0.18	3.07	2.609	0.72
162.3	228	2.844	0.19	3.34	2.612	0.75
166.9	135	3.072	0.18	3.47	2.614	0.79
171.9	74.4	3.330	0.17	3.62	2.615	0.84
176.8	39.2	3.609	0.17	3.82	2.614	0.88
181.3	23.7	3.828	0.18	3.98	2.619	0.88
186.9	9.82	4.210	0.16	4.19	2.618	0.95

TABLE 7 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			High Temperature Absorption			
303.8	687	2.365	0.19	12.31	2.690	1.88
308.3	413	2.586	0.19	12.53	2.688	1.89
313.3	246	2.812	0.19	12.80	2.685	1.93
318.3	156	3.008	0.19	13.08	2.680	1.98
323.3	93.8	3.230	0.19	13.37	2.676	2.04
328.6	50.9	3.495	0.19	13.79	2.670	2.10
333.4	29.4	3.734	0.18	14.34	2.661	2.19
			0.248M 3-Acetylphenanthrene			
			Low Temperature Absorption			
165.0	676	2.372	0.17	3.89	2.651	0.84
169.1	293	2.735	0.15	4.22	2.652	0.94
175.1	150	3.025	0.13	4.44	2.649	1.04
180.9	64.2	3.395	0.14	4.61	2.653	1.03
188.9	27.5	3.763	0.15	5.02	2.658	1.05
196.8	15.5	4.013	0.19	5.42	2.666	1.00
199.5	10.6	4.177	0.21	5.31	2.670	0.96
205.9	6.52	4.388	0.20	5.55	2.670	1.01
			High Temperature Absorption			
294.0	1213	2.118	0.16	10.29	2.699	1.85
297.9	767	2.317	0.14	10.63	2.686	2.00
301.0	439	2.560	0.15	11.11	2.704	2.01
304.7	384	2.617	0.14	10.88	2.685	2.03
308.5	219	2.861	0.14	11.46	2.701	2.07
312.4	168	2.977	0.14	11.11	2.682	2.07
316.1	101	3.200	0.14	11.74	2.695	2.15
323.4	38.7	3.614	0.14	12.00	2.680	2.23

TABLE 8 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR SUBSTITUTED PHENOLS

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.519M p-Nitrophenol				
		Low Temperature Absorption				
127.6	244	2.814	0.20	8.36	2.716	0.67
133.9	128	3.094	0.19	8.97	2.712	0.72
138.4	87.9	3.258	0.18	9.23	2.707	0.78
142.6	50.8	3.496	0.18	9.62	2.705	0.81
147.7	27.2	3.768	0.18	10.11	2.703	0.83
152.9	14.6	4.037	0.19	10.60	2.703	0.84
		High Temperature Absorption				
233.8	241	2.820	0.26	55.98	2.697	2.01
238.6	143	3.047	0.26	58.87	2.696	2.06
242.6	89.8	3.249	0.27	61.85	2.698	2.10
243.7	54.5	3.465	0.27	65.17	2.695	2.18
251.9	34.0	3.670	0.26	69.16	2.691	2.26
257.0	20.0	3.900	0.26	73.33	2.675	2.38
261.9	12.5	4.106	0.25	76.52	2.662	2.50
266.8	7.21	4.344	0.24	80.37	2.635	2.64
		0.250M 2,4-Dinitrophenol				
163.6	637	2.398	0.14	6.41	2.626	1.17
170.8	202	2.896	0.13	6.82	2.625	1.25
177.6	85.5	3.270	0.12	7.23	2.620	1.37
184.2	26.7	3.775	0.13	7.68	2.620	1.40
189.4	11.3	4.149	0.13	8.06	2.616	1.48
195.2	6.91	4.362	0.14	8.57	2.624	1.45
200.6	4.31	4.567	0.14	8.92	2.626	1.49
205.6	2.28	4.844	0.15	9.31	2.625	1.53
		0.498M 3,5-Dichlorophenol				
226.4	64.8	3.390	0.24	23.84	2.646	1.41
231.6	35.5	3.652	0.27	24.27	2.653	1.35
235.9	19.1	3.922	0.30	24.58	2.656	1.31
241.0	10.9	4.163	0.33	25.07	2.660	1.27
245.9	6.71	4.375	0.35	25.47	2.662	1.26
251.0	4.84	4.517	0.38	25.92	2.665	1.23

TABLE 8 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.910M 2,4,6-Trimethylphenol				
204.0	317	2.701	0.18	4.35	2.495	0.51
208.9	115	3.140	0.20	4.47	2.503	0.50
214.0	48.0	3.521	0.23	4.66	2.513	0.48
219.0	22.1	3.858	0.24	4.84	2.522	0.48
224.4	12.6	4.103	0.26	5.00	2.529	0.48
230.0	6.21	4.409	0.25	5.07	2.536	0.49
234.4	3.47	4.661	0.25	5.25	2.538	0.51
		0.591M 2,4,6-Tri-t-butylphenol				
294.1	159	3.001	0.21	2.65	2.601	0.54
299.9	87.6	3.259	0.21	2.64	2.593	0.55
304.7	53.5	3.482	0.21	2.64	2.588	0.55
309.5	29.9	3.726	0.21	2.61	2.582	0.56
314.0	21.4	3.872	0.21	2.62	2.578	0.56
318.8	12.04	4.121	0.19	2.58	2.572	0.59
323.9	8.12	4.292	0.18	2.57	2.568	0.61
		0.412M 2,4,6-Trichlorophenol				
		Low Temperature Absorption				
91.7	433	2.565	0.18	2.41	2.668	0.37
96.0	129	3.091	0.21	2.60	2.667	0.37
100.4	59.2	3.430	0.22	2.76	2.667	0.38
106.5	21.6	3.868	0.20	2.96	2.665	0.42
111.3	9.82	4.210	0.21	3.24	2.664	0.43
		High Temperature Absorption				
209.9	150	3.026	0.27	8.62	2.668	0.85
214.8	81.6	3.290	0.28	8.53	2.668	0.84
222.2	27.2	3.767	0.33	8.48	2.669	0.79
228.3	13.4	4.076	0.37	8.47	2.670	0.76
234.7	7.04	4.355	0.39	8.47	2.670	0.74
239.8	5.24	4.482	0.42	8.42	2.671	0.72
246.4	2.91	4.738	0.43	8.24	2.670	0.72

TABLE 8 continued....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	ε_∞	μ(D)
		0.342M 2,4,6-Tribromophenol Low Temperature Absorption				
108.1	96.8	3.216	0.31	2.76	2.664	0.36
114.6	29.3	3.736	0.32	2.96	2.661	0.38
118.7	13.4	4.075	0.32	3.13	2.658	0.39
124.8	6.36	4.399	0.36	3.34	2.655	0.39
128.9	5.05	4.498	0.39	3.31	2.655	0.38
134.3	3.40	4.671	0.44	3.26	2.653	0.37
137.5	2.88	4.743	0.46	3.25	2.653	0.36
		High Temperature Absorption				
220.1	145	3.042	0.28	4.23	2.627	0.66
225.0	70.0	3.357	0.30	4.17	2.626	0.65
229.7	41.9	3.580	0.31	4.13	2.624	0.64
234.9	25.4	3.797	0.32	4.08	2.622	0.64
239.7	15.6	4.008	0.32	3.99	2.621	0.64
244.9	10.5	4.178	0.33	3.92	2.619	0.63
249.2	6.28	4.404	0.31	3.87	2.617	0.65
		0.240M 2,4,6-Triiodophenol Low Temperature Absorption				
83.9	261	2.786	0.25	2.71	2.616	0.42
89.5	106	3.179	0.31	2.89	2.620	0.40
93.4	50.8	3.496	0.34	3.02	2.624	0.40
99.2	23.2	3.836	0.37	3.15	2.627	0.40
105.2	12.9	4.090	0.40	3.22	2.628	0.40
110.9	6.17	4.412	0.47	3.35	2.631	0.39
116.0	4.90	4.512	0.57	3.34	2.634	0.36
		High Temperature Absorption				
274.9	58.5	3.435	0.23	1.97	2.646	0.67
280.0	55.5	3.458	0.24	1.92	2.645	0.66
285.1	31.6	3.702	0.24	1.93	2.643	0.66
289.7	27.9	3.756	0.26	1.95	2.642	0.65
300.4	9.79	4.211	0.21	1.91	2.635	0.72
305.5	7.38	4.333	0.22	1.93	2.633	0.72

TABLE 8 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.309M Pentachlorophenol Low Temperature Absorption				
121.7	733	2.337	0.25	7.80	2.670	0.74
125.4	340	2.671	0.25	8.12	2.667	0.77
130.2	129	3.093	0.24	8.54	2.663	0.81
135.0	45.9	3.540	0.25	8.98	2.659	0.84
139.8	22.1	3.859	0.25	9.29	2.655	0.86
144.8	10.1	4.196	0.26	9.68	2.651	0.88
148.8	6.04	4.421	0.26	9.88	2.648	0.91
		High Temperature Absorption				
209.5	138	3.063	0.35	12.04	2.693	1.01
214.4	71.1	3.350	0.39	11.94	2.694	0.96
218.5	41.2	3.588	0.40	11.97	2.691	0.96
223.7	22.0	3.860	0.45	11.82	2.691	0.92
228.0	11.5	4.143	0.46	11.88	2.688	0.92
232.8	6.89	4.363	0.49	11.81	2.688	0.90
238.0	5.27	4.480	0.53	11.67	2.689	0.87
		0.491M Pentachlorobenzenethiol Low Temperature Absorption				
92.6	629	2.403	0.24	5.61	2.589	0.45
98.8	219	2.861	0.25	5.89	2.590	0.47
103.9	84.1	3.277	0.27	6.13	2.588	0.47
110.6	25.4	3.797	0.31	6.42	2.589	0.46
115.4	12.8	4.093	0.35	6.68	2.589	0.45
123.8	4.87	4.514	0.41	7.07	2.589	0.45
131.7	2.69	4.773	0.46	6.85	2.589	0.43

TABLE 8 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			High Temperature Absorption			
218.9	525	2.482	0.59	10.25	2.679	0.59
226.1	239	2.823	0.57	10.03	2.674	0.60
235.1	82.8	3.284	0.59	9.79	2.670	0.60
244.8	30.1	3.724	0.61	9.47	2.666	0.59
254.6	11.6	4.137	0.64	9.33	2.659	0.58
262.2	6.47	4.391	0.70	9.33	2.656	0.57
268.9	4.09	4.591	0.75	9.21	2.653	0.55
			0.169M Pentabromophenol			
113.9	370	2.634	0.19	2.79	2.598	0.68
119.0	143	3.046	0.20	2.91	2.598	0.69
123.7	65.7	3.384	0.18	3.01	2.593	0.75
129.7	22.9	3.842	0.19	3.10	2.593	0.76
134.6	10.2	4.194	0.21	3.22	2.590	0.76
145.4	3.13	4.706	0.27	3.54	2.590	0.73

TABLE 9 - FUOSS-KIRKWOOD ANALYSIS PARAMETERS AND EFFECTIVE DIPOLE MOMENTS (μ) FOR SUBSTITUTED ANISOLES

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
			0.524M p-Nitroanisole			
212.1	250	2.804	0.20	41.09	2.575	1.90
218.3	137	3.066	0.20	43.20	2.565	1.98
224.5	69.9	3.357	0.20	45.62	2.554	2.07
230.2	42.1	3.578	0.19	47.63	2.546	2.15
235.9	22.7	3.846	0.20	49.90	2.536	2.21
240.6	13.8	4.062	0.20	51.91	2.524	2.29
246.0	8.10	4.293	0.20	54.79	2.517	2.35
250.2	6.65	4.379	0.21	56.40	2.528	2.34
			0.412M 3,5-Dinitroanisole			
188.1	776	2.312	0.18	26.48	2.531	1.73
195.4	266	2.777	0.19	27.89	2.526	1.77
203.8	127	3.099	0.19	30.14	2.514	1.89
213.5	50.3	3.500	0.19	32.54	2.503	2.01
223.7	18.2	3.943	0.20	34.92	2.491	2.10
231.5	9.12	4.242	0.21	37.04	2.487	2.14
241.2	4.15	4.584	0.21	39.45	2.479	2.23
249.0	2.34	4.833	0.22	42.14	2.476	2.27
			0.936M 3,5-Dimethylanisole Low Temperature Absorption			
81.3	184	2.938	0.18	1.87	2.555	0.21
84.7	86.9	3.263	0.18	1.95	2.555	0.22
89.4	29.9	3.727	0.20	2.16	2.557	0.22
94.0	13.2	4.083	0.18	2.29	2.556	0.25
97.8	9.16	4.240	0.22	2.24	2.558	0.24
101.8	7.42	4.332	0.22	2.54	2.560	0.24
106.1	5.27	4.480	0.20	2.59	2.560	0.26
109.3	2.86	4.746	0.20	2.67	2.559	0.27

TABLE 9 continued.....

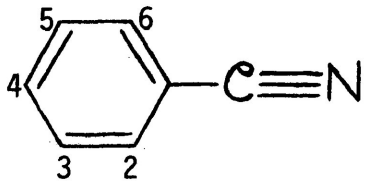
T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.595M 3,5-Dimethylanisole High Temperature Absorption				
170.2	356	2.651	0.17	3.81	2.592	0.55
175.6	172	2.967	0.17	3.90	2.591	0.56
180.3	85.6	3.270	0.18	3.96	2.590	0.56
184.7	46.9	3.530	0.17	4.00	2.586	0.59
190.3	19.6	3.909	0.17	4.06	2.584	0.60
195.9	10.4	4.186	0.18	4.18	2.584	0.59
199.4	6.86	4.366	0.18	4.19	2.583	0.60
		0.324M 2,4,6-Tribromoanisole Low Temperature Absorption				
114.5	268	2.775	0.32	1.80	2.628	0.30
118.5	183	2.939	0.26	1.85	2.627	0.35
123.8	90.1	3.247	0.25	1.97	2.629	0.37
130.6	36.8	3.636	0.23	2.11	2.628	0.41
137.4	13.4	4.076	0.22	2.23	2.626	0.44
144.1	7.13	4.349	0.24	2.41	2.627	0.45
149.6	4.51	4.547	0.26	2.53	2.627	0.45
		High Temperature Absorption				
177.6	284	2.749	0.15	3.29	2.626	0.75
183.7	122	3.114	0.16	3.44	2.627	0.74
190.5	43.2	3.566	0.17	3.54	2.626	0.76
197.9	20.6	3.887	0.19	3.69	2.627	0.74
204.3	11.7	4.133	0.19	3.84	2.626	0.77
211.3	6.05	4.420	0.14	4.02	2.617	0.92
217.0	4.41	4.558	0.22	4.52	2.625	0.80

TABLE 9 continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	ϵ_∞	μ(D)
		0.413M Pentafluoroanisole				
112.3	250	2.803	0.17	5.29	2.582	0.63
118.5	88.7	3.254	0.18	5.61	2.581	0.65
123.5	41.1	3.588	0.19	5.89	2.580	0.66
127.7	19.7	3.907	0.19	6.09	2.580	0.67
134.0	9.11	4.242	0.21	6.44	2.580	0.67
142.7	3.83	4.619	0.24	6.81	2.581	0.68
		0.575M 2,6-Dimethoxynaphthalene				
278.4	187	2.930	0.16	1.99	2.559	0.54
285.4	84.2	3.277	0.17	2.01	2.557	0.52
291.0	24.5	3.814	0.16	2.04	2.554	0.55
296.1	14.8	4.031	0.18	2.11	2.550	0.54
301.4	6.94	4.361	0.15	2.12	2.545	0.59

APPENDIX B

DIAGRAMS OF MOLECULAR STRUCTURES



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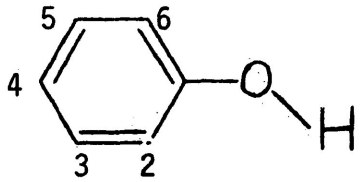
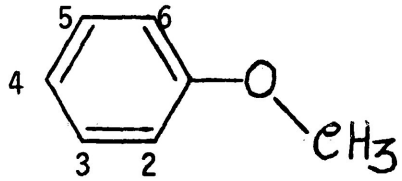
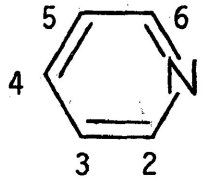


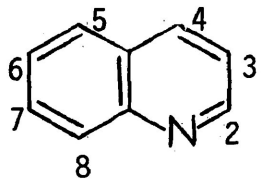
PHENOL



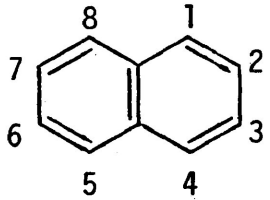
ANISOLE



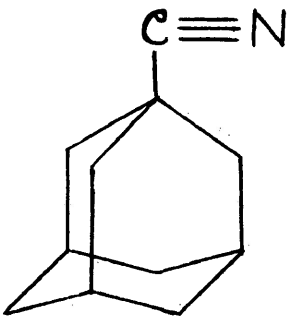
PYRIDINE



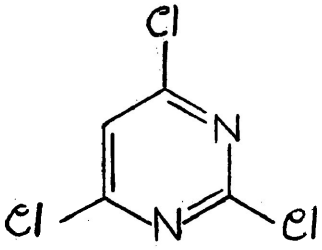
QUINOLINE



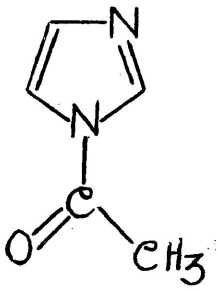
NAPHTHALENE



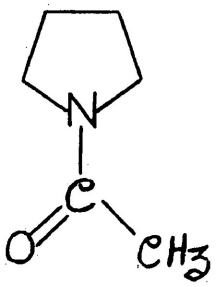
1-ADAMANTANECARBONITRILE



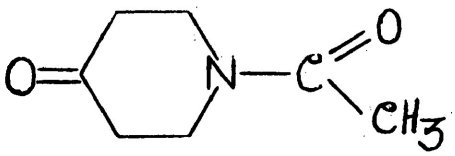
2,4,6-TRICHLOROPYRIMIDINE



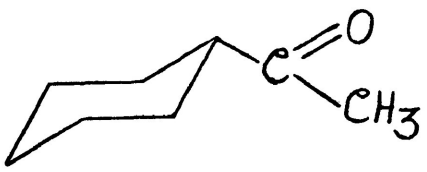
N-ACETYLIMIDAZOLE



N-ACETYLPYRROLIDINE

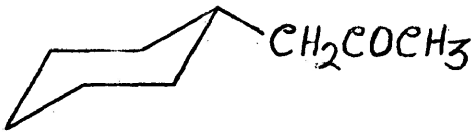


N-ACETYL-4-PIPERIDONE

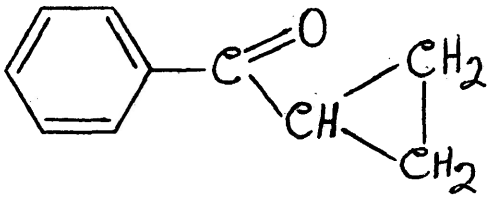


CYCLOHEXYLMETHYL KETONE

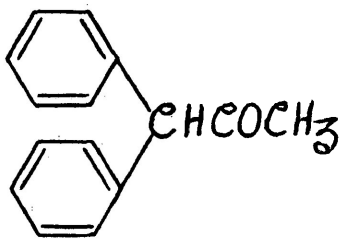
CYCLOHEXYLMETHYL BROMIDE



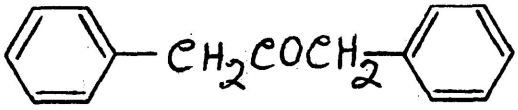
CYCLOHEXYLACETONE



CYCLOPROPYLPHENYL KETONE



1,1-DIPHENYLACETONE



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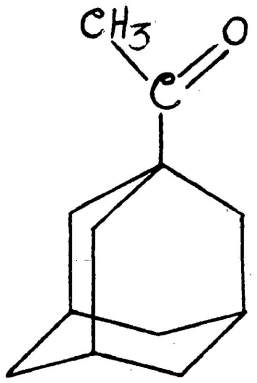
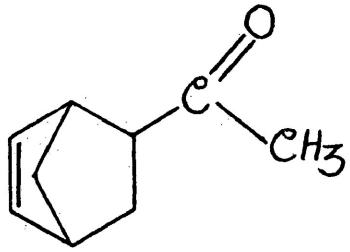
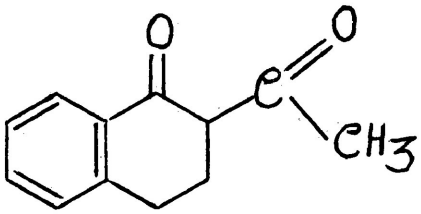


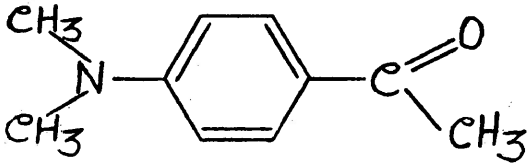
1-ADAMANTYL METHYL KETONE



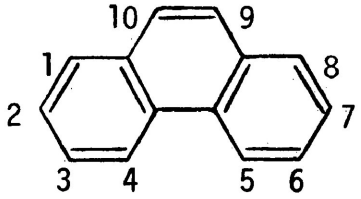
2-ACETYL-5-NORBORNENE



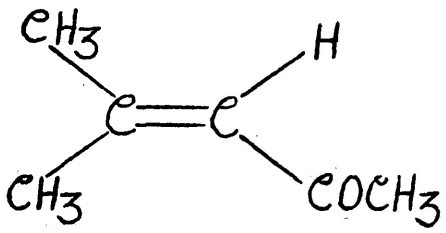
2-ACETYL-1-TETRALONE



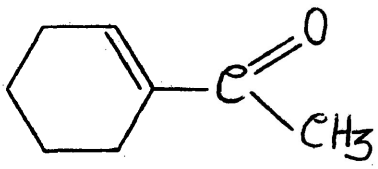
p-N,N-DIMETHYLAMINOACETOPHENONE



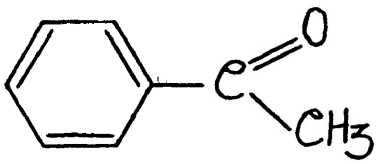
PHENANTHRENE



MESITYL OXIDE



1-ACETYLCYCLOHEXENE



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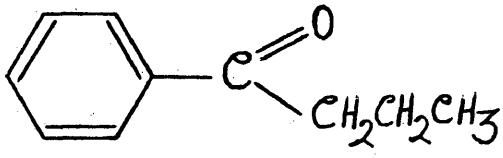
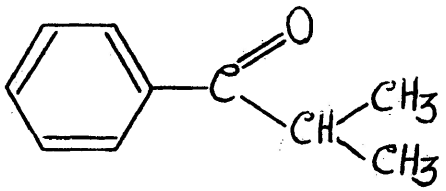
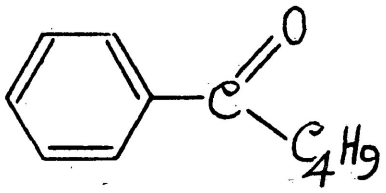


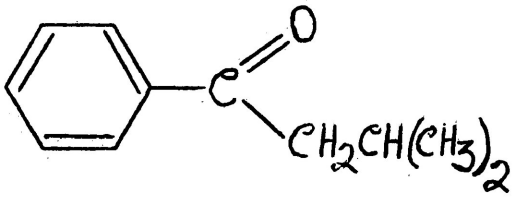
n-BUTYROPHENONE



iso-BUTYROPHENONE



n-VALEROPHENONE



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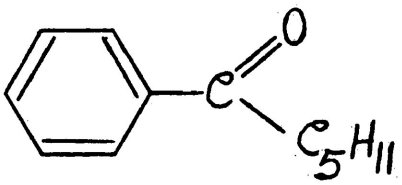

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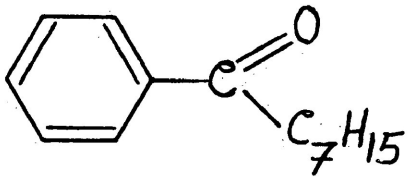
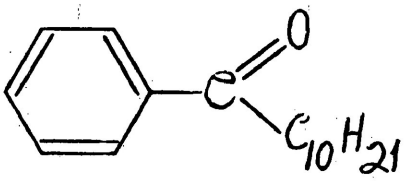


OCTANOPHENONE



UNDECANOPHENONE