Ultrasonic relaxation study in methylcyclohexane and methyl acetate by plano-concave resonator method

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Ultrasonic absorption measurements in methylcyclohexane and methyl acetate have been carried out over the frequency range 0.1–10 MHz at temperatures of 5–60°C using a plano-concave resonator method which is useful for ultrasonic relaxation study around 1 MHz. The results showed a typical spectrum of a single relaxation process, from which the relaxation frequency and strength were determined. The temperature dependence of these parameters gives the activation enthalpy (\( \Delta H^* \)) and enthalpy difference (\( \Delta H \)) between axial and equatorial isomers of methylcyclohexane, and those between cis and trans isomers of methyl acetate. They are: \( \Delta H^* = 10.0 \text{ kcal/mol} \), \( \Delta H = 1.8 \text{ kcal/mol} \), and \( \Delta H^* = 6.6 \text{ kcal/mol} \), \( \Delta H = 3.4 \text{ kcal/mol} \), respectively.

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1. INTRODUCTION

Ultrasonic absorption measurements yield useful information on rotational isomerism of molecules, such as axial-equatorial and cis-trans equilibria.\(^1\)\(^-\)\(^3\) Choi et al.\(^4\) have determined the potential energy parameters characterizing cis-trans rotational isomerism in methyl and ethyl formates using a plano-concave resonator method. This technique has been proved to be particularly useful for relaxation study around 1 MHz, the frequency range too low for conventional resonator to have a sufficient resolution.

Karpovich\(^5\) first suggested that ultrasonic relaxation in methylcyclohexane arises from perturbation of the equilibrium between axial and equatorial conformational isomers shown in Fig. 1(a). There are considerable discrepancies, however, among the conclusion reached by the previous ultrasonic investigators. Pedinoff\(^6\) estimated the enthalpy difference between the isomers \( \Delta H = 1.9 \text{ kcal/mol} \) and the activation enthalpy for the conversion of equatorial into axial isomers to be \( \Delta H^* = 6.4 \text{ kcal/mol} \). Subsequently, Piercy and Subrahmanyan\(^7\) obtained \( \Delta H = 2.9 \text{ kcal/mol} \) and \( \Delta H^* = 10.3 \text{ kcal/mol} \). The discrepancies may be due to the fact that the relaxation frequency lies below 1 MHz where conventional pulse techniques have poor accuracy.

Methyl acetate exhibits an ultrasonic relaxation caused by the perturbation of equilibrium between cis and trans isomers which are schematically shown in Fig. 1(b). Relaxations of similar kind were observed also in methyl and ethyl formates. Bally and North\(^8\) measured absorption on methyl acetate in the frequency range from 1 to 30 MHz at temperatures from 3 to 48°C using pulse technique, and derived potential energy parameters. Their data disagree with those of Pancholy and Mathur.\(^9\) The relaxation frequency exists in a few MHz region, but accurate absorption measurements have been difficult because of low absorption.

The purpose of the present paper is to obtain reliable values of the activation enthalpy and difference between axial and equatorial isomers in methylcyclohexane, and between cis and trans isomers in methyl acetate. The plano-concave resonator method is the most suitable technique for this purpose which performs accurate measurements
2. EXPERIMENT

The plano-concave resonator method has recently been described. A cylindrical resonance cavity which is composed of a quartz transducer and a slightly concaved reflector is filled with a sample liquid, and standing sound waves are established in it. Amplitude of the standing waves is optically probed using Raman-Nath light diffraction and detected with an optical heterodyne system as sweeping the sound frequency. The half-power bandwidth of resonance curve provides ultrasonic absorption in a sample. Use of the concave reflector instead of a flat receiving quartz has a great advantage that the sound diffraction effect is substantially reduced, and $Q$ factor of the resonator increases particularly below 1 MHz. The resonator used in this study has a cavity length of 20 mm and the curvature radius of concave reflector is 200 mm. To determine the ultrasonic absorption coefficient of sample, an instrumental loss of the resonator should be subtracted from the observed spectral width in relative measurements made with ethyl alcohol or methyl alcohol as a reference liquid.

Ultrasonic absorption measurement in methylcyclohexane were carried out at 30–60°C over the frequency range 0.1–2 MHz. The temperature was controlled to within 0.01°C. The velocity was measured at 3 MHz by a pulse-echo overlap method.

The sample was a reagent of spectroscopic grade purchased from Wako Pure Chemical Industries and used without further purification. Measurements in methyl acetate of special grade reagent was made at 5–30°C over the range 0.2–10 MHz.

3. AXIAL-EQUATORIAL ISOMERIC RELAXATION IN METHYLCYCLOHEXANE

Figure 2 shows absorption per wavelength as a function of frequency observed in methylcyclohexane. For a given temperature the frequency dependence of $\mu$ due to a single relaxation process is represented by

$$\mu = 2\mu_m \frac{f/f_r}{1+(f/f_r)^2} + Bcf.$$  (1)

Here $\mu_m$ denotes maximum absorption per wavelength at the relaxation frequency $f_r$, $c$ the velocity, and $f$ the sound frequency. The constant $B$ represents contribution from the classical absorption and other sources, for example, vibrational relaxation. The solid lines in Fig. 2 represent single relaxation curves. The arrows indicate relaxation frequencies.
relaxation curves of Eq. (1), and the arrows indicate
relaxation frequency. Table 1 summarizes the
relaxation parameters determined for methylcyclo-
hexane. We have already reported on the velocity
measurement11) made in this liquid, which showed
a dispersion of 3 m/s in the observed frequency
range from 200 kHz to 1 MHz. The velocity dis-
perion spectra are in very good agreement with the
curves theoretically predicted from the absorption
spectra shown in Fig. 2.

Activation enthalpy $\Delta H^*$ between the axial and
equatorial isomers can be obtained from the tem-
perature dependence of the relaxation frequency
using the Eyring rate equation. Figure 3 shows
the plot of $\ln (f_r/T)$ vs. $1/T$, from which $\Delta H^* = 10.0$
kcal/mol was obtained. Piercy and Subrahmanyam
raised the temperature of this liquid above its normal
boiling point up to 120°C to keep the relaxation
frequency within their measurement range of 0.6–
10 MHz. They obtained $\Delta H^* = 10.3$ kcal/mol which
is in very good agreement with the present value.
Their results of $f_r$ are shown by triangles in Fig. 3
together with those obtained by Pedinoff with a pulse method operating over 0.15–3.5 MHz range.
The activation enthalpy obtained by Pedinoff $\Delta H^* =
6.36$ kcal/mol is in rather poor agreement with the
other two works. The cause of this disagreement is
not clear. However, pulse methods in general lose
accuracy below 1 MHz, the range where very ac-
curate measurements are required to determine $f_r$.
In addition, his experiment was made at frequencies
above $f_r$ and it may not actually be observed.

The temperature dependence of relaxation strength
$2 \mu_m/\pi$ provides the enthalpy difference $\Delta H$
between the two isomers using the following relations

$$\frac{2 \mu_m C_p}{\pi (\gamma - 1)^2} = \left( 1 - \frac{\Delta V}{V} \frac{C_p}{\Delta H \theta} \right)^3 C_1, \quad (2)$$

$$C_1 = R \left( \frac{\Delta H}{RT} \right)^2 \exp \left( -\frac{\Delta H}{RT} \exp \left( \frac{\Delta S}{R} \right) \right) \left( 1 + \exp \left( -\frac{\Delta H}{RT} \right) \right)^2. \quad (3)$$

Here $C_p$ is the specific heat at constant pressure,12)
$\gamma$ the specific heat ratio, $V$ the molar volume and $\theta$
the thermal expansion coefficient evaluated from the
temperature gradient of the density,13) $\Delta V$
time the volume change and $\Delta S$ the entropy change. We
ignored the temperature dependence of the term in
the parenthesis in the right-hand side of Eq. (2)
within the experimental range of 30–60°C. Then
Eq. (2) is a function of only one variable $\Delta H/RT$
with a maximum at $\Delta H/RT = 2.4 R$. We numerically
calculated Eq. (3) varying $\Delta H$ as a running para-
eter until the gradient of the curve agrees with that of
the experimental points. We obtained a good
agreement by setting $\Delta H = 1.8$ kcal/mol as shown
in Fig. 4. Fortunately, the range of $\Delta H/RT$ observed
in this study is close to the maximum point where
the gradient is sensitively dependent on $\Delta H$, and
$\Delta H$ was determined precisely. Booth and Everett14)
reported $\Delta H = 1.75$ kcal/mol for methylcyclohexane

![Fig. 3 The temperature dependence of relaxation frequencies in methylcyclohexane. The closed circles indicate the data by Pedinoff and the triangles by Piercy and Subrahmanyam.](image-url)
The thick solid line represents the best fitted curve of Eq. (3) with \( \Delta H = 1.8 \text{ kcal/mol} \).

from NMR study, which agrees well with our result. They also reported entropy difference \( \Delta S = -0.03 \text{ cal/mol K} \) between the isomers. The substitution of this value into Eq. (3) yields \( \Delta V/V = -0.03 \). The negative sign of \( \Delta V/V \) means that an axial molecule occupies a larger room than an equatorial molecule.

4. ROTATIONAL ISOMERIC RELAXATION IN METHYL ACETATE

Results of absorption measurement in methyl acetate are shown in Fig. 5. The ultrasonic absorption in methyl acetate can be represented by an equation of single relaxation as follows;

\[
\alpha = \frac{A}{f^2 + (f/f_c)^2} + B, \tag{4}
\]

where \( \alpha \) is the ultrasonic absorption coefficient, and \( A \) the relaxation amplitude. The solid lines indicate fitted curves of Eq. (4) and arrows denote the relaxation frequency. Values of the relaxation parameters of methyl acetate are summarized in Table 2. We determined \( \Delta H^* \) and \( \Delta H \) for isomeric conversion from trans to cis with respect to rotation around the axis of C-O bond, and obtained \( \Delta H^* = 6.6 \text{ kcal/mol} \) and \( \Delta H = 3.4 \text{ kcal/mol} \). Again there seems to be disagreement with the previous study by pulse method. Slie and Litovitz\(^{15} \) observed the pressure independence of relaxation frequency and strength and showed that volume difference in ethyl acetate can be neglected. If we assume \( \Delta V = 0 \), then we obtain \( \Delta S = -3.5 \text{ cal/mol K} \) from Eq. (3).

It would be worthwhile to compare the potential barrier \( \Delta E = \Delta H^* + \Delta H \) characterizing cis-to-trans

<table>
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<th>( T ) (°C)</th>
<th>( A ) (( \mu \text{m}^2/\text{g} ))</th>
<th>( B ) (( \mu \text{m}^2/\text{g} ))</th>
<th>( f_c ) (MHz)</th>
<th>( \mu \text{m} ) (10(^{-3}))</th>
<th>( c ) (m/s)</th>
</tr>
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<td>5.0</td>
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<td>( 40 \times 10^{-17} )</td>
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<td>2.18</td>
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<td>40</td>
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</table>
rotation of some acetate and formate esters. The open triangle in Fig. 6 is the result of this work; the two open circles are from our previous study; and the closed points are by other workers. There are two notable features to be described: The barrier in formate esters is larger than that of corresponding acetate esters; and the barrier decreases in the order of methyl, ethyl and isopropyl. It is well known that the carboxyl C-O single bond has partially double bond character at the expense of the neighboring C=O double bond. This effect hinders the smooth rotation around the C-O bond and increases the barrier for the conversion process. The partially double bond character is weakened, however, by the influence of alkyl groups at X and R positions shown in Fig. 6; and larger the alkyl group, stronger the influence. Therefore formate esters have generally higher $\Delta E$ than acetate esters, and $\Delta E$ decreases as the number of C atoms in R increases.

REFERENCES