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## Ultrasonic Studies of Saturated Hydrocarbons at Low Temperatures\*

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Ultrasonic propagation properties of 2-methylbutane, 3-methylpentane, *n*-pentane, 2,3-dimethylbutane, and 2,2-dimethylbutane were studied using a pulse method in the range from 1 mc to 35 mc and from 130°K to 280°K. These studies revealed the existence of an attenuation peak in 2-methylbutane, in 2,3-dimethylbutane, and in 3-methylpentane. These peaks were found to be consistent with a single relaxation process. Activation energies for the relaxation process in 2-methylbutane and 3-methylpentane were found to be about 4.7 kcal/M, and about 3.3 kcal/M in 2,3-dimethylbutane. No absorption was observed in *n*-pentane and 2,2-dimethylbutane. In a mixture of 3-methylpentane and *n*-pentane, measurements at 5 mc showed an absorption peak at the same temperature as in 3-methylpentane, reduced in amplitude in proportion to the reduction in the number of molecules of 3-methylpentane. These observations indicate that the mechanism of absorption is explainable in terms of a hindered rotation (about the middle C—C bond in butanes and about the 2nd and 3rd C—C bonds in 3-methylpentane), leading to potential minima of unequal values for the different rotational isomeric states. Such asymmetry in the different rotational isomers appears to be an essential requirement for ultrasonic absorption in these molecules.

IN recent years a number of physical methods have been used to investigate internal molecular rotation about a single bond as axis. Mizushima<sup>1</sup> has described the development of these investigations and the interpretation of the experimental data that has been accumulated. Through interpretation of infrared and Raman spectra, electron diffraction studies, dielectric constant measurements, and specific heat studies, it has been established that more than one rotational isomer of some molecules exists in the liquid state in appreciable quantities.

When the local free energy barriers for hindered rotation are not too large, and when the difference between the local free energy minima of the various rotational sites is not zero, one expects absorption of sound due to relaxation. Using ultrasonic methods, Karpovich<sup>2</sup> determined the relaxation frequency of a number of organic liquids and attributed the relaxations to a disturbance of the equilibria between rotational isomers. The present paper presents the results of an investigation of the effects of internal rotation in some hydrocarbon liquids on ultrasonic absorption. Liquids were chosen to aid in determining experimentally whether the relaxations observed were indeed due to internal rotation. These liquids were 2-methylbutane, 3-methylpentane, *n*-pentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

### EXPERIMENTAL METHOD

An ultrasonic pulse method was used to obtain acoustic velocity and absorption in the liquids studied. The experimental apparatus was similar to that de-

scribed by Melchor and Petrauskas.<sup>3</sup> The pulse oscillator circuit that was used is essentially that described by Easton.<sup>4</sup> Two quartz crystals were used, one serving as transmitter and the other as receiver. All data were taken with the transmitter-receiver distance lying within the Fresnel region, where a correction for beam spreading is unnecessary.<sup>5</sup> The transmitting and receiving crystals were mounted on a platform so that they could be moved either simultaneously as a unit, or with respect to one another, by means of two calibrated screws. By noting the change in amplitude and the change in transit time of the received acoustic signal when the receiver to transmitter distance was changed by a known amount, the attenuation and velocity of the acoustic signal in a liquid could be determined.

By use of the screw which moved both transmitter and receiver, the difference in velocity and attenuation of two different liquids could be determined *via* the method described by Carstensen.<sup>6</sup> In this method the transmitter is placed in one liquid and the receiver in the other, with a separating membrane or wall between the two liquids. With the transmitter-receiver distance held constant, the relative path length in the two liquids is changed by a known amount, and the corresponding amplitude and transit time changes are observed.

### TEMPERATURE CONTROL

Since the interesting temperature region for the frequencies available was considerably below room temperature, liquid nitrogen was used as the cooling agent. A diagram of the cooling arrangement is shown in Fig. 1. Two tapered copper fins that protruded into

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† Now at DuPont Laboratories.

<sup>1</sup> S. Mizushima, *Structure of Molecules* (Academic Press, Inc., New York, 1954).

<sup>2</sup> J. Karpovich, *J. Chem. Phys.* **22**, 1767 (1954).

<sup>3</sup> J. L. Melchor and A. A. Petrauskas, *Ind. Eng. Chem.* **44**, 716 (1952).

<sup>4</sup> A. Easton, *Electronics* **20**, 124 (March, 1947).

<sup>5</sup> J. M. M. Pinkerton, *Proc. Phys. Soc. (London)* **B62**, 286 (1949).

<sup>6</sup> E. L. Carstensen, *J. Acoust. Soc. Am.* **26**, 858 (1954).

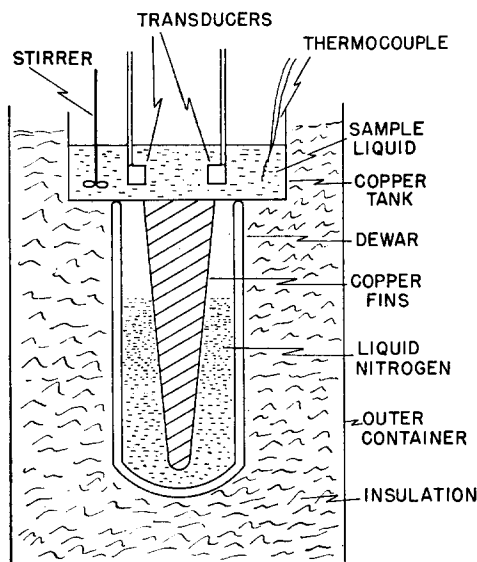


FIG. 1. Temperature control apparatus.

an inner dewar were attached to the copper tank which contained the liquid to be measured. The liquid nitrogen level in this inner dewar, and hence the amount of heat conducted down the copper fins, determined the temperature of the liquid in the copper tank. A thin sheet of polyethylene was wrapped about the tank so that dry air could be circulated to prevent appreciable condensation of water vapor. It was found necessary to stir the liquid vigorously immediately prior to taking acoustic data to keep down thermal gradients during the measurements. Most of the data reported in the present work were taken while the temperature was rising slowly. Temperature was measured by recording the output of a copper-cupron thermocouple on a Brown Elektronik potentiometer. The reference junction of the thermocouple was kept in a water-ice bath. The measuring junction was kept in the liquid, and could be moved about to determine the extent of thermal gradients.

#### SOURCE, PURITY, AND STRUCTURE OF THE LIQUIDS

All of the liquids were supplied by Phillips Petroleum Company and were "pure grade" of at least 99 mole percent purity. Some Eastman Kodak Company practical grade 2-methylbutane was found to yield the same results, within experimental error, as the pure grade liquid.

The carbon skeletons of the hydrocarbons employed in this study are shown in Fig. 2. The probable configurations or stable sites, for 2-methylbutane, 2,2-dimethylbutane, and 2,3-dimethylbutane are shown in the same figure, along with approximate local free energy barrier shapes for rotation about the central single carbon-carbon bond.

#### THEORY

Ultrasonic absorption per wavelength due to a single relaxation process may be expressed by

$$\alpha\lambda = \pi\rho C^2 \frac{\beta_r \omega \tau}{1 + \omega^2 \tau^2} \quad (1)$$

where  $\rho$  is the equilibrium density,  $C$  the phase velocity of the wave,  $\omega$  the angular frequency,  $\beta_r$  the relaxing part of the adiabatic compressibility, and  $\tau$  the relaxation time associated with the particular relaxation mechanism that is involved. If the dispersion of velocity is small, as is the case in most liquids, the attenuation per wavelength,  $(\alpha\lambda)$ , is proportional to

$$\frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

The attenuation per wavelength then peaks when  $\omega\tau=1$ . The width of this peak at half-maximum is about 3.8 octaves, or a factor of about 14 in frequency.

The relaxation times for a three-position or three state model have been considered by Hoffman,<sup>7</sup> under the restrictions of a single jump hypothesis. This model fits the case of 2-methylbutane. As may be seen from Fig. 2, three stable configurations can be obtained, one from the other, by rotation of the ethyl group against the isopropyl group  $120^\circ$  about the central carbon-carbon bond. Stable configurations are obtained when the  $\text{CH}_3$  member (cross-hatched) of the ethyl group occupies any of the three sites 1, 2, or 3,  $120^\circ$  apart. Stable configuration 1 and 3 should have the same

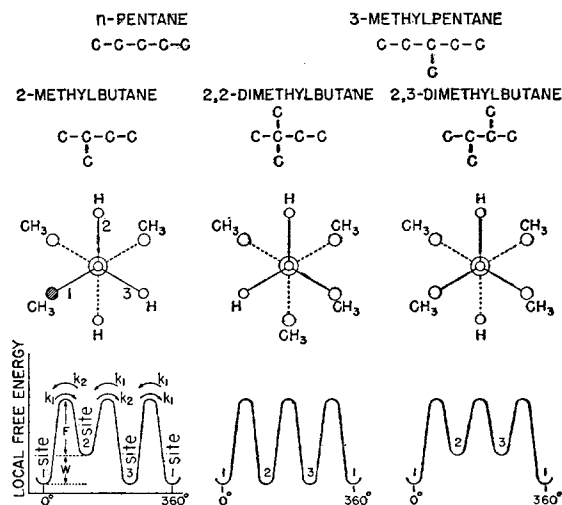


FIG. 2. Upper diagrams: Carbon skeletons of the saturated carbons. Middle diagrams: Stable configurations of 2-methylbutane, 2,2-dimethylbutane, and 2,3-dimethylbutane. Lower diagrams: Local free energy shapes for rotation about the central carbon-carbon bond. Stable configurations for 2-methylbutane are obtained when the  $\text{CH}_3$  member (cross-hatched) of the ethyl group occupies any of the three sites 1, 2, or 3,  $120^\circ$  apart.

<sup>7</sup> T. D. Hoffman, J. Chem. Phys. 23, 1331 (1955).

energy. Configuration 2, however, should have a higher energy because of the proximity of the methyl groups. The local free energy maxima are equivalent when the methyl group passes from site 1 to 2 and from 2 to 3. The maxima may be different when the methyl group passes from site 3 to 1. For the case where sites 1 and 3 are equivalent and more stable than site 2 and all local free energy maxima are equivalent, Hoffman obtains two relaxation times

$$\begin{aligned}\tau_2 &= 1/(k_1 + 2k_2) \\ \tau_3 &= 1/3k_1\end{aligned}\quad (3)$$

where  $k_1$  is the transition probability (specific reaction rate constant) from sites 1 to 3, 1 to 2, and 3 to 2, and  $k_2$  is the transition probability from sites 2 to 1 and 2 to 3.  $\tau_2$  is the relaxation time for transitions from site 2 to both site 1 and site 3, or *vice versa*, and  $\tau_3$  is the relaxation time for transitions from 1 to 3 or 3 to 1. As long as sites 1 and 3 are equivalent, a pressure disturbance would not upset the equilibrium between these two sites and  $\tau_3$  is acoustically inactive.  $\tau_2$  is then the only acoustically active relaxation time.

It is interesting to note that when sites 1 and 3 are more stable than site 2 and when the transition probabilities from sites 1 to 3 and 3 to 1 are equal to  $k_2$  instead of  $k_1$ , the two relaxation times converge and

$$\tau_2 = \tau_3 = 1/(k_1 + 2k_2). \quad (4)$$

The acoustically active relaxation time is the same for this case as for the one considered by Hoffman.

Since the transition probabilities can be written  $k_i = B \exp(-F_i/RT)$  where  $B$  is essentially a constant,  $F_i$  the activation energy per mole for the transition involved,  $R$  the gas constant, and  $T$  the absolute temperature, the acoustically active relaxation time

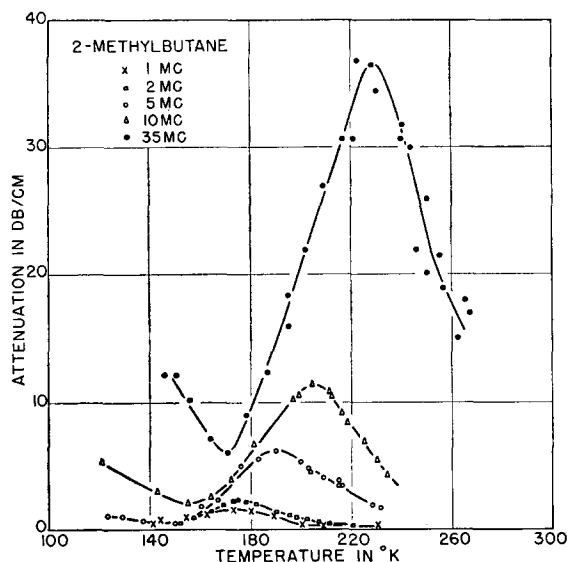


FIG. 3. Acoustic attenuation in 2-methylbutane at frequencies of 1, 2, 5, 10, and 35 mc as a function of the temperature of the liquid.

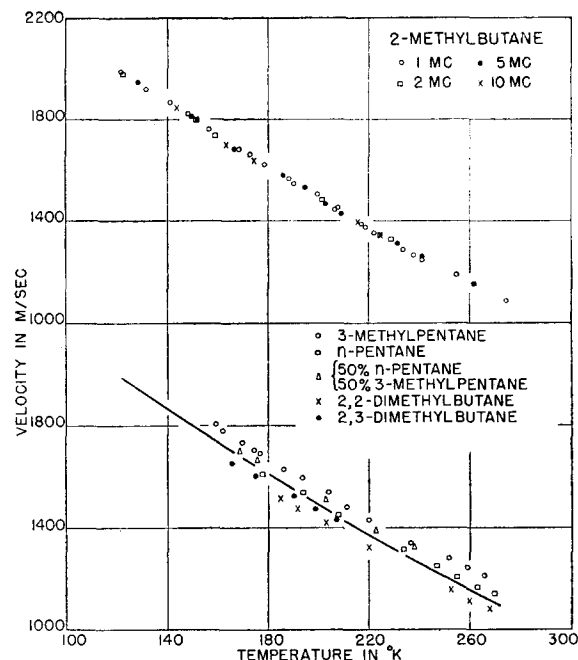


FIG. 4. Upper points: Sound velocity in 2-methylbutane at frequencies from 1 to 10 mc *versus* temperature. Lower curve: Sound velocity in 2-methylbutane transferred from the points above. Lower points: Sound velocity at 5 mc in 3-methylpentane, *n*-pentane, mixture of half *n*-pentane and half 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane.

can be written approximately as

$$\tau = A e^{F/RT}, \quad (5)$$

where  $F$  is the activation energy per mole for the backward reaction. Then since  $\omega_m \tau = 1$  where  $\omega_m$  is the frequency corresponding to maximum attenuation per wavelength

$$\omega_m = \text{const} e^{-F/RT}. \quad (6)$$

This last relation will be used to determine the activation energy for the backward reaction involved in the relaxation processes.

It should be noted that in the case of symmetrical barriers, as in 2,2-dimethylbutane where all three sites are equivalent, a pressure disturbance is not capable of upsetting the equilibrium distribution of molecules between the various sites and no acoustic relaxation should result. There should be at least two non-equivalent sites in order that an acoustically active relaxation time may exist.

## EXPERIMENTAL RESULTS

The acoustic attenuation in 2-methylbutane is presented in Fig. 3 at frequencies of 1, 2, 5, 10, and 35 mc as a function of the temperature of the liquid. Attenuation plotted in db/cm is found to reach a maximum in the temperature range from 170 to 230°K. The temperature at which this maximum occurs increases with increasing frequency. The value of maxi-

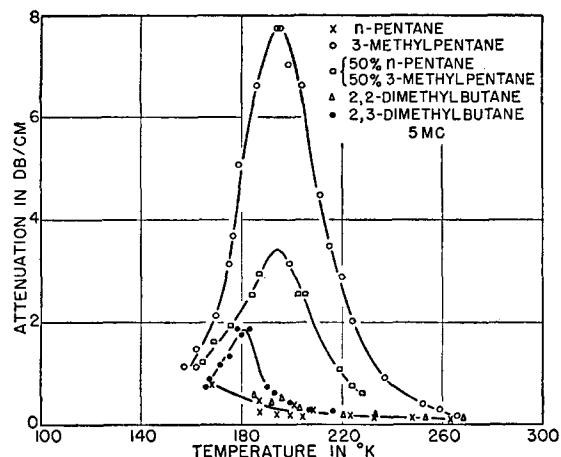


Fig. 5. Attenuation at 5 mc versus temperature in *n*-pentane, 3-methylpentane, half *n*-pentane and half 3-methylpentane mixture, 2,2-dimethylbutane, and 2,3-dimethylbutane.

imum attenuation also increases with increasing frequency. Maximum attenuation varies from about 1.5 db/cm at 1 mc to 27 db/cm at 35 mc. The existence of this peak, and its behavior with increasing frequency is characteristic of relaxation phenomenon. At temperatures below this peak the data at the higher frequencies indicate that the attenuation again rises, but no additional maxima were found. This rise may be due to viscosity increase as the melting or glassy transition temperature is approached.

A composite curve giving the sound velocity in 2-methylbutane at frequencies from 1 to 10 mc is shown in Fig. 4. The velocity decreases from about 2000 m/sec at 120°K to about 1000 m/sec at room temperature. No dispersion could be detected within the experimental accuracy of these velocity data. A gradual change in the slope of the velocity versus temperature curve is observed in the temperature range of 210 to 260°K.

A curve of acoustic velocity versus temperature in 3-methylpentane at 5 mc is included in Fig. 4. Absorption in this liquid was measured at 2, 5, and 35 mc over the temperature region of the relaxation peak. Attenuation per centimeter versus temperature is plotted in Fig. 5 for a frequency of 5 mc, and in Fig. 6 for a frequency of 35 mc. It is interesting to note that these attenuation curves are very similar to the corresponding ones in 2-methylbutane. The peak absorption is slightly higher and the temperature of the peak in this liquid increases with frequency at the same rate as in 2-methylbutane.

Attenuation and velocity in *n*-pentane were measured at 5 and 35 mc. Attenuation per centimeter versus temperature at 5 mc appears in Fig. 5, and at 35 mc in Fig. 6. Velocity at 5 mc versus temperature is included in Fig. 4. No attenuation peak is observed for this liquid in the region of the relaxation peak in 2-methylbutane and 3-methylpentane. However, the increase

in absorption at low temperature manifests itself at a higher temperature than in either of the other two liquids. The general trend of the acoustic absorption with temperature in *n*-pentane is the same as that reported by Koshkin and Nordrev<sup>8</sup> for *n*-hexane, *n*-heptane, and *n*-octane, and is probably characteristic of normal paraffins.

A velocity curve for a mixture of half *n*-pentane and half 3-methylpentane by volume is included in Fig. 4. The velocity in this mixture is intermediate between that of the component liquids. Attenuation in the same mixture is presented in Fig. 5. This attenuation curve exhibits the relaxation peak of 3-methylpentane, reduced in amplitude, but appearing at the same temperature.

Acoustic attenuation in 2,2-dimethylbutane and 2,3-dimethylbutane, for the frequency of 5 mc, is shown in Fig. 5. Attenuation is found to reach a maximum for 2,3-dimethylbutane but not for 2,2-dimethylbutane.

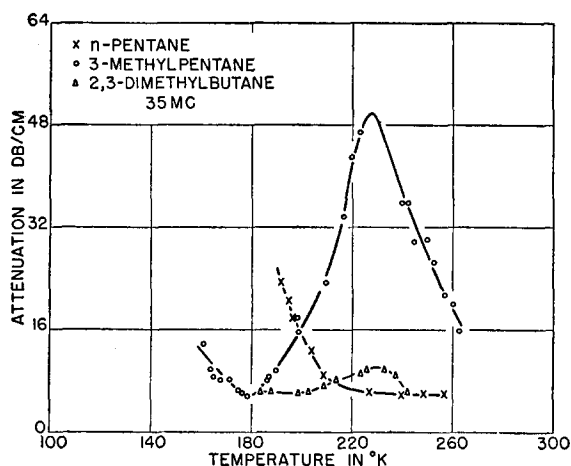


Fig. 6. Attenuation in *n*-pentane, 3-methylpentane, and 2,3-dimethylbutane at 35 mc.

This behavior was expected since all three rotational sites are equivalent in 2,2-dimethylbutane. Figure 6 shows the attenuation in 2,3-dimethylbutane for the frequency of 35 mc. Measurements of attenuation in 2,3-dimethylbutane were carried down to lower temperatures than in 2,2-dimethylbutane because the melting point is lower. The curves of acoustic velocity versus temperature in 2,2-dimethylbutane and 2,3-dimethylbutane at 5 mc are included in Fig. 4.

#### DISCUSSION OF RESULTS

A plot of the attenuation per wavelength as a function of temperature at various frequencies for 2-methylbutane is shown in Fig. 7. These data are cross plotted as a function of frequency, at several temperatures, in Fig. 8. From the curve at 200°K one may observe that the frequency width at half maximum is in excellent

<sup>8</sup> N. I. Koshkin and V. F. Nordrev, Doklady Akad. Nauk. S.S.S.R. 92, 792 (1953).

agreement with the 3.8 octaves calculated for absorption governed by a single relaxation time.

The slope of the curve  $\ln \omega_m$  versus  $1/T$  gives the value of  $F/R$ . In Fig. 9 reciprocal temperature at peak attenuation is plotted as a function of frequency on a logarithmic scale in order to obtain apparent activation energies for the relaxation process in 2-methylbutane, 3-methylpentane, and 2,3-dimethylbutane. Points were taken from the peaks of the attenuation per wavelength versus temperature curves and a straight line was fitted to these points. The inverse of the slope of the line for 2-methylbutane yields an apparent activation energy of about 4.7 kcal/M for the backward reaction, i.e., the one from higher to lower energy.

The fact that acoustic attenuation in 3-methylpentane is very similar to that in 2-methylbutane has been noted in an earlier section. Plots of attenuation per wavelength in 3-methylpentane as a function of temperature are shown in Fig. 10 for three frequencies. Since

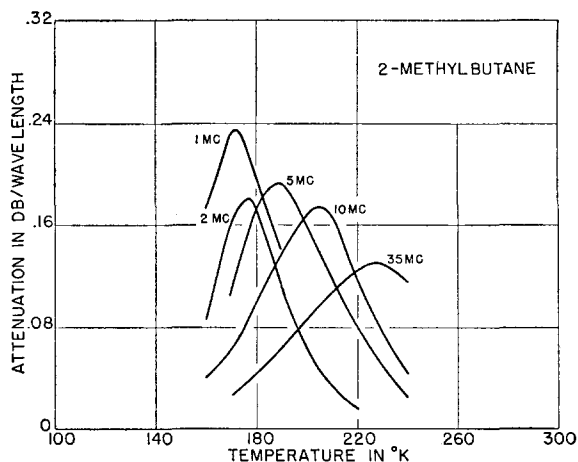


Fig. 7. Attenuation per wavelength versus temperature at the frequencies of 1, 2, 5, 10, and 35 mc in 2-methylbutane.

data were taken at only 3 frequencies, no cross plot of attenuation per wavelength was made. The plot of frequency versus reciprocal temperature at peak attenuation is shown in Fig. 9. The activation energy calculated from this plot is 4.7 kcal/M. This is identical with that found in the same manner for 2-methylbutane.

Finally a similar plot in Fig. 9 for 2,3-dimethylbutane yields an activation energy of 3.25 kcal/M.

### GENERAL DISCUSSION

These results appear to be explainable in terms of a hindered rotation (about the middle C—C bond in the butanes and about the 2nd and 3rd C—C bonds in the 3-methylpentane) leading to potential minima of unequal values. Nonequivalent potential minima for the different rotational isomers appear to be required in order that ultrasonic absorption may occur.

Some idea of the effect of dilution on the relaxation process in 3-methylpentane may be obtained from the

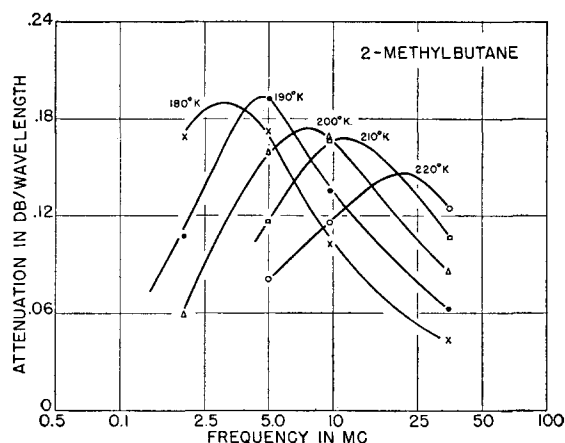


Fig. 8. Attenuation per wavelength versus frequency in mc at temperatures of 180°K, 190°K, 200°K, and 220°K.

study of the 50% by volume mixture with *n*-pentane. The results indicate a reduction in magnitude of the absorption peak by a factor of 0.41. Strictly speaking, one should subtract the portion of the attenuation which is proportional to frequency squared before computing the ratio of the absorptions resulting from the relaxation process. The frequency squared part of the attenuation is ascribed to viscous and other effects, and is not associated with the relaxation mechanism. Now although an exact figure cannot be given, on the basis of our data the major part of the attenuation observed in the vicinity of the absorption peaks unquestionably results from the relaxation process. Further, 39% of the molecules in this mixture are 3-methylpentane. The agreement of this figure with the reduction in the absorption peak indicates a simple dilution effect. This conclusion together with the observation that the relaxation was not changed by the dilution, suggests that an intramolecular process is responsible for the absorption peak. If forces between 3-methylpentane molecules caused the relaxation, these forces would probably change with dilution. The relaxation time would then change and the absorption peak

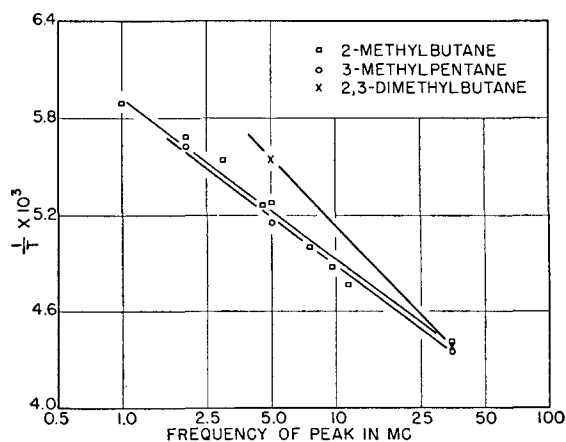


Fig. 9. Plot of  $1/T$  versus frequency at peak attenuation.

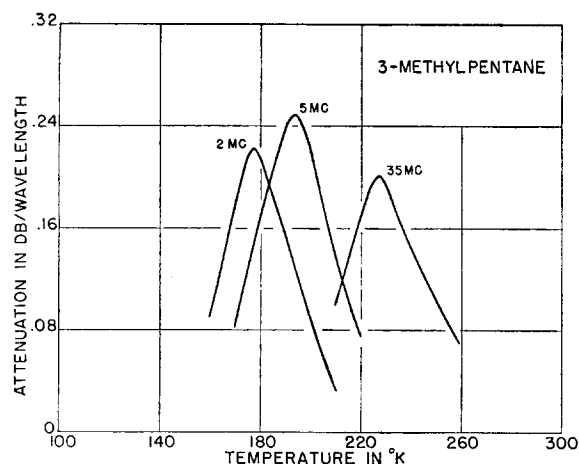


FIG. 10. Attenuation per wavelength in 3-methylpentane versus temperature at 2, 5, and 35 mc.

would change in temperature as well as in magnitude. It seems unlikely that the hydrocarbons studied here should display any appreciable tendency to associate into double molecules at temperatures far removed from the melting point.

From the measurements reported herein the asymmetry of the hydrocarbon molecules due to the methyl side group seems to be necessary for relaxation. Each of the asymmetrical branched chain molecules exhibits the peak in absorption, but the straight chain *n*-pentane and the symmetrical 2,2-dimethylbutane do not. The activation energies for the relaxation process were identical in 2-methylbutane and 3-methylpentane. The barriers hindering rotation of the ethyl groups in these two molecules could very easily be the same. These barriers could then explain the identical activation energies.

The apparent activation energy found for the relaxation mechanism in 2-methylbutane is of the right order of magnitude to suggest that a disturbance of the equilibrium between rotational isomers may be responsible for the observed acoustic effects. Luft's<sup>9</sup> calcu-

<sup>9</sup> N. W. Luft, J. Chem. Phys. **22**, 1814 (1954).

lation of the activation energy for backward reaction also yields 4.7 kcal/M.

Kuratani and Mizushima<sup>10</sup> have demonstrated that 1,1,2-trichloroethane, which has a skeleton structure similar to that of 2-methylbutane, exists in only one form in the solid state but that both isomers exist in appreciable quantities in the liquid state. Szasz and Sheppard,<sup>11</sup> and Brown and Sheppard,<sup>12</sup> have made spectroscopic measurements on 2,3-dimethylbutane and 2-methylbutane in the solid and liquid states. In the crystalline state the spectrum of 2,3-dimethylbutane was simplified indicating a center of symmetry for the stable configuration in the lattice. This evidence suggests that both isomers of 2,3-dimethylbutane exist in the liquid state with only a very small energy difference between the two. The acoustic data presented here also suggest that both isomers exist in appreciable numbers in the liquid state. Although the experimental evidence given by Brown and Sheppard is not so binding in the case of 2-methylbutane, it seems quite probable that this substance also exists in both forms in the liquid state in appreciable quantities.

The evidence supporting an explanation of the absorption peaks found here in terms of rotational isomerism is then: the activation energy found for 2-methylbutane is of the right order of magnitude. The absorption peak is not found in normal pentane where the steric hindrance due to the methyl side group is absent. The same activation energy is observed for 3-methylpentane, which has the methyl side group and two ethyl end groups similar to the one in 2-methylbutane. The dilution effect found in a mixture of 3-methylpentane and *n*-pentane suggests that the relaxation peak is due to an intramolecular process. In 2,2 dimethylbutane all three sites are equivalent and, as expected, no acoustic relaxation was found. Both isomers of 2,3 dimethylbutane are known to exist in the liquid state with a small energy difference between the two.

<sup>10</sup> K. Kuratani and S. Mizushima, J. Chem. Phys. **22**, 1403 (1954).

<sup>11</sup> G. J. Szasz and N. Sheppard, J. Chem. Phys. **17**, 93 (1949).

<sup>12</sup> J. K. Brown and N. Sheppard, J. Chem. Phys. **19**, 976 (1951).