ULTRASONIC RELAXATION DUE TO ROTATIONAL ISOMERISM

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PROEFSCHRIFT

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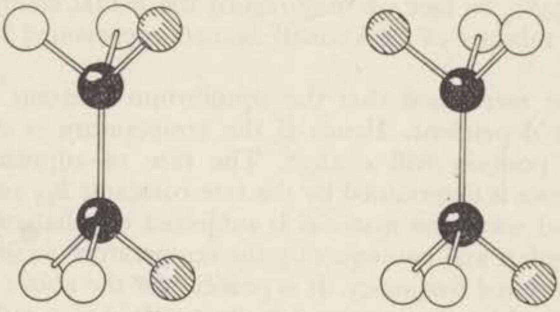
CONTENTS

INTRODUCTION

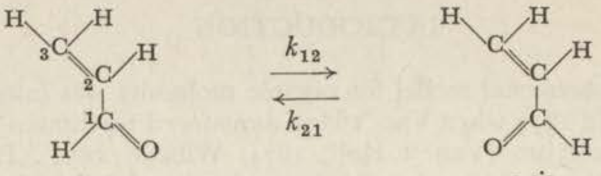
A three-dimensional model for organic molecules was introduced in chemistry in 1874 when Van 't Hoff announced his famous theory on optical isomerism (Van 't Hoff, 1874; Wibaut, 1952). His theory contained the postulate that the four valences of carbon are directed to the corners of a tetrahedron with the carbon atom at the centre. Application of this tetrahedral model to molecules like 1-2-dichloroethane suggested the existence of forms like:



and the absence of this kind of isomerism required the introduction of another postulate, namely that *carbon atoms ordinarily can rotate about a single bond*. This important principle for which now substantial evidence is available implies that the actual 1-2-dichloroethane molecules are a mixture of all sorts of sterical configurations. The conversion of one form into another is very rapid and merely an average property can be measured.

Although the different forms of 1-2-dichloroethane cannot be isolated, there is every reason to believe that they are of different potential energy; for example the electrostatic interaction between the negatively charged Cl atoms is dependent upon the relative position of the CH_2Cl groups (Smyth, 1924; Hückel, 1957). The existence of positions of lower and higher energy implies that rotation about the C-C bond is not completely free but of a so-called restricted type. Restricted or hindered rotation about single bonds is frequently found in organic molecules. Surprisingly it even occurs in a molecule like ethane (Eyring, 1932; Mizushima, 1954).

The type of rotation about a single bond with which we shall be mainly concerned in this thesis is characterised by the fact that the rotation opposing forces are due to resonance. Let us consider the acrolein molecule as an example.



Acrolein

As a result of conjugation between the double bonds the freedom of rotation about the C_1-C_2 bond is restricted. This bond has a partially double bond character and therefore planar structures are stabilised. (Pauling, 1948). In fact we may regard the actual compound as an equilibrium mixture of (rotational) isomers represented by the forms given above.

It may be mentioned that the equilibrium constant is generally temperature dependent. Hence if the temperature is changed the equilibrium position will change. The rate of adjustment to the new conditions is determined by the rate constants k_{12} and k_{21}.

In a sound wave the material is subjected to adiabatic dilatation and compression and consequently the temperature oscillates up and down at the sound frequency. It is possible for the above equilibrium to be perturbed by the temperature fluctuations in a sound wave in which case the equilibrium position oscillates back and forth at the same frequency. In the case of relaxation an appreciable phase difference may develop between the temperature oscillations and the oscillations back and forth of the reaction.

It is the purpose of this thesis to show that from the study of ultrasonic relaxations in liquids direct information may be obtained concerning the mobility of an equilibrium reaction between rotational isomers. For the above given type of reaction this mobility can be changed in a predictable way by decreasing or increasing the conjugation.

In chapter I the theory of ultrasonic relaxation is outlined. It is shown that the equilibrium between rotational isomers may, in principle, lead to anomalous sound absorption. Only those fields of the theory are covered which are of interest for the interpretation of our experiments. No distinction is made between relaxation and retardation processes (Böttcher, 1957; Schrama, 1957); in addition the idea of a continuous spread of relaxation times is ignored (Böttcher, 1952).

The purpose of chapter II is twofold: first to describe the actual equipment that was used for our experiments; and second, to indicate that ultrasonic relaxations in liquids can only be studied over a limited frequency range.

Experimental data are collected and analysed in chapter III. It is shown that, for a number of liquids, the anomalous ultrasonic behaviour is due to perturbation, by the sound wave, of an equilibrium between rotational isomers. A relationship between the ultrasonic behaviour and the chemical structure is established.

CHAPTER I

ULTRASONIC RELAXATION

§ 1.1. Introduction

For a better understanding of ultrasonic relaxation it may be useful to start with a few remarks concerning relaxation phenomena in general. As an early approach to the theory of these phenomena let us consider Maxwell's equation for an elastic substance with friction (Maxwell, 1867; Burgers, 1935).

$$D = \alpha F + \varphi \int_0^t F \, d t , \quad \ldots\ldots\ldots\ldots \tag{1.1}$$

in which F is the applied stress, D is the deformation, t is the time and α and φ are constants. A mechanical model corresponding to Maxwell's equation is given in figure 1. 1.

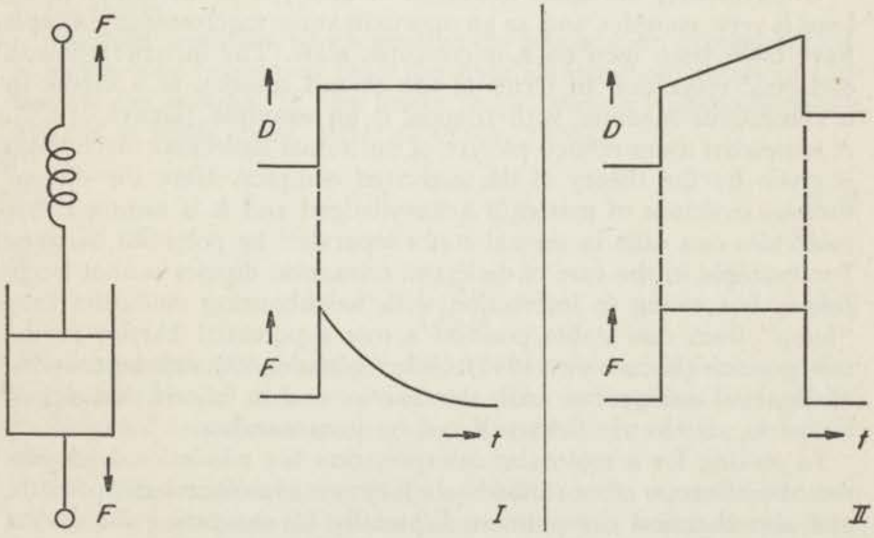


Figure 1.1.
Mechanical model corresponding to Maxwell's equation of state.

If, after an initial perturbation, the deformation D is kept constant (case I) we find $F = F_0\, e^{-t/\tau}$. The constant $\tau = \alpha/\varphi$ has the dimension of a time and it is called the relaxation time of the model. Obviously this model leads to conversion of non-thermal into thermal energy, a characteristic feature of relaxation phenomena. Equation (1.1) is an example of a *dynamic equation of state*. It describes a system which is irreversible and time-dependent.

It is the basic task of theories on relaxation to find the dynamic equation of state and then derive from it the properties of the physical or chemical system under consideration. Frequently this task is carried out in two successive steps:

1. A mathematically convenient dynamic equation of state is assumed for which there may be theoretical justification. Maxwell's equation is an example. Then one checks whether the calculated and experimental values are in agreement. If this is so then it may be regarded as experimental evidence that the employed equation of state is correct.
2. It is attempted to correlate the equation of state with more fundamental properties of matter and preferably to express it in terms of inter or intramolecular structure.

Surely if we want to get down to the roots of the problem we must give more than a mere phenomenological description and pay much attention to the second item.

Unfortunately the exact treatment of this type of molecular problems is very complex and as an approximation macroscopic concepts have often been used on a microscopic scale. The interpretation of dielectric relaxation in terms of the overall rotation of a dipole in a continuous medium with friction is an example (Debye, 1929). A somewhat more refined picture of the actual molecular mechanism is given by the theory of the activated complex. Here the discontinuous structure of matter is acknowledged and it is assumed that molecules can exist in several states separated by potential barriers. For example in the case of dielectric relaxation dipoles cannot freely rotate, but owing to interaction with neighbouring molecules they "jump" from one stable position across a potential barrier to the next position (Kauzmann, 1942). Only molecules with sufficient thermal (kinetic) energy can cross the barrier and it follows that orientation in an electric field will not be instantaneous.

In seeking for a molecular interpretation the relaxational properties of matter are often studied as a function of temperature, pressure and also chemical composition. Especially by comparing the results obtained in related organic compounds the value of a particular mechanism can often be established beyond doubt. This analysis by "chemical modulation" (Böttcher, 1957) will be used in this thesis for the explanation of ultrasonic relaxations discovered in a number of compounds with rotating groups.

The theory of ultrasonic relaxation will now be developed, as far as is necessary for a clear understanding of the following chapters. A more detailed treatment can be found in the literature (DAVIES and LAMB, 1957; MARKHAM, BEYER and LINDSAY, 1951; KNESER, 1949; KITTEL, 1947; VIGOUREUX, 1951; BERGMANN, 1954).

§ 1.2. General theory

Sound waves are essentially harmonic mechanical perturbations which are propagated in a medium. In a solid and also in a very viscous liquid like glass several types of vibrations are possible. We distinguish between transverse waves (oscillations perpendicular to the direction of propagation) and longitudinal waves (oscillations in the direction of propagation). In what follows we simplify matters by confining ourselves to *isotropic fluids* of relatively low viscosity. It can be shown that propagation of ultrasonic transverse or "shear" waves is virtually impossible in this type of medium. This is because "elastic shear waves" can only be realised at extremely high frequencies (MASON, BAKER, MCSKIMIN and HEIS, 1949) which are not accessible to measurement, whereas "viscous shear waves" are damped out in a few oscillations owing to excessive absorption (LAMB and ANDREAE, 1951). Thus there remain longitudinal, that is compressional, waves.

The basic equation, which governs the propagation of compressional waves, can be derived from the hydrodynamic equations of continuity and motion. If non linear (high intensity) phenomena are avoided it reads (JOOS, 1951; COULSON, 1949)

$$\nabla^2 \rho_e = \frac{1}{c^2}\frac{\partial^2 \rho_e}{\partial t^2}, \quad \ldots\ldots\ldots \quad (1.2)$$

with

$$c^2 = \left(\frac{\partial p_e}{\partial \rho_e}\right)_S. \quad \ldots\ldots\ldots\ldots \quad (1.3)$$

The introduction of ρ_e and p_e indicates that we are only interested in the excess density and excess pressure. The suffix S has been added to show that sound wave propagation is essentially adiabatic; t denotes the time.

The differential equation (1.2) is known as the equation of wave motion. It represents all types of wave motion in which the velocity is constant. For the one-dimensional case we find as the most general solution

$$\rho_e = f(t - x/c) + g(t + x/c), \quad \ldots\ldots \quad (1.4)$$

in which f and g indicate arbitrary functions. The special solution

$$\rho_e = R \cos \left[2 \pi \nu \left(t - x/c\right) + \varphi\right] , \quad . \; . \; . \; . \; . \quad (1.5)$$

where φ is a phase angle and ν is the frequency, represents a travelling, planar, harmonic wave of constant density amplitude R. It follows that the constant c must be indentified with the *sound velocity.*

It is to be expected that in an absorbing medium the amplitude of a travelling wave will decrease with increasing travelling distance. Then equation (1.5) must be modified to

$$\rho_e = R\, e^{-\alpha x} \cos \left[2 \pi \nu \left(t - x/c\right) + \varphi\right]; \quad . \; . \; . \; . \quad (1.6)$$

α is the *absorption coefficient* relating to the density amplitude attenuation.

For convenience we introduce complex quantities, indicated by $\wedge$, in which case ρ_e is given by the real part of

$$\hat{\rho}_e = R\, e^{-\alpha x}\, e^{i\left[2 \pi \nu (t - x/c) + \varphi\right]}. \quad . \; . \; . \; . \; . \quad (1.7)$$

This may be written in the form

$$\hat{\rho}_e = \hat{R}\, e^{2 \pi \nu i \left(t - x/\hat{c}\right)}, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1.8)$$

in which c is made complex. We notice that (1.8) also is a special solution of the equation of wave motion (with complex c). It follows from (1.7) and (1.8) that

$$\frac{1}{\hat{c}} = \frac{1}{c} - \frac{\alpha i}{2 \pi \nu}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.9)$$

In a system without relaxation a change in pressure will be followed by a non-delayed density response. Then the excess density ρ_e is uniquely determined by the increase of pressure p_e. For small oscillations it is reasonable to assume a linear relationship between the two quantities (HOOKE's law). This is expressed in the following equations in which the adiabatic *compressibility coefficient* $\beta^\circ{}_s$ is introduced.

$$\beta^\circ{}_s = \frac{1}{\rho_0}\left(\frac{\partial \rho_e}{\partial p_e}\right)_S ; \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.10)$$

ρ_0 is the density of the unperturbed medium and $\beta^\circ{}_s$ is the compressibility coefficient. We write in integral form

$$\frac{\rho_e}{\rho_0} - \beta^\circ{}_s\, p_e = 0. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.11)$$

The relation (1.11) is a static equation of state. It is time-independent and expresses that for a harmonic perturbation ρ_e and p_e will always be in phase. Using (1.10) or (1.11) and (1.3) we obtain for the sound-velocity

$$(c^\circ)^2 = \frac{1}{\rho_0\, \beta^\circ{}_s}. \quad . \; . \; . \; . \; . \; . \; . \quad (1.12)$$

In a medium with relaxation the static equation of state must be replaced by a dynamic one. Instead of (1.11) we introduce the general dynamic equation of state

$$\frac{\dot{\rho}_e}{\rho_0} - \beta_s^{\infty}\, \dot{p}_e + \frac{1}{\tau}\left(\frac{\rho_e}{\rho_0} - \beta^{\circ}_s\, p_e\right) = 0. \quad . \; . \; . \; . \; (1.13)$$

The dots denote time derivatives and τ is a relaxation time. In the case of slow motions we have $\dot{\rho}_e = \dot{p}_e = 0$ and the effective compressibility is equal to β°_s. Alternatively for very fast changes we find a compressibility β_s^{∞}. The relaxational character of (1.13) is clearly demonstrated if, after an initial perturbation, we make $\dot{p}_e = p_e = 0$. Then we have $\dot{\rho}_e + \rho_e/\tau = 0$ with solution

$$\rho = \rho_0 + \rho_e = \rho_0 + C\, e^{-t/\tau}. \quad . \; . \; . \; . \; . \; . \; (1.14)$$

It is of interest that equation (1.13) can easily be derived, for many systems, by the methods of irreversible thermodynamics (Meixner, 1953; Kneser, 1953), that is, without assuming any molecular mechanism.

It will now be shown that (1.13) leads to acoustic equations which are in accordance with the experimentally observed facts. Furthermore the basic principles leading to (1.13) will be examined and "mechanisms" introduced.

The equation of state (1.13) assumes a mathematically somewhat simpler form if only harmonic perturbations are considered. We use the complex notation (1.8)

$$\hat{\rho}_e = R\, e^{2\pi\nu i(t-x/\hat{c})} \quad \text{and} \quad \hat{p} = P\, e^{2\pi\nu i(t-x/\hat{c})}.$$

Substitution in (1.13) gives

$$\frac{\hat{\rho}_e}{\rho_0} - \hat{\beta}_s\, \hat{p}_e = 0 \quad \text{with} \quad \hat{\beta}_s = \beta_s^{\infty} + \frac{\beta^{\circ}_s - \beta_s^{\infty}}{1 + 2\pi\nu i\tau}. \quad . \; (1.15)$$

Thus it appears useful to introduce a complex compressibility coefficient $\hat{\beta}$. Now ρ_e and p_e are no longer in phase. The equation of state (1.15) is formally equivalent to (1.11) and consequently (1.12) is altered to

$$(\hat{c})^2 = \frac{1}{\rho_0\, \hat{\beta}_s}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; (1.16)$$

The fact that $\hat{c}$ is complex reveals that the medium under consideration shows sound absorption. The special solution (1.8) of the equation of wave motion must now be used.

From (1.15) and (1.16)

$$\frac{1}{(\hat{c})^2} = \rho_0\, \frac{\beta^{\circ}_s + \beta_s^{\infty}\,(2\pi\nu\tau)^2}{1 + (2\pi\nu\tau)^2} - \rho_0\, \frac{(\beta^{\circ}_s - \beta_s^{\infty})\, 2\pi\nu\tau}{1 + (2\pi\nu\tau)^2}\, i. \quad (1.17)$$

By comparing the imaginary parts of (1.17) and (1.9) we obtain for the sound absorption coefficient α

$$\frac{\alpha}{\nu^2} = \frac{\pi}{\nu_c} \frac{c}{(c^\circ)^2} \frac{1}{1 + (\nu/\nu_c)^2} \frac{\beta^\circ{}_s - \beta_s{}^\infty}{\beta^\circ{}_s}, \quad \ldots\ldots \quad (1.18)$$

with

$$(c^\circ)^2 = \frac{1}{\rho_o\, \beta_s{}^\circ} \quad \ldots\ldots\ldots \quad (1.19)$$

and

$$\nu_c = \frac{1}{2\,\pi\,\tau}. \quad \ldots\ldots\ldots \quad (1.20)$$

Usually $1/c^2 >> \alpha^2/\nu^2$. Under these conditions we obtain by comparing the real parts of (1.17) and (1.9)

$$c^2 = \frac{1}{\rho_o} \frac{1 + (\nu/\nu)_c{}^2}{\beta^\circ{}_s + \beta_s{}^\infty\, (\nu/\nu_c)^2}. \quad \ldots\ldots \quad (1.21)$$

Equation (1.21) gives the dispersion due to the relaxation. The velocity at very high frequencies ($\nu >> \nu_c$) is found to be

$$(c^\infty)^2 = \frac{1}{\rho_o\, \beta_s{}^\infty}. \quad \ldots\ldots\ldots \quad (1.22)$$

Frequently the dimensionless absorption per wavelength $\mu = \alpha\,\lambda$ is introduced. Since the wavelength $\lambda = c/\nu$, we find for μ

$$\mu = \pi \left(\frac{c}{c^\circ}\right)^2 \frac{\nu/\nu_c}{1 + (\nu/\nu_c)^2} \frac{\beta^\circ{}_s - \beta_s{}^\infty}{\beta^\circ{}_s}. \quad \ldots \quad (1.23)$$

As a representative value for a *liquid* we take: $(\beta^\circ{}_s - \beta_s{}^\infty)/\beta^\circ{}_s = 0.02$ or $\beta^\circ{}_s/\beta_s{}^\infty = 100/98$. The ratio of the sound velocity at infinite and zero frequency is calculated to be: $(c^\infty)^2/(c^\circ)^2 = \beta^\circ{}_s/\beta_s{}^\infty = 1.02$ It is therefore permissible to neglect the frequency dependence of $c/(c^\circ)^2$ and $(c/c^\circ)^2$ in the equations (1.18) and (1.23). We further assume that $c^\circ = 1.500 \times 10^5$ cm/sec and $\tau = 10^{-8}$ sec. The curves obtained with these values are given in figure 1.2. For the maximum value of μ we calculate 3.2×10^{-2}, a considerable absorption. Yet the velocity varies between $c^\circ = 1.500 \times 10^5$ and $c^\infty = 1.515 \times 10^5$ cm/sec, a dispersion of only 1 %. This example shows that in a liquid sound *absorption* measurements yield much more accurate information about a relaxation than do sound *velocity* measurements. It must be mentioned that this is not generally true for a gas.

The effective band width of the μ curve may be defined as "that over which the μ value is not less than half the maximum" (VIGOUREUX, 1951). It follows from (1.23) that the limiting frequencies ν_1 and ν_2 (see fig. 1.2) are then given by the roots of the equation

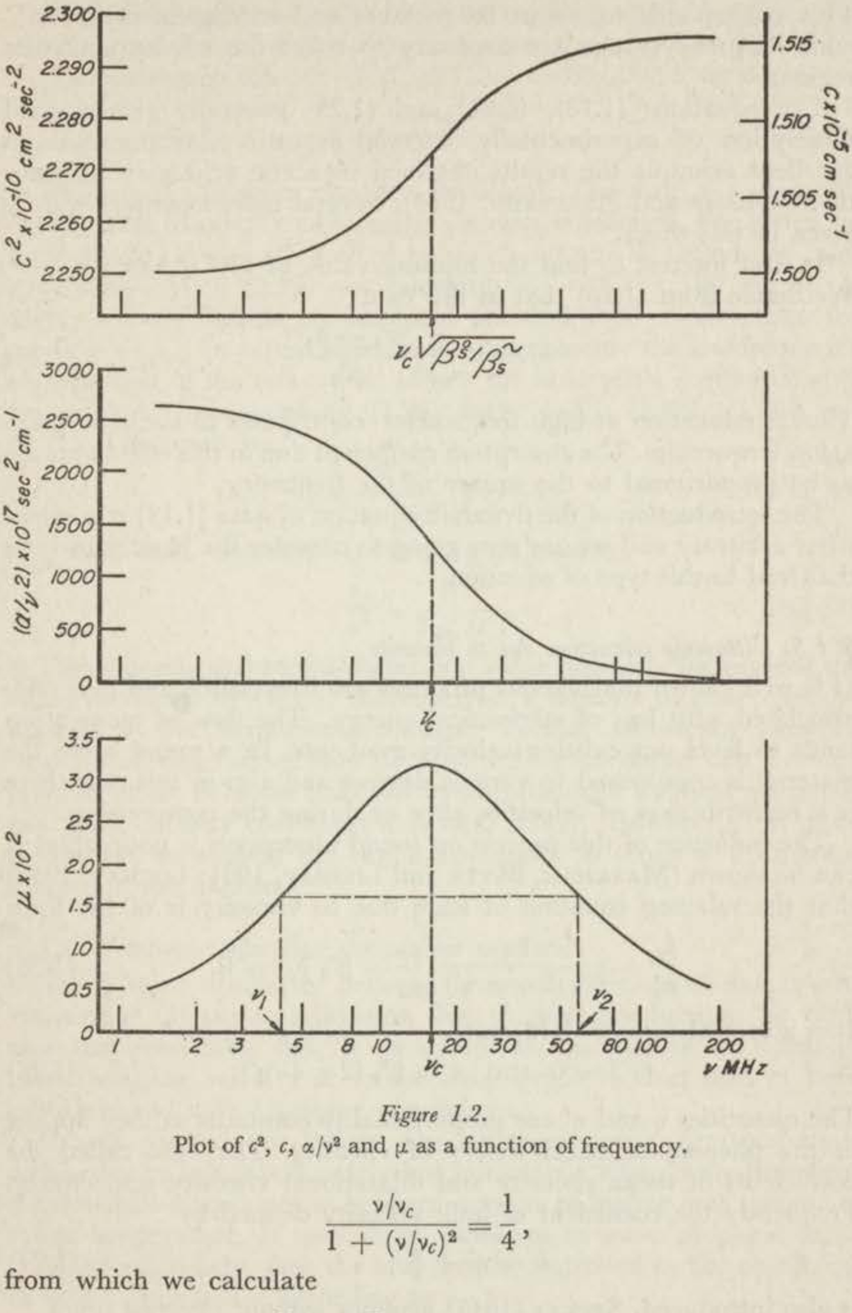


Figure 1.2.

Plot of c^2, c, α/ν^2 and μ as a function of frequency.

$$\frac{\nu/\nu_c}{1+(\nu/\nu_c)^2} = \frac{1}{4},$$

from which we calculate

$$\nu_1/\nu_2 = \frac{2+\sqrt{3}}{2-\sqrt{3}} = 14 \text{ approximately.}$$

This corresponds to about 3.8 octaves and measurements over wide frequency range are necessary to cover the whole relaxation region.

The equations (1.18), (1.21) and (1.23) generally give a good description of experimentally observed acoustic relaxations. As an excellent example the results obtained in acetic acid may be mentioned (Lamb and Pinkerton, 1949). Several more examples will be given in this thesis.

It is of interest to find the limiting value of α/ν^2 if $\nu << \nu_c$.
We derive from (1.18) that in this case

$$\alpha/\nu^2 = \frac{\pi}{\nu_c\, c^\circ} \frac{\beta^\circ_s - \beta_s^\infty}{\beta^\circ_s} \quad \ldots\ldots\ldots \quad (1.24)$$

Thus a relaxation at high frequencies contributes to the absorption at low frequencies. The absorption coefficient due to this effect appears to be proportional to the square of the frequency.

The introduction of the dynamic equation of state (1.13) was somewhat arbitrary and we are now going to consider the basic principles that lead to this type of equation.

§ 1.3. *Ultrasonic relaxation due to viscosity*

It is well known that viscous processes are irreversible and generally associated with loss of mechanical energy. The flow of momentum tends to level out existing velocity gradients. In a sound wave the material is compressed to various degrees and also in this case there is a redistribution of velocities after or during the compression.

The influence of this process on sound absorption is noticeable. It can be shown (Markham, Beyer and Lindsay, 1951; Lindsay, 1951) that the relaxing equation of state due to viscosity is of the form

$$\frac{\dot{\rho}_e}{\rho_0} + \frac{1}{\beta^\circ_s\,(2\eta + \eta')}\left(\frac{\rho_e}{\rho_0} - \beta^\circ_s\, p_e\right) = 0. \quad \ldots\ldots \quad (1.25)$$

It is a special case of (1.13) with

$$\beta_s^\infty = 0 \text{ and } \tau = \beta^\circ_s\,(2\,\eta + \eta'). \quad \ldots\ldots \quad (1.26)$$

The quantities η and η' are proportionality constants as they appear in the phenomenological theory of viscosity. They are called the coefficients of shear viscosity and dilatational viscosity respectively. Frequently the coefficient of bulk viscosity defined by

$$k = \eta' + \tfrac{2}{3}\,\eta \quad \ldots\ldots\ldots\ldots \quad (1.27)$$

is also introduced. Stokes (1845) assumes without rigorous proof

$$k = \eta' + \tfrac{2}{3}\,\eta = 0. \quad \ldots\ldots\ldots \quad (1.28)$$

This relation has been a point of discussion for many years; a general proof cannot be given at the present state of knowledge.

Combination of (1.19), (1.20), (1.26) and (1.28) gives for ν_c

$$\nu_c = \frac{3}{8\pi} \frac{\rho_0 (c^\circ)^2}{\eta}, \quad \ldots \ldots \ldots \quad (1.29)$$

in which η is the shear viscosity coefficient. The ratio η/ρ_0 is sometimes called MAXWELL's kinematic viscosity coefficient. For water we have at 25° C: $\eta = 40 \times 10^{-3}$ poise, $c^\circ = 1.497 \times 10^5$ cm/sec and $\rho_0 = 0.997$. With (1.29) we calculate: $\nu_c = 6.7 \times 10^{10}$ sec^{-1}. If highly viscous liquids are excepted we find that usually (also for gases) $\nu << \nu_c$. In actual practice we only measure the low-frequency contribution of the relaxation. Hence the absorption coefficient may be obtained by combining (1.24) with (1.19), (1.20), (1.26) and (1.27). The result is

$$\frac{\alpha_\nu}{\nu^2} = \frac{2\pi^2}{\rho_0 (c^\circ)^3} \left(\tfrac{4}{3}\eta + k\right). \quad \ldots \ldots \ldots \quad (1.30)$$

Or, if the bulk viscosity k is taken equal to zero

$$\frac{\alpha_\nu}{\nu^2} = \frac{8\pi^2}{3\rho_0 (c^\circ)^3} \eta \quad \ldots \ldots \ldots \quad (1.31)$$

The experimental sound-absorption value normally far exceeds the value predicted by (1.31). Moreover, in a number of materials α/ν^2 appears to be frequency-dependent. Formal agreement between theory and experiment may be obtained by assuming that STOKES' relation (1.28) does not hold and by introducing a frequency-dependent bulk viscosity coefficient k (TISZA, 1942). However, it is more satisfactory to explain the excess absorption in terms of a different relaxation mechanism.

§ 1.4. Ultrasonic relaxation due to heat conduction

There is much similarity between ultrasonic relaxation due to viscosity and ultrasonic relaxation due to heat conduction. In both cases an irreversible flow is set up in the material which tends to cancel existing velocity or temperature gradients and thus in both cases we deal with transport phenomena.

It was pointed out before that ultrasonic wave propagation is adiabatic. In fact this is nearly but not exactly true. Some heat conduction will always occur between regions of higher and regions of lower temperature. If we confine ourselves to wave propagation in the x direction only, then the heat flow is controlled by the coefficient of heat conduction $\varkappa$ according to

$$\psi = -\varkappa \frac{\partial T}{\partial x}, \quad \ldots \ldots \ldots \quad (1.32)$$

where ψ is the heat flow per unit area and per second. This equation introduces a time dependence into the system and consequently a dynamic equation of state is to be expected.

The resultant equation of state is somewhat more complicated than that given by (1.13), the former being dependent on x as well (Markham, Beyer and Lindsay, 1951; Lindsay 1951). Suffice it to say that, similar to the viscosity case, for all practical cases we measure the low-frequency contribution of the relaxation. The sound-absorption coefficient is given by (Kirchhoff, 1868)

$$\frac{\alpha_c}{\nu^2} = \frac{2\,\pi^2}{\rho_o\,(c^\circ)^3}\,(\gamma - 1)\,\frac{M\,\varkappa}{C_p}, \quad \ldots\ldots\ldots \quad (1.33)$$

in which M is the molecular weight, C_p is the molar heat capacity at constant pressure, $\gamma = C_p/C_v$, $\varkappa$ is the heat conduction coefficient, ρ_o is the density and c° is the sound velocity.

The explanation of ultrasonic relaxation in terms of both viscosity and heat conduction is based on a phenomenological rather than a molecular mechanism. If the problem is to be treated in more detail, molecular theories of transport phenomena must be applied.

§ *1.5. Thermal relaxation.*

The theory of acoustic dispersion and absorption due to thermal relaxation was developed by several authors (Einstein, 1920; Herzfeld and Rice, 1928; Kneser, 1931). It occurs whenever a *temperature-dependent* equilibrium system is perturbed by a sound wave. Generally the position of the equilibrium will not change instantaneously when outside conditions are altered; for example, in the case of a chemical equilibrium the rate of adjustment is determined by the rate constants of the reaction. Consequently there will be a time lag between the temperature variations in the sound field and the degree of adjustment of the equilibrium. In other words the temperature variations and the degree of adjustment are not in phase.

Thermal relaxation is of considerable importance for the theory of acoustic dispersion and absorption. Many relaxations described in this thesis will be explained on this basis alone. The necessary theory will now be given, mainly for reference purposes.

We consider systems in which the molecules can exist in two different states (two-state model), for example the ground state and first excited state of a normal vibration or a chemical equilibrium between isomers. These states may be indicated by A and B.

$$A \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} B\,. \quad \ldots\ldots\ldots\ldots \quad (1.34)$$

If the influence of activity coefficients is ignored, as is reasonable for the systems considered in chapter III, then we have for equilibrium (indicated by °)

$$K = \frac{{n^\circ}_B}{{n^\circ}_A} = \frac{{k^\circ}_{12}}{{k^\circ}_{21}} = e^{-({G^\circ}_B - {G^\circ}_A)/RT} = e^{-\Delta G^\circ/RT}, \tag{1.35}$$

where ${n^\circ}_B$ and ${n^\circ}_A$ are the numbers of B and A molecules respectively, $k_{12}{}^\circ$ and ${k^\circ}_{21}$ are rate constants and ΔG° is the Gibbs free energy difference between the appropriate standard states.

The total amount of material be equal to one gram molecule

$$n_A + n_B = \mathcal{N}_A\,. \tag{1.36}$$

From (1.35) and (1.36)

$${n^\circ}_A = \frac{\mathcal{N}_A}{1 + e^{-\Delta G^\circ/RT}}\,. \tag{1.37}$$

It is now assumed that the position of the equilibrium $A \rightleftarrows B$ is only dependent on temperature and not on pressure. For small deviations from equilibrium we have

$$\begin{aligned} k_{12} &= {k^\circ}_{12} + \delta k_{12} = {k^\circ}_{12} + \left(\frac{\partial k_{12}}{\partial T}\right)^\circ \delta T \\ k_{21} &= {k^\circ}_{21} + \delta k_{21} = {k^\circ}_{21} + \left(\frac{\partial k_{21}}{\partial T}\right)^\circ \delta T\,. \end{aligned} \tag{1.38}$$

The rate of adjustment of the number of molecules n_A and n_B will be controlled by the time-dependent rate equation (*first-order reaction*)

$$\frac{d\,n_A}{d\,t} = k_{21}\,n_B - k_{12}\,n_A\,. \tag{1.39}$$

With (1.35), (1.36) and (1.38) this can be written, for small deviations from equilibrium,

$$\begin{aligned} \frac{d\,n_A}{d\,t} &= {n^\circ}_B\,{k^\circ}_{21} - {n^\circ}_A\,{k^\circ}_{12} + \delta\,(n_B\,k_{21}) - \delta\,(n_A\,k_{12}) \\ &= -\,\delta\,n_A\,({k^\circ}_{12} + {k^\circ}_{21}) + {n^\circ}_B\,\delta\,k_{21} - {n^\circ}_A\,\delta\,k_{12} \\ &= -\,\frac{\delta\,n_A}{\tau'} + \left[{n^\circ}_B\left(\frac{\partial k_{21}}{\partial T}\right)^\circ - {n^\circ}_A\left(\frac{\partial k_{12}}{\partial T}\right)^\circ\right]\delta\,T\,, \end{aligned}$$

in which

$$\tau' = \frac{1}{{k^\circ}_{12} + {k^\circ}_{21}}\,. \tag{1.40}$$

It follows from (1.35), (1.36) and (1.40) that this may be written as

$$\frac{d\,n_A}{d\,t} = -\frac{\delta\,n_A}{\tau'} + \frac{1}{\tau'}\left(\frac{\partial\,n_A}{\partial\,T}\right)^\circ.$$

By differentiating with respect to t we obtain

$$\tau' \frac{d^2 n_A}{d t^2} + \frac{d n_A}{d t} - \left(\frac{\partial n_A}{\partial T}\right)^\circ \frac{d T}{d t} = 0 \quad . \; . \; . \; . \; (1.41)$$

Equation (1.41) is now simplified in the same way as (1.13) was simplified to (1.15). If only harmonic perturbations are considered there results, in complex notation,

$$\frac{\partial n_A}{\partial \hat{T}} = \frac{\hat{n}_A}{\hat{T}} = \frac{\left(\frac{\partial n_A}{\partial T}\right)^\circ}{1 + 2\pi\nu i \tau'} . \quad . \; . \; . \; . \; . \; . \; (1.42)$$

It appears that n_A and T are generally not in phase.

The value of $(\partial n_A/\partial T)^\circ$ can be derived from (1.37). For convenience we introduce the internal molar heat defined by

$$C_i = -\frac{\Delta H}{N_A}\left(\frac{\partial n_A}{\partial T}\right), \quad . \; . \; . \; . \; . \; . \; . \; . \; (1.43)$$

with $\Delta H =$ the heat of reaction per gram molecule.

Using (1.37) and the Gibbs-Helmholtz relation

$$\frac{\partial \Delta G^\circ/_T}{\partial T} = -\frac{\Delta H^\circ}{T^2}$$

we derive from (1.43), in the case of equilibrium

$$C_i^\circ = \frac{\Delta H \, \Delta H^\circ}{R T^2} \frac{e^{-\Delta G^\circ/RT}}{(1 + e^{-\Delta G^\circ/RT})^2} . \quad . \; . \; . \; . \; . \; (1.44)$$

If equilibrium is not attained and a phase difference exists between n_A and T then from (1.42) and (1.43)

$$\hat{C}_i = \frac{C_i^\circ}{1 + 2\pi\nu i \tau'} . \quad . \; . \; . \; . \; . \; . \; . \; (1.45)$$

For the total molar heat we find

$$\hat{C}_v = C_v^\infty + \frac{C_i^\circ}{1 + 2\pi\nu i \tau'} \text{ and } \hat{C}_p = C_p^\infty + \frac{C_i^\circ}{1 + 2\pi\nu i \tau'}, \quad (1.46)$$

where C_v^∞ and C_p^∞ denote the molar heat capacities without the reaction contribution.

A frequency-dependent heat capacity will lead to a frequency-dependent adiabatic compressibility. The relation between the isothermal and adiabatic compressibility coefficient is

$$\beta_T = \frac{C_p}{C_v} \beta_s . \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; (1.47)$$

Obviously in the case of thermal relaxation β_T is independent of frequency and real. Therefore

$$\beta_T = \frac{\hat{C}_p}{\hat{C}_v}\,\hat{\beta}_s = \frac{C_p^{\infty}}{C_v^{\infty}}\,\beta_s^{\infty} = \frac{C_p^{\circ}}{C_v^{\circ}}\,\beta^{\circ}_s\,, \quad . \; . \; . \; . \quad (1.48)$$

where C^{∞} and C° indicate molar heats without and with the (total) reaction contribution. Combination of (1.46) and (1.48) gives after an elaborate calculation

$$\hat{\beta}_s = \beta_s^{\infty} + \frac{\beta^{\circ}_s - \beta_s^{\infty}}{1 + 2\,\pi\,\nu\,i\,\tau} \text{ in which } \tau = \frac{C_p^{\infty}}{C_p^{\circ}}\,\tau' . \quad . \quad (1.49)$$

We also have

$$\frac{\beta^{\circ}_s - \beta_s^{\infty}}{\beta_s^{\infty}} = \frac{C_p^{\circ} - C_v^{\circ}}{C_v^{\infty}\,C_p^{\circ}}\,C_i^{\circ} \text{ and } \frac{\beta_s^{\circ} - \beta_s^{\infty}}{\beta_s^{\circ}} = \frac{C_p^{\circ} - C_v^{\circ}}{C_p^{\infty}\,C_v^{\circ}}\,C_i^{\circ} \; . \; . \quad (1.50)$$

Equation (1.49) is equivalent to (1.15) and thus thermal relaxation leads to the same dispersion and absorption formulae as does (1.15).

We conclude from (1.50) that the absorption formulae (1.18) and (1.23) may be written in this case as

$$\frac{\alpha_t}{\nu^2} = \frac{\pi}{\nu_c}\,\frac{c}{(c^{\circ})^2}\,\frac{1}{1 + (\nu/\nu_c)^2}\,\frac{\gamma - 1}{C_p^{\infty}}\,C_i^{\circ} \quad . \; . \; . \; . \quad (1.51)$$

and

$$\mu_t = \pi \left(\frac{c}{c^{\circ}}\right)^2 \frac{\nu/\nu_c}{1 + (\nu/\nu_c)^2}\,\frac{\gamma - 1}{C_p^{\infty}}\,C_i^{\circ}, \quad . \; . \; . \quad (1.52)$$

in which $\gamma = C_p^{\circ}/C_v^{\circ}$. For the low-frequency contribution of a thermal relaxation at high frequencies we obtain with (1.24)

$$\frac{\alpha_t}{\nu^2} = \frac{\pi}{\nu_c\,c^{\circ}}\,\frac{\gamma - 1}{C_p^{\infty}}\,C_i^{\circ}. \quad . \; . \; . \; . \; . \; . \quad (1.53)$$

The equations (1.51), (1.52) and (1.53) will be employed in later sections. Another useful relation is obtained if (1.20), (1.49) and (1.40) are combined

$$\nu_c = \frac{1}{2\,\pi\,\tau} = \frac{C_p^{\circ}/C_p^{\infty}}{2\,\pi\,\tau'} = \frac{C_p^{\circ}}{C_p^{\infty}}\,\frac{k^{\circ}_{12} + k^{\circ}_{21}}{2\,\pi} \quad . \; . \; . \quad (1.54)$$

It is a direct relation between the relaxation frequency ν_c and the rate constants k_{12}° and k_{21}° of the reaction $A \rightleftarrows B$. For many reactions the ratio C_p°/C_p^{∞} may be taken equal to unity to a good approximation.

§ *1.6. Structural relaxation.* (Herzfeld, 1952; Hall, 1948).

Although the sound absorption in many fluids can be explained in terms of thermal relaxation, this in not possible in the case of liquid water where $\gamma = C_p/C_v \approx 1$. Here it is supposed that the liquid can exist in two molecular states of packing, an ice-like structure and a more random structure of smaller volume. Thus we deal essentially with an intermolecular process. The theory can be developed along the same lines as in the case of thermal relaxation, the only difference being that instead of a temperature-dependent equilibrium we assume a *pressure-dependent* equilibrium. The resultant formula for the compressibility is of the form

$$\hat{\beta} = \beta^{\infty} + \frac{\beta^{\circ} - \beta^{\infty}}{1 + 2\,\pi\,\nu\,i\,\tau''}, \quad \ldots\ldots \quad (1.55)$$

with:

$$\beta^{\circ} - \beta^{\infty} = \frac{V}{R\,T}\left(\frac{\Delta\,V}{V}\right)^2 \frac{e^{-\Delta\,G^{\circ}/RT}}{(1 + e^{-\Delta\,G^{\circ}/RT})^2}, \quad \ldots \quad (1.56)$$

in which V is the molal volume of the actual material and ΔV denotes the difference in molal volume between the two states of packing. We notice that again this equation is identical with (1.15). The relaxation time τ'' turns out to be of the order of 10^{-12} sec and for all practical cases is $\nu << \nu_c$ $(= 1/2\,\pi\,\tau'')$. We deal with a relaxation at very high frequencies and it is permissible to use absorption formula (1.24). With (1.19) there results

$$\frac{\alpha_s}{\nu^2} = \frac{\pi\,\rho_0\,c^{\circ}}{\nu_c}\,\frac{V}{R\,T}\left(\frac{\Delta\,V}{V}\right)^2 \frac{e^{-\Delta\,G^{\circ}/RT}}{(1 + e^{-\Delta\,G^{\circ}/RT})^2}. \quad \ldots \quad (1.57)$$

This expression should be compared with the combination of (1.53) and (1.44).

§ *1.7. Other types of relaxation*

There are a variety of other mechanisms that lead to sound absorption. An example is the attenuation due to scattering of sound energy which may occur in inhomogeneous media. There may also be losses due to heat radiation in which case thermal energy is transported not by heat conduction but by heat radiation. If foreign particles are suspended in a medium, friction losses become important because, in general, the particles and the medium move with different velocity. All these additional effects do not contribute significantly to the sound absorption in the systems which we are going to consider and their existence will henceforth be ignored.

§ 1.8. Ultrasonic relaxation in liquids

We are now going to discuss the actually observed acoustic behaviour of matter in terms of the mechanisms just mentioned. Only measurements in *liquids* (and not in gases) will be described in this thesis and therefore we focus our attention on this particular type of fluid. A new type of chemical equilibrium which leads to sound absorption in liquids will appear in the course of the discussion.

From the example given in *§* 1.2 it can be inferred, that although the absorption of sound in a liquid may be considerable, the dispersion is usually less than 1 % and almost negligible. This explains why dispersion measurements are not suitable for investigating acoustic relaxations in liquids.

It may be mentioned that, for liquids, sound absorption values of reasonable accuracy can be obtained within the frequency range 1-250 MHz. An extension to either lower frequencies or higher frequencies is very difficult at the present state of experimental techniques. Further details will be given in chapter II.

We define as the so-called "classical absorption" the sum of the contributions due to viscosity and heat conduction, as given by the equations (1.31) and (1.33)

$$\frac{\alpha_{class}}{\nu^2} = \frac{\alpha_\nu}{\nu^2} + \frac{\alpha_c}{\nu^2} = \frac{2\,\pi^2}{\rho_0\,(c^\circ)^3}\left[\tfrac{4}{3}\,\eta + (\gamma - 1)\,\frac{M\,\varkappa}{C_p}\right] . \;\; . \quad (1.58)$$

Usually, for a liquid, $\alpha_\nu >> \alpha_c$ though mercury is an exception. Equation (1.58) gives a good description of the absorption in monoatomic, simple diatomic and a number of more viscous liquids. Some examples are given in table 1.1.

Table 1. 1.

Sound absorption values of some monoatomic, diatomic and viscous liquids (taken from Markham, Beyer and Lindsay, 1951). The experimental and classical values are compared.

Liquid	Temperature (° K)	Frequency (MHz)	$(\alpha/\nu^2)_{exp}$ (sec^2/cm)	$\frac{(\alpha/\nu^2)_{exp}}{(\alpha/\nu^2)_{class}}$
Helium	4	15	231×10^{-17}	1.12
Argon	85	44.4	10.1×10^{-17}	0.97
Mercury	298	20-1000	6×10^{-17}	1.2
Hydrogen	17	44.4	5.6×10^{-17}	0.97
Olive oil	298	1-4	1250×10^{-17}	1.14
Linseed oil	294	3.16	1470×10^{-17}	1.01

In highly viscous materials like olive oil and linseed oil the viscous contribution is high enough to obscure the influence of other possible mechanisms.

Table 1.2 shows the absorption values of water and some alcohols.

Table 1.2.

Sound absorption values of water and some alcohols (taken from Markham, Beyer and Lindsay, 1951). The experimental and classical values are compared.

Liquid	Temperature ° C	Frequency (MHz)	$(\alpha/\nu^2)_{exp}$ (sec^2/cm)	$\frac{(\alpha/\nu^2)_{exp}}{(\alpha/\nu^2)_{class}}$
Water	25	7-250	21.4×10^{-17}	2.5
Methyl alcohol	20-25	1-250	34×10^{-17}	2.35
Ethyl alcohol	20-25	1-220	54×10^{-17}	2.45
Propyl alcohol	22-28	15-280	75×10^{-17}	2.08
Butyl alcohol	25	1-4	104×10^{-17}	2.02

Again we notice that α is proportional to ν^2 up to the highest frequency that can be reached with conventional experimental techniques. However the experimentally found value exceeds the classical contribution by a factor of 2-3. The liquids mentioned in this table are all associated, that is, the molecules are tied together by strong intermolecular bonds (hydrogen bonds). Hall (1948) has shown conclusively that in the case of water the excess absorption is due to changes in intermolecular structure (as given by 1.57). Unfortunately there are indications (Sette, 1950) that this mechanism fails to explain the total excess absorption in (higher) alcohols.

There are also a large number of non-associated organic liquids in which α/ν^2 is independent of frequency but far greater than the classical value. It can hardly be assumed in these cases that structural relaxation is the cause of the excess absorption. Some examples are listed in table 1.3.

Before we return to this class of liquids we first discuss the behaviour of three compounds in which a frequency dependence of α/ν^2 has been observed. The absorption α/ν^2 of liquid carbon disulphide as a function of frequency is given in figure 1.3.

Table 1.3.

Sound absorption values of non-associated, organic liquids (Data are taken from Markham, Beyer and Lindsay, 1951; Heasell and Lamb, 1956).

Liquid	Temperature ° C	Frequency (MHz)	$(\alpha/\nu^2)_{\text{exp}}$ (sec²/cm)	$\frac{(\alpha/\nu^2)_{\text{exp}}}{(\alpha/\nu^2)_{\text{class}}}$
n-Hexane	21	15	77×10^{-17}	7.7
n-Heptane	22	15	80×10^{-17}	8
Nitrobenzene	25	1-200	74×10^{-17}	5.3
Methyl bromide	2	15	304×10^{-17}	—
Chloroform	25	1-200	364×10^{-17}	36
Carbon tetrachloride	25	1-200	550×10^{-17}	28
Chlorobenzene	25	1-200	146×10^{-17}	18

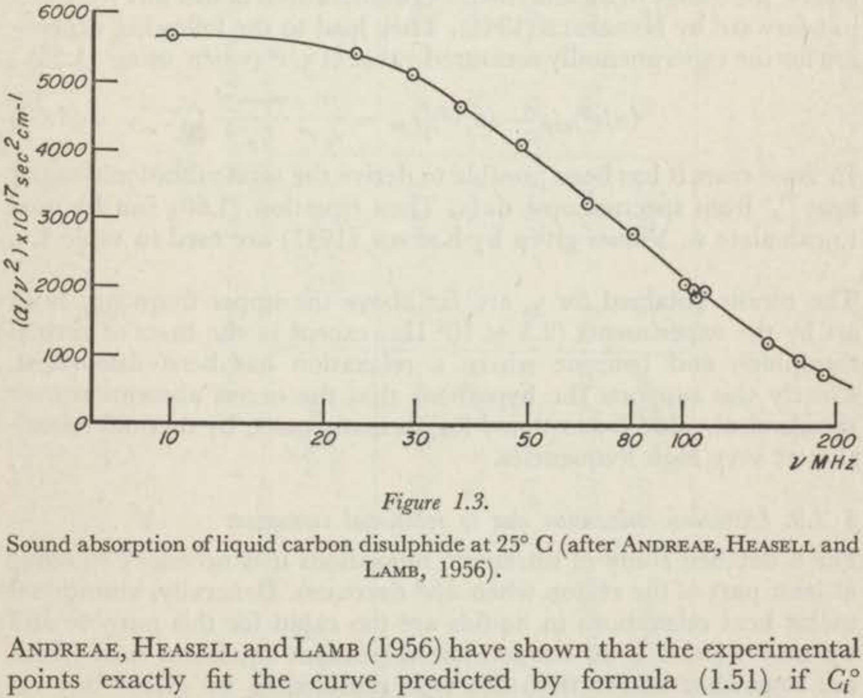


Figure 1.3.

Sound absorption of liquid carbon disulphide at 25° C (after Andreae, Heasell and Lamb, 1956).

Andreae, Heasell and Lamb (1956) have shown that the experimental points exactly fit the curve predicted by formula (1.51) if C_i° is taken equal to the total vibrational molar heat. Apparently it is the finite speed at which thermal energy is transferred from translational to vibrational degrees of freedom which is responsible for this thermal relaxation. The relaxation frequency $\nu_c = 78$ MHz (at 25° C) is high although it lies within the frequency range which is accessible to measurement. For the sum of the rate constants of the equilibrium

$$\underset{\text{energy}}{\text{C S}_2\text{ without vibrational}} \;\underset{k^\circ_{21}}{\overset{k^\circ_{12}}{\rightleftarrows}}\; \underset{\text{energy}}{\text{C S}_2\text{ with vibrational}} . \; . \; . \; (1.59)$$

we calculate with (1.54)

$$k^\circ_{12} + k^\circ_{21} = 2\,\pi\,\frac{C_p^\infty}{C_p^\circ}\,\nu_c \approx 2\,\pi\,\nu_c = 5 \times 10^8 \text{ sec}^{-1},$$

a very fast reaction indeed. It is of interest that the beginning of similar relaxations with even higher ν_c values has been observed in two other compounds namely methylene chloride and benzene (ANDREAE, 1957; HEASELL and LAMB, 1956).

The occurrence of thermal relaxations at high frequencies suggests that the non-explained absorption in the compounds mentioned previously (table 1.3) might very well originate from similar relaxations above the range of measurement. Considerations of this sort were first put forward by HERZFELD (1941). They lead to the following expression for the experimentally measured value of α/ν^2 (when using (1.53))

$$(\alpha/\nu^2)_{exp} - (\alpha/\nu^2)_{class} = \frac{\pi}{\nu_c\, c^\circ}\,\frac{\gamma - 1}{C_p^\infty}\,C_i^\circ . \; . \; . \; (1.60)$$

In some cases it has been possible to derive the total vibrational molar heat C_i° from spectroscopic data. Then equation (1.60) can be used to calculate ν_c. Values given by KNESER (1947) are used in table 1.4.

The results obtained for ν_c are far above the upper frequency limit set by the experiments (2.5×10^8 Hz) except in the cases of carbon disulphide and benzene where a relaxation has been discovered. Clearly this supports the hypothesis that the excess absorption over the classical value is accounted for, in many cases, by thermal relaxation at very high frequencies.

§ 1.9. Ultrasonic relaxation due to rotational isomerism

For a detailed study of ultrasonic relaxations it is necessary to cover at least part of the region when α/ν^2 decreases. Generally, vibrational molar heat relaxations in liquids are too rapid for this purpose and we may wonder if no temperature-dependent equilibria exist which are somewhat slower than the type represented by (1.59) but yet fast enough to be detected by means of ultrasound. Such reversible reactions have been found in a number of cyclohexane derivatives (KARPOVICH, 1954; LAMB and SHERWOOD, 1955).

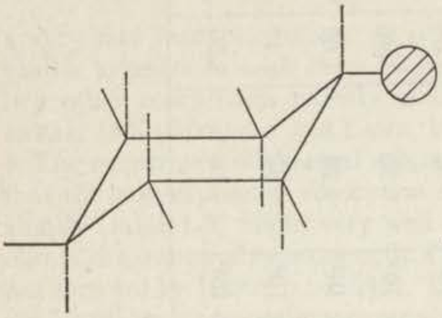
Table 1.4.

Calculation of ν_c for a number of non-associated organic liquids.

Liquid	$(\alpha/\nu^2)_{\mathrm{exp}}$ (sec²/cm)	$(\alpha/\nu^2)_{\mathrm{class}}$ (sec²/cm)	c° (cm/sec)	C_p° (cal/mole degree)	γ	C_i° (cal/mole degree)	ν_c (Hz)
Benzene	850×10^{-17}	8.7×10^{-17}	1.30×10^5	32	1.44	10.6	6.4×10^8
Acetone	27×10^{-17}	7.0×10^{-17}	1.16×10^5	30	1.46	9.7	3.0×10^{10}
Chloroform	364×10^{-17}	10×10^{-17}	0.999×10^5	24	1.60	8.0	2.7×10^9
Carbon tetrachloride	550×10^{-17}	20×10^{-17}	0.923×10^5	31	1.44	12.6	2.0×10^9
Carbon disulphide	6000×10^{-17}	5.0×10^{-17}	1.14×10^5	18	1.56	3.9	0.72×10^8

Normally the carbon atoms of the cyclohexane ring do not lie in a plane but instead two different strain-free configurations, the rigid chair form and the flexible bed form, are preferred. It is known from various experiments that, under ordinary conditions, the majority of cyclohexane molecules are present in the chair form and this also applies to most derivatives (Hazebroek and Oosterhoff, 1951).

An interesting situation arises in the case of mono-substituted compounds like methyl cyclohexane where two *different* chair configurations can be constructed, as illustrated below.



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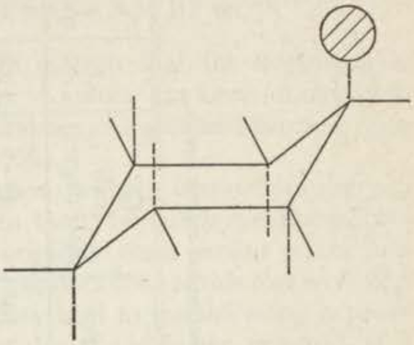


"POLAR"

In reality an equilibrium mixture of both forms exists and it has been shown (Karpovich, 1954) that this equilibrium is responsible for the ultrasonic relaxation observed in methyl cyclohexane near 0.14 MHz (16° C). The corresponding equilibrium in 1,1-dimethyl cyclohexane is not possible as here the polar and equatorial configurations are identical. It follows immediately from (1.44) that C_i° is equal to zero in that case and in fact Karpovich (*l.c.*) found no relaxation in this compound.

The interconversion of the different chair forms involves rotation of all CH_2 groups (in cyclohexane) about the carbon-carbon single bonds. This can only be accomplished if the molecule is put under considerable strain. Clearly this will reduce the magnitude of the rate constants k°_{12} and k°_{21} and it explains why the relaxation frequency in methyl cyclohexane is so low (compare CS_2 where $\nu_c = 78$ MHz).

Sound-absorption measurements in esters were published as early as 1936 (Biquard, 1936) and the results obtained by several authors have revealed a number of acoustic relaxations. For example the relaxation frequency ν_c of methyl acetate is 6.8 MHz at 20° C (Karpovich, 1954) whereas in ethyl acetate it is 11.8 MHz (Pinkerton, 1951). A plot of α/ν^2 versus frequency for both liquids is given in figure 1.4.

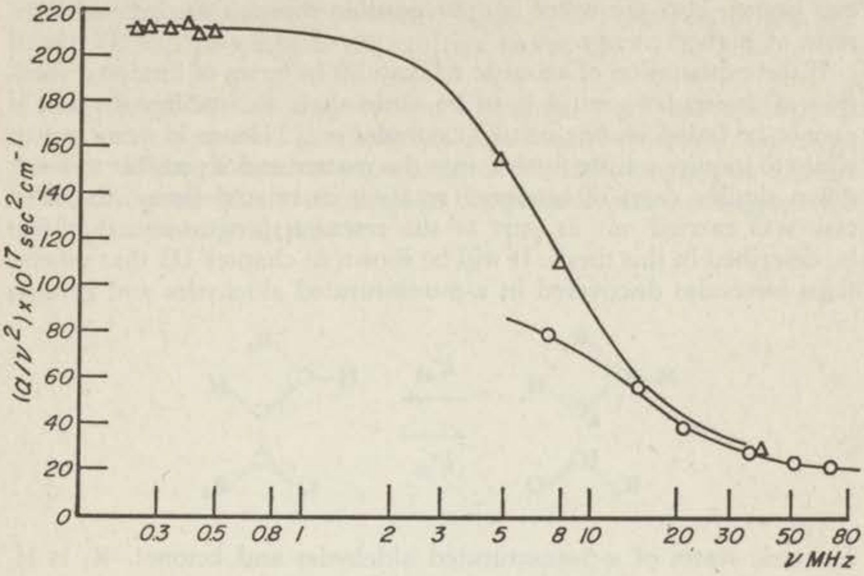
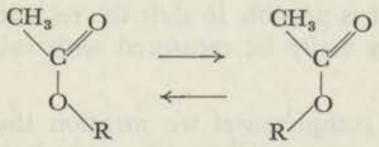


Figure 1.4.

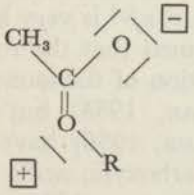
Sound absorption of liquid methyl acetate (Δ) and ethyl acetate (o) at 20° C. (After KARPOVICH, 1954 and PINKERTON, 1951).

It has been suggested (KARPOVICH, 1954) that the anomalous acoustic behaviour of this class of liquids is brought about by perturbation of the following equilibrium between *rotational isomers*

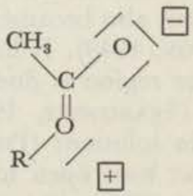


. . . . . (1.61)

It is not immediately clear why this sort of isomerism should exist. However, resonance involving structures like

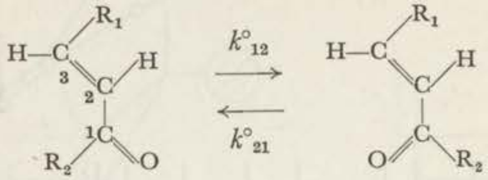


and



will stabilize planar configurations (PAULING, 1948). Apparently rotation about the C-O single bond is not at all free and conversion of one isomer into the other is only possible through an intermediate state of higher energy.

If the explanation of acoustic relaxations in terms of hindered rotation of molecular groups is to be more than an intelligent guess it cannot be based on one or two examples only. Hence it seems worth while to inquire a little further into the matter and if possible to track down similar cases of hindered rotation in related molecules. This task was carried out as part of the research programme that will be described in this thesis. It will be shown in chapter III that relaxations were also discovered in α-β-unsaturated aldehydes and ketones



Isomeric states of α-β-unsaturated aldehydes and ketones. R_1 is H, alkyl or aryl; R_2 is H or alkyl.

Here the freedom of rotation about the C1-C2 single bond is restricted, owing to resonance between the conjugated double bonds. The resonance energy is strongly influenced by R_1 whereas R_2 mainly determines the degree of steric hindrance. Hence by choosing suitable substituent groups the rate constants k°_{12} and k°_{21}, and therefore the relaxation frequency, can be varied between wide limits (see formula 1.54). In this way it is possible to shift the relaxation frequency to a region where it can easily be measured with existing experimental techniques.

For the sake of completeness we mention the carboxylic acids. These liquids are known to show relaxation but up to now it has not been possible to interprete the observed frequency dependence of α/ν^2. In particular acetic acid is of interest as it not only is the liquid in which a relaxation was discovered for the first time (Bazulin, 1936, 1939) but also because the decrease of α/ν^2 is very large (Lamb and Pinkerton, 1949). It has been presumed that the relaxation in the megahertz region is due to perturbation of the monomer-dimer equilibrium (Spakowski, 1938; Freedman, 1953) but recent investigations in solutions (Piercy and Lamb, 1956) have made this explanation at least open to question. Carboxylic acids like formic acid (Bazulin, 1938) and propionic acid (Lamb and Huddart, 1950) behave in a similar fashion.

We finally call attention to toluene. A relaxation at low frequencies was found in this compound by Moen (1951) and confirmed by Beyer (1955). Its cause is still entirely unknown.

It was shown in this chapter that ultrasonic work has opened up a very promising field in studies of rotational isomerism. The next chapter will be devoted to experimental methods. In chapter III the results of measurements obtained in compounds with rotating groups will be discussed in detail.

CHAPTER II

EXPERIMENTAL PART

§ 2.1. Introduction

Systematic measurements of sound-absorption coefficients in liquids were carried out for the first time by BIQUARD (1936). After his pioneer work a variety of methods have been developed. An excellent review on the subject is given by BERGMANN (1954).

In this chapter the principles on which these measurements are based will be discussed first. Following this there will be a brief explanation of the measuring technique that was employed for the work described in chapter III. Examples of actual results will be given to illustrate the method.

Attention will be paid to the problem of why accurate absorption measurements in liquids can only be taken within the frequency interval between 1 and 250 MHz approximately.

§ 2.2. General information

The acoustic output of conventional sound sources like loudspeakers, whistles, sirens, etc. generally drops sharply as the frequency is raised above the audible region. Consequently sources of special design (BERGMANN, 1954) have to be constructed for the ultrasonic range. It is not our present task to describe the different types in detail; we only mention piezo-electric sources because they cover frequencies up to about 1000 MHz. This makes them eminently suitable for scientific purposes.

For example, in our case we used discs (transducers) with diameters between 1.5 and 2.5 cm, specially cut from a quartz single crystal, for generating compressional sound waves. Both top and bottom surface were covered with an isolated thin layer of gold. On application of alternating current to the plating a thickness vibration was set up in the material whereby sound was radiated. In order to increase the acoustic output, the system was always operated near its mechanical resonance frequency or an odd harmonic. Discs of 0.057 to 0.014 cm thickness, corresponding to fundamental resonant frequencies between 5 and 20 MHz, were employed. Owing to practical difficulties — the material is too brittle — the latter figure could not be raised much higher.

Interesting results are obtained if the sound-field in front of a uniformly vibrating disc (piston-source) is probed. It turns out that planar waves can only be detected if the source diameter is several times larger than the sound-wavelength and if the source is not approached too closely. The situation may be compared with the optical case of radiation through a small hole, though boundary conditions differ. Diffraction theory predicts that for a circular hole nearly all energy will be emitted within an angle determined by

$$\sin\delta = \frac{0.61\,\lambda}{r}; \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ (2.1)$$

where λ is the wavelength and $2r$ is the source diameter. The angle δ determines in fact the position of the first diffraction minimum. As an example we take $r = 1$ cm, $\lambda_1 = 0.149$ cm and $\lambda_2 = 0.0149$ cm corresponding to the sound wavelength in water at 1 MHz and 10 MHz respectively. We then calculate $\delta_1 = 5^\circ\,13'$ and $\delta_2 = 0^\circ\,31'$. Hence it follows that a parallel or "pencil" beam can only be produced if the ratio λ/r is sufficiently small whereas for larger values of λ/r considerable "beam spreading" may occur. This has important implications for sound absorption measurements at lower frequencies.

We recall equation (1.6) which determines the absorption of a travelling planar sound wave. It may be expressed as

$$R_x = R_0\, e^{-\alpha x}, \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (2.2)$$

where R_x is the density amplitude, α is the absorption coefficient relating to the excess density (or pressure), x is the distance from an arbitrary origin and R_0 is the density amplitude at the origin. Some authors use the sound intensity I_x rather than the density amplitude R_x. For a harmonic wave I_x is proportional to $R^2{}_x$ so that (2.2) may also be written

$$I_x = I_0\, e^{-2\alpha x}. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ (2.3)$$

It is usually found convenient to eliminate R_0 by measuring R_x for two (or more) different values of x. Then from (2.2)

$$\alpha = \frac{1}{x_2 - x_1}\, ln \frac{R_1}{R_2}. \quad . \ . \ . \ . \ . \ . \ . \ (2.4)$$

Hence all that is needed for an absorption measurement are a sound source, a sound receiver and an instrument to vary the distance between them. It is important to note that only the ratio R_1/R_2 and not absolute values enter the relation (2.4).

For most practical measuring-systems a piezo-electric sound source is employed; however, receivers may differ in design according to which experimental arrangement is preferred. Let us consider the case that two identical quartz transducers are used for both the source and the receiver as shown in figure 2.1.

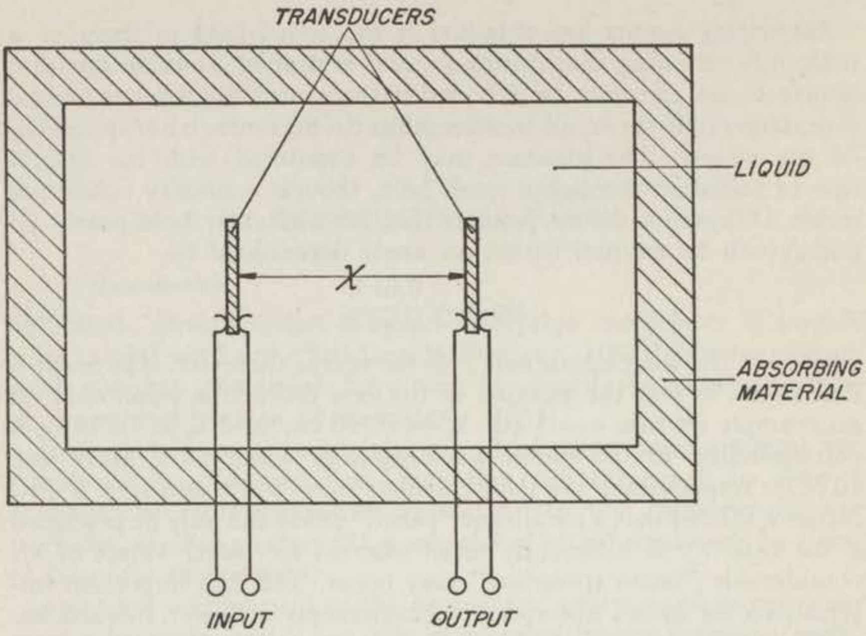


Figure 2.1.

A simple arrangement for sound absorption measurements.

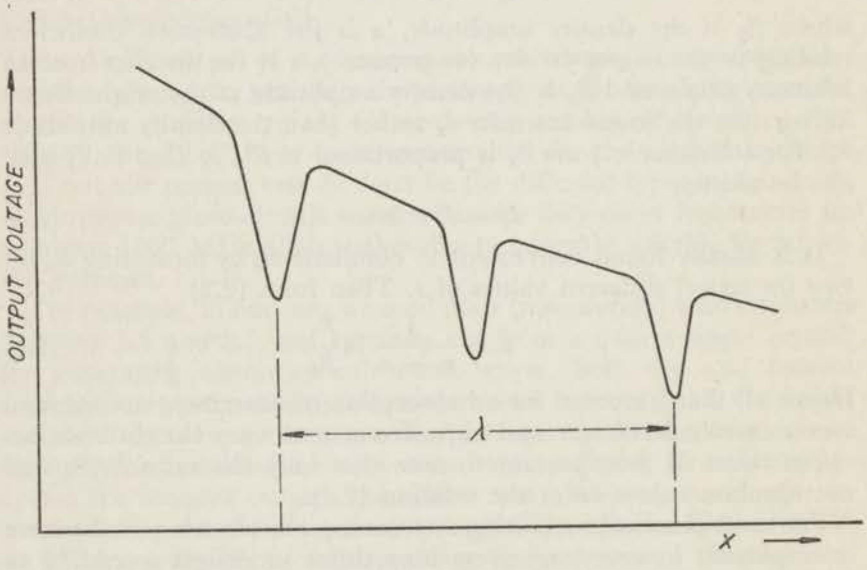


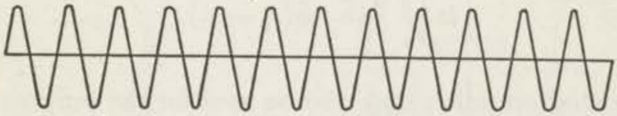
Figure 2.2.

Idealised curve giving the output voltage as a function of distance for continuous-wave excitation.

If alternating current is applied to the source, standing waves may be set up between the two transducers. In addition the absorption of acoustic energy will cause the average output level of the receiver to decrease with increasing x. The situation is characterized by figure 2.2. showing the output voltage as a function of x.

Suffice it to say that this type of curve enables us to calculate the sound-wavelength λ — and from it the sound velocity $c = \lambda\,\nu$ if the frequency ν is known — as well as the absorption coefficient α. It is the well-known interferometer method. However, more accurate absorption values can be obtained if standing waves are avoided altogether. In practice this may be achieved by using intermittent bursts of oscillations ("pulses") rather than a continuous signal (figure 2.3).

Evidently if sound is generated for τ seconds a train of travelling waves will result which is $\tau\,c$ cm long, where c is the sound velocity in cm/sec. Representative values are: $\tau = 10$ μsec, $c = 1.5 \times 10^5$ cm/sec (liquid water at 25° C), $\tau\,c = 1.5$ cm. If we now inquire as to what signal will be received if this system is employed we realise that after every burst of oscillations a sound pulse will be reflected



Continuous wave signal

Bursts of oscillations

Figure 2.3.

back and forth between the transmitting and receiving transducer, thus giving rise to a series of output pulses of diminishing amplitude. Usually the successive pulses received are displayed on the screen of an oscilloscope so that their respective amplitudes can be compared with a calibrated signal (figure 2.4).

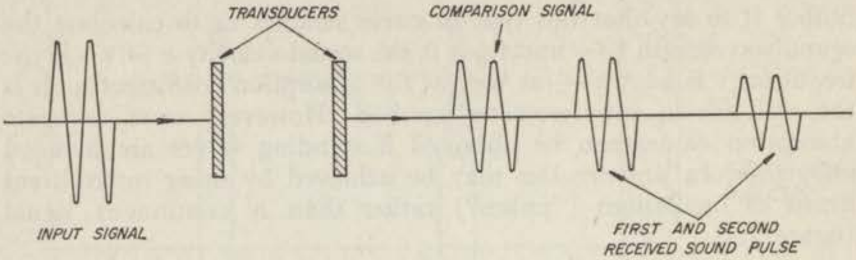


Figure 2.4.

Diagram showing the transmitted and received signal for pulse excitation.

Under the conditions mentioned above the received signal is proportional to the density amplitude of the detected sound pulse. Hence if we measure the output voltage V for the *first received* sound pulse for two (or more) different values of x then the absorption coefficient α can be derived, using (2.4), from

$$ln \frac{V_2}{V_1} = -\alpha\,(x_2 - x_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$

Multiple reflection pulses may also be used for the purpose of calculating α.

The question arises whether a train of travelling waves of finite length may be represented by one single frequency. Fourier analysis predicts that this is only justified provided the (generated) wave packet contains many cycles, the approximate frequency deviation being given by

$$\frac{\Delta\,\nu}{\nu} = \frac{1}{n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.6)$$

where n is the number of cycles per packet. At 10 MHz we calculate for a 10 μsec pulse: $\Delta\,\nu/\nu = 1/100 = 1\,\%$, an accuracy which is ample for our purpose. However at 1 MHz we find for a 10 μsec pulse: $\Delta\,\nu/\nu = 1/10 = 10\,\%$. Apparently longer pulses are required at lower frequencies.

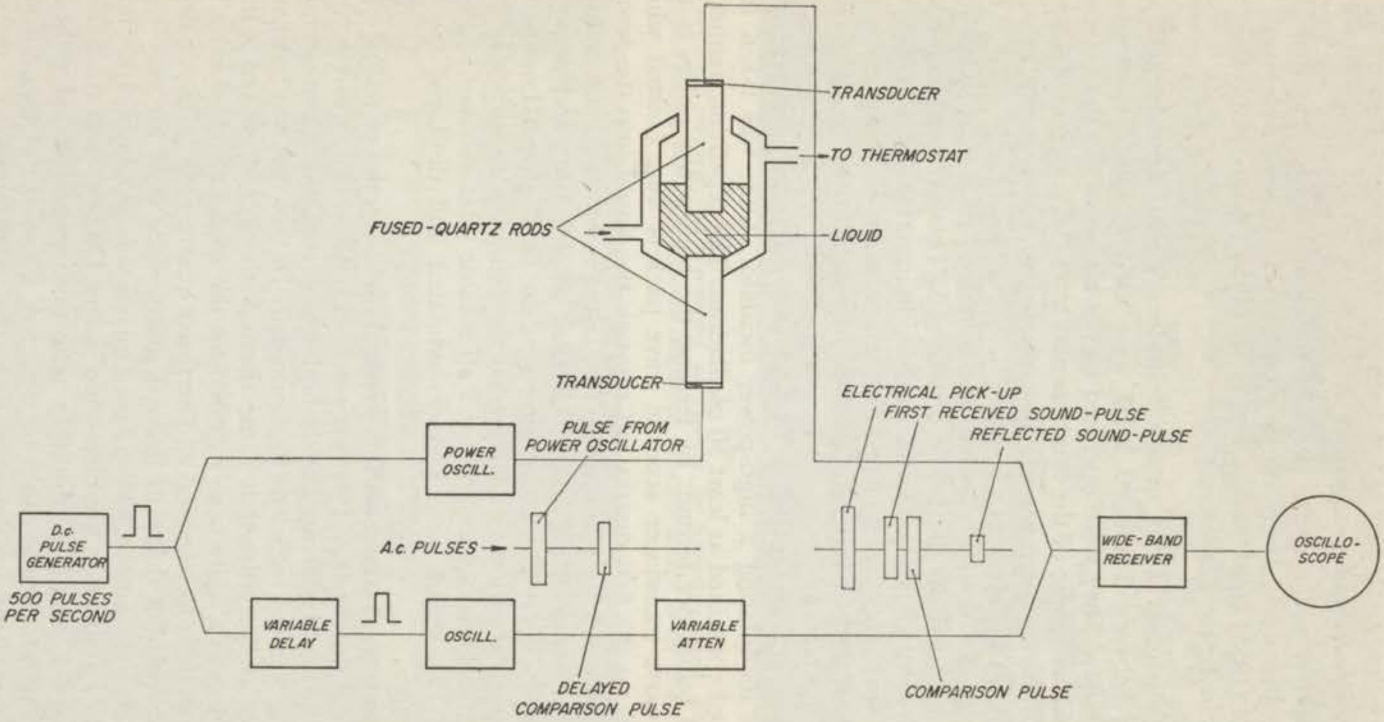


FIG. 2.5. DIAGRAM OF PULSE APPARATUS

§ 2.3. Equipment and measurements

A description will now be given of the actual equipment that was used for the work described in chapter III. It was developed by Andreae (1955) and Heasell and Lamb (1956). A schematic diagram is given in figure 2.5.

Pairs of identical *X*-cut quartz transducers with fundamental frequencies between 5 and 20 MHz were used as sound transmitters and receivers. They were operated in the region of the fundamental or an odd harmonic of the fundamental mode of thickness vibration. The transducers were acoustically coupled to fused quartz rods by means of a thin layer of vacuum oil.

The liquid to be investigated was contained in a glass jacket that accurately fitted on the lower quartz rod. This arrangement effectively prevented contamination of the material as it was only in contact with glass or quartz. The temperature was kept constant by circulating the temperature-controlling liquid through the double wall of the jacket.

Alternating current pulses of 5-25 μsec duration were generated by pulse-modulating a high-power oscillator. Care was taken that each burst contained at least 50 oscillations. The repetition frequency was 500 pulses per second. By feeding the high-power pulses to the lower quartz transducer acoustic wave packets were created which travelled up the first quartz rod through the liquid into the second rod to the receiving transducer. The latter reconverted the acoustic signal into an electrical one which after amplification and demodulation was displayed on the screen of an oscilloscope. Low-power alternating current pulses were used for comparison purposes; they passed through a calibrated piston attenuator (Gainsborough, 1947; Brown, 1949) and were also demodulated and displayed on the oscilloscope.

The picture obtained on the screen showed a series of pulses separated by a time delay. The first received pulse was due to electrical pick-up of signal generated by the high-power oscillator. Even extensive screening was not sufficient to suppress it. In fact this was not really necessary as the pulse that came through the liquid arrived a little later owing to a finite time required for the sound to travel from the bottom to the top transducer. The fused quartz rods (acoustic delay lines) provided a delay to prevent interference even for very short liquid paths (Rapuano, 1947). Fused quartz was chosen because it has a very low absorption for ultrasonic waves (Mason and McSkimin, 1947). As a result of multiple reflection several sound pulses of diminishing amplitude could be detected. Close-ups of two different sets of equipment are shown in figure 2.6. and figure 2.7.

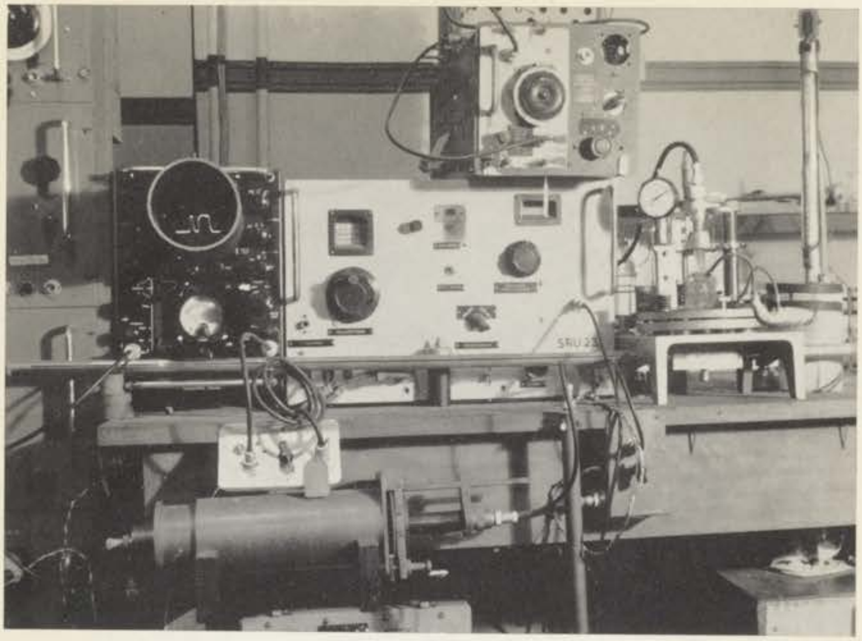


Fig. 2.6.

Photograph showing the experimental arrangement for frequencies above 100 MHz. The first received sound pulse and the comparison pulse can be seen on the oscilloscope screen.

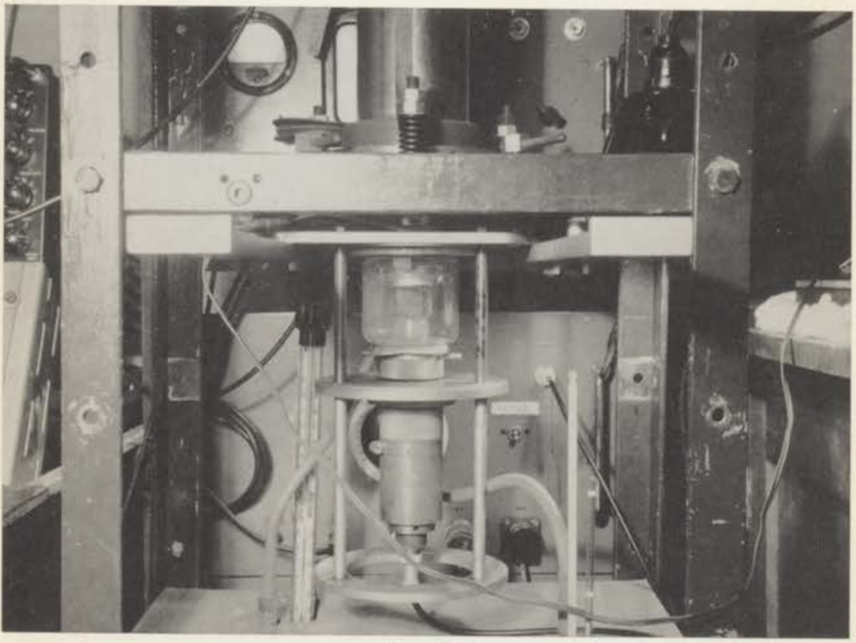


Fig. 2.7.

Detail of the apparatus used for frequencies up to 50 MHz. A liquid-containing double-walled jacket is shown at the centre of this photograph.

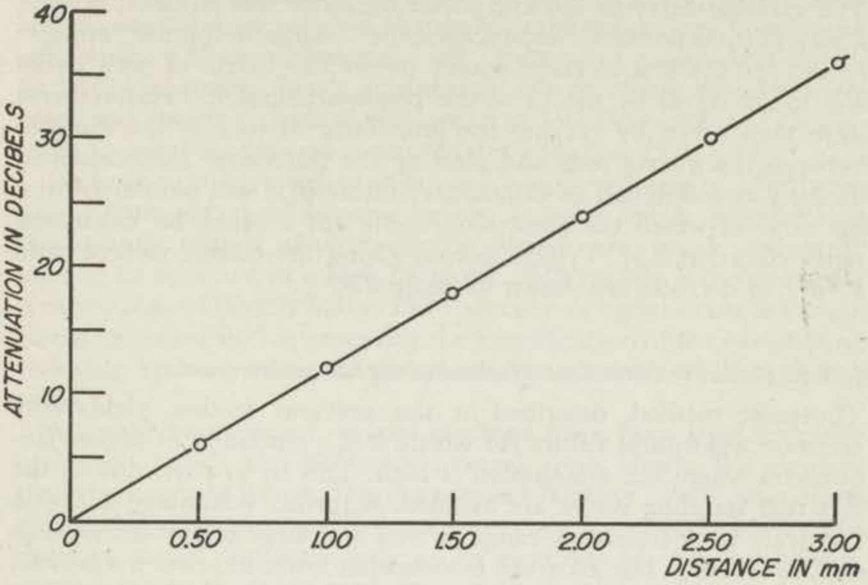


Figure 2.8 a

Attenuation in carbon tetrachloride at 50.17 MHz and 25.0° C.

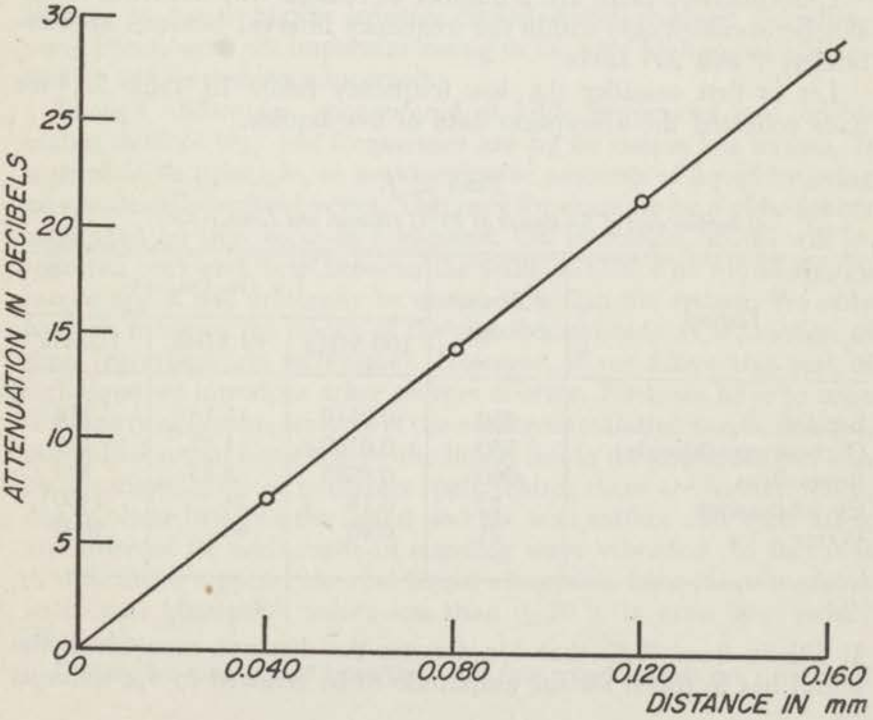


Figure 2.8 b

Attenuation in carbon tetrachloride at 192.4 MHz and 25.1°C.

The variable delay of the low power oscillator was adjusted in such a way that, on the oscilloscope screen, the "comparison pulse" appeared next to the first received sound pulse. The height of both pulses was made equal by means of the piston-attenuator. Measurements were then taken by varying the attenuator as well as the distance between the quartz rods and plotting the (intensity) attenuation in decibels as a function of distance. A linear plot was obtained, from the slope of which the absorption coefficient α could be calculated (with equation 2.5). Typical graphs giving the output voltage ratio V_2^2/V_1^2 in decibels are shown in figure 2.8.

§ 2.4. Frequency limitations of sound-absorption measurements

The pulse method, described in the previous section, yields very accurate absorption values (to within 2 %) especially at higher frequencies where the attenuation is high. This is, in part, due to the fact that standing waves are avoided. A further advantage is that a relatively large frequency range as well as a large temperature range can be covered. The accuracy is somewhat lower at lower frequencies and also for high temperatures and volatile compounds (thermal fluctuations).

Unfortunately there are a number of reasons why accurate values can be obtained only within the frequency interval between approximately 1 and 250 MHz.

Let us first consider the low frequency limit. In table 2.1 we have collected the absorption data of five liquids.

Table 2. 1.

Absorption data of five liquids at 25° C (Heasell and Lamb, 1956).

Liquid	$10^{17}\ \alpha/\nu^2$ sec^2 cm^{-1}	$1/\alpha$ (in cm) at		
		100 MHz	10 MHz	1 MHz
Benzene	850	0.0118	1.18	118
Carbon tetrachloride	550	0.0182	1.82	182
Bromoform	260	0.0385	3.85	385
Cyclohexanone	72	0.14	14	1400
Water	21	0.40	40	4000

It follows from (2.2) that $1/\alpha$ denotes the distance over which the sound has to travel for the amplitude to be reduced to $1/e$ times its original value. Apparently at lower frequencies considerable pathlengths are required before a change of amplitude of any importance will occur. This necessitates the use of excessive amounts of liquid. In addition, unless quartz transducers of very large diameters are employed, beam spreading will occur at low frequencies. This also leads to complications as it invalidates equation (2.2).

Difficulties at high frequencies have a different origin. They arise simply from a lack of acoustic power. It turns out in practice that the acoustic output of piezo-electric transducers, which necessarily have to be operated in a high harmonic, falls rapidly if the frequency is raised above 200-250 MHz. The reduction of signal strength cannot be compensated for by increasing the amplification of the broad-band receiving system, owing to the inevitable presence of background noise.

As could be expected, special methods have been tried for measurements outside the frequency interval given above. We mention the experiment of RINGO, FITZGERALD and HURDLE (1947) who determined the absorption coefficient of mercury up to 1000 MHz. The mercury served simultaneously as an electrode of each transducer, an acoustic transmission medium and an electric shield between the transmitting and receiving crystal transducer. Instead of a pulsed signal continuous wave excitation was chosen which permitted the authors to use a highly sensitive narrow-band receiver. Standing-wave effects were not important owing to the very high sound absorption at the frequencies concerned.

Though difficulties encountered at high frequencies are considerable, those at very low frequencies are by no means less serious. It is possible, in principle, to avoid excessive amounts of liquid by using an acoustically isolated vessel. This may for example be a glass sphere suspended on thin wires in a vacuum. On excitation, sound will be reflected back and forth between the walls and since no sound energy can escape it will gradually be absorbed within the system. We only have to measure the decay of the signal amplitude as a function of time (reverberation technique). However, if we adopt this sort of technique we introduce other sources of error. First, we have to cope with the troublesome features of the numerous standing waves. Second, not only is sound absorbed by the liquid inside the container but also by the material of the container itself. Third, there are friction losses, due to shear between the liquid and the wall surface and these losses are different for each mode of standing wave vibration. In fact is it so difficult to separate the real liquid absorption from the extraneous losses that absorption values less than ± 20 % in error are hardly attainable.

It may be mentioned here that our first experiments on rotational isomerism in liquids with conjugated bonds were carried out by means of a reverberation technique (de Groot and Lamb, 1955). The results did point to the existence of this type of isomerism. Later the much more accurate pulse measurements, described in chapter III, were taken. In this thesis only a few results of reverberation measurements will be quoted.

CHAPTER III

RESULTS AND DISCUSSION OF ULTRASONIC ABSORPTION MEASUREMENTS

§ 3.1. Introduction

In Chapter I it was shown that ultrasonic measuring techniques may be employed in the study of certain temperature-sensitive chemical equilibria in liquids. Examples were given of very fast reactions that had been investigated in this way.

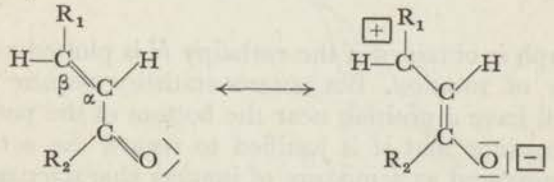
Later it was pointed out that reasonably accurate sound absorption values, which are necessary for this type of investigation, can be obtained only within a limited frequency interval (Chapter II).

As a consequence only a limited range of reactions can be studied by this method, the exact relation between the characteristic frequency and the rate constants being given by the relation (1.54). Hence problems must be carefully selected.

The ultrasonic analysis of such selected problems will be dealt with in the following chapter. It will be shown that ultrasonic measurements may be used to investigate the mobile equilibrium between certain rotational isomers.

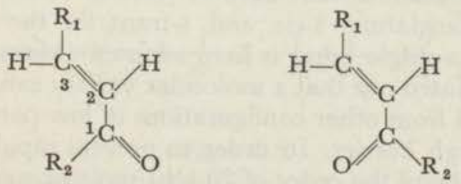
§ 3.2. Analysis of results

The phenomenon of internal rotation may be conveniently exemplified by the α-β-unsaturated aldehydes and ketones, mentioned already in Chapter I. Here resonance of the sort



. . (3.1)

will lend a partially double bond character to the C_1—C_2 bond and hence will stabilise planar configurations. The following forms



s-trans s-cis

. . . . . (3.2)

represent positions of minimum potential energy as is demonstrated in figure 3.1. The Gibbs free energy per mole G is given as a function of the angle of rotation about C_1—C_2.

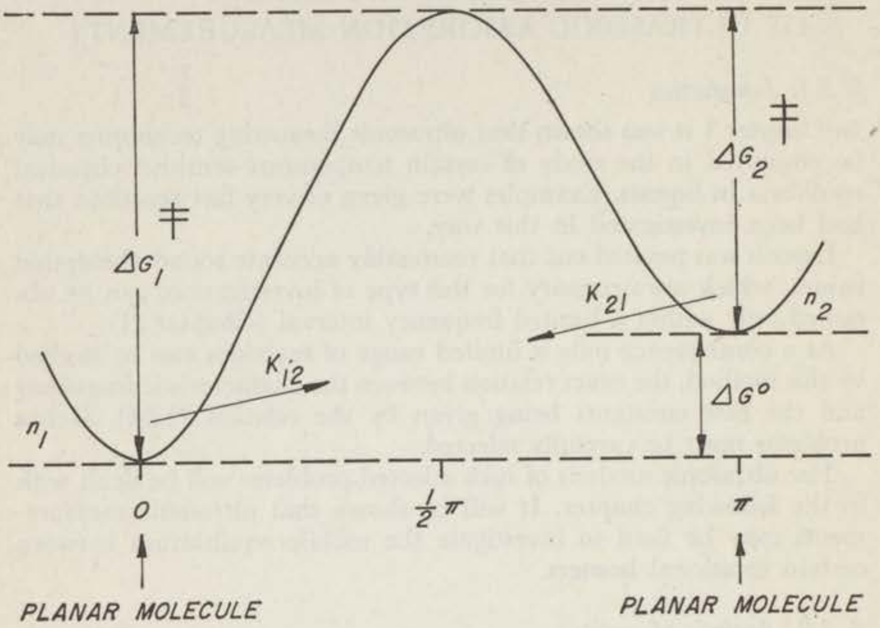


Figure 3.1.

Gibbs free energy as a function of the angle of rotation about the central C-C bond.

A similar graph is obtained if the enthalpy H is plotted as a function of the angle of rotation. Boltzmann-statistics require that most molecules will have a position near the bottom of the potential wells in such a manner that it is justified to regard the actual α-β-unsaturated compound as a mixture of isomers characterized by (3.2). The name *rotational isomers* is frequently used in this connection. In order to avoid confusion with normal (double bond) cis-trans isomerism the nomenclature s-cis and s-trans for the arrangement of groups around a single bond is here adopted (Mulliken, 1942).

It may be pointed out that a molecular variety can only be isolated if it is separated from other configurations of low potential energy by a sufficiently high barrier. In order to prevent rapid interconversion its height must be of the order of 20 kcal/mole or more at room temperature. This figure should be compared with $\Delta H_2^{\ddagger} \approx 5$ kcal/mole which was found for the unsaturated aldehydes (table 3.2).

Apparently there exists a mobile and generally temperature dependent equilibrium

$$\text{s-trans isomer} \underset{k_{21}}{\overset{k_{12}}{\leftrightarrows}} \text{s-cis isomer} . \; . \; . \; . \; . \qquad (3.3)$$

As was discussed in Chapter I, this type of rapid reversible reaction will be perturbed by the temperature fluctuations of a sound wave. Consequently sound relaxation is to be expected at a frequency which, according to equation (1.54), is of the order of $(k_{12} + k_{21})$.

As an illustration, the absorption coefficient for crotonaldehyde divided by the square of the frequency, as derived from our measurements, is given in figure 3.2. α/ν^2 is plotted as a function of log ν at three different temperatures.

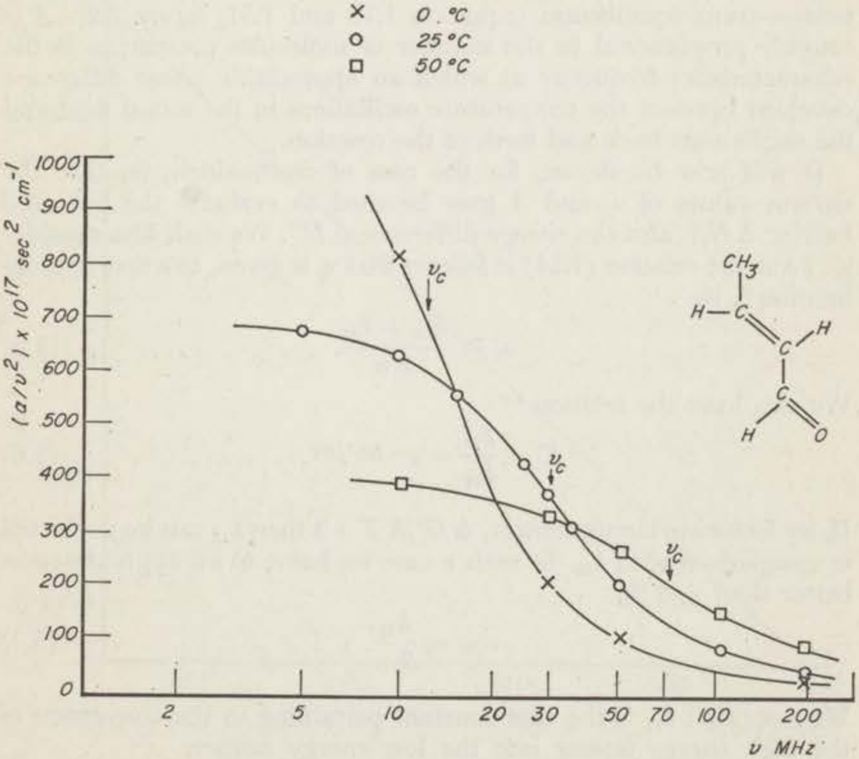


Figure 3.2.

Ultrasonic absorption of crotonaldehyde: liquid distilled in vacuo.

Contrary to the behaviour of compounds like alcohol, acetone, chloroform, etc. where α/ν^2 is a constant for all frequencies accessible to measurement, there is a considerable decrease of α/ν^2 in the case of crotonaldehyde. It will be shown in this chapter, by the method of chemical "modulation", that the above-mentioned equilibrium is responsible for the observed relaxation.

The experimental points of figure 3.2 can be described, with a deviation of less than 2 %, by the algebraic representation

$$\frac{\alpha}{\nu^2} = B + \frac{A}{1 + (\nu/\nu_c)^2}, \quad \ldots\ldots\ldots \quad (3.4)$$

in which different values of B, A and ν_c belong to different curves. This expression is in accordance with theoretical expectations. The constant B includes the classical sound absorption due to viscosity and heat conduction (equation 1.58) as well as contributions resulting from other relaxations at very high frequencies (equation 1.60). The second term with A and ν_c stems from perturbation of the aforementioned s-cis—s-trans equilibrium (equation 1.18 and 1.51, figure 1.2). A is roughly proportional to the number of molecules present; ν_c is the (characteristic) frequency at which an appreciable phase difference develops between the temperature oscillations in the sound field and the oscillations back and forth of the reaction.

It will now be shown, for the case of crotonaldehyde, that the various values of ν_c and A may be used to evaluate the potential barrier $\Delta H_2^\ddagger$ and the energy difference ΔH°. We shall first consider ν_c. From the relation (1.54) it follows that ν_c is given, to a first approximation*, by

$$\nu_c = \frac{k_{12} + k_{21}}{2\pi}. \quad \ldots\ldots\ldots \quad (3.5)$$

We also have the relation **

$$K = \frac{k_{12}}{k_{21}} = e^{-\Delta G^\circ/RT}. \quad \ldots\ldots\ldots \quad (3.6)$$

If, by fortunate circumstances, $\Delta G^\circ/RT > 3$ then k_{12} can be neglected in comparison with k_{21}. In such a case we have, to an approximation better than ± 5 %,

$$\nu_c = \frac{k_{21}}{2\pi}. \quad \ldots\ldots\ldots \quad (3.7)$$

We note that k_{21} is the rate constant pertaining to the conversion of the high energy isomer into the low energy isomer.

---

* The approximation implies that $C_i^\circ << C_p^\circ = C_p^\infty + C_i^\circ$.

** The superscript ° refers to the appropriate standard state.

According to the theory of rate processes (GLASSTONE, LAIDLER and EYRING, 1941), this relation may be written as

$$\nu_c = \frac{1}{2\,\pi}\left[\frac{k\,T}{h}\right] e^{-\Delta G_2\ddagger/RT} = \frac{1}{2\,\pi}\,F_2\left[\frac{k\,T}{h}\right] e^{-\Delta H_2\ddagger/RT} \quad . \;.\; (3.8)$$

where k is BOLTZMANN's constant, h is PLANCK's constant, $F_2 = e^{\Delta S_2\ddagger/R}$ and $\Delta S_2\ddagger$ and $\Delta H_2\ddagger$ are the activation entropy and activation energy respectively. It is seen from the formula that an increase in temperature T will be associated with an increase in relaxation frequency ν_c. The activation energy $\Delta\, H_2\ddagger$ can be obtained from the slope of the plot of log (ν_c/T) against $1/T$ following which the "frequency factor" F_2 and the activation entropy $\Delta\, S_2\ddagger$ can be calculated from equation (3.8). A plot for crotonaldehyde is given in figure 3.3. The actual ν_c values can be found in table 3.2.

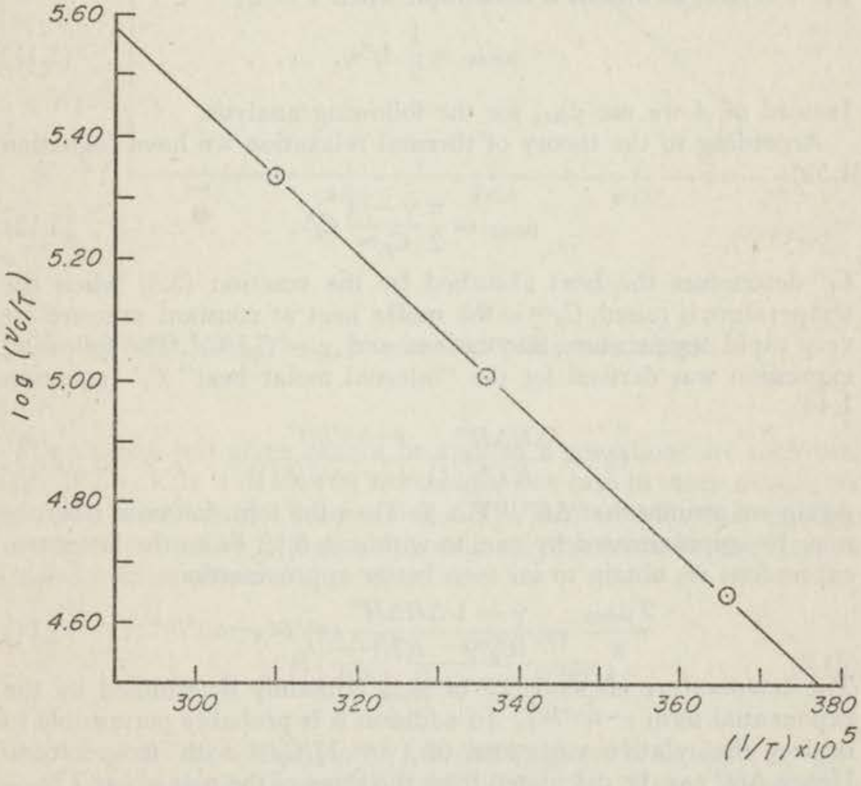


Figure 3.3.

Plot of log (ν_c/T) against $(1/T)$ for crotonaldehyde.

A straight line will generally not be obtained if $(\Delta G^\circ/RT) < 3$. We shall return to this point at a later stage.

There remains to be discussed the value of A in terms of the energy difference ΔH°. For convenience we use the sound absorption per wavelength due to the relaxation introduced in Chapter I. It is defined as

$$\mu = (\alpha - B\,\nu^2)\,\lambda\,, \quad \dots\dots\dots \quad (3.9)$$

where λ is the sound wavelength. With $\lambda = c/\nu$ (c = sound velocity) we derive from (3.4) and (3.9)

$$\mu = \frac{Ac\nu}{1 + (\nu/\nu_c)^2} \quad \dots\dots\dots \quad (3.10)$$

In all cases to be cited in this chapter $\alpha/\nu^2 < 2000 \times 10^{-17}$ sec^2/cm. Hence, referring to the example given in Chapter I, we are justified in neglecting the velocity dispersion, which is less than 1 % (compare figure 1.2). We take for c its low-frequency value c°. The absorption per wavelength attains a maximum when $\nu = \nu_c$;

$$\mu_{max} = \frac{1}{2} A c^\circ \nu_c. \quad \dots\dots\dots \quad (3.11)$$

Instead of A we use μ_{max} for the following analysis.

According to the theory of thermal relaxation we have (equation 1.52)

$$\mu_{max} = \frac{\pi}{2} \frac{\gamma - 1}{C_p^\infty} C_i^\circ \quad \dots\dots\dots \quad (3.12)$$

C_i° determines the heat absorbed by the reaction (3.3) when the temperature is raised. C_p^∞ is the molar heat at constant pressure for very rapid temperature fluctuations and $\gamma = C_p^\circ/C_v^\circ$. The following expression was derived for the "internal molar heat" C_i° (equation 1.44)

$$C_i^\circ = \frac{\Delta H \Delta H^\circ}{RT^2} \frac{e^{-\Delta G^\circ/RT}}{(1 + e^{-\Delta G^\circ/RT})^2} \quad \dots\dots \quad (3.13)$$

Again we assume that $\Delta G^\circ/RT > 3$. Then the term between brackets may be approximated by one, to within $\pm$ 5 %. From the latter two expressions we obtain to an even better approximation

$$\frac{2\,\mu_{max}}{\pi} = \frac{\gamma - 1}{C_p^\infty} \frac{\Delta H \Delta H^\circ}{RT^2}\, e^{\Delta S^\circ/R}\, e^{-\Delta H^\circ/RT} \quad \dots \quad (3.14)$$

The temperature dependence of μ_{max} is mainly determined by the exponential term $e^{-\Delta H^\circ/RT}$. In addition it is probably permissible to neglect the relative variations of $(\gamma - 1)/C_p^\infty$ with temperature. Hence ΔH° can be calculated from the slope of the plot of log $T^2\mu_{max}$ versus $1/T$. Figure 3.4 shows such a plot for crotonaldehyde. The μ_{max} values are compiled in table 3.2.

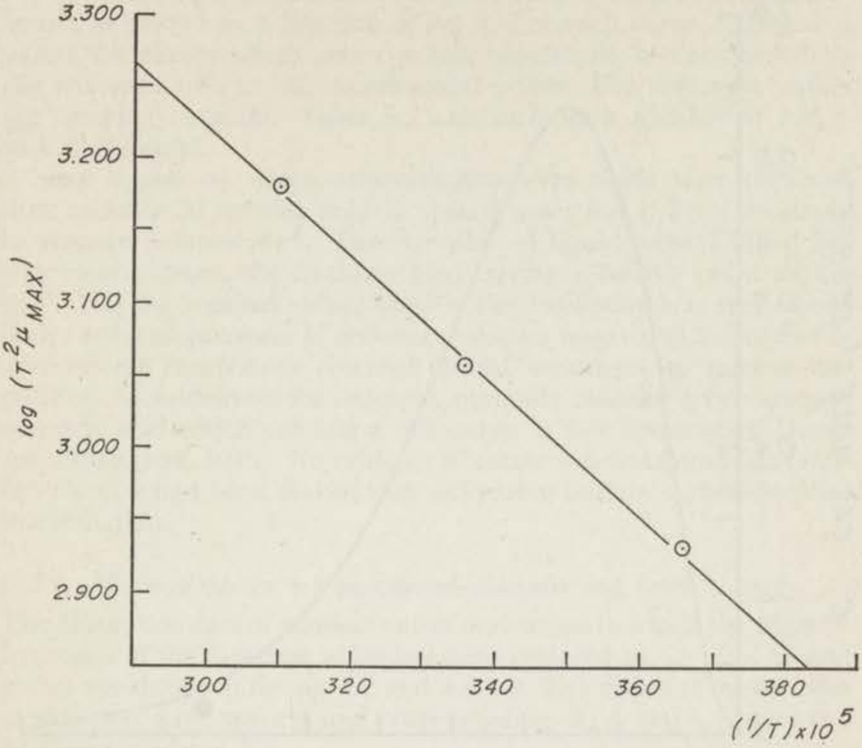


Figure 3.4.
Plot of log (T^2 μ_{max}) against ($1/T$) for crotonaldehyde.

The analysis just given cannot be applied if conditions are such that $\Delta G°/RT < 3$. It is of interest to consider this case in more detail. We simplify equation (3.13) by taking $\Delta H = \Delta H° = \Delta G°$, thus ignoring entropy terms. The following approximate expression for the internal molar heat is obtained

$$C_i^{°\prime} = R\left[\frac{\Delta H°}{RT}\right]^2 \frac{e^{-\Delta H°/RT}}{(1 + e^{-\Delta H°/RT})^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.15)$$

A plot of $C_i^{°\prime}$ as a function of $\Delta H°/RT$ is given in figure 3.5.

A maximum value is reached if $\Delta H°/RT = 2.4$. Hence, considering the relationship (3.12) between μ_{max} and $C_i°$ we infer that μ_{max} will change very little with temperature if $\Delta H°/RT = 2.4$ It will decrease

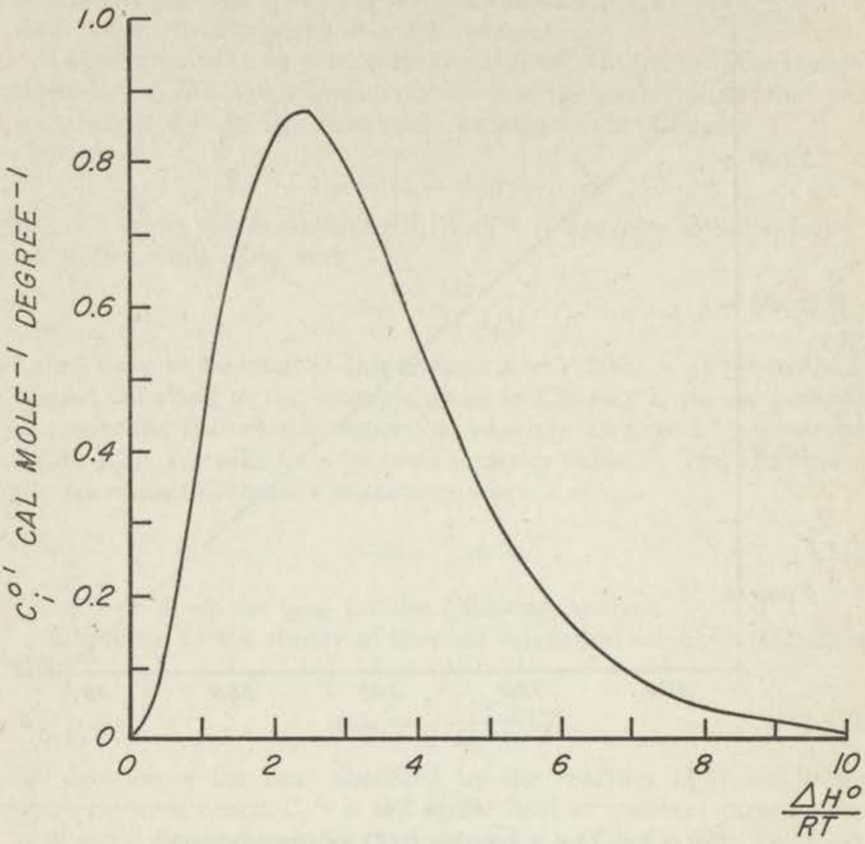


Figure 3.5.
The relaxing molar heat capacity according to equation (3.15).

with rising temperature if $\Delta H°/RT < 2.4$ and it will increase with rising temperature if $\Delta H°/RT > 2.4$. *Thus we are reasonably certain that the necessary condition $\Delta G°/RT > 3$ is fulfilled if μ_{max} increases with rising temperature.* For crotonaldehyde this is shown to be true in table 3.2.

§ 3.3. Measurements in pure liquids

In the next four paragraphs the experimental results obtained for different groups of pure liquids are given. Within each group the chemical properties are varied by systematic substitution and we shall trace the relationship between the chemical structure and the acoustic behaviour. *Measurements were taken at frequencies ranging from 5 to*

200 MHz. In most cases the value of α/ν^2, derived from the measurements, is plotted as a function of log ν. For each curve A, B and ν_c values are chosen which give the best possible fit, as determined by the relation (3.4), to the experimental points. The respective values are compiled in tables. Table 3.2 also includes a number of $\Delta H_2 \ddagger$ and ΔH° values.

Most liquids on which measurements were made were obtained from commercial sources, only in special cases has it been necessary to prepare compounds *. The samples of liquid were distilled before measurement, the fractions used having a boiling point within ± 1° C of the nominal value. Usually the distillation was carried out under reduced pressure. If necessary samples were dried before distillation. Some compounds received special treatment to remove impurities. Acetaldehyde, for example, normally contains a fair amount of acetic acid which exhibits a relaxation at low frequencies. (LAMB and PINKERTON, 1949). No evidence of relaxation was found in acetaldehyde that had been shaken with anhydrous sodium carbonate prior to distillation.

§ 3.4. *Measurements in α-β-unsaturated aldehydes and ketones*

The absorption data of acrolein and of derivatives in which the trans ** hydrogen of the β-carbon atom has been replaced by an alkyl or aryl group are shown in figures 3.2 and 3.6-3.9. The different curves refer to different temperatures and corresponding B, A and ν_c values can be found in table 3.2.

Table 3.1.

Characteristic frequencies, at 25° C, of six acrolein derivatives.

Compound	ν_c at 25° C
Acrolein	176 MHz
Methacrolein	174 MHz
Crotonaldehyde	30.3 MHz
2-Ethyl 3-propyl acrolein	24.6 MHz
Hexyl cinnamic aldehyde	18.2 MHz
Cinnamaldehyde	15.7 MHz

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* Thanks are due to Mr N. M. HAAFKENS and Mr J. BOEKHOLTZ of the Koninklijke/Shell-Laboratorium, Amsterdam, for having prepared methyl vinyl ketone, methyl isopropenyl ketone and furfural acetone.

** For crotonaldehyde and cinnamaldehyde this is known to be correct. In the case of 2-ethyl 3-propyl acrolein and hexyl cinnamic aldehyde it is a likely structure, for steric reasons.

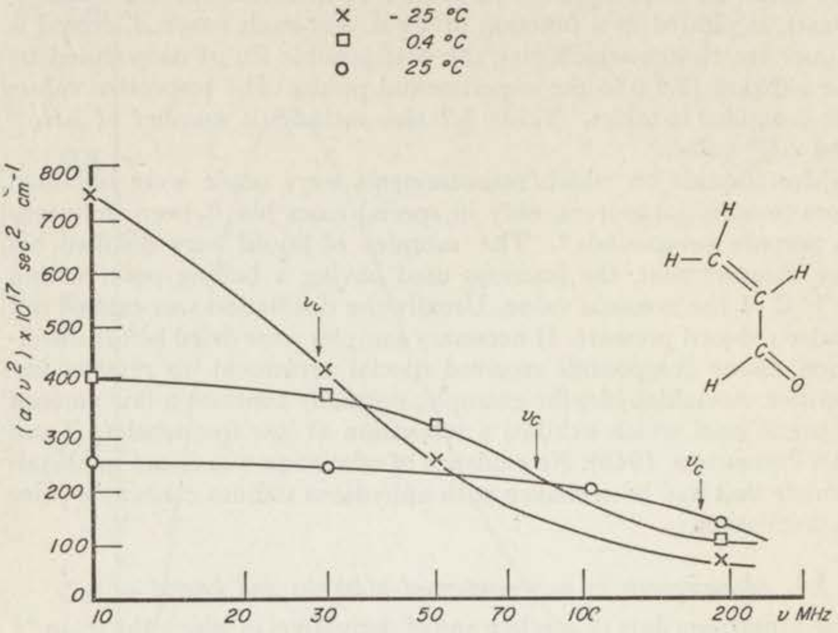


Figure 3.6.

Acrolein: liquid distilled at atmospheric pressure: b.p. = 51 to 52° C.

It will be noticed that for all compounds ν_c decreases with rising temperature in accordance with equation (3.8).

This equation also determines the trend of ν_c when different compounds are compared. In table 3.1 the characteristic frequencies, at 25° C, for six acrolein derivatives are listed.

Let us first consider substitution of β-hydrogen by methyl or phenyl. These substitutions are known to strengthen conjugation thus impeding rotation of the aldehyde group. On the other hand, owing to the fact that the *trans* β-hydrogen atom is replaced, no significant steric influence on this rotation is to be expected. Therefore, assuming that the frequency-factor $F_2\ddagger$ (containing the entropy term) does not change too much, substitution in the order given will lead to a higher potential barrier $\Delta H_2\ddagger$ and a lower characteristic frequency ν_c.

The resonating structures of acrolein involve a positive charge in the region of the β carbon atom but not in the region of the α carbon atom. Hence substitution of α hydrogen by an electron-donating alkyl group is not expected to have much influence on the conjugation. It is pleasing to observe that in fact the characteristic frequencies of

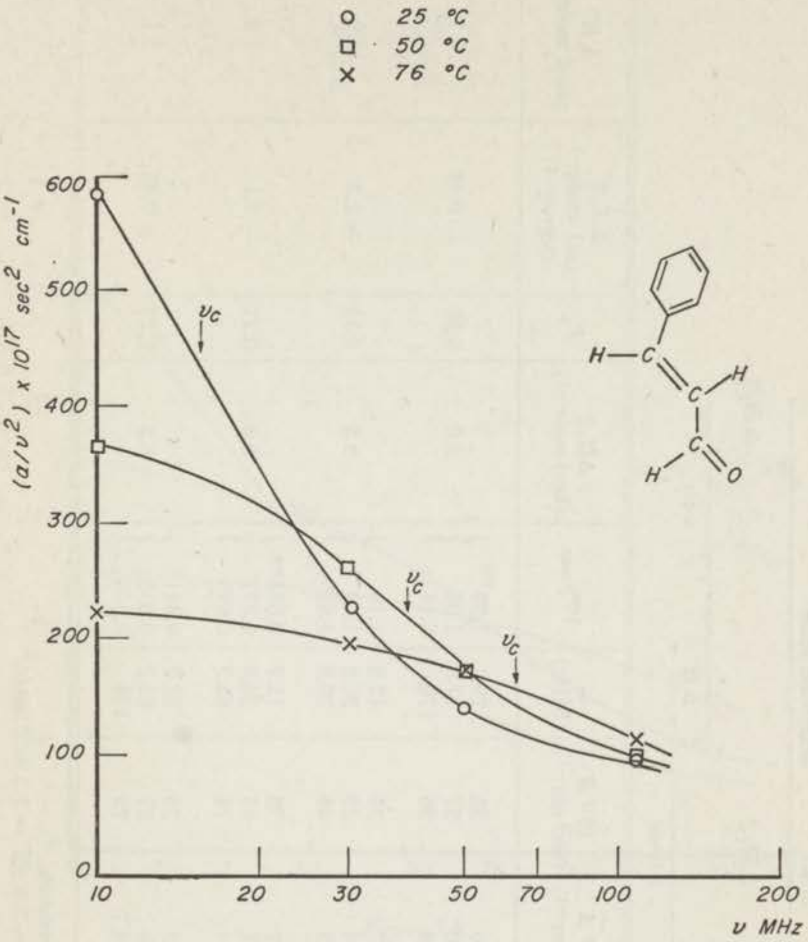


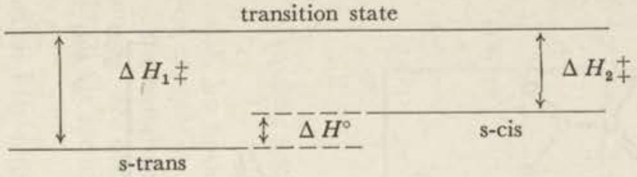
Figure 3.7.

Cinnamaldehyde: liquid distilled in vacuo.

acrolein and methacrolein, at 25° C, appear to be the same within experimental accuracy. Similarly the characteristic frequencies of cinnamaldehyde and hexyl cinnamic aldehyde are of the same order of magnitude and this is also true for crotonaldehyde and 2-ethyl 3-propyl acrolein. Apparently a large α-substituent group only "dilutes" the influence of the active groups; it leads to a lower total absorption.

Measurements at three temperatures are available for acrolein, crotonaldehyde, cinnamaldehyde and methacrolein. For each liquid

Table 3.2.
Absorption parameters and energy values for four α-β-unsaturated aldehydes.



Liquid	T (° C)	10^{-5} c* (cm sec^{-1})	10^{17} A (sec^2 cm^{-1})	10^{17} B (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{max}$	ΔH_2‡ (kcal mole^{-1})	F_2	Δ S_2‡ (cal mole^{-1} degree^{-1})	Δ H° (kcal mole^{-1})
Acrolein	−24.6	1.373	790	38	29.1	1.58	5.0	0.80	−0.44	2.1
	− 0.3	1.273	380	37	77.8	1.88				
	+25.2	1.168	208	36	176	2.14				
Crotonaldehyde	0.0	1.369	1397	24	12.0	1.15	5.5	0.34	−2.2	1.9
	+25.0	1.268	674	29	30.3	1.29				
	+50.1	1.165	355	34	70.0	1.45				
Cinnamaldehyde	+25.1	1.563	722	78	15.7	0.885**	5.6	0.21	−3.1	1.5
	+50.2	1.472	331	63	36.0	0.877				
	+75.8	1.385	154	74	65.2	0.695				
Methacrolein	−24.8	1.408	282	29	22.2	0.441	5.3	1.27	+0.48	3.1
	0.0	1.299	150	27	65.2	0.635				
	+24.9	1.188	94.7	25	174	0.978				

* Velocity values derived from separate measurements.
** μ_{max} changes little with temperature; Δ H° ≈ 2.4 RT = 1.5 kcal/mole.

Note: In obtaining the above energy values from results at three temperatures less weight has been given in each case to the results at the highest temperature since the measured absorption values cover a smaller part of the relaxation region and the value of A is also smaller.

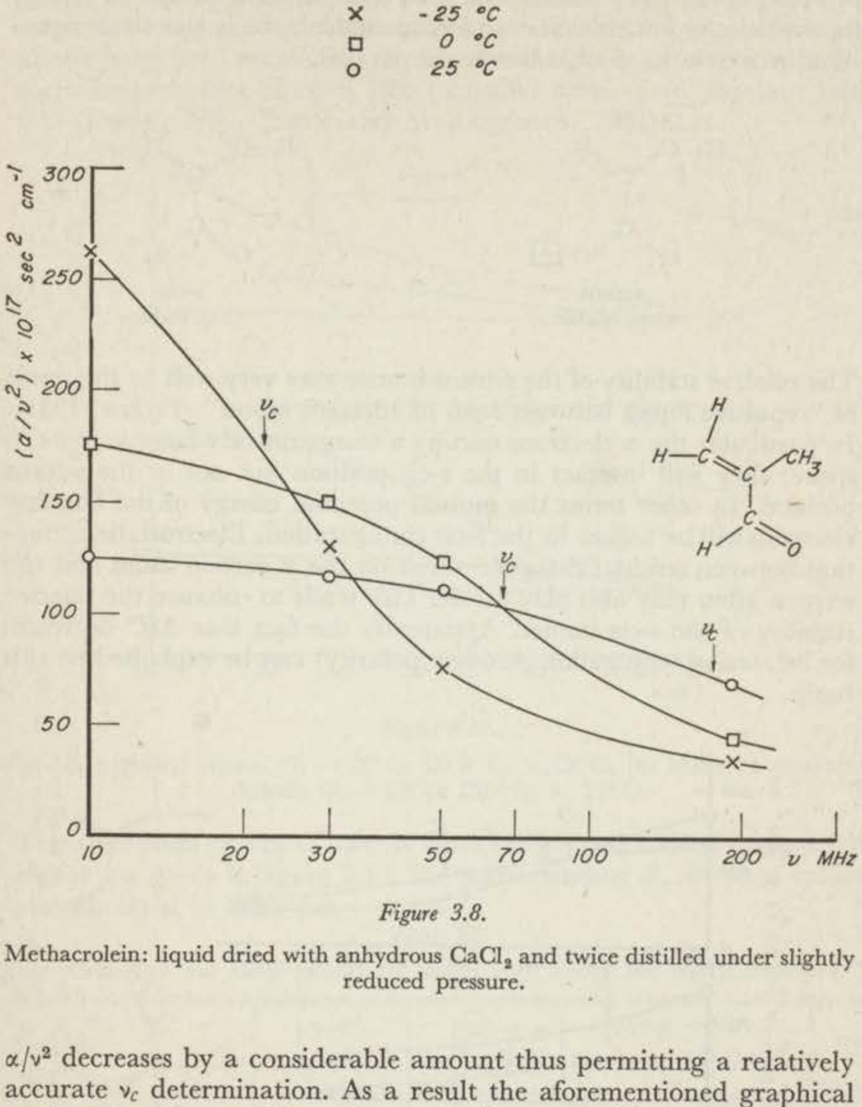


Figure 3.8.

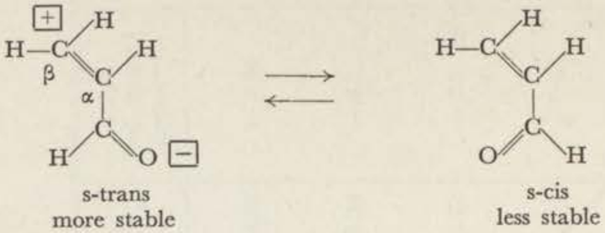
Methacrolein: liquid dried with anhydrous $CaCl_2$ and twice distilled under slightly reduced pressure.

α/ν^2 decreases by a considerable amount thus permitting a relatively accurate ν_c determination. As a result the aforementioned graphical method may be used in order to obtain reasonably accurate values for $\Delta H_2\ddagger$ and ΔH°; these are given in table 3.2. Their estimated accuracy is $\pm 6\,\%$.

It will be noticed that substitution of β hydrogen by alkyl or aryl leads to an increase of $\Delta H_2\ddagger$ while F_2 (or $\Delta S_2\ddagger$) goes down. On the other hand the essentially different α hydrogen substitution leads to an increase of both $\Delta H_2\ddagger$ and F_2.

Electric dipole-moment studies (Bentley, Everard, Marsden and

Sutton, 1949) have shown that the configuration of lowest energy for acrolein, crotonaldehyde and cinnamaldehyde is the s-trans position in which the double bonds are parallel.



The relative stability of the s-trans isomer may very well be the result of "repulsive forces between *bonds* of adjacent atoms" (Pitzer, 1951). In particular the π electrons occupy a comparatively large volume in space; they will interact in the s-cis position but not in the s-trans position. In other terms the mutual potential energy of the bonding electrons will be higher in the s-cis configuration. Electrostatic attraction between residual charges centred on the β carbon atom and the oxygen atom may also play a role. This tends to enhance the relative stability of the s-cis isomer. Apparently the fact that ΔH° decreases for increasing conjugation (stronger polarity) can be explained on this basis.

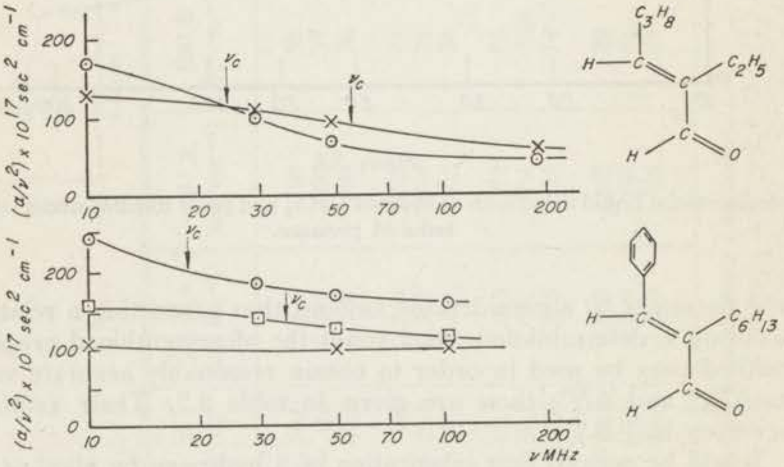


Figure 3.9.

(a) 2-Ethyl 3-propyl acrolein: distilled in vacuo. ⊙,25° C: × ,50° C. (b) Hexyl cinnamic aldehyde: liquid treated with anhydrous Na_2CO_3 in ether solution and distilled in vacuo. ⊙,25° C: ⊡, 50° C: ×,75° C.

The relatively high ΔH° value of methacrolein probably points to attraction between the oxygen atom and the methyl group. Similar effects have been mentioned in the literature to explain the high dissociation constants of acids like trimethyl acetic acid, o-toluic acid etc. (Dippy, 1939; Smith and McReynolds, 1939).

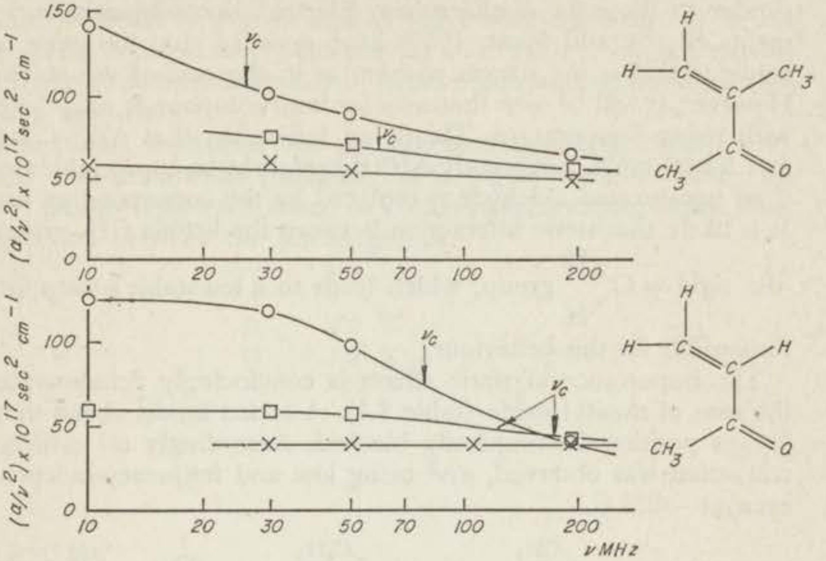


Figure 3.10.

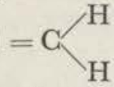
(a) Methyl vinyl ketone. O, — 25° C: □, 0° C: ×,25° C. (b) Methyl *iso*propenyl ketone. O, — 25° C: □,0° C: ×, 25° C.

The absorption curves of methyl vinyl ketone and methyl *iso*propenyl ketone are given in figure 3.10; the corresponding B, A and ν_c values are tabulated in table 3.3.

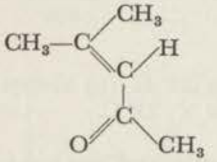
Table 3.3.

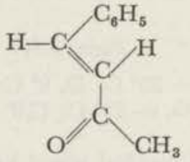
Absorption parameters and sound velocity for methyl vinyl ketone and methyl isopropenyl ketone.

Liquid	T (° C)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{max}$
Methyl vinyl ketone	—24.8	1.451	107	23	80.6	0.626
	— 0.1	1.342	34	25	178	0.406
Methyl *iso*-propenyl ketone	—24.8	1.459	96	59	26.4	0.186
	— 0.1	1.347	28	51	59.6	0.113

These compounds should be compared with acrolein and methacrolein respectively, the difference being that the aldehyde H has been replaced by CH_3. At —25° C the value of the characteristic frequency for methyl vinyl ketone is somewhat higher than for acrolein but, on the other hand, the values for methyl *iso*propenyl ketone are very similar to those for methacrolein. Electric dipole-moment measurements (Estok and Sikes, 1953) have revealed that the more stable configuration is the s-trans position as in the case of the aldehydes. However, it will be seen that now for both compounds μ_{max} decreases with rising temperature. This is an indication that $\Delta H^\circ < 2.4\,RT$ or 1.5 kcal/mole. Apparently ΔH° decreases by an appreciable amount if an unsaturated aldehyde is replaced by the corresponding ketone. It is likely that steric interaction between the ketone CH_3 group and the rigid  $=\mathrm{C}\begin{array}{l}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{array}$ group, which leads to a less stable s-trans form, is responsible for this behaviour.

The importance of steric effects is convincingly demonstrated in the case of mesityl oxide (table 3.4). A scaled model shows that the s-trans position is completely blocked. Accordingly no evidence of relaxation was observed, α/ν^2 being low and frequency-independent even at —25° C.


mesityl oxide
s-cis


benzylidene acetone
s-cis

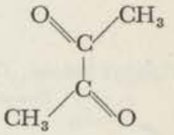

diacetyl
s-trans

Table 3.4.

Absorption values of three unsaturated ketones (10-200 *MHz*).

Liquid	T (° C)	$10^{17}\ \alpha/\nu^2$ ($sec^2\ cm^{-1}$)	$10^{-5}\ c$ ($cm\ sec^{-1}$)
Mesityl oxide	— 24.7 + 24.9	40.9 34.0	1.501 1.287
Benzylidene acetone	+ 50.1	68.1	1.464
Diacetyl	+ 25.0	30.3	1.233

Table 3.4 also contains the absorption data of benzylidene acetone. Unfortunately this compound has a rather high melting point (41° C) which prevents measurements from being taken at lower temperatures. No relaxation could be detected at a temperature of 50° C and up to a frequency of 200 MHz. The s-cis position of benzylidene acetone, in contrast to that of methyl vinyl ketone, appears to be the more stable configuration (Bentley *et al.*, 1949). This is probably due to the combined influence of steric repulsion and stronger conjugation (polarity).

Relaxational behaviour was not observed in diacetyl (table 3.4). In this case the s-trans configuration is highly stabilized since the methyl groups repel each other, as do the oxygen atoms, whilst there is attraction between the unlike groups.

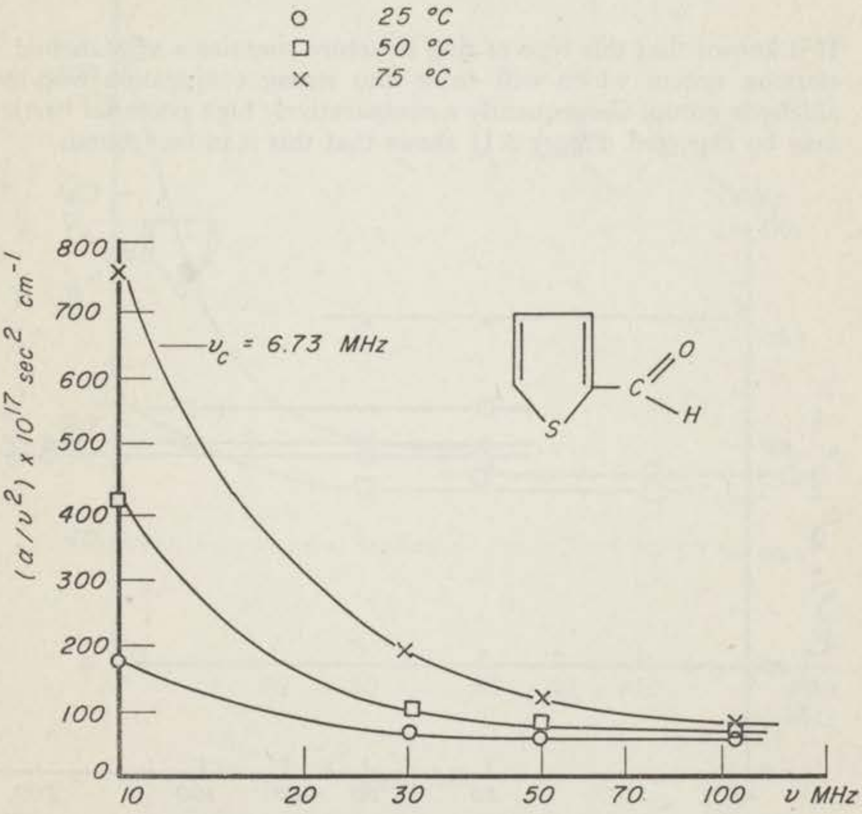
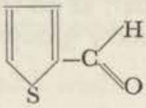


Figure 3.11.

Thiophene 2 - aldehyde: liquid distilled in vacuo.

Acoustic measurements may reveal the existence of rotational isomers. However, the potential barrier $\Delta H_2\ddagger$ must be sufficiently high to reduce the characteristic frequency to a value within or just outside the frequency region which is accessible to measurement. Otherwise the relaxation may escape detection. Hence in order to further investigate the problem of rotational isomerism it is desirable to alter the basic α-β unsaturated aldehyde structure only by degrees. In this way a trend, up or down, of ν_c can be discovered before the relaxation vanishes.

Thiophene 2-aldehyde is an example of such a "modified" structure. Here the α-β double bond is part of an unsaturated ring.



It is known that this type of ring structure contains a very mobile π electron system which will enter into strong conjugation with the aldehyde group. Consequently a comparatively high potential barrier may be expected. Figure 3.11 shows that this is in fact found.

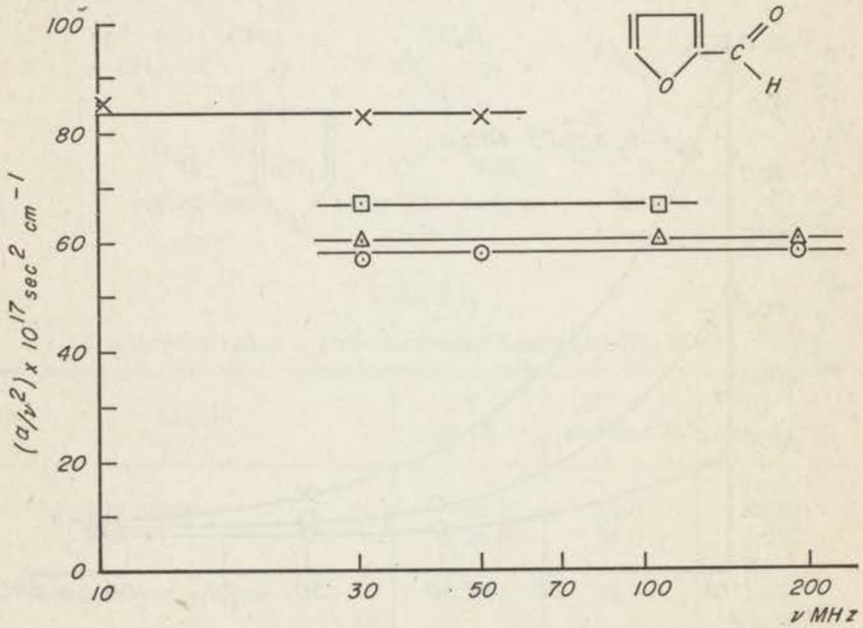


Figure 3.12.

Furfural: liquid distilled in vacuo. ⊙, 0° C: △, 25° C: ⊡, 50° C: ×, 100° C.

Even at + 75° C the characteristic frequency is well below 10 MHz. Still stronger conjugation may be anticipated if sulfur is replaced by oxygen. In furfural not even the "tail" of a relaxation curve is found over the frequency range 10-200 MHz (figure 3.12).

The relaxation is thought to occur at lower frequencies. In fact this has been confirmed by reverberation measurements on this compound over the frequency range 200 kHz to 1 MHz*. It is of interest that in the case of 2-methyl 5-acetyl furane, which is closely related to furfural, the tail of the relaxation curve moves to within the frequency range 10-200 MHz if the temperature is raised (figure 3.13).

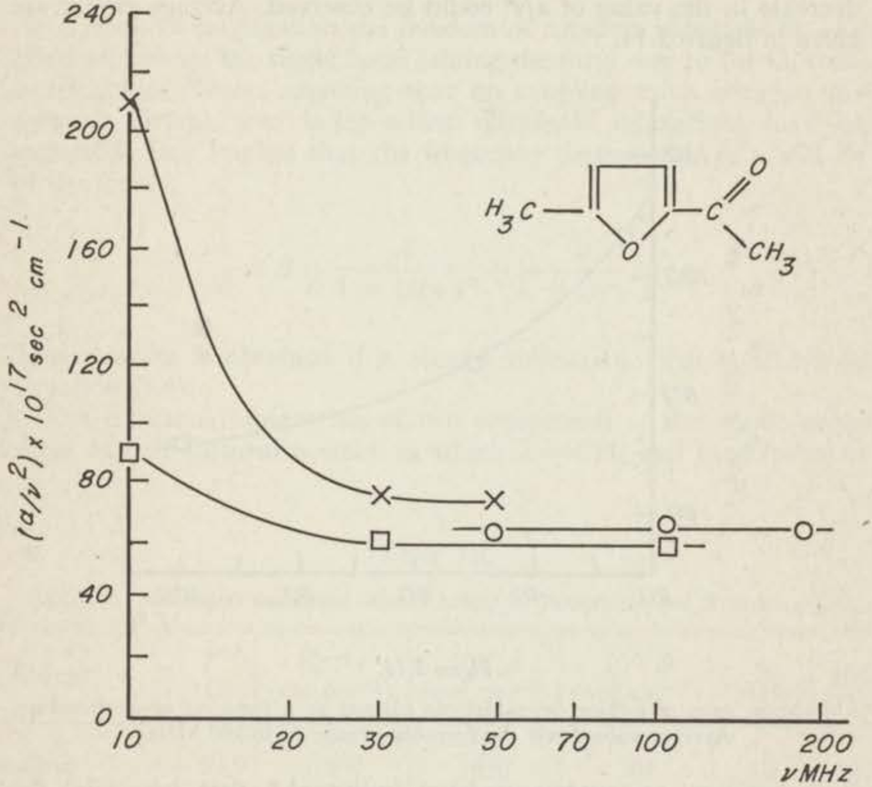


Figure 3.13.

Absorption of 5-methyl 2-acetyl furane. ○,25° C: ☐,75° C: ×,100° C.

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* Thanks are due to Mr D. Hall for carrying out these measurements.

Apparently ν_c is somewhat higher in this case which points to a reduced effective potential barrier. A possible explanation of this can be given in terms of steric hindrance between the furyl ring and the ketone methyl group.

Restricted rotation, arising from conjugation between double bonds, will also occur if an aldehyde group is attached to a benzene ring. However, in that case the planar structures are different — and hence rotational *isomers* exist — only if additional asymmetry is introduced into the ring. Consequently ultrasonic relaxation, due to rotational isomerism, is likely to be found in ortho- and meta-substituted, but not in para-substituted, benzaldehydes. As an example the ultrasonic absorption of *o*-chlorobenzaldehyde was determined over the frequency range 30 to 100 MHz and up to 100° C. Unfortunately no decrease in the value of α/ν^2 could be observed. Average values are given in figure 3.14.

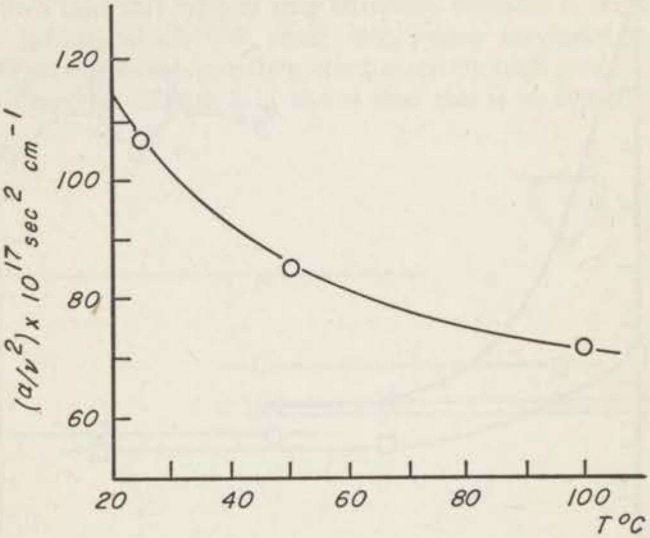

Figure 3.14.

Absorption data of *o*-chlorobenzaldehyde plotted as a function of temperature. Average values over the frequency range 30 to 100 MHz.

Reverberation measurements have indicated * that here also the relaxation falls in an inconvenient low-frequency range.

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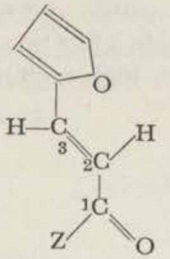
* From pulse measurements between 30-100 MHz at 45° C: $\alpha/\nu^2 = 89 \times 10^{-17}$ sec^2/cm.

From reverberation measurements between 200 kHz - 1 MHz at 45° C: $\alpha/\nu^2 = 465 \times 10^{-17}$ sec^2/cm (DE GROOT and LAMB, 1955).

An interesting situation arises if *two* rotating groups are attached to a rigid molecular framework. We consider the following structure as an appropriate example:



As a result of conjugation the freedom of rotation about the C_1—C_2 bond and about the single bond joining the furyl ring to the C_3 atom is restricted. Hence, assuming that no coupling exists between the rotating groups, two independent ultrasonic relaxations may be expected. This implies that the frequency dependence of α will be of the form

$$\frac{\alpha}{\nu^2} = B + \frac{A'}{1 + (\nu/\nu_c')^2} + \frac{A''}{1 + (\nu/\nu_c'')^2}$$

This relation is obtained if a second relaxation term is added to equation (3.4).

The ultrasonic absorption of two compounds of the above given type, namely furfural acetone in which $Z = CH_3$ and furacrolein in

Table 3.5.

Relaxation parameters and sound velocity values for furacrolein and furfural acetone.

Liquid	T (° C)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{max}$
Furacrolein ($Z = H$)	+ 59.9	1.360	1840	61	13.5	1.69
	+ 79.4	1.293	1150	66	23.0	1.71
	+ 99.8	1.228	617	132	31.4	1.19
Furfural acetone ($Z = CH_3$)	+ 50.1	1.383	1371	67	9.78	0.93
	+ 74.7	1.299	564	67	23.2	0.85

which Z = H, was measured. In neither case has it been possible to establish the existence of two independent relaxation regions. In figure 3.15 the absorption α/ν^2 is plotted as a function of frequency. It appears that a single relaxation mechanism is sufficient to describe the experimental results to within ± 2 %. The relevant relaxation parameters are given in table 3.5. Only measurements at or above 50° C were taken, owing to high melting points.

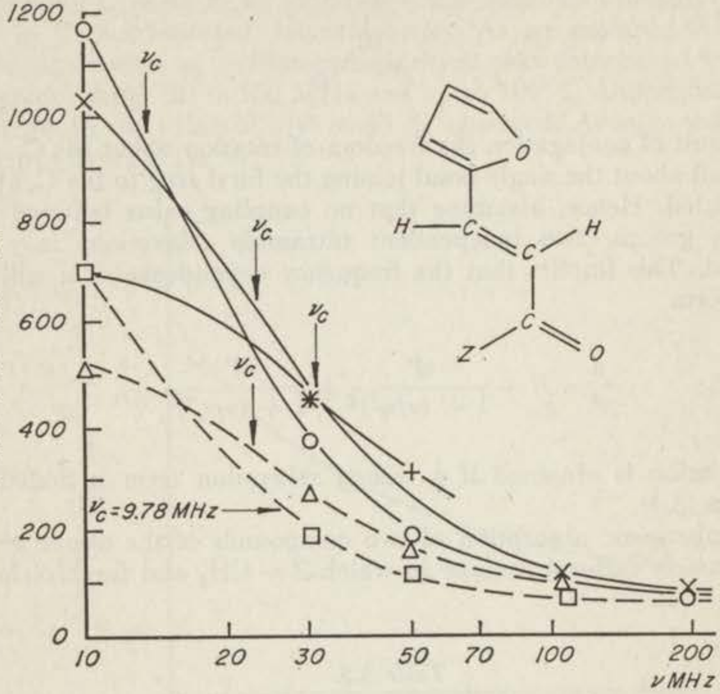
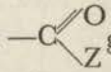


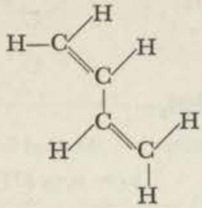
Figure 3.15.

Furacrolein (Z = H): distilled in vacuo: m.p. 50,2° C. ○,60° C: ×,79° C: +,100°C.
Furfural acetone (Z = CH_3). □, 50° C: Δ, 75° C.

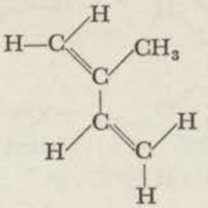
It is possible that relaxation due to rotation of the  $-\mathrm{C}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \diagdown\mathrm{Z}\end{smallmatrix}$ group will not be observed at the temperatures in question because the characteristic frequency associated with this rotation lies far above the frequency range 10-200 MHz (compare for example the characteristic frequencies calculated for acrolein and methyl vinyl ketone). On the other hand there may be close coupling between the rotating groups which leads to a combined relaxation.

§ 3.5. *Butadiene and isoprene*

The chemical structures of butadiene and isoprene are closely related to those of acrolein and methacrolein respectively, the $=O$ being replaced by the $=CH_2$ group.



Butadiene
s-trans



Isoprene

The absorption data derived from measurements in the liquid are collected in table 3.6.

Table 3.6.

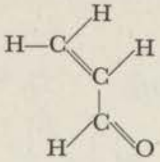
Sound absorption and velocity values for butadiene and isoprene.

T (° C)	ν (MHz)	10.38	30.06	50.24	192.5	$10^{-5}c$ (cm sec^{-1})
	$10^{17}\ \alpha/\nu^2$ (sec^2 cm^{-1})					
-24.8	Butadiene	114	116	110	104	1.201
-24.6	Isoprene	—	54.7	53.7	55.5	1.302
-5.0	Isoprene	—	56.9	55.0	54.5	1.195
$+14.8$	Isoprene	(55)	59.3	58.0	57.8	1.095

Only in butadiene at -25° C there is a sign of incipient relaxation at high frequencies. The characteristic frequency is evidently greater than 200 MHz which indicates a comparatively low $\Delta H_2\ddagger$ value. It is reasonable to assume that low stability of the s-cis isomer, due to steric interaction of the rigid $=CH_2$ groups, is partly responsible for this. Thermal measurements in gaseous butadiene (Aston, Szasz and Brickwedde, 1946) have shown that the activation energy of the reverse reaction ($\Delta H_2\ddagger$) is of the order of 2.6 kcal/mole, which is approximately half the value found for acrolein.

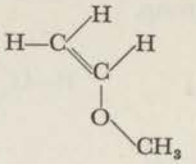
§ 3.6. Vinyl alkyl ethers

In Chapter I it was suggested that the experimental evidence of ultrasonic relaxation in esters may be attributed to perturbation of an equilibrium between rotational isomers. We know that this mechanism is responsible for the anomalous ultrasonic behaviour of α-β-unsaturated aldehydes. It is of interest to compare the chemical structure of both classes of compounds with that of vinyl alkyl ethers.

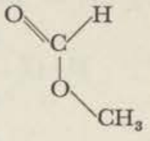


Acrolein

ν_c = 176 MHz at 25° C



Methyl vinyl ether



Methyl formate

ν_c = 0,35 MHz at 25° C

It may be noted that the structure of methyl vinyl ether is intermediate between those of acrolein and methyl formate. Hence if the suggestion concerning the esters is correct then it may be expected that vinyl alkyl ethers will also exhibit ultrasonic relaxation. Three compounds of this type were put to the test. The absorption values and relaxation parameters are given in figure 3.16 and table 3.7.

Table 3.7.

Relaxation parameters and sound velocity values for a number of vinyl ethers.

Liquid	T (° C)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{\max}$
Methyl vinyl ether	—24.8	1.237	272	25*	217	3.64
Ethyl vinyl ether	—24.8	1.255	299	25*	200	3.75
	— 5.7	1.161	169	25*	344	3.37
2-Chloroethyl vinyl ether	—24.7	1.439	130	20*	305	2.85

* Assumed values

It is clear from this figure and this table that our expectations are confirmed by the experiments.

The characteristic frequency of methyl vinyl ether appears to be

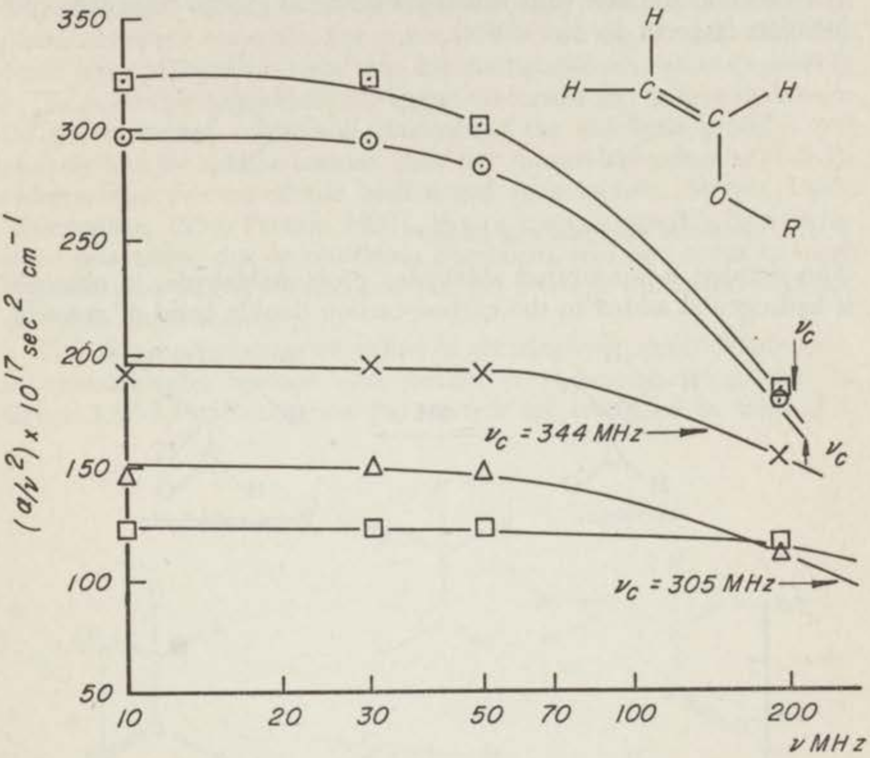
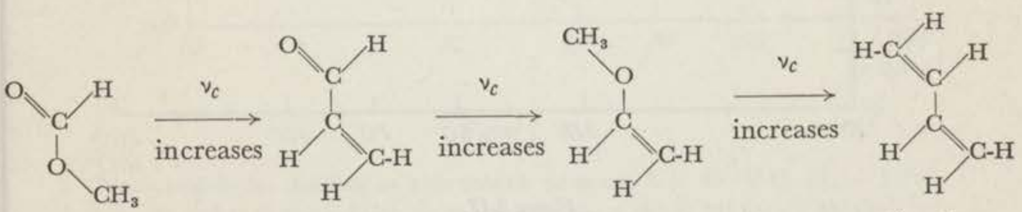


Figure 3.16.

Methyl vinyl ether ($R = CH_3$). ⊙,— 25° C. Ethyl vinyl ether ($R = C_2H_5$). ⊡, — 25° C: ×, — 6° C: □, 15° C. 2-Chloroethyl vinyl ether ($R = CH_2 — CH_2CL$). Δ, — 25° C.

considerably higher than that of both acrolein and methyl formate. With regard to this it is interesting to compare the following changes of chemical structure:



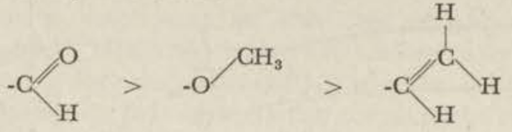
Methyl formate
$\nu_c = 0.35$ MHz
at 25° C

Acrolein
$\nu_c = 176$ MHz
at 25° C

Methyl vinyl ether
$\nu_c = 217$ MHz
at -25° C

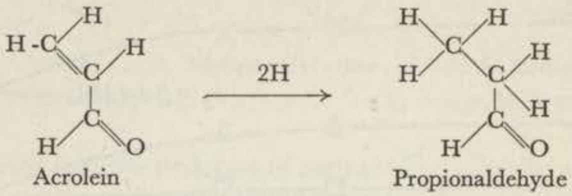
Butadiene
$\nu_c >> 200$ MHz
at -25° C

It seems that the ease with which the different groups enter into conjugation is given by the order:



§ 3.7. *Saturated aldehydes and ketones*

The simplest α-β-saturated aldehyde, propionaldehyde, is obtained if hydrogen is added to the carbon-carbon double bond of acrolein.



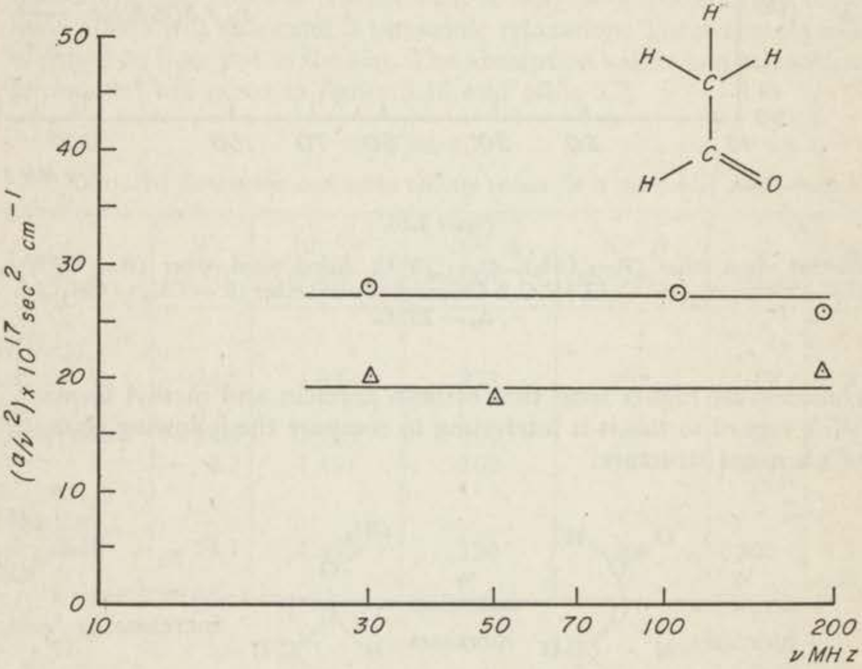


Figure 3.17.

Acetaldehyde: liquid treated with anhydrous Na_2CO_3 and distilled at atmospheric pressure: b.p. 20-21° C. Δ, — 25° C: ⊙, 15° C.

This "simple" addition of hydrogen actually involves a change in character of the molecule. For example, whereas the acrolein molecule tends to be planar, it is clear that this configuration is quite impossible in the case of propionaldehyde. Yet one is inclined to believe that, even for the saturated compound, rotation of the aldehyde group is not entirely free for similar reasons that the internal rotation of 1-2-dichloroethane or even ethane itself is not entirely free (Smyth, 1955; Miszushima, 1954; Pitzer, 1951). Hence it seems possible that ultrasonic relaxation, due to rotational isomerism, will also occur in some α-β-saturated aldehydes and ketones. An attempt was made to check this idea experimentally.

The ultrasonic absorption values of acetaldehyde, propionaldehyde, *n*-butyraldehyde, acetone and methyl ethyl ketone are plotted in figure 3.17-3.19. Relaxation parameters are compiled in table 3.8.

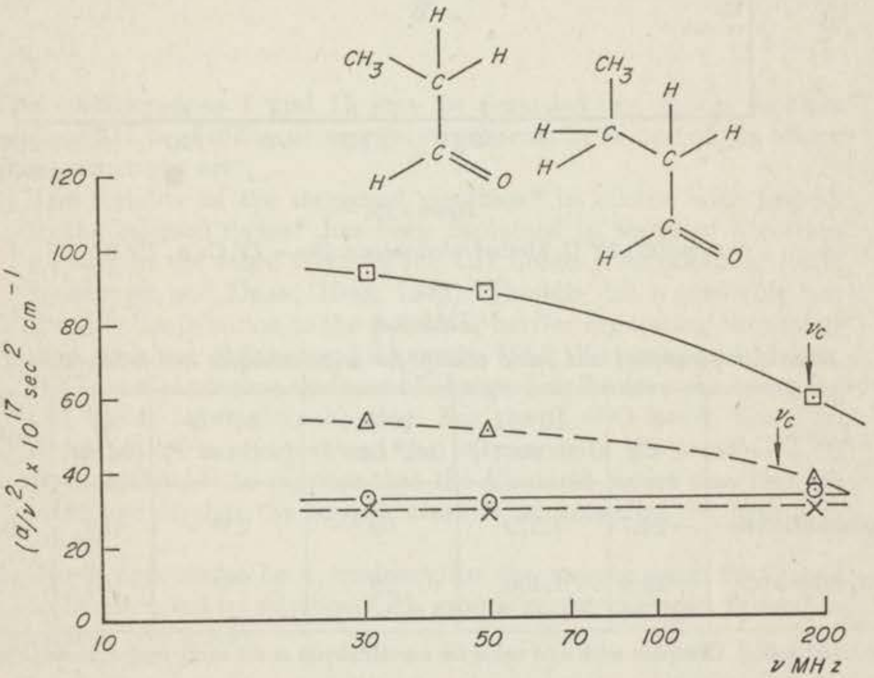


Figure 3.18.

Propionaldehyde: distilled at atmospheric pressure: b.p. 46-48° C. ⊡, — 25° C: ⊙, 25° C. *n*-Butyraldehyde: distilled in vacuo. △, — 25° C: ×, 25° C.

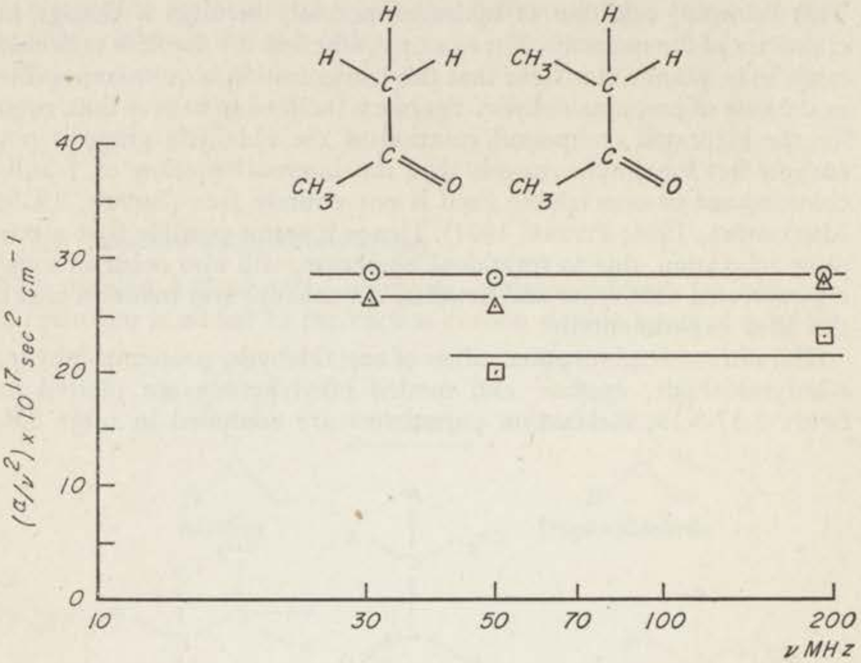


Figure 3.19.

Acetone: ⊙, 25° C. Methyl ethyl ketone: ⊡, — 25° C: △, 25° C.

Table 3.8.

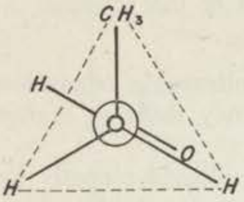
Relaxation parameters and sound velocity for propionaldehyde and n-butyraldehyde.

Liquid	T (° C)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{max}$
Propionaldehyde	— 24.7	1.379	69	25*	189	0.90
n-Butyraldehyde	— 24.8	1.406	29	25*	165	0.34

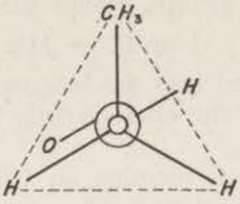
* Assumed values. Compare with α/ν^2 value for acetaldehyde at the same temperature (Fig. 3.17)

A decrease of α/ν^2 is observed for propionaldehyde and *n*-butyraldehyde only at —25° C and at high frequencies. The results of table 3.8 should be compared with those obtained for the corresponding unsaturated compounds acrolein and crotonaldehyde (table 3.2). Note that the characteristic frequency shifts to higher frequencies when the α-β double bond is saturated with hydrogen. This points to a decrease in potential barrier when conjugation between double bonds is no longer possible.

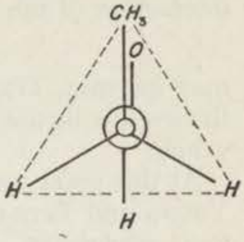
It is still a question which positions of minimum potential energy may be indentified with "rotational isomers" in the case of the saturated aldehydes. There are indications that these positions are as follows (for propionaldehyde):



I



II



III

The configurations I and II may be regarded as optical isomers whereas III is of different energy. Arguments in favour of the above given structures are:

1. The stability of the staggered positions* in ethane with respect to the eclipsed forms* has been explained in terms of a certain ionicity in the sence CH^+ of the CH bonds (Oosterhoff, 1951; Lassettre and Dean, 1948, 1949). Though this is probably not the only contribution to the potential barrier separating the staggered positions (Mason and Kreevoy, 1955; Kreevoy and Mason, 1957) it is clear that this sort of charge distribution will cause the CH bonds to repel each other. For the $C = O$ bond, however, the situation is reversed and the polarity is in the sense C^+O^-. It is reasonable to suppose that the Coulomb forces now become attractive so that the oxygen atom is attracted by the hydrogen atoms.
2. There appears to be a tendency for the oxygen atom in $C = O$ to be attracted by adjacent CH_3 groups as, for example, in methacrolein (see § 3.4).

Both effects tend to stabilise the above given configurations, in particular configuration III; they may very well account for the relatively high potential barrier which must be present in these com-

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* In the eclipsed form of ethane the distance between hydrogen atoms of different CH_3 groups is as short as possible. The staggered configuration is obtained from the eclipsed form by a relative rotation of 60° about the carbon-carbon single bond.

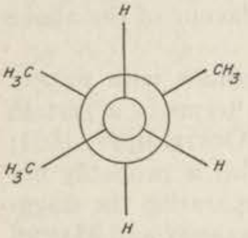
pounds. As far as ultrasonic relaxation is concerned I and II may be regarded as a single species in equilibrium with III. All three configurations are identical if CH_3 is replaced by H in accordance with the fact that no relaxation is observed in acetaldehyde.

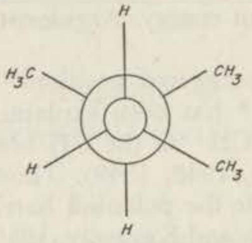
If the aldehyde H of propionaldehyde is replaced by CH_3 (methyl ethyl ketone) no relaxation is found any more. It is likely that this substitution leads to a reduced stability of I and II, owing to steric interaction of the CH_3 groups. Hence the speed of the reaction

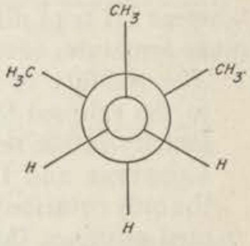
$$\text{I or II} \rightarrow \text{III}$$

may increase. Translated into the language of ultrasonic relaxation theory this means that the characteristic frequency shifts to higher values.

At this point we like to mention an article published recently by Young and Petrauskas (1956). These authors measured the ultrasonic absorption, at low temperatures, of saturated hydrocarbons (alkanes) and discovered relaxations similar to those given in this section. The respective positions of minimum potential energy are (for 2-methyl butane):







Activation energies ($\Delta H_2\ddagger$) of about 3.3 and 4.7 kcal/mole were reported.

§ 3.8. Absorption measurements on solutions of crotonaldehyde

Additional information concerning the molecular process that is involved in a particular ultrasonic relaxation can be obtained from measurements on solutions.

We used solutions of crotonaldehyde because the characteristic frequency lies in a convenient frequency range at 25 °C. Two solvents were chosen, the non-polar liquid *n*-hexane (ε * = 1.87) and the polar liquid acetone (ε * = 21.4). In each case the ultrasonic absorption was measured over the frequency range 10-200 MHz, for three different concentrations. The results are given in figures 3.20-3.21 and in tables 3.9-3.10.

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* ε is the dielectric constant

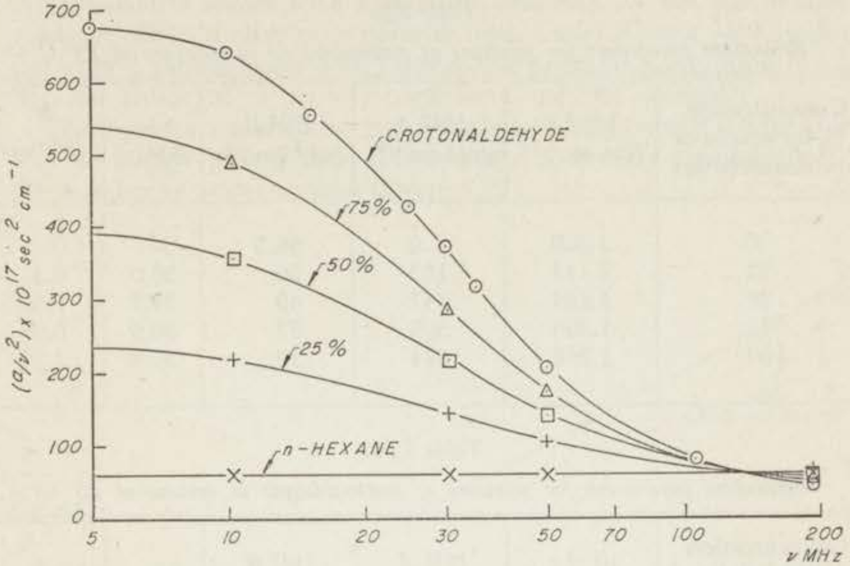

Figure 3.20.

Crotonaldehyde in *n*-hexane at 25° C: concentrations are given in % (by weight) of crotonaldehyde.

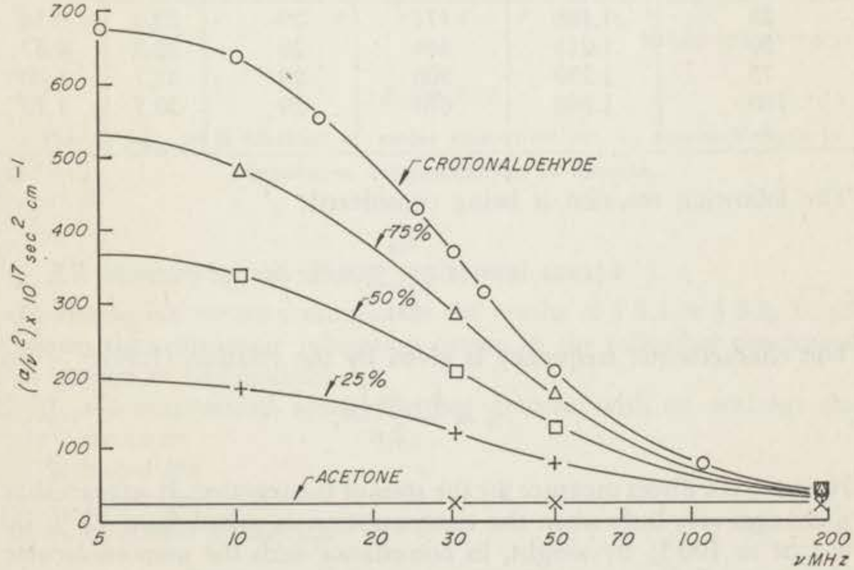

Figure 3.21.

Crotonaldehyde in acetone at 25° C: concentrations are given in % (by weight) of crotonaldehyde.

Table 3.9.

Relaxation parameters for solutions of crotonaldehyde in n-hexane at 25° C.

Concentration (% by weight of crotonaldehyde)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{\max}$
0	1.089	0	59.5	—	0
25	1.111	183	56	30.0	0.31
50	1.151	347	49	29.7	0.59
75	1.205	505	37	30.5	0.93
100	1,268	674	29	30.3	1.29

Table 3.10.

Relaxation parameters for solutions of crotonaldehyde in acetone at 25° C.

Concentration (% by weight of crotonaldehyde)	$10^{-5}\,c$ (cm sec^{-1})	$10^{17}\,A$ (sec^2 cm^{-1})	$10^{17}\,B$ (sec^2 cm^{-1})	ν_c (MHz)	$10^2\mu_{\max}$
0	1.161	0	28.4	—	0
25	1.188	171	29	33.3	0.34
50	1.215	344	29	32.1	0.67
75	1.239	508	29	31.7	1.00
100	1.268	674	29	30.3	1.29

The following reaction is being considered:

$$\text{s-trans isomer} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \text{s-cis isomer}$$

The characteristic frequency is given by the relation (1.54)

$$\nu_c \approx \frac{k_{12} + k_{21}}{2\,\pi}.$$

Hence ν_c is a direct measure for the *speed* of the reaction. It appears that ν_c changes very little when the concentration is raised from 25 % by weight to 100 % by weight, in accordance with the monomolecular character of the reaction*. The reaction is essentially governed by

---

* A different behaviour would be expected for the bimolecular reaction $A + B \rightleftarrows C + D$.

intramolecular forces with negligible influence by the surrounding medium. Even a change in polarity from $\varepsilon = 1.87$ to $\varepsilon = 21.4$ does not alter ν_c significantly. This justifies our previous assumption (§ 1.5) that the influence of activity coefficients may be ignored.

The maximum absorption per wavelength μ_{max}, which is a measure for the energy absorbed by the system, is directly proportional to the number of active centres (figure 3.22).

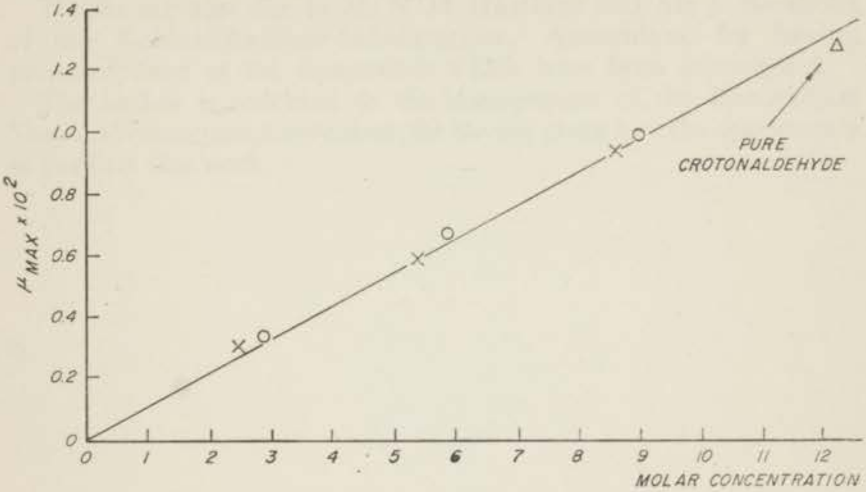

Figure 3.22.

Plot of μ_{max} as a function of molar concentration: ×, crotonaldehyde in *n*-hexane: ○, crotonaldehyde in acetone.

§ 3.9. *Summary of experimental results*

In conclusion we may summarize the results of § 3.4 to § 3.8. It was shown that ultrasonic relaxation occurs in the following compounds or groups of compounds:

1. α-β-unsaturated aldehydes and ketones with or without ring structure
2. butadiene
3. vinyl alkyl ethers
4. saturated aldehydes.

In all cases the observed relaxational behaviour was attributed to perturbation, by the sound wave, of an equilibrium between rotational isomers. The variation of relaxation parameters, as a function of chemical structure, could be explained satisfactorily on the basis of a decreasing or increasing potential energy barrier separating the isomeric states.

Additional information was obtained by investigating the properties of crotonaldehyde in solution. The characteristic frequency was found to be approximately independent of concentration in accordance with the monomolecular nature of the reaction between rotational isomers.

ACKNOWLEDGEMENT

The experimental work described in this thesis was carried out in the Electrical Engineering Department of the Imperial College of Science and Technology (University of London). The author wishes to express his gratitude to Dr J. Lamb for his advice and guidance during the investigation.

Thanks are also due to Mr N. M. Haafkens and Mr J. Boekholtz of the Koninklijke/Shell-Laboratorium, Amsterdam, for having prepared some of the compounds which have been investigated.

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SAMENVATTING

In dit proefschrift wordt het optreden van acoustische relaxatie in vloeistoffen beschreven. Deze relaxatie gaat bij geschikt gekozen frequenties gepaard met dispersie en vooral absorptie van geluid. Hierbij wordt mechanische energie omgezet in warmte, zodat dus irreversibele processen aan de relaxatie ten grondslag moeten liggen. De absorptie van een vloeistof blijkt in sterke mate afhankelijk te zijn van de inter- en intramoleculaire structuur.

In hoofdstuk I wordt nagegaan, welke oorzaken kunnen leiden tot de omzetting van geluidsenergie in warmte. Aangetoond wordt, dat de inwendige wrijving of viscositeit van een vloeistof één van deze oorzaken is. Ook het warmtegeleidingsvermogen is een vloeistofeigenschap, die aanleiding kan geven tot absorptie van geluid. Dit hangt samen met het feit, dat de voorplanting van het geluid een *bijna* volkomen adiabatisch proces is. Temperatuursverschillen, welke bestaan tussen gebieden van hoge druk en van lage druk hebben daardoor steeds een zeker warmtetransport tengevolge. Aangezien dit een irreversibel proces is, zal het leiden tot omzetting van mechanische energie, i.c. geluidsenergie, in warmte.

Het adiabatische karakter van de geluidsvoortplanting impliceert, dat in ieder punt van een geluidsveld de waarde van de temperatuur met de geluidsfrequentie oscilleert. Chemische evenwichten, die gevoelig zijn voor veranderingen van de temperatuur, kunnen op deze wijze worden beinvloed. Aangetoond wordt in hoofdstuk I, dat dit relaxatie tengevolge kan hebben, indien de snelheid, waarmede een evenwicht zich aanpast aan een temperatuursverandering onvoldoende is om de snelle temperatuursfluctuaties in het geluidsveld „bij te houden". Zeer mobiele chemische evenwichten kunnen aldus met behulp van ultrageluidsrelaxatie worden bestudeerd. Een aantal voorbeelden wordt gegeven in § 1.9.

In hoofdstuk II wordt aangetoond, dat bij de huidige stand van de experimentele techniek de geluidsabsorptie van vloeistoffen slechts nauwkeurig kan worden gemeten binnen een beperkt frequentiegebied (ca 1—250 MHz). Dit is een beperkende voorwaarde bij de keuze van het te onderzoeken probleem.

Verder wordt een experimentele methode, de impulsmethode, beschreven, die door ons werd gebruikt voor het verkrijgen van de in hoofdstuk III gegeven geluidsabsorptiewaarden.

In hoofdstuk III wordt aan de hand van uitgebreid feitenmateriaal duidelijk gemaakt, dat de zeer hoge geluidsabsorptie in een aantal klassen van organische verbindingen grotendeels het gevolg is van een verstoring door de temperatuursfluctuaties in een geluidsgolf van een evenwicht tussen rotatie-isomeren.

De eerste groep van verbindingen, waarvoor dit wordt aangetoond, wordt gevormd door de α-β-onverzadigde aldehyden en ketonen (§ 3.4).


s-trans s-cis

Acroleine

De boven gegeven vlakke structuren worden gestabiliseerd door resonantie; ze kunnen echter in elkaar overgaan door rotatie om de C1—C2 band. De energiebarrière, die beide vormen scheidt, is onvoldoende om chemische isolatie der beide vormen mogelijk te maken. Echter blijkt het werkelijk bestaan van bovenstaand evenwicht bijzonder duidelijk uit de geluidsabsorptiemetingen.

Uit de experimenten blijkt, dat een dergelijk soort evenwicht voorkomt in vinyl-alkyl ethers (§ 3.6)


Methyl vinyl ether

en in butadieen (§ 3.5).


Butadieen

Ook hier worden de configuraties links en rechts gestabiliseerd door resonantie.

Getoond wordt nog, dat ultrageluidsrelaxatie tengevolge van rotatie-isomerie zelfs kan voorkomen bij α-β-verzadigde aldehyden (§ 3.7).

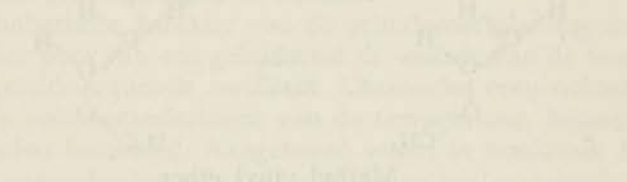
In verbinding (II) [illegible]

[illegible]

Acroleïne

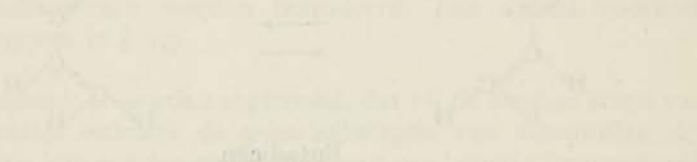
De beide gegeven starre structuren worden gestabiliseerd door resonantie; de laatste echter [illegible] door rotatie om de C—C-band. De energiebarrière, die beide vormen scheidt, is [illegible] om chemische isolatie der beide vormen mogelijk te maken. Echter ligt het evenwicht [illegible] duidelijk uit de gebruikelijke [illegible].

Uit de experimenten blijkt, dat een dergelijk soort evenwicht voorkomt in vinyl-alkyl ethers (§ 3.3)



Methyl-vinyl ether

en in butadieen (§ 3.7).



Butadieen

Uit het voorkomen de configuraties links en rechts gestabiliseerd door resonantie.

Overeenkomstig [illegible] de [illegible] van [illegible] bij [illegible] (§ 3.3).

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Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hieronder enige persoonlijke gegevens.

Nadat ik in 1945 de middelbare schoolopleiding (H.B.S.-B) te Leiden had voltooid begon ik in hetzelfde jaar met de studie in de Faculteit der Wis- en Natuurkunde van de Rijksuniversiteit te Leiden. Door persoonlijke omstandigheden moest deze studie in 1948 een jaar worden onderbroken. Het candidaatsexamen (natuurkunde en scheikunde met wiskunde) werd afgelegd in december 1949.

In de tijd tussen het candidaatsexamen en het doctoraalexamen was ik eerst assistent bij prof. dr E. Havinga (van 1 juli 1951 tot 1 januari 1952) en daarna bij prof. dr C. J. F. Böttcher (van 1 januari 1952 tot 1 april 1953). Het afleggen van het doctoraal examen (hoofdvak physische chemie, bijvak organische chemie) geschiedde op 29 september 1953.

Onmiddellijk hierna vertrok ik naar Engeland om daar gedurende een jaar te studeren aan het Imperial College of Science and Technology (Universiteit van Londen). Dit verblijf werd mogelijk gemaakt, doordat de Esso Development Company een beurs had verschaft. Onder leiding van dr J. Lamb werden ultrageluidsabsorptiemetingen uitgevoerd met behulp van een nagalmmethode. Een en ander werd vastgelegd in een „thesis", waarvoor het Diploma of Membership of the Imperial College in Electrical Engineering werd toegekend.

Vervolgens werkte ik gedurende een half jaar in het physisch laboratorium van de Universiteit te Leuven onder leiding van prof. dr A. J. F. van Itterbeek. De onderzoekingen, waaraan ik medewerkte, hadden betrekking op het Ramanspectrum van vaste waterstof en het meten van de geluidssnelheid in vloeistoffen langs optische weg. Gedurende deze periode ontving ik een toelage door bemiddeling van de Gemengde Technische Commissie van het Nederlands-Belgisch Cultureel Accoord.

Op 1 juni 1955 trad ik in dienst van het Koninklijke/Shell-Laboratorium, Amsterdam (N.V. De Bataafsche Petroleum Maatschappij). De Directie van dit laboratorium stelde mij in de gelegenheid nogmaals ruim een jaar in het reeds genoemde laboratorium van het Imperial College te werken. Het onderzoek, dat toen werd verricht onder supervisie van dr J. Lamb en in nauw overleg met de promotor prof. dr C. J. F. Böttcher, wordt in dit proefschrift beschreven.

STELLINGEN

STELLINGEN

I

De acoustische relaxatie, die door Lawley en Reed is gevonden in acetaldehyde bij circa 1 MHz, is het gevolg van verontreiniging met azijnzuur.

L. E. Lawley en R. D. C. Reed, Acustica **5**, 316 (1955).
Dit proefschrift, hoofdstuk III.

II

Waarschijnlijk zijn bij geluidsabsorptiemetingen boven 250 MHz aanzienlijk betere resultaten te verkrijgen indien:

a) van continue excitatie wordt gebruik gemaakt,
b) de lengte van de door het geluid af te leggen weg harmonisch wordt gevariëerd.

Het ontvangen signaal kan dan fase-gevoelig worden versterkt.

Dit proefschrift, hoofdstuk II.

III

De introductie door Parthasarathy en Guruswami van een gewijzigde Stokes-Kirchhoff formule voor de geluidsabsorptie in vloeistoffen wordt onvoldoende gemotiveerd, bovendien leidt deze gewijzigde formule tot onjuiste conclusies.

S. Parthasarathy en D. S. Guruswami, Ann. Physik **16**, 31 (1955),
Ann. Physik **16**, 287 (1955).

IV

De opvatting van Barrer en Stuart, volgens welke er een onzekerheid bestaat in de toepassing van de vergelijking van Clapeyron op het drie-fasen evenwicht

$$\text{gas} + \text{water} \rightleftarrows \text{hydraat},$$

vanwege het feit, dat het hydraat een niet stoichiometrische samenstelling heeft, is onjuist.

R. M. Barrer en W. I. Stuart,
Proc. Roy. Soc. (London) **242A**, 172 (1957).

V

Asymmetrische peroxyden kunnen door verhitting uiteenvallen in een groot en een klein radicaal. Volgens Vuillemenot, Messiet en Banderet bestaat er een groot verschil in reactiviteit van deze radicalen ten aanzien van de polymerisatie van acrylonitril en methylmethacrylaat. De argumenten, waarmee deze bewering wordt gestaafd, zijn onvoldoende.

J. Vuillemenot, J. Messiet en A. Banderet,
Compt. rend. acad. sci. **246,** 1042 (1958).

VI

De vermindering van de quantumopbrengst, die bij fluorescentie van oplossingen van fluoresceïne en thionine als gevolg van het toenemen van de concentratie wordt gevonden, is volgens Lavorel te wijten aan de vorming van een dimeer; de door hem verschafte experimentele gegevens rechtvaardigen deze uitspraak niet.

J. Lavorel, J. Phys. Chem. **61,** 1600 (1957).

VII

De dispersie van de diëlectrische constante, die door Rehfeld is waargenomen in mengsels van *n*-propylalcohol en koolstoftetrachloride tussen 10 en 14,5 kHz, moet volgens hem worden toegeschreven aan „netwerkvorming" van de moleculen; in feite zijn echter ionogene verontreinigingen de oorzaak.

K. Rehfeld, Naturwissenschaften **44,** 415 (1957).

VIII

Het onderscheid, dat von Stackelberg en zijn school tussen „Doppelhydrate" en „Mischhydrate" menen te moeten maken, berust op een onjuiste interpretatie van het thermodynamisch gedrag van gashydraten, waarin twee soorten gasmoleculen voorkomen.

M. von Stackelberg en W. Meinhold, Z. Elektrochem. **58,** 40 (1954).
M. von Stackelberg en H. Frühbuss, Z. Elektrochem. **58,** 99 (1954).

IX

Een ziektekostenverzekering behoort aangepast te zijn aan de maatschappelijke positie van de te verzekeren persoon. Indien zij eenmaal gesloten is, behoort zij niet wegens verandering van die positie door de verzekeraar te kunnen worden beëindigd.

X

Het is noodzakelijk, dat men komt tot een wijze van schifting, die de nodige waarborgen biedt, dat ongeschikte leerlingen niet op een school voor middelbaar of voorbereidend hoger onderwijs worden toegelaten.