A Kinetic Study of the Thermal Unimolecular Reactions of Some Small Ring Hydrocarbons.

by

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CHAPTER 1.

The Theories of Unimolecular Reactions.

A study of the kinetics of chemically reacting systems, a wide and rapidly expanding field of chemical research, has attained its prominence not solely because of the data it can provide concerning the rates of reactions. The subsequent application of these data can result in the elucidation of the actual mechanism of a reaction.

The first important attempt to provide a reasonable basic mechanism for any chemical reaction was made by Arrhenius[1] in 1889. He observed that the rate constant for the acid-catalysed inversion of cane sugar was strongly temperature dependent. Rate constants at temperatures T_1 and T_o were related by the equation

$$K_{T_1} = K_{T_o} \exp [A(T_1 - T_o) / T_1 T_o]$$

Arrhenius postulated the existence of an energy barrier between the reactants and products of a reaction, which had to be overcome. Only those molecules of the system with a high energy content were capable of reacting. These were referred to as active molecules. The application of the van't Hoff Isochore to the equilibrium existing between the active and inactive molecules led to a second order rate constant of the form:

$$K = A \exp(-q/RT) \qquad \text{Equation 1.}$$

where q is the heat of formation of the active molecules.

An early idea suggested that these active molecules obtained the extra energy by a collision process. It was soon pointed out, however, that this could not account for first-order reactions, a few of which had been observed, since the rate constant would then be dependent upon concentration. To overcome this difficulty the Radiation Hypothesis was developed by Perrin[2], Trautz[3] and W.C.M.Lewis[4]. They assumed that the absorption of almost monochromatic radiation of frequency E/h by an individual molecule, where E is the critical increment in energy and h is Planck's constant, was followed by dissociation. This being so, k would be independent of concentration, even at low pressures. An extension by Tolman[5] applied statistical mechanics to the rate of a chemical reaction. The derivation of an Arrhenius-type equation required two further assumptions. At all times the statistical state of maximum probability had to be maintained and also activation resulted from the absorption of an extended range of frequencies.

Simultaneously, criticisms of the Hypothesis were made. Examining the available experimental data, Langmuir[6] found that there was little evidence of absorption bands occurring in molecules which included a frequency corresponding to activation. He favoured an idea already suggested by Lewis[7] that the internal energy of the molecule was the source of the energy of activation.

In 1922 the foundation of many of the theories of unimolecular reactions, subsequently developed, was laid by Lindemann[8]. Completely discarding the Radiation Hypothesis, he returned to the belief that molecular collisions were the source of the energy required for reaction. He suggested that the internal motions of the molecule might occasionally carry it into an unstable configuration favourable for dissociation, in which rotation would cause the molecule to fly apart. The implication of this was that a time lag existed between collisional activation and dissociation. Provided that the concentration of gas was high, the chance of a molecule undergoing further collisions, causing deactivation, before an unstable configuration was attained, became appreciable. This produced a steady state of molecules being activated and deactivated by collision, with just a few reaching the dissociation configuration whilst energized. This being so, the number of molecules dissociating is proportional to the almost constant number of activated molecules present which in turn is proportional to the concentration of the gas, giving a first-order reaction. Lindemann predicted, on the basis of his mechanism, that at lower concentrations the rate would tend towards the second order. With fewer molecules present, the time between collisions would be comparable to the lifetime of the active molecules; most of these would then have a chance to dissociate, giving a rate dependent upon the collision of active molecules. This prediction was soon confirmed by studies of the decomposition of propionic aldehyde [9] and azomethane[10]. These, thought to be unimolecular reactions, showed a change to second-order kinetics at low pressures.

Lindemann did not attempt to show that the collision theory could produce a sufficient number of activated molecules to account for observed reaction velocities Christiansen and Kramers[11] maintained that neither radiation nor collisions were able to furnish a sufficient number of activated molecules. This disagreed with calculations by Rodebush[12], who, rejecting the Radiation Hypothesis, expanded the Lindemann theory to give a clearer picture of the unstable configuration. Activation of a molecule involved the acquisition of a certain critical energy within a specific degree of freedom by means of collision. The rate of reaction was not dependent upon the number of activated molecules present but was equal to the rate at which molecules acquired this critical energy. The theoretical equation which he derived for the rate constant gave good agreement with experimental data available for the thermal decomposition of dinitrogen pentoxide[13].

Lewis and Smith[14] agreed that collisional activation was possible, if the internal energy of the molecules as well as the translational energy was considered. This idea, upon which later theories were to depend for their success, was not pursued since it was shown at the same time that radiation was equally capable of producing a sufficient number of activated molecules. Weight was given to this by agreement with the experimental data for dinitrogen pentoxide.

The first important extension of the Lindemann theory came from Hinshelwood[15]. He pointed out that the number of molecules reacting in a system was much larger than was possible assuming the energy of activation confined to a few degrees of freedom. For propionic aldehyde the factor was 400. The probability of a molecule possessing a total energy greater than E after collision had, until this time, been set equal to exp (-E/RT) but, strictly speaking, this is only the probability of the energy being in two degrees of freedom. If there are 2n degrees of freedom the probability is approximately

$$\frac{(E/RT)^{\frac{1}{2}n-1} \exp(-E/RT)}{(\frac{1}{2}n-1)!} \qquad \text{Equation 2.}$$

which, for reasonable values of n, is much larger than exp (-E/RT). This development emphasised the significance of the complexity of the molecule in allowing a distribution of energy in several degrees of freedom. Using the results for propionic aldehyde it was found necessary to consider between 12 and 14 of the 24 degrees of freedom to account for the rate of reaction.

To calculate the number of molecules reacting, the dissociation rate constant was made proportional to the probability given by equation 2. An inherent assumption of this statement is that the rate constant is independent of the magnitude of the excess energy above the minimum energy E for reaction. The theory failed to produce an Arrhenius-type high concentration rate expression but gave an equation

$$d \ln k / dt = \left[E - (\tfrac{1}{2}n-1)\, RT\right] / RT^{2}$$

A similar treatment by Fowler and Rideal[16] led to the conclusion that, whilst activation by collision was not proved, it was a definite possibility. The weakness of their argument lay in the method of activation of the molecules. This led to the improbable consequence that a collision of two molecules with very little internal energy of their own but with a large energy capacity might result in almost complete transfer of energy to one of them.

Rice and Ramsperger[17] elaborated on the Hinshelwood theory and this was soon followed by a very similar treatment from Kassel[18]. The latter showed that, without modification, the theory leads to the equation for the first-order rate constant at any pressure p

$$k = \frac{k_\infty}{1 + \beta / p} \qquad \text{Equation 3.}$$

where k_∞ is the high pressure rate constant and β is a constant at any fixed temperature. If the theory holds over a wide pressure range a plot of 1/k versus 1/p should be linear. Slater (ref; 19 p.20) generalizes this in the form:

"Any theory dividing molecules into just two classes, those incapable of dissociation, and those capable of having a fixed specific rate, gives a linear relation between 1/k and 1/p."

Results for diethyl ether, dimethyl ether and azomethane definitely disagree with the requirements of the simple theory. They all produce plots showing considerable curvature. So, although the consideration of a reasonable number of degrees of freedom of a molecule is capable of accounting for the order of magnitude of reaction rates for most unimolecular reactions it is not able to account quantitatively for the variation of the specific rate constant with pressure.

In his theory Kassel envisaged a model in which the bonds of the molecule were treated as harmonic oscillators which, by means of small coupling forces, could pass energy from one to another. Classical mechanics was applied to the system. Dissociation occurred when one particular bond (two degrees of freedom) accumulated at least a certain minimum energy to cause its rupture. Further, the specific dissociation rate constant increased with the excess energy content of the bond above the minimum quantity. The main point of difference with the Rice-Ramsperger model was that they required only one degree of freedom to possess at least a certain minimum energy for reaction.

The Lindemann theory of unimolecular reactions may be represented by a three-stage mechanism as follows:-

$$A + M \xrightarrow{k_1} A^* + M \qquad \text{Activation.}$$

$$A^* + M \xrightarrow{k_2} A + M \qquad \text{Deactivation.}$$

$$A^* \xrightarrow{k_a} \text{Products} \qquad \text{Reaction.}$$

A denotes an inactive molecule that is, one which possesses insufficient energy to enable it to reach a reacting state, and A* is an activated molecule. If the conditions existing at the beginning of the reaction are considered, only pure reactant is present; the products are not yet formed in sufficient quantities to have any effect so that M can then by identified as any molecule of reactant gas. This condition places considerable restriction on any kinetic studies but it will be shown later that, certainly in isomerization reactions and apparently in decomposition reactions, the gradual change in M from reactant to product has no observable influence on the reaction at reasonable pressures. Volpe and Johnson[20] have suggested a means of analyzing any effects in the low pressure region.

The rate of production of activated molecules $d[A^*]/dt$ is given by the expression

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_a[A^*]$$

where the square brackets indicate concentration of the species. Assuming that a steady state of activated molecules exists

$$\frac{d[A^*]}{dt} = 0$$

or $$[A^*] = \frac{k_1[A][M]}{k_2[M] + k_a} \qquad \text{Equation 4.}$$

The rate of the unimolecular decomposition of A, $-d[A]/dt$

$$= k_{exp}[A]$$

where k_{exp} is the experimentally-determined rate constant. Since the rate of decomposition of A is equal to the rate of formation of products

$$-\frac{d[A]}{dt} = \frac{d[\text{Products}]}{dt}$$

but, from the reaction sequence

$$\frac{d[\text{Products}]}{dt} = k_a[A^*]$$

Thus $$k_{exp}[A] = k_a[A^*]$$

Substituting for $[A^*]$ from equation 4.

$$k_{exp}[A] = \frac{k_a k_1[A][M]}{k_2[M] + k_a}$$

or $$k_{exp} = \frac{k_a k_1 [M]}{k_2 [M] + k_a} \qquad \text{Equation 5.}$$

At high pressures, where the time between collisions is shorter than the lifetime of activated molecules, the majority of activated molecules are deactivated before they have chance to react. Under these conditions $[M] k_2 >> ka$, so that

$$k_\infty = \frac{k_1}{k_2} k_a \qquad \text{Equation 6.}$$

where k_∞ is the high concentration rate constant, and is independent of pressure. At very low pressures the rate of reaction becomes very much greater than the rate of deactivation

$$k_2 [M] << k_a$$

and $$k_{exp} = k_1 [M]$$

The experimental rate constant is dependent upon pressure and the reaction becomes second-order. This type of behaviour, which may be regarded as typical of a unimolecular reaction has been designated the name of "quasi-unimolecular". It follows that, at intermediate pressures the order of the reaction lies somewhere between first and second. The mathematical treatment confirms the predictions made earlier by Lindemann.

A mathematical expression for the overall rate constant, at a pressure sufficiently high to maintain the Maxwell-Boltzmann distribution of energy, can be obtained using equation 6. (k_1/k_2) and k_a are evaluated for a molecule containing energy in the range E to E + dE, where $E \geqslant E_o$, the minimum energy required per molecule for reaction to occur. The expression is integrated over all possible values of E from E_o to infinity.

k_a (E) is the specific reaction rate constant of molecules with total energy E. It can be shown (see, for example Ref.19 p 30) that the probability of one oscillator in a molecule having an energy greater than E_o when the molecule has energy in the range E to E + dE is proportional to

$$\left(\frac{E - E_o}{E}\right)^{s-1}$$

where s is the number of harmonic oscillators in the molecule. This is simply equal to the probability that the remaining (s-1) oscillators have an energy less than $E - E_o$. k_a (E) is proportional to this quantity or, introducing a proportionality constant, A,

$$k_a\,(E) = A\left(\frac{E - E_o}{E}\right)^{s-1} \qquad \text{Equation 7.}$$

Slater (Ref.19. p.31) compares the significance of A in the internal energy changes of a molecule to that of the effective collision frequency in over-all energy changes. $A\Delta t$ is the probability that, in time Δt, there is an internal energy change in the critical oscillator.

k_1/k_2 (E) represents the fraction of molecules having internal energy E in the s oscillators

$$\frac{k_1}{k_2}(E) = \frac{1}{\Gamma(s)(kT)^s} \cdot E^{s-1} \cdot e^{-E/kt}$$

Equation 8.

Substituting these values,

$$k_\infty = \frac{A}{\Gamma(s)(kT)^s} \int_{E_0}^{\infty} \left(\frac{E - E_0}{E}\right)^{s-1} \cdot E^{s-1} \cdot e^{-E/kT} \, dE$$

Repeated integration by parts, or identification of the integral with the gamma function leads to

$$k_\infty = A \exp(-E_A/RT)$$

where $E_A = N.E_0$. N being the Avogadro number. This is of the Arrhenius form and identifies A with the frequency factor of the Arrhenius equation.

At low pressures, equation 5 is used to derive an expression for k_{exp} in terms of quantities that can be measured. The treatment is similar to that at high pressures; k_1 k_2 and k_a are determined when an activated molecule has an energy in the range E to $E + dE$, $E \geqslant E_0$ and the final expression integrated over all possible values of E from E_0 to infinity.

At high pressures the assumption is made that the Maxwell-Boltzmann distribution of energies is maintained. This is tantamount to saying that only a small fraction of the activated molecules react, so that the rate of activation is almost equal to the rate of deactivation The latter quantity can be calculated from the kinetic theory expression for the number of collisions of activated molecules with other molecules, assuming deactivation at every collision. At low pressures this is no longer true since an appreciable number of activated molecules react. The rate of activation is in no way influenced by the rate of deactivation or the rate of reaction and this enables it to be set equal to the rate of deactivation which would exist if an equilibrium number of activated molecules were present.

k_a (E) and k_1/k_2 (E) are again given by equations 7 and 8 so that it only remains to determine an expression for $k_2(E)$, the rate constant for the deactivation of molecules with energy E. Approximately

$$k_2\,(E) \quad = \quad \lambda . Z$$

where Z is the collision frequency of the activated molecule and λ is a constant ($\leqslant 1$) which is equal to the fraction of activated molecules that are deactivated by collisions. As has been pointed out by Benson (Ref 21 P.233) this is a very rough approximation since it assumes that the rate of deactivation is independent of the internal energy of the colliding molecules. At high pressures λ should equal unity unless more than one collision is required to reduce an active molecule to an inactive state.

The collision frequency of activated molecules with all other molecules is, from the kinetic theory,

$$Z = \pi.\sigma^2\sqrt{\frac{8kT}{\pi.\mu}} \qquad \text{Equation 9.}$$

where σ is the collision diameter and μ the reduced mass. $[M]$ is set equal to the pressure of the gas, p.

Substitution of these various quantities gives the expression

$$k_{exp} = \frac{A}{\Gamma(s)(kT)^s}\int_{E_o}^{\infty}\frac{E^{s-1}\exp(-E/kT)\left(\frac{E-E_o}{E}\right)^{s-1}dE}{1 + \frac{A}{\lambda Zp}\left(\frac{E-E_o}{E}\right)^{s-1}}$$

Substituting $y = \dfrac{E-E_o}{kT}$

$$k_{exp} = \frac{k_\infty}{(s-1)!}\int_0^{\infty}\frac{\exp(-y)\,y^{s-1}\,dy}{1 + \frac{A}{\lambda Zp}\left(\frac{y}{y+b}\right)^{s-1}} \qquad \text{Equation 10.}$$

where $b = E_o/kT = E_A/RT$, E_A denoting the energy of activation of the reaction.

Representation of a molecule as a system in which the oscillators are classical, is not very accurate. Kassel[22] attempted to improve the approach to the problem by an extension of his theory, using the more elegant quantum approach, considering two possible models. In the simpler of these the molecule consists of s quantized oscillators, all of the same frequency ν coupled to each other by small forces. This is a necessary feature so as to permit transfer of energy between the oscillators. Reaction occurs when at least the energy $E_o = mh\nu$ accumulates in one critical oscillator, m being the number of quanta of energy.

Using statistics, Kassel showed that, if there are n quanta of energy in the s oscillators of a molecule, the probability that the critical oscillator contains at least m of them $(m < n)$, assuming that no reaction occurs and hence that equilibrium is established, is

$$b_n = \frac{n!\ (n - m + s - 1)!}{(n - m)!\ (n + s - 1)!}$$

so that the specific dissociation rate constant

$$k_n = Ab_n$$

A being a proportionality constant.

The probability that any molecule has n quanta of energy at equilibrium, assuming no reaction, is

$$f_n = \alpha^n (1-\alpha)^s P_n$$

where $\alpha = \exp(-h\nu/kT)$

and $P_n = \frac{(n + s - 1)!}{n! \; (s - 1)!}$

P_n is the statistical weight of a system of s degrees of freedom containing n quanta of energy. It is equal to the number of ways of distributing n indistinguishable objects in s boxes.

The high concentration rate constant k_∞ is found to be

$$\begin{aligned} k_\infty &= \sum_{n=m}^{\infty} k_n f_n \\ &= A\alpha^m \\ &= A \exp(-E_0/kT) \end{aligned}$$

The general rate constant

$$k = \sum_{n=m}^{\infty} \frac{f_n k_n}{1 + k_n/k_2[M]} \qquad \text{Equation 11.}$$

The second quantum model considers the case of s oscillators of frequency ν and r of frequency μ, where $\mu = \nu t$, t being an integer. Dissociation requires the accumulation of energy $mh\nu$ in one of the slow oscillators. This also leads to an Arrhenius-type high concentration rate constant. Slater

(Ref 19. p.28) points out that the only molecular model giving the Arrhenius rate is one containing a set of degenerate oscillators. The advantage of such a set is that it permits the interchange of energy which the dissociation model requires. Unfortunately, except in the case of complete degeneracy the general concentration rate constant becomes cumbersome, especially in the extreme but most realistic model of a set of oscillators whose frequencies are rational (but not all integral) multiples of the slowest and critical oscillator.

The theoretical work of Kassel and others was concerned primarily with the variation of the relative rate (k/k_∞) with concentration or pressure. The comparative simplicity of the approach would not permit an absolute estimate of the magnitude of k_∞ and, in particular, the pre-exponential A factor of the Arrhenius equation. It had been observed that the A factors for many reactions then thought to be unimolecular but subsequently shown not to be so were approximately 10^{13} $\sec^{-1}$, which is of the order of a vibrational frequency. Attention was focussed on this rather than on the differing energies of activation.

Polanyi and Wigner[23] in 1928 attempted to estimate k_∞. The work provided the nucleus around which the Slater theory was to develop twenty years later. The model that they used is a simple molecule consisting of equal masses in a linear chain. The distribution of the normal frequencies of vibration within it are estimated. The molecule dissociates when a link in the chain becomes excessively stretched. The length of this link varies as a sum of the different normal-mode vibrations; when all of the modes come into phase a critical stretch occurs. This leads to a high-concentration rate constant,

$$k_\infty = 1{\cdot}15\,\nu\,\exp(-E_0/kT) \qquad \text{Equation 12.}$$

where ν is the highest normal frequency. A continuation of this promising work had to wait because of the lack of a suitable mathematical treatment of phase effects and also because attention was diverted to rate calculations using a concept of flow over a critical surface in phase space, the precursor of the transition state theory.

In the development of the Slater theory the polyatomic molecule is seen as a system of classical harmonic oscillators. The high-concentration rate constant is derived in terms of the frequency with which the normal vibrations of these oscillators come sufficiently into phase to give a critical distortion of a molecular coordinate, which will be specified. The frequency is dependent upon the energies in the individual normal modes. The problem reduces in fact, to a relation between the rate constant and the time lag between the collision of a molecule and its reaction.

The n independent internal coordinates $q_1, q_2, \cdots, q_n$ which define the molecule, may be resolved into normal coordinates with frequencies $\nu_1, \nu_2, \cdots, \nu_n$. These are assumed to be independent so that the energies and phases of the different modes of vibration remain unchanged between collisions unless dissociation occurs. This is more rigorous than the Kassel treatment in which the light coupling between oscillators permits the flow of energy between them.

Dissociation of the molecule can occur if and when it has a particular critical internal configuration such that an internal coordinate q attains a critical value q_0. Between collisions any coordinate is expressed as a function of time by

$$q=\sum_{i=1}^{n}\alpha_i \sqrt{\varepsilon_i} \cos 2\pi(\nu_i t+\psi_i) \qquad \|\alpha_i\| \neq 0$$

The amplitude factor α is a constant, characteristic of the particular coordinate q which is being considered, and may be calculated from the force constants and kinetic energy coefficients of the molecule. This requires a full spectroscopic study and vibrational analysis of the molecule. ε_i is the energy and ψ_i the initial phase in the i th mode.

q can only reach the critical value q_o if

$$\sum_{i=1}^{n} |\alpha_i| \sqrt{\varepsilon_i} \geqslant q_o$$

which leads on to the result that the minimum total energy for dissociation E_o.

$$\frac{q_o^2}{\sum_{i=1}^{n} \alpha_i^2} \quad (\alpha > 0)$$

A molecule which has the energy E_o may not be "interesting" ie. likely to go on to dissociate at some time as the energy distribution may be unfavourable.

Assuming an equilibrium distribution of energetic molecules at high concentrations, the specific dissociation rate k of a molecule with internal mode energies $\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_n$, is equated to one half of the probability that an internal coordinate q reaches the critical value q_o (the factor $\frac{1}{2}$ is introduced since q can only approach q_o from values less than q_o)

Integration over the entire range of energies of the internal modes (0 to ∞) gives the expression

$$k_\infty = \nu \exp(-E_o/kT)$$

which is of the Arrhenius form, with E_o the minimum energy required for dissociation. ν may be calculated since it is a weighted root mean square of the normal frequencies of the normal modes and lies between the greatest and the least of them.

An equilibrium distribution is not maintained at lower concentrations where the general rate constant is given by

$$k = \frac{\nu \exp(-E_o/kT)}{\left(\frac{n-1}{2}\right)!} \int_0^\infty \frac{x^{\frac{1}{2}(n-1)}\exp(-x)dx}{1 + x^{\frac{1}{2}(n-1)}\,\theta^{-1}}$$

Equation 13.

where $\theta = \left(\frac{w}{\nu}\right) f_n \left(E_o/kT\right)^{\frac{1}{2}(n-1)}$

and $f_n = (4\pi)^{\frac{1}{2}(n-1)} \left(\frac{n-1}{2}\right)! \; \mu_1\mu_2\cdots\mu_n.$

The μ_i are related to the amplitude factors. The value of n cannot exceed the total number of normal modes of vibration in the molecule (3x-6 for a non-linear and 3x-5 for a linear molecule of x atoms), although it can be less either because q_o is a "symmetry coordinate" and will not be affected by some of the modes or because the effect of some modes on q_o may be so small as to be negligible.

A more realistic quantum mechanical treatment of the harmonic oscillator model by Slater produces rate constants at high, low and intermediate concentrations which all approach the corresponding classical forms at high temperatures. It requires an energy of activation at high concentrations which is temperature dependent and an A-factor involving a negative entropy of activation.

Slater has critically compared his theory with the RRK theory throughout its development. This has been further expanded by Gill and Laidler[24], in particular at the low concentration region. Before proceeding to give details of more recent theories it is informative to look at some of the points made in the comparisons.

A Lindemann-type mechanism provides the foundation of both theories, leading to essentially the same first-order rate constants at high concentrations and predicting a limiting low concentration rate equal to the rate of activation. The RRK second-order rate constant

$$= \frac{Z}{(s-1)!}\left(\frac{E_o}{kT}\right)^{s-1} \exp\left(-E_o/kT\right) \qquad \text{Equation 14.}$$

whilst for the Slater theory it is

$$Z\left(\frac{4\pi E_0}{kT}\right)^{\frac{1}{2}(n-1)} \prod_{k=1}^{n} \mu_k \qquad \text{Equation 15.}$$

For a given E_0 and s or n, the rate given by equation 15 is always less than that given by equation 14, a consequence of the necessary but not sufficient condition for reaction that the molecule has energy E_0, which reduces the rate of energization in the Slater theory. Whilst it may be valid to assume harmonicity of the oscillators at moderate pressures, there is justifiable reason to question this at very low pressures when the time between collisions becomes appreciably long. Even if the flow of energy between normal modes is very slow the interval may be of sufficient length for this to be appreciable. In view of the present knowledge of molecular vibrations, the restriction that the modes of vibration should be harmonic is unrealistic although insufficient grounds for discarding the theory. Gill and Laidler conclude that the approach is an accurate representation of the decomposition of activated molecules. It permits the calculation of the rate constant at any concentration once the energy of activation has been experimentally determined.

In the RRK theory s is estimated by a comparison with the experimental results to give the best fit, invariably leading to a value significantly less than the total number of degrees of vibrational freedom in the molecule. But since the theory does not take into consideration the various symmetries of the molecular vibrations and their respective effects upon the mode of reaction, this is not incompatible. Similarly n may be equal to the total number of modes of vibration but a value less than this is normally required for agreement. It is quite legitimate to ignore those having small values of ν and use a correspondingly smaller value of n.

The general rate expressions of the two theories can be equated if (y+b) in the Kassel integral is replaced by b, and f_n in the Slater theory is ignored. The equations are identical if

$$n = 2s-1$$

Slater quoting actual values (ref 19. p.175), considers the approximation to be reasonable but Schlag, Rabinovitch and Schneider[25] have evaluated the Kassel integral for four values of b and various values of s, compared the fall-off curves with those given by the Slater equation and found divergance from this relation for avalue of n less than 8. At about 18, n = s.

Both theories predict that for an increase in temperature fall-off of the unimolecular rate constant should commence at a higher pressure. Slater shows that the shift may be expressed as

$$\Delta \log p = \tfrac{1}{2} n \log (T_1/T_2) \qquad \text{Equation 16.}$$

Prior to the Slater theory of unimolecular reactions, a more fundamental approach to chemical kinetics had been made, which came to be known as the theory of absolute reaction rates or the transition state theory. Expanding a concept used by Marcelin[26] in 1914 that a rate may be considered as a flow over a critical surface in phase space, Eyring[27,28], the chief exponent of the theory, derived certain rate equations soon after 1930. These enabled the rate of a chemical reaction to be calculated using only the fundamental properties of the reactant molecules.

The transition state involves a critical intermediate configuration termed the activated complex, which occurs at the highest point of the energy path along which the reaction proceeds. The activated complex differs from the reactant molecules only in that motion in one direction, along the reaction coordinate, has no potential barrier and hence results in decomposition at a definite rate. Within the molecule a vibrational degree of freedom is replaced by translational motion.

The mathematical treatment of the rate of a reaction requires the application of quantum statistics and statistical mechanics to the system. The only necessary assumptions are that the rate of reaction is given by the rate of passage of activated complexes through the transition state and that an equilibrium distribution of activated complexes is maintained throughout the reaction. It is then possible to calculate, first, the potential energy content of the activated complex, second, the rate of passage of activated complexes over the energy barrier and third, the equilibrium concentration of activated complexes, by the application of statistical mechanics. The general equation for the rate constant is

$$k_r = \kappa \cdot \frac{kT}{h} \cdot \frac{Q^{\ddagger}}{Q} \cdot \exp\left(-E_0/RT\right)$$

Equation 17.

Q is the complete partition function of the normal molecule and $Q^{\ddagger}$ the partition function of the "modified" activated complex which excludes the reaction coordinate. Q can be calculated since such constants as the moment of inertia and the vibrational frequencies can be obtained from spectroscopic data. It is more difficult to estimate $Q^{\ddagger}$ although, in principle, it can be determined theoretically.

In a unimolecular reaction the translational degrees of freedom of the initial and activated states are identical and those for rotation and vibration will not differ greatly. $Q^{\ddagger}/Q$ then becomes equal to $1/f_v$, where f_v is the vibrational partition function of the reaction coordinate in the normal molecule. This reduces equation 17 to the Arrhenius form.

E_o can be identified with the experimental energy of activation of the reaction only if an account is taken of the difference between the zero-point energy of the reactant and activated complex. Generally this is small so that $E_o = E_a$.

κ is a transmission coefficient introduced to compensate for the possibility that some activated complexes, after crossing the energy barrier, may be reflected back instead of going to products. In most calculations κ is set equal to unity.

If $K^{\ddagger}$ is the equilibrium constant for activated and initial states, then

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q} \cdot \exp(-E_o/RT)$$

and substituting into equation 17

$$k_r = \kappa \cdot \frac{kT}{h} \cdot K^{\ddagger}$$

$K^{\ddagger}$ is also related to the standard free energy change of the process, $\Delta G^{\ddagger}$, by the equation

$$-\Delta G^{\ddagger} = RT \ln K^{\ddagger}$$

and since $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$$k_r = \kappa \cdot \frac{kT}{h} \cdot \exp(\Delta S^{\ddagger}/R). \exp(-\Delta H^{\ddagger}/RT)$$

which expresses the rate constant in terms of thermodynamic quantities. In practice $\Delta H^{\ddagger}$ can be identified with the experimental activation energy, $\Delta S^{\ddagger}$ is the entropy change accompanying the formation of the activated complex.

At approximately 300°c, $\frac{kT}{h}$ has a value of about 10^{13} sec^{-1}, of the order of a vibrational frequency. Because the rotational partition functions and the vibrational frequencies of the reactants and activated complexes for most unimolecular reactions are very similar, the theory predicts an A factor of the order of 10^{13} sec^{-1}. If $10^{13} \exp(-E_a/RT)$ is considered to be a 'normal' rate constant, $\exp(\Delta S^{\ddagger}/R)$ determines whether the reaction will proceed faster or slower than 'normal'. If $\Delta S^{\ddagger}$ is positive, corresponding to a more probable or 'looser' activated complex, the reaction proceeds faster than normal.

Slater (ref.19.ch.6) has adapted his harmonic model to consider the approach of the transition state theory. Employing classical mechanics, a high-concentration rate constant is obtained, corresponding to the basic formula of the theory, that is

$$k_{\infty} = \frac{kT}{h} \cdot \frac{Q^{\ddagger}}{Q} \cdot \exp\left(-E_0/RT\right)$$

A consideration of anharmonicity within the model introduces a saddle point, bringing it more into line with the activated complex.

In view of the success of the transition state theory as a means of calculating high-concentration rate constants, a suitable extension of it to a more general concentration is required. Trotman-Dickenson[29] regards this advance into a non-equilibrium region as a fundamental contradiction of the equilibrium postulate of the theory, an opinion which is opposed by Giddings and Eyring[30], who calculate the specific rate for the dissociation of activated molecules with total energy E using an equilibrium theory. It is necessary to assume that some sort of equilibrium exists between activated complexes and active molecules in order to derive a Rice-Ramsperger-Kassel expression.

Thiele and Wilson[31] have extended Slater's[32] high pressure classical unimolecular rate expression and Slater himself has used the transition state method on his classical harmonic model to consider the case of two simultaneous reaction coordinates.

Slater (ref.19.ch.9.) introduces a new approach to rate theory to provide a way of extending the transition state to general concentrations. The hypothesis that dissociation, like collision, is a random process, in quasi-unimolecular reactions is discarded. From a consideration of the life-time between activation and dissociation of a molecule, whose classical state can be defined precisely when it is activated, an equation is established for the general rate constant. This, at high concentrations, is identical to the equation from the transition state theory.

The absolute theory of reaction rates, which gives no consideration to the lifetime of molecules between activation and dissociation, would not appear to be suitable for extension to include a general-concentration rate constant but Slater regards his new rate as a correct generalization.

A more realistic theory is also presented by Slater (ref. 19. ch. 10) which combines quantum mechanics with the harmonic oscillator model. Marcus and Rice[33] have also developed a quantum mechanical transition-state formulation as an extension of the HKRR theory which permits the possibility excluded by the Slater theory of a large increase in entropy of the activated complex during its formation. The reaction sequence in the Marcus treatment[34] may be considered as:-

$$A + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_a} A^+$$

$$A^+ \xrightarrow{k_3} \text{Products}$$

in which A^* and A^+ denote the excited or active molecule and activated complex respectively, while M is any third body capable of deactivating A^*. Application of a steady-state treatment to A^* and A^+ leads to the equation

$$k_{uni} = \frac{k_a\,(k_1/k_2)}{1 + k_a/k_2 p} \qquad \text{Equation 18.}$$

where p is the pressure of the gas. k_a and k_1/k_2 are conveniently evaluated as functions of the energy of the active molecule A^*, considering a small energy range. k_{uni} is then obtained by an integration over all possible energies so that equation 18 is replaced by

$$k_{uni} = \int \frac{k_a \, d(k_1/k_2)}{1 + k_a/k_2 p} \qquad \text{Equation 19.}$$

$d(k_1/k_2)$ is the fraction of active molecules having energy within a specified range. The rate constant for deactivation, k_2, is assumed to be energy-independent and is equated to the kinetic theory collision frequency. If deactivation does not occur at every collision this has to be multiplied by an efficiency factor. The specific dissociation rate constant, k_a, is assumed to be proportional to the number of ways of distributing non-fixed energy among the degrees of freedom of the activated complex and of the active molecule.

The vibrational zero-point energy associated with A^* and A^+ together with the potential energy of the newly broken bond of the activated complex is 'fixed' within the molecule. The remaining 'non-fixed' energy of the active molecule and its activated complex, denoted by E^* and E^+, is available for distribution amongst their various degrees of freedom. $E^*-E^+=E_a$, where E_a is approximately equal to the strength of the breaking bond.

Using this method in which the number of ways of distributing the 'non-fixed' energy is evaluated, Marcus has developed equations for $d(k_1/k_2)$ and k_a. The combination of quantum mechanics the transition state theory and a sound knowledge of mathematical manipulations leads to a final general concentration rate equation:-

$$k_{uni} = \frac{kT}{h} \cdot \frac{P^+}{P} \cdot \frac{\exp(-E_a/kT)}{\Gamma(1 + r/2)} \cdot \int_{w=0}^{\infty} \frac{w^{r/2} e^{-w} dw}{1 + aw^{r/2}}$$

Equation 20.

in which $w = E^+/kT$. P^+ is the partition function for all degrees of freedom of A^+, excluding the internal translational motion along the reaction coordinate and P is the partition function for A. a is given by

$$a^{-1} = P_1 hk_2 p\Gamma(1+r/2)N^*(E_a)\sum_{E_i=0}^{wkT} D(E_i)/P_3^+$$

where P_1 is the partition function of the two rotational degrees of freedom of the active molecule possessing the larger moments of inertia whilst P_1^+ is the corresponding partition function for the activated complex. P_3^+ is the product of P_1^+ and the vibrational and rotational partition functions of the activated complex. $D(E_i)$ is the degeneracy of those degrees of freedom termed 'inactive', containing energy E_i in which transfer of energy to the breaking bond only occurs with sufficient rapidity when the molecule becomes essentially an activated complex. The energy is not available during the process of rupture. r is equal to the total number of rotational degrees of freedom of the molecule, regardless of degeneracy. $N^*(E_a)$ denotes the number of energy or quantum states per unit energy of the degrees of freedom with energy E_a which participate in intramolecular energy transfer. It is calculated by a classical treatment in preference to the extremely long computational method required by quantum mechanics. Unfortunately, this can give a considerable overestimate of the number of quantum states. Compromising methods of performing the calculation, which give a good estimate of the number of complexions, have been suggested which are comparatively rapid. Whitten and Rabinovitch[35] have simplified the quantum statistical calculation for molecules with low and moderate energies by grouping the vibrational frequencies into a small number of degenerate sets. For the majority of complex molecules considered, five such sets are sufficient to give an adequate representation to within a few per cent. Anharmonic corrections can be introduced into the calculation, a factor which has been shown by Thiele and Wilson[36] to be essential for a simple molecule. Schlag et al.[37] have confirmed this for the molecule CD_4 although the error involved with a complex molecule such as cyclopropane by ignoring anharmonicity is small.

Semi-classical approximations which can be introduced into the calculation have been described by Schlag and Sandsmark[38] and also by Lin and Eyring[39]. Both give good agreement with an absolute determination of the number of quantum states except when the energy of the system is small.

The main features in the development of the theories of unimolecular reactions have been briefly outlined in the preceding pages. The success or failure of any such theory is, of necessity, dependent upon agreement with the available experimental data. Within the region of the kinetics of unimolecular reactions, the availability of reliable precise information has been preceded by the theoretical progress, thereby creating a situation in which more than one theory is in agreement with the experimental results. The absence of any distinguishing criterion has led to this state of confusion. In retrospect, it is remarkable that the acceptance of the Kassel theory was mainly due to its good agreement with the data available for many reactions subsequently found not to be true unimolecular processes.

A unimolecular reaction which has received considerable attention is that of the thermal isomerization of cyclopropane to propylene, first studied by Chambers and Kistiakowsky[40] in 1934, and re-examined by Trotman-Dickenson[41] et al in 1953. An investigation over a wide pressure range revealed the predicted decline in the rate constant with a decrease in pressure. Slater[42] has applied his theory extensively to the isomerization, since the necessary vibrational data is available. A theoretical fall-off curve was obtained, having the same shape as the experimental plot. However, the theoretical absolute value of the pressure, for a given value of k/k_∞, was more than three times the experimental result.

The success of the theoretical and experimental studies of cyclopropane has prompted a vigorous programme of research involving many of its derivatives, in particular alkyl-and alkenyl-cyclopropanes, providing a prolific source of data. Similar studies on cyclobutane[43] and cyclobutene[44] have shown that these also undergo simple unimolecular reactions, thereby greatly extending the potential source of compounds.

The purpose of this research was to study the kinetics of the unimolecular reactions of certain cyclopropanes and cyclobutenes which, from an a priori consideration of their structures, might shed some light onto the complex problems surrounding the mechanism of unimolecular reactions.

The research was greatly assisted by the availability of modern analytical techniques and apparatus, enabling results of a reasonable precision to be obtained.

CHAPTER 2.

Description of Gas-Handling and Analytical Apparatus.

2.1. Pumping System and Gas Sampler

The general gas-handling high vacuum apparatus, constructed entirely of Pyrex glass, is shown diagramatically in figures 1 and 2. The two sections shown were supported either side of a rectangular 'bedstead' framework each being directly connected to the 20mm. internal diameter (i.d.) main backing line A. The pumping system, separated from A by an 8mm horizontal bore stopcock B, consisted of a two-stage mercury diffusion pump D surmounted by a 'cold finger' trap C and backed by a single stage rotary pump. Liquid oxygen was used as the coolant in C. With this system the pressure of the apparatus could be reduced to between 10^{-4} and 10^{-5}mm. The pressure of the vacuum line was measured by a Speedivac Model B4 Gauge connected to a Pirani head fitted at the B 14 socket P or by the McLeod Gauge.

The remainder of the apparatus shown in Figure 1 was used for the storage of liquids, the introduction of gaseous samples into the reaction vessel V and their subsequent removal for analysis.

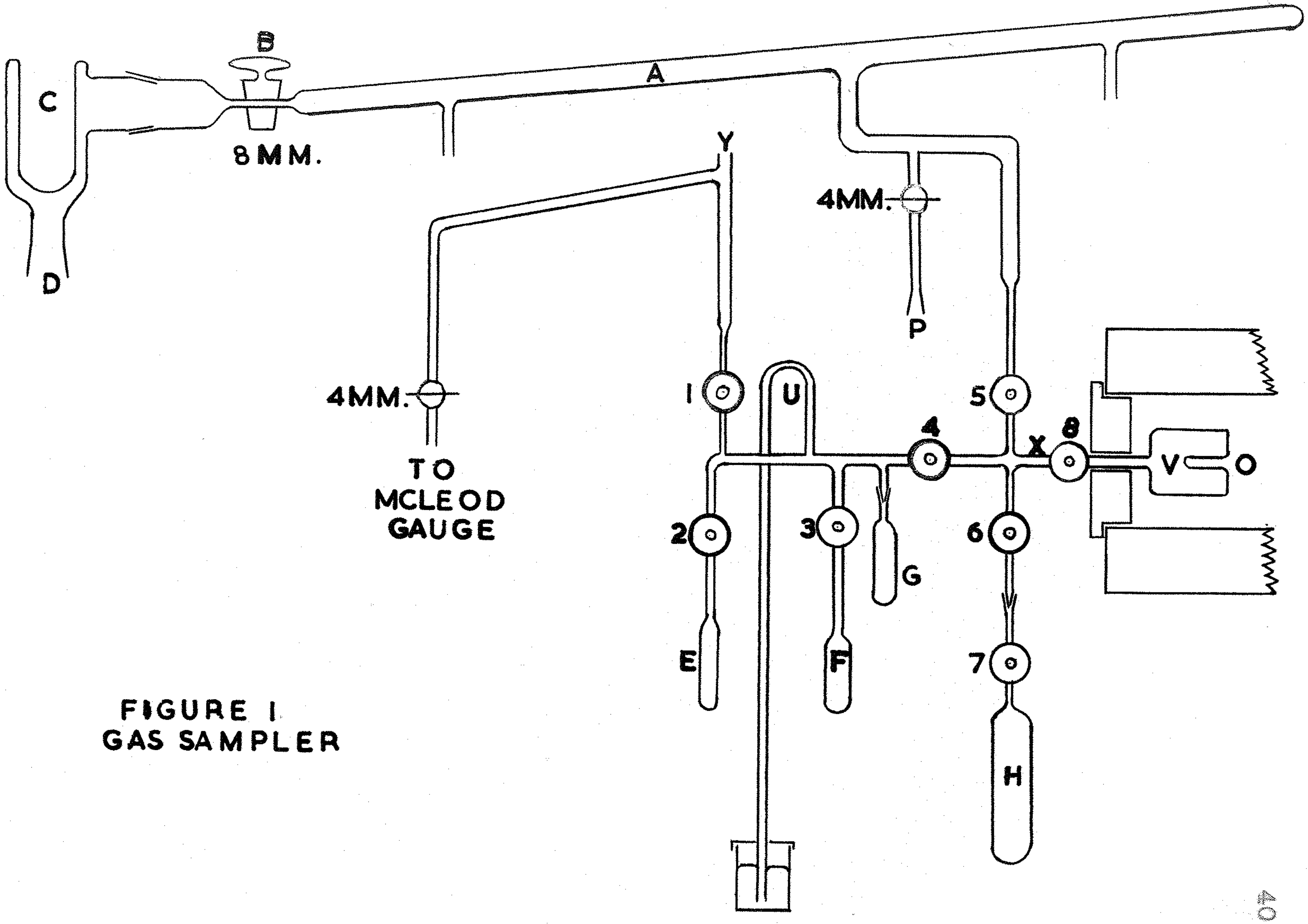


FIGURE I
GAS SAMPLER

Taps 1 to 8 were greaseless valves containing Viton A diaphragms. Their use eliminated the presence of any stopcock grease within this section of the apparatus and thus prevented the absorption of any vapour onto the taps. Tubes E and F were used for the storage of the liquids being studied. The B7 ground glass joint connecting the bulb G to the vacuum line was sealed with black wax. By varying the volume of G the size of samples introduced into the reaction vessel could be altered. After reaction, a gas sample was frozen from V into the gas pipette H (volume 150 ml.) cooled to -186°C in liquid oxygen. 2mm.i.d. capillary tubing was used within this section of the apparatus with the exception of the connection between valves 5 and 6 which was 4mm.i.d. tubing. By mounting valve 8 close to the side of the furnace or oil thermostat, the deadspace of the reaction vessel was reduced to only 0·2% of the total volume. The apparatus in this form was used for all kinetic studies apart from a modification (see section 2.7) during the investigation of the isomerization of 3-methylcyclobutene at pressures below 2mm.

2.2. Gas Sampling Procedure.

The following procedure was adopted when carrying out a typical kinetic run. With valves 4,5,6,7 and 8 open, the entire system was pumped down to a pressure of between 10^{-4} and 10^{-5}mm., as indicated on the McLeod Gauge (0·1 - 0·0001mm. range) or the Pirani Gauge. Valve 4 was closed and vapour of the liquid sample in either E or F allowed to expand into G until the mercury manometer U indicated the desired pressure. Valves 5 and 6 were closed and valve 4 opened so that the sample in G expanded into the reaction vessel. Simultaneously a stop watch was started. After 10 seconds valve 8 was closed, the pressure of the gas measured on the manometer and then valves 5 and 6 reopened.

The sample, after heating in the reaction vessel for the required time interval, was removed by closing valves 4 and 5, opening valve 8 at the appropriate moment and freezing into H immersed in liquid oxygen. 20 seconds was allowed for freezing before closing valves 6 and 7 and removing the pipette from the vacuum line. To reduce any fractionating effects, the pipette was then immediately flash heated in hot water to vaporise the sample.

The stop watch used for timing the kinetic runs was checked for its accuracy at regular intervals.

The watch was compared over a two-hour interval with the time signals broadcast by the BBC and regulated if necessary to give an accuracy better than 0·1%.

2 3 Vacuum Distillation Apparatus.

The apparatus shown in figure 2 was used for the purification of compounds. It was designed to permit the rapid transfer of larger quantities of vapours than in the gas sampling apparatus. The subsidiary backing line W was of 12mm. i.d. tubing. With the exception of the greaseless diaphragm valve 9 ground-glass stopcocks were used throughout. These had an oblique 4mm. diameter bore and were greased with Apiezon M. With the exception of the manometer, made of 2mm. i.d. capillary tubing, the remainder of the tubing had a 7mm. i.d.

The Podbielniak distillation column M was connected to the vacuum line via either stopcock 10 or the needle valve 11. The bulb N was capable of containing about 30ml. of the liquid being fractionally distilled, which was allowed to reflux under its own vapour pressure. The fractionating column K was a 50cm. x 4mm. i.d. tube. This contained a close-fitting spiral of 22 gauge nichrome wire with approximately 10 turns to the inch.

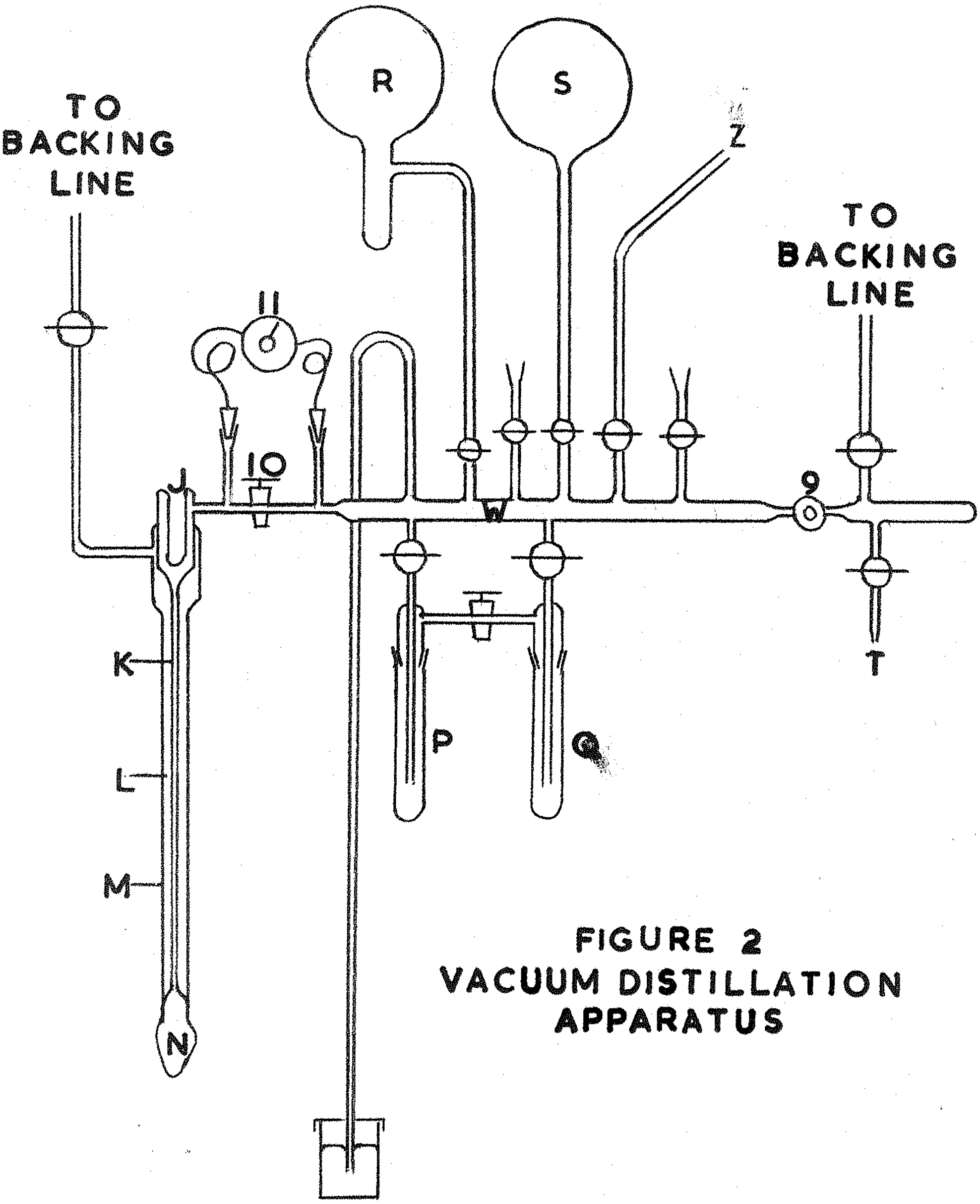


FIGURE 2
VACUUM DISTILLATION
APPARATUS

Surrounding it was a vacuum jacket L connected direct to the main backing line. At the top of the column was a 'cold-finger' trap J. Suitable coolants were selected for N and J so that a reasonable rate of refluxing was maintained without K becoming blocked with liquid. The fine control of the needle valve used in preference to tap 10 enabled vapour to be drawn off from the top of the column at a slow rate and frozen into P or Q. This was capable of giving a very high reflux ratio (as high as 100:1).

The progress of the distillation was followed by periodically freezing a sample of the distillate into a gas pipette connected at T and analysing it on the chromatographic apparatus. Purified product was transferred from P or Q to the gas sampling side of the apparatus via Y - Z.

Tubes P and Q were also used for trap - to - trap distillations from -78^{o}c to -186^{o}c as a means of purifying and degassing liquid samples.

R and S were 2-litre glass bulbs for the storage of non-condensable gases. They were not used throughout this work.

2.4. Apparatus for Preparing Mixtures of Gases.

The study of the effect of inert gases on the thermal isomerization of 3-methylcyclobutene required the preparation of mixtures of gases having a known composition. The apparatus used consisted essentially of a cylindrical vessel with a fixed volume of approximately 45ml , closed at either end by a diaphragm valve. This was surrounded by a water jacket whose temperature could be maintained to within 2° C of the laboratory temperature with an accuracy of ± 0·2° C. The vessel was connected to two liquid storage vessels (20ml. capacity), a 2-litre gas storage vessel and a 12mm. i.d mercury manometer. Diaphragm valves were used throughout. The pumping system was identical to that described in section 2.1.

Gas from one of the storage vessels was expanded into the fixed volume. After allowing 10 minutes for an equilibrium of temperature to be established, the pressure was measured on the manometer using a cathetometer The gas within the vessel was then frozen into a 500ml. storage container which was immersed in liquid oxygen and possessed a magnetically-operated paddle stirrer. By a repetition of this procedure a mixture of gases could be prepared. The contents of the storage container were flash heated and stirred for at least forty-eight hours before use to ensure that the mixture was homogeneous.

2.5. Temperature Control of the Furnace.

The cylindrical Pyrex reaction vessel V (fig.1) had a volume of approximately 150ml. It possessed a thermocouple well O. For kinetic studies in the temperature range 330-490°C the vessel was placed within an electrically-heated horizontal furnace. This was an insulated cylindrical tube 15cm. in diameter and 47cm. long with removable insulated covers. The heating element was wound round the exterior of the tube. The temperature of the furnace was maintained by a Sunvic Resistance Thermometer Controller Type R.T.2. A complete circuit diagram is shown in figure 3. The detecting element was a 10-ohm platinum resistance thermometer (2) mounted in one of the end covers close to the perimeter of the furnace (1). This formed one arm of a Wheatstone Bridge circuit which was used to operate a thermal cycling unit. The unit consisted of two similar bimetallic strips which operated a hot-wire vacuum switch, short circuiting the resistance R_1, and giving proportional control of the heating system.

The heating element of the furnace was fed from the mains supply via an A.C. voltage stabiliser.

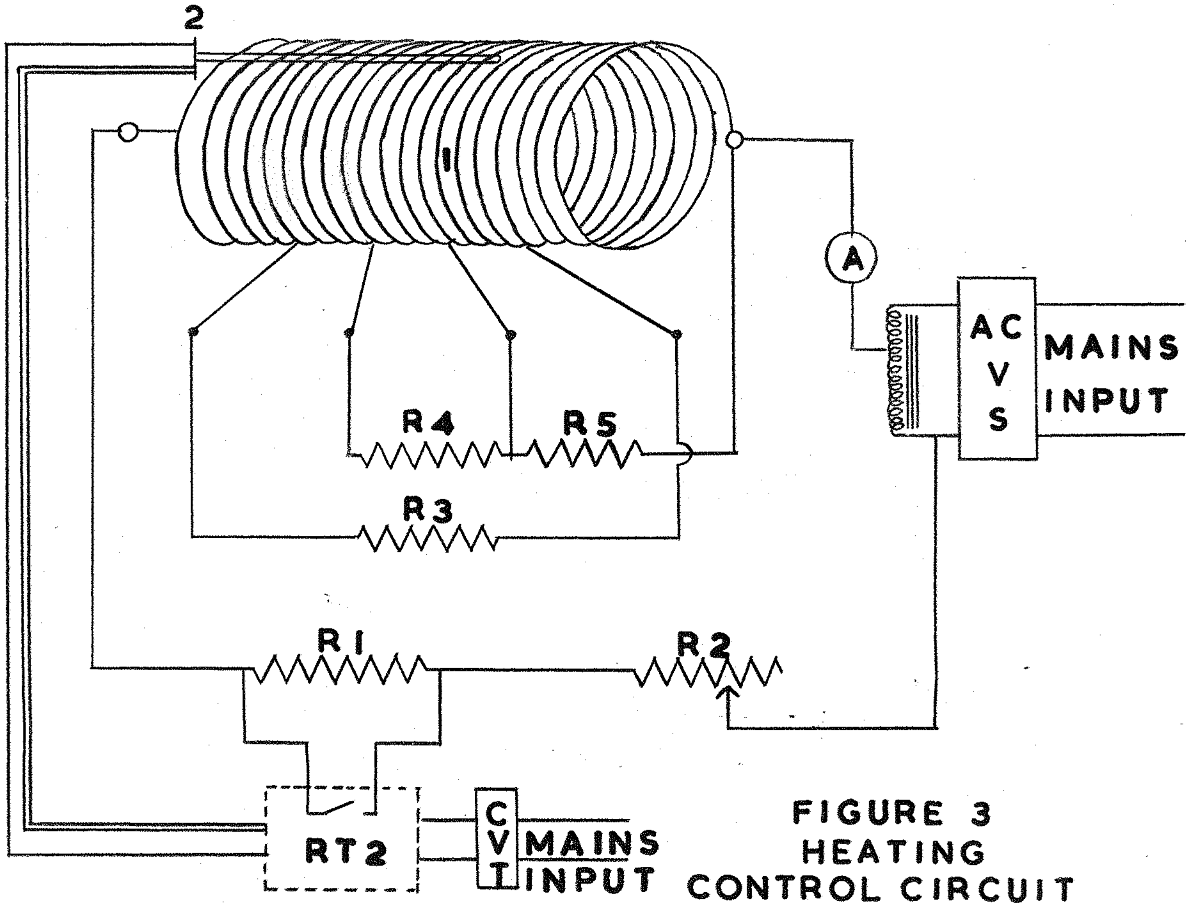


FIGURE 3
HEATING
CONTROL CIRCUIT

a Variac transformer and the resistances R_1 and R_2. At any particular temperature setting of the controller the Variac was adjusted to give an approximately equal on-off cycling time of the furnace current. The R.T.2 was able to control the temperature to within 0·1°C.

The furnace winding was tapped at four points along its length and resistances R_3, R_4 and R_5 shunted between them. By a suitable adjustment of these resistances the temperature gradient over the section of the furnace in which the reaction vessel was situated was only 0·3°C.

A platinum/platinum-13% rhodium thermocouple with compensated leads was used to measure the temperature of the furnace. It was inserted through the end of the furnace into the reaction vessel well O. A double cold junction was used which was immersed in water in a Dewar vessel. The temperature of the junction could be measured to within 0·1°C using a mercury-in-glass thermometer. The e.m.f. of the thermocouple was measured by a Tinsley Potentiometer Type 3387 B connected to a sensitive galvanometer (0·2µA/cm.) which could detect a temperature change of 0·1°C over the complete range. A cold junction connection was applied to the potentiometer reading before calculating the temperature of the furnace. The accuracy of the thermocouple had previously been checked by a calibration against a standard platinum resistance thermometer.

2.6. The Oil Thermostat.

The investigation of the thermal isomerization of 3-methylcyclobutene and 1.3-dimethylcyclobutene was performed over the temperature range 120-175°C. A high-temperature oil thermostat containing Ultra Therm 250 grade oil was used to maintain the temperature of the reaction vessel within this range. A 150 ml. spherical Pyrex bulb was used for sample pressures above 1mm although this was replaced by a 30ml. bulb when the pressure was increased above 15mm. These were mounted vertically in the oil bath. The oil was constantly stirred to maintain an even temperature distribution throughout. A mercury contact thermometer immersed in the bath controlled the mean temperature to better than ± 0·02°C. It actuated a relay switch controlling the heating element. This cycling mechanism produced a short-term temperature fluctuation of ± 0·08°C but the mean temperature remained constant. The on/off cycling time of the heater was about one minute, considerably shorter than the time of a kinetic run and therefore of no consequence.

The temperature of the thermostat was measured by two mercury-in-glass thermometers covering the ranges 100-150°C and 150-200°C respectively. They were standardised against National Physical Laboratory calibrated thermometers.

The diaphragm valve fitted at the exit of the reaction vessel had a 2mm. bore. It was mounted immediately above the cover plate of the thermostat, reducing the deadspace to less than 0·2%. A 1mm. bore valve was used in conjunction with the 30ml. vessel so that it possessed about the same deadspace.

2.7. Low Pressure Apparatus

During normal kinetic runs in which the sample pressure was above 1mm. a time interval of 20 seconds was sufficient to obtain almost complete transfer of gas from the reaction vessel to the pipette through 2mm. capillary tubing. Whilst studying the isomerization of 3-methylcyclobutene, the pressure was varied down to 0·01mm. In order to maintain reasonable sample sizes a 1-litre reaction vessel was used over the range 0·01-1·0mm. This was mounted horizontally in the thermostat and the accompanying gas sampling system suitably modified as shown in figure 4. The reaction vessel V and gas pipette W into which the sample was frozen after reaction were connected by 12mm. i.d. tubing although the diaphragm valve 12 had a bore of only 10mm. This valve gave the reaction vessel a 0·4% deadspace. By using wide tubing a time of 20 seconds was still sufficient to obtain complete removal of the sample from the reaction vessel. The system was evacuated through valve 13 and samples introduced from G (fig.1) via valve 14. Two McLeod Gauges were connected to the apparatus for measuring the pressure of samples. A covered the range 5·0–0·1mm. The relative heights of the mercury columns were measured using the cathetometer and the pressure calculated. B, covering the range 0·1–0·0001mm., had a direct-reading scale. During kinetic runs the mercury column of the gauge not in use was maintained at its maximum height.

The sampling procedure required only a slight modification. When the system had been completely evacuated valve 13 was closed and, with valve 12 open, valve 14 opened to admit sample from G. At the same time the stop-watch was started. After 15 seconds valve 12 was closed, the mercury in the McLeod

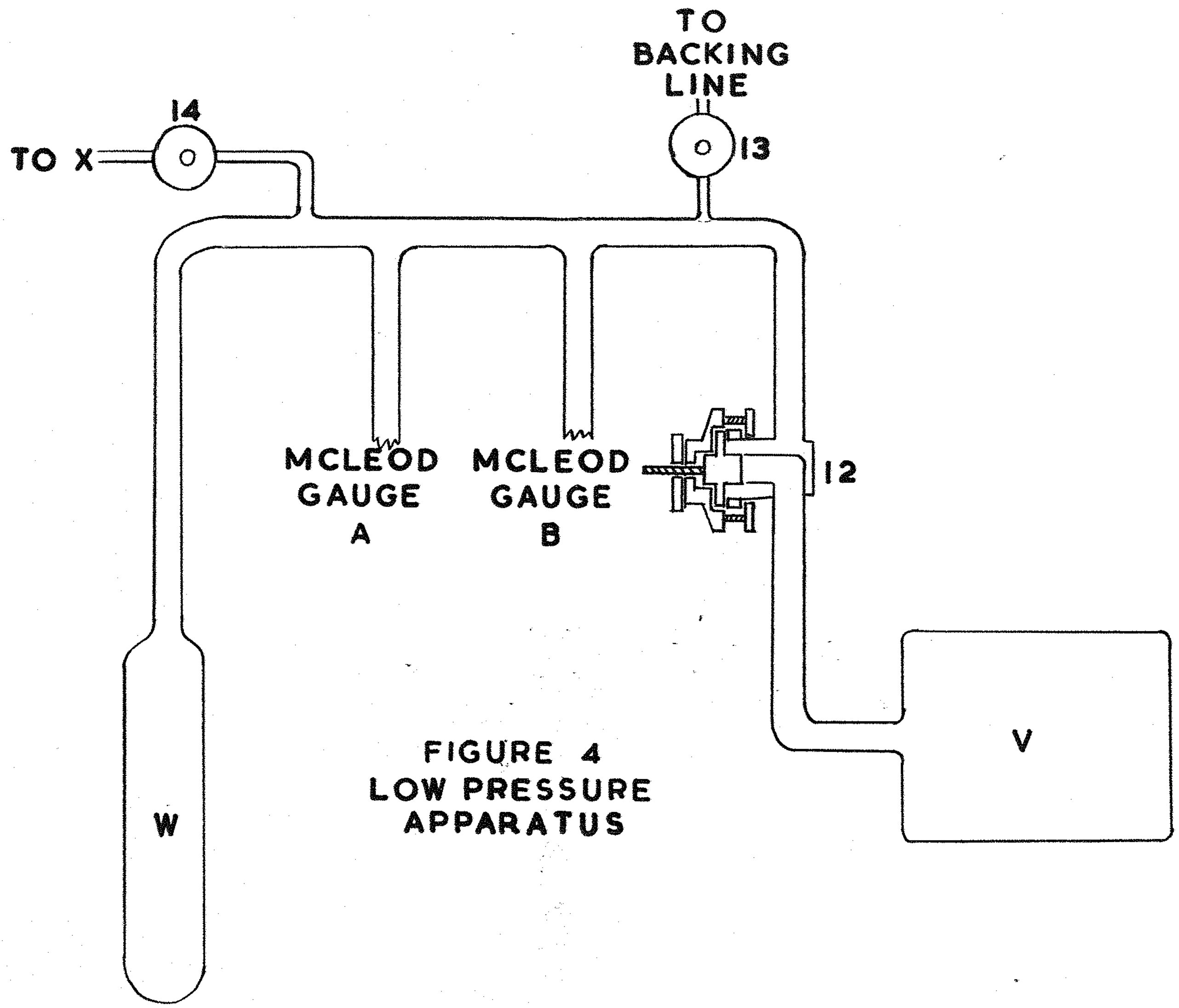


FIGURE 4
LOW PRESSURE
APPARATUS

Gauge raised to the required level valve 13 opened and the pressure measured. At the end of a run valves 13 and 14 were closed, 12 opened at the appropriate moment so that the sample was frozen into W immersed in liquid oxygen. After 20 seconds valve 12 was shut, valve 14 opened, W flash heated and the sample transferred through the capillary tubing to the gas pipette H immersed in liquid oxygen. Between 10 and 15 minutes was allowed for this.

2.8. Analytical Apparatus.

The technique of gas chromatography was employed for the analysis of reaction mixtures. The apparatus used in the first section of this research was the same as employed in earlier work[45], but various modifications were made in later stages which will be described below. The complete analytical apparatus is shown in figure 5.

Hydrogen was used as the carrier gas through the chromatography column. It was fed direct from the cylinder valve head through a rotameter (R) to the apparatus. With an inlet pressure of 8lb./sq.in. and the outlet at atmospheric pressure the flow rate, as shown on the rotameter, was about 25ml.per minute. After passing through the reference side of the

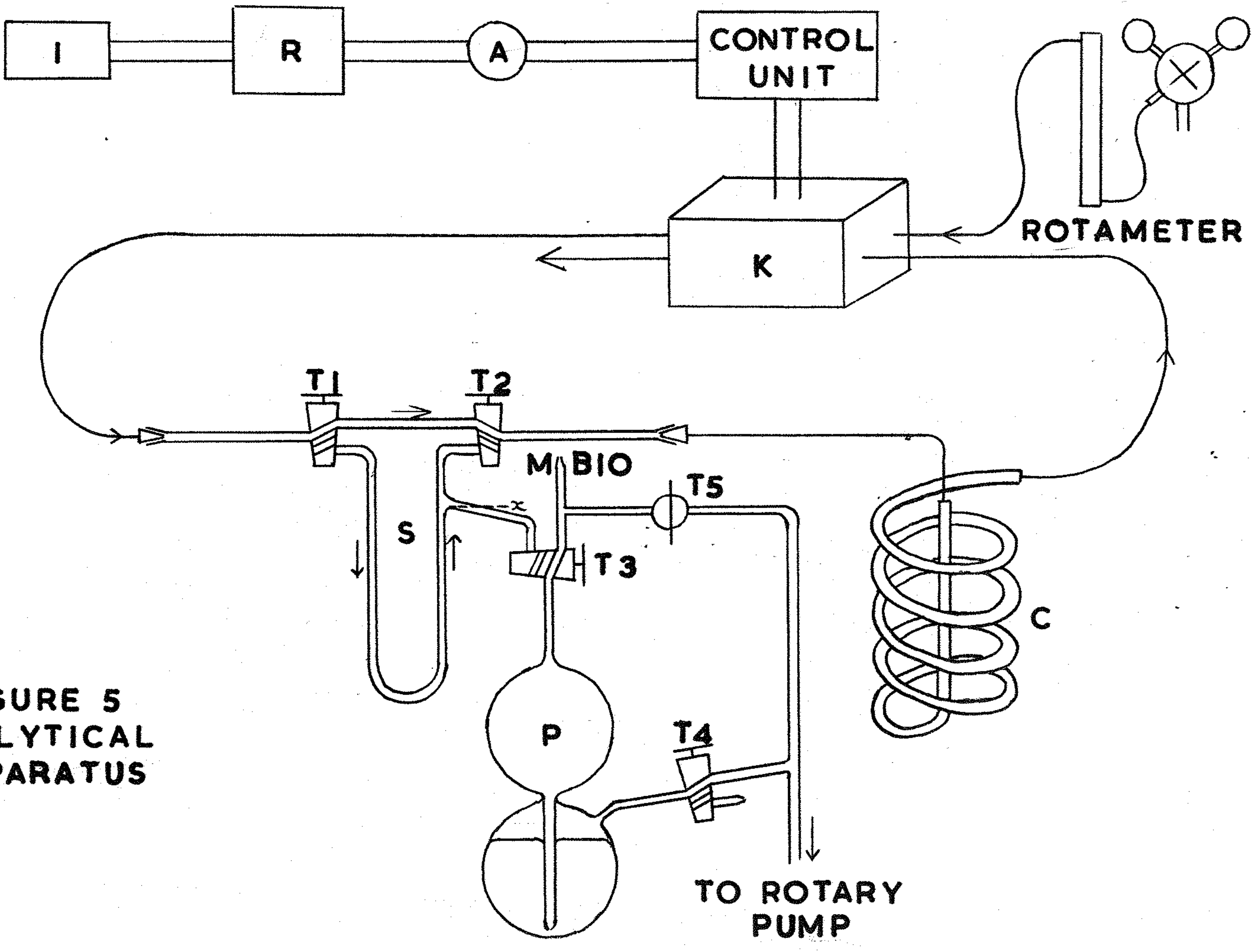


FIGURE 5
ANALYTICAL
APPARATUS

katharometer, the gas was directed either through the sampler S or along the by-pass, depending on the positions of taps T_1 and T_2, and thence into the chromatography column C. Finally the hydrogen passed through the detector side of the katharometer and out into the atmosphere.

A sample for analysis was transferred from the gas pipette inverted on the B10 cone M to S via the Toepler pump P. To prevent the retention of any sample on the taps T_1,T_2,T_3 and T_5 as well as the joint M, these were lubricated with a special fluorocarbon grease which did not absorb hydrocarbons appreciably. T_1 and T_2 were also spring-loaded to prevent their ejection by the pressure of the carrier gas. With these taps in the position shown, the U-tube of the sampler, having a volume of about 2.5ml.,was evacuated by sharing with the pump P three or four times. Tap T_5 was closed, the valve on the gas pipette opened and the sample shared with the pump. Taps T_3 and T_4 were rotated, causing mercury to rise into P and forcing the sample into S. If necessary this process could be repeated two or three times to get almost complete transfer of material. Finally the mercury was raised to the level x. When compounds were purified on the analytical column S was increased to 10ml. so that larger samples could be injected.

The gas sample was swept onto the chromatography column by turning taps T_1 and T_2 and letting hydrogen pass through S for about 20 seconds. The taps were then returned to their original positions. Sample sizes varied between 0·5 and 30 μ mole.

The detector used in the chromatographic system was a Gow-Mac Thermal Conductivity Katharometer K with tungsten filaments. A control unit, consisting of a Solartron transistor power supply unit Type No. AS 1200, capable of delivering 300m A at 8 volts powered the katharometer. This replaced an earlier control unit (see ref. 45) which used accumulators. During normal working conditions a current of 200 mA was used, 300 mA being used only when maximum sensitivity was required for very small samples. The sensitivity was adjusted by a 100 ohm ten-turn helipot inside the control unit. This also contained two 2 ohm ten-turn helipots, one having a low resistance in parallel with it, which acted as the fine and coarse controls for adjusting the base line of the recorder. The resistances on the reference and detector sides of the katharometer together with the fine and coarse controls, formed the arms of a Wheatstone Bridge circuit. Any change in the thermal conductivity of the gas flowing through the detector side of the katharometer compared to the reference side produced an out-of-balance e.m.f. in the circuit. This was displayed on the recorder R.

The signal from the katharometer was fed first through a variable attenuator A, a Tinsley Universal Shunt Type 3000. This enabled the signal transmitted to the recorder to be reduced if necessary by the factors 2 5,10 20,50 100 and 500. For the work on 1,1,2,2,-tetramethylcyclopropane, isopropenylcyclopropane and 1,2,3 -trimethylcyclopropane the signal was fed to a Sunvic R.S.P.2 recorder having a 0-1·0m V range. The areas of the peaks were integrated using a retransmitting slidewire fitted to the recorder which was connected to five accumulators. The signal produced drove a low-inertia dc motor (I) coupled to a revolution counter (see ref.45).

In the later work a Speedomax Type G recorder having 0-1·0 and 0-5·0m V ranges, was used in conjunction with a Perkin-Elmer Model 194 printing integrator. The retransmitting slidewire of the recorder produced a signal proportional to the position of the shaft driving the recorder pen. The signal voltage was compared to the voltage produced by a tachometer generator driven by a servo motor. Any voltage difference, after amplification, was fed to the motor, producing a change in the speed of rotation of its shaft and hence a change in the output voltage of the generator. A digital printing counter geared to the servo motor/tachometer shaft recorded the number of turns of the shaft which is proportional to the area beneath the pen trace At full-scale deflection the integrator gave 6000 counts per minute.

The chromatography columns were contained within 0·17"i.d. copper tubing wound into a spiral. The solid support was 40-60 mesh Chromosorb. Column B was 12 feet long and contained, as the stationary phase, 20% w/w of dinonyl phthalate. This was used for the kinetic studies of 1,3-dimethylcyclobutene. The remainder of the analytical work was performed on column A a 30 ft. column containing 20% w/w of di-2-cyanoethyl ether. Both columns had been made prior to the commencement of this work (ref.45).

Two columns were prepared containing a saturated solution of silver nitrate in ethylene glycol as the stationary phase. They were used as an extension to column A during part of the work with 1,2,3 -trimethylcyclopropane. One column was contained in a 6 ft. length of plastic tubing and the second in a 16 ft. x 0·17" i.d. copper spiral. 40-60 mesh Chromosorb was washed in acetone to remove any fine dust. 20% by weight of a saturated solution of silver nitrate in ethylene glycol was added to a slurry of the solid in acetone. After thorough mixing, the acetone was removed under reduced pressure. The plastic tube was suspended vertically, and suction from a water pump applied at the lower end which was blocked with a glass wool plug. Solid was added slowly from the top, tapping the column at frequent intervals to ensure an even packing. When filled, the ends of the tube were plugged with brass connections. The copper tube was filled in a similar manner although the spiral was extended to assist the operation and rewound when filled.

The components of the analytical system were linked by 1mm. i.d. copper capillary tubing fitted with $\frac{1}{4}$" diameter brass end pieces. The connectors were brass couplings with $\frac{1}{4}$" i.d. copper sleeves. Brass B10 cones and glass B10 sockets sealed with black wax connected the sampler to the system. The chromatography column was contained in a 6" diameter Dewar vessel, filled with water. Its temperature was regulated by a circulation of water from an external bath whose temperature was controlled to within ± 0·2°C by a Tecam Tempunit.

The exit tube from the sample side of the katharometer terminated in a B10 brass cone thus providing a link to an apparatus for trapping out samples from the gas flow.

Throughout all the analytical work the integrated area of each peak of the chromatogram was set proportional to the mole per cent of the constituent. The error introduced by this assumption is negligible for isomeric hydrocarbons since the determination of calibration factors has shown that, for such compounds, the values are almost equal to unity. The factors need only be used if the various constituents of a mixture being analysed differ considerably in their respective molecular weights. A correction to the data obtained during the kinetic investigation of 1,1-diethylcyclopropane was not considered necessary although the molecular weights of three of the components being analysed were 98 whilst that of the fourth (2-ethylbuta-1,3-diene) was 82. The relevant calibration factor would be close to unity.

2.9. Analysis of Liquid Samples.

Liquid samples from the preparative work were analysed on a Perkin-Elmer Model 451 Fractometer. They were injected into the carrier gas stream through a serum cap using a microlitre hypodermic syringe A 2 metre x ⅛"o.d. silicone column and a flame ionisation detector with nitrogen as the carrier gas were used for general analyses. The usual sample volume injected was 0·25 microlitre.

The fractometer was conveniently adaptable to preparative purification using a 6 ft. x 1"o.d. silicone column and a sample splitter. The latter allowed only a small fraction of the sample to pass through the hot wire detector. The carrier gas was nitrogen.

The purification of 1,3-dimethylcyclobutene was carried out on the machine, injecting ½ml. samples from a syringe. The product was frozen out of the gas stream by passing it through two 6 ft. x ¼"i.d. glass spirals immersed in liquid oxygen.

2.10. Infra-red Spectra of Gas Samples.

The gas phase infra-red spectra of compounds were obtained using a 5ml. gas microcell with a path length of 5cm. After evacuating the cell by connecting to the vacuum line, about 30mm. pressure of the sample was introduced. The analysis was performed on a Unicam S.P.200 Spectrometer, each spectrum being calibrated using the absorption bands of polystyrene at 1029, 1603 and 2851cm^{-1}.

2.11 Mass Spectra.

Mass Spectra of gas samples were obtained using a Metropolitan-Vickers MS3 Spectrometer. The machine was calibrated up to a mass-to-charge ratio of 96 using samples of 1-methyl-1-cyclohexene and toluene. By a comparison of the spectra with those published by the American Petroleum Institute (API), a calibration graph of (m/e) against the magnet current (milliamps) was plotted.

2.12. Nuclear Magnetic Resonance Spectrum.

The NMR spectrum of 1,1-diethylcyclopropane was obtained using a Varian Type A60 NMR Spectrometer.

CHAPTER 3

Preparation of Materials.

3.1. Preparation of 2,4-dimethylpent-2-ene.

2,4-Dimethylpent-2-ene was prepared by the reduction of di-isopropyl ketone to 2,4-dimethylpentan-3-ol, using the Meerwein-Pondorff-Veerley reaction followed by dehydration of the alcohol.

(a) Reduction of di-isopropyl ketone.

The ketone was reduced using a method described by Vogel[46]. Clean aluminium foil (13.8g.) and mercuric chloride (0.5g) were refluxed with 300ml. of isopropyl alcohol which had previously been dried by refluxing over calcium oxide for 30 minutes followed by distillation. When boiling, 2ml. of carbon tetrachloride was added and the mixture refluxed for eight hours. By this time all of the metal had dissolved. The solution was cooled and diluted to one litre with dry isopropyl alcohol to give an approximately half-molar solution of aluminium isopropoxide.

Di-isopropyl ketone (41g.,0.4mole.) was added to the solution of aluminium isopropoxide contained in a two-litre flask fitted with a 15 inch fractionating column packed with glass tubes. The flask was heated in an oil bath maintained at 115°C. This was sufficient to keep the temperature at the top of the column between 65 and 70°C thereby allowing the acetone produced in the reaction to distill off. The distillation was continued until four drops of the distillate, added to 5ml. of a 0.1% solution of 2,4-dinitrophenylhydrazine gave no precipitate after standing for thirty seconds.

The remaining isopropyl alcohol was distilled off under a slightly reduced pressure, the residue cooled to 40°C and 230ml. cold 6N sulphuric acid added slowly with constant cooling. Two liquid layers were formed, the upper one containing the alcohol. This was separated off, washed once with water and distilled at 80-90°C whilst the pressure was gradually reduced from 275 to 60mm., thus removing the remaining isopropyl alcohol.

The impure alcohol was obtained by distilling the remaining liquid at 30mm. pressure, collecting the fraction boiling between 80 and 85°C. The product was dried over anhydrous potassium carbonate, decanted and fractionally distilled through the 15 inch column maintained at 132°C by an external heating jacket. The alcohol boiled at 138°C at 764mm.(Lit.b.p.= 139°C) Chromatographic analysis on a 4ft. silicone column showed it to be almost pure. Yield = 30g. % Yield = 75%.

(b) Dehydration of the alcohol.

The alcohol (4.5ml.) was dehydrated by refluxing with 5ml. conc.sulphuric acid and 5ml.water. The fraction distilling from the top of the column below 90°C was collected. Further purification was achieved by a fractional distillation in vacuo using the Podbielniak column. The final product contained 5% of impurities.

An alternative method of dehydration, due to Robinson and Slater[47], required the formation of the xanthate by the Chugaev reaction. The alcohol (4.5ml.) and sodium (4g.) were refluxed in 30ml. dry toluene on an oil bath for five hours. The liquid was decanted from excess sodium, 80ml.dry ether added, followed by 4ml.carbon disulphide and 5ml methyl iodide. After refluxing for an hour on a water bath, water was added to the product in a separating funnel, the upper layer separated and dried over calcium chloride. The solvents, toluene and ether were distilled off and the remaining liquid heated under reduced pressure at 200°C in a flask fitted with an air-cooled reflux condenser. Vapour from the top of this was cooled in a water condenser and frozen into a trap immersed in a mixture of Drikold and acetone at -78°C. Analysis of the product on the chromatographic column A showed it to contain one main product and about 5% of a second product. (Lit.b.p. = 83.4°C).

3.2. Preparation of isopropenylcyclopropane.

Isopropenylcyclopropane was synthesised by reacting methyl magnesium iodide with methylcyclopropyl ketone to give, on hydrolysis, dimethylcyclopropylcarbinol. Dehydration of the alcohol produced the required isopropenylcyclopropane. Van Volkenburg et al.[48] used four different methods of dehydration and found that the best yield (80%) was obtained using conc. sulphuric acid.

(a) Preparation of dimethylcyclopropylcarbinol.

A 500ml. 3-neck round bottomed flask was fitted with a dropping funnel, glycerol-sealed stirrer and reflux condenser. Methyl iodide (22ml.) was added slowly to magnesium turnings (7g.) in 100ml. dry ether. The contents of the flask were stirred continuously during the addition. After refluxing for an hour and cooling, methylcyclopropyl ketone (20g) in 50ml.

ether was added slowly. followed by further refluxing for 60 hours. Addition of 30ml. of a saturated solution of ammonium chloride produced the alcohol in the upper ethereal layer. This was separated washed with water and the ether distilled off. The alcohol was dried over anhydrous sodium sulphate, decanted and distilled under reduced pressure. 19.4g. of the alcohol was obtained (78% yield).

(Lit.b.p. = 123.4°C).

(b) Dehydration of dimethylcyclopropylcarbinol.

One drop of conc. sulphuric acid was added to 10g. of alcohol in a 100ml. flask attached to a 15 inch packed fractionating column, still-head and water condenser. The column was surrounded by an electrically-heated air jacket maintained at 60°C. The liquid was gently refluxed, collecting the portion distilling between 65 and 75°C. This was further purified by fractional distillation in a Podbielniak column at -10°C. giving a final product which was better than 99.5% pure.

Boiling point = 70°C (Lit.b.p. = 70.3°C).

Yield = 6.0g. (73%).

3.3. Preparation of cis-and trans-1,2,3-trimethylcyclopropane.

1,2,3-trimethylcyclopropane was prepared by the bromination of 3-methylpentan-2,4-diol using a method suggested by Bartleson et at.[49]. Ring closure was by a modification of the Gustavson reaction in which bromine was eliminated with zinc dust. At first aqueous n-propyl alcohol was used as a solvent for the reaction but this gave a very poor yield of product. Repetition of the experiment, using dioxan instead, was more satisfactory.

(a) Bromination of 3-methylpentan-2,4-diol.

A 1-litre 3-neck flask, fitted with a mercury-sealed mechanical stirrer, a -50 to 0°C thermometer, calcium chloride tube and dropping funnel, was immersed in a lagged beaker containing Drikold and carbon tetrachloride. The diol (100g.,0.86mole.) and 50ml. chloroform (added to reduce the viscosity of the mixture on cooling) were stirred and cooled to -24°C. 61ml. phosphorus tribomide (0.63mole.) was added dropwise at a rate such that the temperature in the flask remained below -15°C. This took almost 8 hours. Stirring was stopped and the contents allowed to warm to room temperature over a period of two days, giving an amber-coloured liquid. The liquid was allowed to stand for seven days by which time two layers had separated. The upper one, containing the dibromide, was separated, washed rapidly with two 200 ml. portions of ice water, dried over anhydrous sodium sulphate, decanted and distilled under reduced pressure. The yield was 106g. (51%).

(b) Reduction of 2.4-dibromo-3-methylpentane.

Dioxan was purified using a method given by Vogel (ref.46,p.175). 400ml. of the liquid was refluxed for 12 hours with 5.5ml. conc.hydrochloric acid and 40ml.water, whilst a slow stream of nitrogen was bubbled through the solution to sweep away any liberated acetaldehyde. The solution was cooled, potassium hydroxide pellets added slowly, with shaking, until no more dissolved. The dioxan was decanted, more potassium hydoxide pellets added to remove the adhering aqueous liquor, decanted and refluxed for 12 hours with excess sodium. The solvent was distilled off and stored under nitrogen.

A 500ml.3-neck flask was equipped with a 0-100°C thermometer, glycerol-sealed mechanical stirrer, reflux condenser and a dropping funnel. 100ml.dioxan was stirred with 30ml. water, 50g oxygen-free zinc dust (washed with N hydrochloric acid and water) and 90g. of the disodium salt of ethylenediaminetetraacetic acid.

After cooling to 0°C by immersing the flask in an ice bath, 2 4-dibromo-3-methylpentane (51g.) was added dropwise over a period of eight hours. The reaction mixture was then stirred at room temperature for 40 hours and the product separated by distillation, collecting between 56 and 75°C. The impure 1,2,3-trimethylcyclopropane was washed twice with ice-cold water and separated. It was further purified by cooling to -78°C in Drikold and acetone and adding bromine until a yellow colour persisted. The liquid was allowed to stand at 0°C for two hours, washed twice with ice-cold sodium carbonate solution, once with ice-cold water, dried over calcium chloride and fractionally distilled in a Podbielniak column at -25°C. Two fractions were collected, the first containing predominantly the trans-1,2,3-trimethylcyclopropane and the second most of the cis-isomer. Both fractions contained impurities. cis-1,2 3-trimethylcyclopropane was purified by gas chromatography using the analytical apparatus with column A. This was also used for purifying the trans-isomer but analysis on the column extended with a 16ft column containing, as the liquid phase, a saturated solution of silver nitrate in ethylene glycol, showed the compound to be still very impure. No further attempt at purification was attempted. (Lit.b.p. cis-,65-67°C; trans-,59.7°C.).

3.4. Preparation of 3-methylpent-2-ene.

Dehydration of 3-methylpentan-2-ol with conc. sulphuric acid or through the xanthate (see section 3.1 (b)) gave a complex mixture of olefins. 3-Methylpentan-3-ol was dehydrated by decomposing the xanthate formed using sodium hydride. Sodium hydride may be used in preference to sodium as it often produces a higher yield of product. (see reference (2)).

5g. of a 50% dispersion of sodium hydride in oil was washed three times with petroleum ether (80-100°C). To a stirred suspension of the hydride in 70ml. of ether was added dropwise 4.2g. of 3-methylpentan-3-ol. The mixture was refluxed for three hours and then treated successively with 7ml. of carbon disulphide and 7ml. of methyl iodide. After each addition the mixture was refluxed for three hours. Water was added slowly to dissolve the solid material, the ether layer separated, dried over anhydrous magnesium sulphate, decanted and the ether distilled off. The residual liquid was added dropwise into a 10ml. flask containing glass beads, heated in an oil bath to 260°C.

The flask was connected to a semi-micro fractionating column and condenser. The olefins produced by the decomposition of the xanthate were collected in a tube immersed in a mixture of acetone and Drikold.

The product was fractionally distilled, collecting liquid distilling between 60 and 70°C. This contained about 90% of the cis-and trans-3-methylpent-2-ene. A third product, identified by its retention time on the chromatographic column, was 2-ethylbut-1-ene.

(Lit.b.ps. cis-,70.5°C. trans-,67.6°C.)

3.5. Preparation of 1,1-diethylcyclopropane.

Addition of dibromocarbene across the double bond of 2-ethylbut-1-ene, gave 1,1dibromo-2,2-diethylcyclopropane. The bromine atoms were removed by a reduction reaction used by Doering and Hoffmann[50] employing sodium and aqueous methanol, to give 1,1-diethylcyclopropane.

(a) Addition of dibromocarbene to 2-ethylbut-1-ene.

The method was the same as that used by Skell and Garner[51]. Potassium (20g.) was added to an excess of redistilled tert-butanol, heated in a flask fitted with a reflux condenser. The excess alcohol was distilled off under reduced pressure by heating the flask on a steam bath. The solid potassium tertbutoxide was broken up, the flask fitted with a glycerol-sealed stirrer, dropping funnel, caustic potash drying tube and a thermometer (0 to -50°C range). The apparatus was immersed in a lagged beaker containing Drikold and carbon tetrachloride at -24°C. After cooling the contents for 15 minutes, 2-ethylbut-1-ene (84g. 1mole.) was added and the mixture stirred rapidly until the temperature had fallen to -24°C. Then bromoform (90ml. 1mole.) was added over a period of 1 hour such that the temperature remained below -10°C. Stirring was continued for a further two hours and then the flask allowed to warm to room temperature. After adding 200 ml. petroleum ether (40-60°C fraction) and 300ml. water, stirring was recommenced until all the solid had dissolved. The ether layer was separated, the aqueous layer extracted three times with 20 ml. petroleum ether, the extracts combined, dried over anhydrous sodium sulphate and the ether and unreacted olefin distilled off.

Yield of unpurified dibromo compound = 236g.

(b) Reduction of 1,1-dibromo-2,2-diethylcyclopropane.

0.5mole. (128g.) of the dibromo compound was dissolved in 400ml. of ether, 150g. of sodium added together with 750ml. of methyl alcohol and 25ml. of water over a period of 3 days, followed by the addition of a further 400ml. of water. After shaking the solution, the ether layer was separated and distilled through a 2ft. packed fractionating column fitted with a Fenske distillation head until all of the ether had been removed. The residual liquid was fractionated in a semi-micro apparatus, collecting a fraction distilling between 80 and 89°C. Methanol and any water present in the sample were removed by the addition of powdered anhydrous calcium chloride. The liquid was decanted and further purified using a spinning band distillation column maintained at atmospheric pressure. Four fractions were collected over the temperature range 84-90°C the largest fraction boiling between 87 and 89°C. V.P.C. analysis on a silicone column indicated an 80% purity, there being one other compound present. The analytical column A was used for the final purification, giving a sample of 1 1-diethylcyclopropane with a purity better than 99.5%. (Lit.b.p. 88.7°C).

3.6. Preparation of 3-ethylpent-1-ene.

A contrathermodynamic isomerization of 3-ethylpent-2-ene, using successively hydroboration, isomerization and displacement, produced 3-ethylpent-1-ene.

Sodium borohydride and boron trifluoride diethyl etherate in diglyme solution were used for the hydroboration, a method given by Brown and Subba Rao[52].

(a) Hydroboration of 3-ethylpent-2-ene and isomerization.

A 500ml. 3-neck flask was fitted with a glycerol-sealed stirrer, pressure-equilibrated dropping funnel, nitrogen inlet and outlet. 3-Ethylpent-2-ene (20g. 0.2mole) in 50ml. diglyme (diethylene glycol dimethyl ether) and 90ml. of a molar solution of sodium borohydride (3.4g) in diglyme were poured into the flask. Freshly distilled boron trifluoride diethyl etherate (17g.0.12mole) in 25ml. diglyme was put in the dropping funnel. The complete apparatus was thoroughly flushed with nitrogen The liquid in the flask was stirred whilst the solution of boron trifluoride was added over a period of about one hour, at the same time cooling the flask in running water. The reaction mixture was left in the flask overnight. Then the stirrer was replaced by a condenser and the solution refluxed for an hour.

(b) Displacement of 3-ethylpent-1-ene.

Brown and Subba Rao[53] observed that the addition of an excess of a terminal olefin was capable of displacing a more volatile terminal olefin from an organoborane. 25ml. of 1-octene was poured into the flask equipped with a 2ft. fractionating column and Fenske distillation head. The flask was heated until the liquid was boiling vigorously. Diethyl ether separated off as the first fraction. The second fraction, boiling between 82 and 87°C, was collected over a period of 9 hours. V.P.C. analysis on a silicone column and on the analytical column A showed that the product was about 70% pure. Chromatographic separation was used to obtain a pure specimen of 3-ethylpent-1-ene which was used to obtain an infra-red spectrum in the gas phase. This was identical to the spectrum of an authentic sample, as published by the American Petroleum Institute (A.P.I.) (Lit.b.p. = 85°C).

3.7. Preparation of 2-ethylpent-1-ene.

A Wittig reagent or alkylidene phosphorane was used to convert the carbonyl group of a ketone ($>C=O$) into a carbon-carbon double bond ($>C=CH_2$) employing the experimental procedure of Greenwald et al.[54]. The reaction of methylenetriphenylphosphorane with ethyl n-propyl ketone produced 2-ethylpent-1-ene.

(a) Preparation of methylenetriphenylphosphorane.

Sodium hydride (0.033mole. 1.6g. of a 50% dispersion in mineral oil) was washed in a 100ml.3-neck flask with five portions of iso-pentane to remove the oil. The flask was fitted with a serum cap, a reflux condenser with calcium chloride drying tube and a nitrogen inlet. It was then immersed in an oil bath placed on an electrically heated magnetic stirrer and all air swept out with nitrogen. Dimethyl sulphoxide (17ml.), dried by distillation under reduced pressure from calcium hydride, was injected using a 10ml. hyperdermic syringe. The oil bath was maintained at a temperature of 75-80°C for 45 minutes and then the flask, containing the solution of methylsulphinyl carbanion, was cooled in ice. Methyltriphenylphosphonium bromide (11.9g.,0.033mole) stored in a vacuum desiccator, was dissolved in 35ml. of warm dimethylsulphoxide, and injected into the flask. The resulting dark red liquid was stirred for ten minutes at room temperature before use.

(b) Reaction with ethyl n-propyl ketone.

Freshly-distilled ethyl n-propyl ketone (4.0g. 0.038mole.) was added to the solution of methylenetriphenylphosphorane. When the liquid had been stirred for 30 minutes it was distilled under reduced pressure, collecting the distillate in a trap immersed in a Drikold-acetone mixture. This was fractionally distilled in a semi-micro apparatus, thereby obtaining a fraction boiling in the range 92-96°C The chromatogram of a sample using the analytical column A indicated a purity of approximately 65%. A sample which was purified chromatographically, was used to obtain the infra-red and mass spectra of the compound.

3.8. Preparation of 1 3-dimethylcyclobutene.

The irradiation of conjugated dienes as a suitable method of forming cyclobutene derivatives was suggested by Crowley[55]. A solution of 2-methylpenta-1,3-diene in iso-pentane was irradiated to give 1,3-dimethylcyclobutene.

(a) Dehydration of 4-methyl-4-pentene-2-ol.

Two drops of concentrated sulphuric acid was added to 50g. of 4-methyl-4-pentene-2-ol in a 100ml. round-bottom flask attached to a 2ft. packed fractionating column, surrounded by a heating jacket, and a condenser. The jacket was electrically heated to 60°C. The liquid in the flask was heated until boiling and then the rate of heating adjusted so that product distilled slowly from the top of the fractionating column. The product was redistilled, using a 10cm. Vigreaux column, most of the liquid distilling over at 76°C. Its V.P.C. analysis on a silicone column showed it to be almost pure.

Yield = 24g.(60%). Lit.b.p. = 76°C.(cis-and trans-).

(b) Irradiation of 2-methylpenta-1,3-diene in iso-pentane solution.

The light source for irradiation was a 500W medium pressure mercury lamp, contained within a water-cooled quartz jacket which, itself, was surrounded by a cylindrical Pyrex vessel fitted with a water-cooled double wall condenser. To ensure complete condensation of the volatile solvent during irradiation a Drikold-acetone trap was placed above the condenser. A 3ml. sample of the methylpentadiene was added to 250ml. of iso-pentane contained between the quartz and Pyrex jackets, and irradiated. 50μl. samples were withdrawn from the solution at regular intervals and analysed on a Perkin-Elmer Fractometer using a silicone column and flame ionisation detector, enabling the progress of the isomerization to be followed. Irradiation for fifteen hours was found to be sufficient to give over 80% conversion to 1,3-dimethylcyclobutene, provided that the outer surface of the quartz jacket was kept free of polymer. Therefore it was cleaned every 8 hours by a combination of immersion in hot chromic acid and washing with "Ajax".

On completion of the irradiation, the solution was fractionally distilled to remove most of the solvent which was subsequently used for the irradiation of further samples. The combined impure 1,3-dimethylcyclobutene from the irradiation of 8 samples was further fractionated to remove more iso-pentane.

A 6ft.x 1in. diameter silicone preparative column maintained at room temperature in the Perkin-Elmer Fractometer was used for the final purification. The carrier gas was nitrogen. 0.5ml. samples were injected and the product trapped out in two 6ft.x $\frac{1}{4}$in. glass spirals immersed in liquid oxygen. The 1,3-dimethylcyclobutene contained 0.4% impurity.

3.9. Additional compounds used.

1. 1,1,2,2-Tetramethylcyclopropane.

An American Petroleum Institute Standard Sample was used for the investigation of this compound. It had a stated purity of 99.96± 0.03%. The liquid was degassed before use.

2. 3-Methylcyclobutene.

The sample of 3-methylcyclobutene used in this work had been prepared previously[56] by Dr. H. M. Frey. The purity was 99.5%. Apart from degassing the liquid no further attempt at purification was made.

3. 2-Ethylbuta-1,3-diene.

A sample of 2-ethylbuta-1,3-diene was generously donated by the "Veb Leuna-Werke 'Walter Ulbricht'".

4. 3-Ethylpent-2-ene.

A commercial sample was supplied by the Eastman Kodak Company. This was used for identification and for the preparation of 3-ethylpent-1-ene.

5. Inert Gases.

(a) Carbon dioxide.

The commercial solid Drikold was subjected to three trap-to-trap distillations (-78 to -186°C) to remove water and any non-condensable gases and stored as a gas.

(b) n-Pentane and iso-Pentane.

Phillips Pure Grade samples of these two compounds were used having a stated minimum purity of 99Mole%. They were degassed.

(c) neo-Pentane.

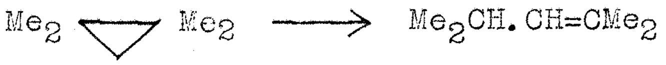
neo-Pentane (Matheson C.P. grade), with a stated minimum purity of 99.0%, was frozen into a trap and degassed.

CHAPTER 4

EXPERIMENTAL RESULTS.

4.1. The Thermal Structural Isomerization of 1,1,2,2-Tetramethylcyclopropane.

1,1,2,2-Tetramethylcyclopropane, when heated in the temperature range 435-484°C undergoes a first-order structural isomerization to 2 4-dimethylpent-2-ene



This is accompanied by some cracking of the olefin to give other products.

Initially several runs were carried out at the same temperature for identical lengths of time to ensure reproducibility of the system. It is necessary to confirm that a reaction vessel is "aged" otherwise the rate of the reaction is not reproducible. In all subsequent work the kinetic data was obtained using reaction vessels that had been "aged". This process required leaving a sample in the vessel for about eight hours.

Preliminary runs at 452°C with various pressures of the tetramethylcyclopropane showed that the rate constant for the isomerization was independent of pressure from 22.5 to 2.0mm. Detailed studies were therefore undertaken at 5mm. pressure at six temperatures. At each temperature between seven and thirteen runs were carried out in which the decomposition varied from 5 to 50%. The shortest run was 2 minutes and the longest 150 minutes. Ignoring the cracking products, plots of the logarithm of the percentage of undecomposed cyclopropane against time were only linear up to about 35% decomposition. However, if allowance was made for the formation of cracking products linear plots were obtained up to 50% decomposition. Rate constants, calculated from these plots by the method of least squares, are shown in Table 1.

TABLE 1. Rate Constants for the Isomerization of 1,1,2,2-Tetramethylcyclopropane.

Temp.(°C)	434.8	440.9	452.0	462.4	473.0	483.6
$10^5 k$ (sec^{-1})	3.81	5.62	11.8	20.4	39.2	75.9

The Arrhenius plot of the logarithm of the rate constant against the reciprocal of the absolute temperature is shown in figure 6. It gave a good straight line. The frequency factor and energy of activation were calculated by the method of least squares, giving

$$k_\infty = 10^{15.83} \exp(-64{,}400/RT)\,\text{sec}^{-1}$$

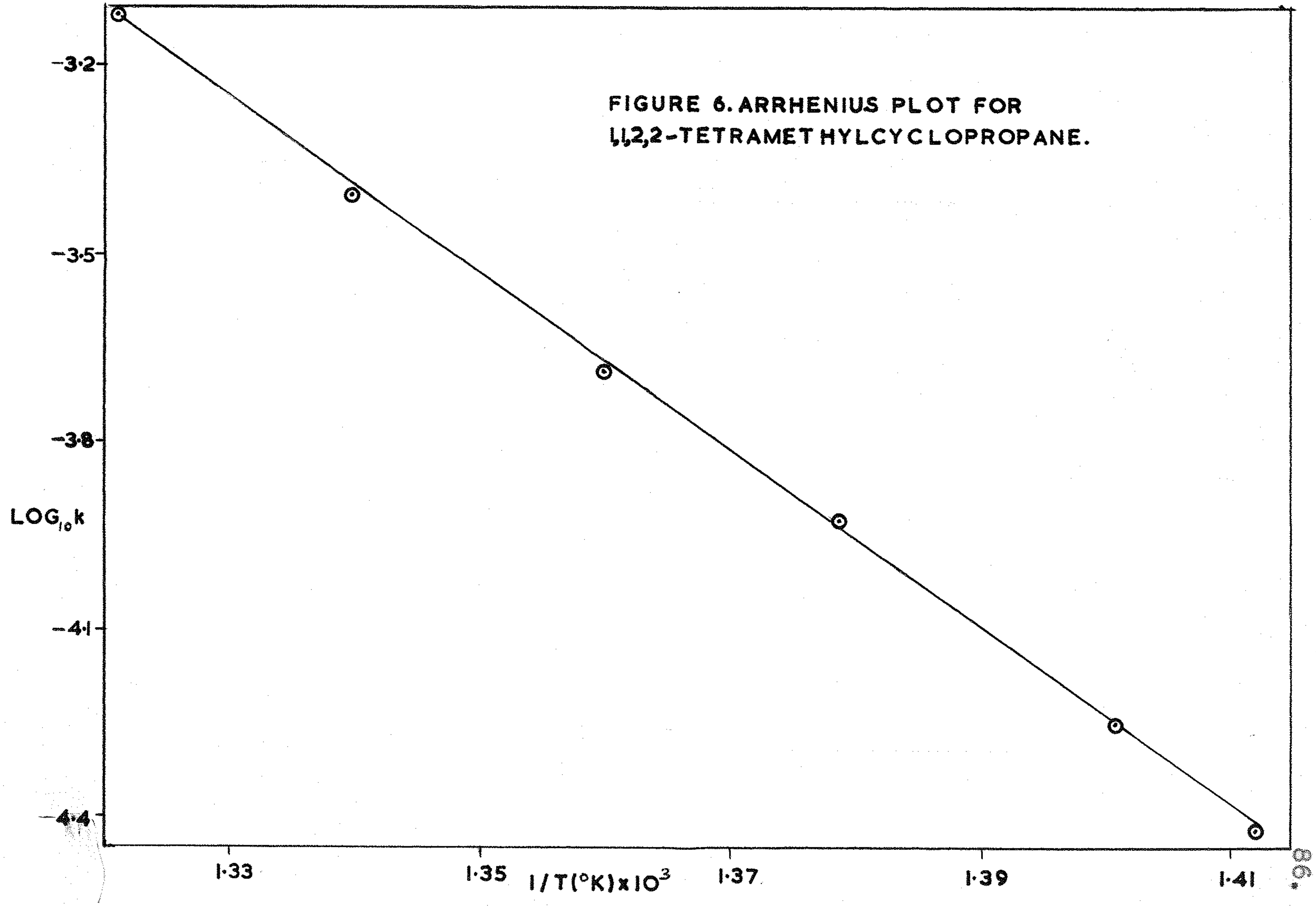


FIGURE 6. ARRHENIUS PLOT FOR 1,1,2,2-TETRAMETHYLCYCLOPROPANE.

The estimated maximum error in the energy of activation is ± 1.5 kcal./mole. This value is attributed partly to the temperature fluctuation of the furnace and partly to the error introduced by the production of cracking products.

To ensure that the rates were for a homogeneous reaction several runs were carried out in a reaction vessel packed with glass tubes. This gave it a surface-to-volume ratio 5.8 times greater than the unpacked vessel. The rates obtained, after correcting for a 1° temperature difference between the two reaction vessels, were identical.

The addition of radical-chain inhibitors to reaction samples, such as nitric oxide and propene, provide a means of detecting any such component in a reaction. Since the product of the reaction, 2,4-dimethylpent-2-ene, is itself a powerful inhibitor, their addition was unnecessary in this reaction. The linearity of the first-order plots at low-percentage decomposition indicated that any such component was not present to a significant extent.

The product of the reaction was identified in two ways. A sample was isolated from the reaction mixture by trapping out the peak from the chromatography column using a U-tube with a four-way stopcock immersed in liquid oxygen. It was connected to the outlet from the detector side of the katharometer using a B10 joint. It's infra-red spectrum, obtained using the gas microcell, agreed with the spectrum for 2,4-dimethylpent-2-ene, published by the A.P.I.

With the chromatography column A maintained at 30°C and a hydrogen flow rate of 20ml./minute. 1,1,2,2-tetramethylcyclopropane had a retention time of 11 minutes and the product 14 minutes. This was in agreement with the retention time of the sample of 2,4-dimethylpent-2-ene which was prepared.

It has been stated earlier that, at high-percentage conversions, appreciable quantities of cracking products, that is, molecules containing less than seven carbon atoms, were formed. Making the crude approximation that the integrated area of a peak is proportional to the mole percentage of the compound, one-fifth of the total products resulting from 60% decomposition of the cyclopropane were due to cracking reactions. This gives a gross overestimate of the truth since no account has been taken of two factors. First, whilst the chromatographic calibration factors for isomeric compounds are almost equal to unity, when there is a difference of molecular weights this is no longer true. A failure to consider these factors leads to an overestimate of those compounds with the lower molecular weights. Second since at least two molecules of cracking products result from one molecule of olefin, these are again overestimated. This in no way affects the general shape of a graph plotting the percentage of cracking products against the percentage of isomerization. The graph has zero slope at zero decomposition and positive curvature at all other values, implying that the cracking products arise from the secondary decomposition of 2,4-dimethylpent-2-ene.

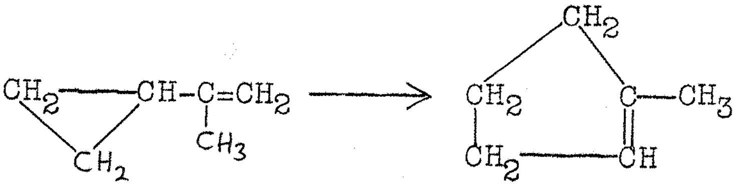
Apart from cracking reactions, there was also evidence that 2,4-dimethylpent-2-ene was isomerizing to other seven-carbon olefins at a rate considerably slower than the primary reaction. At high-percentage conversions a definite shoulder appeared on the chromatographic peak due to 2 4-dimethylpent-2-ene. The tail of this peak was trapped out using a U-tube immersed in liquid oxygen. The mass spectrum indicated a compound of formula C_7H_{14}, but the cracking pattern failed to agree with that of any single seven-carbon olefin which was available. The infra-red spectrum, obtained using the gas microcell, had absorption bands at 900, 910, 1000 and 1805 cm.$^{-1}$, characteristic of an olefin with a terminal double bond ($>C=CH_2$). It seemed probable that at least two isomeric olefins were present but as the secondary isomerization was not directly related to the main purpose of this work, the complete solution was not pursued.

The influence of pressure on the rate of the reaction was studied over the range 22.5-0.5mm. A slight fall-off of the rate constant occurred at about 0.5mm. Because of the design of the apparatus sample sizes were small at this pressure and the analysis inexact so that precise information was not obtained.

The available experimental evidence given here indicates that the isomerization is a true unimolecular reaction.

4.2. The Thermal Structural Isomerization of Isopropenylcyclopropane.

Between 332 and 386°C isopropenylcyclopropane isomerizes to 1-methylcyclopentene by a first-order reaction.



A series of runs at 365°C in which the pressure was varied between 21 and 0.5mm. showed that, within this range, the rate constant was independent of the pressure.

In detailed studies at 5mm. at least nine runs were carried out at each of eight temperatures in which the isomerization varied from 5 to 64%. Plots of the logarithm of the percentage of undecomposed isopropenylcyclopropane against time were linear over the complete range. The rate constants were calculated from the slopes of these graphs by the method of least squares. Their values are given in Table 2.

TABLE 2. Rate Constants for the Isomerization of Isopropenylcyclopropane.

Temp. (°C)	332.2	337.2	345.8	356.9
10^5k (sec.$^{-1}$)	3.32	4.53	8.34	17.0
Temp. (°C)	364.5	371.1	381.6	386.4
10^5k (sec.$^{-1}$)	27.7	42.4	80.1	107

Using these values, the Arrhenius plot, shown in figure 7, gave a good straight line. Calculation

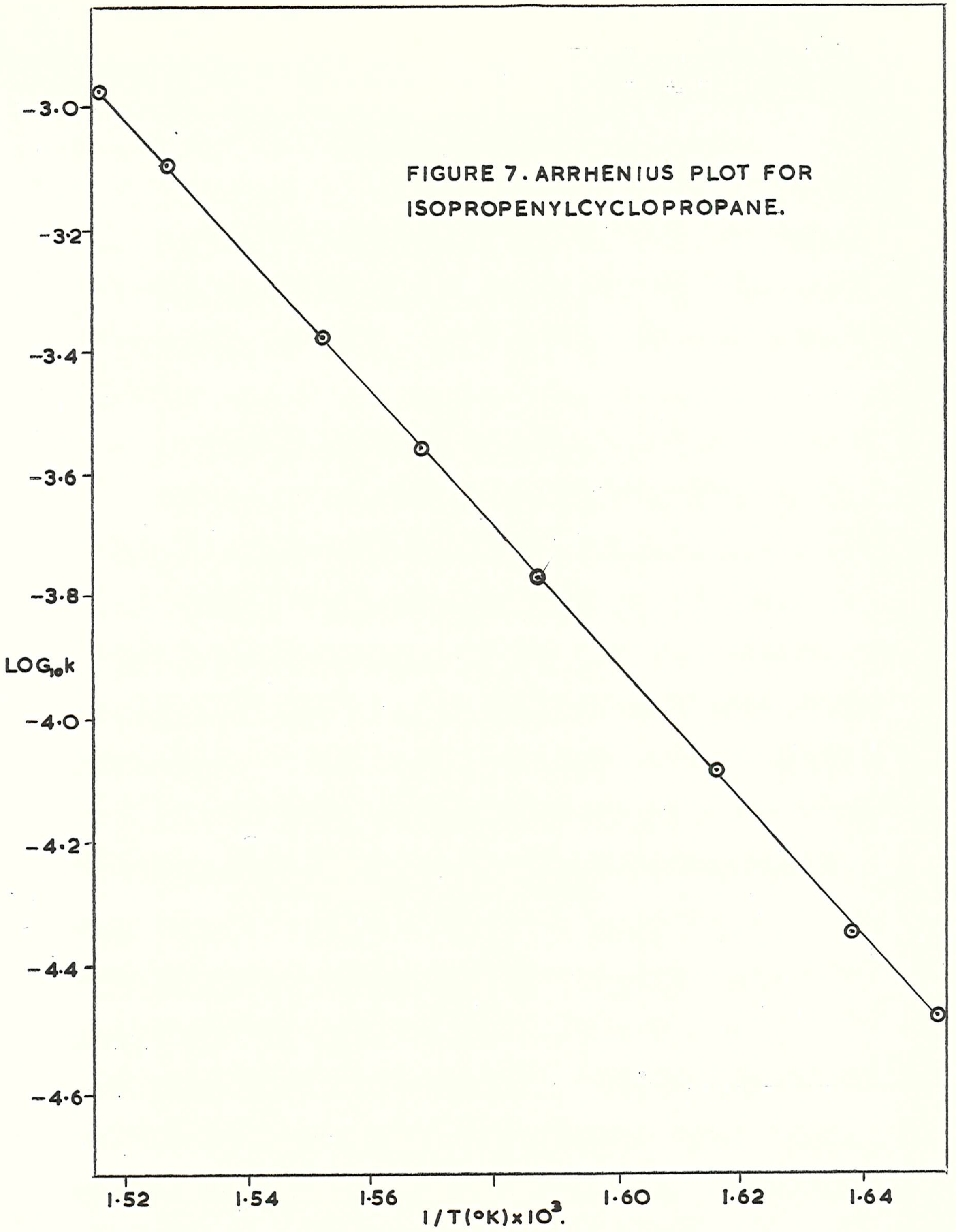


FIGURE 7. ARRHENIUS PLOT FOR ISOPROPENYLCYCLOPROPANE.

of the A factor and energy of activation by the method of least squares gives·

$$k_{\infty} = 10^{13.89} \exp(-50,900/RT)\sec^{-1}$$

The standard deviation of the energy of activation was only eleven calories per mole., clearly indicating the high reproducibility of the results. In fact the probable error in the value is estimated as ± 600 calories, resulting largely from uncertainties in the temperature of the reaction vessel.

Runs were carried out at 356°C using a packed reaction vessel with a surface-to-volume ratio eleven times greater than the unpacked one. The mean value of the rate constant was 1.7% less than for the unpacked vessel, after correcting for a temperature difference. This small difference has no significance and verifies that the isomerization is a homogeneous reaction.

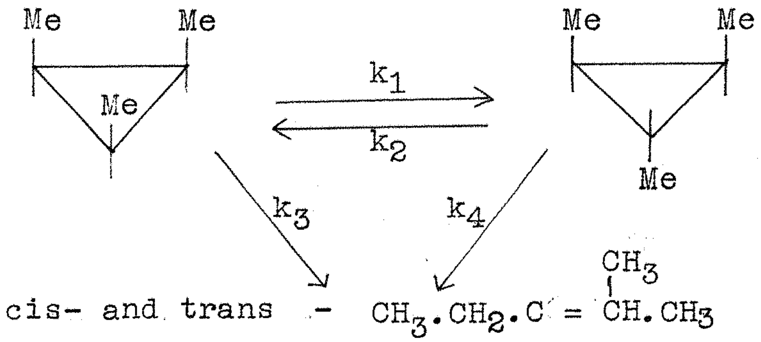
A consideration of 1-methylcyclopentene as an inhibitor confirmed the absence of radical reactions in the system. No deviation from the linearity of the first-order plots occurred with increase of the product.

The product was identified using the infra-red spectrum of a sample trapped from the effluent gas of the chromatography column. It was identical to the spectrum published for 1-methylcyclopentene by the A.P.I.

On the basis of this experimental work it is concluded that the thermal isomerization of isopropenylcyclopropane to 1-methylcyclopentene is a homogeneous unimolecular reaction.

4.3. The Thermal Geometrical and Structural Isomerization of 1,2,3-Trimethylcyclopropane.

The thermal isomerization of cis-1,2,3-trimethylcyclopropane was studied between 395 and 452°C. It underwent a reversible geometrical isomerization to give an equilibrium mixture of the cis- and trans-isomer. A parallel structural isomerization of both occurred at a much slower rate, the products being almost equal quantities of cis- and trans-3-methylpent-2-ene. In runs carried almost to completion increasing quantities of 2-ethylbut-1-ene were identified. The yield of this olefin, plotted as a function of the percentage reaction, gave a curve of zero initial slope and positive curvature. It was, therefore, a secondary product formed from the 3-methylpent-2-ene. Other olefins were formed but these amounted to less than 1% of the total product.



Preliminary runs at 428°C, using various pressures of cis-1,2,3-trimethylcyclopropane, revealed that the rate constants for the geometrical isomerization were independent of pressure from 12.5 to 3.5mm. and had fallen by only 2% from this "high-pressure limit" at 0.5mm. The reaction was studied in detail at eight temperatures with a sample pressure of 2.5mm. This gave values of the rate constants within 1% of the high-pressure limit. For each temperature at least ten runs were analysed in which the percentage of the trans-isomer formed was between 4 and 66%.

The values of the equilibrium constant for the reversible isomerization are required at each temperature in order to calculate the individual rate constants k_1 and k_2. With the exception of the two lowest temperatures, these were determined by isomerizing samples of the cis-isomer for increasing lengths of time until successive analyses differed by less than 0.2%. Time increments were such that, if equilibrium had not been reached, the variation would have been detectable.

At 395 and 405°C an attempt was made to determine the equilibrium constant commencing with a synthetic mixture of the two isomers having a composition close to the equilibrium value. A constant value could not be obtained due to an impurity in the trans-isomer not resolved by column A. The use of a 16ft. column, containing a saturated solution of silver nitrate in ethylene glycol, as the stationary phase in conjunction with A revealed impurities but at least one of them appeared only as a shoulder on the main peak. It could not be resolved even when the chromatography columns were immersed in an ice bath.

The ratio cis: trans-isomer (K_1) is not equal to the true equilibrium constant K but, as shown in Appendix 2, is given by the expression

$$K = K_1\left[1+(k_3-k_4)/k_1(1+K_1)\right]$$

In this work both k_3 and k_4 were small compared with k_1 and k_2 so that K was assumed equal to K_1. Values of the equilibrium constant K_1 are given in Table 4. A plot of the logarithm of K_1 against the reciprocal

TABLE 4. Equilibrium Values for the Geometrical Isomerization of 1,2,3-Trimethylcyclopropane.

Temp.(°C)	411.8	420.6	427.5	435.6	443.7
K_1	2.84	2.80	2.74	2.67	2.64

of the absolute temperature gave a good straight line. From its slope ΔH for the cis-trans-isomerization was calculated as 2.3 kcal./mole. The value of K_1 at other temperatures was found by extrapolation of the line. This can lead to only a slight error in the calculated value of k_1, as shown by the following calculation. An error of 0.7% in the experimental value of the trans-isomer, which would give a ratio cis: trans well off the log ratio-1/T plot, produces a 2.8% error in the calculated value of k_1.

The appropriate rate equation for a reversible first-order isomerization is derived in Appendix 2. It is

$$2.303 \log\left[T_e/(T_e-T)\right]=(k_1+k_2)t$$

where T_e is the equilibrium percentage and T the percentage after a time t of the trans-isomer. Plots of the logarithm of (T_e-T) against time gave very good straight lines over the complete range of isomerization. The slope and the intercept on the y-axis were calculated by the method of least squares at each temperatures. The former led to a value of (k_1+k_2) and the latter to a value of T_e which was compared with the experimental value. Agreement between the two was always better than 0.4%.

The calculated values of k_1 obtained at the eight temperatures studied are shown in Table 5.

TABLE 5. Rate Constants for the cis-trans-Isomerization of cis-1,2,3-Trimethylcyclopropane.

Temp.(°C)	395.1	404.6	411.8	420.6
$10^4 k_1$ (sec.$^{-1}$)	0.690	1.29	2.08	3.69
Temp.(°C)	427.5	435.6	443.7	451.7
$10^4 k_1$ (sec.$^{-1}$)	5.80	9.54	15.4	24.5

An Arrhenius plot of these values shown in figure 8, gave a very good straight line. The A factor and energy of activation were calculated by the method of least squares, whence

$$k_1(\text{cis}\rightarrow\text{trans})=10^{15.78}\exp(-60{,}950/RT)\,\text{sec.}^{-1}$$

The statistical probable error is only 15 cal./mole., but the maximum uncertainty in the energy of activation is about ± 600 cal./mole., due mainly to possible fluctuations in the temperature of the reaction vessel.

The results of several runs at 435°C using the

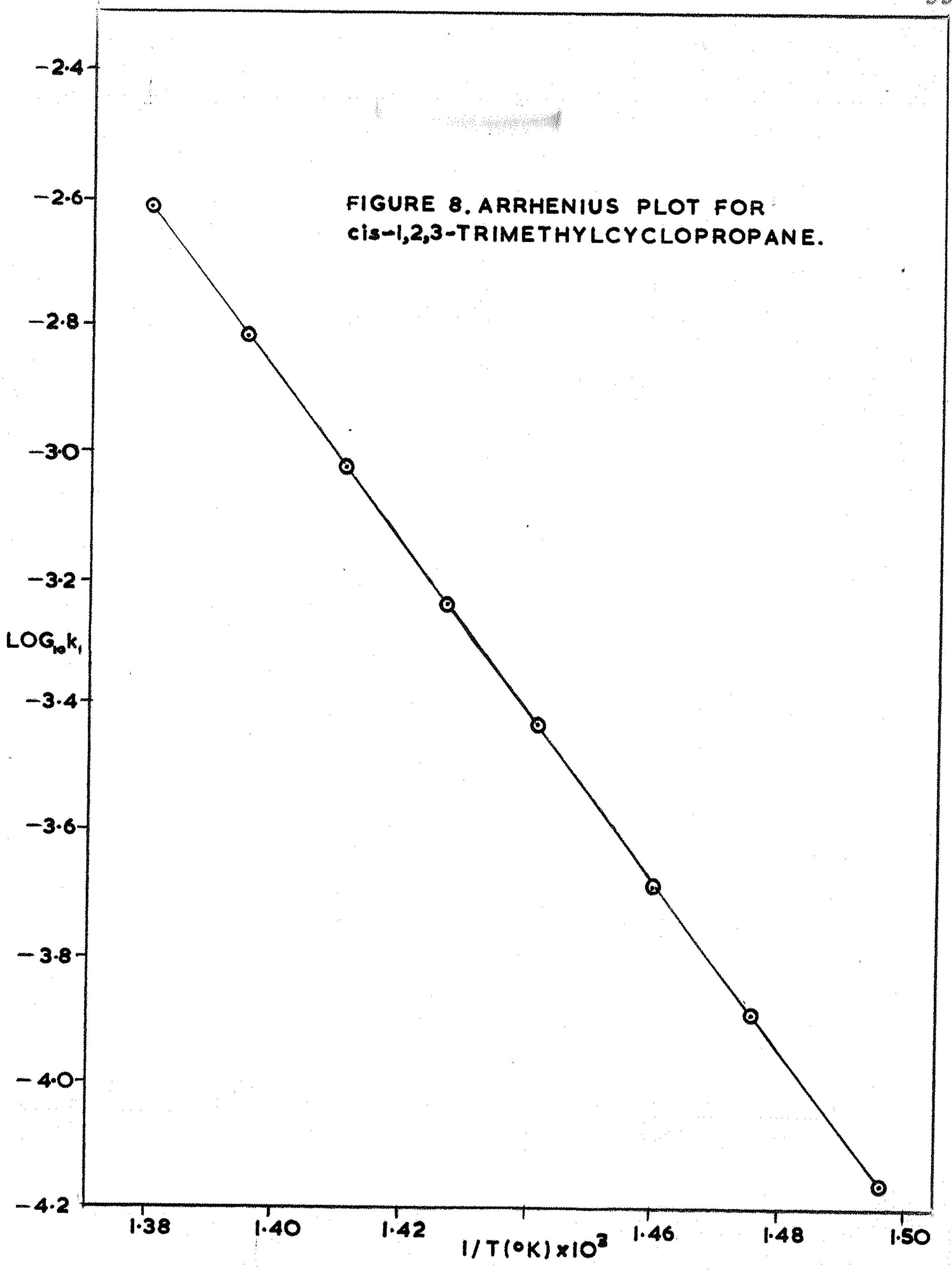


FIGURE 8. ARRHENIUS PLOT FOR cis-1,2,3-TRIMETHYLCYCLOPROPANE.

packed reaction vessel gave a value of the rate constant 3% lower than using the unpacked vessel. A difference of this magnitude has no significance and is most likely due to variations in the external geometries of the reaction vessels and in their exact location within the furnace leading to small differences in the mean temperature of the reaction vessels. The reaction is therefore homogeneous.

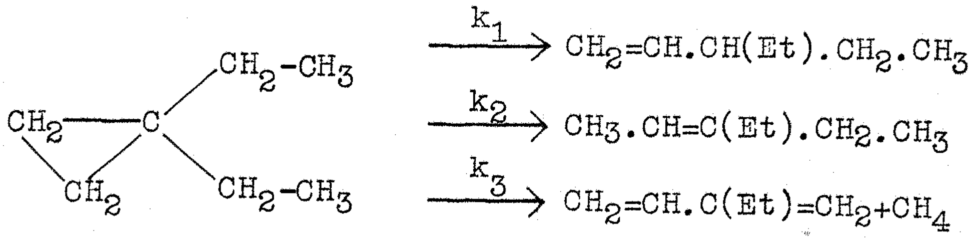
All of the kinetic results described so far were obtained using cis-1,2,3-trimethylcyclopropane as the starting material but it is equally feasible to commence with the trans-isomer. Experimentally it is less desirable since equilibrium exists at about 75% trans-1,2,3-trimethylcyclopropane. A few runs were performed using it as the starting material. The results lacked precision but they established that the trans-isomer is capable of undergoing isomerization to the cis-isomer. Because of the difficulty of purifying the trans-1,2,3-trimethylcyclopropane which was synthesised, a sample was obtained by heating a quantity of the cis-isomer in the furnace followed by chromatographic separation of the trans-isomer.

The products of the structural isomerization were identified as cis- and trans-3-methylpent-2-ene by a comparison of retention times with those of the authentic samples which were prepared.

The experimental results obtained for the geometrical isomerization of 1,2,3-trimethylcyclopropane are in agreement with it being a true unimolecular reaction.

4.4. The Thermal Isomerization and Decomposition of 1,1-Diethylcyclopropane.

In the temperature range 425-475°C 1,1-diethylcyclopropane undergoes a first-order reaction to give as the principle products, 3-ethylpent-1-ene 3-ethylpent-2-ene, 2-ethylbuta-1,3-diene and methane



3-Ethylpent-1-ene and 3-ethylpent-2-ene are the products of a 'normal' cyclopropane isomerization but this is the first reported example of a substituted cyclopropane decomposing to a diene by the elimination of a molecule of methane.

Initially, a series of runs was made at 454°C in which the pressure of the reactant gas in the reaction vessel was varied between 16.0 and 0.2mm. No decline in the rate constant was observed at 1.0mm. but at 0.2mm. it had fallen by 5% of the high pressure limit. Detailed studies were undertaken at 4.5mm. at eight temperatures. At each one eight or nine runs were analysed in which the percentage of products varied from 6.5 to 31.5%. The chromatograms showed three major and six minor products. The plots of the logarithm of the percentage of undecomposed cyclopropane against time were linear over the entire range studied. The overall rate constant was calculated from the slope of the graph by the method of least squares giving the values listed in Table 7. The Arrhenius plot using these figures is shown in figure 9. The A factor and energy of activation were calculated from it giving an equation for the overall rate constant

$$k_\infty(\text{overall}) = 10^{15.74} \exp(-64{,}900/RT)\text{sec.}^{-1}$$

The absence of any significant heterogeneous reactions was shown by the analysis of a few runs at 452°C in the packed reaction vessel. After correcting for a

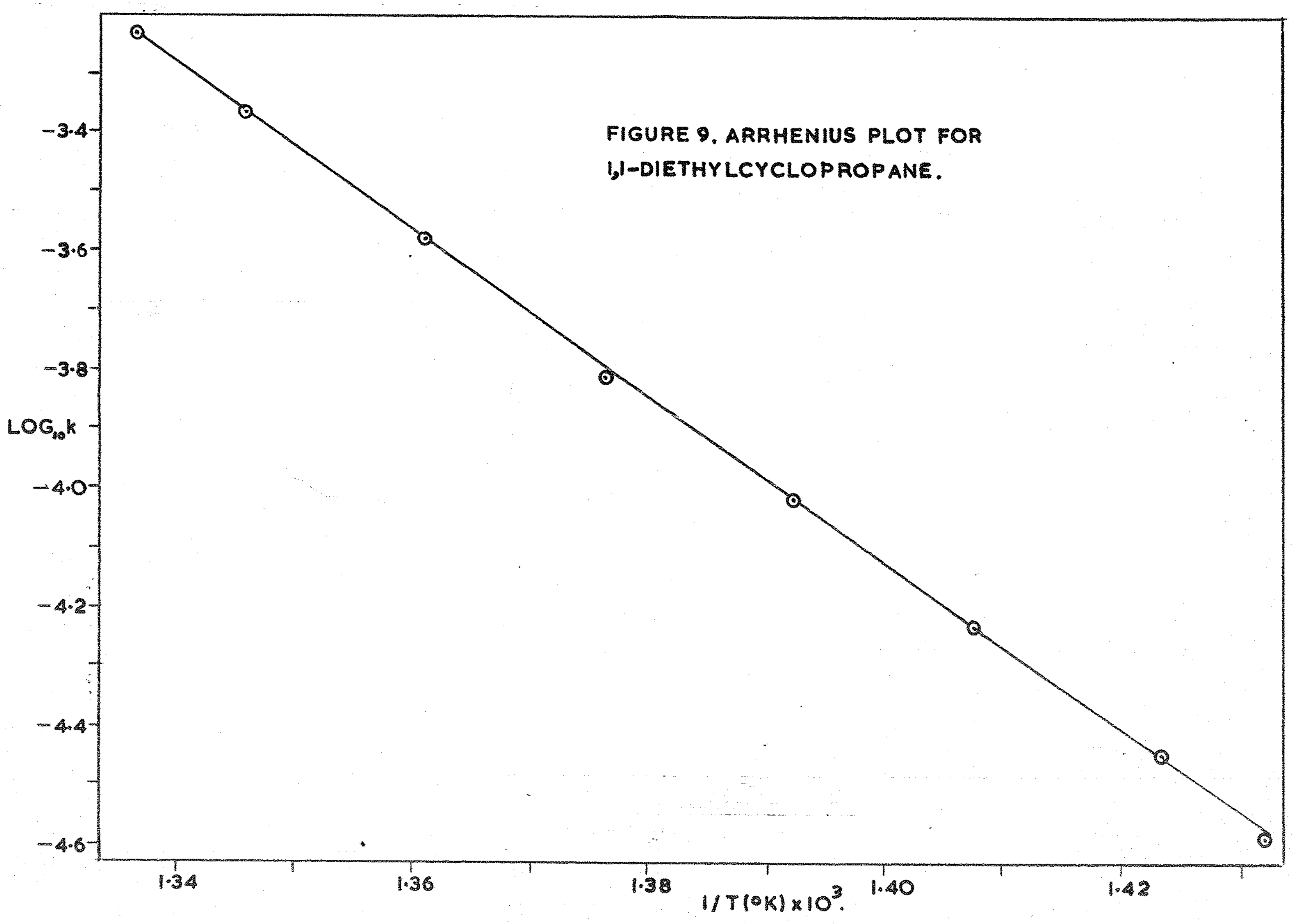


FIGURE 9. ARRHENIUS PLOT FOR 1,1-DIETHYLCYCLOPROPANE.

temperature difference, the rate constant was only two per cent higher than the corresponding value for the unpacked vessel.

The linearity of the rate plots, despite the formation of products which can act as efficient radical chain inhibitors, confirmed the absence of such components.

3-Ethylpent-1-ene and 3-ethylpent-2-ene were identified as products of the reaction by comparing their retention times with those of authentic samples. Using column A maintained at 33°C and a hydrogen flow rate of 25ml./min. the retention times were:

3-Ethylpent-1-ene	13 minutes
1,1-Diethylcyclopropane	16 minutes
3-Ethylpent-2-ene	22 minutes

The infra-red spectra agreed with those published for the two compounds by the A.P.I.

The third major product had a retention time of twenty-five minutes. It was originally thought to be an olefin containing seven carbon atoms, produced by a rearrangement reaction of the other two products. The mass spectrum of a sample was in agreement with the molecular formula C_7H_{14} although the peaks corresponding to the C_7 fragments were small. This is not an uncommon feature of mass spectral cracking patterns. Absorption bands at 900,1000 and 1800 cm.$^{-1}$ in the infra-red spectrum could be attributed to a terminal double bond in the olefin. On this evidence the compound was thought to be 2-ethylpent-1-ene. Petrov[57] had observed that the isomerization of 3-ethylpent-2-ene in the presence of aluminosilicates, produced, after hydrogenation, 3-methylhexane.

The photolysis of ketene with 2-ethylbut-1-ene and diazomethane with 2-methylpent-1-ene, both of which should give 2-ethylpent-1-ene, failed to give a product with a retention time of 25 minutes.

By two independent methods it was established that the compound was the product of a primary reaction. First, plots of its percentage against the percentage of the total product were linear, passing through the axes close to zero. Similar plots for 3-ethylpent-1-ene and 3-ethylpent-2-ene were also linear. Second, runs carried out at 453°C using 3-ethylpent-1-ene and 3-ethylpent-2-ene as the starting materials, gave results which showed that their secondary decomposition could account for no more than 18% of the observed quantities of the third product in a typical run.

The final evidence that 2-ethylpent-1-ene was not the product came when a synthesised sample of it was found to have a retention time of only 18 minutes.

The mass spectrum of a second sample of the product which was pure, possessed no peaks corresponding to C_7 fragments. The analysis indicated a molecular formula C_6H_{10}. Contamination by 3-ethylpent-2-ene had caused the original error. The product was therefore a diene, formed in a reaction involving the elimination of a molecule of methane. No quantitative measurements of the methane were made since some additional methane would almost certainly be formed from the minor cracking reactions.

Hively[58] has determined the relative retention times of many hydrocarbons on a 2.5 metre column containing di-2-cyanoethyl ether using helium as the carrier gas. Some of these values are given in Table 6. The relative retention times of the three products of the thermal reaction of 1,1-diethylcyclopropane were 1.0 (3-ethylpent-1-ene), 1.9 (3-ethylpent-2-ene) and 2.2. Comparison of the last figure with the value in Table 6 for 2-ethylbuta-1,3-diene suggested that this was the product, a fact

TABLE 6. Relative Retention Times of Some Hydrocarbons on a 2.5 Metre Column Containing Di-2-cyanoethyl Ether.

Compound	Relative Retention Time
3-Ethylpent-1-ene	1.0
3-Ethylpent-2-ene	2.1
2-Ethylbuta-1,3-diene	2.5
2,3-Dimethylbuta-1,3-diene	2.8

which was confirmed using a sample of the compound. Its retention time on the analytical column was identical to that of the third product.

Although the data was not very precise, a graphical plot of the percentage of minor products against the percentage of reaction had positive curvature, showing these to be secondary products.

In Appendix 2 an equation is derived for the rate constant k_i for any one of n parallel first-order reactions. It is related to x, the percentage of the product of the particular reaction formed in time t, by the expression

$$\frac{x}{100} = \frac{k_i}{\sum_{i=1}^{n} k_i}\left[1 - \exp\left(-t\sum_{i=1}^{n} k_i\right)\right]$$

where $\sum_{i=1}^{n} k_i$ is the rate constant for the overall reaction.

At each temperature graphs were plotted of $(x/100)$ against $\exp(-t_i\sum_{i=1}^{n}k_i)$ for each of the three products. These are shown in figure 10 using the experimental results at 462°C. The data was corrected for the decomposition to secondary products by assigning one-third of their total percentage to each of the main products. The error introduced by this approximation was small as the total percentage of secondary products never exceeded 1.8%. The values of the individual rate constants k_1,k_2 and k_3 were calculated from the slopes of the lines by the method of least square. These are given in Table 7. The Arrhenius plots, using these values, gave good straight lines. The A factors and energies of activation were calculated, from which the individual rate constants were found to be given by the equations

$$k_1(\text{3-ethylpent-1-ene}) = 10^{14.95}\exp(-63{,}800/RT)\,\text{sec}^{-1}.$$

$$k_2(\text{3-ethylpent-2-ene}) = 10^{14.84}\exp(-63{,}400/RT)\,\text{sec}^{-1}.$$

$$k_3(\text{2-ethylbuta-1,3-diene}) = 10^{15.44}\exp(-65{,}900/RT)\,\text{sec}^{-1}.$$

Thus, the thermal reaction of 1,1-diethylcyclopropane involves three parallel unimolecular processes which are homogeneous and free from radical components.

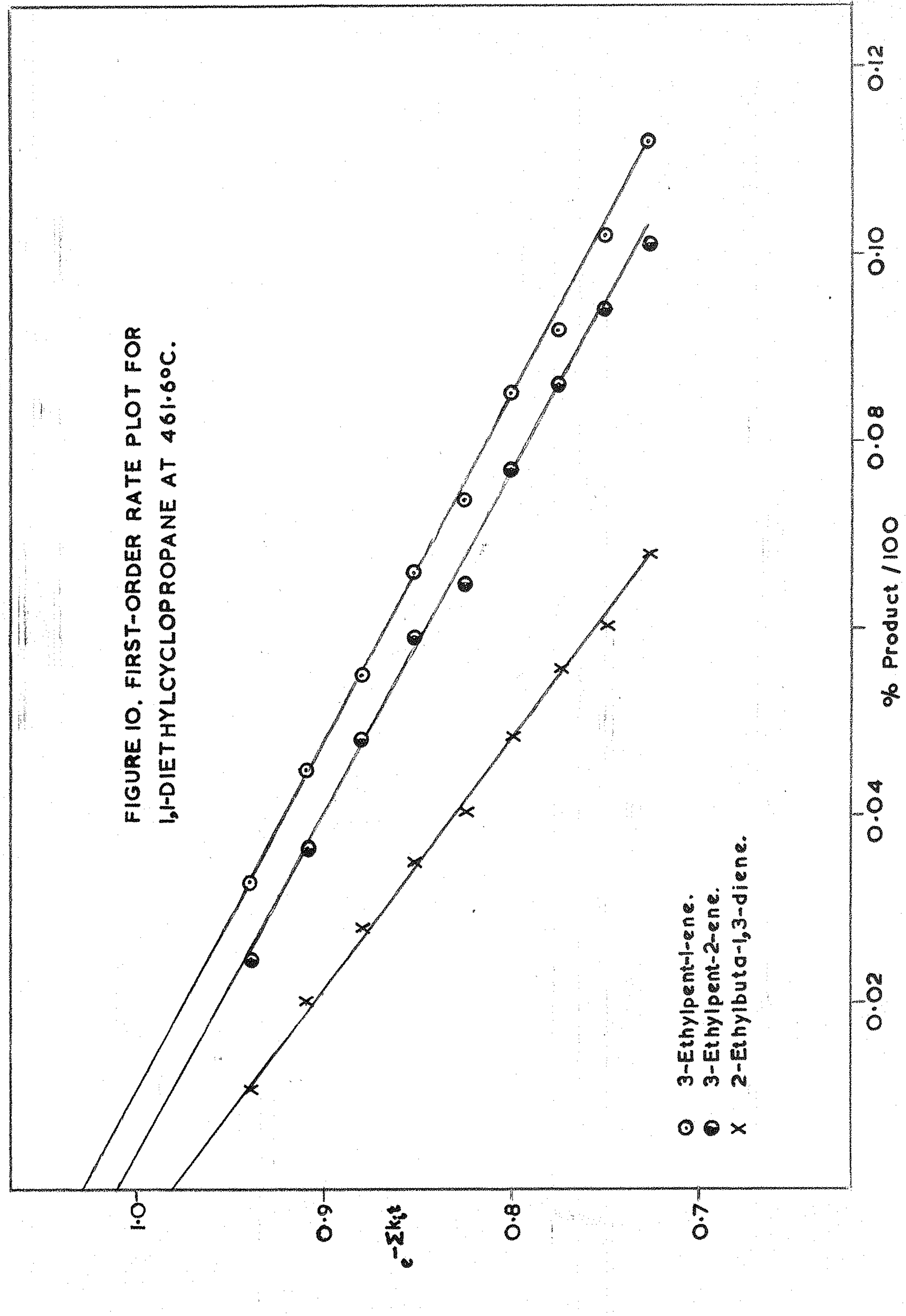


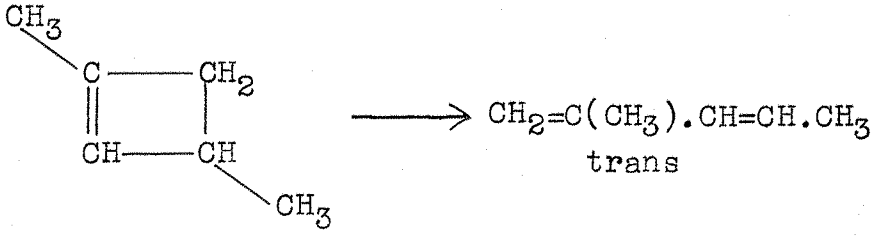
FIGURE 10. FIRST-ORDER RATE PLOT FOR 1,1-DIETHYLCYCLOPROPANE AT 461·6°C.

TABLE 7. Rate Data for the Thermal Reaction of 1,1-Diethylcyclopropane.

Temp. (°C)	425.0	429.3	437.1	445.0
10^5k(overall)sec^{-1}.	2.58	3.57	5.84	9.63
10^5k_1(sec^{-1}.)	0.979	1.22	2.15	3.43
10^5k_2(sec^{-1}.)	0.941	1.33	2.19	3.56
10^5k_3(sec^{-1}.)	0.606	0.946	1.56	2.38
Temp. (°C)	453.3	461.6	469.9	475.1
10^5k(overall)sec^{-1}	15.5	26.6	43.1	58.6
10^5k_1(sec^{-1}.)	5.51	9.71	14.3	22.1
10^5k_2(sec^{-1}.)	5.92	9.65	15.8	20.3
10^5k_3(sec^{-1}.)	3.92	7.04	11.9	15.7

4.5. The Thermal Structural Isomerization of 1,3-Dimethylcyclobutene.

A structural isomerization of 1 3-dimethylcyclobutene occurs in the temperature range 121-175°C. The product of the reaction is trans-2-methylpenta-1,3-diene.



Preliminary runs at 144°C showed that the rate constant for the isomerization was independent of pressure over the range 140-0.25mm. A sample pressure of 6.0mm. was used for the complete kinetic study, which enabled many of the runs to be analysed in duplicate. The reaction was investigated at ten temperatures in which the isomerization varied from 12 to 80%. The shortest run was 3 minutes and the longest one 816 minutes. A typical plot of the logarithm of the percentage of undecomposed dimethylcyclobutene against time is given in figure 11. It is linear over the complete range studied. The rate constant at each temperature was calculated from the slope of the graph. The values obtained are given in Table 8. The graph of the logarithm of the rate constant against the reciprocal of the absolute

TABLE 8. Rate Constants for the Thermal Isomerization of 1,3-Dimethylcyclobutene.

Temp.(°C)	120.9	133.2	138.5	143.7	148.6
10^4k(sec^{-1}.)	0.213	0.774	1.31	2.20	3.44
Temp.(°C)	152.6	158.4	163.9	168.6	174.4
10^4k(sec^{-1}.)	5.06	8.63	13.9	20.4	32.3

temperature gave a very good straight line. A least squares calculation of the A factor and energy of

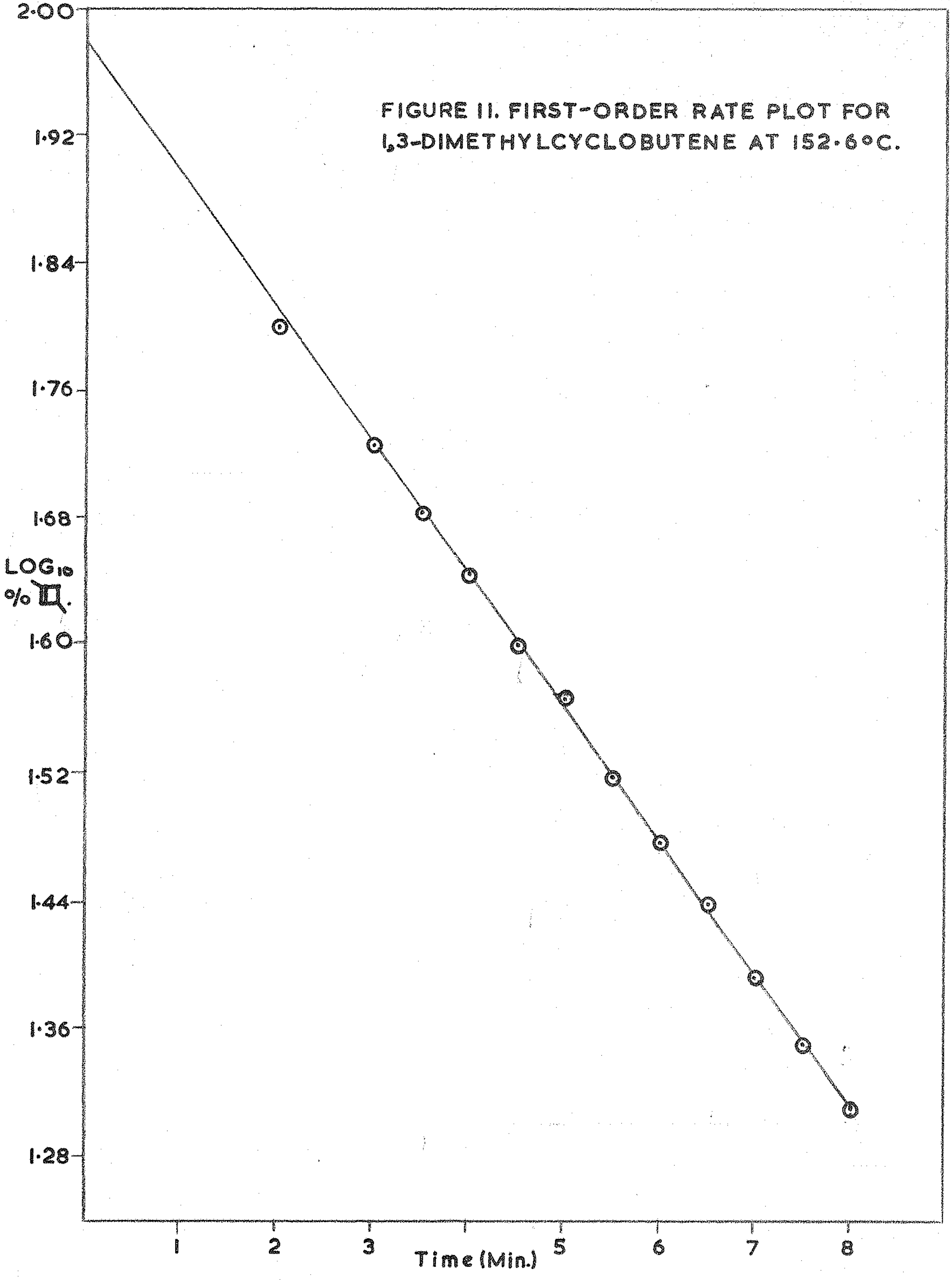


FIGURE 11. FIRST-ORDER RATE PLOT FOR 1,3-DIMETHYLCYCLOBUTENE AT 152·6°C.

activation resulted in the following equation for the high pressure rate constant:

$$k_{\infty} = 10^{13.65}\exp(-33{,}000/RT)\,\mathrm{sec}^{-1}.$$

The statistical probable error of the energy of activation is only 12cal./mole. but the maximum uncertainty in its value does not exceed ± 300 cal. This error is due to possible fluctuations of the temperature of the reaction vessel and the limitation of the precision with which it could be measured.

The rate constant for the isomerization was determined at 153°C in the packed reaction vessel. The difference between this and the value determined using the normal vessel was only 0.9%. The chromatography column B was maintained at 39°C during the analysis; the hydrogen flow rate was 30ml./min. With these conditions the retention times of 1,3-dimethylcyclobutene and trans-2-methylpenta-1,3-diene were 12 minutes and 28 minutes respectively. The product of the reaction was identified with the compound used to synthesise the dimethylcyclobutene by their identical retention times.

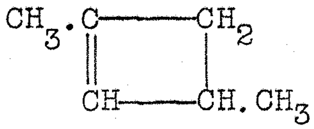
The vapour pressure of 1,3-dimethylcyclobutene was measured between 22.25 and -4.35°C using the apparatus described in section 2.4. From the data the boiling point of the compound was calculated. The logarithm of the vapour pressure, measured in mm., was plotted against the reciprocal of the absolute temperature. The equation of the straight line obtained was calculated as

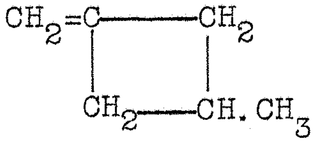
$$\log p_{mm.} = 7.858 - 1633/T$$

Extrapolation of the line to p = 760mm. gives the boiling point as 55.2°C and, from the slope the latent heat of vaporization (ΔH_v) = 7.47 kcal./mole. The Trouton Constant, using these figures, is 22.8cal. $deg.^{-1}mole^{-1}$. which is a 'normal' value.

Gil-Av and Herling[59] have verified that a catalyst of finely-divided sodium on alumina causes a reversible isomerization to give an equilibrium mixture of methylenecyclobutane and 1-methylcyclobutene, commencing with either pure compound. The analogous reaction was studied using 1,3-dimethylcyclobutene. 2g. of clean sodium was melted onto 3g. of alumina in an evacuated glass tube. ½ml. of the 1.3-dimethylcyclobutene was frozen onto the catalyst and left at room temperature for three hours. The sample was transferred to a 500ml. glass vessel containing a magnetically-operated stirrer and mixed for at least

48 hours before analysis. The procedure was repeated thereby establishing that an equilibrium mixture had been formed containing the starting material and a product with a retention time of 17 minutes. Assuming a similar type of isomerization, the product was 3-methylmethylenecyclobutane.





At 23°C the equilibrium mixture contained 76% of the cyclobutene. The results were not very reproducible thus preventing a study of the variation of the equilibrium with temperature.

On the basis of the experimental results given above it is concluded that the thermal isomerization of 1,3-dimethylcyclobutene is a true homogeneous unimolecular reaction.

4.6. The Thermal Structural Isomerization of 3-Methylcyclobutene at Low Pressures.

In studies reported earlier[56], 3-methylcyclobutene was found to undergo a first-order structural isomerization to trans-penta-1,3-diene in the temperature range 113 to 156°C. The rate constant was independent of pressure above 25mm. and the high pressure rate constant was given by the equation

$$k_\infty=10^{13.53} \exp(-31,550/RT)\,\mathrm{sec}^{-1}$$

A preliminary investigation showed that at 7mm. pressure the rate constant was about 2.5% below the high pressure limit and at 0.9mm. had fallen by 13%.

By suitably modifying the apparatus, the decline of the rate constant with pressure was studied in detail at the two temperatures 123.5 and 148.5°C over the pressure range 45.0-0.010mm. The first-order rate constant for the isomerization was calculated at each pressure from a single run. Samples were analysed using the chromatographic column A maintained at room temperature. The inlet pressure of the hydrogen carrier gas was 7.5lb./sq.in., giving a flow rate of 20ml./min. With these conditions the retention times of 3-methylcyclobutene and trans-penta-1,3-diene were 10 minutes and 26 minutes respectively.

The time intervals for which samples were in the reaction vessel were such that the percentage of product was between 25 and 29% at the lower temperature; at the higher temperature the value was between 56 and 71%. The shortest run had a duration of 14 minutes so that any timing errors were negligible.

Gas sample pressures above 5mm. were measured using a cathetometer on a 2mm. i.d. mercury manometer

All other pressures were determined using the McLeod gauges described in section 2.7. Samples with a pressure above 1mm. were heated in the 150ml. spherical Pyrex reaction vessel. Below 1mm. the modified apparatus shown in figure 4 (p.53) was used in which the reaction vessel had a volume of 1 litre. This ensured that, even at the lowest pressure, the sample size was sufficiently large for accurate analysis. The sensitivity of the analytical apparatus was increased to its maximum when the sample pressure in the reaction vessel was less than 0.1mm. The katharometer current was increased to 300mA and the recorder range changed from 0-5.0mV to 0-1.0mV.

The results obtained at the two temperatures are listed in Tables 14 and 15 (Appendix 3). The high pressure rate constants were estimated by extrapolating a plot of 1/k against 1/p to 1/p = 0. These were in close agreement with the values $1.38\times10^{-4}\text{sec}^{-1}$. and $1.48\times10^{-3}\text{sec}^{-1}$. calculated using the Arrhenius equation. Schlag and Rabinovitch[70] have suggested that the extrapolation of a plot of $1/k$ against $1/p^{\frac{1}{2}}$ is a better method of estimating k_∞ since it shows less curvature. This plot and the corresponding one for 1/k against 1/p at 148.5°C are shown in figures 16 and 17. (Appendix 3). Whilst a linear extrapolation in figure 17 gives a more accurate value of k_∞ than a linear extrapolation of figure 16, the value of $1.63 \times 10^{-3} sec^{-1}$. is a considerable overestimate of the correct figure. On the other hand a curved extrapolation of figure 16 is more accurate than a similar extrapolation of figure 17. Therefore, if values of the rate constant are available close to the high pressure limit, the curved extrapolation of a plot of $1/k$ against $1/p$ is to be preferred as a method of estimating k_∞ .

The graphs shown in figures 13 and 15 (Appendix 3) are plots of $\log k/k_\infty$ against $\log p$ at the two temperatures. A fall-off of the rate constant commences at 12mm. at 148.5°C and 7mm. at 123.5°C. This agrees with the theoretical prediction that fall-off commences at a higher pressure at higher temperatures.

Johnson and White[60] have derived certain consistency tests using the general Lindemann theory of unimolecular reaction rates set out on p.9 (Chapter 1). These provide a means of determining whether a set of data fulfills the requirements of the general theory before using it to test more detailed theories.

They can also reveal any serious experimental errors in the results.

If a_i, b_i and c_i are the rate constants for activation, deactivation and reaction of the energy state i, respectively, then the moments ν_1, ν_2, ν_3 etc. are defined as follows. The n th. moment of c_i/b_i over Tolman's distribution function is $\nu_n = \langle c^n/b^n \rangle^T_{Av}$ where Tolman's distribution function is

$$T_i^{\,1} = a_i c_i M/(b_i M + c_i)$$

M is the concentration of the gas, measured in moles/cc. Johnson and White show that

$$\nu_1 = (k_\infty - k)M/k$$

and
$$\nu_{n+1} = (k_\infty \nu_n^\infty - k\nu_n)M/k$$

ν_1 converges to the finite value ν_1^∞ at infinite pressure which may be determined by extrapolating a plot of ν_1 against $1/M$ (or $1/\nu_1$ against $1/M$) to $1/M = 0$. ν_2 is then computed using the recursion formula, ν_2^∞ found by extrapolation and ν_3 computed. However as ν_2 contains the accumulated errors of k, k_∞, ν_1 and ν_1^∞, excellent experimental data are required to prevent its overinterpretation. Certain inequality relations exist between the moments which can prevent this and check the consistency of the results. These are

$$\nu_2/\nu_1^2 \geqslant 1$$

and $$\nu_1\nu_3/\nu_2^2 \geqslant 1$$

The moments ν_1, ν_2 and ν_3 were calculated using the data for 3-methylcyclobutene at 148.5°C and the consistency tests applied. The various quantities are listed in Table 16 (Appendix 3). The first inequality holds over the complete pressure range but the second one fails at the higher pressures. Flowers and Frey[61], applying the tests to data for 1,1-dimethylcyclopropane, also obtained failure at this point although a decrease of less than 1% in the value of the high pressure rate constant was sufficient for the inequality to hold over the entire pressure range. The consistency tests are sufficiently satisfactory to justify the application of the more detailed Kassel integral to the results.

The Kassel integral equation for the first-order rate constant, equation 10 (p.15), was evaluated for several values of the parameter s at the two temperatures. These are listed in Table 17 (Appendix 3). A molecular diameter of 7.0 Å was used for 3-methylcyclobutene together with the experimental high pressure A factor and energy of activation. The Kassel integral was evaluated by using the

Gauss-Laguerre quadrature formula[62] (Appendix 4). The summation was carried out using an Autocode programme on a Ferranti Pegasus computer.

No attempt was made to integrate Slater's[19] expression and determine the value of n giving the same shaped curve as the experimental results. It may be calculated for the classical model from the shift of the fall-off curve with temperature. The experimental shift in log p was 0.2 log units, giving by equation 16, p.26., n = 15. Schlag et al.[63] have compared the values of n and s for different values of b. When b = 40, n = 15 is equivalent to s = 12.

Previous studies have shown that an inert gas present in a reaction mixture is capable of transferring energy so helping to maintain the Maxwell-Boltzmann distribution of energies. In so doing the rate constant is increased towards the high pressure limit, but never exceeds it.

The effect of the addition of four "inert gases", carbon dioxide, n-pentane, iso-pentane and neo-pentane, on the rate of isomerization of 3-methylcyclobutene was investigated in the fall-off region at 123.5°C. The fall-off curves obtained are shown in figures 13 and 14. Figure 14 also shows the theoretical curve when s = 12 for reference. The relative efficiency (E_p) of an inert gas, pressure for pressure, in transferring energy was calculated by the method described by Trotman-Dickenson (ref.29,p.83.). The relative efficiency (E_c), collision for collision, was calculated using the equation

$$E_c = E_p\,(\sigma_1/\sigma_{12})^2(2\mu_{12}/m_1)^{\frac{1}{2}}$$

where σ_1 and m_1 are the molecular diameter and molecular weight of 3-methylcyclobutene and σ_2 and m_2 the corresponding quantities for the inert gas. Then

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2$$

and

$$\mu_{12} = m_1 m_2/(m_1 + m_2)$$

The values of E_p and E_c together with the results obtained by other workers for carbon dioxide are given in Table 9. The molecular diameter of carbon dioxide was given in reference 62 whilst the values for the pentanes were the same as used by McGrath and Ubbelohde[65].

The efficiencies of a wide variety of inert gases have been determined by workers, but of these, only a few have been hydrocarbons. Those which have been studied have had low molecular weights with the exception of toluene, because of the high temperatures required for the isomerization reaction involved.

TABLE 9. Relative efficiencies of inert gases in transferring energy.

Compound	Molecular Diameter(Å)	E_p	E_c	Reference.
3-Methylcyclobutene.	7.0	1	1	
Carbon dioxide	4.1	0.32	0.48	
	"	0.13	0.26	61
	"	0.38	0.49	64
	4.0	0.27	0.3	44(b)
n-Pentane	5.8	1.09	1.32	
iso-Pentane	5.3	0.96	1.25	
neo-Pentane	5.2	0.85	1.12	

At these temperatures more complex molecules would decompose and possibly interfere with the reaction. The low temperature required for the isomerization of 3-methylcyclobutene provided the opportunity to determine the relative efficiencies of hydrocarbons with molecular weights almost identical to those of the reactant and product.

CHAPTER 5.

Discussion

In the thirty years that have elapsed since Chambers and Kistiakowsky[40] first reported the thermal unimolecular isomerization of cyclopropane, the publication of experimental data derived from studies of its many derivatives has been quite prolific. The potential of the cyclopropanes, treated as a single class of compounds, was soon recognised as a source of many kinetic data. By employing subtle changes in the substituents of the ring, the key to the mechanism of their reactions and unimolecular processes in general might be found. Prior to 1934 the progress of the theories of unimolecular reactions had depended upon the results of reactions surrounded by justifiable uncertainty. Of all the early examples quoted, the decomposition of dinitrogen pentoxide remains the only reaction still believed to be unimolecular.

The study of the isomerization reactions of cyclopropanes has revealed that they can be subdivided into three general classifications, although this in no way infers that the mechanism of each is different.

Results have been obtained by the author from certain cyclopropanes covering all the categories.

The first type of isomerization is shown by the vinylcyclopropanes. The carbon-carbon double bond may be considered as conjugated to the cyclopropane ring since the latter possesses some properties typical of an olefinic double bond. Vinylcyclopropane itself isomerizes to cyclopentene[66] whilst more recent work has shown that 1-methyl-1-vinylcyclopropane[67] and isopropenylcyclopropane both produce 1-methylcyclopentene. The rate constants for the three reactions are given by the equations:

Vinylcyclopropane $k=10^{13.5}\exp(-49,600/RT)\mathrm{sec}^{-1}$.

1-Methyl-1-vinylcyclopropane

$k=10^{14.11}\exp(-49,350/RT)\mathrm{sec}^{-1}$.

Isopropenylcycloprpane $k=10^{13.89}\exp(-50,900/RT)\mathrm{sec}^{-1}$.

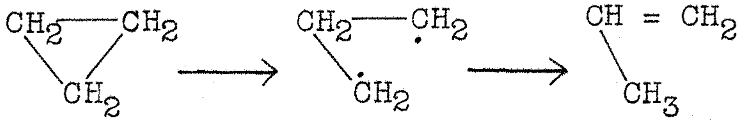
The reactions are characterised by 'normal' A factors close to $10^{13}\mathrm{sec}^{-1}$ and energies of activation of about 50kcal./mole.

The hydrogen atoms of cyclopropane project either side of the plane of the ring. Replacement of some of these hydrogen atoms by other atoms or groups can result in the formation of geometric isomers, possessing either a cis-or trans-configuration. The first compound which was investigated for kinetic data was the symmetrically deuteriated 1,2-cyclopropane-d_2[68]. The results showed that a reversible geometric isomerization can occur at elevated temperatures to give eventually an equilibrium mixture of the two isomers. Other examples have subsequently been investigated. The author gives results for 1,2,3-trimethylcyclopropane whilst other workers have reported on 1,2-dimethylcyclopropane[69], 1-ethyl-2-methylcyclopropane[70] and 1,2-dideuterio-3-methylcyclopropane[71]. The reactions are characterised by A factors greater than 10^{15} sec^{-1} and energies of activation close to 60 kcal./mole.

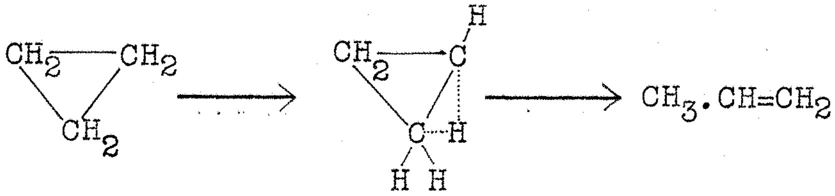
The third category includes cyclopropane itself; in general it includes compounds obtained by replacing some or all of the hydrogen atoms of the ring with other atoms, notably deuterium and tritium, or alkyl groups. By far the largest volume of work, both experimental and theoretical has been concerned with this group of compounds. Some of the theoretical aspects will be presented first so as to give an up-to-date viewpoint of the mechanism of cyclopropane reactions, this will be followed by a consideration of the experimental results and their relevance to the particular theories.

The isomerization of cyclopropanes within this classification requires the rupture of the ring and the shift of a hydrogen atom to give an olefin as the final product. Those compounds quoted as examples of geometric isomerization may also be included here since, by parallel reactions, they also undergo structural isomerization but at a considerably slower rate. Summarising the results for structural isomerizations, the A factors lie between 10^{15} and 10^{16} sec^{-1}. whilst the energy of activation is in the range 62-66 kcal./mole. The introduction of additional strain into the ring causes a considerable reduction in the energy of activation.

The isomerization of cyclopropane to propene has been discussed in terms of two possible mechanisms, both suggested by Chambers and Kistiakowsky.[40] By analogy with the cracking of paraffins, in their first mechanism a carbon-carbon bond breaks and this is followed by a shift of a hydrogen atom to the end of the diradical



The second mechanism favoured by Slater when testing his theory, requires that a hydrogen atom on one carbon atom of the ring should approach a non-adjacent carbon atom so that migration can occur. This is followed by ring opening.



Since the inception of the two mechanisms, which will be designated the names 'trimethylene diradical' and 'hydrogen migration', the ultimate goal has been to accept one in preference to the other. The pendulum of decision has swung in both directions.

Corner and Pease[72], the first to reinvestigate the isomerization of cyclopropane, explained the results on the basis of a simple three-stage mechanism involving the trimethylene diradical. A feature of it was that added inert gas should have no effect on the first-order rate constant in the fall-off region. Using hydrogen as the inert gas this was found to be so. Pritchard et al[41] have since pointed out that the efficiency of hydrogen in intermolecular energy transfer is small and the pressures added by Corner and Pease so small that any effect was concealed by the rather large experimental error. These workers also pointed out that, using this theory with the experimental results, the observed rate constant should become independent of pressure at low pressures, $\log k/k_\infty$ having a limiting value of -0.80. Values below -1.0 have been observed with no indication of the approach of a limiting value. The mechanism was therefore rejected.

As a means of testing his theory, Slater[42] used the results for cyclopropane in conjunction with the two mechanisms. Taking as his critical coordinate the distance between a hydrogen atom and a non-adjacent carbon atom, there are twelve equivalent coordinates in the molecule. He calculated the A factor as being 4.0×10^{14} whereas the experimental value is about 15×10^{14}. A theoretical decline of the rate constant was obtained but at a pressure $3\frac{1}{2}$ times the experimental value.

Using the trimethylene diradical, with only three equivalent coordinates, the first-order rate is only given at excessively high pressures.

The error of regarding the trimethylene intermediate as a radical with a lifetime sufficiently long to permit its detection led to the acceptance of the hydrogen migration mechanism as supported by the Slater theory.

McNesby and Gordon[73] pyrolyzed cyclopropane in the presence of deuterium. A failure to obtain any deuteriated propylene or cyclopropane was given as evidence for the absence of a radical chain reaction. A similar conclusion was reached by Weston[74] after studying the tritium isotope effect in cyclopropane. At high pressures the kinetic isotope effect is that for the decomposition of the activated molecule; if this involves breaking a bond to an isotopically labelled atom the effect can be predicted. The activation and deactivation steps are without an isotope effect. He predicted a decline in the effect to zero at low pressures, a result which was confirmed experimentally. On the basis of the rupture of a carbon-carbon bond no isotope effect would be expected.

The possible existence of a diradical which cannot be detected by conventional methods was established by Seubold[75]. He calculated that the subsequent recyclization or rearangement, an exothermic intramolecular process, occurs much more rapidly than the attack on a radical inhibitor such as toluene or nitric oxide.

The simultaneous geometric and structural isomerization of 1,2-cyclopropane-d_2 was investigated by Rabinovitch et al.[68]. Of three possible mechanisms suggested for the geometric isomerization, the only acceptable one involved the trimethylene diradical in a reversible recyclization. The absence of any 1,1-cyclopropane-d_2 in the product excluded a radical or hydrogen migration mechanism. It was found preferable to treat the structural isomerization as a hydrogen migration process.

Later work[76], in which vibrationally excited cis-1,2-cyclopropane-d_2 was formed from methylene and trans-ethylene-d_2, showed that the ratio of the geometric and structural rate constants differed only slightly from the value given by thermal studies. The energy of the cyclopropane was estimated as 95 kcal./mole., appreciably higher than the average molecule in the thermal studies; its failure to influence the ratio was taken to indicate a similar transition state for either reaction.

A value of $n = 14$[77] gives agreement between the Slater theoretical equation and the experimental decline of rate constant with pressure for cyclopropane-d_2, a finding difficult to correlate with the hydrogen migration mechanism. The removal of symmetry in the cyclopropane ring by tritium substitution can increase the number of normal modes participating in the reaction coordinate by as much as seven[78] and a similar effect would be predicted with 1,2-cyclopropane-d_2 towards a value of 20 or 21. Smith[79] was able to give a simple explanation of the geometric isomerization in terms of a partial hydrogen migration without ring-opening. In the transition state one of the methylene groups becomes coplanar with the ring. This configuration predicts a value of n similar to that for the structural isomerization, a result which is more difficult to account for with a simple ring-opening mechanism.

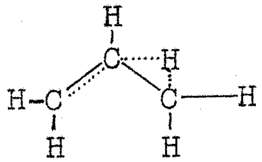
Benson[80] considers two objections to Smith's mechanism. First, any reasonable assignment for the frequency of a CH_2 twist (900-$1200 cm.^{-1}$) leads to an activation energy of between 100 and 150 kcal./mole. This is in complete disagreement with the observed activation energies which never exceed 65 kcal./mole. Second, the frequency factor for the mechanism will never exceed $10^{15} sec^{-1}$, an order of magnitude too low for the geometric isomerization of 1,2-dideuteriocyclopropane.

The possibility of the reaction coordinate being complex, with the carbon-carbon stretch an important component of it, was propounded by Rabinovitch and Michel[81] Applying the Slater theory to their results for the geometric isomerization of cis-butene-2 the fall-off was given using n = 28. A comparison of the values of n for other unimolecular reactions reveals their relatively large magnitude, in support of a complex coordinate.

Equations derived by Marcus in his absolute theory of unimolecular reaction rates have been used by Diesen and Rabinovitch[82] to compare the decomposition behaviour of chemically activated sec-butyl radicals. All of the vibrational degrees of freedom were taken as active, suggesting a complex reaction coordinate.

Although the removal of degeneracy by deuterium and tritium does not lead to the predicted increase in the value of n, the substitution of a methyl group does. Chesick[78] has found agreement between his studies of methylcyclopropane and the Kassel theory using s = 19.(s = 12 or 13 for cyclopropane). Fall-off occurred at 1/30th of the pressure observed for cyclopropane. Two possible conclusions can be reached from these data. First, the replacement of the C-H bond by C-C leads to an increase in the value of s or n whereas C-D and C-T do not. Alternatively the presence of the methyl group provides additional vibrational modes in which energy can be distributed. This would contribute towards the breaking of the molecule, assuming the transference of energy between the modes, which is contrary to a postulate of the Slater theory.

Isotopic studies have been extended to cyclopropane-d_6 by Blades[83]. The kinetic isotope effect was observed, as with cyclopropane-t_1, and by an identical argument, the results were put forward as favouring the hydrogen migration mechanism rather than the simple diradical process. On the other hand, Benson and Nangia[84] have shown that the diradical mechanism predicts a pressure effect if a more complex reaction coordinate is considered. Their transition state has a structure about midway between trimethylene and propylene, containing a bridged hydrogen atom perpendicular to the C-C-C plane.



A value of the frequency factor for the high-pressure rate constant and an expression for k_H/k_D, using the available frequencies, gives excellent agreement with the experimental values.

It is slightly ironical that this transition state embodies the features of both mechanisms originally put forward for the isomerization of cyclopropane. Nevertheless it deserves a serious consideration and has received support from results published by Setser and Rabinovitch[71]. Having thoroughly investigated the geometric and structural isomerization of 1,2-dideuterio-3-methylcyclopropane, they found that the results can only be adequately explained if the C-H, C-D and C-C bonds are all considered in the mechanism.

Benson[80] has criticised the hydrogen migration mechanism on the grounds that the simultaneous stretching and deformation of a C-H bond which will permit transfer to an adjacent group would require energies in excess of 120 kcal./mole.

Apart from a consideration of the reaction coordinate which is concerned in the mechanism of cyclopropane isomerizations, there is a second criterion by which the Slater theory can be distinguished from other theories. One of its requirements is that transfer of energy between the vibrational modes of the molecule is forbidden. The restriction is not made in the Kassel and Marcus theories.

The ability to produce 'hot' or vibrationally excited molecules has given a means of examining the possible process of intramolecular energy transfer. Whereas in thermal reactions the energy is evenly distributed throughout the molecule, in 'hot' molecules it may be located in one particular section.

The addition of methylene to isobutene gives an excited form of 1,1-dimethylcyclopropane[85] which, if not deactivated by collisions, isomerizes to 2-methylbut-2-ene and 3-methylbut-1-ene, the ratio of the products being 1.65. The thermal study of the isomerization gave a value of 0.96. As the energy of activation for both reaction paths is the same the difference between these ratios cannot be attributed to the higher energy content of the cyclopropane produced from isobutene and methylene. The distribution of the energy may be different and because of its very slow or non-existant transfer, the reaction to 2-methylbut-2-ene might be favoured. This conclusion would be in agreement with the

Slater theory.

Similar studies of the reaction of methylene with propylene and cyclopropane by Butler and Kistiakowsky[86] failed to reach the same conclusion. Both reactions produce 'hot' methylcyclopropane, but if slow energy transfer is assumed, a difference would be predicted between the isomerization of the compound formed from methylene and propylene and that formed from cyclopropane and methylene, where the excess energy is concentrated within the methyl group. The average yields of the four butenes from either reaction were identical, a result in agreement with energy transfer as proposed by the RRKM theory.

Likewise activated sec-butyl radicals[87] formed from either but-1-ene or cis-but-2-ene and hydrogen atoms involve different processes and yet the radicals decompose at virtually the same rates.

A calculation of the pressure dependence of rate constants using the Marcus quantum formulation of the RRK theory does not require the use of adjustable parameters. Using the necessary data for cyclopropane, methylcyclopropane and cyclobutane Wieder and Marcus[88] have obtained good agreement with the experimental results. This supports the assumption that energy exchange occurs between the various vibrational modes all of which participate in the process.

A group of compounds which possess similar structures, such as the alkyl cyclopropanes, apart from providing many examples of unimolecular reactions, have an additional advantage. They can provide a means of following the influence of a variety of substituents inserted into the ring. Besides reducing the degeneracy of the reaction path from the maximum value of twelve for the structural isomerization of cyclopropane itself, the size and chemical nature of the substituents would be expected to influence the path of the reaction and its rate. The truth of this is clearly shown by the isomerization of methylcyclopropane to butene-1, butene-2(cis- and trans-) and isobutene. The first two compounds are formed by the rupture of a ring carbon-carbon bond having the methyl group at one end; for the production of isobutene the breaking bond has only hydrogen atoms linked to the carbon atoms. The latter reaction has an energy of activation approximately 2.3 kcal./mole. higher than the other. Similar results have been obtained from the kinetic data for the structural isomerization of 1,2-dideuterio-3-methylcyclopropane[71] and 1,2-dimethylcyclopropane[89], and in the latter case a further reduction in the energy of activation has been found if the methyl groups have the cis- rather than the trans-configuration.

Thus the substituents in a cyclopropane ring can have a very real influence upon the reaction path and the energy of activation. A comparison of the A factors and energies of activation might be expected to give some quantitative measure of their effects. Unfortunately results still lack precision and the method of calculating these quantities is not sufficiently exact to permit a worthwhile comparison. The experimental uncertainties may exceed the expected variation between compounds. The method of least squares is frequently used to calculate the A factor and energy of activation from a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature. Roseveare[90] has pointed out that even this can be a questionable method which does not give an equal weighting to all of the points.

In view of these uncertainties, a more useful approach to the comparison can be made by calculating the rate constants of the different reactions at a fixed temperature. Further, if we postulate that the A factors for a particular type of cyclopropane reaction are almost equal after allowing for any difference of degeneracy in the reaction path the comparison becomes more significant.

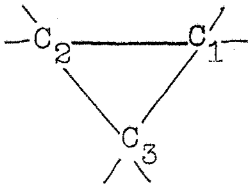
Gowenlock[91] has reviewed Arrhenius factors and concludes that they bear a relation to the reaction mechanism. The magnitude of the A factor gives some indication of the nature of the transition state, a value greater than 10^{13}sec^{-1} suggesting a 'loose' structure in which there is partially hindered or free rotation. Substituent groups would be expected to impose some restriction on this motion. However the fundamental mechanism for the structural isomerization of a cyclopropane will be very similar for different compounds so that the postulate is not unreasonable. The rate constant then provides a method of comparing the energetics of the reactions and the influence of molecular structure.

The rate constants for the structural isomerization of several cyclopropanes have been calculated at 730°A and are given in Table 10. The true rate constants are given in the second column. Their relative values provide some measure of the influence of the structure on the reaction velocity but they are also dependent upon the degeneracy of the reaction paths. When cyclopropane isomerizes to propane there

TABLE 10. Rate Constants for the Structural Isomerization of Certain Cyclopropanes.

Compound	Rate Constant $x10^5(sec^{-1})$ 730°A	Path Degeneracy	Rate Constant $x10^5(sec^{-1})$ Corrected
Cyclopropane	6.46	12	6.46
Methylcyclopropane	9.60	10	11.5
1,1-Dimethylcyclopropane[92]	20.0	8	30.0
1,1-Diethylcyclopropane	20.0	8	30.0
1,1,2,2-Tetramethylcyclopropane.	34.8	4	104

are twelve possible ways of transferring a hydrogen atom to a non-adjacent carbon atom whereas for 1,1,2,2-tetramethylcyclopropane there is a maximum of four ways by which the exchange can occur. Probability alone therefore predicts a slower rate for the latter compound, if the shift of the hydrogen atom is a rate-controlling part of the mechanism. Cyclopropane-d_6[83] has been found to isomerize at a slower rate than cyclopropane which can only be caused by the different type of atom being transferred. Multiplying the rate constants by appropriate factors (12/path degeneracy) eliminates the effect of degeneracy; the corrected values are given in the fourth column. For reference, the carbon atoms of the cyclopropane ring will be labelled as follows:



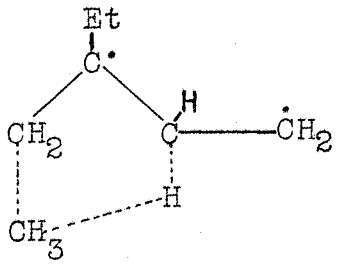
The results of earlier workers show that the rate constant increases from the value for cyclopropane as one methyl group and then a second is substituted onto the C_1 atom. The replacement of a hydrogen atom by the larger methyl group might produce some additional steric repulsion between it and those hydrogen atoms at C_2 and C_3 which lie on the same side of the plane of the ring. This introduces additional strain into the C_1-C_2 and C_1-C_3 bonds so that a lower energy of activation would be required for their rupture. The effect in these examples is only small. More important as an aid to the reaction is the partial stabilization of the diradical by the substituent groups. When the C_1-C_2 bond breaks in the 1,1-dimethylcyclopropane molecule, a tertiary carbon atom is at one end of the diradical. The reaction in which the C_2-C_3 bond breaks will not be affected by these factors which accounts for the slower rate of isomerization.

Although it is perhaps fortuitous that the rate constant for the isomerization of 1,1-diethylcyclopropane is identical to that for 1,1-dimethylcyclopropane, their similarity is significant. The larger ethyl groups will have little additional effect on the C_1-C_2 and C_1-C_3 bonds or upon the diradical which is formed. The energies of activation are expected to be similar and so it follows that the A factors are also. The conclusion is in agreement with the original assumption that the larger substituents in the ring do not alter appreciably the form of the transition state.

Substitution is further increased in the molecule of 1,1,2,2-tetramethylcyclopropane with two methyl groups on C_1 and C_2. The higher rate constant is to be expected because of the greater steric repulsion of the four groups, weakening the C_1-C_2 bond. In addition the rupture of this bond gives two tertiary carbon atoms which have a stabilizing effect on the diradical.

The kinetic results obtained for 1,1,2,2-tetramethylcyclopropane and 1,1-diethylcyclopropane cannot be used to distinguish between the two suggested reaction paths which have been discussed or lend support to a mechanistic theory combining the two. Nevertheless it is necessary to consider a possible mechanism for the reaction in which 1,1-diethylcyclopropane decomposes to 2-ethylbuta-1,3-diene and methane. Work by Chesick[93] has confirmed that the interpretation of the result is correct, since he has established that buta-1,3-diene is a product of the thermal reaction of ethylcyclopropane.

No evidence was obtained to suggest that this reaction involves radicals anymore than the 'normal' cyclopropane isomerization. Therefore a mechanism is favoured which is a molecular process. As in the isomerization reactions, ring opening occurs initially to give a diradical. This orientates itself into a transition state, considered as a five-membered ring, which is represented as



The reaction requires the breaking of a second carbon-carbon bond and the migration of a hydrogen atom. This is in accordance with the higher energy of activation than is required for the isomerization to 3-ethylpent-1-ene and 3-ethylpent-2-ene. The difference is only about 2.3 kcal./mole.,(as this reaction path is favoured by the 4 kcal./mole. resonance energy of the conjugated diene.)

The A factor is also higher for the decomposition reaction, pointing to a 'looser' complex in which rotation is free or only partially hindered. The rather rigid five-membered ring which has been proposed might be expected to be characterized by a somewhat lower A factor.

The problem of elucidating an acceptable mechanism for the geometric isomerization of the cyclopropanes has not proved to be such a contraversial issue. Although several suggestions have been put forward, one has come to the fore as being most plausible. The mechanism was proposed by Rabinovitch et al.[68] and again it involves the formation of a diradical intermediate. Its validity has not been definitely proved, nor has it been possible to discard an alternative idea due to Smith[94] that the isomerization can occur via a partial hydrogen migration without ring opening.

The main features of the diradical mechanism are that, after rupture of a carbon-carbon bond, a hindered rotation can occur about one or both of the remaining bonds. This is followed by a reversible recyclization of the diradical. By analogy with the considerations made during the discussion of the structural isomerization of cyclopropane, the velocity of the reaction is expected to be dependent upon the substituents in the ring.

The A factors, energies of activation and rate constants at 710°A for five compounds that undergo a geometric isomerization are given in Table 11. They may all be considered as having the same path degeneracy. For 1,2-dideuterio-3-methylcyclopropane two values of each of the quantities are quoted. The first (a) is for the isomerization of the cis-isomer to the trans- and cis,trans-isomers; the second (b) is for the isomerization of the cis,trans-isomer to the cis- and trans-isomers.

TABLE 11. Rate Constants for the Reversible Geometric Isomerization of Certain Cyclopropanes.

Compound	A factor sec^{-1}.	Energy of Activation kcal./mole.	Rate Constant $x10^4(sec^{-1}.)$ $710^{\circ}A$.
1,2-Cyclopropane-d_2 (trans → cis)	16.0	64.2	1.70
1,2-Dimethylcyclopropane (cis → trans)	15.25	59.4	8.96
1,2,3-Trimethylcyclopropane (cis → trans)	15.78	61.0	10.3
1-Ethyl-2-methylcyclopropane (cis → trans)	15.08	58.9	8.94
1,2-Dideuterio-3-methyl	(a)15.3	60.4	4.90
cyclopropane	(b)15.4	60.7	5.14

1,2-Cyclopropane-d_2 is seen to differ from the others in two ways. First, the energy of activation is about 4 kcal./mole. higher, accounted for by a stronger carbon-carbon bond when deuterium atoms are at either end rather than the larger methyl and ethyl groups. Second, the A factor is higher. This may be attributed to a 'looser' transition state than is formed in the remaining examples. If the diradical mechanism is accepted, a configurational change in a molecule results from the rotation of a deuterium atom, methyl or ethyl group about a carbon-carbon single bond. The larger methyl and ethyl groups will cause a greater hindrance to the rotation, an effect which is associated with a smaller A factor.

The values of the rate constants for the geometric isomerization of 1,2-dimethylcyclopropane, 1,2,3-trimethylcyclopropane and 1-ethyl-2-methylcyclopropane are very similar. From a consideration of the geometries of the molecules this is to be expected. It does seem however, that an A factor of 15.78 for 1,2,3-trimethylcyclopropane is too high. A figure similar to that obtained for 1,2-dimethylcyclopropane would be more in accordance with expectation.

The difference in the enthalpy of formation (ΔH) of the cis- and trans-1,2,3-trimethylcyclopropane was calculated to be 2.3 kcal./mole. The values found for 1,2-dimethylcyclopropane and 1-ethyl-2-methylcyclopropane were 1.07 and 1.2 kcal./mole. respectively. These values may be ascribed to the difference in repulsion produced when the substituent groups are in the cis-and trans-orientations. Additional strain is introduced into the molecule if the groups are in the cis-configuration. Similar values of ΔH are therefore to be expected for 1,2-dimethylcyclopropane and 1-ethyl-2-methylcyclopropane.

A comparison of the cis- and trans-configurations of 1,2,3-trimethylcyclopropane reveals that additional repulsion in the cis-isomer occurs between C_1 and C_2 and also between C_1 and C_3. The repulsion between C_2 and C_3 is identical for both, so that twice the value found for 1,2-dimethylcyclopropane is to be expected, in good agreement with the experimentally-determined 2.3 kcal./mole.

Kinetic studies of vinylcyclopropane and its derivatives have only received slight attention. The fundamental nature of the isomerization does not seem to lend itself to suitable adaptations by which the cyclopropane reaction mechanism can be probed. Despite this, it is of theoretical interest as a way of studying the influence of an exocyclic double bond on a reaction. In accordance with the preceding discussions, the isomerization can be considered as involving a diradical intermediate. The rate equations for the three known examples were given on p.125. The reactions are characterised by 'normal' A factors and lower energies of activation than found for the geometric and structural isomerization of cyclopropanes. The products of the reactions are cyclopentene or 1-methylcyclopentene.

The isomerization of isopropenylcyclopropane to 1-methylcyclopentene is most easily understood in terms of the formation of the diradical

$$\underset{1}{\cdot CH_2}.CH_2.\underset{3}{\dot{C}H}.C(Me):CH_2 \longleftrightarrow \underset{1}{\cdot CH_2}.CH_2.CH:C(Me).\underset{5}{CH_2}\cdot$$

Ring closure at the 1-3 position regenerates the cyclopropane; at positions 1-5 it yields 1-methylcyclopentene. Although there is a similarity with the other cyclopropane mechanisms, the lower energy of activation (51 kcal./mole.) is attributed to the delocalization or allylic resonance energy of the cyclopentene diradical which, for allyl itself, has been calculated[95] as 17-18 kcal./mole.

The energy of activation for the geometric isomerization of 1,2-cyclopropane-d_2 is 64 kcal./mole., a value 13 kcal./mole. higher than for isopropenylcyclopropane. This is close to the value suggested for the mechanism. The 4-5 kcal./mole. difference between theory and experiment is possibly due to the steric requirements of the transition state, imposing some restriction on the diradical. Benson et al.[96] have suggested a value of 12 ± 1 kcal./mole. for the allylic resonance in the methylallyl radical but this would suggest complete delocalization of the electron in the transition state leading to the methylpentene, contrary to the model used when discussing these reactions. It also disagrees with the A factor being considerably smaller than the value for the geometric isomerization of dideuteriocyclopropane. Even allowing for the slight difference in path degeneracy the value does indicate a rather restricted transition state.

The cyclcpropanes are not the only cyclic hydrocarbons capable of undergoing a unimolecular transformation. Studies have now been extended to cyclobutane,[43] cyclobutene[44] and a few of their derivatives. Their structural isomerization differs from that of the alkyl cyclopropanes since the shift of a hydrogen atom is not involved in the reaction.

Cyclobutene[44] was observed to isomerize to buta-1,3-diene at an appreciable rate at 150°C a temperature considerably lower than required for the cyclopropanes and cyclobutanes. Later work with 1-methylcyclobutene[97], 1,2-dimethylcyclobutene[98], 3-methylcyclobutene[56] and 1,3-dimethylcyclobutene was in agreement with isomerization occurring at low temperatures. The product in all cases was a conjugated diene.

The accepted mechanism of the isomerization of cyclobutenes is that, due to the influence of the ring double bond, the C_3-C_4 bond breaks to form a diradical. Overlap of the π orbital of the C_1-C_2 bond with the orbitals containing the unpaired electrons leads to the formation of the conjugated diene.

The A factors and energies of activation together with the rate constants calculated from the Arrhenius equation at 420°A for these isomerizations are given in Table 12. The A factors are all between 10^{13} and 10^{14} sec^{-1}, the 'normal' value for a unimolecular reaction but considerably lower than for cyclopropanes and cyclobutanes. This indicates a more rigid transition state which is structurally very similar to the original cyclobutene. The energies of activation are approximately 30 kcal./mole. less

TABLE 12. A factors, Energies of Activation and Rate Constants for the Cyclobutenes.

Compound	log A	Energy of Activation (kcal./mole)	Rate Constant $x10^{4}$(sec^{-1}) at 420°A.
Cyclobutene	13.26	32.70	1.74
1,3-Dimethylcyclobutene.	13.65	33.02	2.95
3-Methylcyclobutene.	13.53	31.55	12.6
1-Methylcyclobutene.	13.79	35.10	0.331
1,2-Dimethylcyclobutene.	13.84	36.04	0.120

than the values for cyclopropanes and cyclobutanes a definite indication that the opening of the ring by the rupture of a carbon-carbon bond is energetically comparatively easy. A comparison with the cyclobutanes shows that, apart from the normal ring strain, the presence of the double bond introduces a considerable additional strain to the breaking bond.

Goldish et al.[99] have studied the molecular structure of cyclobutene in the gas phase by electron diffraction and find that the angle stress at $\angle C_3-C_2=C_1$ is most likely greater than at $\angle C_2-C_3-C_4$. This will tend to lengthen the C_3-C_4

bond which breaks. The resonance energy of the conjugated diene formed during the reaction may also contribute towards a lowering of the energy of activation.

The substitution of methyl groups into the cyclobutene ring produces a marked alteration in the energy of activation for the reaction. The magnitude of the effect is seen more clearly by comparing the rate constants for the isomerization of the cyclobutenes at 420°A, bearing in mind the fact that these also reflect any changes in the A factors. The values are given in Table 12.

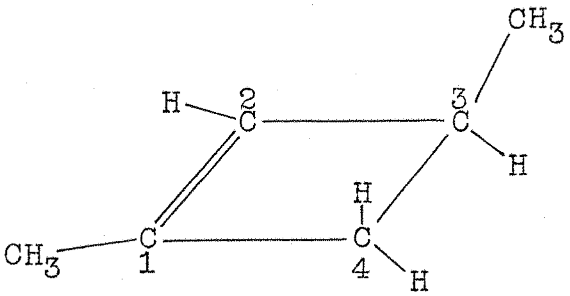
The first significant observation that can be made from the results is that the effect of methyl substitution in the ring is strongly dependent upon its exact location. If the methyl group is at either end of the ring double bond the energy of activation is increased by between 2 and 3 kcal./mole. The increment is greater when methyl groups are at both ends of the double bond. Simultaneously the A factor increases.

Steric repulsion exists between the methyl group on C_1 and the hydrogen atom or methyl group on C_2 which are coplanar. The breaking of the C_3-C_4 bond will permit twisting about the C_1-C_2 bond to relieve the repulsion giving more freedom to the transition state. The increase in the energy of activation is due to the electron donating properties of the methyl group which slightly increases the length of the double bond and so removes some of the strain from the C_3-C_4 bond.

In contrast, methyl substitution at C_3 reduces the energy of activation. The A factor is greater than for cyclobutene so that the rate of isomerization increases by a factor of seven. Additional steric repulsion is to be expected with a methyl group present which will weaken the C_3-C_4 bond. Frey[56] has also suggested that the methyl group may partially stabilize the diradical. Either or both effects would account for the lower energy of activation.

The molecule of 1,3-dimethylcyclobutene has one methyl group on the double bond and the other at the end of the C_3-C_4 single bond. From the preceding discussion, the first tends to decrease the rate of isomerization whilst the second increases it. The similarity of the rate constants for cyclobutene and 1,3-dimethylcyclobutene is therefore to be expected.

3-Methylcyclobutene and 1,3-dimethylcyclobutene isomerize to give only the trans-isomer of the diene which is formed. This observation provides additional information of the mechanism. A consideration of the stereochemistry of the reactant and product provides an adequate explanation. The molecule of 1,3-dimethylcyclobutene is



All of the carbon atoms in 2-methylpenta-1,3-diene are coplanar whereas in the cyclobutene molecule the methyl group on C_3 lies above the plane of the ring. Hence, as the 1,3-dimethylcyclobutene molecule progresses along the reaction path towards the transition state, the stretching of the C_3-C_4 bond is not the only structural change which occurs. Simultaneously the methyl group on C_3 must begin to rotate into the plane of the ring. It can rotate in two directions, towards or away from C_4. Sterically, rotation away from C_4 is preferred which can only result in the formation of trans-2-methylpenta-1,3-diene.

One of the essential requirements of any theory of unimolecular reactions which is based on the general Lindemann mechanism is that, at a sufficiently low pressure, there should be a decline in the first-order rate constant towards a second-order limit. The pressure at which fall-off commences depends upon the complexity of the molecule. For cyclopropane fall-off has already begun at 1000mm., for methylcyclopropane it begins slightly below 100mm. and for 1,1- and 1,2-dimethylcyclopropane at about 16mm. A detailed study of the decline of the first-order rate constant with pressure for a unimolecular reaction provides a means of critically examining the theories which have been developed.

Hauser and Walters[44(b)] have extensively investigated the dependence of the rate constant on pressure for the isomerization of cyclobutene to buta-1,3-diene from 23 to 0.015mm. at two temperatures. Agreement between the experimental results and the curve computed from the classical form of the Kassel integral was obtained for s=10, assuming unit collisional deactivation efficiency. Preliminary investigations showed that a similar decline occurred for 3-methylcyclobutene over a similar pressure range so a more detailed investigation was undertaken.

A comparison of experimental results with the transition state theory and the Marcus absolute rate theory provides the most conclusive means of establishing a theory of unimolecular reactions. Because these theories are so fundamental, a considerable quantity of data for each compound is required, including a complete vibrational analysis of the molecule. Weider and Marcus[88] have successfully applied their theory to several of the simple compounds including cyclopropane and cyclobutane.

The need for precise data together with the problems of the computational work involved in the absolute theories has led many workers to resort to a comparison with the relatively simple rate expressions derived by a classical treatment, notably the Kassel integral equation. The usefulness of this equation lies in the comparison of the fall-off behaviour of compounds rather than an absolute analysis of a single compound.

The successful application of consistency tests to the rate data for the isomerization of 3-methylcyclobutene showed that the reaction was in agreement with the general Lindemann mechanism and justified a comparison of the results with the more detailed Kassel theory.

The Kassel integral was computed using various values of the parameter s for the two temperatures at which the decline of the rate constant with pressure was studied. The collision efficiency λ was set equal to unity.

If the theory correctly predicts the value of k/k_∞ at any pressure over the range studied, then the overall shape of the theoretical and experimental curves should be identical. They may not superimpose on each other because of the uncertainties in the collision diameter, A factor and energy of activation. However any error in these quantities simply displaces the complete theoretical curve along the pressure axis.

Setting s=14 in the integral gave good agreement with the experimental value of k/k_∞ over part of the pressure range as shown in figure 15, but there was considerable divergance at the lowest pressures. The experimental fall-off was more rapid than predicted by the theory. Better agreement in the overall shape of the curves was obtained with s=12 but this necessitated shifting the theoretical curve along the pressure axis by 0.58 log units for fall-off to occur in the correct pressure region. The shift may be accounted for by setting λ equal to 0.26. A similar discrepancy in the shape of the curves was found in the low-pressure region for cyclopropane with $s=13$[41]. By assuming a larger collision diameter, the curve for $s=12$ gave a more satisfactory fit. With the collision efficiency set equal to unity one particular value of s accounted for the observed fall-off for methylcyclopropane and 1,1-dimethylcyclopropane. The curvature of the theoretical plot changes with s for larger values only by a small degree as the latter increases. Therefore, for these two compounds which have higher s values, agreement between the overall shape of the theoretical and experimental fall-off curves can be obtained over a small range of values of s. Because of the lack of any further knowledge, s has been determined by the curve fitting the experimental points with $\lambda=1$.

The isomerization of cyclobutene has been studied over almost the same pressure range. A satisfactory fit of the results with the theoretical curve was obtained with s=10 and λ=1, using the classical form. There was some uncertainty in the accuracy of the points at the lowest pressures which were apparently too high. It might therefore be necessary to assume smaller values of s and λ for complete correspondence of the overall shapes. Until a check is made, a comparison of the s value assigned to cyclobutene and 3-methylcyclobutene cannot be made.

A comparison between 3-methylcyclobutene and cyclopropane shows that similar values of s are required although the former molecule has four extra atoms giving it twelve additional modes of vibration. A direct comparison of the significance of this result cannot be made because of the considerable difference in the energy of activation for the two reactions, but two explanations can be given. First if a reaction has a smaller energy of activation, the process of transferring the energy to a specific bond in the molecule would be expected to require the participation of a smaller number of oscillators. Second, the accumulation of a certain quantity of energy in a carbon-carbon bond of the ring is simpler than the more complex requirement of a cyclopropane isomerization which also involves the transfer of energy into a carbon-hydrogen bond. The ring carbon-carbon bonds form an important link for energy transfer through a cyclopropane molecule, but, because of their more remote location, the flow of energy into the carbon-hydrogen bonds is statistically more improbable. Thus a greater number of the vibrational degrees of freedom have to participate to produce a configuration which will lead to reaction. The isomerization of a cyclobutene only requires the accumulation of energy in a ring carbon-carbon bond.

The assumption of unit collisional efficiency infers that every collision between an activated molecule and any inactive one results in deactivation. An efficiency less than one means that more than one collision of the activated molecule is required to cause deactivation. Jones and Davidson[100] have been able to calculate λ in the thermal decomposition of ozone. Their value is 0.039. The Marcus theory has been applied to the isomerization of several compounds[88]. Agreement between theory and experiment was obtained for cyclopropane and cyclobutane if the respective collision efficiencies were 0.25 and 0.20. These findings cast considerable doubt on the assumption of unit collisional deactivation efficiency.

Certain kinetic studies have led to a determination of the relative efficiencies of inert gases in the energy transfer process occurring during deactivation. The ability of inert gases to maintain the high pressure rate constant of a unimolecular reaction in the fall-off region provides a method of determining the efficiencies on a pressure-for-pressure and collision-for-collision basis. Attention has been mainly confined to the non-condensable gases and compounds of small molecular weight whose relative efficiencies have been less than that of the reactant molecule.

The conditions existing at the commencement of a reaction were considered when deriving the Kassel classical expression for the first-order rate constant. This avoided the need to consider the influence of the product upon the reaction. In practice reactions are followed to a high percentage decomposition, thereby assuming that the reactant and products have the same efficiency in maintaining the distribution of energies. If they do not, some curvature of the rate plot is to be expected as the reaction proceeds. This has never been observed but Volpe and Johnson[20] have shown that any curvature resulting from a product having a different activating efficiency to the reactant will be concealed by experimental error.

The collision efficiencies of the three isomeric pentanes were determined during the study of the thermal isomerization of 3-methylcyclobutene. With the possible exception of toluene, no previous attempt had been made to determine the relative efficiencies of hydrocarbons with molecular weights similar to those of the reactant and product. The results obtained in this work are of considerable interest since they lend support to the possibility that the collision efficiency of 3-methylcyclobutene is less than one.

The collision efficiency of n-pentane, averaged over seven runs, was 1.32 compared to 3-methylcyclobutene whilst the values for iso- and neo-pentane were 1.25 and 1.12 respectively. If the assumption that deactivation occurs on every reactant-reactant collision is true then no inert gas can have a collision efficiency greater than 1. The above results can only mean that the original assumption is incorrect for 3-methylcyclobutene and gives some support to the earlier finding that agreement between the Kassel integral and the experimental results required $s=12$ and $\lambda=0.26$. Doubt is now cast upon all quantitative interpretations of unimolecular reactions which can only be cleared away by a complete solution to the problems of collision efficiency.

Comparisons have been made to give some guide to the parameters which are important in determining energy transfer efficiencies. There appears to be no correlation with molecular complexity[64] but there does seem to be one with boiling point. For the pentanes these are 36°C(normal), 30°C(iso-) and 9°C(neo-). The collision efficiencies are therefore seen to decrease with the boiling point.

A further consideration of the parameter λ is deferred until Appendix 1.

There was close agreement between the theoretical and experimental shift of the fall-off curves with temperature. The Slater classical treatment relates the parameter n to this shift. The value of n calculated in this way for 1,1-dimethylcyclopropane was 29 whereas the value of n corresponding to $s=23$ is 19. This difference was well outside the experimental error. The identical calculation for

3-methylcyclobutene gave n=15, equivalent to s=12. The agreement is good although it must be remembered that a value of λ less than one has been assumed when setting s equal to 12.

The results obtained from the kinetic study of the thermal reactions of the cyclopropanes and cyclobutenes summarised in this work have been critically examined in relation to the modern theories of unimolecular reactions and the proposed mechanisms. A close agreement with the results for structurally similar compounds has been obtained. A qualitative analysis has been made of the influence of substituents in a cyclic hydrocarbon on the reaction path. Some doubt still surrounds the mechanism of cyclopropane isomerization reactions although interpretations in this work have favoured the diradical mechanism which does seem to present a more realistic model. It seems more capable of explaining the experimental observations and may be used to discuss the structural and geometric isomerization of cyclopropanes. A similar mechanism has been used to describe the isomerization of cyclobutenes.

Two significant results have been obtained by applying the Kassel integral to the rate data for

3-methylcyclobutene in the fall-off region. First, a smaller value of s is required in the integral than for a corresponding cyclopropane with an almost identical number of atoms in it. Second, a collision efficiency of less than one is required for complete agreement between theory and experiment over the entire pressure range. This is given support by the finding that the isomeric pentanes, used as inert gases, are relatively more efficient than 3-methylcyclobutene in the energy transfer process. No longer does there seem to be any justifiable reason for assuming that $\lambda=1$ in the Kassel integral. As a consequence considerable uncertainty must be attached to the values of s assigned to the various compounds whose first-order kinetics have been extensively studied in the fall-off region.

A determination of collision efficiencies of inert gases in a region close to the high-pressure limit of a reaction will be of interest. At these pressures only a slight decline in the collisional deactivation efficiency is expected on account of a larger number of activated molecules proceeding to product rather than undergoing deactivation. If an inert gas has an efficiency greater than the reactant molecule this will be clear evidence that more than one collision of an activated molecule is required to cause deactivation.

APPENDIX 1.

An Alternative Method of Estimating the s Parameter

A study of the decline of the first-order rate constant with pressure for 3-methylcyclobutene produced results which enabled a comparison to be made with theoretical curves computed from the Kassel integral. A value was assigned to the parameter s to give agreement between theory and experiment. At the lowest pressure, 0.01mm., the rate constant had declined to one-third of the high pressure limit.

An accurate comparison is only possible if the fall-off can be followed into the low pressure region where a rapid decline in the value of the rate constant occurs. The scatter of the experimental points close to the high pressure limit is such as to give agreement with the theoretical curves for a range of value of s.

The necessity to study fall-off over a wide pressure range has imposed a severe restriction on the compounds to which the theories of unimolecular reactions can be applied. The decline of the first-order rate constant for a cyclopropane with more than five carbon atoms does not begin until the pressure is about 1mm. A lower pressure limit of 0.01mm.

is set by the apparatus in order to obtain results of worthwhile accuracy. It is therefore instructive to examine a possible method of determining s using only the data obtained close to the high pressure limit. At the same time a method is given of further examining the collision efficiency λ for those compounds whose s value is already known.

The pressure p in the Kassel integral (equation 10, p.15.) is replaced by 1/m and the expression for k_{exp} differentiated with respect to m. Then

$$\left(\frac{\partial k_{exp}}{\partial m}\right) = -\frac{k_{\infty}C}{(s-1)!}\int_{0}^{\infty}\frac{y^{2s-2}e^{-y}dy}{\{1+mC[y/(y+b)]^{s-1}\}^{2}(y+b)^{s-1}}$$

$$= \underset{m\to o}{Lt} -\frac{k_{\infty}C}{(s-1)!}\int_{0}^{\infty}\frac{y^{2s-2}e^{-y}dy}{(y+b)^{s-1}} \qquad \text{Equation 1.}$$

where $C=A/\lambda Z$ and $b=E_{A}/RT$. The collision frequency Z is equal to $N\sigma^{2}(8\pi kT/\mu)^{\frac{1}{2}}$ in which σ is the collision diameter and μ the reduced mass. Since the right-hand side of the equation is independent of m, a plot of k_{exp} against m should be linear as m tends to zero, that is, close to the high pressure limit. The slope can be calculated from the experimental results, substituted into the equation, assuming $\lambda=1$ and s calculated. Alternatively if s has already been determined from fall-off results, λ can be recalculated instead of assuming it again equal to unity. If the Kassel theory accounts for the behaviour of a compound participating in a unimolecular reaction over the complete range of pressures, the values of s and λ should be the same, whichever method of calculation is used.

The integral in equation 1 can be computed by Gauss-Laguerre Quadrature. Most of the results were obtained by this method using an Autocode programme similar to that for the Kassel integral. Marcus[101] has described an alternative method of calculation, used for the earlier section of the work, by which the integral can be evaluated quite rapidly using a hand calculating machine.

Before examining any experimental results, the limitations of the calculations are considered using theoretical results for 1,1-dimethylcyclopropane. These show the range of fall-off over which a plot of k against m can be treated as linear. The Kassel integral was computed over the pressure range 200-0.45mm. for s=23 and b=43.17, assuming $\lambda=1$. The graph of k plotted against m appeared linear between 200 and 45mm. corresponding to 0.6% fall-off of the high pressure rate constant. The limiting slope was calculated by least squares to be -1.60×10^{-4} mm./sec., which, inserted in equation 1, gave

λ=1.29. The method is obviously not very satisfactory so that only a brief consideration will be given to the calculations by the method using experimental data for cyclopropane, methylcyclopropane and 1,1-dimethylcyclopropane.

At 470°C the limiting slope was -4.88×10^{-5}mm./sec., using the results over a range of 15% fall-off. This gave λ equal to 4.25. Using the same value of the slope and with s=27, λ equalled 1.07, but it was not possible to find values of s and λ which would give complete agreement between the Kassel equation, the high pressure equation and the experimental results. The same discrepancy was found for cyclopropane and methylcyclopropane. The value of s required to give λ=1, using data close to the high pressure limit was four or five greater than the value determined from fall-off results.

Johnston and White[60] have related k/k_∞ to m by the equation

$$k/k_\infty = 1-\nu_1^\infty m+\nu_2^\infty m^2-\nu_3^\infty m^3+ \cdots$$

For small values of m

$$k/k_\infty = 1-\nu_1^\infty m$$

so that a plot of k against m should be linear with a slope equal to $-\nu_1^\infty k_\infty$. Alternatively the slope can be found indirectly from ν_1^∞ which is obtained by extrapolating a plot of ν_1 against m to m=o.

Theoretical values of ν_1 were computed for 1,1-dimethylcyclopropane with s=23 and b=43.17. The extrapolation of a plot of $1/\nu_1$ against m to m=o gave $\nu_1^\infty = 1.019 \times 10^{-8}$m./cc. The high pressure rate constant at 469.8°C was 4.65×10^{-4}sec^{-1} and so the limiting slope was calculated to be -2.19×10^{-4}mm./sec. This gave a value of $\lambda = 0.95$, thereby showing this calculation to be a preferable method of estimating λ.

First of all the experimental results for cyclopropane at 500°C were used. Johnston and White found ν_1^∞ to be equal to 60.1×10^{-8}m./cc by extrapolation. At this temperature $k_\infty = 6.17 \times 10^{-4}$sec^{-1}., so that the limiting slope was equal to -1.78×10^{-2} mm./sec, a factor of 10 higher than calculated from the plot of k against m. Assuming a collision diameter of 5.5Å, when s=13, the collision efficiency was calculated as 1.07.

This more promising method of estimating the magnitude of the limiting slope of the k vs m plot was applied to the experimental results of other workers for the compounds methylcyclopropane, 1,1-dimethylcyclopropane and cyclobutane. The results are summarised in Table 13. The values of λ computed using s given by fall-off results are not equal to 1 but agreement is much closer than in the earlier calculations.

TABLE 13. Collision Efficiencies.

Compound	s	Temp(°C)	$\nu_1^{\infty} \times 10^8$(m./cc.)	λ
1,1-Dimethyl-cyclopropane	23	449.6	0.253	2.81
" "	23	469.8	0.323	2.99
" "	25	469.8	0.323	1.13
Methylcyclo-propane	19	490.6	8.70	0.77
Cyclobutane	19	449	2.91	2.39
" "	21	449	2.91	1.00

The original method of calculating the limiting slope was inexact for two reasons. First, the region of fall-off considered for calculating it was too wide and second, there was a lack of reliable experimental data close to the high pressure limit which could be used.

Earlier in this work results have been given for the decline of the first-order rate constant with pressure for the thermal isomerization of

3-methylcyclobutene. At 148.5°C a pressure range was studied in detail in which the rate constant was within 5% of the high pressure limit. The graph of k against 1/pressure is shown in figure 12. The slope was calculated by the method of least squares, including all the points, and was equal to $-2.47x10^{-4}$ mm./sec.

The moment ν_1 was also calculated and plotted against m. By extrapolation to m=o ν_1^{∞} was equal to $0.690x10^{-8}$m./cc , giving a limiting slope of $-2.70x10^{-4}$mm./sec. The agreement between these limiting slopes, as calculated by the two methods, was good, confirming that if accurate data for the decline of the rate constant can be obtained which is within 5% of the high pressure rate constant, a reliable estimate of the slope can be made.

Finally the calculated values of λ for 3-methylcyclobutene are considered. The results were

	s=12	s=14
Limiting slope = $-2.47x10^{-4}$mm./sec.	λ=11.4	λ= 3.7
Limiting slope = $-2.70x10^{-4}$mm./sec	λ=10.4	λ= 3.4

The poor agreement when s=12 clearly reveals that, although this figure gives a fall-off curve having the correct shape, it fails to give the correct high

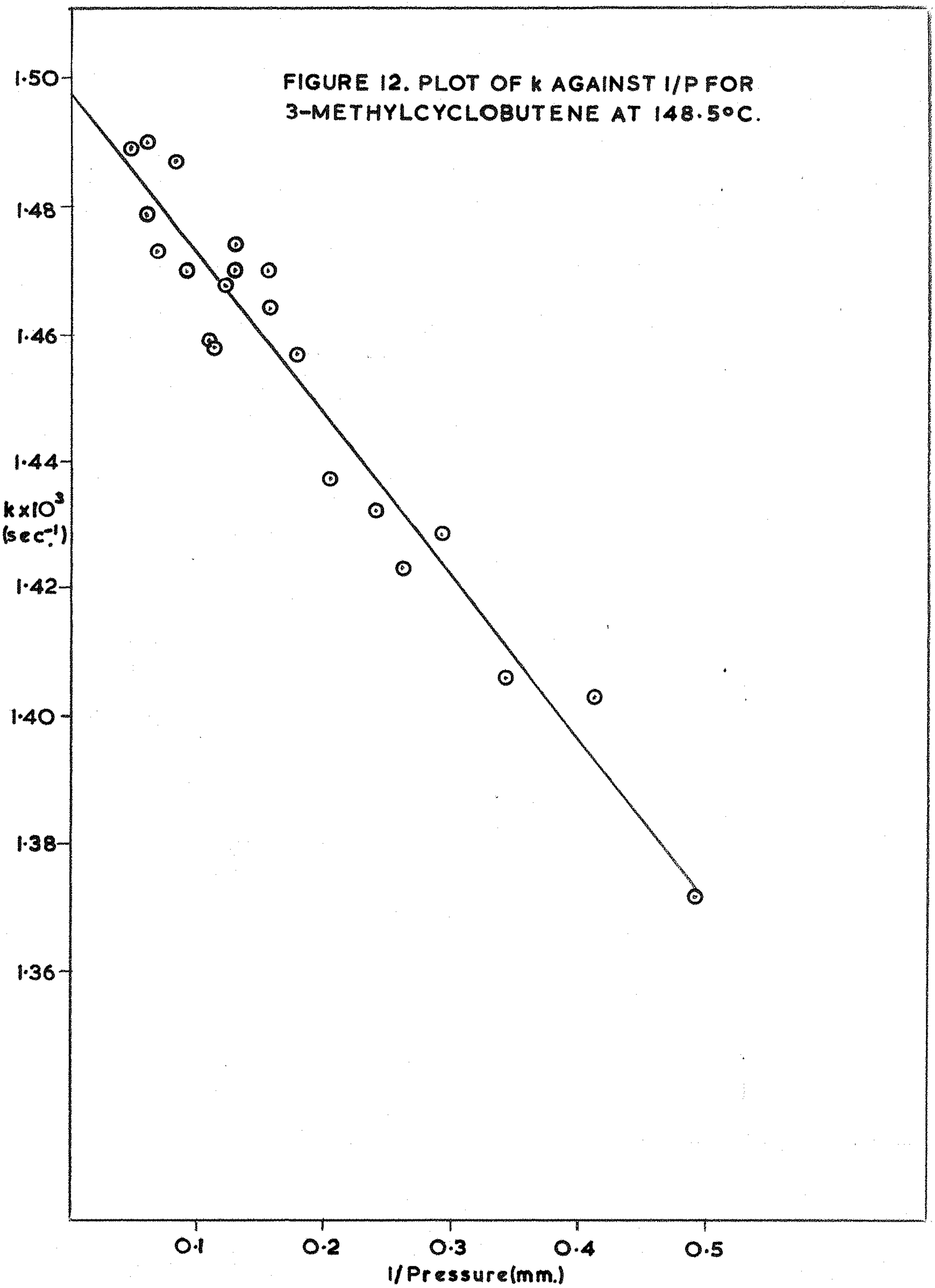


FIGURE 12. PLOT OF k AGAINST 1/P FOR 3-METHYLCYCLOBUTENE AT 148·5°C.

pressure results. This is to be expected since the value of λ calculated using s=12 has not taken into account the fact that the latter figure was obtained assuming λ=0.26. It does seem, therefore, that s=12 is unable to account completely for the kinetics of 3-methylcyclobutene in the high and low pressure regions. However with s=14 the agreement is as good as was obtained for the other compounds whose results have been used

The failure of specific values of s and λ to account for the kinetics of a unimolecular reaction in the high and low pressure regions raises some doubts on the validity of the assumptions made during the development of the theory. Assuming λ=1 in the Kassel equation a value of s is given which, when applied to the high pressure data, produces a hypothetical value greater than one. Since λ cannot exceed unity, a value considerably less than this would seem to be necessary in the low pressure region.

λ, apart from being a measure of the collision efficiency, is a constant which is multiplied by the collision frequency to allow for the conditions at low pressures when a reasonable number of activated molecules go on to react rather than undergoing collisional deactivation. The importance of this is dependent upon the pressure but some decline in λ can be anticipated. Further research is required to establish whether the assumption of $\lambda=1$ is reasonable even close to the high pressure limit.

The results derived from a consideration of experimental data obtained close to the high pressure region have shown that, if λ is assumed equal to one, quite a good estimate of the s parameter can be made by a calculation of the limiting slope.

APPENDIX 2.

Derivation of Rate Equations.

Throughout these derivations letters without square brackets will be used to denote the concentration of reactants and products.

1. Rate Equation for a First-Order Reversible Geometric Isomerization.

The reaction may be represented by

$$C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} T$$

Initially only the cis-isomer is present with a concentration C_o. The rate of formation of T at a time t, dT/dt, is given by

$$dT/dt = k_1C - k_2T \qquad (1)$$

At equilibrium dT/dt = 0 so that

$$k_1C_e = k_2T_e \qquad (2)$$

where C_e and T_e are the equilibrium concentrations of the two isomers. As

$$T = C_o - C \qquad (3)$$

then $$C_e = C_o - T$$

Substituting for C_e in (2),

$$k_1(C_o-T_e) = k_2T_e$$

or
$$k_1C_o = (k_1+k_2)T_e \tag{4}$$

C in (1) is replaced by C_o-T and k_1C_o is substituted from (4) so that

$$\frac{dT}{T_e-T} = (k_1 + k_2)dt$$

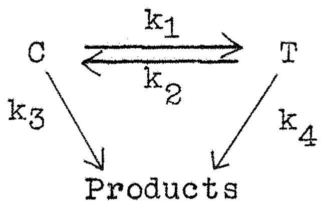
This expression is integrated between the limits 0 and T at time zero and t to give

$$\ln\left(\frac{T_e}{T_e-T}\right) = (k_1+k_2)t$$

2. Equation for the 'true' Equilibrium Constant.

If a parallel structural isomerization reaction occurs simultaneously with a reversible geometric isomerization, the ratio of the equilibrium concentrations of C and T is not equal to the 'true' equilibrium constant k_2/k_1.

The reaction scheme is



The rate of formation of the cis-isomer is

$$dC/dt = k_2T-(k_1+k_3)C$$

whilst that of the trans-isomer is

$$dT/dt = k_1C-(k_2+k_4)T$$

At equilibrium $\frac{dC}{dt}\Big/\frac{dT}{dt} = K_1$

Combining the three equations

$$K_1 = \frac{k_2T-(k_1+k_3)C}{k_1C-(k_2+k_4)T}$$

Rearranging $\frac{k_2+K_1(k_2+k_4)}{k_1+k_3+K_1k_1} = \frac{C}{T} = K_1 \qquad (5)$

If the 'true' equilibrium constant K equals k_2/k_1, substituting for k_2 in (5),

$$K_1 = \frac{Kk_1+K_1(k_1K+k_4)}{k_1K_1+k_1k_3}$$

whence $\underline{\underline{K = K_1\left[1+(k_3-k_4)/k_1(1+K_1)\right]}}$

3. Rate Equation for a Parallel First-Order Reaction.

The reaction scheme for three parallel reactions is

$$A \quad \begin{array}{l} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \\ \xrightarrow{k_3} D \end{array}$$

With only A present initially, the rate of decomposition of A at time t is

$$-dA/dt = (k_1+k_2+k_3)A$$

or $-dA/A = \Sigma k_i dt$

where $\Sigma k_i = k_1+k_2+k_3$

Integrating between the limits a and A at time zero and t,

$$\ln (a/A) = \Sigma k_i t \tag{6}$$

If the concentration of B at time t is x,

$$dx/dt = k_1 A. \tag{7}$$

Substituting A from (7) in (6)

$$ak_1 = \exp(t\Sigma k_i)dx/dt.$$

or $$dx = ak_1 \exp(-t\Sigma k_i)dt$$

Integrating between the limits of 0 and x at time zero and t,

$$\underline{\underline{\frac{x}{a} = \frac{k_1}{\Sigma k_i}\left[1-\exp(-t\Sigma k_i)\right]}}$$

Similar expressions exist for k_2 and k_3. If x is expressed as a percentage product, a = 100%.

APPENDIX 3.

Results for the Isomerization of 3-Methylcyclobutene.

TABLE 14.

Rate Constants for the Isomerization of 3-Methylcyclobutene at 123.5°C

Pressure (mm.)	10^4k (sec^{-1})	Pressure (mm.)	10^4k (sec^{-1})	Pressure (mm.)	10^4k (sec^{-1})
∞	1.39*	2.09	1.34	0.092	0.889
45.0	1.39	1.31	1.30	0.087	0.876
27.4	1.40	1.15	1.25	0.078	0.841
21.5	1.39	1.07	1.25	0.070	0.817
17.9	1.39	0.972	1.24	0.067	0.809
12.9	1.38	0.797	1.21	0.059	0.804
9.71	1.37	0.624	1.21	0.054	0.787
7.00	1.38	0.504	1.17	0.046	0.747
5.48	1.37	0.353	1.14	0.038	0.692
4.66	1.37	0.261	1.10	0.029	0.660
3.94	1.38	0.225	1.07	0.025	0.633
3.29	1.35	0.195	1.03	0.020	0.574
3.06	1.35	0.151	0.993	0.012	0.485
2.78	1.35	0.130	0.958	0.010	0.476
2.53	1.34	0.102	0.921		

*Extrapolated value from a plot of 1/k against 1/pressure.

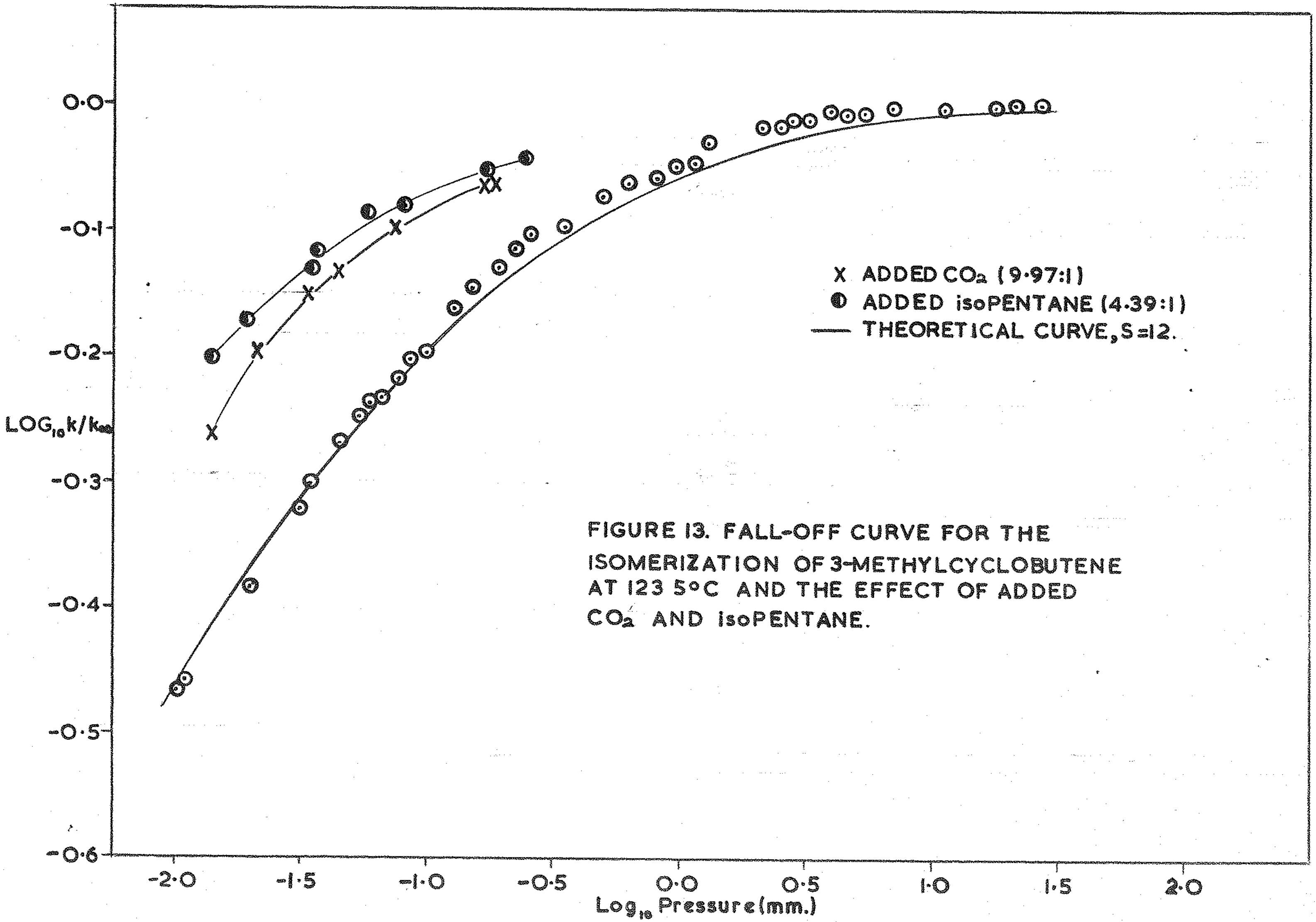


FIGURE 13. FALL-OFF CURVE FOR THE ISOMERIZATION OF 3-METHYLCYCLOBUTENE AT 123 5°C AND THE EFFECT OF ADDED CO_2 AND isoPENTANE.

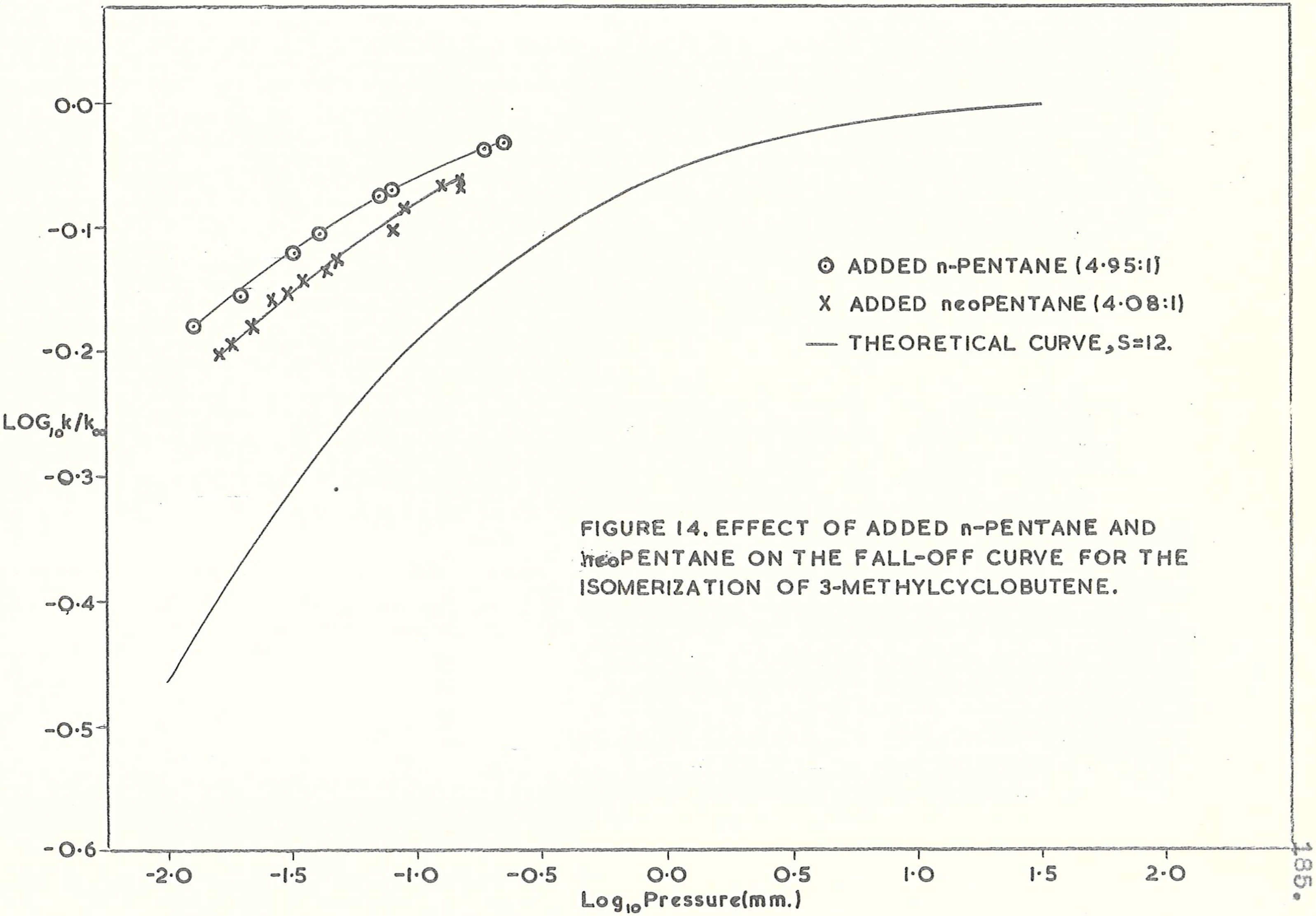


FIGURE 14. EFFECT OF ADDED n-PENTANE AND neoPENTANE ON THE FALL-OFF CURVE FOR THE ISOMERIZATION OF 3-METHYLCYCLOBUTENE.

TABLE 15.

Rate Constants for the Isomerization of 3-Methylcyclobutene at 148.5°C.

Pressure (mm.)	10^3k (sec^{-1})	Pressure (mm.)	10^3k (sec^{-1})	Pressure (mm.)	10^3k (sec^{-1})
∞	1.49*	2.04	1.37	0.114	0.915
32.3	1.50	1.64	1.34	0.111	0.895
20.7	1.49	1.13	1.32	0.097	0.880
16.7	1.49	1.10	1.30	0.091	0.858
15.1	1.47	0.934	1.28	0.086	0.841
12.2	1.49	0.860	1.27	0.080	0.827
11.0	1.47	0.675	1.24	0.078	0.824
9.25	1.46	0.634	1.22	0.071	0.805
8.86	1.46	0.613	1.21	0.068	0.790
8.18	1.47	0.540	1.20	0.061	0.762
7.59	1.47	0.503	1.20	0.057	0.740
6.49	1.46	0.437	1.17	0.053	0.727
5.61	1.46	0.365	1.14	0.045	0.693
4.90	1.44	0.281	1.09	0.036	0.653
4.16	1.43	0.214	1.04	0.029	0.594
3.85	1.42	0.211	1.02	0.023	0.559
3.42	1.43	0.156	0.978	0.017	0.487
2.92	1.41	0.148	0.969	0.012	0.429
2.43	1.40				

* Extrapolated value from a plot of 1/k against 1/pressure.

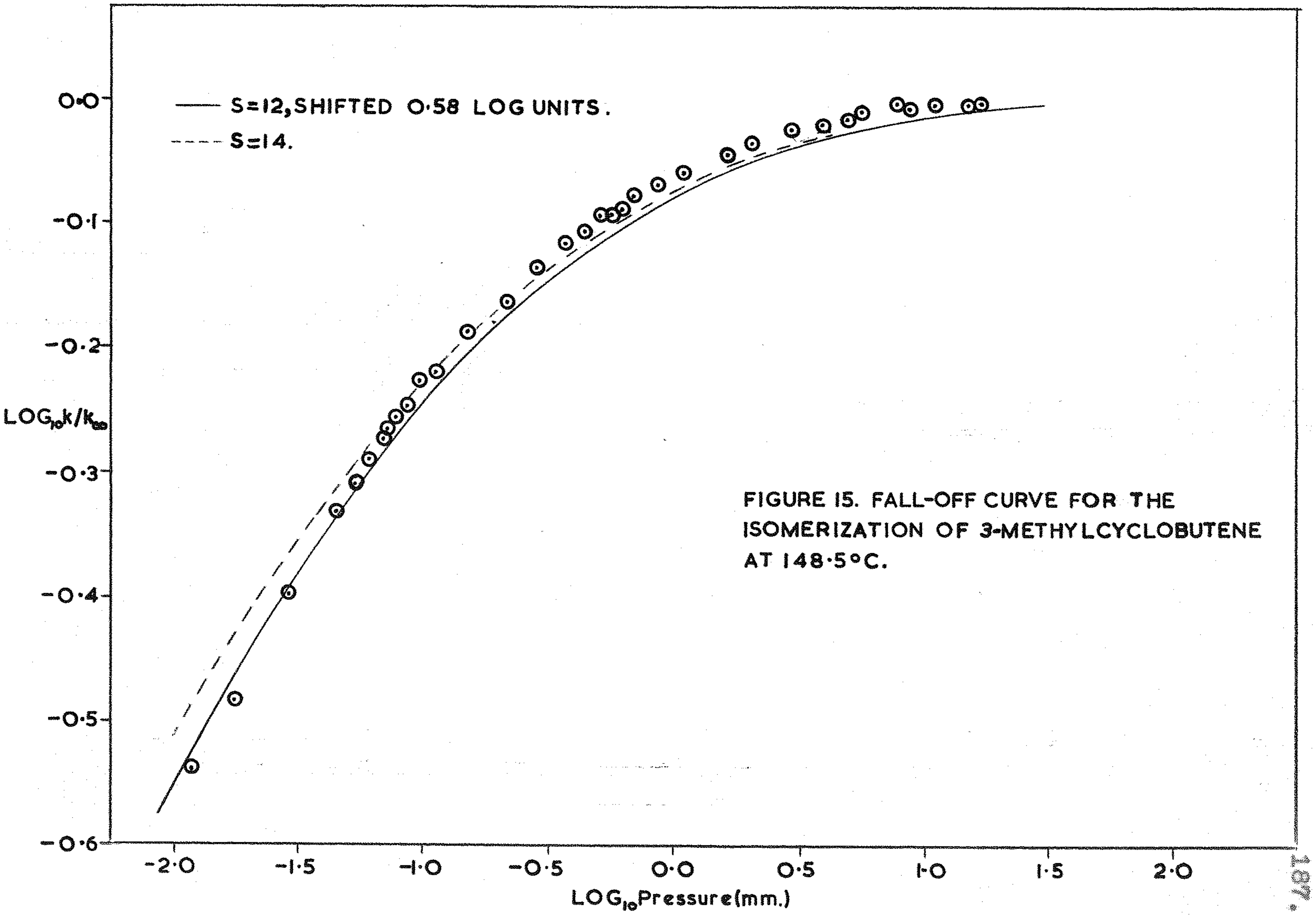


FIGURE 15. FALL-OFF CURVE FOR THE ISOMERIZATION OF 3-METHYLCYCLOBUTENE AT 148·5°C.

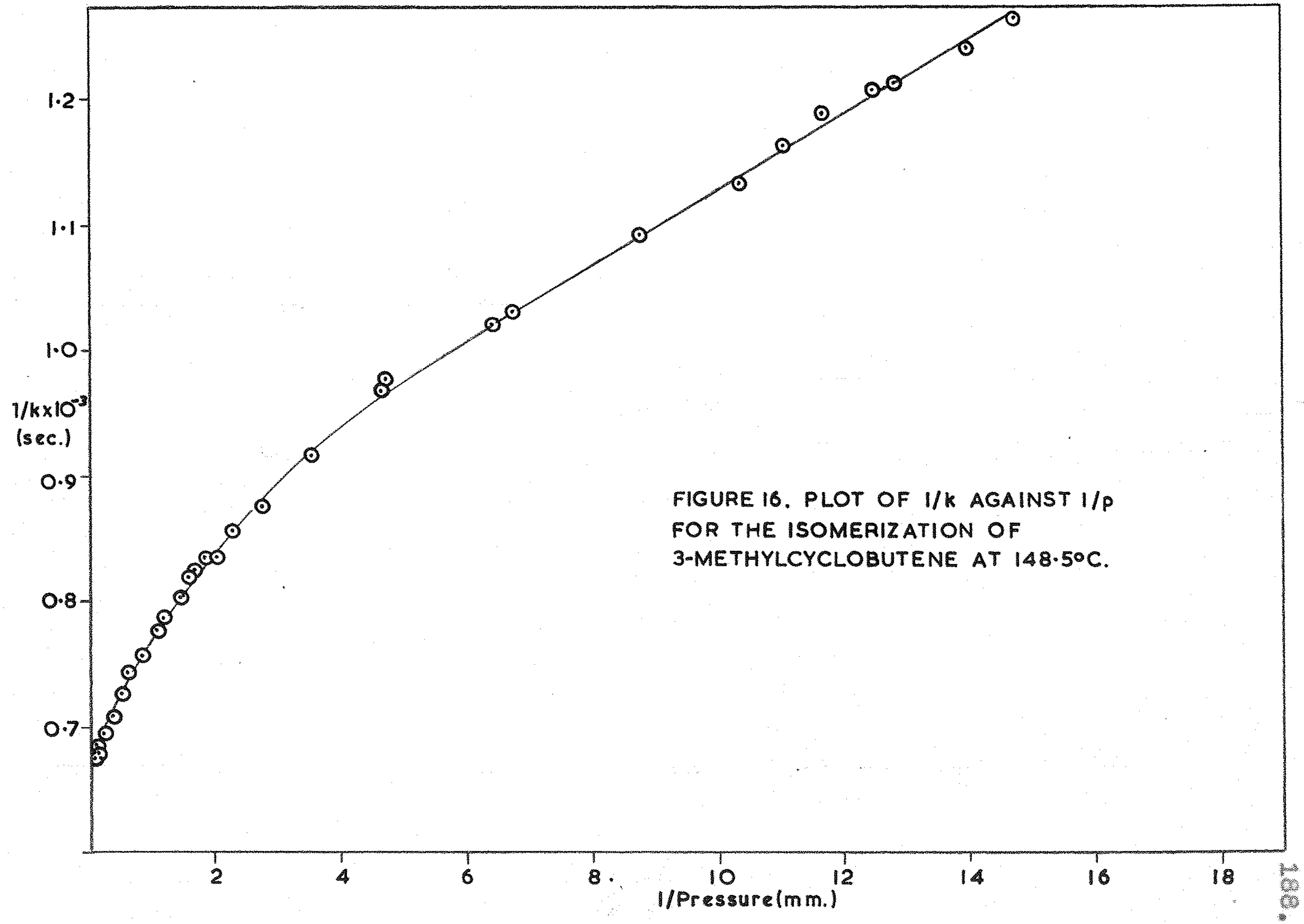


FIGURE 16. PLOT OF 1/k AGAINST 1/p FOR THE ISOMERIZATION OF 3-METHYLCYCLOBUTENE AT 148·5°C.

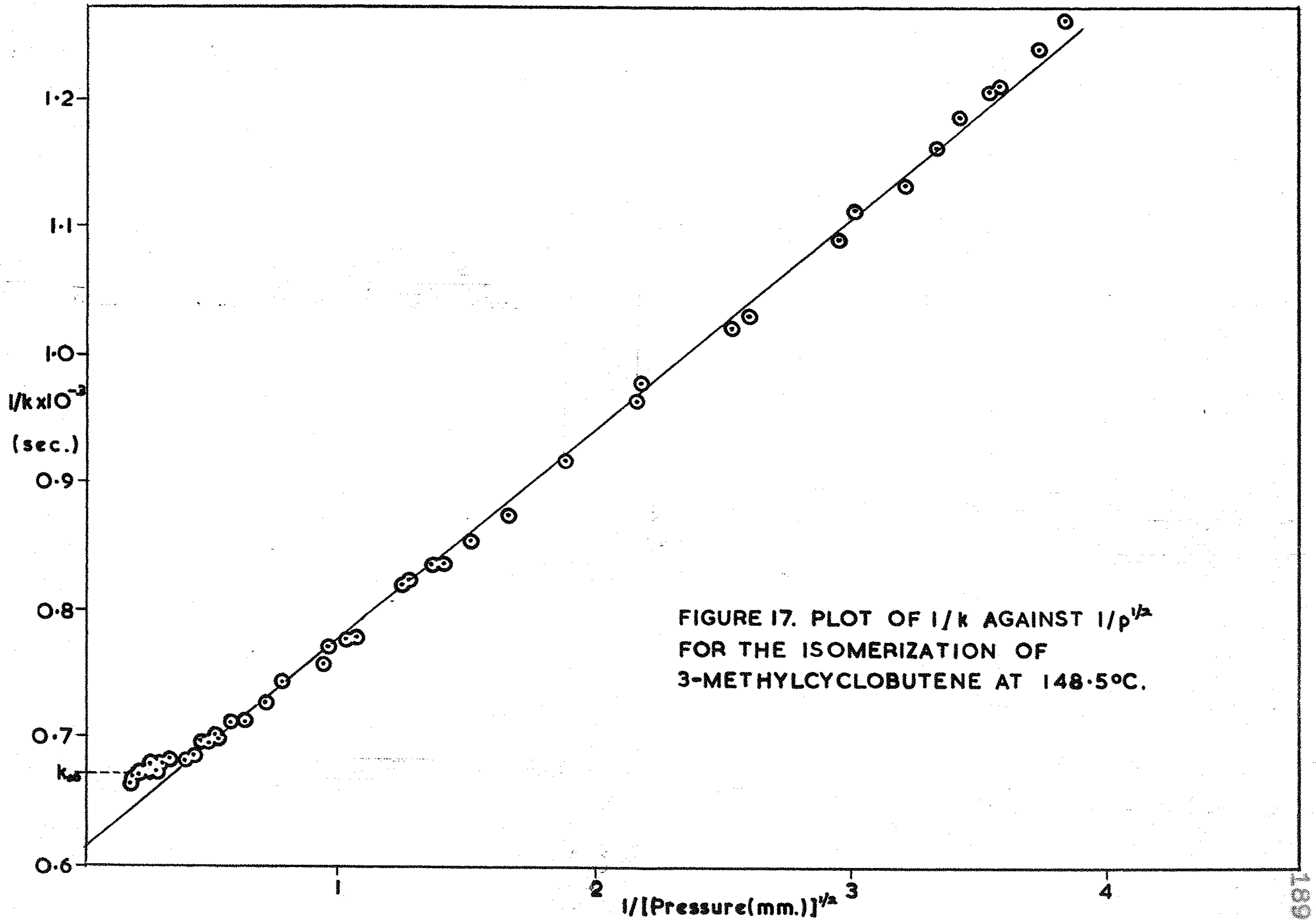


FIGURE 17. PLOT OF $1/k$ AGAINST $1/p^{1/2}$ FOR THE ISOMERIZATION OF 3-METHYLCYCLOBUTENE AT 148·5°C.

TABLE 16.

Consistency Tests.

10^8M (m/cc)	10^3k (sec^{-1})	$10^8\nu_1$	$10^{16}\nu_2$	ν_2/ν_1^2	$10^{24}\nu_3$	$\nu_1\nu_3/\nu_2^2$
∞	1.487	0.690	0.970	2.04	-	-
35.2	1.459	0.676	0.965	2.11	0.821	0.58
33.7	1.458	0.671	1.11	2.47	-	-
18.7	1.437	0.649	1.21	2.87	-	-
15.8	1.432	0.608	1.71	4.63	-	-
14.6	1.423	0.658	0.925	2.14	1.30	1.00
13.0	1.428	0.538	2.35	8.12	-	-
11.1	1.406	0.640	0.996	2.43	3.32	2.14
9.24	1.403	0.553	1.65	5.40	-	-
7.75	1.372	0.650	0.757	1.79	2.28	2.59
6.22	1.343	0.667	0.602	1.35	2.94	5.41
4.29	1.319	0.547	0.993	3.32	0.429	0.24
4.17	1.296	0.614	0.740	1.96	1.55	1.74
3.56	1.284	0.562	0.842	2.67	1.00	0.79
3.27	1.268	0.565	0.800	2.51	1.10	0.97
2.41	1.218	0.532	0.748	2.64	1.05	1.00
2.06	1.197	0.498	0.739	2.98	0.957	0.87
1.66	1.166	0.458	0.702	3.35	0.889	0.83
1.39	1.140	0.422	0.664	3.73	0.834	0.80
1.07	1.089	0.391	0.590	3.86	0.786	0.88
0.816	1.036	0.355	0.518	4.11	0.713	0.94
0.592	0.9775	0.308	0.439	4.63	0.787	1.26
0.564	0.9686	0.302	0.427	4.68	0.598	0.99
0.434	0.9148	0.271	0.369	5.02	0.523	1.04
0.421	0.8954	0.278	0.366	4.74	0.524	1.09
0.344	0.8584	0.252	0.325	5.11	0.467	1.11

TABLE 17.

Theoretical Computation of the Kassel Integral.

b	Pressure (mm.)	s				
		11	12	13	14	15
37.7	121.60	0.977	0.987	0.992	0.995	0.997
	38.300	0.942	0.965	0.979	0.987	0.992
	12.160	0.874	0.918	0.947	0.966	0.978
	3.8300	0.766	0.836	0.887	0.922	0.946
	1.2160	0.625	0.716	0.789	0.845	0.886
	0.3830	0.469	0.569	0.658	0.731	0.792
	0.1216	0.323	0.418	0.508	0.592	0.664
	0.0383	0.206	0.281	0.364	0.443	0.521
	0.0122	0.120	0.177	0.240	0.309	0.379
40.0	121.60		0.991	0.995	0.997	0.998
	38.300		0.976	0.986	0.992	0.995
	12.160		0.943	0.965	0.978	0.986
	3.8300		0.878	0.919	0.947	0.965
	1.2160		0.776	0.840	0.888	0.922
	0.3830		0.639	0.725	0.793	0.847
	0.1216		0.490	0.584	0.667	0.738
	0.0383		0.345	0.435	0.523	0.601
	0.0122		0.224	0.302	0.379	0.460

APPENDIX 4.

The Evaluation of Integral Equations by Gauss-Laguerre Quadrature.

An integral of the type $\int_0^\infty \exp(-x)f(x)dx$ can be evaluated by a transformation into a summation using Gauss-Laguerre Quadrature[62] such that

$$\int_0^\infty \exp(-x)f(x)dx = \sum_{i=1}^{n} H_i f(a_i)$$

A choice of particular values of the variable a_i, which are substituted into f(x), and the corresponding weighting factors H_i ensures that the error of the transformation is negligible. The final summation of n terms is equivalent to expressing the integrand as a polynomial of 2n-1 terms.

The a_i are the zeros of the nth Laguerre polynomial

$$L_n(x) = e^x\left[\frac{d^n}{dx^n}\left(e^{-x}x^n\right)\right]$$

These zeros and the weighting factors have been calculated for several values of n. For the majority of the calculations the values when n=15 were used, as given by Salzer and Zucker[102]. Values when n=32 also became available but, within the limit of precision required, these gave identical results. They had the disadvantage of considerably increasing the computer time for programmes.

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