STUDIES OF UNIMOLECULAR REACTIONS

THE THERMAL DECOMPOSITION OF AZOMETHANE

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ABSTRACT

The thermal decomposition of azomethane alone and in the presence of added gases has been reinvestigated in a static reaction system to see if the reaction could still be regarded as a true unimolecular reaction and, as such, used to test the detailed theories of unimolecular reactions and to obtain information about the efficiencies of added gases in energy transfers with the reactant molecules.

The reaction was followed in the temperature and pressure ranges (502-593°K) and (0.2 - 975 mm.) by measurement of the nitrogen which was produced by the primary reaction

$$CH_3N{=}NCH_3 \rightarrow CH_3 + N_2 + CH_3 \ .$$

As predicted by theory, the experimental first-order rate constant and the activation energy both fall away from their high-pressure values with decreasing pressure. However, work with toluene and propylene as added gases showed that the reaction is complicated by a short chain process. A possible mechanism for the chain decomposition of azomethane is discussed and suggestions are made as to how this may be verified by experiment. These chains account for about 50 per cent of the reaction at higher pressures, but they can be entirely inhibited by the presence of excess propylene. The rate constants for the fully inhibited reaction are given by

$$k_\infty = 10^{15.7} \exp(-51{,}200/RT) \text{ sec.}^{-1}$$

Surface reaction was eliminated by seasoning the reaction vessel with allyl bromide.

Because of the complexity of the reaction the interpretation of the rate/pressure and activation-energy/pressure curves as a detailed test of unimolecular theory is doubtful but the indications are that these can only be accounted for by the quasi-unimolecular nature of the reaction.

There are four current theories of unimolecular reactions which are chiefly associated with the names of Hinshelwood, Kassel, Eyring and Slater.

Little attention has been paid in the past to treating these theories as a whole. In this thesis the particular theories are developed from general arguments and then compared. In particular, the dependence of the first-order rate constant and the activation energy on pressure is noted. The significance of the experimental activation energies and frequency factors in terms of the theories is discussed in detail. In general, the high-pressure activation energy should be equal to the bond dissociation energy of the rupturing bond and the high-pressure frequency factor should lie within the range of molecular vibration frequencies. However, there is an important exception: if reaction involves the simultaneous rupture of more than one bond then the high-pressure activation energy is not necessarily related to the dissociation energies of the bonds in a simple manner and the high-pressure frequency factor is greater than normal.

The previous work on the thermal and photochemical decomposition of azomethane and some of the more reliable work on energy transfer in other systems are also summarised.

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PREFACE

Some attempt has been made to make the material in each chapter self-contained. For example, in chapters 9 and 10, which discuss the experimental work, the reasons for the various sets of experiments, the previous work and the theoretical background are briefly outlined. it is to be hoped that by this the thesis has not been made to appear needlessly repetitive. In general, internal references to a section merely state the chapter and section numbers, but references to equations, figures and tables are explicit. For example, (2.13) refers to section 13 of chapter 2, whilst (equation 2.13) refers to equation 13 of chapter 2. For simplicity a common system has been used for the reaction and equation numbers. The tables and diagrams follow the appropiate chapters.

CONTENTS

CHAPTER 1.

GENERAL BACKGROUND & PURPOSE OF STUDY.

(1.1) GENERAL BACKGROUND: A unimolecular reaction may be defined as a reaction in which the chemical transformation is an event happening to a single molecule. In principle, unimolecular reactions are the simplest of reactions, but in practice they have proved difficult to handle, both theoretically and experimentally.

In 1922 Lindemann[1] suggested that collisional activation was compatible with first-order kinetics provided that the time interval between collisions was much less than the lifetime of the activated molecules which could subsequently undergo unimolecular decomposition. When the frequency of the collisions becomes of the same order as the lifetime of the activated molecules then the rate constant falls away from its limiting "high pressure" value. Thus Lindemann predicted that the first-order rate constant should be a function of pressure. Such behaviour is often described as being quasi-unimolecular, and the experimental rate-pressure curves can be used as a test of the more refined theories of unimolecular reaction.

In the experimental field more detailed investigation has shown that chemical reactions are often very complex. In particular it has been realised that the thermal decompositions of many organic compounds, which were originally believed to be examples of simple unimolecular reactions, are in fact complicated by concurrent radical and molecular processes; furthermore, the radicals which may be present in the system often set up reaction chains. As a result the number of reactions for which the existing experimental data can be used to test the theories of unimolecular reaction has become embarassingly small.

Before 1925 the only known gaseous unimolecular reaction was the decomposition of nitrogen pentoxide, in which the rate-controlling step was assumed to be

$$N_2O_5 \rightarrow N_2O_3 + O_2 \ . \qquad (1)$$

Trautz and Winkler[2] had suggested that the isomerisation of cyclopropane was also unimolecular but their data were inconclusive. There was, therefore,

some justification for the belief that no unimolecular reactions existed. However, during the years 1926 and 1927 Hinshelwood[3,4,5,6] investigated the gaseous decomposition of several organic compounds and the kinetic results appeared to give convincing support to Lindemann's concepts. In particular, the first-order rate constants fell off as the pressure decreased. But it is now known that the reactions are complex and that they cannot be regarded as confirming the correctness of the theories. Also in 1927 Ramsperger[7,8] investigated the decomposition of azomethane and this alone of the classic unimolecular reactions has survived the test of time and subsequent research.

To-day numerous unimolecular reactions involving organic compounds† are known, and these may be conveniently divided into three classes:-

(i) Isomerisations.
(ii) Molecular Eliminations.
(iii) Radical Eliminations.

Few of these, however, have been investigated in such a manner as to make them a useful test of the detailed theories. In this respect the work of Pritchard, Sowden and Trotman-Dickenson[9] on the isomerisation of cyclopropane is the best investigation of a reaction of the first class, whilst Kern and Walters[10] have investigated the decomposition of cyclobutane, which is a reaction of the second class. Azomethane is still the only reasonable investigation of a radical elimination reaction. The study of such reactions usually presents considerable experimental difficulties. Often the reaction is complicated by chain processes, for the radicals formed in the primary split may react further with the substrate to give a complex overall reaction pattern. This difficulty can be overcome by the Toluene Carrier technique in which the radicals are removed by reaction with toluene, but the method cannot be applied to all compounds and the pressure and temperature ranges are limited.

(1.2) PURPOSE OF THE RESEARCH: For thirty years the thermal decomposition of azomethane has found a place in text-books as an example of a unimolecular reaction. Originally the decomposition was taken to be mainly the molecular

† More recently the unimolecular decompositions of radicals have also been studied.

process

$$CH_3N = NCH_3 \rightarrow C_2H_6 + N_2 . \qquad (2)$$

By simple pressure-time measurements Ramsperger[8] obtained good first-order constants for the individual runs and the rate-constant/pressure data appeared to be in agreement with unimolecular theory. Later work by Rice and Sickman[11] confirmed Ramsperger's results in a general way although a greater variation in rate with initial pressure was found and it was no longer clear that the first-order rate constant was becoming pressure independent at high pressures. All the work was done without analysing the products. When Riblett and Rubin[13] carried out such analyses they found that the reaction was far more complex than was originally assumed. Research on the photolysis of azomethane has also emphasised the complexity of the reaction and the insufficiency of pressure measurements as a means of following its progress. It therefore seemed important to re-investigate the decomposition to see if the reaction could still be regarded as a true unimolecular reaction and used to test the detailed theories.

By adding chemically inert gases to a quasi-unimolecular system and by studying their effect on the rate of decomposition information may be obtained about their efficiencies in energy transfer processes involving the upper vibrational levels[12]. But the data have been limited on the whole to small molecules which tend to be structurally uninteresting. In this research it was hoped to add a range of the larger hydrocarbons, C_3- C_6, and to study the effect of structure on energy transfer efficiency. This is not possible in the case of cyclopropane or cyclobutane because at the temperatures required for reasonable rates of reaction the added hydrocarbons would also be decomposing, and so provide unwanted complexities.

However, the research developed along entirely unexpected lines, for later work showed that the reaction was complicated by a short chain process, so that the decomposition of azomethane could not be regarded as a simple example of a unimolecular reaction. In writing this thesis I have attempted to compromise between a strictly historical approach in describing the work and a logical interpretation in the light of later findings, and it is to be hoped that this has not given rise to obscurity and inconsistency.

CHAPTER 2.

THE THEORETICAL TREATMENT OF UNIMOLECULAR REACTIONS.

(2.1) SUMMARY: Molecules are treated as classical vibrating systems which dissociate when they pass through a critical boundary in phase space, and expressions are derived for the overall rate of decomposition in terms of the specific rate constants of the individual states. The particular theories of Hinshelwood, Kassel, Eyring and Slater are developed from the general arguments and then compared. Emphasis is laid on how these theories may be tested by experiment. In particular, the dependence of the first-order rate constant and activation energy on pressure is noted.

It is shown that, in general, the high-pressure activation energy should be equal to the bond dissociation energy of the rupturing bond in a thermal dissociation reaction, and that the frequency factor should lie within the range of molecular vibration frequencies (10^{12} - 10^{14} sec.$^{-1}$). Exceptions to these generalisations are noted and possible reasons for the divergences discussed.

(2.2) INTRODUCTION: Although unimolecular reactions are the simplest of the elementary chemical reactions, the theoretical attempts to account for the magnitude of their Arrhenius parameters have proved to be complex. There are four current theories, which are associated with the names of Hinshelwood, Kassel, Eyring and Slater. Most authors prefer one or the other, and scant attention has been paid to treating the theories as a whole. But as there can be only one correct theory it seems that the several approaches require a synthesis. The purpose of this chapter is to emphasise the basic similarity of the theories, the points at which they differ and how they may possibly be elaborated or modified. In particular, attention will be focussed on the predictions of the theories to see if experiment can be used to test their relative merits.

The internal energy of a molecule is composed of electronic, vibrational, and rotational energy, and for many purposes these may be considered to be independent of each other. The energy difference between two electronic levels in saturated molecules is approximately 100 kcal. per mole whilst the

vibrational and rotational levels are separated by approximately 1 kcal. and 0.1 kcal. respectively. The activation energies of many unimolecular reactions lie between 25 and 60 kcal. per mole, so that rotational energy would hardly be expected to make an important contribution to the energetics of the reaction, and for most thermal reactions there is not sufficient energy to make electronic excitation important. All the theories, therefore, treat the molecule as a vibrating system.

In general, the complex motions of the n atoms of a polyatomic molecule can be represented by a superposition of (3n-6) simple normal mode vibrations which correspond to the (3n-6) degrees of vibrational freedom and these normal vibrations may be thought of as a set of harmonic oscillators[14,15]. The basic connection between a set of oscillators and a molecule is that both are energy stores, but there are closer parallelisms depending on the detailed nature of the model adopted. The internal motion of the molecule can be represented by the motion of a point in a (3n-6)-dimensional hyperspace and reaction is envisaged as the passage of the point through a certain boundary[16,17].

However these conditions are so general that little particular information can be derived from them. In order to proceed further, more detailed assumptions must be made, the choice of which is influenced by what are believed to be the properties possessed by molecules undergoing unimolecular reaction.

(2.3) THE LINDEMANN MECHANISM: Not every molecular state is a suitable one for reaction. If they were, chemical reactions would proceed at room temperature and the temperature coefficient of reactions would be extremely small. Molecules capable of reacting must possess energy in excess of the average; such are called activated molecules and the process whereby they gather this excess energy is called activation. If molecules are activated by collisions, which are by nature bimolecular, it is difficult to see at first sight why reactions are not kinetically of the second order.

Lindemann[1] pointed out that collisional activation was compatible with first-order kinetics provided the interval between collisions was short compared to the mean lifetime of the activated molecules. This argument can be summarised in terms of the well known Lindemann reaction scheme

$$A + A \rightleftharpoons A^* + A \qquad (1)$$

$$A^* \rightarrow B + C \ . \qquad (2)$$

A^* represents the activated molecules, and for a stationary concentration of these it is easy to show that the first-order rate constant (k) for the reaction is

$$k = -\frac{d[A]}{dt} \times \frac{1}{[A]} = k_2 \frac{k_1[A]}{k_{-1}[A] + k_2} \ . \qquad (3)$$

This mechanism of collisional activation (reaction 1) followed by either collisional deactivation (reaction -1) or decomposition (reaction 2) is common to all the theories.

(2.4) GENERAL BASIS OF THE THEORIES: The dissociation frequency of a molecule in the i^{th} state will be symbolised k_i; it will also be referred to as the specific rate constant of that state.

If there are N molecules per cc. in the system and if g_i is the proportion in the i^{th} state then k, the first order rate constant, is given by

$$k = -\frac{1}{N} \cdot \frac{dN}{dt} = \sum_i k_i g_i \ , \qquad (4)$$

the summation being over all molecular states.

At high pressures the rates of collisional activation and deactivation are sufficiently great, compared with the rate of reaction, to maintain a Maxwell-Boltzmann energy distribution of the molecules and the high pressure rate constant k_∞ is given by

$$k_\infty = \sum_i k_i f_i \ , \qquad (5)$$

where f_i is the proportion of molecules in the i^{th} state under equilibrium conditions.

At lower pressures the collision frequency is not sufficiently great to maintain this equilibrium and the number of molecules in the activated states are depleted from their Maxwell-Boltzmann distribution by reaction (2).

By the Principle of Microscopic Reversibility the number of molecules

entering a state i due to collisional energisation per cc. per second is equal to the number leaving it due to collisional deactivation and reaction. This is the basis of the stationary state assumption used in deriving equation (3). Thus under equilibrium conditions the number energised per cc. per second equals the number de-energised per cc. per second. This is equal to $\omega N f_i$ where ω is the collision frequency per molecule. Even when equilibrium is not maintained, the number of energisations per cc. per second into a given state is the same since collisional activation takes place between two unactivated molecules and these are still present in their equilibrium distribution. However, under non-equilibrium conditions the number de-energised per cc. per second is $\omega N g_i$, where g_i is the fraction of molecules in the i^{th} state, and the number reacting per cc. per second is $k_i N g_i$. Thus

$$\omega N f_i = \omega N g_i + k_i N g_i$$

$$\text{or} \qquad g_i = \frac{\omega}{\omega + k_i} f_i \quad . \tag{6}$$

By combining (4) and (6) it will be seen that the general rate at any pressure is given by

$$k = \sum_i k_i f_i \frac{\omega(p)}{\omega(p) + k_i} \quad . \tag{7}$$

Here we have written $\omega(p)$ to emphasise that the collision frequency is a function of pressure.

This argument assumes every collision undergone by activated molecules to be deactivating and Kassel[18] has shown that this is plausible on the basis of a simple physical model. Rössler[19] has found that when an excited iodine molecule collides with a foreign molecule a transfer of vibrational and rotational energy occurs in almost every case. More recently, however, Johnston[20-23] has presented data to indicate that energy transfer does not necessarily occur on every collision.

(2.5) KASSEL'S MODEL: Kassel[18] considers that the molecule may be pictured as a set of loosely coupled harmonic oscillators all possessing the same frequency, and that reaction occurs when a specified oscillator acquires an

energy greater than a certain critical value ϵ_o. Only classical oscillators will be considered, but the theory can be developed in a similar manner for quantised oscillators.

For a system of s non-coupled (i.e. independent) classical oscillators the probability that the total energy lies in the range $(\epsilon, \epsilon+d\epsilon)$ is

$$f(\epsilon)d\epsilon = \frac{1}{(s-1)!}\left(\frac{\epsilon}{kT}\right)^{s-1}\exp\left(-\frac{\epsilon}{kT}\right)\frac{d\epsilon}{kT}. \qquad (8)$$

The effect of coupling the oscillators is to make all molecules which possess energy $\epsilon \geqslant \epsilon_o$ capable of reaction. Thus $f(\epsilon)d\epsilon$ is the natural definition of the activated fraction in the range $(\epsilon, \epsilon+d\epsilon)$.

Also for a system of s non-coupled classical oscillators, the probability that one particular oscillator possesses energy $\epsilon \geqslant \epsilon_o$, when the total energy is in the range $(\epsilon, \epsilon+d\epsilon)$, is $\left(1-\frac{\epsilon_o}{\epsilon}\right)^{s-1}$. Kassel then assumes that the specific rate constants will be of the form

$$k(\epsilon) = \lambda\left(1-\frac{\epsilon_o}{\epsilon}\right)^{s-1}, \quad \epsilon \geqslant \epsilon_o, \ \lambda = \text{constant} \qquad (9)$$

$$= 0 \qquad , \quad \epsilon < \epsilon_o.$$

Thus the high pressure rate is given by

$$k_\infty = \int_o^\infty k(\epsilon) f(\epsilon) d\epsilon$$

$$= \int_o^\infty \lambda\left(1-\frac{\epsilon_o}{\epsilon}\right)^{s-1}\frac{1}{(s-1)!}\left(\frac{\epsilon}{kT}\right)^{s-1}\exp\left(-\frac{\epsilon}{kT}\right)\frac{d\epsilon}{kT} \qquad (10)$$

$$= \lambda \exp\left(-\frac{\epsilon_o}{kT}\right). \qquad (11)$$

The general rate is

$$k = \int_o^\infty k(\epsilon) f(\epsilon)\frac{\omega(p)}{\omega(p)+k(\epsilon)}d\epsilon$$

$$= \frac{k_\infty}{\Gamma(s)}\int_o^\infty \frac{x^{s-1}\exp(-x)}{1+\frac{\lambda}{\omega}\left(\frac{x}{b+x}\right)^{s-1}}dx, \qquad (12)$$

where $x = \frac{\epsilon-\epsilon_o}{kT}$ and $b = \frac{\epsilon_o}{kT}$.

† In the development of the formulae, k, the gas constant per molecule, is used since ϵ refers to the energy of a molecule. But experimental activation energies are usually given in calories per mole when the molar gas constant R is employed. The molecular gas constant is equal to the molar gas constant divided by the Avogadro Number.

It should be noted that the same high pressure formula is obtained for a set of non-coupled oscillators. Since these are orthogonal, and, therefore cannot exchange energy, a more stringent definition of activated molecules must be adopted, namely that activated molecules must possess at least an energy ϵ_0 in the oscillator which is associated with the rupturing bond. If $G_{s,1}(\epsilon,\epsilon_0)\,d\epsilon$ is the probability that the total energy in an s-oscillator system is $(\epsilon,\epsilon+d\epsilon)$ and also that more than ϵ_0 is in one particular oscillator, then this is the natural definition of the fraction of activated molecules in the range $(\epsilon,\epsilon+d\epsilon)$. If the frequency of dissociation of such molecules is λ' then

$$
\begin{aligned}
k_\infty &= \int_0^\infty k(\epsilon) f(\epsilon)\, d\epsilon \\
&= \int_0^\infty \lambda' G_{s,1}(\epsilon,\epsilon_0)\, d\epsilon \\
&= \int_0^\infty \lambda' \left(1-\frac{\epsilon_0}{\epsilon}\right)^{s-1} \frac{1}{(s-1)!}\left(\frac{\epsilon}{kT}\right)^{s-1} \exp\left(-\frac{\epsilon}{kT}\right)\frac{d\epsilon}{kT} \\
&= \lambda' \exp\left(-\frac{\epsilon_0}{kT}\right) \quad . \qquad (13)
\end{aligned}
$$

The general rate now becomes

$$
k = k_\infty \frac{\omega(p)}{\omega(p)+\lambda'} \quad , \qquad (14)
$$

which is the same form of rate expression as derived on the basis of the Hinshelwood model (equation 18), although it is to be noted that the definition of $f(\epsilon)\,d\epsilon$ in the two theories is different. This is an example of the peculiarly passive role adopted by the Kassel oscillators under certain circumstances - a property which has been remarked upon by Slater[24]. Essentially it is due to the fact that the oscillators cannot interchange energy and hence the molecule degenerates into a one-oscillator system.

(2.6) HINSHELWOOD'S MODEL: Hinshelwood's model[5,25,26] is a particular case of Kassel's in which the dissociation probability of all activated molecules is assumed to be the same and is given an arbitary value λ''.

Thus

$$k(\epsilon) = \lambda'' \qquad \epsilon \geq \epsilon_o \,, \tag{15}$$
$$= 0 \qquad \epsilon < \epsilon_o \,,$$

and

$$k_\infty = \int_{\epsilon_o}^{\infty} \lambda'' \frac{1}{(s-1)!} \left(\frac{\epsilon}{kT}\right)^{s-1} \exp\left(-\frac{\epsilon}{kT}\right) \frac{d\epsilon}{kT} \tag{16}$$

$$= \lambda'' \frac{1}{(s-1)!} \left(\frac{\epsilon_o}{kT}\right)^{s-1} \exp\left(-\frac{\epsilon_o}{kT}\right) \quad \text{for } \epsilon_o \gg skT \,. \tag{17}$$

The general rate is

$$k = k_\infty \frac{\omega(p)}{\omega(p) + \lambda''} \,. \tag{18}$$

(2.7) SLATER'S MODEL: Slater's treatment[27,28] is much more precise than Kassel's or Hinshelwood's and involves fewer assumptions. The molecules are again treated as an assembly of classical vibrating systems, but dissociation now occurs when the internal modes come sufficiently into phase to carry a specified internal co-ordinate q past a critical value q_o. For a thermal dissociation q may be taken as the bond elongation and for an isomerisation it will be the change in bond angle. Suppose the n normal modes of vibration can be assigned energies $(\epsilon_1, \epsilon_2, \cdots, \epsilon_n)$ where $\sum_i^n \epsilon_i = \epsilon$, then the frequency with which q is carried past q_o may be defined as the specific rate constant of the state and is written $L(\epsilon_1, \epsilon_2, \cdots, \epsilon_n)$. Thus

$$k_\infty = \int_o^\infty \cdots \int L(\epsilon_1, \epsilon_2, \cdots, \epsilon_n) f(\epsilon_1, \epsilon_2, \cdots, \epsilon_n)\, d\epsilon_1\, d\epsilon_2 \cdots d\epsilon_n$$

$$= \int_o^\infty \cdots \int L(\epsilon_1, \epsilon_2, \cdots, \epsilon_n) \left(\frac{1}{kT}\right)^n \exp\left(-\sum_i^n \frac{\epsilon_i}{kT}\right) d\epsilon_1\, d\epsilon_2 \cdots d\epsilon_n \tag{19}$$

$$= \frac{\nu_1 \nu_2 \cdots \nu_n}{\nu_1' \nu_2' \cdots \nu_{n-1}'} \exp\left(-\frac{\epsilon_o}{kT}\right)$$

$$= \bar{\nu} \exp\left(-\frac{\epsilon_o}{kT}\right) \,. \tag{20}$$

Here $\nu_1, \nu_2, \cdots, \nu_n$ denote the n normal mode frequencies and $\nu_1', \nu_2', \cdots, \nu_{n-1}'$ the frequencies obtained by fixing q at any value. The ratio $\frac{\nu_1 \nu_2 \cdots \nu_n}{\nu_1' \nu_2' \cdots \nu_{n-1}'}$ will, therefore, be a frequency $\bar{\nu}$ which lies between the greatest and least of

the frequencies of the normal vibrational modes. ϵ_o is the minimum total energy which the modes must possess for q to attain the value q_o.
The general rate is

$$k = \int_o^\infty \cdots \int L(\epsilon_1, \epsilon_2, \cdots, \epsilon_n) f(\epsilon_1, \epsilon_2, \cdots, \epsilon_n) \frac{\omega(p)}{\omega(p) + L(\epsilon_1, \epsilon_2, \cdots, \epsilon_n)} d\epsilon_1 d\epsilon_2 \cdots d\epsilon_n \qquad (21)$$

and this can be put into the form

$$k = \frac{k_\infty}{\Gamma(\frac{1}{2}n + \frac{1}{2})} \int_o^\infty \frac{\chi^{\frac{1}{2}(n-1)} \exp(-\chi)}{1 + \chi^{\frac{1}{2}(n-1)} \Theta^{-1}} d\chi \qquad (22)$$

where $\frac{\epsilon - \epsilon_o}{kT} = \chi$ and Θ is a function of ω and hence of p. It will be noticed that this is remarkably similar to Kassel's general rate (equation 12), provided $n = 2s$. However, the physical meaning of this is obscure.

Recently Slater[29] has developed the theory to cover the case of quantum systems. The results are similar to the classical case except that the high pressure activation energy is found to be slightly temperature dependent.

(2.8) EYRING'S MODEL: THE THEORY OF ABSOLUTE REACTION RATES: The theory of Absolute Reaction Rates or Transition State theory is largely associated with the name of Eyring[30] and may be regarded as a particular method for solving the rate of transfer of molecules across the critical boundary in phase space.

A narrow region adjacent to the boundary is considered and the molecules therein are regarded as the activated species or complexes. This region is identified with the transition state which is situated at the top of the potential barrier between the initial and final states (see 2.9). The rate constant for the reaction is simply the frequency of transition of molecules through the region multiplied by the fraction of activated molecules. The latter is calculated by means of Statistical Thermodynamics, and it can be shown that

$$k_\infty = \frac{kT}{h} \frac{\phi_\ddagger}{\phi} \exp\left(-\frac{\epsilon_o}{kT}\right) , \qquad (23)$$

where ϵ_o is the difference in energy between the initial and activated states at 0°K, ϕ is the partition function of the initial state, and $\phi_\ddagger$ is the partition function of the activated state with the reaction co-ordinate "frozen".

If the rotational partition functions of the activated complex and the initial state are similar, it is easy to show that equation (23) reduces to

$$k = \frac{\prod^{3n-6} \nu_i}{\prod^{3n-7} \nu_\ddagger} \exp\left(-\frac{\epsilon_o}{kT}\right) : \tag{24}$$

$$\text{thus} \qquad k = \bar{\nu}' \exp\left(-\frac{\epsilon_o}{kT}\right) . \tag{25}$$

This is analogous to equation (20); thus if vibrational energy alone is considered the theory may be regarded as a particular case of Slater's treatment. But in principle Absolute Reaction Rate theory has the advantage that it considers all types of energy.

From time to time attempts have been made to extend the theory to the pressure-dependent region, but such a procedure involves a fundamental contradiction. The theory of Absolute Reaction Rates is based on the assumption that an equilibrium concentration of activated complexes is maintained and cannot be extended to a region in which this is not the case.

(2.9) <u>POTENTIAL ENERGY SURFACES AND ACTIVATION ENERGIES:</u> In the introduction to this chapter it was pointed out that the internal motion of a molecule can be represented by the motion of a point in $(3n-6)$-dimensional phase space, and that reaction is envisaged as the passage of this point through a certain critical boundary. Obviously the strict calculation of the energy surface over which the point is constrained to move would be prohibitively difficult. But the dissociation of a molecule by the reaction $A - B \rightarrow A + B$ is formally similar to the dissociation of a diatomic molecule. It might, therefore, be expected that the potential surface along the reaction co-ordinate would be similar to that of a diatomic molecule. Even the calculation of the potential surface of a diatomic molecule proves a difficult task and the procedure is only briefly outlined here.

As two atoms approach one another from infinity along their line of centres various forces must be considered. They are -

(i) Coulombic forces (Electrostatic interactions)
(ii) van der Waals forces (Polarisation interactions)
(iii) Chemical bonding forces (Exchange interactions)

The latter are the most important and arise from the Pauli Exclusion Principle when applied to the bond-forming electrons. These forces are calculated by the methods of Wave Mechanics. The net effect is shown in the interaction energy curve, more commonly called the potential energy curve, for a diatomic molecule (Figure 2.1).

This is the more modern explanation of the "quasi-elastic" forces which had long been recognised in molecules and the potential energy curve can also be considered from this less exact, but nevertheless very convenient, viewpoint. If the elastic forces (normal mode vibrations) were simple harmonic in character the potential energy curve for a diatomic molecule would be a parabola. B ecause of the known anharmonic nature of the vibrations the actual curve will be of the form shown in Figure 2.1. A very convenient empirical expression of this curve is the Morse equation

$$U(r) = D[1 - \exp(-a\overline{r-r_e})]^2 . \qquad (26)$$

The bond dissociation energy D(A - B) is defined as the increase in internal energy at absolute zero in the ideal gas state for the reaction $A - B \rightarrow A + B$. That is with respect to Figure 2.1

$$D(A - B) = D . \qquad (27)$$

It is assumed here that the vibrations are classical; if the vibrations are quantised the argument is similar but allowance has to be made for the zero-point energy.

The theories of Kassel, Eyring and Slater all equate the high pressure activation energy E_∞ with the critical energy ϵ_o (see 2.10). In Kassel's theory ϵ_o is the minimum energy which the oscillator associated with reaction must possess before reaction can occur. In Slater's case ϵ_o is the minimum energy which the internal modes associated with the breaking bond must possess for reaction, whilst in Eyring's model it is the difference in energy between the initial and activated states at 0°K. Thus in all three cases

$$D(A - B) = \epsilon_o = E_\infty . \qquad (28)$$

That is to say, the high-pressure activation energy should be equal to the bond dissociation energy of the rupturing bond.

If reaction involves the simultaneous rupture of two bonds according to the scheme A-B-A → A + B + A, the activation energy is not necessarily twice D(AB-A) but might be expected to be close to the value D(AB-A) + D(A-B), which by Hess's Law must be equal to the total internal energy change in the reaction.

It has already been stated (2.8) that the activated complex is associated with the potential energy maximum, which is generally to be found between the initial and final states. However, it will be seen that the Morse curve for the dissociation of A-B gives no such maximum and the question of the location of the activated complex arises. Eyring[30] has shown that if the rotational energy is taken into account the dissociation curve has a very slight maximum, or, in other words, the recombination reaction has a very small positive activation energy. Thus, in principle, the location of the complex may be obtained. Appreciable activation energies for the recombination of radicals are due to other causes, such as steric effects, and in these cases $E_\infty = \epsilon_0 > D(A\text{-}B)$.

(2.10) ACTIVATION ENERGY AS A FUNCTION OF PRESSURE: The experimental high-pressure rate constant is defined by

$$E_\infty = RT^2 \frac{d(\ln k_\infty)}{dT} \tag{29}$$

and so should equal the critical energy ϵ_0 on the basis of the Kassel and Slater models. Slater[28] has shown that, at constant pressure, the experimental activation energy E_0 in the low-pressure region should be approximately $\frac{1}{2}n$ RT less than the high-pressure value. Thus

$$\epsilon_0 = E_\infty = E_0 + \tfrac{1}{2}nRT . \tag{30}$$

The corresponding approximation for Kassel's model is

$$\epsilon_0 = E_\infty = E_0 + sRT . \tag{31}$$

The basis of this decrease may be explained along simple physical lines. Tolman[31,32] has shown quite generally that the experimental activation energy E is equal to the average energy of all the molecules which react in unit time ($\bar{\bar{\epsilon}}$), minus the average energy of all molecules ($\bar{\epsilon}$). This is strictly true only under equilibrium conditions but Kassel[84] has shown that the result

is approximately the same under non-equilibrium conditions. Thus at high pressures

$$\epsilon_0 = E_\infty = \bar{\bar{\epsilon}}_\infty - \bar{\epsilon}_\infty . \tag{32}$$

Now the average energy of a molecule containing n vibrational modes is nRT † so that

$$\bar{\epsilon}_\infty = nRT \tag{33}$$

Therefore

$$\bar{\bar{\epsilon}}_\infty = \epsilon_0 + nRT \tag{34}$$

At lower pressures the number of activated molecules are depleted from their equilibrium concentration by reaction (2), that is, the equilibrium distribution $f(\epsilon)d\epsilon$ is changed to some new distribution $g(\epsilon)d\epsilon$. Since the specific rate of dissociation $k(\epsilon)$ increases with ϵ, the highest energy states will be the most affected and the maximum of the $k(\epsilon)g(\epsilon)d\epsilon$ curve falls away from the high pressure value $\epsilon_0 + nRT$ (see Fig. 2.2).

Recently Slater[33] has made some detailed calculations of this effect and has shown that

$$E = E_\infty - \tfrac{n}{2} RT\, g(\theta) \tag{35}$$

where

$$g(\theta) = \theta \frac{d(\ln I_n\theta)}{d\theta} . \tag{36}$$

$I_n(\theta)$ is the integral $\frac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})} \int_0^\infty \frac{x^{\frac{1}{2}(n-1)} \exp(-x)}{1 + x^{\frac{1}{2}(n-1)}\theta^{-1}}\, dx$ of equation (22).

It can be shown that as $p \to \infty$, $\theta \to \infty$ and hence $g(\theta) \to 0$, and that as $p \to 0$, $\theta \to 0$ and hence $g(\theta) \to 1$. The main decrease in activation energy occurs in the region where the rate has fallen off to half the high-pressure value.

In the case of Hinshelwood's model (see equation 17)

$$E_\infty = RT^2 \frac{d(\log k_\infty)}{dT} = \epsilon_0 - (s-1)RT . \tag{37}$$

$$\therefore \quad \bar{\bar{\epsilon}}_\infty = \epsilon_0 + RT . \tag{38}$$

† It should be noted that the maxima of the curves shown in Fig. 2.2 will not correspond exactly to $\bar{\bar{\epsilon}}_\infty$ and $\bar{\epsilon}_\infty$ since the most probable energy is not the same as the average energy. But the approximation is sufficiently good for our purpose.

Since the specific dissociation rates of the activated molecules are the same it might be expected that all states will be equally depleted under non-equilibrium conditions so that $\bar{\epsilon}$ and hence E will retain their high pressure values. In any case $\bar{\epsilon}$ cannot fall below ϵ_0, so the activation energy cannot decrease by more that RT.

(2.11) THE FREQUENCY FACTORS OF UNIMOLECULAR REACTIONS: In Kassel's theory the high-pressure frequency factor λ can be identified with the frequency of internal energy transfers between the loosely coupled oscillators and this would not be expected to be greater than their vibration frequency. Using a more stringent definition of activated molecules a second frequency factor λ' was obtained and was shown to be equal to the frequency of dissociation of the activated molecules. Since these not only possess the requisite energy but also have it localised in the oscillator which is associated with the rupturing bond, there is some justification for believing that the dissociation frequency λ' will be the same as the vibration frequency. Now molecular vibration frequencies lie in the range $10^{12} - 10^{14}$ sec.$^{-1}$

Thus

$$\lambda \leqslant 10^{12} - 10^{14} \text{ sec.}^{-1}$$

$$\lambda' = 10^{12} - 10^{14} \text{ sec.}^{-1}$$

For Slater's and Eyring's models the high-pressure frequency factors were shown to lie between the greatest and least of the frequencies of the molecular vibrations which contribute towards the reaction co-ordinate. Thus

$$\bar{\nu} = \bar{\nu}' = 10^{12} - 10^{14} \text{ sec.}^{-1}$$

The frequency factors of the majority of thermal decompositions of organic molecules do indeed lie in the range $10^{13.0 \pm 1.5}$ sec.$^{-1}$ and these are regarded as normal. However, certain unimolecular decompositions have been found to have frequency factors which are higher than these values. The compounds are generally ketones and metal alkyls[34,35] and they all possess one common feature, namely that after the breaking of one bond the dissociation energy of a second bond is very much less than that of the first bond. That is, with respect to scheme A-B-C → A-B + C → A + B + C, D(AB-C) ≫ D(A-B). In other words, the change in internal energy for the reaction A-B-C → A + B + C is of

the same order as for the reaction A-B-C → A-B + C. Recognition of this lop-sided thermochemistry has lead Pritchard[34] to suggest that high frequency factors are associated with a mode of decomposition which produces three fragments in one step by the simultaneous breaking of two bonds. However, although this suggestion may well be correct, the treatment is far from satisfactory.

Essentially, Pritchard expresses his rate in the Hinshelwood form (equation 17) but treats the oscillators as normal mode vibrations. On the basis of this model λ'' is interpreted as the frequency of dissociation of activated molecules, that is, it is the reciprocal of their lifetime.

Now it is generally agreed that the lifetime of the complex molecules which undergo unimolecular decomposition is very much greater than 10^{-13} sec. because of the time required for the redistribution of energy into a suitable configuration for reaction. Thus for a molecule containing 10 vibrational modes the lifetime has been calculated to be 10^{-4} sec.[27]. However, to get high frequency factors Pritchard has to arbitrarily assign to the various λ'', values which are close to 10^{13} sec.$^{-1}$ and so in effect assumes that activated molecules react on every vibration.

Pritchard states that the molecule may collect energy for activation through a considerable number of normal mode vibrations and it is this number which determines the fall-off characteristics of the rate constant, but he has to assume that this is not the same as the number of normal modes which contribute to the reaction co-ordinate. But comparison with Slater's more precise theory shows that the normal mode vibrations which contribute to the activation also contribute to the reaction co-ordinate.

However, there is a more serious objection which is associated with the phase relations of the normal vibrations, for not only must the requisite energy be localized within the vibrations but they must also be moving sufficiently in phase to carry the two co-ordinates, associated with the two breaking bonds, past their critical value. Pritchard makes no allowance for this in the calculation of his frequency factors. Slater's is the only model which deals with the contribution of several vibrational modes in the correct manner, and it has been shown there that, for the rupture of one bond, the resultant frequency factor cannot be greater than the largest frequency of the contributing modes.

The problem of high frequency factors may be approached in another way by returning to the bond-oscillator model of Kassel, in which the oscillators are identified with chemical bonds rather than with normal mode vibrations. If chemical reaction is associated with more than one bond the natural extension of the Kassel model is the assumption that the necessary condition for reaction is the localization of the critical energy ϵ_o in z of the s oscillators, where $1 < z < s$. This is similar to the suggestion made by Peard, Stubbs and Hinshelwood[36] when they discussed the high frequency factors in the thermal decomposition of paraffins.

If these oscillators are lightly coupled the high-pressure rate constant will be given by

$$k_\infty = \int_o^\infty \lambda H_{s,z}(\epsilon,\epsilon_o) f(\epsilon) d\epsilon \ , \tag{39}$$

where $f(\epsilon)d\epsilon$ is the probability that total energy is in the range $(\epsilon,\epsilon+d\epsilon)$ and $H_{s,z}(\epsilon,\epsilon_o)$ is the probability that, if the total energy is $(\epsilon,\epsilon+d\epsilon)$, ϵ_o or more is in the z oscillators.

If the oscillators are not coupled then a more stringent definition of activated molecules must be used, namely that these must possess energy ϵ_o localized in the z oscillators which are associated with the rupturing bonds. The high-pressure rate constant now becomes

$$k_\infty = \int_o^\infty \lambda' G_{s,z}(\epsilon,\epsilon_o) d\epsilon \ , \tag{40}$$

where $G_{s,z}(\epsilon,\epsilon_o)$ is the probability that the energy in an s-oscillator system is $(\epsilon,\epsilon+d\epsilon)$ and also that at least ϵ_o is in z particular oscillators. Obviously, by definition,

$$H_{s,z}(\epsilon,\epsilon_o) f(\epsilon) d\epsilon \equiv G_{s,z}(\epsilon,\epsilon_o) d\epsilon \ , \tag{41}$$

so that both expressions for the rate constants will reduce to similar forms (the same form if $\lambda = \lambda'$). Recently Slater[33] has evaluated $H_{s,z}(\epsilon,\epsilon_o)$ and $G_{s,z}(\epsilon,\epsilon_o)d\epsilon$ and has shown that

$$\int_o^\infty G_{s,z}(\epsilon,\epsilon_o) d\epsilon = \frac{\exp\left(-\frac{\epsilon_o}{kT}\right)\left(\frac{\epsilon_o}{kT}\right)^{z-1}}{(z-1)!}\left(1+\frac{z-1}{\left(\frac{\epsilon_o}{kT}\right)}+\cdots+\frac{(z-1)!}{\left(\frac{\epsilon_o}{kT}\right)^{z-1}}\right) . \tag{42}$$

For $z = 2$ equations (37) and (38) reduce to

$$k_\infty = \text{const.} \exp\left(-\frac{\epsilon_o}{kT}\right)\left[\frac{\epsilon_o}{kT}+1\right] \ ,$$

where the constant term equals λ or λ'. Now these terms have the same significance as in the simpler model, so tentatively we may equate them with the value of "normal" frequency factors. For an activation energy of 40 kcal. at 500°K $E/RT \approx 40$. Thus the frequency factor of reactions which are associated with the simultaneous rupture of two bonds should be some 40 times greater than the normal value, i.e. $10^{14.6 \pm 1.5}$ sec.$^{-1}$. When reaction is associated with three bond-oscillators, as it might be for the reaction R.CO.CO.R $\rightarrow$ R + CO + CO + R, then the frequency factor should be about 1,600 times greater than the normal value, i.e. $10^{16.2 \pm 1.5}$ sec.$^{-1}$.

Using the transition state model Evans and Rushbrooke[37] have associated the high frequency factors with a large entropy of activation. This large entropy is supposed to be caused by the anharmonic nature of the oscillator which is associated with reaction in Kassel's model. Pictorially it corresponds to a greater looseness of the transition state in the anharmonic case. But these ideas are only qualitative, and the hypothesis does not indicate why some molecules should have high entropies whilst others do not. Slater[16] has considered the effect of anharmonic corrections to the internal co-ordinate q which is associated with the rupturing bond. He finds that the frequency factor is only altered by about 2% and that the change is in the opposite direction to that suggested by Evans and Rushbrooke. However, if the arguments were extended to include the other (n-1) co-ordinates this might not be so. It has also been suggested that high frequency factors might arise if the phase distribution after an activating collision was not statistical but was such that $(q - q_0)$ was likely to reach zero very soon after collision; however the mathematical treatment of such a problem would be extremely difficult.

(2.12) ENERGY TRANSFER BETWEEN MOLECULES: If activation takes place by collision it is to be expected that the addition of gases, which are themselves chemically inert, will increase the rate of reaction in the pressure-dependent region. Starting with a pressure p_a of reactant A, which has associated with it a first-order rate constant k_a, by the addition of a pressure P_i of inert gas X the rate constant may be increased to k_b, which corresponds to a pressure p_b of reactant (see Fig. 2.3).

In terms of the Lindemann scheme we have

$$A + A \rightleftharpoons A^* + A \qquad (1)$$

$$A + X \rightleftharpoons A^* + X \qquad (1')$$

$$A^* \rightarrow B + C \,. \qquad (2)$$

Using the steady state treatment it is easy to show that

$$k_b = k_2 \frac{k_1 p_b}{k_{-1} p_b + k_2} = k_2 \frac{k_1 p_a + k_1' p_i}{k_{-1} p_a + k_{-1}' p_i + k_2} \,. \qquad (43)$$

Whence

$$\frac{p_b - p_a}{p_i} = \frac{k_1'}{k_1} + \frac{p_b}{k_2}\left(k_{-1}\frac{k_1'}{k_1} - k_{-1}'\right). \qquad (44)$$

But

$$\frac{k_1}{k_{-1}} = \frac{k_1'}{k_{-1}'}, \text{ since both equal } \frac{[A^*]}{[A]}, \qquad (45)$$

Thus

$$\frac{k_{-1}'}{k_{-1}} = \frac{k_1'}{k_1} = \frac{p_b - p_a}{p_i} \,. \qquad (46)$$

$\frac{k_{-1}'}{k_{-1}}$ may be taken as a measure of the efficiency of X, relative to A, in deactivating A-molecules, whilst $\frac{k_1'}{k_1}$ is the efficiency of X, relative to A, in activating A-molecules. Thus, in general, $\frac{p_b - p_a}{p_i}$ may be regarded as the relative efficiency of X in energy transfers with A-molecules, or more explicitly, as the relative efficiency of X in transfer processes which involve the activated states of the A-molecules. The ratio $\frac{p_b - p_a}{p_i}$ is symbolised α_p, the subscript p being used to emphasise that the calculations are on a pressure-to-pressure basis rather than on a collision-to-collision basis.

(2.13) COMPARISONS BETWEEN THE THEORIES:

General Model: All the theories have the Lindemann mechanism of collisional activation in common and treat the molecules as vibrating systems.

High-Pressure Rate: The theories of Kassel, Slater and Eyring predict that the high-pressure rate will be of the form

$$k_\infty = A \exp(-E/RT) \,. \qquad (47)$$

The Hinshelwood expression (equation 17) is more complex, but this could not be distinguished experimentally from the simpler expression.

General Rate: Only the theories of Hinshelwood, Kassel and Slater can be used when there is not an equilibrium distribution of molecules; they all predict that the rate constant should decrease with decreasing pressure. However, the rate/pressure curves calculated on the basis of the Hinshelwood model are much steeper than the experimental curves (see Fig. 11.1). Furthermore, from equation (18) it will be seen that the theory predicts a negligible separation between two curves at different temperatures when, in fact, the experimental separation is considerable, and that the predicted separation is in the wrong direction. These inadequencies stem from the failure to allow for the greater reactivity of the more energetic molecules.

To evaluate the Kassel integral (equation 12) we require to know, besides the kinetic data - (i) the number of effective oscillators, (ii) the molecular diameter, (iii) the molecular weight, and (iv) the pressure. Of these, (ii), (iii) and (iv) are required in the calculation of the collision frequency ω. ϵ_0 is given the value of the high-pressure activation energy (E_∞). The value of s is chosen to give the best fit between the theoretical and experimental curves over a range of temperatures. The main criticisms of the theory are its arbitrary nature and the fact that the oscillators are not well defined, but have a status somewhere between normal vibrational modes and chemical bonds.

The high-pressure activation energy is the only kinetic datum which is required by the Slater theory (equation 22). n is not arbitrary and $\bar{\nu}$ is calculated from the properties of the normal unexcited molecule. Furthermore, the theory allows for the different vibrational characteristics of molecules and, without arbitrary assumptions, predicts that the specific rate constant of a molecule will be a function of the energy which it possesses in excess of the critical value. Thus Slater's theory involves fewer assumptions and is more rigorously developed than Kassel's. However, its elegance is offset by a practical difficulty, for it requires a complete knowledge of the vibrational structure of the molecule. It is difficult to obtain these data and, even when known, the calculations are tedious. But calculations have been performed for some "idealised" molecules.

In actual fact the predicted rate/pressure curves of both theories are remarkably similar and they both fit the experimental results closely, so it is impossible to say on this basis which theory is superior (see Fig. 11.1).

Activation Energies: At high pressures, when there is an equilibrium distribution of molecules, the theories of Kassel, Slater and Eyring identify the critical energy with the experimental activation energy (equation 29), but in Hinshelwood's theory (equation 37) the activation energy should be less than the critical energy. Thus only in the first case can the bond dissociation energy be identified with the activation energy.

Hinshelwood's theory indicates that the activation energies at high and low pressures should be the same, but those of Kassel and Slater require the high-pressure activation energy to be, respectively, sRT and $\frac{1}{2}$nRT greater than the low-pressure value (see 2.10). Eyring's theory cannot be extended to low pressures since an equilibrium distribution of activated molecules is not maintained in that region.

The determination of activation energy as a function of pressure is important not only as a test of the theories but it can also yield information about the number of oscillators which contribute to the reaction co-ordinate. It has been pointed out that the rate/pressure curves are not sensitive to the exact value of n or s, so that the measurement of the total change in activation energy, $\frac{1}{2}$nRT or sRT, should be the best way of determining these values. Moreover, the shape of the activation-energy/pressure curve might be expected to give some information about the detailed nature of the specific rate constant function.

Frequency Factors: Comparisons between the frequency factors predicted by the various theories have already been made in section 2.11.

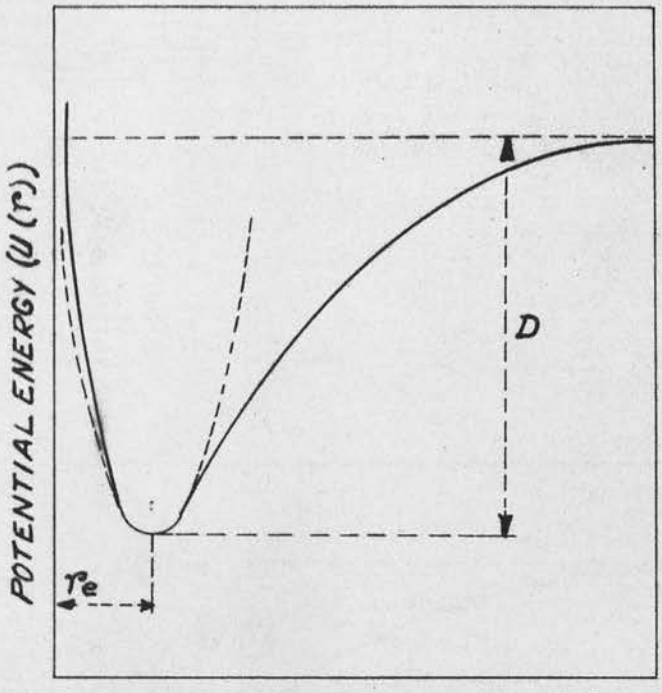


FIG. 2·1. POTENTIAL ENERGY CURVE FOR A DIATOMIC MOLECULE.
THE DASHED CURVE SHOWS THE VARIATION IN POTENTIAL ENERGY WITH INTERNUCLEAR DISTANCE IF THE VIBRATION WAS SIMPLE HARMONIC IN CHARACTER. r_e IS THE EQUILIBRIUM NUCLEAR SEPARATION, AND D IS THE DISSOCIATION ENERGY.

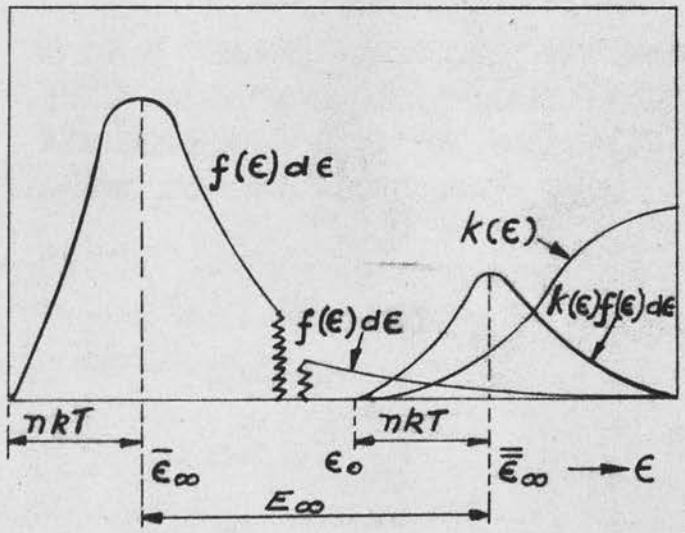


FIG. 2·2 DISTRIBUTION FUNCTION $f(\epsilon)d\epsilon$, SPECIFIC DISSOCIATION RATE $k(\epsilon)$ AND THEIR PRODUCT AS A FUNCTION OF ENERGY.

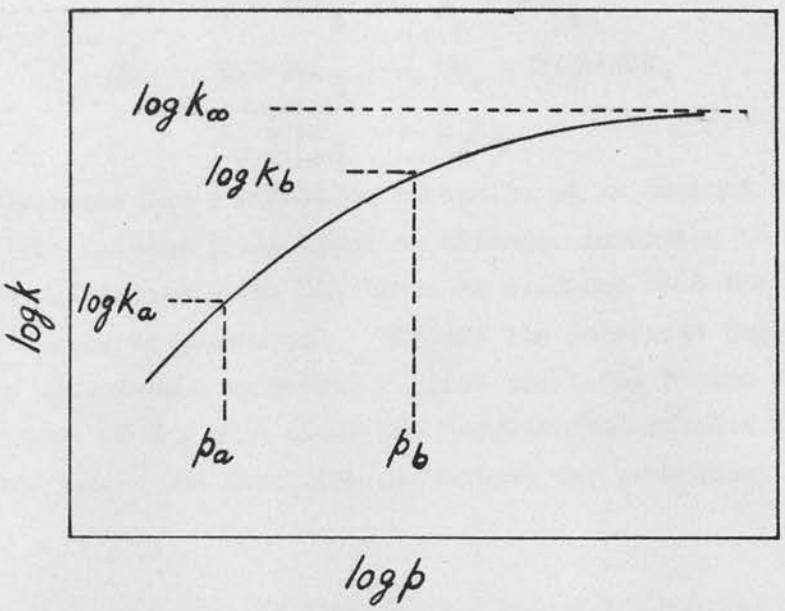


FIG. 2·3 THE METHOD OF DETERMINING THE RELATIVE EFFICIENCIES OF GASES IN ENERGY TRANSFERS WITH REACTING MOLECULES IN UNIMOLECULAR REACTIONS.

CHAPTER 3.

THE PHOTOCHEMICAL DECOMPOSITION OF AZOMETHANE.

(3.1) SUMMARY: Within the temperature range 24 - 160°C the variation in the rate of production of nitrogen, methane and ethane with absorbed intensity and azomethane concentration may be accounted for quantitatively by the reactions

$$CH_3N{=}NCH_3 \xrightarrow{h\nu} N_2 + 2CH_3 \qquad (1)$$

$$CH_3 + CH_3N{=}NCH_3 \longrightarrow CH_4 + CH_2N{=}NCH_3 \qquad (2)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \ . \qquad (3)$$

There is no evidence for a molecular mechanism or an excited molecule mechanism. The quantum yield based on nitrogen formation is unity, and is independent of temperature; but there is evidence that the yield increases at higher temperatures. Besides the permanent gases, complex compounds are also formed by methyl radical additions to the substrate. A summary of some of the more important experimental results is given in Tables 3.1 and 3.2. The text also deals with the inadequacy of the early studies.

(3.2) INTRODUCTION: The photolysis of azomethane has been investigated more thoroughly than the thermal reaction and both the mechanism and kinetics appear to be fairly well understood. It will, therefore, provide a valuable background in discussing the thermal reaction.

Until the work of Jones and Steacie[38] in 1953 there was little understanding of the reactions involved. This was due to the lack of knowledge, both qualitative and quantitative, of radical reactions, especially radical abstractions and radical combinations. For instance, the combination of two methyl radicals to form ethane was considered too unlikely a reaction to account for the ethane observed, and the likelihood that methane could be formed by a hydrogen-abstraction reaction such as

$$CH_3 + CH_3N{=}NCH_3 \longrightarrow CH_4 + CH_2N{=}NCH_3 \qquad (2)$$

was not envisaged.

The early work would appear now to be only of historic interest, but it will serve to emphasise three points. (i) The insufficiency of pressure measurements as a means of following the reaction. (ii) The need for quantitative analyses in the elucidation of mechanism. (iii) The complexity of the reaction.

(3.3) EARLY STUDIES BASED ON PRESSURE MEASUREMENTS: The first work was done in 1927 by Ramsperger[39]. He followed the decomposition by measuring the pressure increase, assuming for every molecule decomposed 2.04 molecules were formed. This appeared reasonable since he had previously concluded that the reaction was mainly the molecular process

$$CH_3N{=}NCH_3 \rightarrow C_2H_6 + N_2. \qquad (4)$$

For the pressure and temperature ranges 1-257 mm., 20 - 100°C, he found the temperature coefficient to be zero and obtained a quantum yield of 2. Ramsperger suggested that this yield could be explained on the basis of short energy chains in which the activated ethane formed in the primary act transferred its excess energy *in toto* to another azomethane molecule.

(3.4) Forbes, Heidt and Sickman[40] pointed out that if this mechanism were operative it was difficult to understand how the quantum yield was both pressure and temperature independent, and they suggested that the high yields were due to Ramsperger's poor optical technique. They, therefore, reinvestigated the reaction. At room temperatures the quantum yield decreased as the reaction progressed, approached unity at low pressures and diminished at high, and the authors explained this decrease in yield by collisional deactivation of the excited azomethane. This effect was especially noticeable at longer wave-lengths, which is reasonable if the life of the excited molecule depends in an inverse way upon the energy it contains.

(3.5) ANALYSES OF THE REACTION PRODUCTS: However, by carrying out analyses of the products of the reaction, Burton, Davis and Taylor[41] showed that the decomposition was more complex than previously suspected

and that the overall reaction did not even approximately follow equation (4). The percentage of nitrogen formed exceeded that of hydrocarbons and, although ethane was the main hydrocarbon at low temperatures, at higher temperatures the amount of ethane formed decreased and methane became the main hydrocarbon product. This cast doubt on the validity of the previous results, which were obtained solely on the basis of pressure measurement. Such calculations assumed either an overall decomposition giving nitrogen and ethane, or a pressure increase which was proportional to the amount of azomethane decomposed in a single simple reaction, and Burton, Davis and Taylor suggested that the low yields of Forbes, Heidt and Sickman could be explained on this basis.

(3.6) DIVERGENCE OF YIELDS BASED ON NITROGEN ESTIMATION AND PRESSURE INCREASE:

These conclusions were justified by later work. Blacet and Taurog[42] obtained quantum yields of 1 on the basis of molecules of nitrogen formed per quantum absorbed, but on the basis of pressure increase the yield was only 0.75. Cannon and Rice[43] also found that the yields based on pressure increase and nitrogen formation did not agree and that the ratio of the total pressure increase to nitrogen produced decreased with increasing pressure. To explain this they suggested that at low pressures methyl radicals reacted on the surface to form ethane, whilst at higher pressures they added to the azomethane (see section 3.7).

(3.7) FORMATION OF ETHANE AND METHANE AND THE NATURE OF THE PRIMARY STEP:

Besides pointing out the unsatisfactory nature of the data based on pressure-time measurements, the main contribution of Burton, Davis and Taylor was the suggestion that methyl radicals could add to azomethane by reactions such as

$$CH_3 + CH_3N{=}NCH_3 \rightarrow CH_3N{-}N(CH_3)_2 \qquad (5)$$

$$CH_3 + CH_3N{-}N(CH_3)_2 \rightarrow (CH_3)_2N{-}N(CH_3)_2 \qquad (6)$$

$$2CH_3N{-}N(CH_3)_2 \rightarrow \begin{matrix}(CH_3)_2N{-}NCH_3\\ |\\ (CH_3)_2N{-}NCH_3\end{matrix} \qquad (7)$$

However, the reactions which they suggested for the production of methane

and ethane are highly speculative. In the final paper of the series Davis, Jahn and Burton[44] showed that in the presence of nitric oxide practically no hydrocarbon gas was produced. There was, however, no inhibition in the formation of nitrogen, which indicated that no chains were involved. But it should be borne in mind that nitric oxide has been observed to have both a catalytic and an inhibitory effect, and it is conceivable that these two effects roughly balance each other. The work indicated, contrary to the conclusions in the first two papers, that the primary step is predominantly the radical reaction

$$CH_3N{=}NCH_3 \longrightarrow N_2 + 2CH_3 \qquad (1)$$

and that molecular rearrangement to ethane and nitrogen is unimportant. They suggested that the ethane and methane arise by (unspecified) reactions involving the complex addition products mentioned above, but they give no real experimental evidence for this conclusion.

It is now well known that the photochemical decomposition yields methyl radicals. These have been detected by the para-ortho hydrogen method and by the Paneth mirror technique[45]. Blacet and Taurog[42] have used azomethane to sensitise the decomposition of acetaldehyde, and more recently Herzberg and Shoosmith[46] have produced methyl radicals by the flash photolysis of azomethane.

(3.8) Flowers and Taylor[47] also photolysed azomethane and explained their results on the basis of a scheme whereby both methane and ethane arise from reactions of the complex radicals -

$$CH_3 + (CH_3)_2\,N{-}N(CH_3) \longrightarrow CH_4 + \text{liq.} \qquad (8)$$

$$CH_3 + (CH_3)_2\,N{-}NCH_3 \longrightarrow C_2H_6 + CH_3N{=}NCH_3 \qquad (9)$$

$$CH_3 + (CH_3)_2\,N{-}N(CH_3) \longrightarrow C_2H_6 + C_2H_6 + N_2\,. \qquad (10)$$

It will be seen that the last of these reactions gives an overall process of chain length two. If such reactions are possible then methyl radicals

should also react directly with azomethane by the reaction

$$CH_3 + CH_3N{=}NCH_3 \rightarrow N_2 + CH_3 + C_2H_6 \qquad (11)$$

and this would also give rise to a chain reaction.

(3.9) AZOMETHANE-HYDROGEN MIXTURES: Flowers and Taylor[47] studied azomethane-hydrogen mixtures. In the temperature range 20 - 200°C they found the rate of formation of ethane to be independent of hydrogen. At low temperatures the rate of methane production was decreased, but it increased with temperature faster than for azomethane alone.

Kuchler[48] also studied azomethane and azomethane-hydrogen mixtures, following the reaction by measurement of the nitrogen evolved. At 3130 Å he obtained a quantum yield of 2 which was independent of pressure and of temperature up to 200°C. In the presence of a threefold excess of hydrogen the yield rose from 2 at 20°C to 6 at 225°C.

(3.10) ACTIVATED MOLECULE MECHANISM: In the work, already mentioned, of Blacet and Taurog[42] the reaction was followed by total analysis in the pressure range 49 - 80 mm., and the authors revived the activated molecule mechanism by suggesting the scheme

$$CH_3N{=}NCH_3 \rightarrow CH_3N{=}NCH_3^* \text{ (electronically excited)} \qquad (12)$$

$$CH_3N{=}NCH_3^* \rightarrow C_2H_6 + N_2 \text{ (in absence of NO only)} \qquad (13)$$

$$CH_3N{=}NCH_3^* \xrightarrow{NO} X \,.$$

But in the experiments of Davis, Jahn and Burton[44], nitric oxide was present in only one-tenth the concentration of azomethane so it must possess a very high efficiency in removing excess energy even although this is in the form of electronic energy. Cannon and Rice[43] studied the reaction up to pressures of 390 mm. of azomethane and 683 mm. of carbon dioxide and their quantum yields at room temperature remained unity throughout, showing no indication of a collisional deactivation process.

(3.11) RECENT WORK: This rather confused picture has been largely clarified by the more recent work of Jones and Steacie[38]. Using light of wave length 3660 Å they were able to show that, for the ranges 10 - 100 mm. and 24 - 191°C, the rates of production of the permanent gases were consistant with the scheme

$$CH_3N{=}NCH_3 \xrightarrow{h\nu} N_2 + 2CH_3 \qquad (1)$$

$$CH_3 + CH_3N{=}NCH_3 \longrightarrow CH_4 + CH_2N{=}NCH_3 \qquad (2)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \,. \qquad (3)$$

Like previous workers they also obtained higher molecular weight products. Analyses of these by mass spectra indicated that a mixture of substances was present with the main peaks at mass numbers 72 and 88. It is likely that these are parent peaks corresponding to methyl ethyl diimide and tetramethyl hydrazine which could be formed by the reactions

$$CH_3 + CH_2N{=}NCH_3 \longrightarrow C_2H_5N{=}NCH_3 \qquad (15)$$

$$2CH_3 + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2N{-}N(CH_3)_2 \,. \qquad (5)\ \&\ (6)$$

The quantum yield, which was unaffected by change of pressure, was approximately 0.9 in the temperature range 24 - 159°C, but had risen to 1.13 at 194°C. At this temperature the thermal reaction is not important (5% reaction would take 8 days) and the question may well be asked whether the increase in yield is real or merely within experimental error. Steacie[50] has reported that at 260°C the quantum yield is 2, and at the same temperature Forbes, Heidt and Sickman[40] observed that the quantum yield had increased by 50%.

At 30°C the quantum yield was not affected by the presence of carbon dioxide. In agreement with the results of Cannon and Rice[43] this appears to rule out an excited molecule mechanism.

On the basis of the rates of methane and ethane production, Jones and Steacie calculated the rate expression for the metathetical reaction of methyl radicals with azomethane (reaction (2)) to be

$$k_2 = 10^{11.1} \exp(-7{,}600/RT) \text{ sec.}^{-1} \text{ Moles}^{-1} \text{ cc.} \qquad (16)$$

On the basis of an assumed mechanism and material balance considerations, the rate constant for the addition of methyl radicals to azomethane was found to be

$$k_5 = 10^{10.7} \exp(-6,300/RT) \text{ sec.}^{-1} \text{moles}^{-1} \text{ cc.} \qquad (17)$$

but this value must be accepted with caution.

(3.12) CONCLUSIONS: Although the main pattern of the low-temperature photolysis appears to have been elucidated, there are still some points which need clarification.

(a) Davis, Jahn and Burton have shown that nitric oxide does not affect the yield of nitrogen. This, together with the unit quantum yields, is taken as evidence of the non-existence of chains. But it should be borne in mind that the effect of nitric oxide is complex; Smith and Hinshelwood[49] have shown that it can simultaneously catalyse and inhibit a reaction. It would, therefore, be interesting to see whether propylene gives the same results. Furthermore, the original work with nitric oxide was not very accurate. Unit quantum yields by themselves are not unambiguous evidence for the non-existence of short chains.

(b) Accurate studies at somewhat higher temperatures than those reported by Jones and Steacie would indicate if short chain processes become of importance as the temperature is increased as they do in the photolysis of acetone. Steacie[50] has stated that the quantum yield at 260°C is 2, but does not give the source.

(c) The studies of the photolysis in the presence of hydrogen, in particular the high quantum yields obtained by Kuchler, need reinvestigation.

TABLE 3.1. SOME OF THE IMPORTANT EXPERIMENTAL CONDITIONS AND RESULTS IN THE PHOTOLYSIS OF AZOMETHANE.

Authors	Wavelength of light (Å)	Temp. range (°C)	Int. Press. Azomethane (mm.)	Temp. Coeff.	Quantum Yields	Analyses	Rate Determination	Percent. Decomp.
Ramsperger	~3660	20-100	12-257	0	2		pressure increase	
Forbes, Heidt & Sickman	3660-3350	25-226	181-664	0	≤ 1		pressure increase	
Burton, Davis & Taylor	~3660	room	13.5-102	-	-	total	-	<20
Burton, Davis & Taylor	~3660	-22.5-223	~100	-	-	total	-	10
Davis, Jahn & Burton	~3660	20-222	40-105	-	-	total	-	-
Blacet & Taurog	3660	30	49-80	-	1.75	total	pressure increase & N_2 analysis	2
Cannon & Rice	3660	30	66-390	-	0.74-1.11	nitrogen	pressure increase & N_2 analysis	<10
Kuchler	3130	20-200	90-300 100-300	0	2 2-6(H_2)	nitrogen	N_2 analysis	<1
Flowers & Taylor	unfiltered mercury arc	20-200	22-57	-	-	total	-	30
Jones & Steacie	~3660	24-191	10- 125	0	.87-1.13	total	N_2 analysis	<6

TABLE 3.2. ANALYSES OF PRODUCTS OF PHOTOLYSIS OF AZOMETHANE

Authors	Temp. (°C)	Int. press. Azomethane (mm.)	Permanent Gases expressed as percentage						High M.W. Compounds	Percentage Decomp.
			CH_4	C_2H_6	C_3H_8	unsatd.	H_2	N_2		
Burton, Davis & Taylor	room	13.5-102	0-5	37-45	0-15	0-.9	0	52-58	obsvd.	<20
Burton, Davis & Taylor	20	100	3	42	0	0	0	55	obsvd.	10
	223	100	23	4.9	45	0	0	69		
Blacet & Taurog	30	49-80	6.5	37	0	0	1.9	54	obsvd.	<2
Flowers & Taylor	30	57	7	42	0-1	.6	0	50	obsvd.	30
	197	37	33	3.2	0	.8	0	63	obsvd.	
Jones & Steacie	24	11	1.6	47	<1	0	0	51.4		
	24	81	6.7	38.8	<1	0	0	54.5	obsvd.	<6
	191	41	30.9	1.5	0	0	0	67.6		
	191	92	30.8	.7	0	0	0	68.5		

CHAPTER 4.

THE THERMAL DECOMPOSITION OF AZOMETHANE.

(4.1) SUMMARY: In the thermal decomposition of azomethane the rate-controlling step appears to be the primary reaction $CH_3N{=}NCH_3 \rightarrow 2CH_3 + N_2$, and, as in the photolysis, there is no evidence for the molecular reaction $CH_3N{=}NCH_3 \rightarrow C_2H_6 + N_2$, which was suggested by Ramsperger. Since the products are similar to those obtained in the photolysis, viz:- methane, ethane, traces of ethylene and "liquid", it appears likely that the reactions following the primary step are also similar to those which occur in the photolysis. Studies with azomethane-nitric oxide mixtures do indicate, however, that short chains may be present. The high-pressure rate based on pressure measurements is given by

$$k_\infty = 10^{16.2 \pm .3} \exp(-51,300 \pm 1,200/RT) \text{ sec.}^{-1} \qquad (1)$$

but it is shown that these measurements are inadequate in determining the rate of the primary reaction. Inert gases are able to increase the rate in the pressure-dependent region and this is considered to be evidence that the rate-pressure curves cannot be explained solely on the basis of a varying chain length or a reaction of complex order. The carbon-nitrogen bond strengths in azomethane are discussed and the effect of surface on the reaction noted.

(4.2) EARLY WORK BASED ON PRESSURE MEASUREMENTS: The thermal reaction was first investigated by Ramsperger[7,8] for the temperature and pressure ranges 290-330°C and .26-707.9 mm. The reaction was followed by total-pressure measurements on the assumption that 2.04 molecules of product were formed by every azomethane molecule which reacted. This was reasonable in that the reaction was assumed to be predominantly

$$CH_3N{=}NCH_3 \rightarrow N_2 + C_2H_6 \ . \qquad (2)$$

The limiting high-pressure rate constant was given by

$$k_\infty = 10^{16.5} \exp(-52,500/RT) \text{ sec.}^{-1} \qquad (3)$$

Rice and Sickman[11,51] reinvestigated the reaction for the ranges 290 - 310°C and .41 - 24.8 mm. The main purpose of the work was to study the effect of added gases on the reaction but they also did a considerable amount of work with pure azomethane. With the aid of a Huygens manometer the rates were calculated for 3 - 10% reaction from the change in total pressure. A few runs were also carried out up to pressures of 190 mm. using the McLeod gauge technique of Ramsperger.

The rate expression for the reaction $A \rightarrow zB$ is

$$k.t = 2.303 \log \frac{(z - 1) P}{zP_o - P} \quad , \tag{4}$$

where P_o is the initial pressure, and P is the total pressure at time t. The rate constants were calculated on the assumption that z = 2.00, but it should be noted that they found the ratio of the final pressure to the initial pressure, when the reaction was allowed to go to completion, to be 2.17. This is considerably higher than the ratio found by Ramsperger. But, under the experimental conditions used, the rate constant is lowered by 25 per cent when z is changed from 2.00 to 2.17. Thus, although the shape of the fall-off curve may be correct, little reliance can be put on its absolute position unless the number of moles of product formed from each mole of azomethane under the experimental conditions are accurately known. Indeed Taylor and Jahn[52] found that although for 100 per cent decomposition the ratio of the initial to the final pressure was 2.17, for 50 - 90 per cent decomposition only 1.95 moles of product were formed for every mole of azomethane which had reacted.

Although there is general agreement between the results of Ramsperger and Rice & Sickman, it will be observed from Figure 9.4 that the latter's rates show a greater variation with initial pressure and it is no longer clear that the first-order constants are becoming pressure independent at high pressures. The value of the high-pressure rate is, therefore, a matter of speculation, but the authors give

$$k_\infty = 10^{15.9} \exp(-50,200/RT) \text{ sec.}^{-1} \tag{5}$$

(4.3) ANALYSES OF PRODUCTS: All the above work was done without recourse to analyses of the products. When such analyses were carried out by Riblett and Rubin[13] they found that the overall reaction could not even be approximated to by reaction (2); in particular, large quantities of methane were observed. The results of some of their experiments are given in Table 4.1.

Taylor and Jahn[52] also analysed the reaction products and obtained similar results, the main difference being that they found even less ethane than did Riblett and Rubin.

The rate constants which may be derived on the basis of pressure increase, azomethane consumption and nitrogen production are shown in Table 4.2. The rates based on pressure measurements were calculated on the assumption that 1 mole of reactant formed 1.95 moles of product in the case of Taylor and Jahn, and 2.10 moles in the case of Riblett and Rubin.

The rates based on nitrogen analyses and total pressure measurements are in fairly good agreement, but the rates based on azomethane analyses are considerably higher. This is consistent with the view that the rate-controlling step for the overall process is

$$CH_3N{=}NCH_3 \rightarrow CH_3 + N_2 + CH_3 \qquad (6)$$

and that the methyl radicals formed react with azomethane, effectively removing it from the reaction system.

Although the nitrogen and total-pressure rates agree fairly well, it is obvious, because of the complexity of the reaction, that conclusions based on pressure data alone must be accepted with extreme reserve. In particular, photolysis studies have shown that the ratio of the quantum yields obtained by measurement of the nitrogen formed and by pressure increase is not independent of the initial pressure of azomethane (see 3.6).

(4.4) THE FORMATION OF RADICALS AND THE NATURE OF THE PRIMARY STEP: There is considerable evidence that methyl radicals are formed in the thermal decomposition. Leermakers[53] and Rice & Evering[54] have shown that mirrors are removed when azomethane is decomposed by the usual Rice-Paneth technique. Azomethane has also been used to sensitize the thermal decomposition of acetone, and more recently Lossing, Ingold and Henderson[83], using mass spectrometry, have detected methyl radicals in the pyrolysis of azomethane.

In the presence of a twofold excess of nitric oxide Jahn and Taylor[55] found that azomethane decomposed with only a very small pressure increase, and that the composition of the gaseous products was completely altered. One mole of nitrogen was obtained per mole of azomethane decomposed and very little else- about 0.1 mole of hydrocarbons and carbon dioxide. This indicates that the direct split to ethane and nitrogen does not occur and that the primary process is entirely reaction (6). More recently Page, Pritchard and Trotman-Dickenson[56] have been able to account semi-quantitatively for the rate of ethane production on the basis of methyl radical combination. This is further evidence that ethane does not arise from a molecular reaction.

Since the primary step and the products of the reaction appear to be similar to those in the photolysis, we may suppose for the present that the reaction schemes of the thermal and photochemical reactions are similar (see 3.11). To account for the traces of ethylene, which some workers have reported, Page, Pritchard and Trotman-Dickenson have suggested that ethyl radicals, and hence ethylene, are formed from the decomposition of $C_2H_5N{=}NCH_3$.

(4.5) CHAIN PROCESSES: All authors have concluded that there is little evidence for the existence of chains in the thermal decomposition of azomethane. Rice and Sickman[11] write -

> "We believe the constancy of α (the relative efficiency of inert gas) over a range of pressures and two temperatures is strong evidence in favor of the view that the azomethane decomposition is not a chain reaction, or at least that the chain length is independent of pressure and temperature over that range."

And Steacie[57] states -

> "The evidence favors the idea that while azomethane decomposes by a radical mechanism it does not do so by a chain mechanism."

Besides the unit quantum yields obtained in the photolysis studies and the effect of inert gases on the thermal reaction, the main evidence for this belief rests on the work of Leermakers[58], who concluded that at 275°C ethyl radicals do not initiate chains in azomethane. But examination shows that little reliance can be placed on this work.

The method employed by Leermakers was as follows:- He investigated the kinetics of the decomposition of lead tetraethyl in a static system by total-pressure measurements and found

$$k = 10^{12.1} \exp(-36{,}900/RT) \text{ sec.}^{-1} \quad (7)$$

He then studied azomethane-lead tetraethyl mixtures. Using Ramsperger's data he was able to allow for the pressure increase due to azomethane alone and hence to obtain rate constants for the decomposition of lead tetraethyl in the presence of azomethane. Now if the ethyl radicals were inducing chains, Leermakers argued, these simple assumptions would not be correct and the calculated rate should be greater than for lead tetraethyl alone. Careful analysis of Leermaker's data shows that the calculated rate constants are affected considerably by variations of the experimental parameters within the limits of the experimental reproducibility and may be as much as 20 per cent in error. Moreover, at 275°C the rate constant for the decomposition of lead tetraethyl is some fifty times greater than the rate constant for azomethane, so the method is quite unsuited for the detection of short chains. In fact, Leermaker's rate constants for lead tetraethyl in the presence of azomethane show a decrease of 25 per cent at 260°C and 15 per cent at 275°C over the constants obtained for lead tetraethyl alone. This may well be due to the addition of ethyl radicals to azomethane.

There does, in fact, appear to be some evidence that short reaction chains are involved. Thus the quantum yield at 260°C is significantly greater than at temperatures below 190°C (see 3.11). Furthermore, the rates obtained by Jahn and Taylor[55] in the presence of nitric oxide are lower by a factor of two than the rates for pure azomethane. But this was not emphasised as the authors were mainly interested in showing the primary step to be a radical split rather than a molecular rearrangement. From analysis of azomethane consumption Taylor and Jahn[52] found the high-pressure rate to be given by

$$k_\infty = 10^{16.5} \exp(-52{,}500/RT) \text{ sec.}^{-1}, \quad (8)$$

whilst the rates for the inhibited reaction, on the basis of both azomethane analysis and nitrogen formation, are best represented by the expression

$$k_\infty = 10^{15.8} \exp(-51{,}400/RT) \text{ sec.}^{-1} \quad (9)$$

But the experimental results had a wide scatter and it should be noted (see Table 4.2) that in the uninhibited reaction the rates based on azomethane analysis are greater than those based on nitrogen analysis.

(4.6) COMPLEX ORDER: Pease[59] has emphasised that the absence of long chains by no means demands that the reaction be of first order, and he has pointed out that if the reaction was 1.5 order the data of Rice and Sickman would be fitted equally well. However, a calculation of the 1.5-order rate constant gives

$$k_{1.5} = 10^{17.9} \exp(-47{,}700/RT) \text{ (moles cc.}^{-1})^{-\frac{1}{2}} \text{ sec.}^{-1} \qquad (10)$$

and the temperature-independent term is excessively large. Furthermore, the experiments of Rice and Sickman were over a comparatively limited pressure range, and over a more extensive pressure range Pease's hypothesis does not appear so convincing. The ability of chemically inert gases to increase the rate in the pressure-dependent region is also evidence against this idea.

(4.7) EFFECT OF INERT GASES: In section 2.12 it was pointed out that inert gases could activate and deactivate the substrate molecules on collision by energy transfer processes involving the high vibrational states of the substrate, and that addition of inert gas to a system in the pressure-dependent region resulted in an increased rate of reaction.

Ramsperger[60] found that the efficiency of ethane was similar to that of azomethane, whilst the efficiency of nitrogen was very much less. However, the experiments were few in number and only over a very limited range of pressures. Sickman and Rice[61] obtained the relative efficiencies with respect to azomethane of a series of gases, of which carbon dioxide was the most extensively studied. The initial pressure of azomethane was varied between .3 and 9 mm. and the ratio of the pressure of carbon dioxide to azomethane between 1 and 50, and throughout this range the relative efficiency of carbon dioxide was equal to .20 $\pm$ .04. If there is a chain reaction in the thermal decomposition of azomethane this would appear to be strong evidence that the chain length is independent of pressure in the range studied and that the pressure dependence of the rate is a true reflection of the unimolecular nature of the reaction.

One might expect that the efficiency of an inert gas would increase with molecular complexity. Although the data of Sickman and Rice (Table 4.3) are not contrary to this, the range of gases studied is too small to confirm the hypothesis. In this respect the high value for deuterium is most surprising. Unfortunately they do not give their results for hydrogen, but note that in this case the efficiency was not constant but depended upon the composition of the mixture, increasing as the percentage of hydrogen was increased. This they attributed to the reaction, with azomethane, of hydrogen atoms which are formed by the reaction of methyl radicals with hydrogen. This observation is interesting in view of the surprisingly high photochemical yields obtained with azomethane-hydrogen mixtures (see 3.9).

They also found that the efficiencies of ethane and propane were not constant but depended on the pressure of the mixture, increasing as the pressure decreased. They suggested that this inconstancy was due to the occurrence of side reactions which resulted from the hydrogen abstraction

$$CH_3 + RH \rightarrow CH_4 + R \quad . \qquad (11)$$

The free radical R was then assumed to be capable of further reaction. In the case of ethane $R \equiv C_2H_5$ and it is difficult to see why ethyl radicals should be very different in their behaviour from methyl radicals. Admittedly, they can disproportionate to form ethylene and ethane but this reaction can hardly explain the inconstancy, and if the high values of the efficiency are associated with the decomposition of ethyl to ethylene and a hydrogen atom, it is hard to understand why the effect becomes more pronounced at low ethane pressures.

(4.8) RECENT WORK: More recently Page, Pritchard and Trotman-Dickenson[56] have studied the decomposition at higher temperatures (390 - 450°C) by the Toluene Carrier technique. The rate constants for the decomposition in the presence of 15 mm. of toluene are given by

$$k = 10^{14} \exp(-46{,}000/RT) \text{ sec.}^{-1} \qquad (12)$$

The authors suggest that the larger activation energies found at higher pressures in static systems are associated with the decomposition of the

chain-carrying radical $CH_2N{=}NCH_3$. In view of their results they point out that, although the dependence of the rate constant on pressure may be real, the shape of the curve is influenced by factors other than energy transfer so that the reaction cannot be used to test the theories of unimolecular reaction.

The rate constants and activation energies obtained at 15 mm. agree very well with the early work of Ramsperger and Rice & Sickman in static systems, so presumably the chain carrying radical is not decomposing at 15 mm. in static systems either. Using Ramsperger's data, at 20 mm. the activation energy is 46.3 kcal., whilst at 100 mm. it is 49.5 kcal. This is hard to understand on the basis of Page, Pritchard and Trotman-Dickenson's suggestion, even if the $CH_2N{=}NCH_3$ radical is destroyed on the walls of the reaction vessel.

They also present some interesting ideas on the values of the bond strengths in azomethane. They assume that the nitrogen and methyl radicals are formed in two stages by the reactions

$$CH_3N{=}NCH_3 \rightarrow CH_3N{=}N + CH_3 \qquad (13)$$

$$CH_3N{=}N \rightarrow CH_3 + N_2 , \qquad (14)$$

of which the first is assumed to be rate determining. From thermochemical arguments it can be shown that $D_1(CH_3NN - CH_3) + D_2(H_3C - NN) \approx 22$ kcal. If D_1 is identified with the experimental activation energy, then D_2 must be a negative bond dissociation energy. In other words reaction (13) is exothermic. This is evidence that the $CH_3N{=}N$ radical will have no appreciable lifetime.

The bond dissociation energy D_1 would be expected to be less than 81 ± 2 kcal., which is the strength of the normal C-N single bond[62,63], since the $CH_3N{=}N$ radical is stabilized by the formation of a three-electron bond[64]. A similar "reorganisation energy" causes D_2 to have its negative value.

(4.9) SURFACE REACTION: Rice and Sickman[11] are the only authors who have noted a surface effect in the reaction. When they packed the original reaction vessel the rates tended to be slow and erratic. The packing was

removed and placed in a new reaction vessel but the results were again irregular. They then tried a new packing in a third reaction vessel; the first runs were high but those following, though still irregular, agreed fairly well with those obtained in the original unpacked reaction vessel. They also noted that there appeared to be some indication that the surface became more inert after it had been used for some time. But they did not attempt to season their reaction vessels and there is no report in the literature of other authors doing so. Ramsperger also packed his reaction flask and reported that the rate constants were not altered.

However, when Heidt and Forbes[65] investigated the reaction in a quartz vessel they found that the rate constants were only half as great as Ramsperger's; unfortunately no further details were given.

TABLE 4.1. PRODUCTS FROM THE THERMAL DECOMPOSITION OF AZOMETHANE.

Authors	Temp. (°C)	Int. Press. (mm.)	Moles per Mole Azomethane Decomposed							Percentage Decomp.
			CH_4	C_2H_6	C_3H_8	unsatd.	H_2	N_2	liquid	
Taylor & Jahn	292	129	.76	.08	-	.02	.01	.73	.35	64
	336	119	.75	.10	-	.04	-	.77	.30	77
Riblett & Rubin	340	125	.38	.27	-	-	-	.68	.40	47
	339	124	.51	.32	-	-	-	.72	.30	71

TABLE 4.2. RATE CONSTANTS FOR THE THERMAL DECOMPOSITION OF AZOMETHANE.

Authors	Temp. (°C)	Int. Press. (mm.)	$k \times 10^4$ sec.$^{-1}$		
			Analysis by Measurement of		
			Pressure	Nitrogen	Azomethane
Taylor & Jahn	292	129	1.05	1.00	1.59
	310	114	6.5	5.8	8.56
	325	141	20.0	16.2	25.6
	336	119	35.3	30.1	48.8
Riblett & Rubin	340	125	67	-	101

TABLE 4.3. RELATIVE EFFICIENCIES OF GASES IN TRANSFERRING ENERGY IN THE THERMAL DECOMPOSITION OF AZOMETHANE.

Substance	$CH_3N{=}NCH_3$	N_2	CO	CH_4	H_2O	CO_2	D_2	He
α_p	1.00	.19	.12	.23	.41	.20	.66	.12
α_c	1.00	.21	.13	.20	.46	.25	.37	.07

α_p = relative efficiency on pressure-to-pressure basis.
α_c = relative efficiency on collision-to-collision basis.

CHAPTER 5.

THE THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF ACETONE.

(5.1) INTRODUCTION: It has become apparent from this research that the reactions of azomethane bear a close similarity to those of acetone. The salient characteristics in the decomposition of the latter are summarised in this section, but the discussion is of the briefest since the subject has been extensively reviewed by Steacie[66] and less fully by Laidler[67].

(5.2) THE THERMAL REACTION: Para-ortho hydrogen studies and the sensitised decomposition of ethers by acetone have shown that radicals are formed in the decomposition to some extent. Methyl radicals can start chains at temperatures above 520°C, but inhibition studies of the sensitised and non-sensitised decomposition have shown that these chains are short. The effect of nitric oxide is complex; it both inhibits the reaction, by stopping chains, and catalyses the reaction. At lower temperatures chains are not propagated by the introduction of radicals.

Despite its complexity, the reaction obeys first-order kinetics. Probably the most reliable Arrhenius parameters are those determined by Clark and Pritchard[68] using the Toluene Carrier technique, who found

$$k = 10^{14.1} \exp(-70{,}900/RT) \text{ sec.}^{-1}$$

Since the total pressure was only 13 mm., it is not certain that these parameters are true high-pressure values.

The overall reaction can be represented by the plausible scheme

$$CH_3COCH_3 \rightarrow 2CH_3 + CO \quad (1)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (2)$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 \quad (3)$$

$$2CH_2COCH_3 \rightarrow CH_3COCH_2CH_2COCH_3 \quad (4)$$

$$CH_2COCH_3 \rightarrow CH_2CO + CH_3 \quad (5)$$

(5.3) THE PHOTOCHEMICAL REACTION: The photolytic decomposition of azomethane and acetone also appear to bear a striking similarity. Thus inhibition experiments have shown that there is no molecular mechanism. At the lower temperatures used in the photolysis no chains occur since the chain-carrying reaction

$$CH_2COCH_3 \rightarrow CH_2CO + CH_3 \qquad (5)$$

has an activation energy of 48 kcal.[69] and the CH_2COCH_3 radicals are primarily removed by radical combinations at the walls. At low temperatures carbon monoxide and ethane are the main permanent gases produced, but at higher temperatures methane becomes the major hydrocarbon.

CHAPTER 6.

ENERGY TRANSFER PROCESSES IN THERMAL DECOMPOSITION REACTIONS.

(6.1) INTRODUCTION: In this chapter we shall summarise some of the work on energy transfer processes in quasi-unimolecular systems. This subject has already been reviewed in some detail by Trotman-Dickenson[103] so we shall merely select a few of what appear to be the more important and reliable results. However, we shall mention the work on the thermal decomposition of nitryl chloride in some detail because this has been published since Trotman-Dickenson's review.

(6.2) THE THERMAL DECOMPOSITION OF NITRYL CHLORIDE: Cordes and Johnston[104] studied the thermal decomposition of nitryl chloride at low pressures and in the temperature range 180° to 250°C, and confirmed the mechanism of Schumacher and Sprenger[105], who had stated that the main reactions were

$$NO_2Cl \rightarrow NO_2 + Cl \qquad (1)$$

and

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2 \,. \qquad (2)$$

From this mechanism and the assumption of a steady-state concentration of chlorine atoms it is easy to show that the experimental first-order rate constant is $2k_1$. Cordes and Johnston's results show quite clearly that below 5mm. the reaction is first order in reactant throughout a single run and that the first-order rate constants are themselves first order in initial concentration. It would therefore appear that this study offers a clear-cut example of a quasi-unimolecular reaction showing second-order kinetics, and as such it is unique.

According to the Lindemann theory, the rate in the second-order region is determined by the rate of activation of nitryl chloride by collision. By the Principle of Microscopic Reversibility this rate is also proportional to the rate of deactivation by collision. In the second-order region

equation (2.43) reduces to

$$k_b = k_1 p_a + k_1' p_i \quad . \qquad (3)$$

Thus, to determine the effect of added gases on the rate of energy transfer to and from the reactant, Volpe and Johnston[23] plotted the experimental first-order rate constant against the concentration of added gas. The slope of this line gives the second-order rate constant for activation by the foreign gas, and the intercept divided by the concentration of reactant gives the corresponding second-order rate constant for the reactant. It will be seen from (2.12) that this method of determining the relative efficiencies of gases is different from the method used in this research although the principle behind the methods is the same.

Since activation and deactivation take place only on collision it is instructive to normalise these relative efficiencies so as to obtain relative efficiencies per collision (ρ). This is done by multiplying k_1'/k_1 by $(\mu_{AX}/\mu_{AA})^{\frac{1}{2}}(\sigma_{AA}/\sigma_{AX})^2$. μ and σ are reduced masses and kinetic collision diameters, and A and X refer to the reactant and the added gas.

In Column 2 of Table 6.1 we have given the values of the relative efficiencies per collision of the various added gases used by Volpe and Johnston. From their results these authors have drawn the following conclusions:- (i) For a non-polar gas, the factors which determine the boiling point are also those which determine the relative efficiency of the gas in energy transfer. Thus they found an almost linear increase in ρ with boiling point. This may be compared with the similar variation in the third-order rate constant for the recombination of iodine atoms in the presence of a third body, as found by Russel and Simons[86]. (ii) For constant molecular weight and number of atoms, the gases with permanent dipole moments have larger efficiencies than those which have no moments. (Compare O_2/HCl, SiF_4/CCl_2F_2, CO_2/NO_2). (iii) For spherical molecules of roughly the same mass there is no correlation between relative efficiency in energy transfer and molecular complexity, that is, the number of oscillators in the molecule. (Compare Xe, SiF_4, SF_6.)

(6.3) THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE IN THE PRESENCE OF NITRIC OXIDE: These results appear to be in agreement with the earlier work by Wilson and Johnston[21], who studied the effect of added gases on the thermal decomposition of nitrogen pentoxide in the presence of nitric oxide (see Table 6.1).

(6.4) THE THERMAL DECOMPOSITION OF CYCLOPROPANE AND CYCLOBUTANE: Pritchard, Sowden and Trotman-Dickenson[9,106] studied the thermal isomerisation of cyclopropane and the thermal decomposition of cyclobutane. They, too, added gases to the system and, employing the same method as was used in this research (see 2.12), they obtained the relative efficiencies of a series of gases. Those efficiencies, which are on a collision-to-collision basis, are given in the last two columns of Table 6.1. Contrary to the conclusions of Volpe and Johnston, their results indicate that the efficiency in energy transfer increases with increasing molecular complexity but that a maximum efficiency is soon reached beyond which no further increase occurs for still more complex molecules. This, the authors suggest, indicates that all the more complex molecules have unit efficiencies. Therefore the assumption made in the derivation of the theories of unimolecular reactions, that deactivation occurs on every collision, is probably correct.

(6.5) THEORETICAL CONSIDERATIONS: The suggestions of Pritchard, Sowden and Trotman-Dickenson seem to be reasonable because it is the high vibrational energy levels which are involved and these are close together, that is, the vibrational quanta are small and energy transfer between translational energy and vibrational energy should occur readily since the non-adiabatic condition required for efficient energy transfer is automatically fulfilled[12]. An adiabatic collision corresponds to a "soft, slow" collision, when the readjustments of translational energy on collision do not occur quickly enough to affect the fast internal molecular movements. A non-adiabatic collision corresponds to a "hard, quick" collision, that is, one acting against the molecule with a large force for a short time. In this case the time taken for the translational energy change is of the same order as the period of a molecular vibration. A crude mechanical analogy can be devised

for this situation: A "soft" collision would be expected to merely accelerate the molecule as a whole without any considerable "compression of the springs" (bond-oscillators). On the other hand, a "hard" collision would be expected to cause considerable compression, that is, to vibrationally excite or de-excite the "springs", depending on the phases of the latter. Furthermore, for the high vibrational levels not only are the energy levels closely spaced ("scrambled" might be a not altogether inappropriate term), but the potential energy function is strongly anharmonic (see Fig. 2.2) so that the harmonic oscillator selection rules governing vibration-vibration transitions are relaxed.

As regards the effect of structure, one would expect that complex molecules could effect energy transfers involving larger amounts of energy than could simple molecules and that the routes for these transfers would be more numerous.

However, these conclusions are not borne out by Johnston and Volpe's work, and these authors consider it very doubtful whether deactivation occurs on every collision between activated and unactivated reactant molecules. Until this point is clarified by further energy transfer studies there is no complete quantitative theory of unimolecular reactions.

Notwithstanding these differences, it is impressive that, although the studies were carried out using different reactions, different reaction temperatures and in different regions of the rate-pressure curves, the efficiencies of the different gases which are common to all the studies are similar. This suggests that the general principles behind the methods are correct but that some or all of the reactions have unsuspected minor complexities which mask the true trends in the relative efficiencies or that the added gases do not comprise a sufficiently wide range to show up the main common trends.

TABLE 6.1. RELATIVE EFFICIENCIES PER COLLISION OF VARIOUS GASES IN ENERGY TRANSFER.

Unimolecular reaction of:	Nitryl chloride	Nitrogen pentoxide	Cyclo-propane	Cyclo-butane
Temperature (°C)	203	50.5	492	448
Total-pressure range (mm.)	3 - 9	.1 - 3	(9 - 30)	2 - 11
Reacting molecule	1.00	1.00	1.00	1.00
He	.15	.07	.05	.07
Ne	.22	.09	-	.12
A	.30	.15	.07	.21
Kr	.36	.21	-	-
Xe	.46	.19	-	-
H_2	.15	-	.12	.10
N_2	.34	.23	.07	.21
O_2	.34	-	-	-
Cl_2	.50	-	-	-
CO	-	-	.08	-
NO	-	.30	-	-
HCl	.63	-	-	-
CO_2	.49	.39	-	-
H_2O	-	-	.74	.44
N_2O	.48	-	-	-
NO_2	1.38	-	-	-
CH_4	-	-	.24	.38
S_1F_4	.51	-	-	-
CCl_4	.49	.67	-	-
CCl_2F_2	.71	-	-	-
SF_6	-	.44	-	-
$C_6H_5CF_3$	-	-	.75	.85
$C_6H_5CH_3$	-	-	1.10	1.12
$C_6H_3(CH_3)_3$	-	-	.89	1.23

CHAPTER 7.

PREPARATION AND PURIFICATION OF MATERIALS.

(7.1) SUMMARY: 1,2-dimethylhydrazine dihydrochloride was prepared by the method of Hatt and the free hydrazine was obtained from it by reaction with aqueous sodium hydroxide. The solution so obtained was added very slowly and with constant stirring to a suspension of mercuric oxide. After stirring for a further two hours the azomethane, formed in 60-70% yield, was distilled off by heating the reaction vessel on a water bath and collected in a spiral trap cooled to -78°C. The gas was dried, purified by trap to trap distillation and the purity checked by gas chromatography before being stored at the temperature of liquid nitrogen.

The sources of the various added gases are given in Table 7.2. They, too, were dried, distilled and had their purities checked by gas chromatography before being stored in the apparatus.

Both the azomethane and added gases were degassed before each run.

(7.2) PREPARATION OF AZOMETHANE: In the early kinetic studies azomethane was prepared by the oxidation of dimethylhydrazine in aqueous solution with potassium chromate [7,70]. However, Jahn[71] states that this method gives poor yields and that the azomethane is impure. He prepared it by the method of Diels and Koll[72], in which the dihydrochloride is oxidised with cupric chloride. Although the yields are better, the preparation is still tedious and low yields may still be obtained if fresh samples of dihydrochloride are not used. It was decided, therefore, to modify the procedure and to oxidise dimethylhydrazine with yellow mercuric oxide, as recommended by Renaud and Leitch[73].

(i) Preparation of 1,2-dimethylhydrazine dihydrochloride:

(a) $2PhCOCl + N_2H_4.H_2SO_4 \xrightarrow{(NaOH)} PhCONH.NHCOPh.$

(b) $Me_2SO_4 + PhCONH.NHCOPh \xrightarrow{(NaOH)} PhCO(Me)N.N(Me)COPh.$

(c) $PhCO(Me)N.N(Me)COPh \xrightarrow{(HCl)} MeNH.NHMe.2HCl.$

Me = CH_3. Ph = C_6H_5.

1,2-dimethylhydrazine dihydrochloride was prepared by the method given by Hatt in "Organic Syntheses"[74]. Several modifications to the recommended procedure were adopted, but as these are only of specialised interest for preparative purposes, they have been given in an Appendix at the end of the thesis.

(a) Dibenzoylhydrazine was prepared by reacting hydrazine sulphate with benzoyl chloride under alkaline conditions. (b) On treating this with dimethyl sulphate, again under alkaline conditions, dibenzoyldimethylhydrazine was obtained. (c) The two benzoyl groups were removed by acid hydrolysis to yield dimethylhydrazine dihydrochloride.

(ii) Preparation of 1,2-dimethylhydrazine:

$$MeNH.NHMe.2HCl \xrightarrow{(OH^-)} MeNH.NHMe.$$

Originally dimethylhydrazine dihydrochloride was dissolved in chloroform (or ether) and the theoretical amount of barium hydroxide required to liberate the free base was added. After mechanical agitation and filtration of the sludge, the chloroform (or ether) was distilled off leaving dimethylhydrazine, which was then purified by distillation. However, later work showed that this tedious stage could be omitted by simply preparing the dimethylhydrazine *in situ*.

(iii) Preparation of Azomethane:

$$MeNH.NHMe.2HCl \xrightarrow{(OH^-)} MeNH.NHMe \xrightarrow{HgO} MeN{=}NMe$$

13.3g. of dimethylhydrazine dihydrochloride were added to 10 g. of sodium hydroxide solution and shaken for 15 minutes. This hydrazine solution was then added very slowly, by means of a dropping funnel, to a suspension of 74 g. of yellow mercuric oxide contained in a three-necked Quickfit flask. Besides the funnel, the flask was provided with a mercury-seal stirrer and an outlet to a spiral trap which was cooled to -78°C. (Care must be exercised at this stage, as rapid addition may result in EXPLOSION, and the addition should be accompanied by constant stirring.)

After addition of the hydrazine, the mixture was stirred for a further two hours. The azomethane, obtained in 60 - 70% yield, distilled over when the flask was heated on a water bath. It is advisable to have a calcium

chloride drying tube between the collecting trap and the reaction flask.

The azomethane was then thoroughly dried by passing it into the storage system of the kinetic apparatus via a large drying tube. Three different drying agents were employed - (i) calcium chloride, (ii) sodium sulphate/potassium hydroxide, (iii) phosphorus pentoxide/sodium sulphate/potassium hydroxide - and all appeared to be equally effective.

(7.3) PURIFICATION & GAS CHROMATOGRAPHIC ANALYSES OF AZOMETHANE: The azomethane samples were purified by several trap to trap distillations before storage and by thorough degassing before each run. In all, four samples of azomethane were prepared, and in every case the rate constants obtained with the fresh sample agreed with those from the previous sample.

The second sample was analysed by Dr. J. Knox and Mr. J. Falconer using gas chromatography. Employing an 80% celite/20% dioctyl phthalate column Dr. Knox obtained one sharp peak which showed the general purity of the sample and Mr. Falconer was unable to detect any ethane or methane in a large sample which he analysed on a silica gel column.

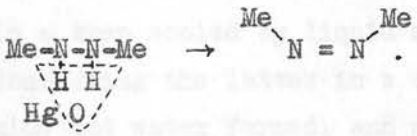
The third and fourth samples were analysed by means of the chromatography unit which was used by the author to study Cis-Trans Isomerisations. The experimental conditions are summarised in Table 7.1.

TABLE 7.1 EXPERIMENTAL CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSES OF AZOMETHANE.

Column	Column Length	Column Packing	Column Temperature	Carrier Gas	Detector Gauge
A	6ft.	activated alumina	100°C	H_2	Thermal Conductivity
B	12ft.	firebrick (80%) dioctyl phthalate (20%)	20°C	H_2	" "
C	6ft.	firebrick (80%) nitrobenzene (20%)	20°C	H_2	" "

Columns A and C showed the absence of C_1- C_5 hydrocarbons, whilst Column B showed the general purity of the sample. Less than .1 per cent of impurity could have been detected.

The work of Dr. Knox, who used celite columns, and the later work, in which firebrick columns were used, indicated that the synthesis of azomethane was stereospecific since the columns were capable of distinguishing between cis- and trans-butene but in no case were isomers of azomethane detected. It seems likely, therefore, that the mechanism for the oxidation of dimethylhydrazine is



(7.4) PREPARATION & PURIFICATION OF ADDED GASES: The pertinent data with respect to the sources of the various added gases and their gas chromatographic analyses are given in Table 7.2. The gas chromatographic analyses of carbon dioxide, cyclopropane, propylene and trans-2-butene were carried out on columns A and C (see Table 7.1) whilst the pentanes were examined on column B. In each case less than .1 per cent impurity could be detected. Mr. J. Falconer analysed the propane.

All the gases were dried over phosphorous pentoxide and potassium hydroxide, purified by several trap to trap distillations before storage, and degassed before each run.

TABLE 7.2 SOURCES AND GAS CHROMATOGRAPHIC ANALYSES OF ADDED GASES.

Added gas	Source	Gas Chromatographic Analysis
Propylene	Dehydration of isopropyl alchol	no impurity detectable
Cyclopropane	B.O.C. Medical Division	trace propane < .1%
Propane	B.P.C. sample	.2% isobutene, no olefines
Trans-2-butene	D.S.I.R. Teddington	no impurity detectable
Cyclopentane	D.S.I.R. Teddington	no impurity detectable
Normal Pentane	M & B n-pentane distilled	.05% cyclopentane
Carbon dioxide	I.C.I. Drikold	no impurity detectable
Toluene	Sample from purified material used by Mr. S.J.W. Price for Toluene Carrier work.	--

CHAPTER 8.

THE APPARATUS AND EXPERIMENTAL TECHNIQUE.

(8.1) SUMMARY: The thermal decomposition of azomethane alone and in the presence of added gases was studied in a static reaction system. The amounts of reactant and added gas were determined from their pressure either in the reaction vessel or in a gas burette (B). After reaction the non-condensable methane and nitrogen formed were measured in a gas burette (V), the condensable gases having been retained in a trap cooled by liquid nitrogen. The nitrogen was freed from methane, by combusting the latter in a copper oxide furnace and freezing out the carbon dioxide and water formed, and measured in the burette (V). First-order rate constants were calculated on the basis of nitrogen production.

(8.2) APPARATUS: The apparatus, which was constructed from Pyrex glass, was an arrangement whereby any desired amount of azomethane and added gas could be fed into a static reaction system and the nitrogen formed in the reaction analysed.

RUNS 7 - 84.

Pumping System: The pumping system consisted of a two-stage mercury diffusion pump backed by a rotary oil pump. The pressure, which was read on a McLeod gauge, could be reduced to 10^{-5} mm. after 40 - 60 minutes pumping.

Storage System: The azomethane and added gas were stored in two two-litre Pyrex bulbs which were fitted with traps and manometers so that the gases could be degassed before use. There were also two more traps which were used in the purification of the materials by trap to trap distillations.

Reaction and Analysis System: The reaction and analysis system is shown in Figure 8.1. The gas burette B was provided with three calibrated volumes and a calibrated capillary. R_1, the larger of the two reaction vessels used, was 20 cm. long and had a volume of 608.5 cc. The three-stage quartz mercury diffusion pump P (made by Thermal Syndicate) was joined to the rest of the apparatus by Picein-sealed ground-glass joints which had been individually ground to give a good fit; it was characterised by its ability to work

against a moderately high backing pressure. T_1 was a wide-bore trap and T_2 a pump-down trap. The Toepler pump T was fitted with a non-return mercury float valve F and so could also serve as a gas burette V. The small quartz tube C of approximately 20 cc. capacity was packed with copper oxide catalyst which was used in the oxidation of methane. This was also joined to the rest of the apparatus by Picein-sealed ground-glass joints. The apparatus was provided with a low-vacuum line and connections to this are symbolised L.

Furnaces and Temperature Control: The small furnace F_2 had a heating element of Nichrome wire which was wound on a quartz former. It required 200 watts and could be raised to 650°C in 10 minutes.

Furnace F_1, housing the reaction vessel, was of conventional design. The main heating element was wound on a heavy iron former and required 600 watts at 300°C. This was tapped at two points so that the temperature profile could be altered by shunt resistances.

The reaction vessel was surrounded by a close fitting Pyrex Dewar flask, the annular volume of which was 170 cc. The latter was connected by capillary tubing to a mercury contact manometer. This arrangement formed a gas thermometer and the temperature was maintained constant by means of a subsidiary winding (100 watts) which was switched on and off by the mercury manometer acting as a contact device for a Sunvic H.V.S. relay. The subsidiary element was wound on a thin copper former which fitted the Dewar flask closely.

RUNS 85 - 99.

Modifications: For the work at the highest pressures (670-975 mm.) the apparatus was modified, as shown in Figure 8.2, by removal of B and the insertion of a small trap T_3 and a 250 cc. bulb S which was provided with a manometer M_2. The small reaction vessel R_2 was of 50.2 cc. capacity.

RUNS 100 - 169.

In the preliminary work with added gases, B was replaced and a small mixing vessel M inserted between it and the reaction vessel R_1.

RUNS 170 et seq.

In the later work with added gases, the mixing vessel was removed so that the burette led directly to the reaction vessel. Pressures were read on a mercury or butyl phthalate manometer M_3 and there was a direct connection via t_3 to the added gas storage system.

(8.3) PROCEDURE:

THE THERMAL DECOMPOSITION OF AZOMETHANE:

Runs 7 - 67: Initial Pressures 0.2 - 40 mm.: The whole system was pumped down to 10^{-5} mm. and the azomethane degassed. By allowing the azomethane storage trap to come to room temperature the required amount of reactant was introduced into the calibrated bulbs B and its volume, pressure and temperature noted.

The azomethane was then transferred into the reaction vessel R_1 by opening the three-way tap t_1 and rapidly raising the mercury. The initial pressure of the gas in the reaction vessel was calculated from the Ideal Gas Laws and the temperature of the reaction recorded at several instances throughout the run.

The products of the reaction were admitted into a wide-bore trap T_1, which was cooled by liquid nitrogen, and the non-condensable methane and nitrogen pumped away, by means of the mercury pump P and Toepler pump T working in series, into the calibrated volumes V where the volume, pressure and temperature were recorded. The second trap T_2 was used to catch any of the condensable gases which might have passed through T_1 as a fine mist and any dissolved organic material pumped out of tap grease by the mercury diffusion pump. When liquid oxygen was used as a refrigerant T_2 was used as a pump-down trap to condense any ethane or ethylene which passed through T_1.

The nitrogen was freed from methane by passing the gas into the copper oxide furnace C, F_2. It was then measured by passing it back into the calibrated volumes V, the carbon dioxide and water formed in the combustion being removed by T_2.

The experimental rate constants k were derived from the expression

$$k.t = 2.303 \log \frac{p_1 v_1 T_2}{p_1 v_1 T_2 - p_2 v_2 T_1} \qquad (1)$$

where p_1, v_1, T_1 are the pressure, volume and temperature of azomethane in the burette B

and p_2, v_2, T_2 are the pressure, volume and temperature of nitrogen in the calibrated volumes V.

In most cases $T_1 \approx T_2$ so that (1) reduces to the simpler expression -

$$k.t = 2.303 \log \frac{p_1 v_1}{p_1 v_1 - p_2 v_2} \quad . \qquad (2)$$

The necessary corrections to this equation for dead-space volume and flowage of reactant into the dead space are considered in (8.6).

Runs 68 - 71; 85 - 99; Initial Pressures 170 mm.; 670 - 975 mm.: In the medium-pressure work the azomethane was fed directly into the reaction vessel R_1 and the pressure measured on the mercury manometer M_1. In the work at the highest pressure the required amount of azomethane was vapourised into the small storage bulb S and this azomethane then transferred into the small trap T_3 which was cooled by liquid nitrogen. The tap t_2 was then closed and the gas rapidly introduced into the reaction vessel by warming the trap T_3 with boiling water.

The rate constants k were calculated from the expression

$$k.t = 2.303 \log \frac{p_a v_a T_2}{p_a v_a T_2 - p_2 v_2 T} \qquad (3)$$

where p_a, v_a, T are the pressure, volume and temperature of the azomethane in the reaction vessel, and the other symbols have their previous significance.

THE EFFECT OF ADDED GASES ON THE REACTION:

Runs 100 - 169: In the preliminary work with added gases the azomethane was measured out in the burette B and transferred into the mixing vessel M which was cooled by liquid nitrogen. The added gas, which had been degassed, was then likewise measured and condensed into the mixing vessel. There the gases were "flash boiled", by warming the vessel with boiling water, and allowed to mix for 15 - 20 minutes.

The rate constants were calculated from equation (2) after allowance had been made for the volume of the mixing vessel.

Runs 170 et seq: In the later work a simpler and more satisfactory procedure was adopted. The azomethane was measured in the burette B and fed directly into the furnace. The added gas was then immediately added by opening t_3.

The experimental rate constants were calculated from (2), allowance being

made, especially for runs 219 et seq. when the small reaction vessel was used, for any dead-space.

By subtracting the calculated pressure of azomethane from the total initial pressure, the pressure of added gas was obtained. Depending on the pressure range either a mercury or a butyl phthalate manometer $\underline{M}_3$ was used to measure the total pressure in the reaction vessel. The butyl phthalate manometer was 5.24 times as sensitive as a mercury manometer and so was ideal for use up to pressures of 50 mm. Hg. For higher pressures (Runs 197 et seq.) the simple mercury manometer was sufficiently accurate.

(8.4) DATA & CALCULATIONS FOR SAMPLE RUN:

Run 196: Added gas propylene.

Reactants.

$CH_3N{=}NCH_3$: Burette Vol. = 5.32 cc. Press. = 30.10 cm.Hg. Temp. = 19.5°C

Press. in reaction vessel (p_a) = $\dfrac{5.32 \times .98 \times 30.10 \times 549.9 \times 10}{608.5 \times 292.5}$ †

= 4.84 mm. Hg.

C_3H_6: Butyl phthalate manometer reading = 267.7 mm.
Sensitivity of manometer = 5.24
Total pressure in reaction vessel = 51.10 mm. Hg.
Propylene pressure in reaction vessel = 51.10 - 4.84 = 46.26 mm. Hg.

Time: Reaction time = 45.5 min.

Temperature: * Thermocouple e.m.f. = 10.38 ± .01 mV, 10.38 ± .01 mV
e.m.f. corrtd. for temp. gradient = 10.39 mV
Cold junction = 21.85°C 21.91°C
Hot junction (calcd.) = 549.9°K

Products:

$CH_4 + N_2$: Burette Vol. = 1.016 cc. Press. = 12.3 cm. Hg. Temp. = 19.8°C

N_2: Burette Vol. = .339 cc. Press. = 26.0 cm. Hg.

Rate Constant: $k = 2.303 \log \dfrac{.98 \times 5.32 \times 30.10}{.98 \times 5.32 \times 30.10 - .339 \times 26.0} / 45.5 \text{ min.}^{-1}$

$= 12.70 \times 10^{-4} \text{ min.}^{-1}$

$= 2.12 \times 10^{-5} \text{ sec.}^{-1}$

k (corrtd. to 549.4°K) = $2.03 \times 10^{-5} \text{ sec.}^{-1}$

† .98 is the dead-space correction.
* See section 8.6.

(8.5) THE COPPER OXIDE FURNACE: The copper oxide furnace, which was used to oxidise the methane to carbon dioxide and water, gave considerable trouble in the early part of the work. Since this method does not appear to have been used for the removal of methane in the presence of such small quantities of nitrogen, which had subsequently to be accurately determined, some description is warranted.

Originally the small quartz tube C was packed with short lengths of cupric oxide wire and a flow system employed whereby the gases were continuously circulated over the hot oxide. But even at 700°C the oxidation of methane was not effective and at this temperature considerable quantities of oxygen were evolved, by the dissociation of cupric oxide to cuprous oxide and oxygen[75,76] which interfered with the nitrogen determination. Because of these difficulties it was decided to employ a static system and to use Arneil's catalyst[77,78,79,80]. This consists of cupric oxide (99%) and ferric oxide (1%) supported on finely ground kaolin and allows the use of a lower oxidation temperature. It was hoped that any oxygen formed would reach an equilibrium value above the catalyst and on slow cooling would recombine with the cuprous oxide.

At temperatures above 610°C the methane was totally oxidised in 10 - 12 minutes. However, the catalyst appeared to absorb impurities very readily. Thus if air was admitted for a period of time or if a fresh batch of catalyst was used, it had to be pumped for several hours at 600°C before it was suitable for use. This is in agreement with the results of other workers who have found that cupric oxide readily absorbed gases and water vapour.[81] As a precautionary measure the catalyst was heated and pumped free of any impurities before each analysis and after every combustion it was allowed to cool slowly in an attempt to reproduce equilibrium conditions.

Despite these precautions, a small amount of non-condensable gas, which varied from 0 to 0.7×10^{-3} cc. at N.T.P., could be pumped out of the furnace after the latter had been heated to temperatures above 610°C. This was assumed to be oxygen which had not recombined and proved to be one of the most troublesome features of the analysis. The amount of nitrogen formed varied from 4.5 cc. to 5×10^{-3} cc. at N.T.P. and since it was hoped to do accurate rate determinations the "oxygen corrections" could be significant.

The actual experimental runs were interspersed with numerous blank runs to estimate the "oxygen correction" and great care had to be taken at the low pressures to keep the correction to a minimum. This was both time consuming and laborious.

At the beginning of the work with added gases it was decided to try a new form of catalyst mixture which was made by intimately grinding together 1.8% ferric oxide and 98.2% cupric oxide. This catalyst was found to be entirely satisfactory. 97 - 100% of the methane was oxidised in the static system at temperatures above 610°C in 10 - 12 minutes. After combustion, the furnace was allowed to cool very slowly to allow any oxygen time to recombine with cuprous oxide. It was found that there was no significant "oxygen correction" so that this appears to have been associated with the kaolin.

(8.6) POSSIBLE SOURCES OF ERROR IN ESTIMATION OF RATE CONSTANTS:

(a) Temperature: The temperature was measured by means of a thermocouple in conjunction with a Doran D.C. potentiometer. The thermocouple was constructed from commercial thermocouple wire which was provided with a calibration scale. Nevertheless it was standardised at the boiling points of mercury and water. In both cases the temperature calculated from the observed e.m.f. was within the tolerance quoted ($\pm$ 3°C up to 400°C).

The cold junction was contained within a Dewar flask filled with water and the hot junction in the axial well of the reaction vessel. The temperature (T°C) of the latter was calculated from the formula -

$$T = 24.51\,\phi + (20.30 \pm \delta)$$

where ϕ is the observed e.m.f. in millivolts and δ is the variation from 20°C of the cold junction.

Despite the most careful packing of the ends of the furnace the temperature varied by 4½°C along the reaction vessel. However, the temperature profile was determined and the necessary correction made to obtain the "average" temperature of the reaction vessel. Throughout all the sets of experiments the temperature profile varied only very slightly and the corrections were all within $\pm$ .25°C of each other, so that even if the temperature profile correction was in error the relative temperatures would not be affected.

The period of the Sunvic H.V.S. relay was 5-6 minutes and in this time the temperature had an amplitude of 0.3 - 0.5°C. Moreover, the gas thermometer was sensitive to variations in room temperature and it was calculated that an increase of 2°C in the latter decreased the thermostating temperature of the furnace by .4°C. To minimise these errors the temperature of the reaction was determined at frequent intervals throughout the run.

The following summarise the possible errors involved in the measurement of temperature:-

Constant Errors.		Variable Errors.	
Thermocouple tolerance	± 3°C.	Thermocouple reading	± .05°C.
R.V. temp. gradient	± .5°C.(estimate)	Cold junction "	± .05°C.
		Thermostat fluctuation	± .1°C. (estimate)
			± .2°C.

Thus the maximum possible error in the relative temperatures of a set of runs is ± .2°C, which would give a 4% reproducibility in the rate constant. However, the absolute value of the temperature may be some 3°C in error.

(b) Dead Space and Flow: Dead space and flow of reactants into the dead space, unless allowed for, can cause errors which, though constant with a group, are variable throughout the whole range of experimental conditions . Since the volume of the connecting tubing around the reaction vessel was kept at a minimum the dead-space corrections were generally small. When the large reaction vessel was used the corrections to the rate constants were approximately 3%, but for the final runs (219 et seq.), when the small reaction vessel was used, the correction was about 20%.

(c) Estimation of Azomethane and Nitrogen: The pressures and volumes of the azomethane and nitrogen were generally measured in a burette and their concentration calculated from the Ideal Gas Laws. Any systematic error so incurred must be very small. The van der Waals constants for azomethane are not known but they are probably similar to those for butane. If this is so then it can be shown that the use of the Ideal Gas Law results in an error which is less than ½%. More serious are the errors involved in reading the burettes and possible calibration errors in the determination

of the volumes of the capillaries and bulbs. At the lowest pressures used, only 0.005 cc. of nitrogen at N.T.P. was formedand this gave a pressure of 2.7 cm.Hg. when contained within the calibrated volume (.153 cc.) of the capillary of V. A total reading error here of 7% would not be unreasonable and to this must be added the constant error, if any, of the calibration.

General Conclusions: It will be noted that several of the possible sources of error discussed here are constant within a group of experiments carried out under similar conditions. Thus the reproducibility within a given group was considerably better than the above remarks suggest. For the first group of runs carried out (7 - 23), when the experimental technique had not been perfected, the fractional standard deviation was 5%. In the subsequent groups the deviations were not greater than this; for example the set of standardisation runs (191 - 192, 215 - 218) had a fractional standard deviation of 2½%.

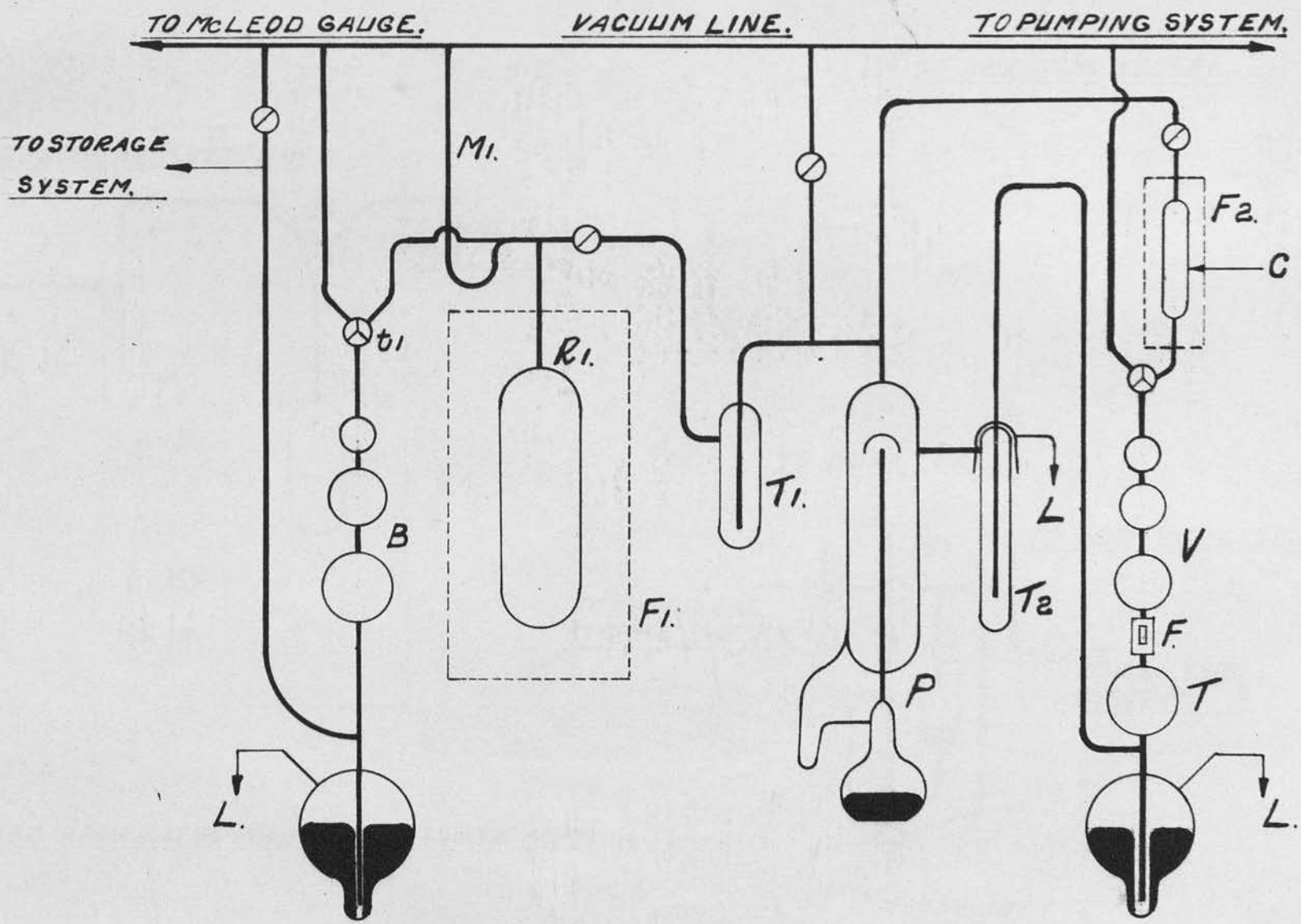
(8.7) LIMITS TO THE EXPERIMENTAL TEMPERATURE AND PRESSURE RANGES:

Temperature range: 502 - 593°K.
Pressure range: 0.2 - 975 mm.

At 502°K it required 190 minutes for 6% reaction in the high pressure region and it was not convenient to follow slower reactions especially as any small leak of air into the furnace would cause an error in the nitrogen analysis. On the other hand, at 593°K it required only 5 minutes for 8% reaction, at pressures of 1 mm., and an error of 15 seconds in the estimation of the reaction time would result in a 5% error to the rate constant. Thus if runs had been carried out at higher temperatures the finite time required to transfer the reactant from the burette to the reaction vessel could have caused a serious error.

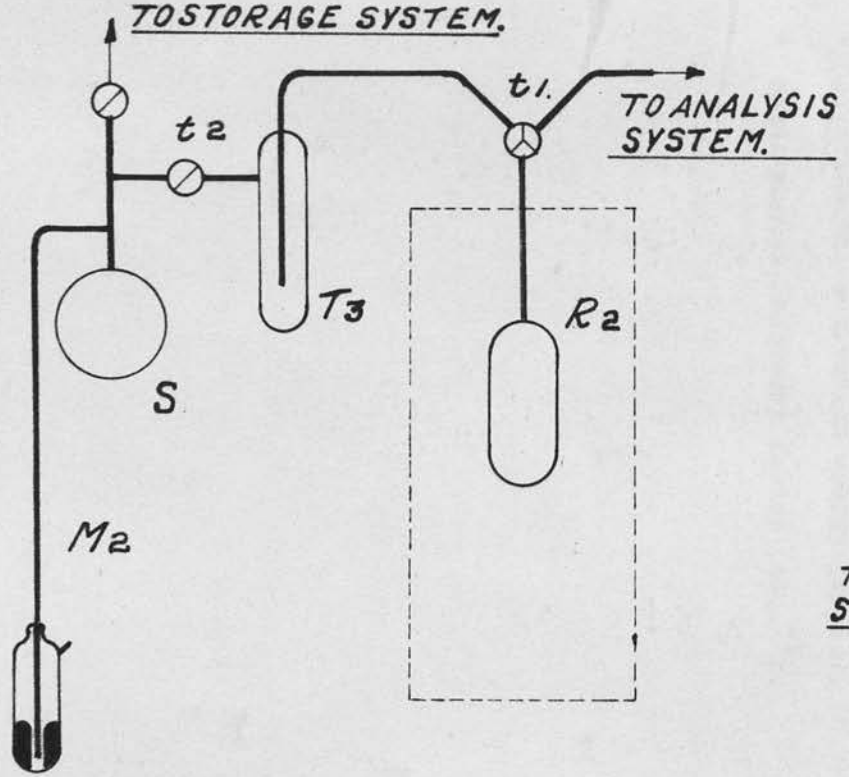
Pressures of about 950 mm. were the highest which could be used because of the danger of "streaking" in the three-way tap t_1; the low pressure limit of 0.2 mm. was determined by the sensitivity of the analysis (see 8.6(c)).

FIG. 8·1

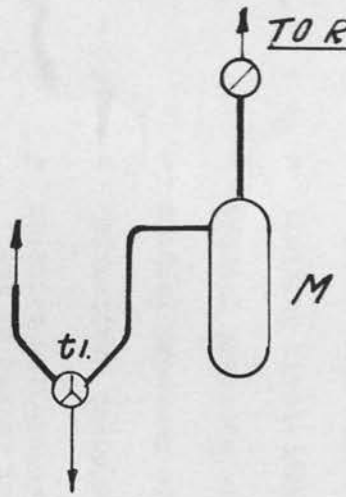


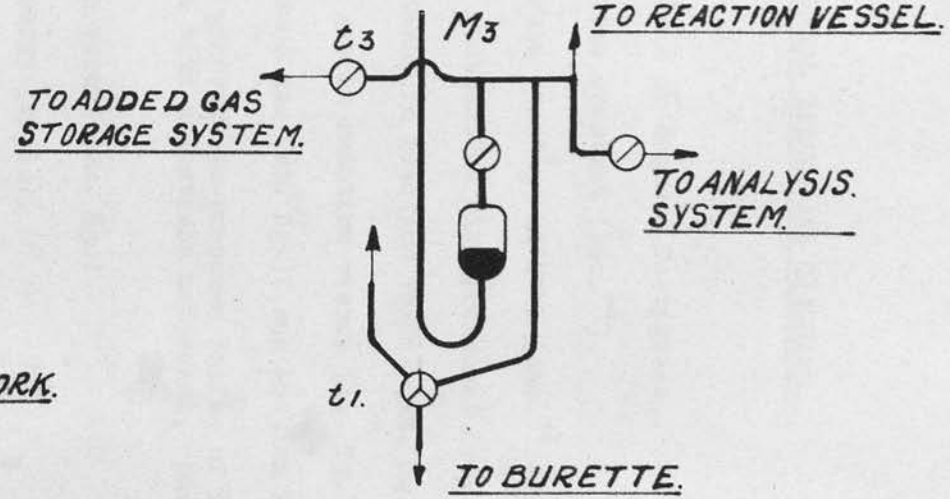
THE REACTION AND ANALYSIS APPARATUS.

FIG. 8·2



MODIFIED APPARATUS FOR HIGH PRESSURE WORK.





MODIFIED APPARATUS FOR ADDED GAS WORK.

SYMBOLS USED IN EXPERIMENTAL TABLES AND DIAGRAMS.

T = temperature in degrees Kelvin or degrees Centigrade.

k = experimental first-order rate constant ($sec.^{-1}$).

k^T = experimental first-order rate constant at T °K ($sec.^{-1}$).

k_∞ = limiting first-order rate constant at high pressures ($sec.^{-1}$).

p_a = initial pressure of azomethane in reaction vessel (mm. Hg.).

P_i = initial pressure of added gas in reaction vessel (mm. Hg.).

$p_a - p_b$ = "effective" pressure of added gas (mm. Hg.); see section 2.12.

α_p = relative efficiency, on a pressure-to-pressure basis, of inert gas in energy transfers with azomethane molecules; see section 2.12.

$P = P_i + p_a$ = total pressure in reaction vessel (mm. Hg.).

E = experimental activation energy (kcal.).

A = experimental frequency factor ($sec.^{-1}$).

CHAPTER 9.

THE THERMAL DECOMPOSITION OF AZOMETHANE AND THE EFFECT OF ADDED GASES ON THE REACTION.

(9.1) SUMMARY: The experimental work on the thermal decomposition of azomethane alone and in the presence of added gases is reviewed chronologically, although occasionally the results of later work are anticipated. The early work is concerned with the accurate determination of the first-order rate constant and the activation energy as functions of pressure. Details are also given of work with carbon dioxide and various hydrocarbons as added gases and of attempts to calculate the relative efficiencies of these in energy transfers with azomethane molecules. However, analysis of the results indicates that the reaction is more complex than previously suspected and detailed comment on the results as a test of unimolecular theory is postponed.

(9.2) THE VARIATION OF THE FIRST-ORDER RATE CONSTANT AND THE ACTIVATION ENERGY WITH PRESSURE:

This section of the research was carried out to see if the thermal decomposition of azomethane could be used to test the theories of unimolecular reaction. It has been shown that the first-order rate constant (k) of a unimolecular reaction should be a function of pressure and should tend toward a limiting value (k_∞) at high pressures. The shape of this rate-constant/pressure curve can be used as a test of theory. In particular, it yields information about the effective number of vibrational modes or oscillators which the molecules possess. The theory also predicts that the experimental activation energy, which is defined by the equation

$$E = RT^2 \frac{d(\log_e k)}{dT},$$

should be a function of pressure (see 2.4, 2.10, 2.13).

In previous kinetic studies the rates were determined by total pressure measurements. The inadequacy of this method has already been remarked upon and in this work the reaction was followed by measuring the nitrogen which was formed (see 4.2, 4.3).

RESULTS: The results of experiments carried out in the temperature and pressure ranges (502.4 - 593.4°C) and (0.2 - 975 mm.) are given in Table 9.1 and the limits to the ranges are discussed in section 8.7. The rate constant for a given pressure and temperature was obtained by interpolation of the rate-constant/pressure curve at that temperature. Runs 7 - 23 (see Table 9.2 and Fig. 9.1) showed that the rate constant at a given pressure and temperature was independent of the percentage decomposition provided the latter was limited to less than 10 per cent, and all subsequent decompositions were kept within this limit.

Figure 9.2 shows how the Arrhenius plot for a given pressure was constructed by pressure interpolations at several temperatures. The rate constants for a variety of pressures and temperatures are given in Table 9.3. The frequency factors and activation energies for the various pressures were calculated by the method of Least Squares[85] and these are shown in Table 9.4. The values of the rate constants at 563°K (k^{563}) were calculated from the Arrhenius Equation using the values of A and E given in the preceding columns. The standard errors of estimate[85] of the frequency factor and activation energy at 20 mm. were $10^{\cdot 8}$ sec.$^{-1}$ and 0.7 kcal.; for the other pressures the errors were less, having values of approximately $10^{\cdot 2}$ sec.$^{-1}$ and 0.5 kcal.

In Figure 9.4 the rate constants at 563°K have been plotted against the initial azomethane pressure and it will be observed that they show the expected variation with pressure. The rate constant corresponding to the pressure 794.3 mm. has not been plotted since later work showed that the high-pressure work was not reliable (see 10.6).

In Figure 9.5 the experimental activation energies have been plotted as a function of pressure. The diagram shows that the activation energy falls away from its high-pressure value with decreasing azomethane pressure.

REMARKS: Only the runs at the highest pressures, approximately 800 mm., were carried out in the small reaction vessel, volume 50.2 cc.; for all other runs the large reaction vessel, volume 608.5 cc., was used. The slightly high values found for the rate constants, activation energy and frequency factor at 794.3 mm. will be discussed later. However, at this stage we may anticipate the later work by stating that the reaction was found to be complicated by a

chain process. But this difficulty was not realised originally and the preliminary evidence appeared to support, in a pleasing manner, the general conclusion of previous workers, namely that azomethane was a satisfactory example of a unimolecular reaction. Because of this complication detailed discussion of the work is postponed.

(9.3) THE EFFECT OF ADDED GASES: Chemically inert gases can increase the rate of a unimolecular reaction in the pressure-dependent region by virtue of their ability to activate and deactivate the chemically reactive molecules by energy transfer. Knowing the increase in rate which a given amount of inert gas produces, it is possible to calculate its efficiency, relative to the chemically reactive substrate, in such energy transfer processes. Generally, this will simply be termed the efficiency of the gas (see 2.12).

Some work on energy transfer in azomethane systems had already been carried out by Sickman and Rice[61], but the added gases consisted of small, structurally uninteresting molecules and few conclusions could be drawn from their results. Although we hoped to investigate a much wider range of added gases it appeared wise to perform some check experiments with a gas which had been used by Sickman and Rice. Carbon dioxide was the gas studied most fully and this they found to have an efficiency of .20 ± .04 on a pressure-to-pressure basis.

(9.4) ADDED GAS CARBON DIOXIDE:

Temperatures: 534.5°K, 554.5°K, 561°K.
Pressure ranges: Azomethane (p_a) 0.4 - 2.8 mm. Carbon dioxide (P_i) 20.0 - -59.1 mm.
Results: Table 9.5.

The value of α_p obtained was .20 ± .06. Although the results varied by 60 per cent throughout the experiments, the reproducibility within a given group was better (approximately 20 per cent). The Doran potentiometer which was used for measuring the temperature of the reaction gave considerable trouble at this period due to "dead spots" on one of the variable resistances and this may have been the reason for the poor reproducibility, for the subsequent work was much more consistent. Later in the research a different technique for introducing

and measuring the gases in the reaction vessel was employed and this also resulted in a considerable improvement in reproducibility (see 8.2, 8.3). However, it should be noted that a 5% error in the rate constant results in a 17% error in α_p so that this method is limited in the accuracy with which the relative efficiencies can be determined since it is difficult to obtain a reproducibility in rate constant which is better than 5%.

There were no obvious trends in α_p with varying azomethane pressure or carbon dioxide pressure, but the large scatter in results would mask any small systematic change.

(9.5) HYDROCARBONS AS ADDED GASES: After the work with carbon dioxide, it was decided to investigate the effect of gases which were structurally more complex. Such molecules, by possessing more vibrational modes or effective oscillators, should be better agents for energy transfer (see 6.5).

The pentanes were chosen for two reasons: (i) They are molecules of roughly the same complexity as azomethane and so might be expected to have efficiencies which are close to unity. (ii) McGrath and Ubbelohde[87] had shown that cyclopentane was only one hundredth as effective as normal pentane in energy transfers involving the low vibrational states and, although we did not expect it, we wished to see if there was any carry-over of such an effect to the higher vibrational states.

NORMAL PENTANE:

Temperatures: 556°K, 554.5°K, 555°K.
Pressure ranges: Azomethane (p_a) 0.4 - 0.5 mm. Pentane (P_i) 15.2 - 21.9 mm.
Results: Table 9.6.

The value of α_p obtained was .44 ± .02. Neglecting runs 141 and 144, the reproducibility in the value of α_p (10 per cent) was much better than it was for carbon dioxide. α_p does show a tendency to decrease as P_i is changed from 15 to 20 mm., but this is within the limits of experimental error.

CYCLOPENTANE: The experimental conditions were similar to those for normal pentane and the results are shown in the same table. Neglecting runs 137 and 143, the value of α_p is .44 ± .02.

As expected, the relative efficiencies of the two gases are similar but the low values obtained were somewhat surprising. For a molecule to be an effective energy-transfer agent it is possible that it has to possess a close structural similarity to the reacting molecule and by studying the effect of 2-butene, which is isoelectronic with azomethane, it was hoped to obtain some information about the possibility of such an effect.

TRANS-2-BUTENE:

Temperature: 553.8°K.

Pressure ranges: Azomethane (p_a) 0.4 - 0.5 mm. Trans-2-butene (P_i) 16.7-32.7 mm.

Results: Table 9.7.

The efficiency of trans-2-butene was less than that of carbon dioxide and this unexpectedly low value indicated that it was acting not merely in the role of an inert gas. It was decided, therefore, to study the effect of hydrocarbons over a much wider range of conditions to see if this difficulty could be resolved.

NORMAL PENTANE:

Temperature: 553.8°K.

Pressure ranges: Azomethane (p_a) .4 - 2.7 mm. Pentane (P_i) 9.2 - 37.4 mm.

Results: Table 9.8.

Figure 9.6 (insert) shows how, for a given pressure of azomethane, the efficiency of normal pentane decreases as the pressure of pentane is increased. It also shows how, for a given pressure of added gas, the efficiency decreases as the initial azomethane pressure is increased. A more direct interpretation of the work is obtained by plotting the experimental rate constant, for a given azomethane pressure, as a function of the pressure of added gas. This has been done in Fig. 9.6. The two curves are the calculated rate-constant/pressure curves for inert gases with efficiencies .75 and .50, and it will be seen that, as the pentane pressure is increased, the rate constant falls away from the expected value.

It would appear from these results that the thermal decomposition of azomethane is more complex than previously suspected; discussion of the significance of the results is therefore delayed.

(9.6) SURFACE REACTION:

Results: Table 9.9.

Previous investigations appeared to indicate that surface reaction plays a minor role in the thermal decomposition of azomethane and that after a few runs the reaction vessel becomes seasoned and the runs reproducible (see 4.9).

Air was inadvertently allowed into the reaction vessel after run 65, and the rates of the subsequent runs were found to be three to six times greater than that of 65. The reaction vessel was then conditioned by permitting a run to proceed for two days, when it was noticed that a considerable quantity of dark brown liquid had formed in the cooler parts of the tubing leading to the reaction vessel. After this the rates returned to their normal values. Such accelerations in the rate of decomposition were always observed after the reaction vessel had been opened to the atmosphere and prior to conditioning (see 10.6).

TABLE 9.1. THE THERMAL DECOMPOSITION OF AZOMETHANE

RATE CONSTANTS AT VARIOUS TEMPERATURES AND INITIAL PRESSURES.

Run	Temp. (°C)	$k \times 10^5$ ($sec.^{-1}$)	$k^T \times 10^5$ ($sec.^{-1}$)	p_α (mm.)	$\log k^T + 7$	$\log p_\alpha$
7	257.1	.465	.460	7.75	1.663	.889
8	256.7	.340	.350	6.56	1.544	.817
9	256.7	.488	.503	12.27	1.702	1.089
10	255.6	.735	.765	42.00	1.884	1.623
11	256.1	.337	.368	5.61	1.566	.749
12	256.9	.390	.394	6.09	1.596	.785
13	256.7	.365	.376	5.72	1.575	.757
14	257.1	.580	.574	18.50	1.759	1.267
15	256.7	.577	.594	20.04	1.774	1.302
16	257.0	.603	.603	19.72	1.780	1.295
17	256.7	.523	.539	20.17	1.732	1.305
18	256.7	.593	.611	23.14	1.786	1.364
19	256.9	.473	.478	19.66	1.679	1.294
20	256.9	.527	.532	19.73	1.726	1.295
21	256.8	.610	.622	23.91	1.794	1.379
22	257.0	.600	.600	20.84	1.778	1.319
23	257.0	.620	.620	23.31	1.792	1.368
25	303.7	30.5	31.4	21.85	3.497	1.340
27	303.9	27.1	27.4	14.81	3.438	1.171
28	304.1	31.2	29.9	22.33	3.476	1.349
29	304.5	15.6	14.8	2.91	3.170	.464
30	304.4	26.8	25.7	13.52	3.410	1.131

Run	Temp. (°C)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	p_a (mm.)	log k^T +17 (sec.$^{-1}$)	log p_a (mm.)
31	279.9	4.24	4.28	14.43	2.631	1.159
32	279.6	4.57	4.73	21.03	2.675	1.323
33	280.2	3.25	3.17	7.31	2.501	.864
34	280.4	2.90	2.74	4.19	2.438	.622
35	280.4	4.82	4.66	17.94	2.668	1.254
36	238.4	.0826	.0834	14.57	0.921	1.164
37	238.5	.0918	.0918	17.81	0.963	1.251
38	238.5	.1036	.1036	24.63	1.015	1.391
39	270.0	1.92	1.92	17.15	2.283	1.234
40	270.3	2.17	2.13	22.78	2.328	1.358
41	270.4	2.18	2.12	20.81	2.326	1.318
42	270.2	1.48	1.45	7.38	2.161	.868
43	270.6	1.56	1.47	5.63	2.167	.751
44	270.4	1.37	1.31	5.29	2.117	.724
45	270.6	1.40	1.31	5.61	2.117	.749
46	270.6	2.24	2.14	24.79	2.330	1.394
47	271.5	.955	.955	.982	1.980	$\bar{1}$.992
48	271.5	.883	.883	.614	1.946	$\bar{1}$.788
49	271.5	.751	.751	.641	1.876	$\bar{1}$.807
50	271.3	.992	1.012	1.156	2.005	.063
51	271.7	.840	.823	.205	1.915	$\bar{1}$.312
52	271.5	.617	.617	.192	1.790	$\bar{1}$.283
53	271.5	.598	.598	.207	1.777	$\bar{1}$.316

Run	Temp. (°C)	$k \times 10^5$ ($sec.^{-1}$)	$k^T \times 10^5$ ($sec.^{-1}$)	p_∞ (mm.)	$\log k^T$ ($sec.^{-1}$)	$\log p_\infty$ (mm.)
54	305.9	9.83	9.51	.675	2.978	$\bar{1}$.829
55	304.8	5.65	6.21	.313	2.793	$\bar{1}$.496
57	304.6	5.35	6.09	.257	2.785	$\bar{1}$.410
58	305.5	7.08	7.08	.438	2.850	$\bar{1}$.642
59	305.3	5.89	6.05	.285	2.782	$\bar{1}$.455
60	305.8	7.89	7.65	.498	2.884	$\bar{1}$.697
61	305.8	11.43	11.19	1.196	3.049	.078
62	305.7	10.98	10.82	.998	3.034	$\bar{1}$.999
63	320.4	28.4	28.4	1.060	3.453	.025
64	320.4	20.0	20.0	.485	3.301	$\bar{1}$.686
65	320.3	16.4	16.6	.325	3.220	$\bar{1}$.512
66E	320.3	12.7	12.9	.192	3.111	$\bar{1}$.283
67	320.6	28.7	28.3	1.016	3.452	.007
68	260.3	1.19	1.19	168.0	2.076	2.225
69	293.3	20.4	20.4	174.5	3.310	2.242
70	274.0	4.26	4.26	178.0	2.629	2.250
71	286.2	11.8	11.8	176.0	3.072	2.245
85	274.1	4.62	4.70	678.0	2.672	2.831
86	274.3	4.83	4.83	676.5	2.684	2.830
87	261.3	13.69	1.37	877.0	2.137	2.943

Run	Temp. (°C)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	p_α (mm.)	$\log k^T + 7$ (sec.$^{-1}$)	$\log p_\alpha$ (mm.)
88	229.5	.0521	.0516	919.5	0.713	2.964
89	229.6	.0593	.0583	870.0	0.766	2.940
90	229.2	.0696	.0708	791.5	0.850	2.899
91	229.4	.0584	.0584	763.3	0.766	2.883
93	262.1	1.568	1.57	791.0	2.196	2.898
94	262.2	1.635	1.62	802.0	2.210	2.904
95	261.9	1.616	1.65	936.5	2.218	2.972
96	246.2	.352	.370	975.0	1.568	2.989
97	246.7	.430	.430	820.4	1.634	2.914
98	246.7	.401	.401	781.4	1.603	2.893
99	246.6	.378	.382	753.2	1.582	2.877

Runs	T(°K)	Runs	T(°K)
7 - 23	530	63 - 64	593.4
25 - 30	577	68 - 71	temp. in col. 2 + 273
31 - 35	553	85 - 86	547.3
36 - 38	511.5	87	534.3
39 - 46	543	88 - 91	502.4
47 - 53	544.5	93 - 95	535.1
54 - 62	578.5	96 - 99	519.7

TABLE 9.2. RATE CONSTANTS FOR VARIOUS PERCENTAGE DECOMPOSITIONS.

Run	$k^{530} \times 10^5$ (sec.$^{-1}$)	p_α (mm.)	percent. decomp.
7	.460	7.75	5
8	.350	6.56	4
9	.503	12.27	4
11	.368	5.61	4
12	.394	6.09	4
13	.376	5.72	4
14	.574	18.50	2
15	.594	20.04	2
16	.603	19.72	1
17	.539	20.17	1
18	.611	23.14	9
19	.478	19.66	1
20	.532	19.73	8
21	.622	23.91	1
22	.600	20.84	10
23	.620	23.31	4

TABLE 9.3. RATE CONSTANTS AT VARIOUS TEMPERATURES AND PRESSURES.

Run	p_α (mm.)	T (°K)	$\frac{1}{T} \times 10^3$ (°K)	log k + 7 ($sec.^{-1}$)
7 - 23	20	530	1.887	1.770
7 - 23	5	530	1.887	1.563
24 - 30	20	577	1.733	3.475
24 - 30	5	577	1.733	3.260
31 - 35	20	553	1.808	2.676
31 - 35	5	553	1.808	2.457
36 - 38	20	511.5	1.955	0.980
39 - 46	20	543	1.842	2.312
39 - 46	5	543	1.842	2.108
47 - 53	1	544.5	1.836	1.985
47 - 53	.2	544.5	1.836	1.780
54 - 62	1	578.5	1.729	3.035
54 - 62	.2	578.5	1.729	2.690
63 - 67	1	593.4	1.685	3.445
63 - 67	.2	593.4	1.685	3.120
68	158.5	533.3	1.875	2.065
69	158.5	566.3	1.766	3.305
70	158.5	547	1.828	2.625
71	158.5	559.2	1.788	3.065
85 - 86	749.3	547.3	1.827	2.690
88 - 91	749.3	502.4	1.990	0.800
93 - 95	749.3	535.1	1.869	2.204
96 - 99	749.3	519.7	1.924	1.590

TABLE 9.4.

ACTIVATION ENERGIES, FREQUENCY FACTORS & RATE CONSTANTS AT 563°K FOR VARIOUS INITIAL PRESSURES.

p_a (mm.)	E (kcal.)	log A ($sec.^{-1}$)	$\log k^{563}$ ($sec.^{-1}$)
0.2	46.2	13.12	$\bar{5}.19$
1.0	47.5	13.94	$\bar{5}.50$
5.0	50.1	15.23	$\bar{5}.79$
20.0	51.6	16.03	$\bar{4}.01$
158.5	52.0	16.38	$\bar{4}.20$
794.3	52.9	16.82	$\bar{4}.29$

TABLE 9.5. ADDED GAS CARBON DIOXIDE.

Run	Temp. (°K)	$k \times 10^5$ ($sec.^{-1}$)	$k^T \times 10^5$ ($sec.^{-1}$)	$\log k^T + 5$ ($sec.^{-1}$)	p_b (mm.)	p_a (mm.)	P_i (mm.)	α_p
102	560.9	2.69	2.71	.433	-	.81	-	-
103	561.5	5.91	5.62	.750	4.84	.74	29.51	.14
104	561.4	6.11	5.87	.769	5.43	.71	33.29	.14
105	561.2	2.42	2.37	.375	-	.61	-	-
106	560.7	2.62	2.70	.431	-	.84	-	-
107	560.9	5.69	5.74	.759	5.19	.75	20.40	.22
108	560.9	6.66	6.73	.828	7.85	.84	26.94	.26
109	561.4	6.92	6.65	.823	7.59	2.77	25.80	.19
110	561.9	6.42	5.85	.767	5.43	2.42	20.73	.15
111	560.9	6.57	6.64	.822	7.59	2.31	28.39	.19
112	533.5	.851	.936	$\bar{1}$.971	15.67	2.32	50.98	.26
113	534.5	.914	.914	$\bar{1}$.961	14.62	2.29	57.16	.22
114	534.5	.678	.678	$\bar{1}$.831	-	5.45	-	-
115	554.8	4.46	4.33	.637	7.94	.42	52.80	.15
116	554.5	4.80	4.80	.681	10.35	.41	52.65	.19
117	554.1	2.16	2.24	.350	-	1.25	-	-
118	554.2	2.28	2.35	.371	-	1.20	-	-
119	554.5	4.65	4.65	.668	9.62	.42	56.50	.16
120	553.7	2.31	2.49	.396	-	1.50	-	-
121	554.2	4.49	4.63	.666	9.44	.45	59.10	.15
122	554.2	4.54	4.68	.670	9.66	.47	58.50	.16
123	554.1	3.58	3.72	.571	5.13	.41	21.67	.22
124	554.5	3.77	3.77	.576	5.43	.44	19.95	.25
126	554.9	1.82	1.75	.243	-	.836	-	-
127	555.3	2.12	1.96	.292	-	.827	-	-

Runs	102 - 111	112 - 114	115 - 127
T(°K)	561	534.5	554.5

TABLE 9.6. ADDED GASES NORMAL PENTANE AND CYCLOPENTANE.

N = normal pentane, C = cyclopentane, CO_2 = carbon dioxide standard.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	$\log k^T + 5$ (sec.$^{-1}$)	p_b (mm.)	p_α (mm.)	P_i (mm.)	α_p
129 N	556.3	4.94	4.82	.683	7.24	.47	15.20	.45
130	556.5	2.70	2.58	.412	-	1.20	-	-
131 N	556.4	5.13	4.95	.695	7.94	.44	16.17	.46
132	555.9	4.03	4.06	.608	-	4.83	-	-
133	554.9	2.25	2.46	.391	-	.96	-	-
134 C	555.1	4.72	5.08	.706	8.71	.45	18.30	.45
135	555.3	3.91	4.17	.620	-	5.53	-	-
137 C	555.8	4.34	4.41	.644	5.37	.45	17.93	.27
138 C	555.6	4.75	4.91	.691	7.94	.47	17.87	.42
139 N	555.8	5.07	5.15	.712	9.33	.44	19.52	.45
140 C	555.8	4.82	4.90	.690	7.76	.46	18.06	.40
141 N	556.1	5.27	5.23	.718	9.77	.60	18.10	.50
142 C	554.1	3.74	3.87	.588	9.77	.63	20.09	.45
143 C	554.3	3.51	3.57	.553	7.24	.52	20.75	.32
144 N	554.2	3.40	3.49	.543	6.76	.52	21.85	.29
145	554.5	2.80	2.80	.446	-	3.48	-	-
147	555.0	2.97	2.97	.473	-	3.75	-	-
148 N	555.0	3.80	3.80	.580	8.91	.39	20.20	.42
149 N	555.1	3.79	3.76	.575	8.51	.49	19.76	.41
150 CO_2	555.0	3.62	3.62	.559	7.41	.46	29.95	.23
151 N	555.4	3.94	3.81	.581	8.91	.41	20.95	.41
152 CO_2	555.2	3.87	3.81	.581	8.91	.46	31.80	.26

Runs	129 - 141	142 - 145	147 - 152
T(°K)	556	554.5	555

Runs 130, 132, 133, 135, 145 and 147 were standardisations with pure azomethane.

TABLE 9.7. ADDED GAS TRANS-2-BUTENE.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	$\log k^T + 5$ (sec.$^{-1}$)	p_b (mm.)	p_a (mm.)	P_i (mm.)	α_p
163	553.5	2.80	2.87	.458	4.47	.44	16.70	.24
164 CO_2	553.2	3.78	3.97	.599	10.96	.49	35.10	.30
165	553.8	3.34	3.34	.524	6.92	.41	32.65	.20

$T = 553.8$ °K

For comparison Run 164 was carried out with carbon dioxide as the added gas.

TABLE 9.8. ADDED GAS NORMAL PENTANE.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	$\log k^T + 5$ (sec.$^{-1}$)	p_b (mm.)	p_a (mm.)	P_i (mm.)	α_p N_2/CH_4	
163	554.1	4.30	4.19	.622	18.62	.42	37.35	.49	.40
164	553.8	3.32	3.32	.521	7.59	.45	9.18	.78	.50
165	554.2	3.72	3.60	.556	10.23	.43	18.40	.53	.39
166	554.2	3.48	3.36	.526	7.94	.49	9.46	.79	.48
167	554.4	3.89	3.70	.568	11.22	.45	19.29	.56	.40
168	553.9	3.03	3.01	.479	5.25	2.18	9.61	.32	.58
169	553.9	3.31	3.28	.516	7.24	2.73	22.98	.20	.46

$T = 553.8$ °K

TABLE 9.9. THE EFFECT OF SURFACE ON THE RATE OF REACTION.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	p_a (mm.)	Remarks.
65	320.3	16.4	.325	r.v. conditioned.
66 A	320.3	87.6	.209	r.v. opened to air.
66 B	320.3	91.1	.200	
66 C	320.2	51.4	.194	
66 E	320.6	12.7	.192	r.v. reconditioned.

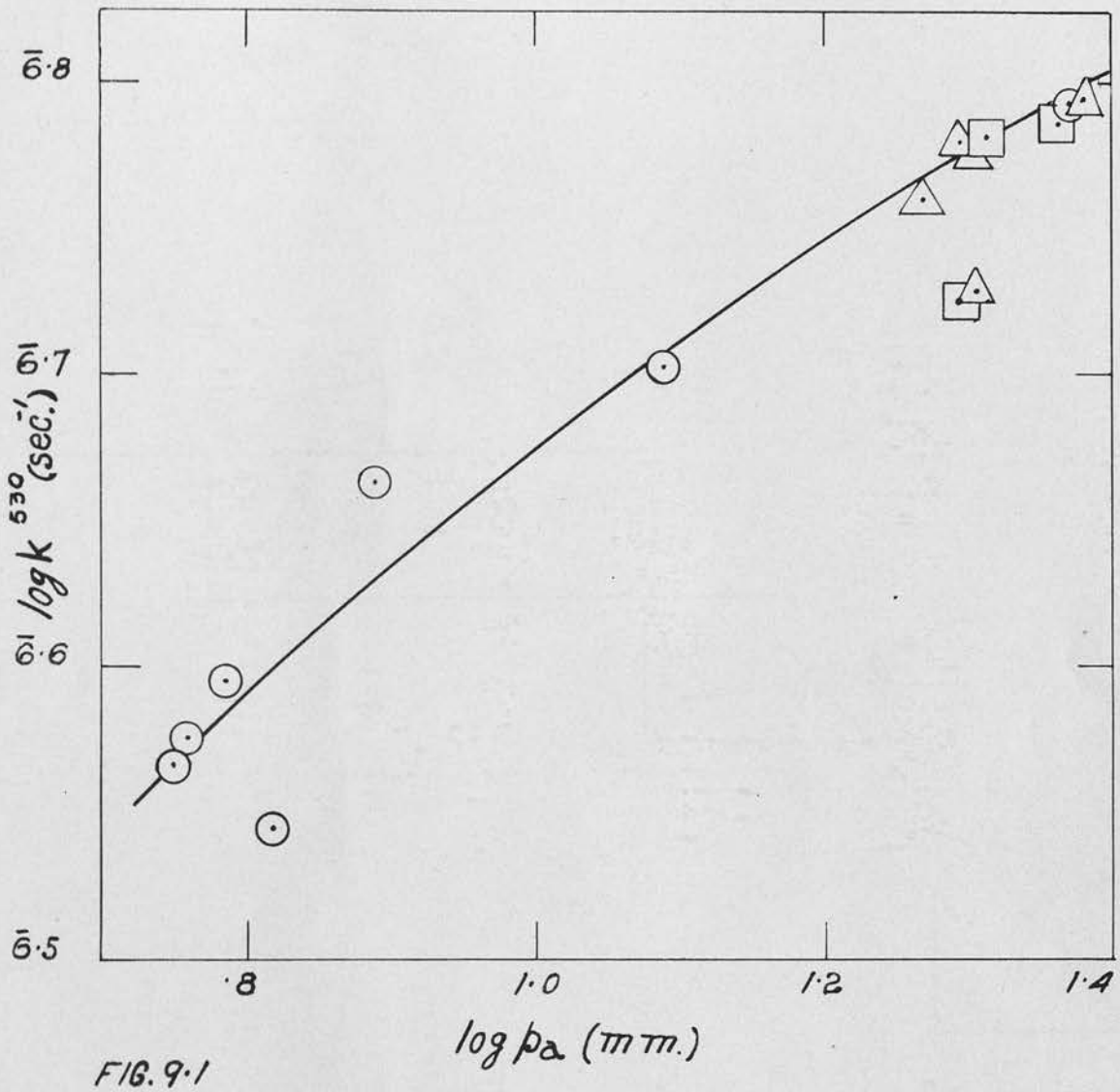


FIG. 9·1

RATE CONSTANTS FOR THE DECOMPOSITION OF AZOMETHANE FOR VARIOUS PERCENTAGE DECOMPOSITIONS.

△ 1 - 2 PERCENT.

⊙ 4 - 5 PERCENT.

⊡ 8 - 10 PERCENT.

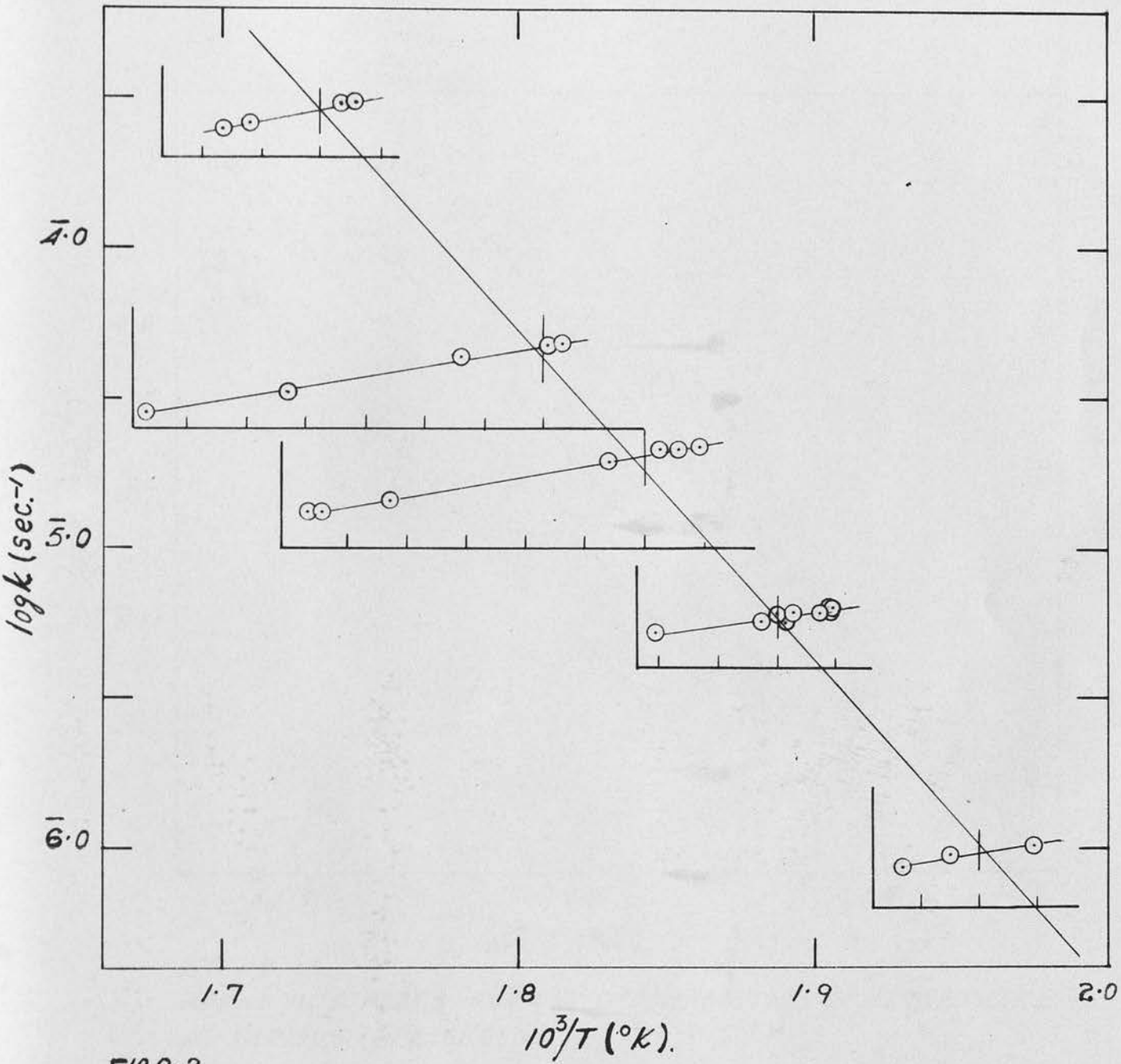


FIG. 9·2

ARRHENIUS PLOT FOR 20 m m. PRESSURE OF AZOMETHANE OBTAINED BY INTERPOLATION OF THE EXPERIMENTAL RATE CONSTANTS OVER A RANGE OF PRESSURE. THE MINOR ABSCISSAE ARE FOR LOG (AZOMETHANE PRESSURE). ARRHENIUS PLOTS FOR OTHER PRESSURES WERE OBTAINED IN A SIMILAR MANNER.

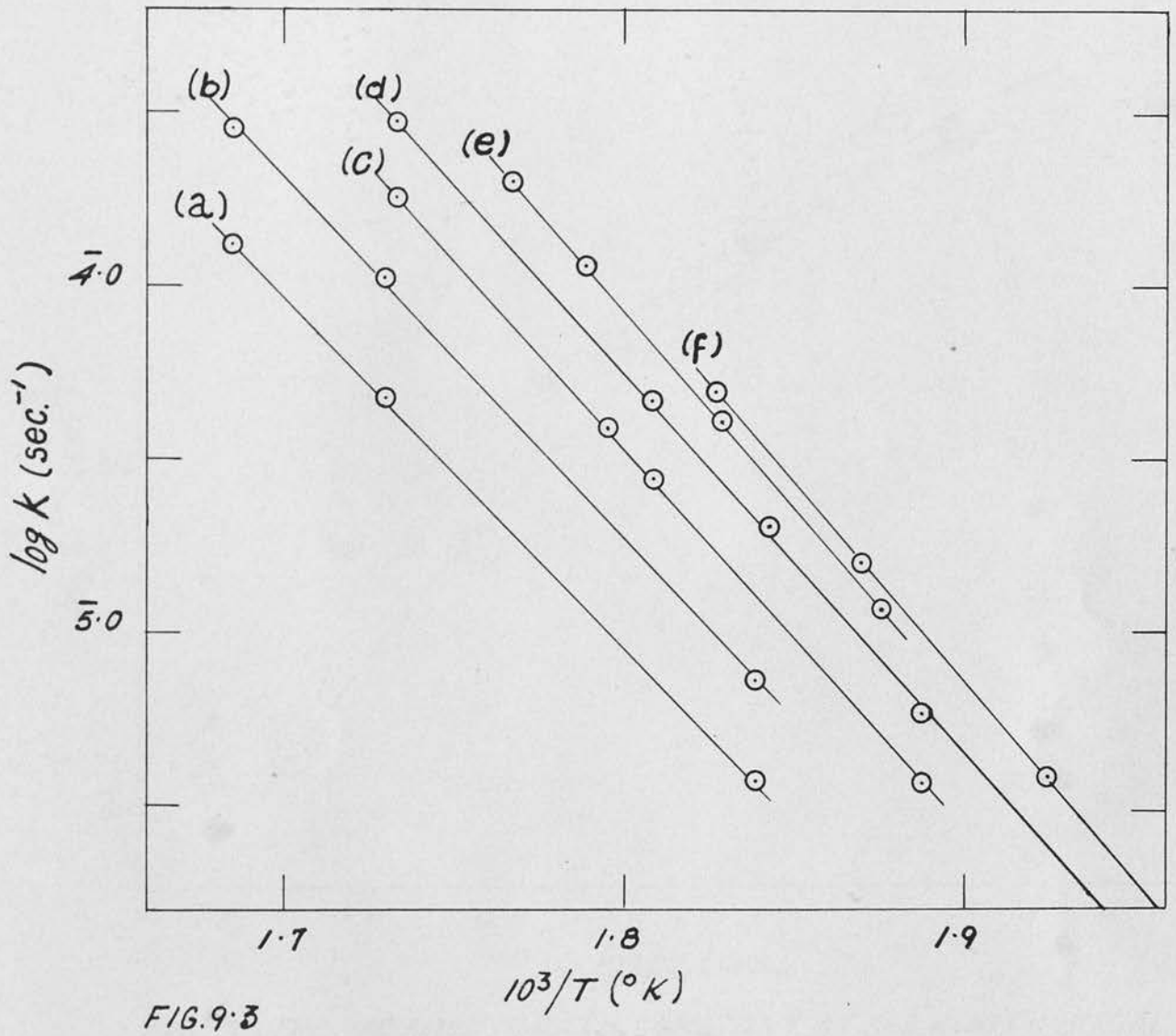


FIG. 9·3

ARRHENIUS PLOTS FOR THE DECOMPOSITION OF AZOMETHANE AT VARIOUS PRESSURES.

PLOT	a	b	c	d	e	f
p_a (mm.)	0·2	1·0	5·0	20·0	158·5	794·3

PLOTS (d) AND (f) ARE EXTENDED PAST THE EXPERIMENTAL POINTS SHOWN BECAUSE RATE DETERMINATIONS WERE MADE, IN THOSE CASES, AT TEMPERATURES BELOW THOSE WHICH APPEAR ON THE PLOT. IN THE CALCULATION OF THE ACTIVATION ENERGIES AND FREQUENCY FACTORS ALL THE EXPERIMENTAL POINTS WERE USED.

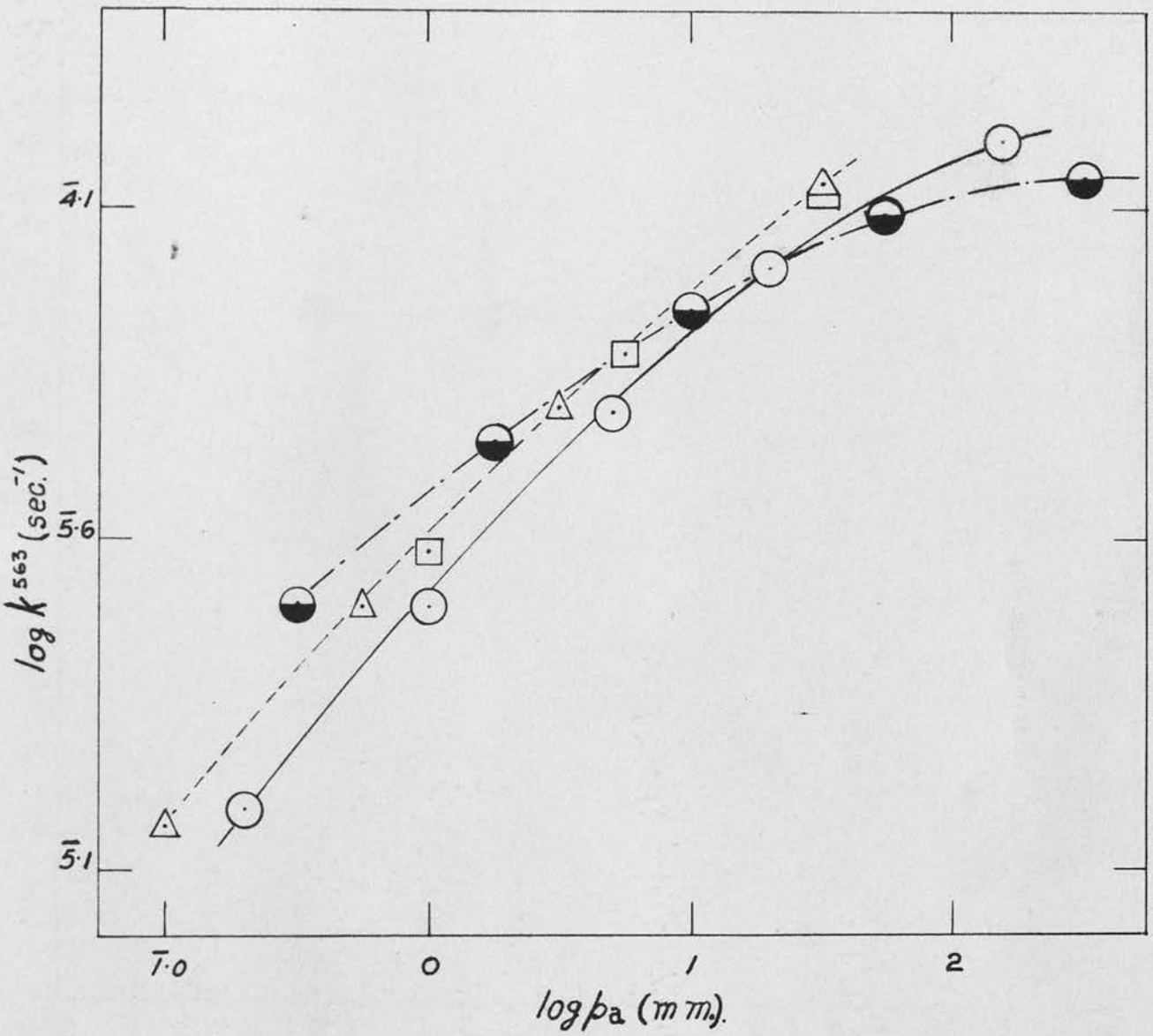


FIG. 9A. THE VARIATION IN RATE CONSTANT AT 563°K WITH INITIAL PRESSURE FOR THE THERMAL DECOMPOSITION OF AZOMETHANE.

- ◒ RAMSPERGER.
- ⊡ RICE AND SICKMAN.
- △ Mc. COY.
- ⊙ THIS WORK.

THE RATE OBTAINED AT THE HIGHEST PRESSURE IN THIS WORK HAS NOT BEEN PLOTTED AS IT IS BELIEVED TO BE UNRELIABLE.

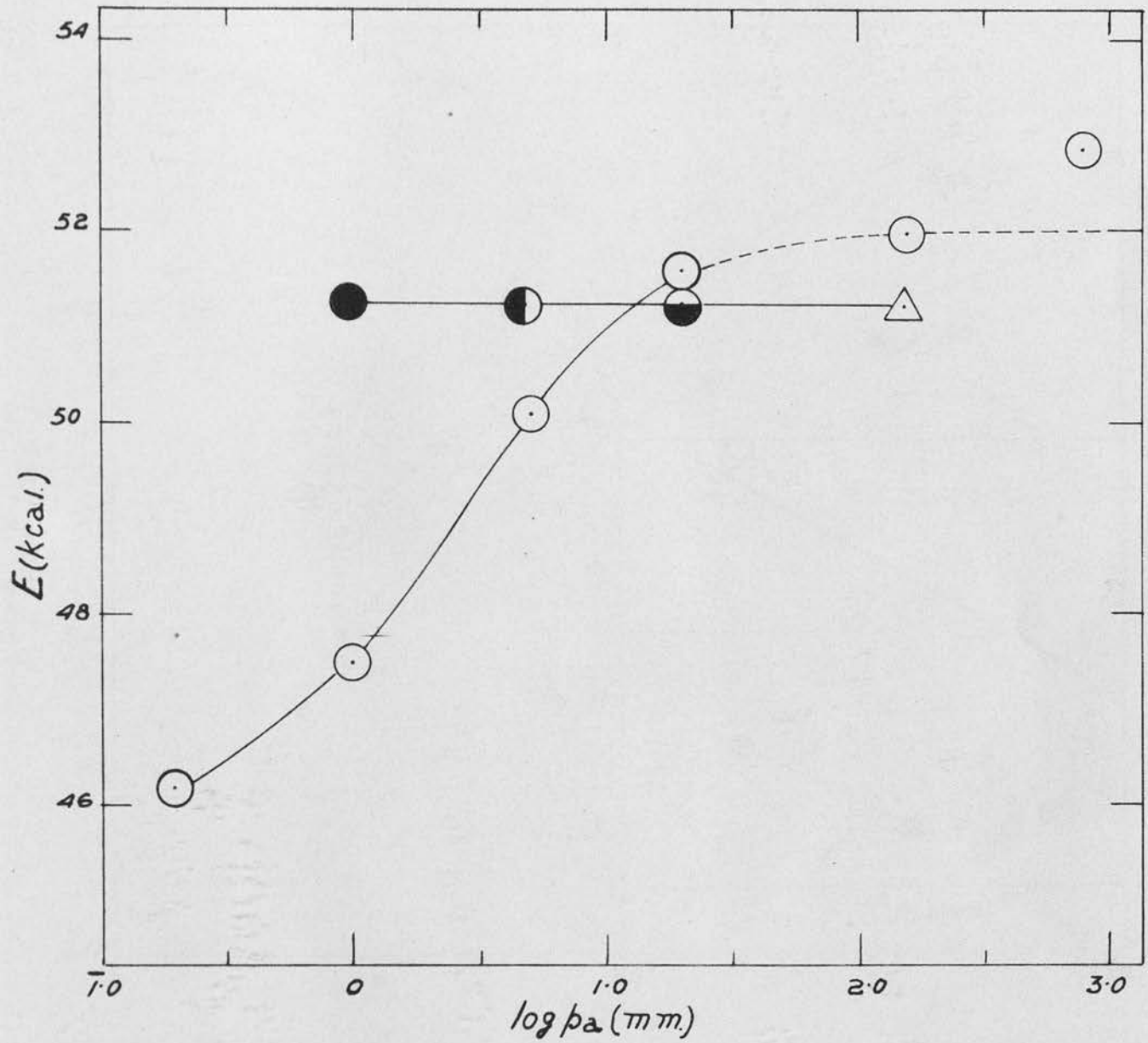


FIG. 9·5 PLOT OF EXPERIMENTAL ACTIVATION ENERGY AGAINST THE LOG OF INITIAL AZOMETHANE PRESSURE.

⊙ PURE AZOMETHANE

●◐◒ AZOMETHANE IN PRESENCE OF EXCESS PROPYLENE.

△ AZOMETHANE IN PRESENCE OF EXCESS PROPYLENE, BUT ABSCISSA IN TERMS OF TOTAL PRESSURE.

THE ACTIVATION ENERGY FOR THE HIGHEST PRESSURE / IS NOT RELIABLE.

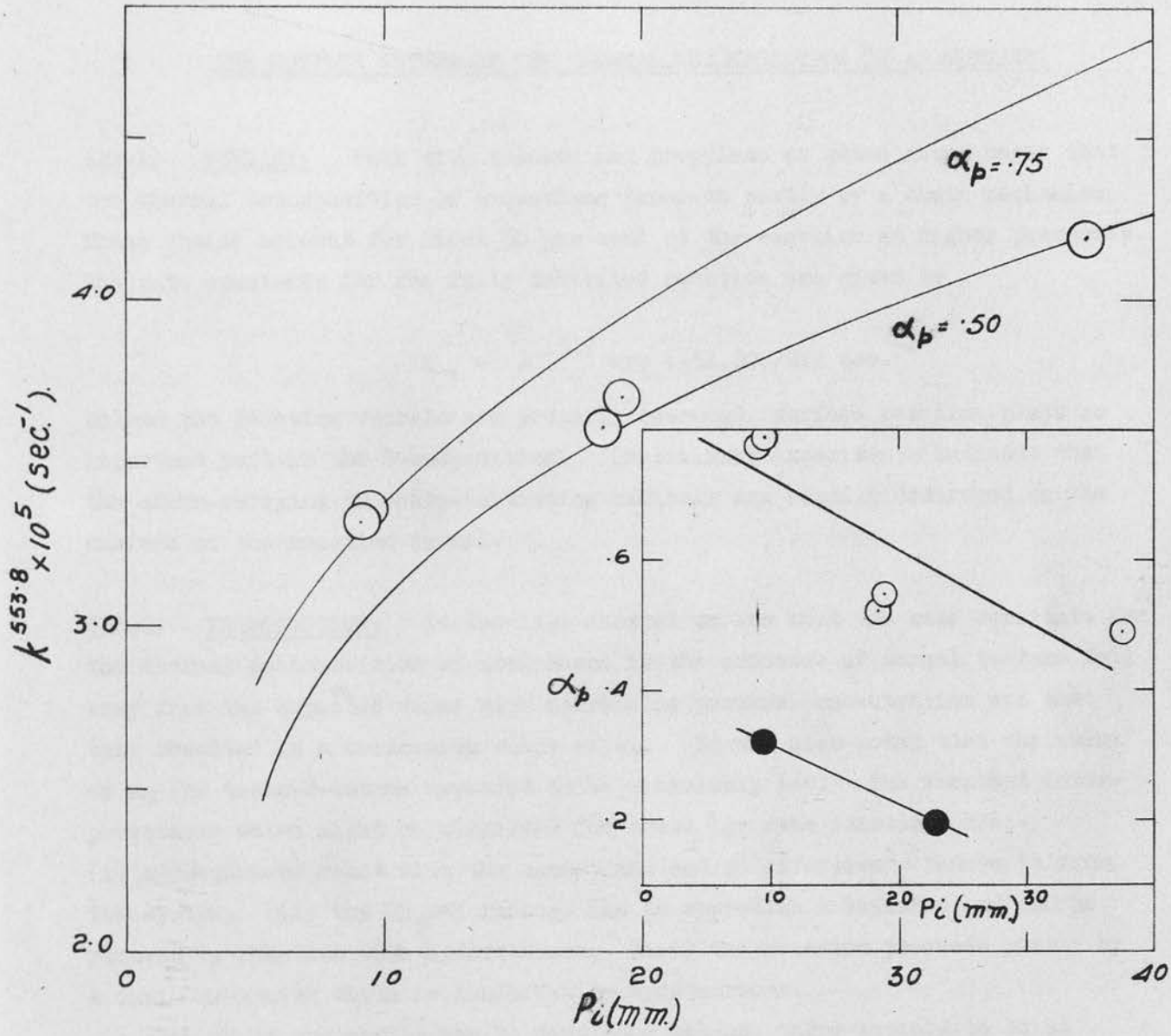


FIG. 9·6. TO SHOW THE DECREASE IN α_p AS THE PRESSURE OF NORMAL PENTANE (P_i) IS INCREASED.

⊙ AZOMETHANE PRESSURE (p_a) ~ ·45 mm.

● AZOMETHANE PRESSURE ~ 2·75 mm.

IN THE MAIN DIAGRAM THE RATE CONSTANTS AT 553·8° K HAVE BEEN PLOTTED AGAINST P_i. THE FULL CURVES REPRESENT THE RATE-PRESSURE CURVES THAT WOULD BE OBTAINED FOR GASES WITH EFFICIENCIES OF ·75 AND ·50. IN THE INSERT DIAGRAM THE VALUES OF α_p HAVE BEEN PLOTTED AGAINST P_i.

CHAPTER 10.

THE COMPLEX NATURE OF THE THERMAL DECOMPOSITION OF AZOMETHANE.

(10.1) SUMMARY: Work with toluene and propylene as added gases shows that the thermal decomposition of azomethane proceeds partly by a chain mechanism. These chains account for about 50 per cent of the reaction at higher pressures. The rate constants for the fully inhibited reaction are given by

$$k_\infty = 10^{15.7} \exp(-51{,}200/RT) \text{ sec.}^{-1} \quad (1)$$

Unless the reaction vessels are properly seasoned, surface reaction plays an important part in the decomposition. Preliminary experiments indicate that the chain-carrying or chain-initiating radicals are readily destroyed on the surface of the reaction vessel.

(10.2) INTRODUCTION: In the last chapter we saw that the rate constants for the thermal decomposition of azomethane in the presence of normal pentane fell away from the expected value with increasing pentane concentration and that this resulted in a decreasing value of α_p. It was also noted that the value of α_p for trans-2-butene appeared to be singularly low. The simplest interpretations which might be suggested for these low rate constants are:- (i) hydrocarbons react with the azomethane and so effectively remove it from the system, (ii) the $CH_3N{=}N$ radical has an appreciable lifetime and can be removed by reaction with hydrocarbons, (iii) the reaction proceeds partly by a chain mechanism which is inhibited by hydrocarbons.

The first suggestion may be dismissed because there appears to be no plausible mechanism. Admittedly methyl radicals will react with hydrocarbons to form alkyl radicals and these radicals will react with azomethane either by addition or by hydrogen abstraction. But it is difficult to see why they should be more effective in this respect than the methyl radicals which have been removed from the system by reaction with the hydrocarbon.

If the $CH_3N{=}N$ radical has an appreciable lifetime and can react with hydrocarbons the $[N_2]/[CH_4]$ ratio should tend to zero as the hydrocarbon

concentration increases, since all the nitrogen is formed by the reaction

$$CH_3N{=}N \rightarrow CH_3 + N_2. \qquad (2)$$

Table 9.8 shows that this is not so in the case of normal pentane. With increasing pentane concentration the $[N_2]/[CH_4]$ ratio decreases rapidly from the value 1.3, which is characteristic of pure azomethane, and tends towards a limiting value of 0.4, which is to be expected if most of the methyl radicals are removed by hydrogen abstraction reactions with normal pentane so that two methane molecules are formed for every nitrogen molecule. Furthermore, it has been shown that the carbon-nitrogen bond in the $CH_3N{=}N$ radical has a negative bond dissociation energy and so the radical would not be expected to have an appreciable lifetime (see 4.8).

Thus the only reasonable interpretation of the results would appear to be in terms of a chain mechanism, and this chapter deals mainly with the work confirming this idea. It should be noted that the effect cannot be explained in terms of chains which are initiated by hydrogen atoms resulting, with alkene, from the unimolecular decomposition of alkyl radicals. If this were so, the chain reaction would become increasingly important as the hydrocarbon pressure was increased. That is, the rate constants would exceed the values which would be obtained if α_p remained constant as the pressure of hydrocarbon was increased. The chains must, therefore, be a property of azomethane itself.

The two best-known chain inhibitors are nitric oxide and propylene, but the results with the former are often difficult to interpret since it can both catalyse and inhibit a reaction[49]. The same difficulty has not been observed with propylene, but the overall reaction of propylene with radicals is known to be complex[88], so it was decided to use first a "cleaner" inhibitor. In this respect toluene appeared to be suitable, for it was thought that methyl radicals must be responsible for initiating the chains and these would be removed by the reaction

$$CH_3 + CH_3C_6H_5 \rightarrow CH_4 + CH_2C_6H_5 \cdot \qquad (3)$$

The benzyl radical, $CH_2C_6H_5$, is stabilized by resonance; it therefore forms no complications in the system, being removed by reaction with another of its kind to form dibenzyl .

(10.3) INHIBITION OF THE CHAIN REACTION BY TOLUENE:

Temperature: 549.4°K.

Pressure ranges: Azomethane (p_a) 0.4-2.8 mm. Toluene (P_i) 4.1-23.7 mm.

Results: Table 10.1.
Table 10.2 shows the results for similar experiments with carbon dioxide as added gas.

The effect of toluene on the rate of decomposition of azomethane for various initial pressures of the latter is shown in Fig. 10.1; for comparison, two rate constants with carbon dioxide as the added gas have also been plotted. The results for toluene show the same general trend as did those for normal pentane, that is, a falling away in rate constant from the value which would be obtained if α_p remained constant as the pressure of toluene is increased. Indeed, at the highest pressure of azomethane used (2.8 mm.) the rates did not increase at all but remained more or less constant. In Table 10.1 some of the $[N_2]/[CH_4]$ values have been tabulated and it will be observed that the ratios do not decrease indefinitely with increasing toluene concentration but tend towards a limiting value of 0.6. This is to be expected if the predominant reactions, in the presence of toluene, are

$$CH_3N{=}NCH_3 \rightarrow N_2 + 2CH_3 \qquad (4)$$

$$2CH_3 + 2CH_3C_6H_5 \rightarrow 2CH_4 + 2CH_2C_6H_5 \qquad (3)$$

$$2CH_2C_6H_5 \rightarrow (CH_2C_6H_5)_2 \,. \qquad (5)$$

(10.4) INHIBITION OF THE CHAIN REACTION BY PROPYLENE:

Temperature: 549.4°K.

Pressure ranges: Azomethane (p_a) 0.9-19.8 mm. Propylene (P_i) 2.9-191.1 mm.

Results: Table 10.3.

Propylene possesses a great advantage over toluene in that it can be used over a much wider pressure range. Fig. 10.2 shows its effect on the rate of decomposition of azomethane. To facilitate comparison between the results with toluene and those with propylene, some of the results with the latter

have been plotted in the insert figure using a larger abscissa scale. In Fig. 10.3 the results have been plotted on a logarithmic scale and the rate constants obtained with pure azomethane have been added for reference. It will be observed that for the highest pressure of azomethane the rates actually decreased, with increasing concentration of propylene, to a limiting value, and that this limit is independent of the initial pressure of azomethane. $[N_2]/[CH_4]$ ratios have not been recorded since the fate of methyl radicals in the presence of propylene is more complex than in the presence of toluene. Not only can they undergo hydrogen abstraction reactions with propylene but they can also undergo addition reactions and the products so formed can react still further to give a most complex overall scheme[88].

The results, together with those for toluene, are most convincing evidence for the existence of a chain process in the thermal decomposition of azomethane. We therefore wished to determine the rate expression for the fully inhibited reaction.

(10.5) ARRHENIUS PARAMETERS FOR THE INHIBITED REACTION: Three pressures of azomethane were used:- .93 mm., 4.7mm., 19.7 mm.; in each case it was ascertained that sufficient propylene had been added to bring the rate constants to their limiting value. The results are given in Table 10.4 and the Arrhenius plots constructed from these values are shown in Fig. 10.4. To separate the plots, the abscissae have been displaced relative to one another. The activation energies and frequency factors were calculated by the method of Least Squares[85] and are given in Table 10.5. It will be seen that the rate of the high-pressure inhibited reaction is given by

$$k_\infty = 10^{15.7} \exp(-51{,}200/RT) \text{ sec.}^{-1} \qquad (1)$$

and that this rate is independent of the concentration of azomethane. The average values for the standard errors of estimate[85] of the frequency factors and activation energies given in the Table are $10^{.15}$ sec.$^{-1}$ and 0.25 kcal.

(10.6) SURFACE REACTION:

Results: Tables 10.6 and 10.7.

As before, it was found that, after the reaction vessel had been opened to

the atmosphere, the rate constants of reactions carried out in the unconditioned vessel were very much greater than those in properly conditioned vessels (see Table 10.6).

Maccoll[89] has found that allyl bromide can be used to condition a reaction vessel, that is, to make the surface inactive. After run 99 the reaction vessel was conditioned before each group of runs, or if there was any reason to suspect that air had leaked into the vessel, by reacting allyl bromide in it overnight at about 400°C. Several standardizations with pure azomethane were carried out throughout the course of this later work to ensure that no serious error had been incurred in the early work due to surface effects. The rates obtained with the large reaction vessel agreed well with the early work, but the original high-pressure work using the small reaction vessel (runs 85 - 99) was found to be seriously in error.

The small reaction vessel was used for run 219 et seq. Prior to this, several reactions had been carried out in the vessel to obtain products for gas chromatographic analyses. It might be thought, therefore, that the vessel would have been sufficiently seasoned (see the observations of Rice and Sickman, section 4.9). The rates were indeed reproducible (runs 219 - 221), but on conditioning the vessel with allyl bromide the rate fell by 37% (run 223); further conditioning had no effect (run 224). These rates are considerably less than those originally obtained with the small reaction vessel. Preliminary work (runs 223 - 225) indicates that the rate-constant/pressure curve for reactions in the small reaction vessel is displaced by approximately .25 log k units from the rate-constant/pressure curve obtained using the large vessel (see Fig. 10.5). This was a most unexpected result and would indicate that the chains are terminated very readily on the surface, since the small reaction vessel has the larger surface-to-volume ratio. It is interesting to note that the limiting rate in the presence of excess propylene, when all the chains are inhibited, is still the same as that obtained using the large reaction vessel, so the displacement of the curve does not seem to be due to any gross error.

TABLE 10.1. ADDED GAS TOLUENE.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	P_a (mm.)	P_i (mm.)	N_2/CH_4
171	548.6	1.50	1.60	.94	5.36	.78
172	549.4	1.67	1.67	.48	8.36	.71
173	549.7	1.44	1.40	.48	4.06	.77
174	549.7	1.68	1.63	2.72	9.80	.79
175	549.2	1.60	1.63	2.78	18.94	.68
176	549.4	1.66	1.66	1.32	19.44	.63
177	550.2	2.01	1.88	.43	19.61	.63
178	550.1	1.74	1.64	.94	12.55	.64
179	549.3	1.59	1.60	.92	23.73	.61

$T = 549.4$ °K

TABLE 10.2. ADDED GAS CARBON DIOXIDE.

Run	Temp. (°K)	$k \times 10^5$ (sec.$^{-1}$)	$k^T \times 10^5$ (sec.$^{-1}$)	$\log k^T + 5$ (sec.$^{-1}$)	p_b (mm.)	p_a (mm.)	P_i (mm.)	α_p	N_2/CH_4
180	550.6	2.527	2.274	.357	5.69	.93	25.14	.19	1.35
181	550.5	2.048	1.858	.269	3.39	.94	9.10	.27	1.41
182	550.7	2.908	2.596	.414	8.51	.92	51.61	.15	1.45

$T = 549.4$ °K

TABLE 10.3 ADDED GAS PROPYLENE.

Run	Temp. (°K)	$k \times 10^5$ ($sec.^{-1}$)	$k^T \times 10^5$ ($sec.^{-1}$)	$\log k^T + 5$ ($sec.^{-1}$)	P_a (mm.)	P_i (mm.)
183	549.6	1.78	1.75	.243	.93	30.57
184	550.4	1.87	1.72	.236	.96	16.37
188	547.7	1.47	1.68	.225	.97	21.12
189	548.0	1.72	1.92	.283	.96	50.34
190	548.2	1.23	1.35	.130	.96	3.47
191	548.5	.921	.990	$\bar{1}$.996	.96	-
192	549.8	2.10	2.03	.308	4.91	-
193	548.7	1.95	2.07	.316	4.82	2.88
194	551.8	2.26	1.81	.258	4.91	7.28
195	549.9	1.92	1.84	.265	4.79	12.04
196	549.9	2.12	2.03	.308	4.84	46.26
197	548.3	1.77	1.93	.286	4.79	30.20
198	548.5	1.97	2.12	.326	4.82	147.2
200	548.4	1.89	2.04	.310	4.82	85.70
205	549.4	2.06	2.06	.314	.95	67.00
206	549.6	2.25	2.22	.346	.92	191.1
207	550.2	2.34	2.18	.338	19.7	126.6
208	547.5	1.92	2.22	.346	19.8	173.2
214(CO_2)	547.1	3.13	3.73	.572	4.80	376.4
215	548.3	2.72	2.97	.473	25.36	-
216	548.5	1.89	2.03	.308	4.39	-
217	547.7	2.37	2.71	.433	12.91	-
218	548.9	3.22	3.36	.526	38.29	-

$T = 549.4\,^{\circ}K$

For comparison run 214 was carried out using carbon dioxide as the added gas. Runs 191, 192, 215-218 were standardisations with pure azomethane.

TABLE 10.4 ADDED GAS PROPYLENE.

Run	Temp. (°K)	$\frac{1}{T} \times 10^3$ (°K)	$k \times 10^5$ ($sec.^{-1}$)	log k + 5 ($sec.^{-1}$)	p_a (mm.)	P_i (mm.)
198	548.5	1.823	1.97	.295	4.8	147.2
202	568.1	1.761	9.72	.988	4.7	134.3
203	524.3	1.907	.219	$\bar{1}$.340	4.6	135.9
204	511.7	1.954	.0687	$\bar{2}$.837	4.7	140.1
205/206	549.4	1.820	2.20	.342	.93	190.0
209	568.1	1.761	10.77	1.032	.93	150.1
212	534.8	1.870	.609	$\bar{1}$.785	.94	147.1
213	573.2	1.744	15.01	1.176	.92	144.1
207/208	549.4	1.820	2.20	.342	19.8	170.0
210	568.3	1.760	10.51	1.021	19.6	141.4
211	526.4	1.900	.284	$\bar{1}$.453	19.8	157.7

TABLE 10.5 ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE THERMAL DECOMPOSITION OF AZOMETHANE IN THE PRESENCE OF EXCESS PROPYLENE.

p_a (mm.)	P_i (mm.)	log A ($sec.^{-1}$)	E (kcal.)
0.93	144 - 190	15.7	51.2
4.7	134 - 147	15.7	51.2
19.7	141 - 170	15.7	51.2

TABLE 10.6 THE EFFECT OF SURFACE ON THE RATE OF REACTION.

Run	$k^T \times 10^5$ (sec.$^{-1}$)	P_a (mm.)	P_i (mm.)	Remarks.
				Large reaction vessel
184	1.72	.96	16.37	r.v. opened to air
185	17.1	.93	29.29	
186	14.9	.95	32.95	
187	13.6	.89	38.51	r.v. reconditioned
188	1.68	.97	21.12	
				Small reaction vessel
219	3.70	207.9	-	
221	3.82	256.6	-	r.v. incompletely conditioned
222	3.09	224.4	380	r.v. reconditioned
223	2.35	232.3	-	

$T = 549.4\ ^\circ K.$

Runs 184-188, and 222 were carried out in the presence of propylene.

TABLE 10.7 THE EFFECT OF THE SURFACE TO VOLUME RATIO ON THE RATE OF REACTION.

Run	$k^T \times 10^5$ (sec.$^{-1}$)	p_a (mm.)	P_i (mm.)	Remarks
				Large reaction vessel
191	.990	.96	-	
192	2.03	4.91	-	
215	2.97	25.36	-	
216	2.03	4.39	-	Runs with pure azomethane
217	2.71	12.91	-	
218	3.36	38.29	-	
205	2.06	.95	67.0	
206	2.22	.92	191.1	
207	2.18	19.7	126.6	Runs in the presence of propylene
208	2.22	19.8	173.2	
				Small reaction vessel
223	2.35	232.3	-	
224	2.52	218.6	-	Runs with pure azomethane
225	1.57	15.22	-	
226	2.71	207.6	382	Runs in the presence of propylene
227	2.28	9.2	580	

T = 549.4 °K.

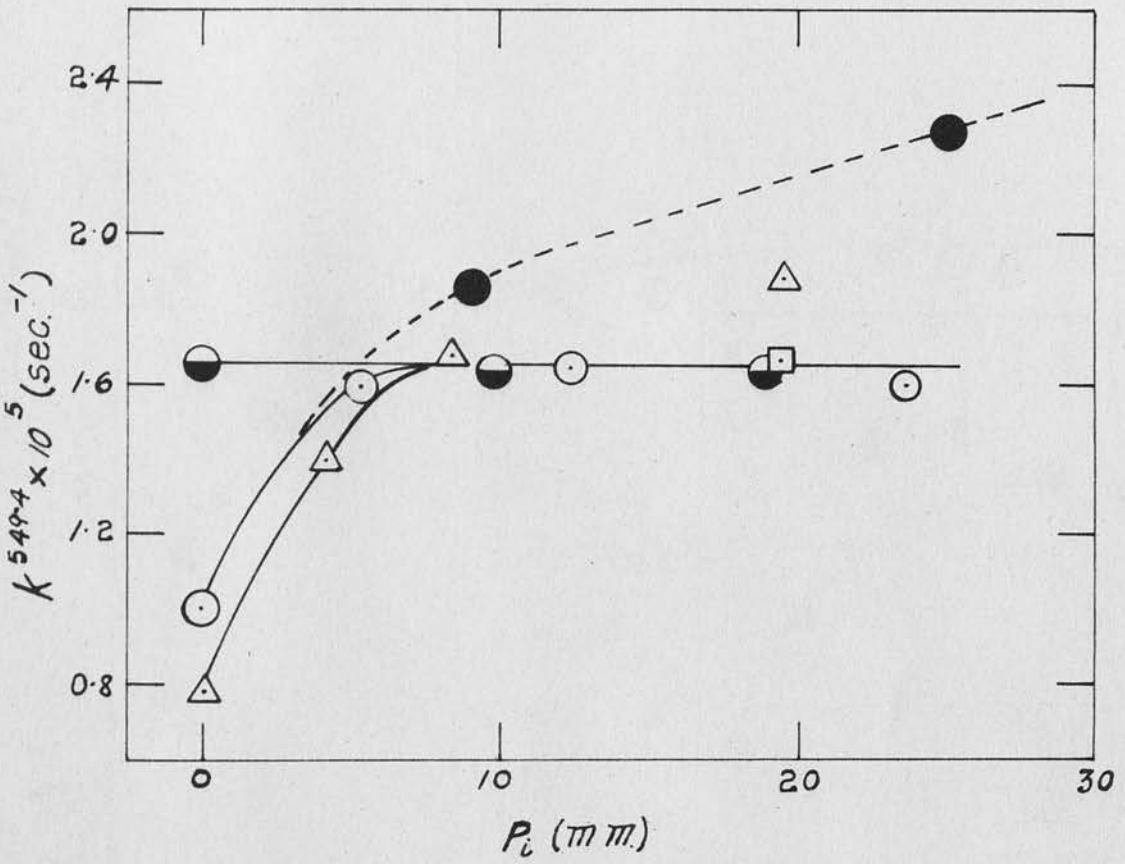


FIG. 10·1 RATE CONSTANTS AT 549·4°K FOR THE DECOMPOSITION OF AZOMETHANE IN THE PRESENCE OF TOLUENE. FOR COMPARISON TWO RATE CONSTANTS WITH CARBON DIOXIDE AS ADDED GAS ARE ALSO GIVEN.

P_i = PRESSURE OF TOLUENE OR CARBON DIOXIDE.

	AZOMETHANE PRESSURE.	ADDED GAS.
△	~ ·45 mm.	TOLUENE.
⊙	~ ·94 mm.	TOLUENE.
●	~ ·94 mm.	CARBON DIOXIDE.
⊡	~ 1·32 mm.	TOLUENE.
◒	~ 2·75 mm.	TOLUENE.

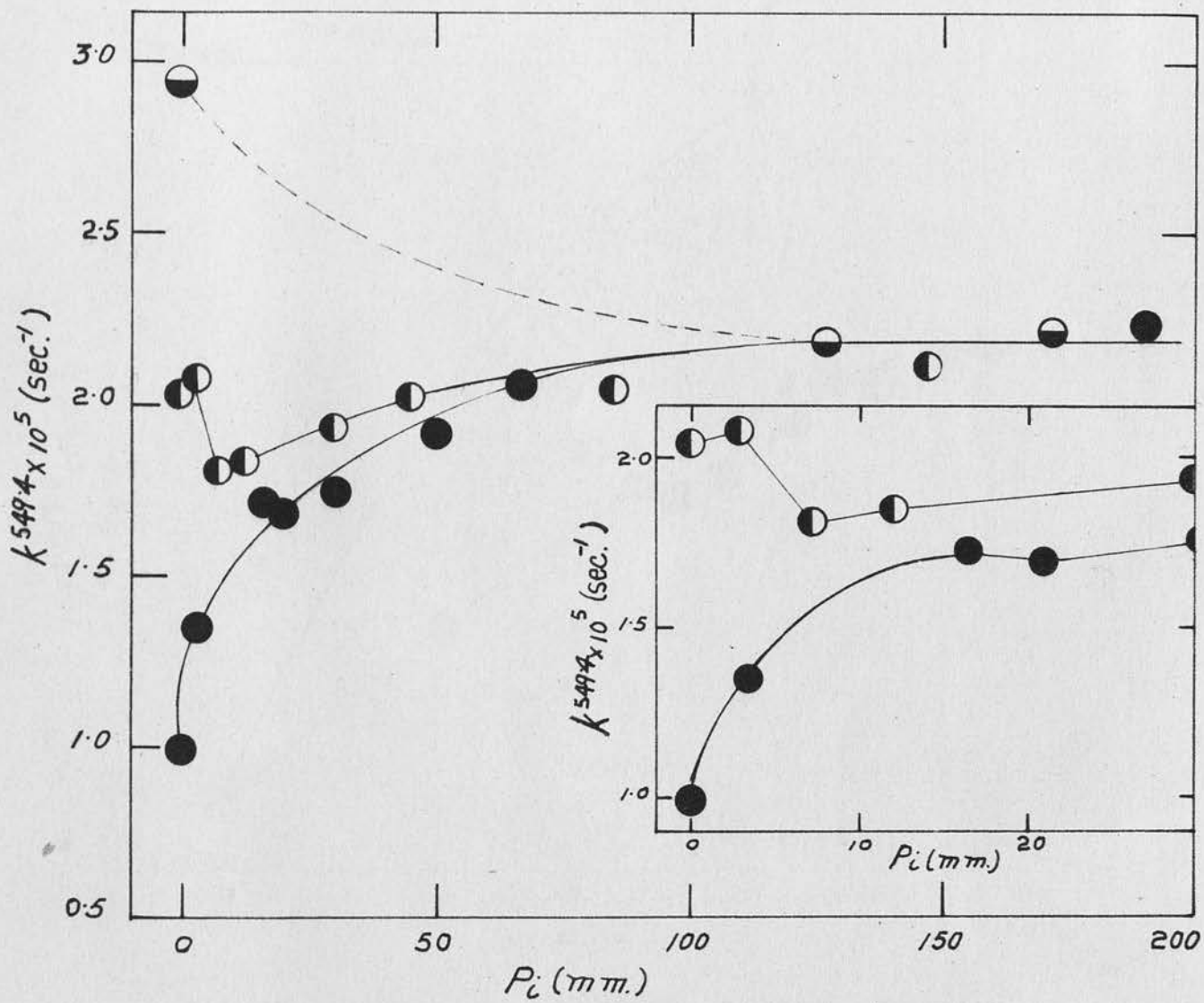


FIG.10·2 RATE CONSTANTS AT 549·4°K FOR THE DECOMPOSITION OF AZOMETHANE IN THE PRESENCE OF PROPYLENE.

- ● AZOMETHANE PRESSURE ~ 0·9 mm.
- ◐ AZOMETHANE PRESSURE ~ 4·7 mm.
- ◒ AZOMETHANE PRESSURE ~ 19·7 mm.
- P_i PRESSURE OF PROPLYENE.

IN THE INSERT DIAGRAM THE ABSCISSA HAS BEEN MAGNIFIED TO MAKE IT COMPARABLE WITH THE ABSCISSA OF FIG.10·1.

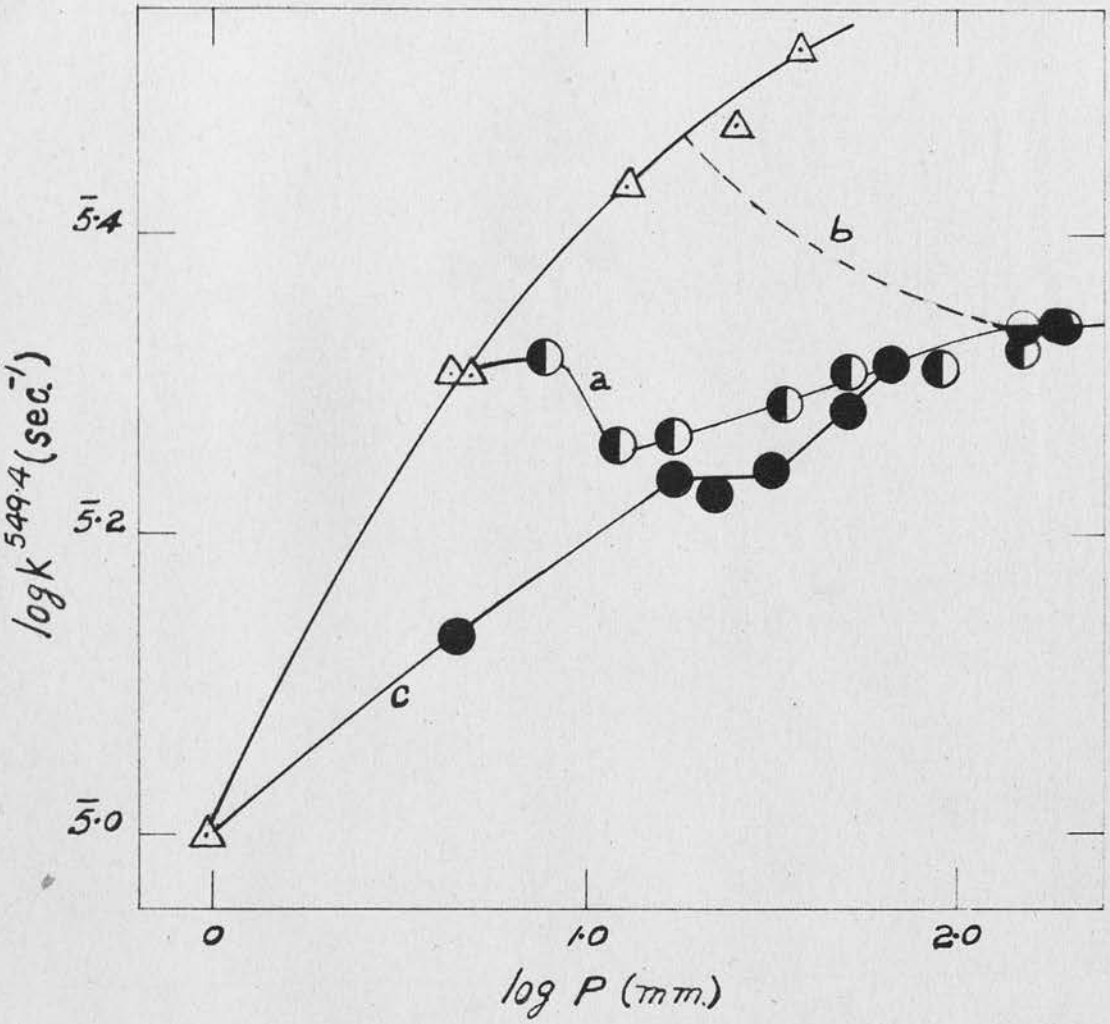


FIG. 10·3 TO SHOW THE EFFECT OF PROPYLENE ON THE RATE CONSTANTS FOR THE DECOMPOSITION OF AZOMETHANE.

P = PRESSURE OF AZOMETHANE + PRESSURE OF PROPYLENE.
△ RUNS WITH PURE AZOMETHANE.
●◐◒ RUNS WITH AZOMETHANE + PROPYLENE.
● AZOMETHANE PRESSURE ~ 0·9 mm.
◐ AZOMETHANE PRESSURE ~ 4·7 mm.
◒ AZOMETHANE PRESSURE ~ 19·7 mm.

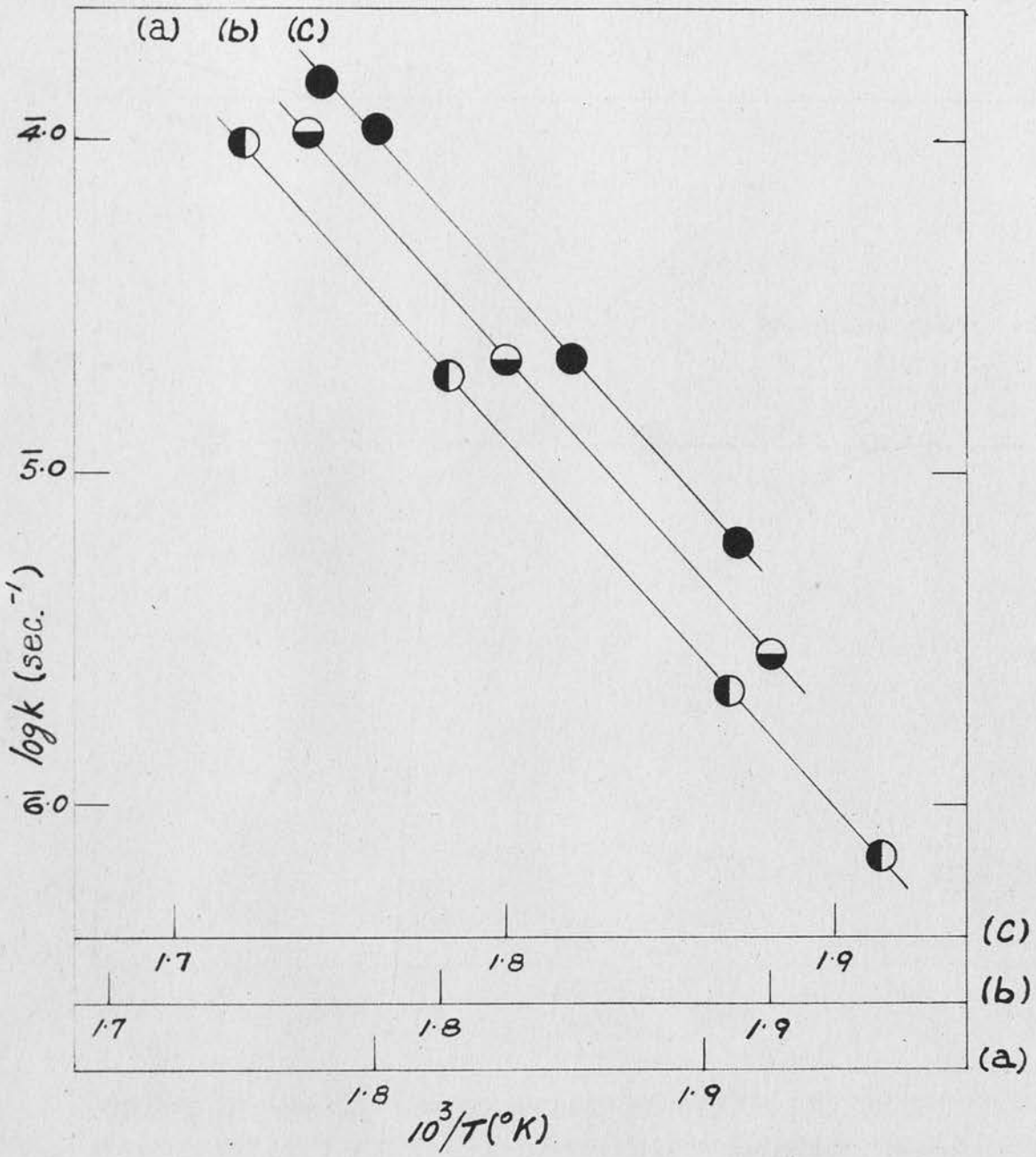


FIG. 10·4 ARRHENIUS PLOTS FOR THE DECOMPOSITION OF AZOMETHANE IN THE PRESENCE OF EXCESS PROPYLENE.

PLOT.	AZOMETHANE PRESSURE (mm).	PROPYLENE PRESSURE (mm).
(C)	·9	144-190
(a)	4·7	134-147
(b)	19·7	141-170

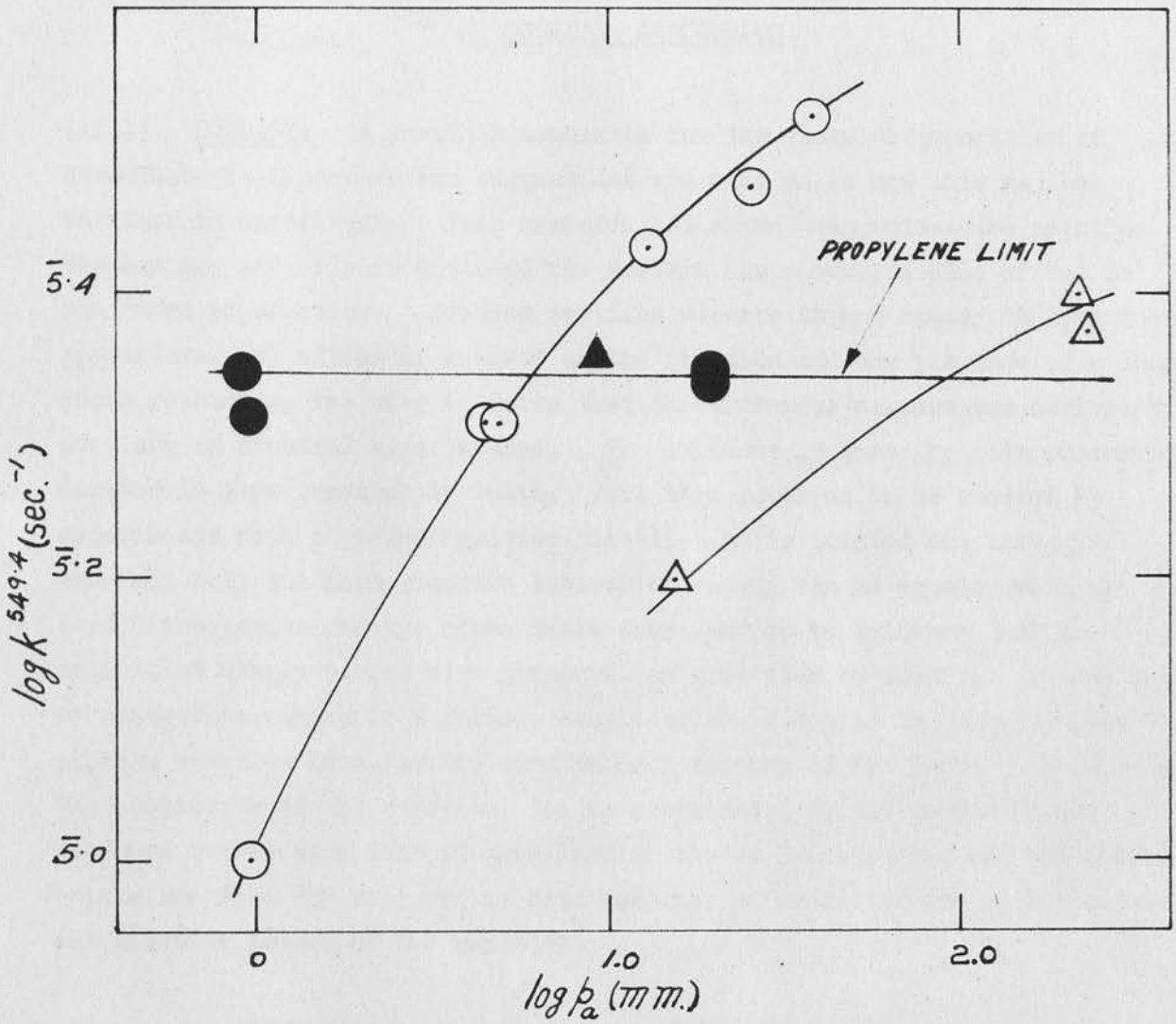


FIG.10·5 TO SHOW THE EFFECT OF THE SURFACE TO VOLUME RATIO ON THE RATE CONSTANTS FOR THE DECOMPOSITION OF AZOMETHANE.
p_a = PRESSURE OF AZOMETHANE.

⊙ RUNS WITH PURE AZOMETHANE IN LARGE REACTION VESSEL.
△ RUNS WITH PURE AZOMETHANE IN SMALL REACTION VESSEL.
● RUNS IN LARGE REACTION VESSEL IN THE PRESENCE OF EXCESS PROPYLENE (67-191 mm.).
▲ RUN IN SMALL REACTION VESSEL IN THE PRESENCE OF EXCESS PROPYLENE (580 mm.).

CHAPTER 11.

GENERAL DISCUSSION.

(11.1) SUMMARY: A possible mechanism for the chain decomposition of azomethane is discussed and suggestions are made as to how this may be verified by experiment. This research has shown that unless the reaction vessels are properly conditioned the surface has a considerable effect on the rates of reaction. Because previous workers do not appear to have fully appreciated the effect of surface on the reaction and the presence of a short chain mechanism, the view is taken that the Arrhenius expressions derived by them are of doubtful significance. The evidence is that the rate expression derived in this research is valid. But this requires to be checked by experiments with a packed reaction vessel. It is pointed out that, in general, only the high-pressure activation energy can be equated with the bond dissociation energy, since there does seem to be evidence that the activation energy varies with pressure, as predicted by theory. In the case of azomethane, there is a further complication, since it is possible that the primary reaction involves the simultaneous rupture of two bonds. Because of the complexity of the reaction, the interpretation of the rate-constant/pressure curves as a test of unimolecular theory is doubtful, but the indications are that the fall-off in rate can only be accounted for by the quasi-unimolecular nature of the reaction.

(11.2) CHAIN PROCESS: The inhibiting effect of toluene and propylene on the rate of the thermal decomposition of azomethane is convincing evidence for the existence of a chain mechanism. At the highest pressure used in the large reaction vessel (158.5 mm.) the chain process accounted for some 50% of the total reaction. These results for the thermal decomposition may be compared with the quantum yields of 1.5 and 2.0 which have been reported for the photolysis at 260°C (see 3.11). It will also be remembered that Jahn and Taylor[55] found that the rate constants, in the presence of a two-fold excess of nitric oxide, were only about half as large as those for pure

so that the activation energy of reaction (3) should be considerably less than the strength of the normal carbon-nitrogen single bond (81 ± 2 kcal.). The diazomethane would then decompose by the reaction

$$CH_2N{=}N \longrightarrow CH_2 + N_2 \quad . \tag{5}$$

Due to the large "reorganisation" energy in the formation of nitrogen this reaction, too, should have a reasonable activation energy (see 4.8). Reaction (5) accounts for the increased amount of nitrogen formed in the uninhibited reaction. In the inhibited reaction the chain-initiating methyl radicals are removed by reaction with toluene or propylene and the chain scheme (4), (3), (5) cannot take place.

Although diazomethane has been used with success in the photolytic production of methylene radicals[90], little kinetic work has been done on the thermal decomposition because of the dangerously explosive nature of the reaction. Steacie[91] performed a few experiments and found the main products to be ethylene and nitrogen. The ethylene is believed to be formed by the reaction

$$CH_2 + CH_2N{=}N \longrightarrow C_2H_4 + N_2 \quad , \tag{6}$$

rather than by the direct combination of two methylenes as was once believed[92]. The best expression for the few rate constants which were determined by Steacie is

$$k = 10^{14.4} \exp(-36{,}000/RT) \text{ sec.}^{-1} \tag{7}$$

This means that reaction (5) will be proceeding rapidly in the temperature range used in this study. It would be unwise to equate the activation energy with the bond dissociation energy $D(H_2C\text{-}NN)$.

The detection of methylene radicals in the azomethane system would afford substantial confirmation of the suggested chain process. The detection of ethylene cannot be used as proof of their existence. It will be remembered that Jones and Steacie[38] postulated the formation of methyl ethyl diimide by the radical combination

$$CH_3 + CH_2N{=}NCH_3 \longrightarrow C_2H_5N{=}NCH_3 \quad . \tag{8}$$

The diimide could then decompose by the reaction

$$C_2H_5N{=}NCH_3 \rightarrow C_2H_5 + N_2 + CH_3 \quad , \tag{9}$$

and the ethyl radicals would disproportionate to form ethylene and ethane -

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \quad . \tag{10}$$

Knox and Trotman-Dickenson[93] have shown that methylene radicals react with propylene to form methylcyclopropane -

$$CH_2 + CH_3CH{=}CH_2 \rightarrow CH_3\overset{\diagdown}{\underset{\diagup}{CH}}{-}CH_2 \quad . \tag{11}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2$$

This molecule contains an excess energy of 78 kcal. and, unless deactivated by collision, isomerises to form mixed butenes. But the detection of butenes in azomethane/propylene systems would not be unambiguous evidence for the existence of methylene radicals. Rust, Seubold and Vaughan[88] studied the reaction of methyl radicals with propylene in the temperature range 200-235°C and found 1-butene and 2-butene among the products. These are formed by the disproportionation of butyl radicals or by the reaction of methyl radicals with allyl radicals -

$$C_4H_9 + C_4H_9 \rightarrow C_4H_8 + C_4H_{10} \tag{12}$$

$$CH_3 + CH_2{-}CH{=}CH_2 \rightarrow C_4H_8 \quad . \tag{13}$$

Above 250°C it is also possible that some of the butyl radicals undergo a unimolecular decomposition to butene and a hydrogen atom[94]. The butyl radicals are formed by addition of methyl radicals to propylene, and allyl radicals arise when methyl radicals abstract hydrogen from propylene -

$$CH_3 + CH_2{=}CH{-}CH_3 \rightarrow C_4H_9 \tag{14}$$

$$CH_3 + CH_2{=}CH{-}CH_3 \rightarrow CH_4 + CH_2{=}CH{-}CH_2 \quad . \tag{15}$$

This difficulty of finding a reaction which is unique to methylene is common to most schemes which might be suggested for the detection of these

radicals, since reactions involving CH_2 are formally similar to those involving CH_3 followed by loss of a hydrogen.

However, if the butenes are formed by rearrangement from "hot" methylcyclopropane then the ratio $\frac{\text{methylcyclopropane + butenes}}{\text{methylcyclopropane}}$ should decrease as the total pressure is increased due to the stabilisation of the methylcyclopropane by collisional deactivation.

A few runs were carried out over a range of pressures with azomethane/propylene mixtures to obtain products for gas chromatographic analyses, and the experimental conditions and results for two sample runs have been recorded in Table 11.1. Propylene, by reacting very readily with the chain-initiating methyl radicals, inhibits the formation of the products sought. But by using roughly equal quantities of azomethane and propylene it was hoped that there would still be enough chain reaction present. In (10.6) it was pointed out that the chains appear to be terminated readily on the surface of the reaction vessel, so there should be much less chain reaction in the small vessel. Run 226 (Table 10.7) was carried out using the same pressures of azomethane and propylene as were used in the gas chromatographic runs at high pressures and by comparing the rate constant with the limiting rate constant in the presence of excess propylene it will be seen that there is little chain reaction. However, this difficulty was not appreciated at the time the gas chromatographic runs were carried out. Thus it appears that these preliminary experiments were poorly designed for the detection of methylene radicals in the system and it is not surprising that the results recorded in Table 11.1 are inconclusive.

Recently Frey and Kistiakowsky[95] have shown that "hot" methylcyclopropane can also be formed by the reaction of methylene radicals with cyclopropane. This might be a better reaction to test for methylene radicals since cyclopropane does not inhibit chains so readily as propylene. If the suggestion about chain termination at the walls of the vessel proves to be correct, it would be necessary to carry out the high-pressure work in the large reaction vessel. For moderate pressures of azomethane and cyclopropane, large total pressures could still be obtained by adding carbon dioxide to the system.

(11.3) EFFECT OF SURFACE ON THE REACTION: In the last two chapters and in the second section of this chapter mention was made of the effect of surface on the rate of reaction. The rates in unconditioned vessels were found to be several times greater than those in properly conditioned vessels (see Tables 9.9 and 10.5). Such large surface effects have not been reported in the previous work. Indeed, Rice and Sickman[11] alone record having observed a surface effect when they packed their reaction flasks, and they state that this effect is not very important. Ramsperger[8] reported that packing the reaction vessel had no effect on the rate. The other authors do not report either seasoning or packing their reaction vessels (see 4.9).

The difference between our findings and those of Ramsperger and Rice & Sickman may be due to the different methods of analysis - our rates were based on the amount of nitrogen formed whilst the early rates were in terms of total pressure measurements. However, the discrepancy could be due to a more subtle effect. It appears that the chain reaction becomes less important as the surface-to-volume ratio is increased, so that the effect of packing the reaction flask could be twofold - first, a decrease in the amount of chain reaction, secondly, an increase in the amount of surface reaction - and it is conceivable that these two effects roughly balance one another. Experiments are planned to check this hypothesis and to see if the rate-constant/pressure curves obtained after the surfaces have been made inert by thorough seasoning can be displaced by packing the vessel.

The need for careful experiments to investigate the effect of surface on rates of reactions does not appear to have been always appreciated. Thus, for the thermal isomerisation of 1,2-dichloroethylene we were able to obtain rate constants which were 1,000 times smaller than those reported by Jones and R. L. Taylor[96] for the (supposedly) homogeneous reaction. This finding is in agreement with recent work by Rabinovitch and Hulatt[97]. It should also be emphasised that reproducible rate constants by no means require the reaction to be homogeneous. In both the isomerisation of 1,2-dichloroethylene and the thermal decomposition of azomethane reproducible rate constants were obtained which could be lowered by subsequent conditioning. Thus a similarity between the rates obtained in a packed vessel with those obtained in the unpacked vessel is not necessarily evidence for the non-

existence of a surface reaction unless it has been previously ascertained that both surfaces are in the same state.

(11.4) ARRHENIUS PARAMETERS FOR THE THERMAL DECOMPOSITION: In Table 11.2 we have gathered together the frequency factors and activation energies obtained in the various researches. The inadequacy of the early work by Ramsperger[8] and by Rice and Sickman[11] has already been discussed (see 4.2). To this must now be added a fresh criticism - namely that the rates do not refer to a non-chain process. In this respect the work by Page, Pritchard and Trotman-Dickenson[56], in which the Toluene Carrier technique was used, is still valid, since the chain-initiating methyl radicals are removed by the reaction

$$C_6H_5CH_3 + CH_3 \rightarrow C_6H_5CH_2 + CH_4 \quad . \qquad (16)$$

The benzyl radicals then combine to form dibenzyl and so cause no complication. However, it is unfortunate that the authors did not investigate the possibility of surface reaction by packing the vessel. There is no report in the work of Taylor and Jahn[52,55] that they conditioned their reaction vessel or that they checked the effect of packing. Furthermore, because of the complexity of the overall reaction, the rates based on azomethane consumption cannot be identified with the elementary reaction

$$CH_3N{=}NCH_3 \rightarrow 2CH_3 + N_2 \quad . \qquad (17)$$

Thus, in view of discussion in the last two sections, it is perhaps not too harsh to say that the results of previous work are of doubtful significance. The rate expression found in this research for the fully-inhibited reaction can only be accepted as giving the correct Arrhenius equation for reaction (17) when it has been established by further experiment that a large variation in the surface-to-volume ratio does not affect the rate of decomposition.

In the work of Page, Pritchard and Trotman-Dickenson the total pressure in the flow system was only 15 mm. Thus the values obtained for the frequency factor and activation energy are not necessarily the same as those which would be obtained at high pressures. It will be remembered that the

theories of Kassel, Eyring and Slater identify only the high-pressure activation energy with the bond dissociation energy (see 2.9); thus, since the theories also indicate that the activation energy should be a function of pressure, we cannot use an activation energy which is obtained in the pressure-dependent region as a measure of the bond dissociation energy of the rupturing bond. This important concept does not seem to have been appreciated by some authors. Cottrell[98], for instance, referring to the work of Page et al., gives $D(CH_3NN-CH_3)$ the value 46 kcal.

But in the case of azomethane there is an objection to identifying even the high-pressure activation energy with the bond dissociation energy. The frequency factors obtained at high pressures are larger than would normally be expected. Thus, following Pritchard's[34] suggestion for the mode of decomposition of certain ketones and metal alkyls, it seems likely that azomethane decomposes by a simultaneous rupture into three fragments by reaction (17) rather than by the two-stage process:

$$CH_3N{=}NCH_3 \rightarrow CH_3N{=}N + CH_3 \ , \tag{18}$$

$$CH_3N{=}N \rightarrow CH_3 + N_2 \ . \tag{19}$$

For a reaction A-B-A → A + B + A involving the simultaneous rupture of two bonds, the critical energy ϵ_0 must be localized in the bond-oscillators which are associated with the reaction, and Pritchard assumes that

$$\epsilon_0 = D_1(AB-A) + D_2(A-B) \ . \tag{20}$$

Thus we have, for the theories of Kassel, Eyring and Slater,

$$E_\infty = D_1 + D_2 \ . \tag{21}$$

For azomethane, Page, Pritchard and Trotman-Dickenson have estimated that $D_1 + D_2 = 22$ kcal. This does not agree with the experimental value of E_∞.

It is interesting to note that molecules which possess high frequency factors have a plane of symmetry which is perpendicular to the rupturing bonds. It might be imagined that this symmetry would facilitate internal

energy transfers, that is, coupling of the bond oscillators should be especially easy.

It is perhaps not out of place to re-emphasise at this point that, although reaction may involve the simultaneous rupture of two carbon-nitrogen bonds, it is not necessary that the minimum energy required for reaction should be equal to twice the strength of a normal carbon-nitrogen single bond (2 x 81 kcal.)[62,63]. As the carbon-nitrogen bonds are broken, the two σ-electrons which are associated with the bonds and which would normally end up in the 2p atomic orbitals of nitrogen, in fact are accommodated in the vacant π2p molecular orbital. This large "reorganisation" energy means that the activation energy can be much less than 2 x 81 kcal.

(11.5) THE RATE CONSTANT AS A FUNCTION OF PRESSURE: In Fig. 9.4 we showed the variation in the first-order rate constant with initial azomethane pressure. The results of McCoy[99], who carried out a mass spectrometric study of the reaction, and of Ramsperger[8] and Rice & Sickman[11], who followed the reaction by pressure measurements, have been added for comparison. McCoy's method of analysis is not known since the work does not appear to have been published. The data have been taken from a report by Willbanks[100] in which McCoy's experimental rates have been plotted.

In view of the complexities mentioned in 12.2 and 12.3 it may well be asked if the experimental work can be used to test the theories of unimolecular reaction. The inadequacy of the work by Ramsperger and by Rice & Sickman has already been mentioned, and the experimental conditions

employed by McCoy are not known. The discussion will therefore be limited to the results obtained in this research.

The surface-to-volume ratio of the small reaction vessel was approximately $2\frac{1}{2}$ times greater than the surface-to-volume ratio of the large vessel, but the rates obtained in the presence of excess propylene were the same for both vessels (see Fig. 10.5). We shall therefore assume that when the vessels were seasoned with allyl bromide all the surface reaction was inhibited. Of course, this should be checked by experiments over a wider range of surface-to-volume ratios using a packed reaction flask.

In the pressure range 0.2 - 158.5 mm. there is a tenfold change in rate constant and we know that the chain reaction accounts for about 50% of the reaction at high pressures. Thus, even if the chain length did vary, it could account for only part of the change in rate which is observed experimentally. Furthermore, it is likely that the proportion of chain reaction for runs carried out in the small reaction vessel is different from that for runs in the large reaction vessel; nevertheless, the shapes of the two fall-off curves are similar. This also indicates that the dependence of the rate on pressure is not a property of the chain reaction. Lastly, the value of α_p for carbon dioxide does not vary appreciably over a large range of pressures and this would not be so if the shape of the fall-off curve was affected by factors other than energy transfer. Thus all the indications are that the rate-constant/pressure curves can only be accounted for in terms of unimolecular theory. There is, therefore, some justification for comparing our results with the theoretical rate-constant/pressure curves, and this we have done in Fig. 11.1.

The position of the Hinshelwood curve is dependent upon the choice of λ'' (see equation 2.18). This has been chosen to give the best fit with the experimental points and the diagram clearly shows the inadequacy of the model. Recently E. W. Willbanks[100] has evaluated the Kassel integral (see equation 2.12) with the aid of a high-speed digital binary computer and the Kassel curve in the diagram is that obtained by him for $M = 58.1$, $E_\infty = 50.4$ kcal. per mole, $\sigma = 4.7$ Å and $s = 12$ (see 2.13). No specific

calculations can be made for Slater's model since a vibrational analysis of azomethane has not been performed. However, calculations have been made[28] for a hypothetical molecule having $M = 50$, $E_\infty = 55.6$ kcal., $\sigma = 5$ Å, $n = 13$, $\bar{\nu} = 5 \times 10^{13}$ sec.$^{-1}$ The values of $\log k/k_\infty$ and $\log p_\alpha$ were calculated from the general parameters $I_n(\theta)$ and θ which have been tabulated. The absolute position of the curve is not certain; dependent on how the n vibrational modes contribute to the reaction coordinate, p_α/θ can vary from a minimum value of 9×10^{-6} to a "representative" value of 7×10^{-4}. The p_α's here are "representative" pressures. It should be pointed out that the slopes of the Kassel and Slater curves are not sensitive to the values of s and n; the main effect of a change in these values is a change in the position of the curves.

(11.6) ACTIVATION ENERGY AS A FUNCTION OF PRESSURE: Both the Kassel and the Slater theories predict that the activation energy should decrease with decreasing pressure in the region in which the rate constant is also found to be pressure-dependent. However, there is little experimental evidence to confirm this important prediction. Mills and Johnston[101] found that for the decomposition of nitrogen pentoxide in the presence of nitric oxide the energy of activation at the low-pressure limit was 14.5 ± 2 kcal. per mole, whilst at the high-pressure limit the value was 21 ± 2 kcal. per mole. It has also been suggested that the negative activation energy of -2.2 kcal. per mole found by Ingold and Lossing[102] for the combination of methyl radicals is in accordance with the theoretical predictions if the reaction has a zero activation energy at high pressures. But the negative activation energy could also be a result of the change in the effective collision diameter of the methyl radicals with temperature.

Fig. 9.5 shows a most convincing decrease in activation energy with decreasing pressure for the thermal decomposition of azomethane. Because of the presence of chains in the reaction, this cannot be accepted as an experimental verification of the Kassel/Slater models without more detailed examination. It has been shown that the percentage of chain reaction does not vary significantly over the pressure range studied, so the change in activation energy cannot be explained by a change in the proportion of the

chain process in the overall reaction. Moreover, there is little difference between the activation energies of the inhibited and the uninhibited reactions at high pressures (see Fig. 9.5). However, there is a significant difference between the activation energies at 15 mm. determined by Page, Pritchard and Trotman-Dickenson using the Toluene Carrier technique and the value found in this research for the fully inhibited reaction at 190 mm. (see Table 11.2). In the former case there was an excess of toluene so presumably there was little chain reaction. Thus the 5 kcal. difference between the activation energies cannot be explained in terms of a varying chain contribution.

It might also be argued that the change in activation energy is associated with a heterogeneous process at low pressures but this is not consistent with the observed decrease in rate constant and decrease in frequency factor (see Table 9.4).

It would therefore appear that the variation in activation energy with pressure is a result of the quasi-unimolecular nature of the reaction. Recently Slater[33] has made some detailed calculations of this effect and in Fig. 11.2 we have compared the experimental curve with the theoretical curve. From the values of k/k_∞ and $\frac{1}{2}nRT$, tabulated by Slater, E was calculated as a function of log k/k_∞, taking E_∞ = 52 kcal. per mole, n = 15 and T = 563°K. By assuming log $k_\infty^{563} = \bar{4}.30$, E was then calculated as a function of log p_a, using the experimental relationship between log k^{563} and log p_a found in this research (see Fig. 9.4). Although the curves do not agree well it is impressive that the main fall-off in activation energy occurs in precisely the region calculated.

TABLE 11.1

THERMAL DECOMPOSITION OF AZOMETHANE/PROPYLENE MIXTURES.

GAS CHROMATOGRAPHIC ANALYSES FOR BUTENES AND METHYLCYCLOPROPANE.

Columns: Firebrick (52-72 mesh) 80%. Nitrobenzene 20%.

Carrier Gas: Hydrogen

Detection Gauge: Thermal Conductivity

Representative run A(large reaction vessel):

Initial pressure azomethane = 5 mm.

Initial pressure propylene = 8 mm.

Reaction time = 60 min.

Reaction temperature = 565°K.

Analysis for C_4H_8: 1-butene present, 2-butene and/or methylcyclopropane present.

Representative run B (small reaction vessel):

Initial pressure azomethane = 300 mm.

Initial pressure propylene = 300 mm.

Reaction time = 30 min.

Reaction temperature = 565°K.

Analysis for C_4H_8: trace of 1-butene, 2-butene and/or methylcyclopropane undetectable.

TABLE 11.2. ARRHENIUS PARAMETERS FOR THE THERMAL DECOMPOSITION OF AZOMETHANE.

Authors	log A_1 ($sec.^{-1}$)	E (kcal.)	Remarks		
			Total Press. (mm.)	Method of Rate Determination	General
Ramsperger	16.5	52.5	extrap. to ∞	pressure increase	
Rice & Sickman	15.9	50.2	extrap. to ∞	pressure increase	
Taylor & Jahn	16.5	52.5	91-141	$C_2N_2H_6$ decomposed	
Jahn & Taylor	15.8	51.4	331-480	$C_2N_2H_6$ decomposed	twofold excess of NO.
Page, Pritchard & Trotman-Dickenson	14	46	15	N_2 formed	Toluene Carrier system.
This work	15.7	51.2	139-191	N_2 formed	excess propylene.
	16.4	52.0	159	N_2 formed	
	13.1	46.2	0.2	N_2 formed	

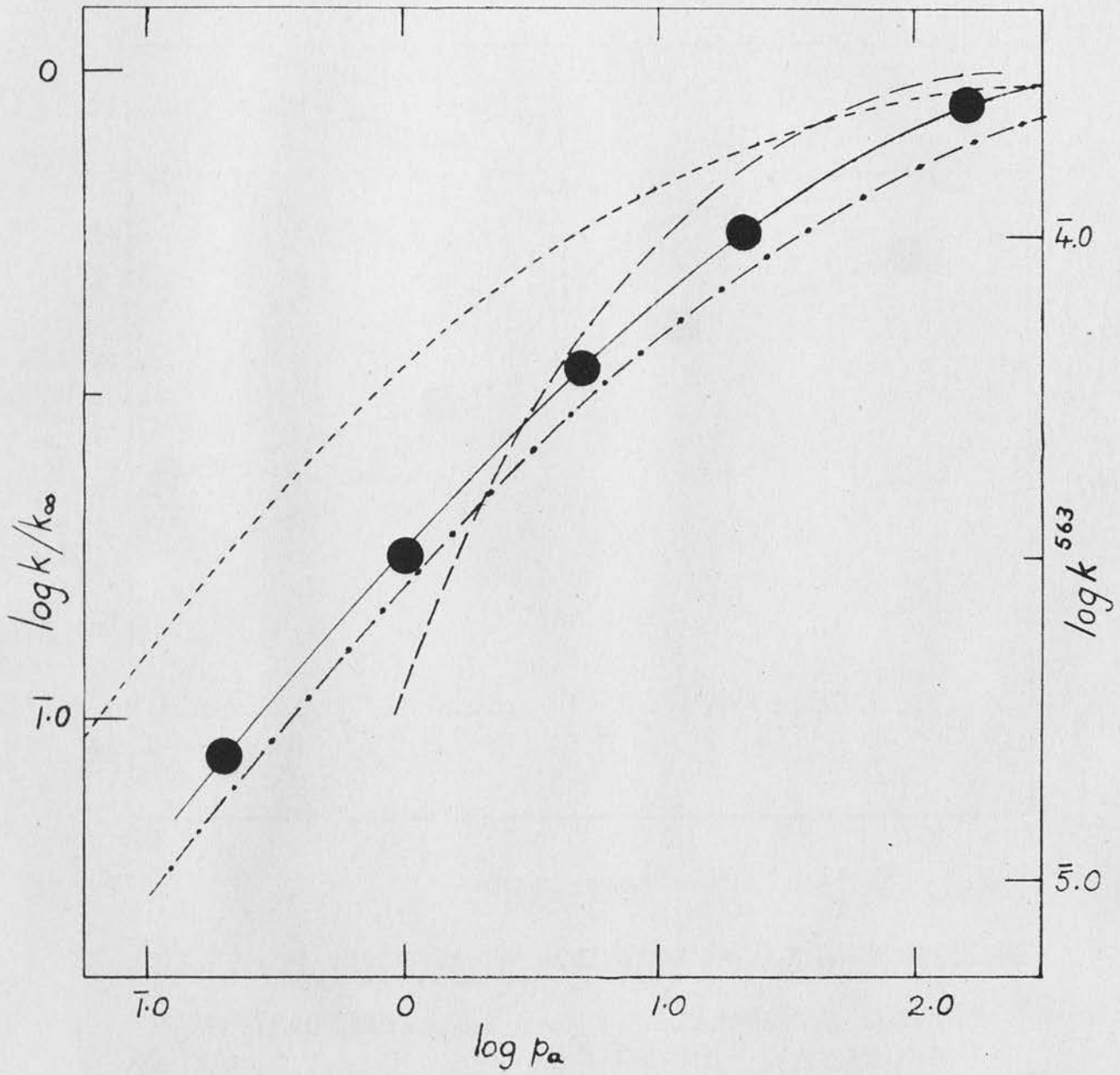


FIG. 11·1 THE VARIATION IN RATE CONSTANT WITH PRESSURE

THEORETICAL CURVES
(ORDINATE $\log k/k_\infty$)

— — — HINSHELWOOD

—·—·— KASSEL (s = 12)

------- SLATER (n = 13)

EXPERIMENTAL CURVE
(ORDINATE $\log k^{563}$)

——— THERMAL DECOMPOSITION OF AZOMETHANE AT 563°K.

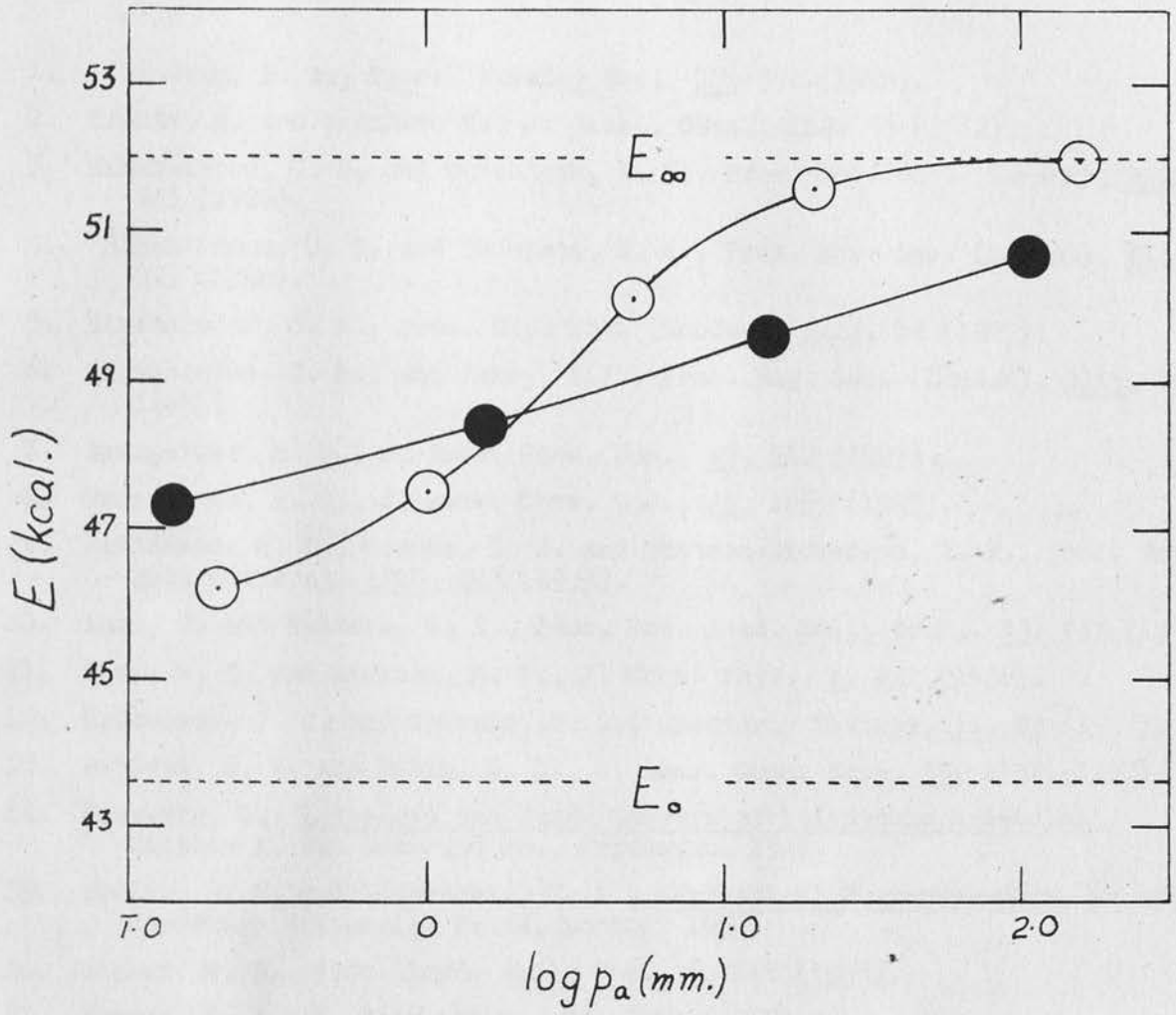


FIG. 11·2 THE VARIATION IN ACTIVATION ENERGY WITH PRESSURE

THEORETICAL CURVE
● SLATER (n = 15)

EXPERIMENTAL CURVE
⊙ THERMAL DECOMPOSITION OF AZOMETHANE

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APPENDIX

MODIFICATIONS TO HATT'S METHOD FOR THE PREPARATION OF 1,2-DIMETHYLHYDRAZINE DIHYDROCHLORIDE.

(a) 1,2-dibenzoylhydrazine:

(i) The saturation with carbon dioxide to precipitate all the dibenzoylhydrazine was carried out by simply adding several lumps of I.C.I. "Drikold".

(ii) The purification of the dibenzoylhydrazine by treatment with acetic acid was found to be unsatisfactory since the basic dibenzoylhydrazine tended to combine with the acid. Indeed, the yield of product obtained by Hatt's method was always greater than the theoretical yield of dibenzoylhydrazine. Furthermore, it was found impossible to dissolve the dibenzoylhydrazine in the amount of acid suggested. Even when much larger amounts of acetic acid were used the material precipitated out very rapidly and filtration had to be carried out on a boiling solution. The product so obtained was examined under the microscope. At 200°C the crystalline form changed and the remaining material melted close to the value given in the literature for dibenzoylhydrazine. On heating a quantity of the original product copious amounts of acetic acid were evolved.

For these reasons the purification was carried out in the following manner. The crude material was washed repeatedly with water, which was saturated with carbon dioxide, and then with alcohol. The first operation removed free base, and the first and second any hydrazine sulphate. B enzoyl chloride was removed by washing with ether. The m.p. of the product so obtained was 238°C. (Literature: 234-235°C, 241°C).

(b) 1,2-dibenzoyl-1,2-dimethylhydrazine:

(i) The material tended to separate from the reaction mixture as an oil, but cooling in ice and adding a 1:1 mixture of ether and petrol ether induced rapid crystallisation.

(ii) It was again found impossible to dissolve the product in the amount of solvent recommended; solution could only be effected in an excess of boiling chloroform. The volume of chloroform was reduced by distillation under reduced pressure. The material could then be extracted by adding an excess of ether/petrol-ether. On reducing the volume of the mother liquor and on adding more ether/petrol-ether more product was obtained. m.p. 83-84°C (Literature: 85°C).

(c) 1,2-dimethylhydrazine dihydrochloride:

Most of the benzoic acid separated out during the reaction and was removed by filtration. It was found more convenient to remove the remaining acid by solvent extraction, using a 1:1 mixture of ether and benzene, rather than by the recommended steam distillation. The crystals, which were obtained after several recrystallisations from ethyl alcohol acidified with hydrochloric acid, still tended to be impure (i.e. the m.p. was low). Pure crystals could be obtained, at the expense of yield, by repeated crystallisations. But this was not found to be necessary since the impure dihydrochloride gave 100% pure azomethane in the final stage of the preparation. m.p. 140-150°C (Literature: 168°C).