STIRRED FLOW THERMOLOYSIS
OF HEXAMETHYLDISILANE

A Thesis presented by
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for the degree of
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To my Mother and Father,
without whose help my higher education
would not have been possible.
I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

Sir Isaac Newton

A short time before his death.
STATEMENT

The experimental work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester, between September 1970 and September 1973.

The work has not been presented, and is not being concurrently presented for any other degree.

January 1974

Signed A.N. KNOWL

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# CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction.</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>The Theory and Application of the S.F.R. Sample Injection Technique.</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>Chemical Reactors.</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>The S.F.R. Under Steady State Conditions.</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Our Experimental Technique - The S.F.R. Sample Injection Technique.</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>An Examination of our Reaction Conditions.</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>A General Method for the Derivation of Rate Constants in Terms of Known Parameters.</td>
<td>26</td>
</tr>
<tr>
<td>2.6</td>
<td>Differences in Temperature and Pressure Between the Reactor and Other Parts of the Flow System: Their Effect on Rate Expressions.</td>
<td>34</td>
</tr>
<tr>
<td>2.7</td>
<td>The Development of Similar Techniques.</td>
<td>40</td>
</tr>
<tr>
<td>2.8</td>
<td>Conclusions Regarding the 'Stirred Flow Reactor Sample Injection Technique'.</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>Apparatus and Experimental Procedure.</td>
<td>44</td>
</tr>
<tr>
<td>3.1</td>
<td>Apparatus - The Flow System.</td>
<td>44</td>
</tr>
<tr>
<td>3.2</td>
<td>Apparatus - The Sampling System.</td>
<td>59</td>
</tr>
<tr>
<td>3.3</td>
<td>Experimental Procedure.</td>
<td>60</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Results.</td>
<td>Page</td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>4.1</td>
<td>Preliminary Experiments and Information.</td>
<td>66</td>
</tr>
<tr>
<td>4.2</td>
<td>Series (1) HEDS Thermolysis in the Absence of m-Xylene.</td>
<td>71</td>
</tr>
<tr>
<td>4.3</td>
<td>Series (2) HEDS Thermolysis in the Presence of Excess m-Xylene.</td>
<td>76</td>
</tr>
<tr>
<td>4.4</td>
<td>Series (3) Thermolysis Experiments at Varied Flow Rates.</td>
<td>79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 5</th>
<th>Discussion.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Evaluation of Rate Parameters.</td>
<td>83</td>
</tr>
<tr>
<td>5.2</td>
<td>Quantitative Consideration of Scheme (1).</td>
<td>86</td>
</tr>
<tr>
<td>5.3</td>
<td>Quantitative Consideration of Scheme (2).</td>
<td>92</td>
</tr>
<tr>
<td>5.4</td>
<td>Tetramethylsilane Formation.</td>
<td>97</td>
</tr>
<tr>
<td>5.5</td>
<td>Comparison with the Results of Other Workers.</td>
<td>99</td>
</tr>
<tr>
<td>5.6</td>
<td>Conclusion.</td>
<td>101</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Appendix I</th>
<th>Preparation and Purification of Compounds.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>103</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Appendix II</th>
<th>Useful Data and Calculations.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>106</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Appendix III</th>
<th>Full Kinetic Results.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>109</td>
</tr>
</tbody>
</table>

References 125
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The basis of the flow system (schematic).</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Graph of [Reactant] v Time.</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>Graph of [Product] v Time.</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Recorder trace of the outflow of inert substance from the reactor.</td>
<td>25</td>
</tr>
<tr>
<td>3.1</td>
<td>The Flow System (Schematic).</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>The Sampling System.</td>
<td>46</td>
</tr>
<tr>
<td>3.3</td>
<td>The Reaction Vessel.</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Furnace Heater - Wiring Diagram.</td>
<td>49</td>
</tr>
<tr>
<td>3.5</td>
<td>Temperature Profile of Furnace.</td>
<td>49</td>
</tr>
<tr>
<td>3.6</td>
<td>Sodium Trap.</td>
<td>53</td>
</tr>
<tr>
<td>3.7</td>
<td>Heating Jacket - for Sample Reservoir.</td>
<td>53</td>
</tr>
<tr>
<td>3.8</td>
<td>The Sampling Valve.</td>
<td>54</td>
</tr>
<tr>
<td>3.9</td>
<td>The Cold Trap.</td>
<td>55</td>
</tr>
<tr>
<td>3.10</td>
<td>The Detector (Schematic).</td>
<td>55</td>
</tr>
<tr>
<td>3.11</td>
<td>A Typical Chromatogram.</td>
<td>63</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Me₃SiH Formation in the absence of Inhibitors. First Order Plots.</td>
<td>73</td>
</tr>
<tr>
<td>4.2.2</td>
<td>'Isomer' Formation in the absence of Inhibitors. 1-5 Order Plots.</td>
<td>74</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Me₃SiH Formation in Xylene. First Order Plot.</td>
<td>78</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Me₄Si Formation in Xylene. First Order Plot.</td>
<td>78</td>
</tr>
<tr>
<td>4.3.3</td>
<td>'Isomer' Formation in Xylene. 1-5 Order Plot.</td>
<td>78</td>
</tr>
</tbody>
</table>
Figure
4.5.1 Formation of Me₃SiH – Arrhenius Plots. 81
4.5.2 Formation of 'TMDS' – Arrhenius Plot. 81
4.5.3 Formation of 'Isomer' – Arrhenius Plots. 82
4.5.4 Formation of Me₄Si – Arrhenius Plots. 82

LIST OF TABLES

Table
3.1 Some Typical Chromatographic Data. 62
5.1.1 Thermolysis of HMDS in the absence of inhibitors: Reaction Scheme (1), and rate parameters. 84
5.1.2 Thermolysis of HMDS in the presence of m-Xylene: Reaction Scheme (2) and rate parameters. 85
5.1.3 Bond Dissociation Energies. 90
5.1.4 Enthalpies of Formation of Gaseous Species. 91
5.2.1 Rate Expressions for the Formation of Me₃SiH in HMDS Thermolysis: No inhibitors. 94
5.2.2 Rate Expressions for the Isomerisation of HMDS: No inhibitors. 95

Tabulated Kinetic Data. 111
Tabulated Rate Constants. 123
CHAPTER ONE

INTRODUCTION
INTRODUCTION

The work described in this thesis, falls naturally into two distinct sections: the development of a novel stirred flow reactor technique for the study of gas phase reactions, and it's application to a kinetic study of the thermolysis of hexamethyldisilane. Full consideration is given to the technique in Chapters Two and Three, and so very little comment will be made here.

The thermolysis of hexamethyldisilane (HMDS) has been undertaken by several groups of workers, with the result that a complex mechanistic behaviour has been revealed\(^1\)\(^-\)\(^8\). This is found to be most simple at high partial pressures of HMDS (>10 torr), and low temperatures (673-780K.)\(^3\)-\(^5\), where virtually only one product, the rearrangement isomer (2,2,4-Trimethyl-2,4-disilapentane) is produced\(^1\)\(^-\)\(^5\). The formation of this product ("the isomer") is now well understood, in terms of a three halves order chain mechanism\(^5\), although the chain length is seen to vary with conditions\(^2\),\(^4\).

At lower pressures of HMDS many more products have been observed\(^6\),\(^7\),\(^8\), but in spite of this the overall rate of reaction was thought to be first order and rate determined by the unimolecular decomposition:

\[
\text{Me}_2\text{SiSiMe}_2 \rightarrow 2\text{Me}_2\text{Si}^* 
\]

This condition is conducive to the kinetic determination of the bond dissociation energy D(Me\(_2\)Si—SiMe\(_2\)), and as a consequence of this, kinetic studies conducted by Haszeldine et. al.\(^6\),\(^7\), and by Davidson and Stephenson\(^8\), produced values for this parameter. (A short discussion on bond dissociation energies (B.D.E.'s) is given below.)

However when measurements by electron impact were included\(^6\),\(^9\), the range of 'values' for D(Me\(_2\)Si—SiMe\(_2\)) was 201-359 kJ mol\(^{-1}\).
The highest figure was based on an appearance potential measurement by Hess, Lampe and Sommer, which was found to be 0.7 eV higher than that observed by two other independent groups of workers. When this discrepancy was accounted for, and allowance made for other errors likely in their method, the resulting value for $D(\text{Me}_3\text{Si}—\text{SiMe}_3)$ was in reasonable agreement with that of Davidson. From careful consideration of Haszeldine's kinetic work, it can be seen that the experimental conditions, which involved very low pressures of HMDS, a vessel of large surface/volume ratio, very high percentage decomposition, and high temperatures, are likely to have enhanced heterogeneous reactions and also chain reactions. Both these effects would have reduced the value of their estimate for $D(\text{Me}_3\text{Si}—\text{SiMe}_3)$. Indeed, their values (205 ±25 and 243 ±17 kJ mol$^{-1}$), when compared with that of Davidson (282 kJ mol$^{-1}$) support this view. A full account of the relative merits of these bond dissociation energy determinations has been given elsewhere.

On the other hand, the kinetic studies of Davidson and Stephenson, were carried out at very low percentage decomposition, and involved elaborate precautions to remove surface reactions. In the face of an extremely difficult analytical problem, (which must also have been experienced by Haszeldine), the peak m/e 203, which was assigned to a combination product, was followed mass spectrometrically. A non-chain mechanism was proposed to explain all the observations, and a value for $D(\text{Me}_3\text{Si}—\text{SiMe}_3)$ of 282 ±8 kJ mol$^{-1}$. was proposed.

This value, and B.D.E. values for other bonds which were calculated using this as a standard, were found to be in close agreement with other independent determinations of B.D.E.'s, and were well accepted. (See Reference (12).)

Nevertheless, in spite of this, there were two discouraging
features of the work. Firstly, the $A$ factor of $10^{13.5}$ (sec$^{-1}$) is low for a unimolecular bond fission and is seen to be in conflict with recent work on the recombination of trimethylsilyl radicals in solution and in the gas phase. Trotman-Dickenson and coworkers obtained a value of $10^{14.25}$ (cm$^3$ mol$^{-1}$ sec$^{-1}$) for the recombination rate constant, from which they estimated a value of $10^{18.4}$ (sec$^{-1}$) for the dissociation $A$ factor. Secondly, the most convincing support for the value of $D(\text{Me}_3\text{Si—SiMe}_3)$ as 282 kJ mol$^{-1}$ are the values of $D(\text{Me}_3\text{Si—H}) = 340$ kJ mol$^{-1}$ and $D(\text{Me}_3\text{HSi—Me}) = 324$ kJ mol$^{-1}$, which result from a kinetic study on the thermal decomposition of trimethylsilane. (See Reference 12.) However, these latter figures rely on a non-chain thermal decomposition of trimethylsilane which might be in doubt, in view of a recent proposal that tetramethylsilane decomposed by a chain process.

In view of these discrepancies we decided to re-investigate the thermolysis of hexamethyldisilane by a chromatographic sampling technique.

The method finally developed is a novel one and is described schematically in Figure 1.1. Pure carrier gas flows steadily through a sampling valve, a stirred flow reactor (S.F.R.), a cold trap, a G.L.C. column, and detector. A 'pulse' of sample vapour, injected into the gas stream at the valve, is carried through the reactor to the cold trap, where it is condensed along with reaction products. On warming the trap, the mixture vapourizes and is resolved, before each component is quantitatively recorded by the detector.

The details of our re-investigation of hexamethyldisilane thermolysis are described in Chapters Four and Five, and a brief discussion of bond dissociation energies, and their determination by kinetic methods is given below.
Bond Dissociation Energies.

The bond dissociation energy \( D \), is normally defined as the enthalpy change \( \Delta H_1 \) in a chemical process, in which one mole of a specified bond is broken; reactants and products being in the ideal gas state. Thus for the process:

\[
A - B (g) \xrightarrow{1} \xleftarrow{-1} A^* (g) + B^* (g)
\]

\[ D(A-B) = \Delta H_1 = \Delta H_f(A^*) + \Delta H_f(B^*) - \Delta H_f(AB) \]  \hspace{1cm} (1,1)

where \( \Delta H_f(A^*) \) is the heat of formation of \( (A^*) \) etc.

Since \( \Delta H_1 \) changes slightly with temperature, then for comparative purposes, a standard temperature at which values may be tabulated and compared, is useful. The temperature normally chosen for this purpose is 298K \(^{19,20}\). In practice however, corrections to 298K, being small, are only made on values which are known precisely.

The values of bond dissociation energies are a quantitative measure of the forces which hold together the parts of a molecule, and as such, provide vital information regarding the rates and mechanisms of radical reactions. Also, because bond dissociation
energies (B.D.E.'s) can be used to evaluate other thermochemical data, including heats of formation, ionisation potentials, and other B.D.E.'s, they are invaluable to the understanding of the chemistry of a series of similar compounds.

There are a number of ways in which B.D.E.'s can be determined directly, which include electronic spectroscopy, measurements of thermal equilibrium, Appearance Potential measurements, and kinetic methods. Electronic spectroscopy is limited to the determination of B.D.E.'s in diatomic molecules, while thermal equilibrium is inapplicable when the radicals produced undergo reactions other than recombination, which is often the case. The most commonly used methods, for the determination of B.D.E.'s in polyatomic molecules, are therefore the measurement of Appearance Potentials, and kinetic methods. The theory and application of the appearance potential method, has been discussed in detail by past members of this group, and since it is not directly relevant to this work, will not be discussed here.

**Kinetic Methods.**

This may be divided into the study of thermolytic reactions and metathetical reactions.

In order that a given B.D.E. may be determined from the kinetic study of a thermolytic reaction, the study must yield an accurate rate constant and Arrhenius parameters which can be identified with the unimolecular homolytic fission of the bond in question. The relationship between the energy of activation of the process, and the B.D.E. is as follows:

\[
D(A\rightarrow B) = \Delta H_1 = \Delta E_+ + RT = E_1 - E_- + \Delta nRT \tag{1.2}
\]

where \(E_1\) & \(E_-\) are the activation energies of the forward
and reverse reactions, and \( \Delta n \) is the change in the number of moles accompanying the reaction. For the process (1) above, \( \Delta n = 1 \).

Since there is very good evidence to suggest that the activation energy for the recombination of radicals is zero\(^{16,24} \) then:

\[
D(A-B) = \Delta H \_1 = E_1 + RT \tag{1.3}
\]

In order to express the value of \( D(A-B) \) at 298K, \( E_1 \) must be corrected from its measured value (which will normally have been obtained at well above 298K) to 298K. This correction roughly cancels with the RT term.

Hence,

\[
D(A-B) \triangleq E_1
\]

The exact relationship between \( D(A-B) \) and \( E_1 \) has been considered by Szwarc\(^{25} \), who has shown that the errors involved are less than 2 kcal. mole\(^{-1} \) up to 1000K.

The problem has therefore been reduced to the determination of the activation energy \( E_1 \). The most serious difficulty here, is quite often not the experimental determination of the Arrhenius activation energy associated with the overall rate of formation or decay of a given compound, but the identification of this parameter with the unimolecular bond fission (1). This requires a clear understanding of the overall mechanism, which is often complex, particularly when an appreciable concentration of products is built up. It is therefore often advisable to study the initial stages of a reaction. Because of this, flow systems have been widely used for the kinetic determination of B.D.E.'s, since they permit reaction times very much shorter than is possible in a static system. Reactions which are simple non-chain processes at low percentage decomposition can therefore be studied by following initial rates, since the reaction will be rate determined by the unimolecular bond fission. However many
thermolytic decompositions involve chain reactions of the Rice Herzfeld type.

The following scheme (X):

\[ M \rightarrow R_1^* + R_2^* \quad (\text{INITIATION}) \]

\[ R_1^* + M \rightarrow R_1H + R_3 \quad (\text{PROPAGATION}) \]

\[ R_3^* + M \rightarrow R_1^* + M' \quad (\text{RE combination}) \]

\[ R_1^* + R_3^* \rightarrow M'' \quad (\text{TERMINATION}) \]

where \( M \) is an organic molecule, and \( M' \) is unsaturated would give:

\[- \frac{d[M]}{dt} = \left( \frac{k_2 k_3 k_4}{k_5} \right)^{\frac{1}{2}} [M] \]

Hence:

\[ E = \frac{1}{2}(E_2 + E_3 + E_4 - E_5) \]

since \( E_2 = 0 \), and \( E_4 \) and \( E_5 \) are normally much smaller than \( E_2 \), then \( E \ll E_2 \).

Regardless of the first order kinetics observed, the overall activation energy \( E \) cannot be related to the unimolecular decomposition, and the use of \( E \) to represent the value of \( D(R_1-R_2) \) would produce an unrepresentative, low, figure.

This type of mechanism can often be simplified by the use of the toluene carrier technique\(^2\); a flow technique in which toluene vapour is used as the carrier gas. Aniline has also been used for this purpose\(^3\). It is required however that the bond under study must be weaker than \( D(\text{PhCH}_2-\text{H}) \) (356kJ) (or \( D(\text{PhNH}-\text{H}) \) 334kJ) as the carrier must be thermally stable under the experimental conditions.
The above scheme would then be reduced to a simple non-chain mechanism, the propagation steps (3) and (4) being replaced by:

\[ R_1^* + \text{PhCH}_3 \rightleftharpoons R_1^+ + \text{PhCH}_2^* \]

the only termination step being the combination of the resonance stabilized benzyl radicals. The overall process is then rate determined by reaction (2). The temperature dependence of \( k_2 \) thus yields \( E_2 \), and hence \( D(R_1-R_2) \).

A full account of all aspects of bond dissociation energies may be obtained from a number of publications .
CHAPTER TWO

THE THEORY AND APPLICATION OF THE

'STIRRED FLOW REACTOR SAMPLE INJECTION TECHNIQUE'
(2.1) Chemical Reactors.

In general chemical reactors may be considered to be of two types, (a) the Static System or Batch Reactor, and (b) the Flow System. Reactions in a static system occur at constant volume, while those in a flow system occur at constant pressure.

It will be shown shortly, that flow systems may be most conveniently divided into two types, (i) the Tube Flow Reactor, and (ii) the Stirred Flow Reactor or Stirred Tank Reactor.

Both types of flow reactor have normally been used under steady state conditions. That is, the experimental conditions at any point within the reactor, do not change throughout the course of the experiment. This is achieved by allowing the reactant(s) (sometimes in the presence of carrier gas or solvent) to flow at a constant rate through the reaction vessel. Because of chemical reaction within the vessel, the effluent will contain reaction products, and the rate of flow of reactant(s) from the vessel will be correspondingly less than that entering. Chemical reaction may therefore be balanced against flow rates.

Kinetic studies conducted in flow systems, are subject to certain restrictions, which do not normally affect similar experiments carried out in a static system. These are: (1) that the extent of mixing (normally due to diffusion and convection) within the reactor should be accurately known, (2) that the effect of any change in volume accompanying the reaction may be accounted for, (3) that the total volume of the reactor is used by the 'reacting stream' on its way through the vessel, and (4) that the temperature throughout the reactor volume should be constant. It is in connection with the first
point that flow reactors may be divided into two types, (a) those in which negligible mixing occurs, and (b) those in which complete mixing occurs. An intermediate degree of mixing is found to be an impracticable condition for kinetic studies. (See page 11.)

Negligible mixing is most nearly achieved in narrow bore tubular reactors, while complete mixing is said to have been achieved in a number of ways which include: mechanical stirring, diffusion in wide bore tubes, a fluidized bed, and forced convection. Reactors which are said to achieve the first condition are known as Tube Flow Reactors, while those said to achieve the latter condition are referred to as Stirred Flow Reactors or Stirred Tank Reactors.

The Stirred Flow Reactor (S.F.R.) has the advantage that, when used in a steady state condition, the kinetic equations associated with it's use are of a simple arithmetic type. Also, complications due to any volume change accompanying the reaction can be removed. These points will be discussed later.

The Mulcahy design of S.F.R. has been fairly well tested, and has been found to produce efficient mixing which utilises the total volume of the reactor. It's spherical shape and efficient mixing have also been found to produce minimum temperature non-uniformities.

For these reasons, the Mulcahy design of reactor was chosen for our work. Our experiments however, do not involve the continuous flow of material through the reactor, merely the passage of a short 'pulse' of reactant vapour. A description and examination of these experiments will be given later.
(2.2) The Stirred Flow Reactor (S.F.R.) under Steady State Conditions.

A clear understanding of the properties of the stirred flow reactor under steady state conditions, will be required in order to consider the more complex conditions existing in our experiments, where a 'pulse' of reactant vapour is passed through the reactor. A short discussion on this topic is therefore given below.

Background.

Bodenstein and Wolgast\textsuperscript{41} were the first to realise that diffusion within a flow reactor could render the usual kinetic expressions invalid, and were the first to derive an expression applicable under "stirred flow" conditions. Their study of the rate of combination of Hydrogen and Iodine in the gas phase was treated in this way, and may be regarded as the first kinetic study conducted in a stirred flow reactor. Langmuir\textsuperscript{42} was the first to discuss the effect of volume change on kinetic expressions, and the first to consider conditions of partial mixing due to convection and diffusion. Further consideration has been given to conditions of incomplete mixing\textsuperscript{43}, but the expressions produced, are sufficiently complicated, to render these conditions of little use for kinetic studies. The most useful advances in stirred flow reactor technique, have therefore been made by the consideration of conditions under complete mixing, and by the development of equipment which most nearly achieves complete mixing.

Much of the general theory has been developed by Denbigh\textsuperscript{44,45}, who has also given particular consideration to studies in the liquid phase\textsuperscript{46}, while Harris\textsuperscript{39}, de-Graaf and Kwart\textsuperscript{29}, Mulcahy and Williams\textsuperscript{35}, 36,40 and Herndon, have considered gas phase conditions. The technique has been developed for liquid phase\textsuperscript{46,47} and gas phase\textsuperscript{29-35}, kinetic studies, and has been extensively applied.
Theoretical Approach: Gas Phase Studies.

There are several useful references on the theory of stirred flow reactors applied to gas phase studies, which differ only in their approach. Herndon's paper is a useful introduction and also provides a concise review of the subject. His type of approach will be used here.

Conditions normally existing in a stirred flow reactor, are achieved by allowing the reactant(s) (sometimes in the presence of carrier gas) to flow continuously through the reactor. Because of chemical reaction within the vessel, the effluent will contain reaction products, and consequently the outlet flow rate of reactant(s) will be less than that entering. These conditions will exist regardless of whether a steady state has been achieved or not, and a mass balance expression involving flow rates, chemical reaction etc., may be set up.

The most general expression of mass balance on any substance, within any reactor, may be stated as follows: At any time $t$, the rate of input minus rate of output, equals the rate of decay plus rate of accumulation. Generation of the substance is regarded as negative decay.

We can now apply this mass balance principle to a single $n$th order reaction occurring in a stirred flow reactor. Let each molecule of reactant 'A' break down to form 'x' molecules of product 'P'.

$$A \rightarrow xP \quad (1)$$

Mass balance equations can be written for both 'A' and 'P'.

The mass balance on 'A' is:

$$n_i(A) - n_e(A) = k V \left( \frac{N}{V} \right)^n + \frac{dN}{dt} \quad 2.2.1$$

\begin{align*}
\text{INFLOW} & \quad \text{OUTFLOW} & \quad \text{DECAY} & \quad \text{ACCUMULATION}
\end{align*}
where:

- $n_i(A)$ is the number of moles of A flowing into the reactor per second.
- $n_e(A)$ is the number of moles of A flowing from the reactor at time $t$.
- $N$ is the number of moles of A within the reactor at time $t$.
- $V$ is the reactor volume.
- $k$ is the $n$th order rate constant for the decay of A to P.

Equation 2.2.1 may be written in a more manageable form when concentration terms are used. Thus we may write:

$$u_i[A]_i - u[A] = kV[A]^N + V \frac{d[A]}{dt}$$

where:

- $u_i$ is the total volumetric inlet flow rate. (cm$^3$.sec$^{-1}$.)
- $u$ is the volumetric exit flow rate. (cm$^3$.sec$^{-1}$.)
- $[A]_i$ is the concentration of A in the inlet pipe. (moles cm$^{-3}$.)
- $[A]$ is the concentration of A in the vessel and in the exit pipe. (moles cm$^{-3}$.)

The concentration of 'A' in the exit pipe is seen to be equal to its concentration within the vessel, but different from that in the inlet pipe. This follows from the assumption of perfect mixing.

With one proviso (see Section 2.6) equation 2.2.2 represents the material balance on A for the reaction (1) above, occurring in a stirred flow reactor under conditions which may, or may not be steady state. The equation is therefore a useful starting point for the derivation of equations applicable to steady state conditions, or to our 'pulse flow' conditions (see Section 2.4).

Application of Herndon's Approach.

Consider the steady state condition specifically.

At steady state:

$$\frac{d[A]}{dt} = 0$$
Equation 2.2.2 then becomes:

\[ u_i[A]_i - u[A] = k V [A]^n \]  

Hence:

\[ k = \left( \frac{u_i[A]_i - u[A]}{V [A]^n} \right) \]  

When there is no volume change accompanying the reaction, or when there is a large excess of inert carrier gas or solvent then:

\[ u_i = u \]

From which we have:

\[ k = \frac{u}{V} \left( \frac{[A]_i - [A]}{[A]^n} \right) \]  

The material balance on product 'P'

The material balance on product under steady state conditions says that the rate of formation is equal to the flow rate from the reactor. Therefore:

\[ u [P] = x k V [A]^n \]  

where \([P]\) is concentration of product within the vessel and the outlet pipe (at reactor temperature).

Equation 2.2.6 assumes that P does not undergo further reaction.

Transposing 2.2.6 we have:

\[ k_{i1} = x k = \frac{u [P]}{V [A]^n} \]  

This holds regardless of a volume change accompanying chemical reaction. In general it can be shown that the simplest expressions result from the use of a material balance on the product, and where all the required measurements are made on the effluent fluid rather than the entering fluid.\[36,37,35,39\]}
More complex reaction schemes.

Consider the following concurrent reactions occurring under steady state conditions in a stirred flow reactor.

\[ A \xrightarrow{} xB \quad \text{Order } n \]
\[ A \xrightarrow{} yC \quad \text{Order } m \]

The material balances for \( B \) and \( C \) are:

\[
\begin{align*}
\frac{\text{d}}{\text{d}t} [B] &= x k_1 V [A]^n \\
\frac{\text{d}}{\text{d}t} [C] &= y k_2 V [A]^m
\end{align*}
\]

Therefore:

\[
x k_1 = \frac{u}{V} \frac{[B]}{[A]^n}
\]

and

\[
y k_2 = \frac{u}{V} \frac{[C]}{[A]^m}
\]

From which it is seen that, with the use of material balances on products, the rate constants of concurrent reactions may be evaluated independently of one another.

A similar approach can be adopted for consecutive reactions or for schemes involving concurrent and consecutive reactions\(^{36,40}\).

Unfortunately, the method described above, relies upon the assumption that the temperature and pressure within the exit pipe, is equal to that within the reactor. This is required in order that the volumetric flow rate within the exit pipe is equal to that within the reactor, and that the concentration of each species within the exit pipe is equal to that within the reactor. This however does not present a serious limitation to the approach as will be seen in Section 2.6.
(2.3) Our Experimental Technique - The Stirred Flow Reactor Sample Injection Technique.

At the time of writing, it appears that all kinetic studies carried out using a stirred flow reactor (except our own), have been done under steady state conditions. Various physical methods have been used to make the required measurements including (a) E.S.R. spectroscopy, (b) mass spectrometry, (c) emission spectroscopy, (d) sampling of the effluent combined with gas chromatography, and (e) the collection of the total effluent over a known period of time.

Our technique bears some superficial experimental similarity to (d) and (e) in terms of the collection and estimation of the reaction mixture. It is, however, fundamentally different from other stirred flow reactor methods, in that we do not pass a continuous stream of starting material through the stirred flow reactor, and do not develop a steady state at any time during our experiments. Because of this, a re-evaluation of the relationship between reaction rate constants and known parameters has been necessary. This is presented in Sections 2.4 and 2.5.

Our method makes use of a single nitrogen carrier gas stream, which passes in turn through the stirred flow reactor, a cold trap, a gas chromatographic column, and detector. The apparatus is fully described in Chapter Three. A pulse of sample vapour is injected into the nitrogen line, and carried rapidly into the well stirred reactor, where it is mixed by forced convection with the nitrogen already present. Once in the reactor, the sample is immediately diminished in quantity by both chemical reaction and the passage of carrier gas through the reactor. The reactant(s), and any products of chemical reaction, are then carried to the cold trap where they are collected at low temperature. After a minimum period of time, calculated to collect greater than 99.95% of the sample mass, the trap is allowed to
warm, and the mixture is resolved before reaching the detector. The method described, thus represents an original approach to the study of homogeneous gas phase reactions. The advantages and disadvantages of this method when compared to the more well established ones, will be discussed in Section 2.8.

(2.4) An Examination of Our Reaction Conditions.

This is illustrated using a simple model reaction:

\[
A \xrightarrow{k_1} x P
\]

The procedure followed, is:

1) Mass balance equations are produced for A and P.
2) Expressions for the values of A and P at any time t within the reactor are derived.
3) Evaluation of the outflow rates of A and P at any time t.
4) Integration of the above expressions gives the total quantities of A and P eluted.
5) The rate constant \( k_1 \) is expressed in terms of these quantities.

In order to follow this procedure two assumptions have been made.

(1) We assume that the rate of mixing within the vessel is very much more rapid than either the rate of chemical reaction or the flow rate. Therefore the concentration of any species, at any point in time, is constant throughout the volume of the vessel.

(2) We assume that the volume of our sample 'pulse' is small compared to the volume of the vessel, and so the time taken for the pulse to enter, is sufficiently short, that a negligible amount of chemical reaction and outflow occur during this time.
It follows from these assumptions, that the pulse of starting material enters the vessel and is mixed to a uniform concentration, before chemical reaction and outflow begin.

It has been found most convenient to build upon these assumptions for the moment, so deriving a working mathematical model, before returning to test the validity of them.

Consider then, the first order reaction:

\[
A \xrightarrow{k_i} x P
\]  

(1)

The general mass balance equation on A, undergoing this reaction in a S.F.R. is equation 2.2.2:-

\[
u_i[A]_i = u[A] + k_i V[A] + V \frac{d[A]}{dt}
\]

2.2.2

On this occasion the differential term does not disappear, because a steady state does not exist. However, from assumptions (1) and (2) above, \([A]_i = 0\). Hence the rate of change of \([A]\) within the reactor is given by:

\[- \frac{d[A]}{dt} = k_i[A] + \frac{u}{V}[A] = \left( k_i + \frac{u}{V} \right) [A]
\]

2.4.1

To find the value of \([A]\) within the reactor at any time \(t\):-

Let \(Q = \left( k_i + \frac{u}{V} \right)\)

Therefore,

\[- \frac{d[A]}{dt} = Q[A]\]

Integrating:

\([A] = [A^o] e^{Qt} = [A^o] e^{-k_i t} e^{\left( \frac{u}{V} \right) t}
\]

2.4.2

where \([A^o]\) is the instantaneous initial value of \([A]\)
To find the value of \([P]\) within the reactor at time \(t\):-

Mass balance in terms of \([P]\) gives:

\[
\frac{d[P]}{dt} = x k_1[A] - \frac{u}{V} [P]
\]

which is insoluble directly. However, if \([A^*]\) represents the value of \([A]\) when there is no chemical reaction, then:

\[
- \frac{d[A^*]}{dt} = \frac{u}{V} [A^*]
\]

and

\[
[A^*] = [A^0] e^{-\left(\frac{u}{V}\right)t}
\]

However, when reaction (1) occurs:

\[
[A^*] = [A] + \frac{1}{x} [P]
\]

i.e.

\[
[P] = x \left( [A^*] - [A] \right)
\]

Substituting for \([A^*]\) and \([A]\) using equation 2.4.4 and 2.4.2:

\[
[P] = x [A^0] e^{-\left(\frac{u}{V}\right)t} - x [A^0] e^{-k_1 t} e^{-\left(\frac{u}{V}\right)t}
\]

Hence:

\[
[P] = x [A^0] e^{-\left(\frac{u}{V}\right)t} \left( 1 - e^{-k_1 t} \right)
\]

From the above expressions, the rates of flow of \('A'\) and \('P'\) from the vessel (\(RA\) and \(RP\) respectively) are:

\[
RA = u [A] = u [A^0] e^{-k_1 t} e^{-\left(\frac{u}{V}\right)t}
\]

\[
RP = u [P] = u x [A^0] e^{-\left(\frac{u}{V}\right)t} \left( 1 - e^{-k_1 t} \right)
\]
To evaluate expressions for the total quantities of 'A' and 'P' flushed from the vessel.

At time $t = 0$ all the starting material 'A' is said to be unreacted within the vessel, and at time $t = \infty$ all starting material 'A' and product 'P' will have been flushed from the vessel.

The total quantity of 'A' flushed from the vessel ($A_t$) will therefore be given by:

$$A_t = \int_0^\infty u [A] \, dt = u [A^0] \int_0^\infty \left( e^{-k_1 t} \cdot e^{-\left( \frac{u}{V} \right) t} \right) \, dt$$

Therefore,

$$A_t = u [A^0] \int_0^\infty e^{-Q t} \, dt = u [A^0] \left[ - \frac{e^{-Q t}}{Q} \right]_0^\infty = \frac{u [A^0]}{Q}$$

Therefore,

$$A_t = \left( \frac{u/V}{k_1 + u/V} \right) V [A^0] \quad 2.4.9$$

This gives the total quantity of 'A' eluted from the vessel.

In the same way the total quantity of 'P' flushed from the vessel ($P_t$) will be given by:

$$P_t = u x [A^0] \int_0^\infty \left( e^{-\left( \frac{u}{V} \right) t} \right) \left( 1 - e^{-k_1 t} \right) \, dt$$

$$= u x [A^0] \int_0^\infty \left( e^{-\left( \frac{u}{V} \right) t} - e^{-Q t} \right) \, dt$$
Integration gives:

\[ P_t = u \times [A^0] \left( \frac{V}{u} - \frac{1}{Q} \right) \]
\[ = \frac{x \cdot k_1 \cdot V \cdot [A^0]}{\left( k_1 + \frac{u}{V} \right)} \]

Let \( k_{11} = x \cdot k_1 \). The rate constant \( k_{11} \) then represents the rate of formation of product 'P'.

Therefore,

\[ P_t = \left( \frac{k_{11}}{k_1 + \frac{u}{V}} \right) V \cdot [A^0] \quad 2.4.10 \]

This gives the total quantity of 'P' eluted from the vessel.

______________________________________________

**Evaluation of the Rate Constant \( k_{11} \).**

Using (2.4.9) and (2.4.10) we have:

\[ \frac{P_t}{A_t} = \frac{\left( \frac{k_{11}}{k_1 + \frac{u}{V}} \right) V \cdot [A^0]}{\left( \frac{u}{V} \right) \frac{V \cdot [A^0]}{k_1 + \frac{u}{V}}} = k_{11} \frac{V}{u} \]

Therefore,

\[ k_{11} = \frac{u}{V} \cdot \frac{P_t}{A_t} \quad 2.4.11 \]

Hence we have a simple expression for the rate constant \( k_{11} \) in terms of measurable parameters.

______________________________________________

Graphs of \([A]\) and \([P]\) versus time are presented in Figures 2.1 and 2.2. These plots are based on equations (2.4.2), (2.4.4), and (2.4.6).

It now remains to assess the validity of the assumptions made at the start of this Section.
FIGURE 2.1 Graph of [Reactant] within the Reactor versus Time (Theoretical).

(See equations 2.4.2 and 2.4.4.)

Set \([A^0] = 1\)

\[
[A] = e^{-\left(\frac{u_2}{V}\right)t} = e^{-\left(\frac{2.63 \times 10^{-2}}{38}\right)t} \quad (\text{eq. } \frac{u_2}{V} = 38 \text{ sec})
\]

\[
\frac{u_2}{V} = 2.63 \times 10^{-2} \text{ sec}^{-1}
\]

\[
\frac{k}{u_2} = 7.89 \times 10^{-3} \text{ sec}^{-1}
\]

\[
k = 0.3 \frac{u_2}{V}
\]

\[
k = 0
\]
(See equation 2.4.6.)

Set $x = [A^0] = 1$
(i) Direct Evidence for their Validity.

A detector was placed close to the exit of the reaction vessel, in order to measure the rate at which a 'pulse' flowed from the vessel. The process was also repeated with the reaction vessel removed in order to account for time delay due to the pipes. These experiments were conducted over the range of flow rates and reactor temperatures used throughout the kinetic experiments, and the results were always the same. Experimental details are given in Chapter Three. A typical recorder trace of response versus time is given in Figure 2.3. This is compared with a peak of the same area, whose shape is defined by the equation (2.4.4), and thus relies on the assumptions (1) and (2) above. From the complete coincidence of the two decay curves after the first few seconds, it is clear that the experimental decay is accurately represented by the theoretical equation (2.4.4). We can therefore say that perfect mixing, utilising the total volume of the reactor, exists throughout most of an experiment. From the very close agreement between the experimental and theoretical peak onsets, it is obvious that each 'pulse' enters the vessel very rapidly compared with the time taken for its removal. Fairly efficient mixing must also exist during this time.

(ii) Indirect Evidence.

(a) The rate constant for the formation of trimethylsilane was found to be independent of the carrier gas flow rate (see Chapter Four). Hence the efficiency of mixing must be independent of flow rate. This in turn strongly implies perfect mixing for the duration of each and every one of our experiments.

(b) Mulcahy and Williams\textsuperscript{35}, Sullivan and Houser\textsuperscript{38}, and Lambert\textsuperscript{22}, have tested the efficiency of mixing within this type of reactor, over the pressure range 2 - 760 torr, residence times.
A trace of the outflow of inert material from the reactor is given under the following conditions: \( u_1 = 0.55 \text{ cm}^3 \text{ sec}^{-1} \), \( u_2 = 0.92 \text{ cm}^3 \text{ sec}^{-1} \). For comparative purposes, a theoretical plot of the same area is shown. This is based on equation 2.4.4. For graphical purposes this equation may be written:

\[ H = H^0 e^{-\left(\frac{H}{xV}\right)(tx)} \]  

where:

- \( H \) = peak height in mm. at time \((tx)\).
- \( H^0 \) = " " " " " " \((tx) = 0.\)
- \( x \) = chart speed in mm. sec\(^{-1} \).
- All other parameters are defined in the text.

\((tx)\) therefore becomes peak width in mm. etc.

Peak area mm\(^2\) is given by:

\[ \text{Area} = \int_0^\infty H \, d(tx) = \int_0^\infty H^0 \, e^{-\left(\frac{H}{xV}\right)(tx)} \, d(tx) \]

Integration gives:

\[ H^0 = \left(\frac{H}{xV}\right) \cdot \text{Area} \]  

where the area is equal to that under the experimental curve, and is therefore known. This expression was used to evaluate \( H^0 \), and all subsequent values of \( H \) were derived from equation (i).

**Delay Time.**

With the vessel and short sections of piping removed, \( (u_1 = 0.50 \text{ cm}^3 \text{ sec}^{-1} \text{ & } u_2 = 0.35 \text{ cm}^3 \text{ sec}^{-1} ) \) the delay time was measured as 19.2 sec. Calculated delay time due to the above sections of pipe = 9.07 sec. Therefore total delay time due to the pipes = 28 sec. Time \( t = 0 \) for the theoretical plot was therefore defined as 26 sec. after injection.
FIGURE 2.3 Recorder Trace of the Outflow of Inert Material from the Reactor.
0.1 - 110 seconds, and temperature 430 - 573K, and have found it to be 'perfect'. This strongly supports the above evidence that perfect mixing exists during our experiments.

Conclusions.

The mixing within the reactor is probably, within the limits of experimental error, perfect during the passage of a 'pulse', and at worst is known to be perfect for the majority of this time. Since the direct measurement described in (i), was found to be independent of temperature, then any minor errors caused through inefficient mixing, would not affect the values of first order activation energies.

The assumption that every 'pulse' enters 'rapidly' is a reasonable one.

Using the model conditions derived from the assumptions (1) and (2), the approach described above, thus provides some insight into the processes involved, and the characteristics of the variables, as our 'pulse' of material passes through the reactor. However, as a method of deriving \( k \) in terms of \( P_t \) and \( A_t \), it is limited to the case of a single first order reaction. A more useful method of deriving these relationships is given in the next section.

(2.5) A General Method for the Derivation of Rate Constants in Terms of Known Parameters.

Consider the concurrent reactions:

\[
A \xrightarrow{k_1} x P_1 \quad \text{Order 1} \quad k_{11} = x k_1
\]
\[
A \xrightarrow{k_2} y P_2 \quad \text{Order n} \quad k_{22} = y k_2
\]

For a steady state reactor, material balance equations on each product are:--
Thus, \( k_{11} = \frac{u}{V} \frac{[P_1]}{[A]} \)

Thus, \( k_{22} = \frac{u}{V} \frac{[P_2]}{[A]^n} \)

However these simple arithmetic relationships are made possible because there is no variation of \([P]\) or \([A]\) with time. In our case the equivalent material balance relationships contain a differential term, that is, for the above reactions we have:

\[
\frac{d[P_1]}{dt} = k_{11} [A] - \frac{u}{V} [P_1] \tag{2.5.1}
\]

and

\[
\frac{d[P_2]}{dt} = k_{22} [A]^n - \frac{u}{V} [P_2] \tag{2.5.2}
\]

which appear to be insoluble.

Therefore, in our pulse experiments:

\( k_{11} V [A] \neq u [P_1] \)

and

\( k_{22} V [A]^n \neq u [P_2] \)

However, since all products and starting material must eventually be flushed from the vessel, the following relationship is true of any product formed in our system:

\[
\left\{ \text{Total amount of product } P_i \text{ formed.} \right\} = \left\{ \text{Total amount of product } P_i \text{ flushed from the vessel.} \right\}
\]

Therefore:

\[
\int_0^\infty k_{11} V [A] \, dt = \int_0^\infty u [P_1] \, dt \tag{2.5.3}
\]
These expressions can be derived from the integration of equations (2.5.1) and (2.5.2) because:

\[ \int_{0}^{\infty} \frac{d[P_i]}{dt} = \left[ V [P_i] \right]_{t=0}^{t=\infty} = 0 \quad 2.5.5 \]

where \( P_i \) represents any product.

So in our system, the assumption that we remove all material from the vessel (by \( t = \infty \)) by flushing with carrier gas, has the same value as the assumption that in a steady state S.F.R., there is no change in the concentration of any species with time. We can therefore produce material balance equations for any product, regardless of the presence of concurrent reactions producing other products. It is also worthy of note that the above method does not require a knowledge of the time dependency of product concentrations. This information can now be applied as follows.

**Derivation of the Rate Constant for a First Order Reaction.**

It will not be important to the proof whether this occurs in the presence of other concurrent reactions or not.

\[ A \xrightarrow{k_1} x P_1 \quad \text{where} \quad k_{11} = x k_1 \]

The integrated material balance on \( P_1 \) is:

\[ \int_{0}^{\infty} k_{11} V [A] \, dt = \int_{0}^{\infty} u [P_1] \, dt \quad 2.5.6 \]
Let $P_{1t}$ and $A_t$ be the total quantities of $P_1$ and $A$ (respectively) flushed from the vessel (by $t = \infty$).

then

$P_{1t} = \int_{0}^{\infty} u [P_1] \, dt \quad 2.5.7$

$A_t = \int_{0}^{\infty} u [A] \, dt \quad 2.5.8$

thus

$\frac{P_{1t}}{A_t} = \frac{\int_{0}^{\infty} u [P_1] \, dt}{\int_{0}^{\infty} u [A] \, dt} \quad 2.5.9$

Substituting into this using equation 2.5.6 we have:

$P_{1t} = k_{11} V \int_{0}^{\infty} u [A] \, dt \quad 2.5.10$

Hence:

$k_{11} = \frac{V}{\int_{0}^{\infty} u [A] \, dt} \quad 2.5.11$

which gives $k_{11}$ in terms of four measurable parameters.

This is identical to equation (2.4.11).
At this point some comment should be made on the equations.

(i) Equation (2.5.11) is an arithmetic relationship, which one might only have expected from the time independent conditions achieved in steady state experiments in a S.P.R.

(ii) In equation (2.5.10) the integrals cancel; this has two important consequences:

(a) Equation (2.5.11) is valid for the first order reaction under consideration, irrespective of the overall time dependency of \([A]\).

(b) The assumption made originally, that no reaction or outflow of material occurs until all \('A'\) has entered the reactor, is not necessary in this case. The only requirements are that at \(t = 0\), \([P_1] = 0\), at \(t = \infty\), \([A] = [P_1] = 0\), and that \([A]\) and \([P_1]\) take positive values for some period of time between these limits.

Derivation of the Rate Constant for a Non-First Order Reaction (Order \(n\)).

For the sake of generalisation we may include the presence of a concurrent first order reaction.

\[
\begin{align*}
A & \xrightarrow{k_1} xP_1 \quad \text{Order 1} \quad k_{11} = xk_1 \\
A & \xrightarrow{k_2} yP_2 \quad \text{Order } n \quad k_{22} = yk_2
\end{align*}
\]

The material balance equation on product \(P_2\) will be:

\[
\int_0^\infty k_{22}V[A]^n \, dt = u \int_0^\infty [P_2] \, dt \quad 2.5.12
\]

from which we have,

\[
\frac{P_{2t}}{A_t} = \frac{k_{22}V \int_0^\infty [A]^n \, dt}{u \int_0^\infty [A] \, dt} \quad 2.5.13
\]
by the same method as above.

However, because the integrals do not cancel, they must be evaluated. For this purpose we are required to express \([A]\) in terms of \(t\). We must therefore rely on the assumption that the 'pulse' has completely entered the reactor before decay processes begin. The relationship between \([A]\) and \(t\) can therefore be found by solving the following equation:

\[
- \frac{d[A]}{dt} = k_2 [A]^n + \frac{n}{V} [A] + k_1 [A] \quad 2.5.14
\]

Let \(Q \equiv \left( k_1 + \frac{n}{V} \right) \)

Thus \(- \frac{d[A]}{dt} = k_2 [A]^n + Q [A] \quad 2.5.15\)

The solution of this differential equation is complicated, but a simple approximate method is satisfactory, provided that at all times during a run:

\(k_2 [A]^n \ll Q [A]\)

This will be the case when only a very small percentage of \(A\) is converted to product \(P_2\). Under these circumstances,

\(- \frac{d[A]}{dt} \triangleq Q [A]\)

and therefore,

\([A] \triangleq [A^o] e^{-Qt}\)

Equation 2.5.13 then becomes:

\[
\frac{P_{2t}}{A_t} \triangleq \frac{k_{22} V}{u} \int_0^\infty \left( [A^o] e^{-Qt} \right)^n dt
\]
\[
\frac{k_{22} V [A^0]^n}{u [A^0]} \int_0^\infty e^{-n Q t} \, dt \\
= \frac{k_{22} V [A^0]^{(n-1)}}{u n}
\]

Rearranging,

\[
k_{22} \triangleq \frac{u V}{V} \frac{P_{2t}}{A_t} \frac{n}{[A^0]^{n-1}}
\]

2.5.16

However, since \( V[A^0] \) represents the total amount of starting material in the vessel initially, and the total number of moles of material collected is given by:

\[
A_t + P_{1t} + P_{2t} + \cdots + P_{nt}
\]

Then

\[
V[A^0] = A_t + P_{1t} \frac{M_1}{M_a} + P_{2t} \frac{M_2}{M_a} + \cdots + P_{nt} \frac{M_n}{M_a}
\]

\[
= A_t + \sum_{i=0}^{\frac{1}{\frac{P_{1t}}{M_a}}}
\]

2.5.17

where \( M_a \) and \( M_i \) are the molecular weights of 'A', and the i th
product, respectively.

Using equation (2.5.17), equation (2.5.16) then becomes:

\[ k_{22} = \frac{u}{V} \frac{P_{2t}}{A_{t}} \left( \frac{n^{n-1}}{A_{t} + \sum_{i=0}^{n} \frac{P_{it} M_{i}}{M_{a}}} \right)^{n-1} \]  \hspace{1cm} 2.5.18

(There is the implicit assumption here that every product is observed as a peak on the gas chromatograph. Strictly speaking this may not be the case, as small quantities of heavy products will produce very low broad peaks that may be imperceptible.)

For the sake of a simple notation:

\[ A_{It} = \left( A_{t} + \sum_{i=0}^{n} \frac{P_{it} M_{i}}{M_{a}} \right) \]  \hspace{1cm} 2.5.19

\( A_{It} \) represents the total amount of 'A' injected into the reactor.

If the total percentage decomposition (i.e. to all products) is very small then:

\[(A_{It})^{n-1} \triangleq A_{t}^{n-1} \]

Hence:

\[ k_{22} = \frac{u}{V} \frac{P_{2t}}{A_{t}^{n-1}} \left( n^{n-1} \right) \]  \hspace{1cm} 2.5.20
(2.6) Differences in Temperature and Pressure Between the Reactor, and Other Parts of the Flow System: Their Effect on Rate Expressions.

Normally in a flow system, the inlet and outlet pipes are at a much lower temperature than the reaction vessel. As a result of this, the volumetric flow rate and concentrations within the pipes, will be seen to be different from those within the vessel. However, the mass balance equations presented in Sections (2.2) to (2.5) (except equation 2.2.1), clearly assume that the concentrations of species within the outlet pipe, are equal to those within the vessel, and in fact rely upon it for their simplicity. For example, in equation (2.2.3):

\[ u_1 [A]_1 - u[A] = k V [A]^n \]

[A] is used to represent the concentration of 'A' within the vessel and outlet pipe.

It is therefore clear that these equations only apply to the reactor, and very short lengths of pipe adjacent to it.

This is not a serious fault in itself, since the terms can be re-defined. However, lack of a clear understanding of it, is likely to lead to important errors in the evaluation of rate constants.

Consider a given mass of gas as it passes through a flow system, from a reactor at temperature \( T_2 \) and pressure \( P_2 \), to some other point \((x)\) at temperature \( T_1 \) and pressure \( P_1 \). The change in its volume from \( V_2 \) to \( V_1 \) will be given by the ideal gas law.

If it takes one second for this mass of gas to leave the reactor, then the volumetric flow rate at this point will be given by \( u_2 \):

\[ u_2 = V_2 \text{ cm}^3 \cdot \text{sec}^{-1} \]
Since the mass flow rate must be constant throughout the flow system, then our given mass of gas will take one second to pass the point (X). The volumetric flow rate will be given by \( u_1 \) at this point:

\[ u_1 = V_1 \text{ cm}^3 \text{ sec}^{-1}. \]

The volumetric flow rate from the reaction vessel, in terms of that measured at point (X) will therefore be:

\[ u_2 = u_1 \frac{P_1 T_2}{P_2 T_1} \]

If the composition of the gas mixture does not change between the reaction vessel and the point (X), then the mass flow rate of the \( n \)th component will not change between these points, and will be given by \( x \) mole sec\(^{-1}\).

Hence \( x = c_1 u_1 = c_2 u_2 \)

The concentration of this, within the reactor, in terms of that measured at the point (X) will therefore be given by:

\[ c_2 = c_1 \frac{P_2 T_1}{P_1 T_2} \]

It is therefore clear that any change in temperature or pressure, throughout the flow system, will cause changes in both the volumetric flow rate and concentration throughout the system. This will effect the evaluation of rate constants in terms of parameters actually measured.
(i) S.F.R. Steady State.

Consider a simple first order reaction. Assume that the concentrations of product and reactant within the outlet pipe, and the volumetric flow rate of effluent, are measured at the point (X) described above.

The appropriate expression for the reaction rate constant is equation (2.2.7). If we introduce the subscript '2' to denote conditions at reactor temperature and pressure we have:

$$ k_{11} = \frac{u_2}{V} \frac{[P]_2}{[A]_2} $$  \hspace{1cm} 2.6.4

If we wish to express $k_{11}$ in terms of the parameters measured at point (X) then, using equations (2.6.1) and (2.6.3) this becomes:

$$ k_{11} = \left( \frac{P_1 T_2}{P_2 T_1} \right) \frac{u_1}{V} \frac{[P]_1}{[A]_1} $$  \hspace{1cm} 2.6.5

Three terms have been 'corrected'. However, we may regard any two of these as having cancelled.

Some workers have chosen to regard this equation as the result of a correction on 'u' specifically $^{30,37,38}$, which will be seen to be a dangerous practice.

For a non first order reaction, the expression equivalent to (2.6.5) is:

$$ k_{11} = \left( \frac{P_1 T_2}{P_2 T_1} \right)^n \frac{u_1}{V} \frac{[P]_1}{[A]_1^n} $$  \hspace{1cm} 2.6.6

All three terms having been corrected again.

Equations (2.6.5) and (2.6.6) may be derived in another way. Since the mass flow rate throughout the system is constant, then the
following mass balance holds:

\[ u_1 \frac{[P]}{[A]}_1 = u_2 \frac{[P]}{[A]}_2 = k_{11} V [A]^n \quad 2.6.7 \]

Therefore:

\[ k_{11} = \frac{u_1}{V} \frac{[P]_1}{[A]_2^n} \]

Correction of the \([A]\) term produces equation 2.6.6 (or 2.6.5 if \(n = 1\)).

It is clear that equation (2.6.6) would not have been derived if the correction had been regarded as one associated specifically with the flow rate term 'u'. Therefore, although these 'correction' terms in the above cases are seen to cancel, it can be dangerous to regard them as being associated specifically with one particular parameter. It would seem most prudent, when working with a steady state S.F.R., to either 'correct' all three terms, or re-evaluate the expressions using an equation of the type 2.6.7.

(ii) S.F.R. Injected Sample.

Let us re-consider the derivation of equation (2.5.11):-

Subscripts '1' and '2' refer to exit pipe and reactor conditions respectively

\[ \frac{P_t}{A_t} = \frac{\int_0^\infty u_1 [P]_1 \, dt}{\int_0^\infty u_1 [A]_1 \, dt} \]

But

\[ \int_0^\infty u_1 [P]_1 \, dt = \int_0^\infty k_{11} V [A]_2 \, dt \]
Therefore,

\[
\frac{P_t}{A_t} = \frac{\int_0^\infty [A]_2 \, dt}{\int_0^\infty [A]_1 \, dt}
\]

But,

\[
[A]_2 = [A]_1 \left( \frac{P_2}{P_1} \right) \left( \frac{T_1}{T_2} \right)
\]

Therefore:

\[
k_{11} = \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right) \frac{u_1}{V} \frac{P_t}{A_t}
\]

An alternative approach is as follows: consider equation 2.5.11 'uncorrected', that is:

\[
k_{11} = \frac{u_2}{V} \frac{P_t}{A_t}
\]

In this case the conditions of temperature and pressure should not affect the values of \(P_t\) and \(A_t\). Only the value of \('u'\) is affected in this way, and so only this needs to be 'corrected'. 'Correction' of \(u_2\) to \(u_1\) produces equation 2.6.8.

By examining the derivation of rate expressions appropriate to non first order reactions occurring in our system, it will be found that the result is analogous to equation (2.6.8). That is, a 'correction' term to the power \(1\) must be introduced. The result is:

\[
k_{22} = \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right) \frac{u_1}{V} \frac{P_t}{A_t} \frac{n}{(A_{lt})^{n-1}}
\]
See equations (2.5.18) and (2.5.19).

Or,

\[ k_{11} = \left( \frac{P_1}{P_2} \right) \frac{u_1}{V} \frac{P_1}{A_n} (n \gamma^{n-1}) \]

See equation (2.5.20).

It can therefore be stated, that all equations applied to our system can be adjusted to include parameters actually measured, by simply multiplying the appropriate equation derived in Section (2.5) by the term:

\[ \left( \frac{P_1}{P_2} \right) \frac{u_1}{V} \frac{P_1}{A_n} (n \gamma^{n-1}) \]

The topic described in this section, is one which I feel has been given insufficient coverage in the literature.

Herndon, and Sullivan and Houser, both state that concentrations within the outlet pipe are equal to those within the reactor, which is very misleading. This can lead workers to neglect concentration and volumetric flow rate changes completely, as Herndon and Lowry appear to have done.

Other workers refer to the adjustment of flow rates, but make no mention of the change in concentration which must accompany it. This can be misleading, but, of more importance, can lead to the incorrect evaluation of non first order rate constants, when using a steady state S.F.R.
The Development of Similar Techniques.

The method described above does not appear to have been used before to study the kinetics of chemical reactions. However, a number of workers in other fields have used the arrangement of a reaction vessel situated between the injection point and the column of a gas chromatograph, as a useful experimental tool. Most noteworthy of these are the exponents of "Pyrolysis Gas Chromatography" [52], and the "Pulse Microreactor Technique" for the study of catalytic reactions [55]. Although none of these workers use a stirred flow reactor, expertise gained in these fields may be usefully applied to the development of the technique described in this thesis. A brief introduction to these techniques is therefore given below.

Pyrolysis Gas Chromatography (P.G.C.) is a rapidly growing technique, which is finding increased application in the field of analytical chemistry, in particular for the identification of unknown compounds [53, 56]. The term P.G.C. encompasses a wide range of techniques [53, 54], in which a mixture of pyrolysis products are resolved and identified by gas chromatography. One of these involves the direct passage of a pulse of sample vapour through a reactor and gas chromatograph. These reactors, sometimes known as microreactors, vary in dimensions, but are all of the tubular type [53, 54]. Although the application of this particular branch of P.G.C. is growing rapidly, it has only recently been used to study the kinetics of a small number of first order homogeneous gas phase reactions [57-60]. Most references cited in the literature, as the application of P.G.C. to these studies, are found to involve the use of a sampling valve and G.L.C. to analyse the contents of a static system, or the effluent from a steady state flow system [23, 61]. Cramers and Keulemans allow a 'pulse' of reactant vapour to partially decompose during it's passage through a narrow (1m. x 1mm I.D.) gold tubular reactor.
This is subsequently analysed by gas chromatography. They test this apparatus by studying the first order kinetics of the thermolysis of (a) Ethyl Acetate and (b) Cyclopropane, and produce rate data in good agreement with that derived from other experiments. However they point out that, because of a lack of knowledge regarding the concentration of the pulse, their method is strictly limited to the study of first order reactions. Non first order reactions can be studied by using this reactor in the 'continuous' mode and sampling the effluent using gas chromatography. Other, non-quantitative, applications of the pulse injection technique are described. The experiments and apparatus described by Kwart and coworkers, and by Sarner et al. are virtually identical with that of Cramers and Keulemans.

The "Pulse Microreactor Technique" was first designed for the study of heterogeneous catalytic reactions, and it is in this field that the technique has been most extensively applied to kinetic studies. In this case a gaseous sample of reactant is carried by an inert gas through a narrow bore tubular reactor packed with a catalyst, and then through a chromatographic column and detector. The technique, which was first proposed by Emmett and coworkers, has been employed for both identification purposes, and for the evaluation of rate constants of surface-catalysed reactions. Theoretical treatment of this technique was first considered by Bassett and Habgood, who restricted themselves to first order reactions, and extended by other workers, to the nth order case. However, because the reaction conditions under consideration here, are distinctly different from our own, their mathematical treatment is of little relevance to the technique presented in this thesis. The popularity of the Pulse Microreactor Technique for the study of heterogeneous catalysis is largely due to the minimal catalyst poisoning.
when compared to analogous steady state experiments. A large number of publications on this subject may be found in the literature.

(2.3) Conclusions Regarding the 'Stirred Flow Reactor Sample Injection Technique'.

(i) A comparison of this technique, with others used to study gas phase kinetics.

The advantages and disadvantages of the more well established methods, have been discussed elsewhere, and so will not be mentioned here.

Advantages of this Technique.

(a) It is a very simple technique, involving relatively inexpensive equipment, which is easily constructed. Very little handling of reactants or products is required.

(b) In contrast with steady state flow techniques, it is extremely economical on reactants.

(c) In contrast with steady state flow techniques, it is very rapid; the time taken to produce each data point, is limited mainly by the retention times of the components.

(d) In common with the steady state S.P.R. technique, very simple arithmetic relationships exist, between rate constants and measured parameters, particularly for first order reactions.

(e) In common with steady state flow techniques, short contact times can be used to study reactions at lower percentage decomposition, and higher temperatures, than in a static system.

(f) Rate data may be obtained on a large number of reaction products simultaneously.
Disadvantages of this Technique.

In common with other flow techniques, it lacks the degree of control which can be achieved with the static method; it can be difficult to change one variable, such as contact time, without to some extent, changing others such as carrier gas pressure.

(ii) Future Work on the Technique.

A form of temperature programming on the "fractional codistillation" column, would greatly improve the peak shape of the heavier reaction products. However, care must be taken to ensure that this does not affect detector sensitivity.
CHAPTER THREE

APPARATUS AND EXPERIMENTAL PROCEDURE
APPARATUS AND EXPERIMENTAL PROCEDURE

All thermolyses were carried out in one flow system. The theory has been discussed in Chapter Two. The apparatus is described below, after which the experimental procedure is discussed.

The Apparatus.

The apparatus can be conveniently divided into two sections, (i) the flow system (Fig. 3.1) and (ii) the sampling system (Fig. 3.2) which are connected by the sampling valve.

(3.1) Apparatus - The Flow System.

Pure nitrogen gas at controlled pressure and flow rate, was passed in turn through the sampling valve, reaction vessel, cold trap, G.L.C. column, and gas density detector. A 'pulse' of sample vapour, injected into the gas stream using the sampling valve, was carried through the vessel and collected at the trap along with reaction products. The trap was allowed to warm, and all species were carried through the column, and recorded separately by the detector.

The Reaction Vessel.

(See Fig. 3.3)

This was of the stirred flow type, and it's properties have been fully described in Chapter Two. The design was first developed for gas kinetic studies by Mulcahy and Williams, from the combustion apparatus of Longwell and Weiss. The quartz vessel consisted of narrow inlet and outlet pipes, and a sphere into which gas entered radially from a smaller sphere at the centre, and flowed out tangentially at (a). The smaller sphere was perforated with 23 holes of 0.5 mm. diameter. The reaction temperature was measured using a
N₂ - nitrogen cylinder ('oxygen free').
PC - pressure controller.
NV - needle valve.
b - drying tube containing dehydrated molecular sieve.
c - 'sodium traps'.
e - G.A.P. flowmeter.
f - 'oxy-trap'
g - sampling valve.
A to B - line heated with 'heat by the yard'.
C - to sampling system - vapour inlet.
D - to vacuum.
TP - thermometer pocket containing thermocouple.
h - reaction vessel.
RT2 - platinum resistance thermometer for Sunvic RT2 controller.
k - septum cap.
j - mercury manometer.
l - cold trap.
m - G.L.C. column.
n - gas density detector.
q - screw clips.
r - flow controller.
s - 'dummy' G.L.C. column - gave improved baseline.
t - G.L.C. oven.
u - capillary constriction (see 's').
v - to soap bubble flow meter or bucket of glass wool.
s, d, & p - see text.
Θ - springham diaphragm tap.
3.2 THE SAMPLING SYSTEM

- Pressure Transducer in heating jacket
- Storage bulbs - Caeous samples
- Storage flasks - Liquid samples
- Sampling valve (heated) (See Fig. 3.8)
- Sample reservoir and heater (See Fig. 3.7)
- To bridge & recorder
- To reaction vessel

Symbols:
- © - Young's greaseless stopcock
- © - Diaphragm tap.
- © - Ground glass greased tap.

To pumps & traps.
Figure 3.3 THE REACTION VESSEL

- Pyrex
- Graded seals
- Quartz 6 mm. O.D.
- Perforated sphere (approx 0.5 cm³)
- Thermocouple pocket (b)

Scale: 5 cm.
chromel/alumel thermocouple placed close to the wall of the vessel at (b).

The volume of the vessel was taken as $54.55 \text{ cm}^3$, being the volume of the bulb ($53.17 \text{ cm}^3$) plus half the volume of the inlet and outlet pipes ($1.41 \text{ cm}^3$). This seemed a reasonable assessment of the reaction space, in view of the fact that the incoming gas probably did not reach maximum temperature, until it entered the bulb. Error caused in this way will in any event be small, and independent of temperature.

The Furnace.

The furnace consisted of a stainless steel tube ($8 \text{ cm}$ in diameter, $25 \text{ cm}$ in length), wrapped with a thin layer of asbestos board and a nichrome heater winding. This was covered with a second layer of asbestos board, and soft asbestos pipe lagging $5 \text{ cm}$ thick. The end walls were of syndanyo $1 \text{ cm}$ thick. Both ends of the steel tube slotted neatly into shallow grooves in these walls.

The reaction vessel was positioned axially within the horizontal furnace, the bulb resting on a firebrick support halfway along its length. The inlet and outlet pipes passed through small holes in the end wall, thus providing them with support.

The heater winding was in four parts, with a variable resistance in parallel with each (Fig. 3.4). The values of these resistances ($R_1$ to $R_4$) were adjusted to achieve a fairly constant temperature along the furnace length. A temperature profile is given in figure 3.5. Power input was adjusted using a 'variac' variable transformer. Temperature control was achieved by switching the resistance $R_5$ in and out of the circuit. This was done using a Sunvic RT2 controller, which utilised a platinum resistance thermometer, situated next to the reaction vessel.
FIGURE 3.4 WIRING DIAGRAM - FURNACE HEATER

Voltmeter.

FIGURE 3.5 TEMPERATURE PROFILE OF FURNACE

Temp. °C

Inches along furnace axis.
Temperature Measurement.

The reactor temperature was measured using a chromel/alumel thermocouple, situated in a quartz pocket adjacent to the vessel wall (Fig. 3.3). The accuracy of the thermocouple was checked against a Rosemount platinum resistance thermometer (Model W.S. 104), and found to be accurate to within +1% (5°C) over the temperature range 673 - 883 K. These errors were random, and are accounted for in Chapter Four.

Control of Flow Rate and Pressure.

(See Fig. 3.1)

The flow rate through a given resistance is controlled by the pressure drop across it. The carrier gas pressure in our system was therefore fixed by our chosen value of flow rate.

Flow control was achieved by means of a B.O.C. pressure controller (a) fitted to the nitrogen cylinder, and a more sensitive pressure controller (d) [Watts 15-2 M 675 (0-25 psi.), donated by I.C.I.] close to the sampling valve. Measured flow rates were found to vary by less than ±1.5% over a matter of days.

Supply of nitrogen to the 'reference' side of the gas density detector, was controlled in a similar way using a simple pressure controller (p), and a sensitive flow controller (r) ('Flowstat Minor' manufactured by C.A. Platon, Croydon).

Measurement of Flow Rate and Pressure.

(See Fig. 3.1)

In order that reaction rate constants may be derived by the method described in this thesis, an accurate assessment of the volumetric flow rate through the vessel is required.

In our system carrier gas from the vessel eventually flows
into the gas density detector, is mixed with 'reference gas', and leaves as effluent. (See 'h' to 'n'.) Precise flow rate measurements on effluent from the detector, were made under ambient conditions, using a 50 cm³ soap bubble flow meter. In order to evaluate the flow rate from the vessel, the 'reference' flow into the detector was switched off at the pressure controller (p), and the screw clips (q). Determination of total effluent flow rate, gave the reference flow by difference. With a knowledge of temperature and pressure conditions, the flow rate from the vessel could be used to calculate the flow rate through it.

Because of the variation in gas viscosity with temperature, the flow rate through the G.L.C. column, reaction vessel, etc. was sensitive to the temperature of the trap (l). When samples were pyrolysed the trap was cooled to -160°C using a slush bath. This produced a flow rate higher than normal. Measurements were therefore made with the trap at slush bath temperature, and at room temperature. The value measured with the trap at slush bath temperature, was the one ultimately used for the evaluation of rate data.

The pressure within the reaction vessel was measured using the mercury manometer (j).

**Purification of Carrier Gas.**

(See Fig. 3.1)

Gas kinetic studies on the thermal decomposition of organo-silicon compounds, have been found in the past, to be extremely susceptible to traces of oxygen and water, which were thought to enhance surface reactions. Therefore, from the outset, great care was taken to remove any trace of these impurities from the 'oxygen-free' nitrogen. The pressure regulator (a) was of a special type, fitted with a non-permeable, stainless steel diaphragm (B.O.C.
model 19 - for special gases). This was to remove the slight possibility of atmospheric oxygen permeating into the nitrogen stream. Before reaching the reaction vessel, the gas was passed through a cylindrical column (2.5 cm. O.D. and 92 cm. in length) packed with dehydrated molecular sieve, and bubbled through molten sodium (Fig. 3.6). This was thought to remove all traces of oxygen and water vapour. The sodium traps were later replaced by an 'oxy trap' (Alltech. Associates) which was at least as effective.

The 'oxy trap' was reduced, and the molecular sieve dehydrated, at regular intervals.

The Sampling Valve.

(See Fig. 3.6)

This was a stainless steel rotary valve, based on the design of Pratt and Purnell, and made by Mr. Cliff Masters of this Department. It consisted of a central key fitted with six 'O' rings, of which four were sloping, and an outer barrel containing six ports. Various ports could be interconnected by rotation of the central key. Ports 3 and 4 were connected externally with a short piece of stainless steel tubing (0.32 cm. O.D.), to form a 'sample loop'. By operation of the valve, this 'loop' could be evacuated, filled with sample vapour, or flushed out with carrier gas. The volume of the 'loop', which included the annular space between the key and the barrel, was found by calculation to be 2.6 cm$^3$.

The Cold Trap.

(See Fig. 3.9 and Fig. 3.1 '1')

The purpose of the trap was two-fold, firstly to provide resolution of both low-boiling and high-boiling compounds, when used in conjunction with a single G.L.C. column, and secondly it gave us
**FIGURE 3.6 SODIUM TRAP**

- Molten sodium
  - 4 cm. deep.

- About 20 1mm. diam. holes.

**FIGURE 3.7 HEATING JACKET FOR SAMPLE RESERVOIR**

(See Fig. 3.2(c).)

- ARALDITE
- HEATER WINDING
- PYREX 25mm. O.D.
- PYREX 14mm. O.D.
Inlet ports connections:

(1) To vacuum system. 
(2) To sampling system. 
(3) & (4) Connected by the sample loop. 
(5) Nitrogen carrier gas in. 
(6) Nitrogen and sample vapour carried to reaction vessel. 

Part of 'O' rings shown thus.
FIGURE 3.9 THE COLD TRAP

To G.L.C. ←

Solid/liquid mixture.

Coil of stainless steel tubing 1/3" O.D.

12 cm. 8 cm.

5.5 cm. ←

7.5 cm. ←

FIGURE 3.10 THE DETECTOR - VERTICAL SECTION (Schematic)

G & F - Thermistor Elements.
some assurance that quantitative collection of the reaction mixture had been achieved.

The trap was a coil, made of an old stainless steel G.L.C. column (0.32 cm. O.D. and 2 m. in length), with most, or all, of it's packing removed. This was cooled to 113K (-160°C), using a slush bath of '40-60' petroleum spirit. Care was taken to ensure that the coil was always completely immersed in the bath, and that the solid/liquid equilibrium was maintained throughout the bath. This was done to ensure that flow rates were accurately reproducible.

The slush bath was left in place for at least five minutes after injection had been made. This allowed for more than 99·95% of the reaction mixture to be collected. For experiments conducted at other than normal flow rates, the time was adjusted accordingly. Collection time will in fact be greater than this, since material can accumulate in the G.L.C. column before the first compound is eluted.

When the coolant was removed, the coil slowly warmed up to room temperature, and the various compounds evaporated off in order of their volatility.

We have found more recently that this is a known separation technique, and is referred to as "Fractional Codistillation".

The Gas Chromatograph.

The gas chromatograph consisted of a single column and a Gow-Mac Gas Density Detector, housed in a home-made oven. The column was of copper tubing 3 m. long and 0.64 cm. O.D., packed with 10% w/v squalane on emacel (60-100 mesh acid washed).

Two ovens were used throughout the course of this work, the second more elaborate one will be described here. This consisted of an aluminium box (61.0 cm. x 25.4 cm. x 30.5 cm.), divided into two compartments by a wall of marinite (2.5 cm.) and aluminium, and
encased in marinite 2.5 cm. thick. The column was situated in one compartment, and the detector was rigidly mounted in the other, which was filled with sand for increased thermal stability. Chromalox heaters (manufactured by G. Bray & Co. Ltd., Leeds) were fitted to the walls, base, and lid, of each compartment. The maximum number were used in order to produce uniform wall temperature, and the finest possible temperature control. Electrical supply was from a 'variac' variable transformer. Temperature control was achieved by using a contact thermometer and relay switch to cut a resistance in and out of series with the heater bank. Each compartment was supplied and controlled separately, but both were run at 81°C.

The Detector.

(See Fig. 3.10)

The gas density detector was a Gow-Mac model 373, fitted with thermistor elements (F and G), which were wired in a Wheatstone bridge. Changes in the balance of the bridge were recorded on a highly sensitive Kipp and Zonen Micrograph (3D5 - 6862) recorder.

The complex theory of operation of gas density detectors, 77-81 has been discussed elsewhere, and so only a brief comment will be given here. Effluent from the G.L.C. column enters the detector at B, and is split into two streams BCE and BDE, while the 'reference gas' entering at A, separates into streams ACE and ADE. If column effluent and reference gas have identical densities, the flow rates AC and AD are equal, the elements are equally cooled, and the bridge is balanced. If however the column effluent (carrier gas and sample) is more dense than the reference gas, then a pressure increase occurs at D, and the flow AD is reduced, while that in AC is increased. If the column effluent is less dense than the reference gas, the converse is true. These changes in flow rate affect the relative temperature
of the two elements, which in turn causes an imbalance of the bridge. The recorder will then quantitatively register the presence of a sample. The peak area produced can be shown to be proportional to the molar quantity of sample present:

\[ A = \frac{N_S (M_S - M_C)}{Y Z} \]  

where:

- \( A \) = Peak area (chart paper).
- \( N_S \) = Molar quantity of sample.
- \( M_S \) = Molecular weight of sample.
- \( M_C \) = Molecular weight of carrier gas.

\( Z \) is a constant representing the sensitivity of the detector under given operating and recording conditions. This will depend upon: detector dimensions and temperature, nature of carrier gas, reference and column flow rates, and the chart speed and amplification of the recorder.

\( Y \) is a constant representing the relative sensitivity at any other chart speed and amplification of the recorder.

Transposing this we have:

\[ N_S = \frac{A}{(M_S - M_C)} Y Z \]  

We can see that, for constant operating conditions of the detector, the molar ratio \( (R_{ij}) \) of compounds \( i \) and \( j \) is given by:

\[ R_{ij} = \frac{N_{Si}}{N_{Sj}} = \frac{\left( \frac{A_i}{M_{Si} - M_C} \right) Y_i}{\left( \frac{A_j}{M_{Sj} - M_C} \right) Y_j} \]  

It is clear from this expression that molar ratios can be
obtained directly from peak areas, with a knowledge of molecular weights and recording conditions.

In order to determine absolute molar quantities, the detector must be calibrated under normal operating conditions. However, with a gas density detector, this can be done using only one, suitably volatile, known compound.

(3.2) Apparatus - The Sampling System.

(See Fig. 3.2)

This was a conventional vacuum system, designed to evacuate the sampling valve loop, and fill it with sample vapour at a known pressure.

The Pumping System.

Pumping was done using a Genevac single-stage rotary pump and a mercury diffusion pump, which were protected from contamination by a trap at 77K.

Pressure Measurement.

Measurement of residual gas pressures was made using a Pirani Gauge and a McLeod Gauge, the system normally being evacuated to within the region of $5 \times 10^{-5}$ torr. Sample vapour pressures were measured using a Bell and Howell pressure transducer (Type 4-327-0003 Range 15 psi.) (Fig. 3.2 b), which had previously been calibrated against a mercury manometer. In order to obtain consistent results, it was found necessary to thermostatically control the transducer body.

Storage of Samples.

Because of the problems associated with the presence of trace
quantities of oxygen and water (see 'Purification of Carrier Gas'), all samples of hexamethyldisilane (HMDS) and xylene were thoroughly degassed, and stored over freshly dehydrated molecular sieve. These compounds were carefully purified before use (see Appendix I). Gases were stored in 5 l. bulbs each equipped with a cold finger, and sealed with a Springham diaphragm tap, while liquids were stored in small flasks sealed with Young's greaseless stopcocks. All taps which came in contact with samples were of the greaseless type.

Handling of Sample Vapour.

For the earlier work, satisfactory hexamethyldisilane (HMDS) vapour pressures were attainable at room temperature. However, later it was found necessary to raise the temperature of the sampling line (including the valve) to about 110°C, to obtain suitable vapour pressures of xylene. The flow system between the sampling valve and the cold trap was therefore also heated.

(3.3) Experimental Procedure.

Setting Up.

Measurements were made at the start of each day, to determine the flow rate of carrier gas from the flow system, with the trap at both room temperature, and at slush bath temperature. In each case the flow meter reading was recorded, and was subsequently used throughout the day, as a check on consistency. The flow rate of nitrogen to the reference side of the detector was also measured.

A Typical Run.

Sample liquid (HMDS or HMDS + xylene), was distilled into the sample bottle (Fig. 3.2 c) and heated. The sampling line was evacuated and sealed off from the rest of the system at tap (3).
Tap (e) was then opened to obtain the required vapour pressure in the sampling line.

The trap (Fig. 3.1, l) was cooled to slush bath temperature, and the flow meter was observed until the required steady flow rate had been reached. At this point the sampling valve was rotated in turn to 'evacuate', and then to 'sample', whereupon sample vapour entered the loop. The vapour pressure was recorded using the transducer, and the sampling valve turned to 'injection' mode. The sample was then carried to the vessel, and slowly flushed from there, with reaction products, to the cold trap.

After the appropriate time, the slush bath was removed, so allowing the trap to warm to room temperature. This caused the mixture to evaporate off, to be resolved, and it's components recorded as separate peaks by the 'micrograph' recorder. Chart speed and sensitivity were adjusted to suit each peak. Some chromatographic data are given in Table 3.1 and a chromatogram is shown in Figure 3.11.

Quantitative Estimation of Reaction Mixture.

Each chromatogram was photostated, and the peaks produced were cut out and weighed. Paper weight was found to be constant to within ±1.3%, and so these weights were representative of peak areas within these limits.

All peak weights were corrected to the same chart speed (20 mm./min.) and sensitivity (1 mV.F.S.D.), and divided by their appropriate molecular weight factors (see 'Gas Density Detector'). For a peak recorded at sensitivity 20 mV F.S.D. and chart speed 10 mm./min. (Y = 20 x 2):

\[
\text{'Corrected weight'} = \frac{\text{Weight}}{(M_s - M_o)} \times (20 \times 2)
\]

3.1.4
### TABLE 3.1

**Some Typical Chromatographic Data.**

**Flow Rates (measured under ambient conditions).**

<table>
<thead>
<tr>
<th>Flow System</th>
<th>Detector Reference Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>(trap at room temperature)</td>
<td>52 cm³.min⁻¹</td>
</tr>
<tr>
<td>(trap at slush bath temperature)</td>
<td>68 cm³.min⁻¹</td>
</tr>
</tbody>
</table>

**Nitrogen Pressure.**

<table>
<thead>
<tr>
<th>Flow System</th>
<th>Nitrogen Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(trap at room temperature)</td>
<td>1696 torr</td>
</tr>
<tr>
<td>(trap at slush bath temperature)</td>
<td>1658 torr</td>
</tr>
</tbody>
</table>

**G.L.C. Column Temperature.**

<table>
<thead>
<tr>
<th>Detector Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>81°C</td>
</tr>
</tbody>
</table>

**Volume of Sample Vapour Injected.**

<table>
<thead>
<tr>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6 cm³</td>
</tr>
</tbody>
</table>

**Sample Vapour Pressure Range (transducer)***

<table>
<thead>
<tr>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 - 220 torr</td>
</tr>
</tbody>
</table>

**Retention Times:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂SiH</td>
<td>3.0 minutes</td>
</tr>
<tr>
<td>Me₄Si</td>
<td>3.8 &quot;</td>
</tr>
<tr>
<td>Me₆Si₂</td>
<td>16 &quot;</td>
</tr>
<tr>
<td>Me₇SiCH₂SiMe₂H</td>
<td>22.5 &quot;</td>
</tr>
<tr>
<td>(Me₂Si - CH₂)₂</td>
<td>27 &quot;</td>
</tr>
<tr>
<td>Me₂C₆H₄</td>
<td>54 &quot;</td>
</tr>
</tbody>
</table>

* Upper limit represents the pressure of gas mixture (HMDS + xylene).
- Change in sensitivity and/or chart speed.

\[ \text{Me}_2\text{SiH} \rightarrow \text{Me}_2\text{SiMe}_2 \rightarrow \text{Me}_3\text{SiH} \rightarrow \text{Me}_3\text{SiMe}_3 \rightarrow \text{Me}_4\text{Si} \rightarrow \text{Me}_5\text{SiMe}_2\text{H} \]

- 27 min.
- 22.5 min.
- 16 min.
- 3.8 min.
- 3 min.
'Corrected weights' were directly proportional to the molar quantities of each compound, and were used for the evaluation of first order rate constants. The evaluation of other rate constants required a knowledge of absolute molar quantities, and so 'corrected weights' were used in conjunction with calibration data representing detector sensitivity (see Appendix II).

Calibration of the Gas Density Detector.

Since the relationship between 'corrected' peak area (or weight!), and molar quantity of sample, is independent of the compound used (see Gas Density Detector and above), it was only necessary to calibrate the detector for one compound. Hexamethyldisilane (HMDS) was chosen for this purpose, and was injected through a septum upstream of the G.L.C. column (Fig. 3.1, k). A Hamilton microsyringe was used to deliver either HMDS liquid or a (10% w/v) solution of HMDS in '40-60' petrol. The operating conditions of the detector, were close to those used for the kinetic studies on the thermolysis of Hexamethyldisilane. A graph of 'corrected peak weight', versus molar quantity of HMDS injected, gave a straight line, whose slope represented the detector sensitivity under those operating conditions. The results are presented in Appendix II.

Examination of Mixing Conditions, and the Residence Time Distribution of a 'pulse' within the Reactor.

To examine these properties, we injected a 'pulse' of inert material (methane) into the carrier gas stream in the usual manner, and measured the rate at which it was eluted from the reactor. This was done by feeding the reactor effluent directly into a Gow Mac thermal conductivity detector (Model 9285), and observing the detector response on the Kipp and Zonen Micrograph Recorder. A needle valve
was fitted after the detector, to take the place of the G.L.C. column. This simple experiment was carried out over a range of temperatures and carrier gas flow rates similar to those used throughout the course of the kinetic studies. This process was then repeated, by-passing the reactor, in order to eliminate the effect of mixing within the inlet and outlet pipes, and the detector itself.

The results of these experiments have been presented in Chapter Two.
CHAPTER FOUR

RESULTS
RESULTS

Hexamethyldisilane (HMDS) was thermolysed over the temperature range 770 K. to 872 K., using the flow technique previously described. The pressure of HMDS was low; initial concentrations being within the range $1.4 \times 10^{-9}$ to $5.5 \times 10^{-7}$ mole cm$^{-3}$.

The principal experiments may be divided into two sections: HMDS thermolysis (1) in the absence of inhibitors, and (2) in the presence of m-Xylene. The majority of these studies were conducted using a carrier gas pressure of 2.1 atmospheres, which produced a flow rate of about $1.4$ cm$^3$. sec$^{-1}$. and a 'residence time' ($V/u_2$) of around 38 seconds. However, a third series of experiments was carried out, with residence times ranging from 29 to 112 seconds. The maximum percentage decomposition was 19%, although most studies were limited to within 5%. The methods used to calculate some of the figures presented here are given in Appendix II, and a list of the kinetic results is given in Appendix III. The results presented here on the formation of 'isomer' and TMDS are restricted to a narrower range of conditions, and involve greater uncertainty, than those for trimethylsilane or tetramethylsilane formation. The reason for this is that G.L.C. operating conditions were optimised for trimethylsilane.

(4.1) Preliminary Experiments and Information.

Reaction Products.

(i) Heterogeneous formation.

In the early stages of the work, small quantities of a number of unidentified compounds were observed. These were partially removed by 'seasoning' of the reaction vessel surface with injections
of trimethylchlorosilane and HMDS vapour. Before the experiments using xylene were carried out, an "oxy trap" was installed for the purification of the carrier gas (see page 52). As a result of this the unidentified compounds were almost completely removed.

It was fairly clear from these observations, that most of the unidentified compounds were formed heterogeneously, and that surface reactivity was enhanced even by minute traces of oxygen or water vapour. The heterogeneous formation of siloxanes and other compounds during the pyrolysis of organosilicon compounds has been well established. In all cases these have been removed by eliminating minute traces of oxygen and water vapour from the reaction vessel.

It was also found, in the initial stages of the work, that the kinetic behaviour was unstable, but consistent results were obtained after the vessel was seasoned. After this, the rate constants for the formation of trimethylsilane and tetramethylsilane decreased slightly over the very long period of continuous use of the vessel in series (1) below. Conversely these values were increased slightly after the vessel had been left unused for some months. There was no systematic change in the rate constants observed throughout series (2) or (3) due to heterogeneity.

(ii) Thermolysis products and their identification.

The principal thermolysis products were trimethylsilane, tetramethylsilane, 2,4,4-trimethyl-2,4-disilapentane (the 'isomer'), and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMD). Each of these was identified by the comparison of their G.L.C. retention times with those of authentic samples. In the case of two compounds (the isomer and TMD), their identity was also confirmed by Mass Spectrometry. These compounds were trapped separately on silica gel held within a
short piece of capillary tubing (0.2 cm. O.D. and 1 cm length), which was fitted to the exit of the gas density detector. Immediately a sample had been collected, the capillary tube was fitted to an insertion probe, and pushed into the ion source of the A.E.I. MS9 Mass Spectrometer. The mass spectrum was run as quickly as possible, since excessive delays tended to yield a spectrum of low intensity. On the other hand, prolonged heating of the probe could yield peaks indicative of siloxanes. The mass spectra produced, were compared with those run on authentic samples of the above named compounds. In each case, very close agreement was obtained between the mass spectra of the "unknown" compounds, and those of the corresponding authentic samples. Distinctive features of the mass spectrum of the 'isomer' were the small molecular ion peak at m/e 146, the larger peak at 145 (parent - H), the very large base peak at 131 (parent - Me), and the large fragment ion peaks at m/e 73 and 59. The spectrum of THDS is characterised by a fairly large molecular ion peak at m/e 144, a base peak at 129 (parent - Me), and fragment ion peaks at 101 and 64. Also metastable peaks at 115.6 and 79.1 indicate the fragmentations: m/e 144 → 129, and 129 → 101 respectively.

Quantitative Measurement of Reactant and Products.

A gas density detector was used for this purpose. This has the advantage that the peaks produced, (when 'corrected'), are directly proportional to the molar quantities of each sample (see Section 3.3). The detector was calibrated so that absolute molar quantities could be measured (see Appendix II).
Calculation of Rate Constants.

(i) First Order Rate Constants.

The appropriate expression is:

\[ k_{ii} = \left( \frac{P_1 \cdot T_2}{P_2 \cdot T_1} \right) \frac{u_1}{V} \frac{P_{iw}}{A_w} \]

(See equations (2.5.11) and (2.6.8).) Since 'corrected peak areas' (or weights) \( P_w \) and \( A_w \) are directly proportional to the molar quantities of each compound, then:

\[ \frac{P_{iw}}{A_i} = \frac{P_{iw}}{A_w} \]

First order rate constants have therefore been evaluated from plots of

\[ \left( \frac{P_1 \cdot T_2}{P_2 \cdot T_1} \right) \frac{u_1}{V} \frac{P_{iw}}{A_w} \]

Slope = \( k_{ii} \)

Where:-

\( k_{ii} \) = Rate constant for first order formation of the \( i \) th product.

\( P_{iw} \) = Corrected peak weight of the \( i \) th product.

\( A_w \) = " " " " HMDS.

\( V \) = Volume of reactor (taken as 54.58 cm\(^3\)).

\( u_1 \) = Volumetric flow rate (measured under ambient conditions).

\( P_1 \) & \( T_1 \) = Ambient pressure and temperature respectively.

\( P_2 \) & \( T_2 \) = Reactor " " " "

Examples of these rate plots are given in Figures 4.2.1 and 4.5.1(1-2).

This method was used for the evaluation of rate constants for the formation of trimethylsilane, tetramethylsilane and TMDS.
(ii) Non-First Order Rate Constants.

The expression used was:

$$k_{jj} = \left( \frac{P_1 T_2}{P_2 T_1} \right) \frac{u_j}{V} \frac{P_{jt}}{A_t^n} n \sqrt{V}$$

See equations (2.5.20) and (2.6.11). If $Z$ is the calibration factor representing the sensitivity of the detector, then:

$$P_{jt} = Z P_{jw}$$
$$A_t = Z A_w$$ etc.

The above expression therefore becomes:

$$k_{jj} = \left( \frac{P_1 T_2}{P_2 T_1} \right) \frac{u_j}{V} \frac{P_{jw}}{A_w^n} n \left( \frac{V}{Z} \right)^{n-1}$$

The three halves order rate constants for the formation of 'isomer' were therefore evaluated from graphs of:

$$\left( \frac{P_1 T_2}{P_2 T_1} \right) \frac{u_j}{V} P_{jw} \text{ versus } A_w^{1.5}$$

$$k_{jj} = \text{slope} \times 1.5 \left( \frac{V}{Z} \right)^{0.5}$$

where $n$ is the order (1.5).

For the values of $Z$ see Appendices II and III. Examples of these rate plots are given in Figures 4.2.2 and 4.3.3.

Errors...

Errors in the measurement of the reactor temperature were random and less than +1%. They are therefore unlikely to affect the slope of the Arrhenius plots, although a small error in the measurement
of $A$ factors is likely. The maximum error in the $A$ factor for trimethylsilane formation in Series (2) (see later), has been calculated as $+0.13$ log units, which lies well within the error limits given. Similar errors may be expected on other $A$ factors. Therefore corrections and adjustments to error limits are not required.

The measurement of volumetric flow rates (see Chapter 3) were reproducible to within 0.3 seconds, which corresponds to 0.6%. Errors incurred in this way are therefore also within the limits determined statistically and given with the Arrhenius parameters. Arrhenius parameters were determined using a least squares programme on a P.D.P. 11 Computer.

(4.2) Thermolysis in the absence of m-Xylene.

In previous studies on the thermolysis of hexamethydisilane, a wide range of product compositions was observed. In view of this, our preliminary re-investigation covered a wide range of temperatures (770-872 K), and initial concentrations ($1.4 \times 10^{-9}$ to $4.7 \times 10^{-7}$ mole cm$^{-3}$), in an attempt to identify all the major reaction products in a single series of experiments. The products observed have been described above, and the kinetic observations are given below.

Trimethylsilane.

The formation of trimethylsilane was found to be close to first order up to about 820 K. Above this temperature there was evidence of an order of about 1.3 at low concentration, which became first order as the concentration was increased. This effect became more pronounced with increasing temperature, until at 861.3 K first order conditions were apparent only at the highest concentrations. Examples of first order rate plots are given in order to illustrate this trend, in Figure 4.2.1. 'First order rate constants' evaluated
from the linear portions of these graphs, are listed in Appendix III.

The temperature dependence of the 'first order rate constant'
so produced is expressed by:

\[
\log_{10} k/\text{sec}^{-1} = 15.32 \pm 0.35 - (294.7 \pm 5.4) \text{ kJ mol}^{-1}/2.303RT
\]

An Arrhenius plot is given in Figure 4.5.1.

**TMDS.**

Although the data available for the formation of TMDS was
less reliable than for trimethylsilane, it was clear that the first
order rate plots exhibited the same characteristics. 'First order
rate constants' were again evaluated from the high concentration
portions of the rate plots, which were linear. The Arrhenius plot of
these rate constants is presented in Figure 4.5.2. This gave:

\[
\log_{10} k/\text{sec}^{-1} = 14.30 \pm 0.61 - (285.4 \pm 9.7) \text{ kJ mol}^{-1}/2.303RT
\]

The activation energy can be seen to be the same as for trimethylsilane
formation, to within the limits of error, although the A factor implies
that the rate constants for the formation of: trimethylsilane ; TMDS
was 10 : 1. This was not the case, the mean of 8 values of this ratio
being 2.74. The temperature dependence of this ratio gave an "A factor"
of 1.42 \pm 0.75 and an "activation energy" of (15.7 \pm 11.8) kJ mol\(^{-1}\),
which must be regarded as not being a meaningful deviation. A more
accurate evaluation, based on the more reliable Me\(_3\)SiH rate constants,
and using the ratio of 2.74 given above, therefore gave:

\[
\log_{10} k/\text{sec}^{-1} = 14.88 - 294.7 \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

**The Isomer.**

The data obtained on 'isomer' formation was more randomly
Figure 4.2.1  \( \text{Na}_2\text{SiH} \) Formation: First Order Rate Plots - Series (1).

\[
\frac{u_2}{V} p_w \times 10^{-6}
\]

- 795.1 K.

\[
\frac{u_2}{V} p_w \times 10^{-5}
\]

- 847.0 K.

\[
\frac{u_2}{V} p_w \times 10^{-5}
\]

- 861.3 K.

\( A_w \) (HMDS)
scattered than for trimethylsilane or tetramethylsilane, but nevertheless the order was found to be 1.5 at the lower temperatures. As the temperature was increased the order increased, particularly at low concentration, until at 871.5 K the overall order was greater than two. The trend is illustrated in Figure 4.2.2. Three-halves order rate constants were evaluated graphically using the linear, high concentration, portions of the rate plots, and gave:

\[
\log_{10} k/cm^3/2 \text{ mol}^{-3/2} \text{ sec}^{-1} = 13.26 \pm 0.65 - (206.5 \pm 10.1) \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

The trend observed here graphically, on the 1.5 order plots, was thus similar but more pronounced than that seen on the first order rate plots drawn for the formation of trimethylsilane. The Arrhenius plot is given in Figure 4.5.3.

**Tetramethylsilane.**

Tetramethylsilane formation was found to be first order. First order rate plots were found to be linear over the whole of the temperature range, and were given by:

\[
\log_{10} k/\text{sec}^{-1} = 13.06 \pm 0.71 - (270.7 \pm 11.1) \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

The Arrhenius plot is given in Figure 4.5.4.

Since there is a clear indication of a slow but continuous change in the kinetic behaviour of HMDS thermolysis, at least above 820 K., no attempt has been made to evaluate accurately the orders of reaction at higher temperatures. For the same reason the rate data will be of limited quantitative significance, as a change of mechanism is implied.
Series (2); HMDS Thermolysis in the presence of Excess m-Xylene.

In view of the complex kinetic behaviour associated with the formation of most products, and because of the presence of TMDS as a major reaction product, it was decided to repeat a number of experiments in the presence of an inhibitor such as toluene. m-Xylene was in fact chosen for this purpose because of its G.L.C. retention time. HMDS was therefore thermolysed over the temperature range 799.5 to 869.2 K. and with initial concentrations of $4.9 \times 10^{-9}$ to $4.3 \times 10^{-7}$ mol. cm$^{-3}$ in the presence of m-Xylene sometimes up to 300 fold in excess. These experiments were interspersed with a small number of runs in the absence of xylene, in order to obtain a direct comparison visually at each temperature. However, because only a small number of these experiments were performed, they are of little quantitative use.

The kinetic behaviour and product formation was found to be altered significantly by the presence of xylene, and is described below.

From the Series (3) experiments it can be seen that up to at least 4.5% decomposition, the rate data obtained are independent of degree of decomposition. The degree of decomposition (see Appendix III) at the highest temperature (869.2 K.) in this series (Series 2) exceeded this limit and therefore the results obtained at this temperature should perhaps be regarded with caution. Also at this temperature, TMDS was formed on three runs where insufficient quantities of xylene were used. These latter runs were therefore not used in the evaluation of rate constants at this temperature.

m-Xylene was found to be stable over the temperature range used in these experiments.
The rate of formation of trimethylsilane was found to be diminished in the presence of xylene. This reduction in rate was found to vary from a factor of 4.5 at 770 K. to 2 at 872 K. The reaction was found to be first order over the whole of the temperature range at all concentrations. A typical first order rate plot is given in Figure 4.3.1. The temperature dependence of the first order rate constant (see Figure 4.5.1) gave the following relationship:

\[
\log_{10} k/\text{sec}^{-1} = 17.53 \pm 0.25 - (336.9 \pm 4.0) \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

This included the value obtained at 869.2 K. However, on the Arrhenius plot, (see Figure 4.5.1) this point was seen to lie exactly on the line drawn through the others. This indicates that the results obtained at this temperature are perfectly valid and not complicated by the increased degree of decomposition. When Arrhenius parameters were computed with the above rate constant omitted, this served to reduce the A factor by only 0.35 log units and the activation energy by only 5.3 kJ mol\(^{-1}\), with the error limits slightly increased. The above Arrhenius parameters therefore relate to the rate of formation of trimethylsilane in the presence of excess m-Xylene.

From the mechanism proposed (see scheme (2) Fig. 5.1.2) we therefore identify the unimolecular dissociation rate constant for the reaction (1) as,

\[
\log_{10} k/\text{sec}^{-1} = 17.25 \pm 0.25 - (556.9 \pm 4.0) \text{ kJ mol}^{-1}/2.505 \text{ RT}
\]

and the bond dissociation energy \(D(\text{Me}_2\text{Si}--\text{SiMe}_2)\) as 337 \pm 4 kJ mol\(^{-1}\).

Except at the highest temperature (869.2 K.), the formation of TMDS was found to be completely suppressed by the presence of xylene.
Figures 4.3.1-3. Product Formation Rate Plots - Series (2).

$\frac{u_2 p_w}{V} \times 10^{-5}$

$\text{Si} \times 831.0 \text{K.}$

- In xylene
- No xylene

$\frac{u_2 p_w}{V} \times 10^{-6}$

$\text{Si}_4 \times 831.0 \text{K.}$

- In xylene
- No xylene

$\frac{u_2 p_w}{V} \times 10^{-5}$

$\text{Isomer} \times 869.2 \text{K.}$

- In xylene
- No xylene
At 869.2 K, TMDS formation was still completely suppressed when the xylene was in excess over the HMDS by a factor of 5 or more.

'The rate of formation of 'isomer' was found to be reduced by the presence of xylene, and close to 1.5 order. A three-halves order rate plot is given in Figure (4.3.3). However in common with the Series (1) experiments, the data obtained was less reliable than for monosilanes. An Arrhenius calculation gave:

\[
\log_{10}k/cm^2/mol^{1/2}sec^{-1} = 16.5 \pm 2.3 - (266.2 \pm 37.2) \text{ kJ mol}^{-1}/2.303RT
\]

Tetramethylsilane.

The formation of tetramethylsilane was found to be first order and unaffected by the presence of xylene. A typical first order rate plot is given in Figure (4.3.2).

The temperature dependence of the rate constant was found to be:

\[
\log_{10}k/sec^{-1} = 13.65 \pm 0.74 - (282.5 \pm 11.7) \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

The Arrhenius plot is given in Figure (4.5.4). The difference between the A factor obtained here and in Series (1) is probably due to some surface reaction occurring during the Series (1) experiments. These results are therefore more likely to relate to the gas phase process. It is clear from Figure (4.3.2) that this is not a genuine effect of the xylene.

(4.4) Series (3) Thermolysis Experiments at Varied Flow Rates.

Thermolysis experiments were carried out at four different flow rates, in order to show that the rate data produced in Series (1)
& (2) were independent of the flow conditions and percentage decomposition. The temperature was kept constant at 813 K. The widest possible range of flow rates was used, and gave residence times ($V/u$) of 29, 38, 68, and 112 seconds respectively. Runs were carried out both with, and without, xylene. The rate constants produced for the formation of trimethylsilane and tetramethylsilane in the presence of, and in the absence of xylene, were found to be constant at all but the longest residence time, where they were found to be slightly increased. The rate data obtained in Series (1) & (2) must therefore be independent of the residence time, since this was always well below 68 seconds (ie. about 38 seconds). Since the maximum percentage decomposition observed using a residence time of 68 seconds was 4.5%, then the rate data obtained in Series (1) & (2) must also be independent of degree of decomposition up to at least this figure. However, since the increase in rate constants at the highest flow rate was observed both with and without xylene, where the degrees of decomposition are different, this must be due to some function of residence time other than degree of decomposition. Therefore 4.5% should not necessarily be regarded as the safe limit of percentage decomposition.

All experiments conducted at 820 K. and below in Series (1), and below 869.2 K. in Series (2), involve less than 4.5% decomposition.

The measured rate constants are presented in Appendix III with all relevant data regarding percentage decomposition and residence times.
Figure 4.5.1 Arrhenius Plots: Me$_2$SiH Rate Constants.

- No xylene
- In xylene

Figure 4.5.2 Arrhenius Plot: TMDS Rate Constants (No Xylene).
Figure 4.5.3 Arrhenius Plots: "Tsohar" Rate Constants.

○ No xylene.
× In xylene.

Figure 4.5.4 Arrhenius Plots: Me₄Si Rate Constants.

○ No xylene.
× In xylene.
DISCUSSION

In view of the results obtained, and described in the previous Chapter, the reaction schemes (1) and (2) are proposed for the thermolysis of HMDS in the absence of inhibitors, and in the presence of xylene, respectively. A preliminary report on this work has already been published. The schemes will be seen to accommodate the facts that the presence of m-Xylene inhibits the formation of trimethylsilane and 'isomer', and completely suppresses TMDS formation.

Trimethylsilane formation is postulated as being a chain process initiated by the dissociation (1) and propagated by the steps (2) - (4). This process would also give rise to the unstable species Me₂Si:CH₂, which would then dimerise to TMDS. The dimerisation of this species, and similar ones, to form four membered ring compounds has been proposed elsewhere. The existence of such species is now supported by much evidence, and is well accepted.

'Isomer' formation is via the propagation reactions (3) and (5), and in fact the reaction mechanism (1) (2) (3) (5) and (6c) has already been proposed for the high pressure isomerisation of HMDS. The relative rates of these processes is a matter for quantitative consideration, as are the expected orders of reaction, which will be seen to depend on the termination steps 6a to 6c.

In the presence of sufficient quantities of m-Xylene, the abstraction reaction (2) will be replaced by (7), although the rearrangement (3) must still occur, since 'isomer' formation is not completely suppressed by xylene. Since the suppression of TMDS means that reaction (4) does not occur in xylene, then from scheme (2), the rate of formation of trimethylsilane is a non-chain process, rate determined by the initial dissociation (1). Since the dissociation
TABLE 5.1.1 - SCHEME (1)

Thermolysis of HMDS in the absence of Inhibitors.

\[
\begin{align*}
\text{Me}_3\text{SiSiMe}_3 & \rightarrow \ 2 \text{Me}_2\text{Si}^* & (1) \\
\text{Me}_3\text{Si}^* + \text{Me}_3\text{SiSiMe}_3 & \rightarrow \ \text{Me}_3\text{SiH} + \text{Me}_3\text{SiSi(Me}_2\text{)CH}_2 & (2) \\
\text{Me}_3\text{SiSi(Me}_2\text{)CH}_2 & \rightarrow \ \text{Me}_3\text{SiCH}_2\text{SiMe}_2 & (3) \\
\text{Me}_3\text{SiCH}_2\text{SiMe}_2 & \rightarrow \ \text{Me}_3\text{Si}^* + \text{Me}_2\text{Si}=\text{CH}_2 & 4' (4) \\
\left(2 \text{Me}_2\text{Si}=\text{CH}_2 \rightarrow \ \text{Me}_2\text{Si} \begin{array}{c} \text{CH}_2 \\ \end{array} \text{SiMe}_2 \right) & (4') \\
\text{Me}_3\text{SiCH}_2\text{SiMe}_2 + \text{Me}_3\text{SiSiMe}_3 & \rightarrow \ \text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H} + \text{Me}_3\text{SiSi(Me}_2\text{)CH}_2 & (5) \\
2 \text{Me}_3\text{Si}^* & \rightarrow \ \text{Me}_3\text{SiSiMe}_3 & (6a) \\
\text{Me}_3\text{Si}^* + \text{Me}_3\text{SiCH}_2\text{SiMe}_2 & \rightarrow \ \text{Me}_3\text{SiSi(Me}_2\text{)CH}_2\text{SiMe}_2 & (6b) \\
2 \text{Me}_3\text{SiCH}_2\text{SiMe}_2 & \rightarrow \ (\text{Me}_3\text{SiCH}_2\text{SiMe}_2)^2 & (6c)
\end{align*}
\]

Rate Parameters.

<table>
<thead>
<tr>
<th>(\log A^*)</th>
<th>(E_a / \text{kJ. mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 17.2</td>
<td>337</td>
</tr>
<tr>
<td>(2) 12</td>
<td>72</td>
</tr>
<tr>
<td>(3) (\geq 13)</td>
<td>(\leq 120)</td>
</tr>
<tr>
<td>(4) 13.5</td>
<td>214</td>
</tr>
<tr>
<td>(5) 12</td>
<td>80</td>
</tr>
<tr>
<td>(6a) 13</td>
<td>0</td>
</tr>
<tr>
<td>(6b) 12</td>
<td>0</td>
</tr>
<tr>
<td>(6c) 11.5</td>
<td>0</td>
</tr>
</tbody>
</table>

*A factor units - see Table 5.1.2.*
TABLE 5.1.2 - SCHEME (2)

Thermolysis of HMDS in the Presence of m-Xylene (RH).

\[
\begin{align*}
\text{Me}_3\text{SiSiMe}_3 & \underset{(1)}{\rightarrow} 2 \text{Me}_3\text{Si}^* \\
\text{Me}_3\text{Si}^* + \text{RH} & \underset{(7)}{\rightarrow} \text{Me}_3\text{SiH} + \text{R}^* \\
\text{R}^* + \text{Me}_3\text{SiSiMe}_3 & \underset{(8,-8)}{\leftrightarrow} \text{RH} + \text{Me}_3\text{SiSiMe}_2\text{CH}_2 \\
\text{Me}_3\text{SiSi(Me}_2\text{)}\text{CH}_2 & \underset{(3)}{\rightarrow} \text{Me}_3\text{SiCH}_2\text{SiMe}_2 \\
\text{Me}_3\text{SiCH}_2\text{SiMe}_2 + \text{RH} & \underset{(9)}{\rightarrow} \text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H} + \text{R}^* \\
2 \text{R}^* & \underset{(10)}{\rightarrow} \text{R}_2
\end{align*}
\]

Rate Parameters.

<table>
<thead>
<tr>
<th>log $A^*$</th>
<th>$E_a$ / kJ. mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 17.2</td>
<td>337</td>
</tr>
<tr>
<td>(7) 12</td>
<td>35</td>
</tr>
<tr>
<td>(8) 11.5</td>
<td>90</td>
</tr>
<tr>
<td>(-8) 12</td>
<td>40</td>
</tr>
<tr>
<td>(3) $\geq 13$</td>
<td>$\leq 120$</td>
</tr>
<tr>
<td>(9) 12</td>
<td>35</td>
</tr>
<tr>
<td>(10) 12</td>
<td>0</td>
</tr>
</tbody>
</table>

* A factors are in units of sec$^{-1}$ (1st order) or cm$^{3/2}$ mol$^{-2.5}$ sec$^{-1}$ (1.5 order).

The figures given in these tables are evaluated in the text.
(1) produces two trimethylsilyl radicals, then its rate is half the overall rate of formation of trimethylsilane in xylene, and is therefore given by:

\[
\log_{10} k/sec^{-1} = 17.23 \pm 0.25 - (33.69 \pm 4.0) \text{ kJ mol}^{-1}/2.303 \text{ RT}
\]

Hence the silicon–silicon bond dissociation energy in hexamethyl-disilane is taken as:

\[
D(\text{Me}_3\text{Si} \longrightarrow \text{Me}_3\text{Si}) = 337 \text{ kJ mol}^{-1}.
\]

The formation of tetramethylsilane is discussed separately in Section (5.4).

A detailed quantitative discussion of the reaction schemes (1) and (2) is given below. A number of thermochemical parameters are also estimated and listed in Tables 5.1.1–5.1.4.

(5.1) Evaluation of Rate Parameters.

In order to consider quantitatively the reaction schemes above, the rate constants of the elementary reactions involved must first be evaluated.

From appearance potential measurements, Davidson, Jones and Tibbals obtained a value of:

\[
D(\text{Me}_3\text{Si-H}) - D(\text{Me}_3\text{Si} \longrightarrow \text{Me}_3\text{Si}) = 31 \text{ kJ mol}^{-1}.
\]

Combining this with the above value for \(D(\text{Me}_3\text{Si} \longrightarrow \text{Me}_3\text{Si})\) gives \(D(\text{Me}_3\text{Si-H}) = 368 \text{ kJ mol}^{-1}\), a value which has recently been supported by the gas phase iodination experiments of Walsh and Wells.

The value of \(D(\text{Me}_3\text{SiCH}_2\text{-H})\) has been estimated as \(406 \text{ kJ mol}^{-1}\) by Kerr et al. If we assume \(D(\text{Me}_3\text{SiMe}_2\text{CH}_2\text{-H})\) to be a little weaker, say \(400 \text{ kJ mol}^{-1}\), then, using

\[
\Delta H_2 = D(\text{Me}_3\text{SiMe}_2\text{CH}_2\text{-H}) - D(\text{Me}_3\text{Si-H})
\]
we obtain a value of 32 kJ mol\(^{-1}\). for the enthalpy of reaction (2).
Since the reverse reaction of (2) is an exothermic hydrogen abstraction by a substituted methyl radical, \(E_{(-2)}\) may be estimated\(^4\) as 40 kJ mol\(^{-1}\). and hence:

\[
E_2 = E_{(-2)} + \Delta H_2 = 72 \text{ kJ mol}^{-1}.
\]

Reaction (5) may be considered in the same way. If

\[
D (\text{Me}_3\text{SiCH}_2\text{Si(Me}_2\text{)}\text{-H}) \text{ is assumed to be slightly less than } D (\text{Me}_3\text{Si-H}), \text{ say 360 kJ mol}^{-1}\text{, then } \Delta H_5 = 400 - 360 = 40 \text{ kJ mol}^{-1}.
\]

Taking \(E_{(-5)}\) as 40 kJ mol\(^{-1}\). (as with \(E_{(-2)}\)), then \(E_5 = 80 \text{ kJ mol}^{-1}\).

Support for these values comes from the work of Davidson, Eaborn and Simmie\(^5\). They studied the isomerisation of HMDS in a static system and obtained a value of 251 \pm 8 kJ mol\(^{-1}\). for the activation energy (\(E\)) of the three-halves order process. From their mechanism

\[
E = \frac{1}{3}(E_1 + 2E_5 - E_6)\text{.}
\]

Using the values estimated here \(E = 248.5\) kJ mol\(^{-1}\), thus providing excellent agreement between the two sets of figures.

Davidson, Eaborn and Simmie\(^5\) have calculated \(A_5\) as \(10^{13.3}\), although they point out that this may be unreasonably high. The abstraction by trimethylsilyl radicals, of chlorine from alkyl halides has been found\(^9\) to have an \(A\) factor of \(10^{11} \text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}\text{, that is, "normal"," and so it may be most reasonable to set } A_5 \text{ as being between these values, say } 10^{12} \text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}\text{. By analogy } A_2 \text{ may be set at the same value.}

There have been two publications recently on the rate of recombination of trimethylsilyl radicals, in the gas phase\(^1\) and in solution\(^1\). The best estimate\(^6\) of \(\Delta S\) for the equilibrium:

\[
\text{Me}_3\text{SiSiMe}_3 \xrightarrow{6a} 2 \text{ Me}_3\text{Si}^*\]

gives \(A_1 / A_{6a} = 10^{4.2} \text{ mol cm}^{-3}\). If this figure is used in
conjunction with our value of \( A_1 \), then \( A_{6a} \) is calculated as \( 10^{13.0} \). This value is seen to lie between the two experimentally determined values of \( 10^{14.2} \) and \( 10^{12.7} \), and may therefore be regarded as reasonable. When allowance is made for the mass and complexity of the \( \text{Me}_3\text{SiCH}_2\text{SiMe}_2 \) radicals, the values of \( A_{6b} \) and \( A_{6c} \) are approximated as \( 10^{12} \) and \( 10^{11.5} \) respectively.

The rate constant \( k_4 \) may be estimated from product analysis. From scheme (1) the relative rates of formation of TMDS : isomer is given by:

\[
\frac{R_{\text{TMDS}}}{R_{\text{iso}}} = \frac{k_4}{2k_5 [\text{HMDS}]} 
\]

If the mean value of this ratio is given by it's value when half the material has left the reactor then:

\[
\frac{(\text{TMDS})_t}{(\text{iso})_t} = \frac{k_4 V}{2k_5 0.5(\text{HMDS})_t}
\]

where the subscript \( t \) represents the total quantities of each compound collected, and \( V \) is the volume of the reactor. Hence:

\[
k_4 = \frac{k_5 (\text{HMDS})_t (\text{TMDS})_t}{V (\text{iso})_t}
\]

From product analysis the mean of six determinations of the above molar ratio gave \( 5.13 \times 10^{-6} \) at 820 K. At this temperature \( k_5 = 8.01 \times 10^6 \), and \( V = 54.58 \text{ cm}^3 \).

Hence \( k_4 = 0.760 \text{ sec}^{-1} \) at 820 K. If \( A_4 \) is \( 10^{13.5} \text{ sec}^{-1} \) (by analogy with similar alkyl radical dissociations\(^2\)), then \( E_4 = 214 \text{ kJ mol}^{-1} \).

It will be seen later that an estimate of \( k_2 \) is not required.
for our purposes, only a lower limit need be set. Reaction (3) is
mildly exothermic ($\Delta H$ being estimated as $-13 \text{ kJ mol}^{-1}$) and is
unlikely to have an activation energy of greater than $120 \text{ kJ mol}^{-1}$.
If we set the $A$ factor at a minimum of $10^{13} \text{ sec}^{-1}$, this probably
represents a minimum set of values for $k_3$.

Turning to scheme (2), $E(-2)$ may be taken as $40 \text{ kJ mol}^{-1}$.
as with $E(-2)$. If $D(\text{MePhCH}_2-\text{H})$ is taken as slightly less than
$D(\text{PhCH}_2-\text{H})$, say $350 \text{ kJ mol}^{-1}$ then, with $D(\text{Me}_3\text{SiMe}_2\text{CH}_2-\text{H})$ as
$400 \text{ kJ mol}^{-1}$ (see above), $\Delta H_8 = 50 \text{ kJ mol}^{-1}$. $E_8$ is thus
$90 \text{ kJ mol}^{-1}$. In the same way, $\Delta H_9$ is calculated as $-10 \text{ kJ mol}^{-1}$.
Since reaction (9) is thus only slightly exothermic, $E_9$ is perhaps
$< 40 \text{ kJ mol}^{-1}$, say $35 \text{ kJ mol}^{-1}$. Reactions (-8) and (9) are
abstractions by substituted silyl radicals, and thus by analogy with
$A_2$, their $A$ factors are set at $10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. $A_8$ may be expected
to be closer to 'normal' and is therefore put at $10^{11.5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
$A_{10}$ is probably about $10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, by analogy with other
recombination rate constants.

From the above bond dissociation energies $\Delta H_7 = -16 \text{ kJ}$,
from which $E_7$ may be put at about $35 \text{ kJ mol}^{-1}$, (7) being just exo-
thermic. $A_7$ is probably similar to $A_2$, i.e. $10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The formation of methane at the highest temperatures used
in series (1) and (2) permits an estimation of its rate of formation.
The molar ratio $\text{CH}_4 / \text{Me}_3\text{SiH}$ was roughly 0.2, which corresponds to
a rate constant of $3.7 \times 10^{-4} \text{ s}^{-1}$ at 870 K. for methane formation.
The most likely route to $\text{CH}_4$ formation is from the reaction:-

$$\text{Me}_3\text{SiMe}_3 \rightarrow \text{Me}_3\text{SiMe}_2 + \text{CH}_4$$  \hspace{1cm} (1b)

The $A$ factor for this reaction may be obtained by an indirect method:
$A_{11}$ can be evaluated by the geometric mean rule,
$$\text{Me}_3\text{Si}^* + \text{Me}^* \rightarrow \text{Me}_4\text{Si}$$  \hspace{1cm} (11)
using the above estimate for $A_{6a}$ combined with the value of $10^{13.5}$ cm$^3$ mol$^{-1}$ s$^{-1}$ for the recombination of methyl radicals$^{14}$. Thus $A_{11} = 10^{13.6}$ cm$^3$ mol$^{-1}$ s$^{-1}$. Using a recent value for the entropy change$^{16}$ of this process $A_{(-11)}$ is then $10^{17.6}$ s$^{-1}$. If we assume $A_{1b}$ is the same as this, then using the above value for the rate constant, $E_{1b} = 350$ kJ mol$^{-1}$. which is identified with $D (\text{Me}_2\text{SiSi(Me}_2\text{-Me})$.

The parameters estimated above are listed in Tables 5.1.1, 5.1.2 and 5.1.3.

**TABLE 5.1.3**

**Bond Dissociation Energies**

<table>
<thead>
<tr>
<th>Bond</th>
<th>$D / \text{kJ mol}^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_2\text{Si-SiMe}_3$</td>
<td>337</td>
<td>This work, 82.</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si-H}$</td>
<td>368</td>
<td>This work, 23, 88, 89.</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiCH}_2\text{-H}$</td>
<td>406</td>
<td>90.</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiCH}_2\text{-H}$</td>
<td>400</td>
<td>5 (Discussed here)</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiCH}_2\text{Si(Me}_2\text{-H}$</td>
<td>360</td>
<td>5</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si-Me}$</td>
<td>350</td>
<td>This work.</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si-Me}$</td>
<td>355</td>
<td>Assumed $&gt; D (\text{Me}_2\text{Si}_2\text{-Me})$</td>
</tr>
<tr>
<td>$\text{HMe}_2\text{Si-Me}$</td>
<td>355</td>
<td>and equal</td>
</tr>
<tr>
<td>$\text{HMe}_2\text{SiCH}_2\text{-H}$</td>
<td>406</td>
<td>Assumed equal to $D (\text{Me}_2\text{SiCH}_2\text{-H})$</td>
</tr>
</tbody>
</table>

With these values we may now consider quantitatively the schemes (1) and (2). However, before this is done, a number of enthalpies of formation will be calculated. These values are of interest in that the figures for molecules are very similar to those given by Pedley et. al. , but the enthalpies of formation of the radicals are very different. This is not surprising in view of the
revised values of bond dissociation energies proposed.

\textbf{TABLE 5.1.4}

\begin{center}
\begin{tabular}{|l|c|}
\hline
\textbf{Enthalpies of Formation of Gaseous Species.} & $\Delta H_f^\circ$ / kJ mol$^{-1}$ \\
\hline
(a) Me$_3$Si* & -11 \\
(b) Me$_3$SiH & -161 \\
(c) Me$_4$Si & -227 \\
(d) Me$_2$Si$_2$CH$_2$ & -177 \\
(e) Me$_2$SiCH$_2$SiMe$_2$ & -190 \\
(f) Me$_2$SiCH$_2$ & -39 \\
(g) *CH$_2$SiMe$_2$H & 27 \\
(h) Me$_2$SiH & 55 \\
(i) Me$_3$SiCH$_2$SiMe$_2$H & -332 \\
\hline
\end{tabular}
\end{center}

\textbf{Enthalpies of Formation.}

The enthalpies of formation given in Table 5.1.4 are calculated by means of the enthalpies of reaction listed below. The following enthalpies of formation$^{93}$ were also required:

\begin{align*}
\Delta H_f^\circ(\text{CH}_3^*)_g &= 139 \text{ kJ mol}^{-1}, \quad \Delta H_f^\circ(\text{Me}_6\text{Si}_2)_g = -359 \text{ kJ mol}^{-1}, \\
\Delta H_f^\circ(\text{H}^*)_g &= 218 \text{ kJ mol}^{-1}. \quad \text{All enthalpies are in kJ mol}^{-1}.
\end{align*}

(a) Me$_3$SiSiMe$_3$ $\rightarrow$ 2 Me$_3$Si* \quad $\Delta H = 337$

$\Delta H_f^\circ(\text{Me}_3\text{Si}^*) = \frac{1}{2} (337 - 359) = -11$

In the same way the enthalpies of the following reactions were used to evaluate the standard enthalpies of formation of the corresponding species in Table 5.1.4. The enthalpies of reaction are given in the text.
(b) Me₃SiH $\rightarrow$ Me₃Si⁺ + H⁺  \[ \Delta H = 368 \]
(c) Me₄Si $\rightarrow$ Me₃Si⁺ + Me⁺  \[ \Delta H = 355 \]
(d) Me₃SiMe₃ $\rightarrow$ Me₃Si₂CH⁺₂⁺ + H⁺  \[ \Delta H = 400 \]
(e) Me₅Si₂CH₂ $\rightarrow$ Me₃SiCH₂SiMe₂⁻⁻⁻  \[ \Delta H = -13 \]
(f) Me₄Si $\rightarrow$ Me₃SiCH₂⁻⁻⁻  \[ \Delta H = 406 \]
(g) Me₃SiH $\rightarrow$ CH₂SiMe₂H⁺ + H⁺  \[ \Delta H = 406 \]
(h) Me₃SiH $\rightarrow$ Me₃SiH⁺ + Me⁺  \[ \Delta H = 355 \]
(i) Me₃SiCH₂SiMe₂H $\rightarrow$ Me₃SiCH₂SiMe₂⁺ + H⁺  \[ \Delta H = 360 \]

(5.2) Quantitative Consideration of Scheme (1).

Since reaction scheme (1) involves three possible termination steps, the overall rate constants have been evaluated using each in turn. The results are presented in Tables 5.2.1 and 5.2.2 for the formation of trimethylsilane and 'isomer' respectively. Because of the short chain length, the simplifying assumptions normally used for the analysis of long chain reactions must be treated with caution.

With reaction (6a) as the termination step, exact solutions are produced for the formation of both trimethylsilane and isomer. However, when considering (6b) as the sole termination step, k₁ is ignored relative to $4k₂k₄/k₆b$, so producing an approximate relationship. At 770 K, k₁ is estimated as being a factor of 2.3 less than the composite rate constant, while at 872 K, the terms are approximately equal. Hence the rate expressions for the formation of trimethylsilane and isomer are a rough approximation of those expected with this termination step, if the calculated ratios of $k₁ : 4k₂k₄/k₆b$ are reasonably accurate. With (6c) as the termination step, the rate expression for the formation of isomer is once again exact. The activation energy for this process has been measured accurately by Davidson, Eaborn and Simmie⁵ and found to be in excellent
agreement with that calculated here (see below). With this termination step however, the expression for the rate of formation of trimethylsilane is only approximate. It results from the assumption that

\[ k_1 \approx \left( \frac{k_1 k_4^2}{4 k_{6c}} \right)^{\frac{3}{2}} [\text{HMDS}]^{-\frac{3}{2}} \]

This relationship is found to be valid at all but the lowest HMDS concentrations where the 6c termination step would not be expected anyway, (see below). With a typical value of [HMDS] of $5 \times 10^{-3}$ mol. cm$^{-3}$, $k_1$ is found to be larger than the composite expression by a factor of 4 at 770 K. and 2 at 872 K. The approximate expression for the rate of formation of trimethylsilane is therefore reasonable, particularly in view of the fact that this termination is most favoured at low temperatures and high HMDS concentrations. The predicted non-chain formation of trimethylsilane with an activation energy of 337 kJ mol$^{-1}$ under these conditions, is in agreement with the observations of Eibom and co-workers$^4,5$, who observed very little trimethylsilane under conditions which favoured the reaction (6c).

The rate expressions presented in Tables 5.2.1 and 5.2.2 are therefore at worst, reasonable representations of the limiting values of the rate expressions expected experimentally.

From the results presented in Tables 5.2.1 and 5.2.2 it is clear that the overall kinetic behaviour of HMDS thermolysis is dependent on the relative concentrations of the radicals $\text{Me}_3\text{Si}^*$ and $\text{Me}_2\text{SiCH}_2\text{SiMe}_2^*$. These ratios have been evaluated using the relationship:

\[ \frac{[\text{Me}_3\text{Si}^*]}{[\text{Me}_2\text{SiCH}_2\text{SiMe}_2^*]} = \frac{k_5}{k_2} \frac{(\text{Me}_3\text{SiH})_t}{(\text{ISOMER})_t} \]

(where $t$ denotes the total quantities of each product collected).
TABLE 5.2.1

Rate Expressions for the Formation of Me₂SiH in Hexamethyldisilane

<table>
<thead>
<tr>
<th>Termination</th>
<th>Order in HMDS</th>
<th>Rate Constant</th>
<th>log₁₀ A</th>
<th>E / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>3/2</td>
<td>( \left( \frac{k_1 k_2^2}{k_{6a}} \right)^{\frac{3}{2}} )</td>
<td>14.1</td>
<td>241</td>
</tr>
<tr>
<td>6b</td>
<td>1</td>
<td>( \Delta \left( \frac{k_1 k_2^2 k_4}{k_{6b}} \right)^{\frac{3}{2}} )</td>
<td>( \Delta 15.4 )</td>
<td>( \Delta 309 )</td>
</tr>
<tr>
<td>6c</td>
<td>1</td>
<td>( \Delta 2 k_1 )</td>
<td>( \Delta 17.5 )</td>
<td>( \Delta 337 )</td>
</tr>
</tbody>
</table>

(\( \Delta \) non-chain)
### TABLE 5.2.2

Rate Expressions for the Isomerisation of Hexamethyldisilane

<table>
<thead>
<tr>
<th>Termination</th>
<th>Order in HMDS</th>
<th>Rate Constant</th>
<th>$\log_{10} A$</th>
<th>$E$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>5/2</td>
<td>$\left( \frac{k_1^\frac{3}{2} k_2 k_5}{k_4^\frac{1}{2} k_{6a}} \right)$</td>
<td>12.6</td>
<td>113</td>
</tr>
<tr>
<td>6b</td>
<td>2</td>
<td>$\Delta \left( \frac{k_1 k_2 k_5^2}{k_4 k_{6b}} \right)^{\frac{1}{2}}$</td>
<td>$\Delta 13.9$</td>
<td>$\Delta 181$</td>
</tr>
<tr>
<td>6c</td>
<td>3/2</td>
<td>$(\frac{k_1 k_5^2}{k_{6c}})^{\frac{1}{2}}$</td>
<td>14.9</td>
<td>249</td>
</tr>
</tbody>
</table>
At 770 K this ratio changed from about 0.3 at medium concentration to about 0.08 at high concentration. The corresponding values at 872 K were 1.7 to 0.6. We would therefore expect the termination step (6a) to become increasingly important with increasing temperature, with the step (6c) becoming less important. The trend should be more marked at the lower concentrations, since the ratio is seen to change more rapidly at lower concentrations. From the Tables 5.2.1 and 5.2.2 the order of the reactions given are predicted to change with the termination steps, and we would therefore expect an increase in order of these reactions with temperature. This effect would be most noticeable at the lower concentrations. These changes in order of reaction have been observed experimentally, exactly as predicted.

(See Figures 4.2.1 and 4.2.2.) Because of the 'mixed mechanism' observed in the series (1) experiments, the Arrhenius parameters produced are of little quantitative value. Nevertheless the results obtained can be seen to lie within the range predicted in Tables 5.2.1 and 5.2.2.

At lower temperatures and higher concentrations, we would expect termination step (6c) to be the most dominant, with the result that the isomerisation reaction would be a 'clean' three-halves order process, with an activation energy of 248.5 kJ mol⁻¹. This is exactly what has been observed between 717 K and 780 K using high pressures of hexamethyldisilane.

It is of interest to note however that TMDS was not observed by these workers, although it was a major reaction product in our own series (1) experiments. However using the estimated values of \( k_4 \) and \( k_5 \) in Table 5.1.1, and a typical value of their HMDS concentration \( (3 \times 10^{-6} \text{ mol. cm}^{-3}) \), the relative rates of formation of isomer : TMDS are calculated as 550 at 717 K and 89 at 780 K. On this basis, TMDS would not be expected to be a reaction product in the higher pressure experiments.
In order that m-Xylene inhibits the formation of TMDS, and the chain formation of trimethylsilane, it is clear from scheme (2) that reaction (9) must be very much faster than reaction (4). Using the estimated values given in Tables (5.1.1) and (5.1.2), the ratio $\frac{k_9}{k_4}$ is seen to vary from $4.4 \times 10^{10}$ at 770 K. to $1.7 \times 10^9$ at 872 K. Since the initial xylene concentrations vary from $5.1 \times 10^{-6}$ mol. cm$^{-3}$. to a minimum of $4.8 \times 10^{-8}$ mol. cm$^{-3}$. then the relative rates of reactions (9) : (4) are calculated as $2.2 \times 10^5$ to $2.1 \times 10^3$ at 770 K. and $8.7 \times 10^3$ to 82 at 872 K. We would expect reaction (4) to be completely suppressed by xylene under all conditions except possibly at the highest temperature and lowest xylene concentrations. This was found to be so experimentally. A similar examination of the relative rates of reactions (7) and (2) reveals that at 770 K., reaction (7) is faster than (2) by a factor which ranges from $7.1 \times 10^4$ to 47. At 872 K. this factor varies from $3.8 \times 10^4$ to 25. These figures justify the exclusion of reaction (2) from scheme (2), although it should be remembered that it is not a requirement for the inhibition of the chain reaction described above.

The presence of xylene caused a reduction in the rate of trimethylsilane formation which varied from a factor of 4.5 at 770 K. to a factor of 2 at 872 K. Hence in the absence of xylene, the chain formation of trimethylsilane varied in chain length from 4.5 to 2. In agreement with the proposed mechanism, the difference between the rate constants for the formation of trimethylsilane in the absence and presence of xylene, was equal to twice the rate constant for the formation of TMDS in the absence of xylene, at all temperatures, to within a few percent.

From the values of the rate constants involved in scheme (2), and using high values for the concentrations of HMDS and xylene,
(1 \times 10^{-7} \text{ and } 1 \times 10^{-6} \text{ mol. cm}^{-3}. \text{ respectively}), \text{ the ratio of radical concentrations was calculated as:–} \quad [\text{Me}_3\text{SiSiMe}_2\text{CH}_2] : [\text{Me}_3\text{SiCH}_2\text{SiMe}_2] : [\text{Me}_3\text{Si}] : [\text{R}^*] = 1 : 17 : 478 : > 3 \times 10^6 \text{ at } 770 \text{ K. Using the lowest concentrations of HMDS and xylene (5 x } 10^{-9} \text{ and } 5 \times 10^{-8} \text{ mol. cm}^{-3}. \text{ respectively), this ratio became } 1 : 342 : 4.2 \times 10^4 : > 5.8 \times 10^7. \text{ At } 872 \text{ K. this latter ratio became } 1 : 1.6 \times 10^3 : 7.9 \times 10^5 : > 1 \times 10^8. \text{ It is therefore clear that under all conditions, the concentration of xylyl radicals is in excess over all others by a factor which is at the very least } > 120. \text{ Under most conditions this factor will be very much larger than this. These calculations therefore justify the choice of reaction (10) as the sole termination step in scheme (2).}

Consideration of scheme (2) gives the following expression for the rate of formation of 'isomer' in the presence of excess xylene (R_{iso}):–

\[
R_{iso} = \frac{k_3 \left( \frac{k_1 k_8^2}{k_{10}} \right)^{\frac{3}{2}} [\text{Me}_6\text{Si}_2]^{3/2}}{k_3 + k_{(-8)} [\text{RH}]} 
\]

However, using the minimum value of \( k_3 \) listed in Table (5.1.1), our estimate of \( k_{(-8)} \), and a high value of [RH] (ie. 10^{-6} \text{ mol. cm}^{-3}.), \( k_3 / k_{(-8)} [\text{RH}] \) is seen to vary from 166 at 872 K. to 38 at 770 K. Hence \( k_3 \gg k_{(-8)} [\text{RH}] \) under all conditions, and so the above expression can be simplified to:–

\[
R_{iso} \propto \left( \frac{k_1 k_8^2}{k_{10}} \right)^{\frac{3}{2}} [\text{Me}_6\text{Si}_2]^{3/2}
\]
We would therefore expect the formation of 'isomer' to be 1.5 order in EMDS and to have an activation energy of 258.5 kJ. mol\(^{-1}\).

Although the rate data available on 'isomer' formation were not as reliable as for monosilanes, the order was found to be close to 1.5 as is illustrated in Figure 4.3.3. This should be compared with Figure 4.2.2, where the order can be seen to be very much higher in the absence of xylene at about the same temperature. The activation energy was found to be about 266 kJ. mol\(^{-1}\), in good agreement with the calculated value.

(5.4) Tetramethylsilane Formation.

In the series (1) experiments the formation of all products except tetramethylsilane was seen to be complex. Tetramethylsilane (TMS) was the only product with a rate of formation which remained first order under all conditions. The rate constants and order of reaction were also seen to be unaffected by the presence of excess m-Xylene. TMS was therefore also unique in this respect. This evidence suggests that the formation of TMS was via a molecular, rather than free radical reaction, which occurred concurrently with the reactions involved in schemes (1) and (2). It was therefore omitted from these schemes, and the following reaction is proposed:

\[ \text{Me}_3\text{SiSiMe}_3 \rightleftharpoons \text{Me}_4\text{Si} + \text{Me}_2\text{Si}^* \]  

(1a)(-1a)

In the absence of xylene, the silylene would insert into an EMDS molecule since this is in a large excess over the reaction products. Insertion into one of the C-H bonds would produce \( \text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{Si}^*(\text{Me}_2)^\text{H} \). Some indirect evidence for this reaction is given in the next section.

If the reaction (1a) was in fact the source of tetramethyl-
silane in our experiments, and was the reaction followed by Stephenson (see Section 5.5), then \( E_{1a} \) is 282 kJ. mol\(^{-1}\). From consideration of the work of John and Purnell\(^{94}\) on the insertion reactions of \( \cdot \text{SiH}_2 \), and the theoretical considerations of Davidson\(^{95}\), we would expect \( E_{(-1a)} > 0 \), and it may be set at 20 kJ. mol\(^{-1}\). Hence \( \Delta H_{(1a)} \) may be calculated as:

\[
\Delta H_{(1a)} = E_{1a} - E_{(-1a)} = 262 \text{ kJ. mol}^{-1}.
\]

but \( \Delta H^o_{(1a)} = \Delta H^o_{(\text{Me}_4\text{Si})} + \Delta H^o_{(\text{Me}_2\text{Si}^\ddagger)} - \Delta H^o_{(\text{Me}_6\text{Si}_2)} \)

Using the values of \( \Delta H^o_{(\text{Me}_4\text{Si})} \) and \( \Delta H^o_{(\text{Me}_6\text{Si}_2)} \) listed in Table 5.1.4, we therefore have:

\[
\Delta H^o_{(\text{Me}_2\text{Si}^\ddagger)} = 130 \text{ kJ. mol}^{-1}.
\]

From this figure, the value of \( D (\text{Me}_2\cdot\text{Si-Me}) \), which may be regarded as the second bond dissociation energy in tetramethylsilane, is evaluated as:

\[
D (\text{Me}_2\cdot\text{Si-Me}) = \Delta H^o_{(\cdot\text{Si})} + \Delta H^o_{(\text{Me}_2\text{Si}^\ddagger)} - \Delta H^o_{(\text{Me}_3\text{Si}^\ddagger)}
\]

\[
= 280 \text{ kJ. mol}^{-1}.
\]

The required enthalpies of formation have been listed in Table 5.1.4. This value is very much less than the estimate of \( D (\text{Me}_3\cdot\text{Si-Me}) \) given in Table 5.1.3. However the increasing stability on the divalent state on descending Group IV b\(^{96}\) is well known. Also there is evidence for at least as large a difference in first and second bond dissociation energies in disilane\(^{94,97}\).
Comparison with the Results of Other Workers.

In Sections (5.1) to (5.3) comparison was made between our results and those of Davidson, Eaborn and Simmie, and excellent agreement was found at a quantitative level. The proposed mechanism for the formation of tetramethylsilane (1a) given in (5.4) also permits an explanation of the apparently conflicting results of Davidson and Stephenson. The latter work was conducted at lower concentrations than ours, that is below $10^{-8}$ mole cm$^{-3}$, and over the temperature range 796 K. to 828 K. The formation of trimethylsilane could not be followed mass spectrometrically because it did not exhibit an intense unique peak. Hence, the "rate of formation" of the fragment $Me_3SiSi(Me_2)CH_2SiMe_2^+$ (m/e 203) was followed, since it was thought to originate from $Me_3SiSi(Me_2)CH_2SiMe_2$, a termination product from a non-chain process rate determined by the initial dissociation. The results obtained were found to be first order and gave the following relationship:

$$\log_{10} k / \text{sec}^{-1} = 13.5 \pm 1.0 - (281.6 \pm 9.2) \text{ kJ mol}^{-1} / 2.303 \text{ RT}$$

The activation energy was therefore identified with $D(Me_3Si-SiMe_3)$. If the chain process described by scheme (1) had been followed, then the observed rate constants would have been greater than those found here in the xylene experiments. However, over the whole temperature range they were found to be less by a factor of at least 2. It is therefore clear that neither the dissociation reaction (1) nor the chain reaction (scheme (1)) was being observed. However, the results given above are seen to be identical with those determined for the rate of formation of tetramethylsilane in series (2), within experimental error. Hence, since the insertion product $Me_3SiSi(Me_2)CH_2Si(Me_2)H$ would give an intense peak at m/e 203, it is probable that the molecular elimination reaction (1a) was being observed in the
earlier work. The radical chain process would be expected to occur concurrently with (1a), and in fact most of the expected products were observed. Trimethylsilane and tetramethylsilane were present under all conditions and were observed gas chromatographically. TMDS was observed mass spectrometrically, but only when the initial concentrations of starting material were greater than $10^{-8}$ mol. cm$^{-3}$.

At lower pressures it may be that the Me$_2$Si=CH$_2$ species could diffuse to the walls more rapidly than it could dimerise, particularly in view of the fact that no inert gas was present. Davidson and Stephenson did not observe the 'isomer', and in fact at these pressures it would not be expected to occur to any great extent.

**Conclusion.**

The reaction schemes (1) and (2) and the thermochemical calculations presented here provide a consistent rationalisation of the results obtained by the author on the thermolysis of hexamethyl-disilane in the absence of inhibitors and in the presence of m-Xylene. The results of other work$^{1-6}$ on HMDS thermolysis are also found to be consistent with these proposals.

Because of the increased magnitude of $D$ (Me$_3$Si—SiMe$_3$) and other thermochemical parameters listed herein, as compared to previously accepted values$^{13}$, a re-assessment of the results obtained on the thermolysis of trimethylsilane and tetramethylsilane is afforded$^{98}$. The thermolysis of tetramethylsilane is at present under re-investigation in this laboratory.
APPENDIX ONE

PREPARATION AND PURIFICATION OF COMPOUNDS
1) Hexamethyldisilane.

This was prepared by the method of Wilson and Smith. 99.

9.1 g. (0.4 g.atoms) of sodium and 63 g. (1.61 g.atoms) of potassium were cut into small pieces and stored over toluene. 200 mls. of dry ethylbenzene and about one quarter of the sodium were added to a 1 litre round-bottomed flask fitted with a thermometer, stirrer, nitrogen bleed, dropping funnel and double-surface water condenser. The dropping funnel and condenser were fitted with calcium chloride drying tubes. Dry, 'oxygen-free', nitrogen was passed through the liquid, while a mixture of 224 g. (2.0 g.mole) of distilled trimethylchlorosilane and 200 mls. of ethylbenzene were added dropwise from the funnel. During this time (4.5 hours) the rest of the sodium and potassium was added. Initially reaction was slow, but when the temperature of the bath was raised to above 50°C a purple colouration appeared, and the reaction proceeded smoothly. The mixture was allowed to reflux with stirring for a further 4 hours.

A still head was fitted later, and the distillate collected until the vapour temperature reached 126°C. The residual liquid was filtered from the solids and, with ethylbenzene washings, was combined with the distillate, and fractionated on a 4 foot column, packed with glass helices and surrounded by a heating jacket. 70 mls. (51 g.) of distillate was collected over the boiling range 111°C-114°C. \(n_D^{20} = 1.4210\) giving a 35% yield.

In order to attain the very high degree of purity required for gas kinetic studies, the distillate was purified by preparative G.L.C. Traces of hexamethyldisiloxane and ethylbenzene were removed in this way. The resulting liquid had a refractive index of \(n_D^{20} = 1.4227\). (Literature value \(n_D^{20} = 1.4228\).) G.L.C. showed a single peak, while the I.R. spectrum showed no traces of Si-O-Si peaks.
at 1055 cm\(^{-1}\) and 522 cm\(^{-1}\) or any 'aromatic peaks'. The high resolution mass spectrum showed no peaks above m/e 149, and a peak height ratio m/e 146:147 of 5:1 indicated the absence of siloxane or heavier materials.

The pure hexamethyldisilane was stored over dried molecular sieve.

2) 2,2,4-Trimethyl-2,4-Disilapentane ('The Isomer').

The method used was that of Kumada et. al.  

1.72 g. (0.01 g.mole) of distilled and thoroughly degassed hexamethyldisilane was sealed in a 50 ml. Carius tube and heated for 4 hours at 450\(^\circ\)C. The resulting liquid had a refractive index

\[ n^2_0 = 1.4140. \]  

(Literature 'isomer' \( n^2_0 = 1.4158 \). Hexamethyldisilane \( n^2_0 = 1.4228 \).) G.L.C. indicated >95% purity with hexamethyldisilane absent, while the I.R. spectrum showed peaks at 1048 cm\(^{-1}\) and 2865 cm\(^{-1}\) indicative of the Si-CH\(_2\)-Si linkage.

As the 'isomer' was required for retention time data only, it was not purified further.

3) meta Xylene.

B.D.H. 'L.R.' grade m-Xylene was found to contain several impurities. These were removed by preparative gas chromatography, only the 'middle' 50% of each peak being collected. The liquid condensed gave a single G.L.C. peak (using the kinetics apparatus described in Chapter 3 (furnace cold)) and had a refractive index

\[ n^2_0 = 1.4971. \]  

(Literature m-Xylene \( n^2_0 = 1.4972 \)) while the I.R. spectrum showed the absence of ortho and para Xylene and other impurities.
4) **Other Compounds.**

Trimethylsilane, tetramethylsilane, and TMDS (1,1,3,3-
Tetramethyl-1,3-disilacyclobutane) were used for the measurement of
retention times. The first was prepared by a previous member of this
group, the second was obtained commercially, while the TMDS was
ddonated by I.C.I. Nobel Division. The trimethylchlorosilane used in
the preparation of HMDS was donated by Dow Corning Ltd., and distilled
by Mrs. Jean Grace of this department.
APPENDIX TWO

USEFUL DATA AND CALCULATIONS
Sensitivity of the Gas Density Detector.

The detector was calibrated under the following operating conditions:

Reference Gas Flow Rate = 73.2 cm$^3$. min$^{-1}$.

Column Gas Flow Rate = 45.6 cm$^3$. min$^{-1}$.

Temperature = 81°C.

The column flow rate was measured with the 'cold trap' at room temperature, since this represented normal recording conditions (although not normal thermolysis conditions — see "measurement of flow rate" — Section 3.1).

Calibration was achieved by injecting HMDS in liquid form into the column gas stream, and recording the peaks produced. All peaks were converted to "corrected peak weights" by calculating their size at a chart speed of 20 mm. min$^{-1}$. and sensitivity of 1 mV. P.S.D., and dividing by a molecular weight factor ($M_s - M_w$) of 118.4. A graph of "corrected peak weights" versus molar quantity of HMDS gave a straight line of computed slope: $(5.41 \pm 0.05) \times 10^3$ grams (corrected paper weight) per mole of sample.

Thus a value of $1.85 \times 10^{-4}$ mole/gram of paper (corrected) was used to convert "corrected peak weights" (recorded at the above flow rates) to molar quantities. See also Chapter Three, pages 58, 61 and 64.

Thus under these conditions:

$Z = 1.85 \times 10^{-4}$ mole/gram.

Slight variations in detector sensitivity throughout Series (2) and the first part of Series (3), caused by minor variations in flow rates, were accounted for using the work of Guillemin and Auricourt. The values of $(Z)$ appropriate to each set of experiments is given in Appendix III.
Linearity of the Detector.

From the calibration experiments, the detector response was found to be linear up to at least $3.5 \times 10^{-5}$ moles, which is greater than the largest sample of HMDS injected.

Calculation of the Range of Initial HMDS Concentrations within the Vessel.

Initial sample sizes $(A_{it})$ were calculated from the equation:

$$A_{it} = Z \left( A_w + \sum_{i} \frac{P_{iw} M_i}{M_a} \right)$$

$A_w$ and $P_{iw}$ are the 'corrected peak weights' of HMDS and the $i$th product respectively.

$M_a$ and $M_i$ are the molecular weights of HMDS and the $i$th product respectively.

The smallest value observed was in Series (1) i.e.

$$A_{it} = 4.14 \times 10^{-4} Z = 4.14 \times 10^{-4} \times 1.85 \times 10^{-4}$$

$$= 7.66 \times 10^{-8} \text{ moles.}$$

The largest value was in Series (3)

$$A_{it} = 1.39 \times 10^{-1} \times 2.14 \times 10^{-4}$$

$$= 2.97 \times 10^{-5} \text{ moles.}$$

The range of HMDS sample sizes was thus:

$$7.6 \times 10^{-8} \text{ to } 3.0 \times 10^{-5} \text{ moles.}$$

Dividing by the volume of the reactor (54.58 cm$^3$) the range of concentrations becomes:

$$1.4 \times 10^{-9} \text{ to } 5.5 \times 10^{-7} \text{ mole cm}^{-3}.$$
Calculation of Percentage Decomposition.

For each given set of conditions, (temperature, flow rate etc.), the extent of decomposition increases with increasing sample size, since there is at least one reaction of order greater than one.

The maximum percentage decomposition at a given set of conditions was thus obtained from the extent of decomposition of the largest injection.

The following equation was used:

\[
\text{% Decomposition} = \frac{\sum_{i=1}^{n} P_{iw} \frac{M_i}{M_a}}{A_w + \sum_{i=1}^{n} P_{iw} \frac{M_i}{M_a}}
\]

The symbols have been explained above.

This method has the implicit assumption that all products are observed on the gas chromatograph, which is probably not strictly true. Nevertheless the values produced are probably reasonable estimates of the true values. The figures are presented, for each set of conditions, in Appendix III.
APPENDIX THREE

FULL KINETIC RESULTS
The results presented below are the data from the individual thermolysis experiments.

The figures in column (F) represent the volumetric flow rate through the reactor divided by the volume of the reactor.

Thus:

$$P\ (\text{sec}^{-1}) \equiv \left( \frac{P_1 T_2}{P_2 T_1} \right) \frac{u_1}{V} = \frac{u_2}{V} = \frac{1}{\text{Residence Time}}$$

For an explanation of symbols see Section 4.1.

The figures in all other columns are 'corrected G.L.C. peak areas' (ie. weights) in arbitrary units (or more strictly grams weight of paper) and are directly proportional to the molar quantities of each compound collected after a thermolysis experiment i.e. $P_{1w}$, $A_w$ etc. (see Section 4.1).

Let: $3MS \equiv$ Trimethylsilane.

$4MS \equiv$ Tetramethylsilane.

$ISO \equiv$ "The isomer" (2,2,4-Trimethyl-2,4-disilapentane)

$TMDS \equiv$ 1,1,3,3-Tetramethyl-1,3-disilacyclobutane.

$HMDS \equiv$ Hexamethyldisilane.

$XYL \equiv$ m-Xylene.

Each horizontal row represents a given experiment or 'injection'.

The numbers in brackets are indices of 10, thus 1·13 (-3) should be read as $1·13 \times 10^{-3}$. A value of (0) means that a particular compound was absent, or present in a sufficiently small quantity to be undetectable on the chromatogram. The symbol (-) means that no accurate measurement was made, and does not imply the absence of a compound. The symbol ($XYL$) in the right hand column means that excess xylene was used in the experiment, but the amount was not measured accurately.

'Corrected peak areas' (weights) may be used to calculate absolute molar quantities by multiplying by the appropriate calibration
factor \( Z \) (in moles/unit or more correctly moles per gram weight of paper). \( Z \) values are given at the top of each section.

'D' represents the maximum value of percentage decomposition under the experimental conditions given. (See Appendix II).

Rate constants evaluated graphically from the data presented here, are listed at the back of this Appendix.

The results below are presented in chronological order.
## Series (1) Thermolysis of Hexamethyldisilane without added m-Xylene.

**Temp. = 841.6K.**  
Residence Time (average) = 38.3 seconds.  
\[ Z = 1.85\ (-4). \]
\[ D = 7.5\%. \]

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<th>ISO</th>
<th>TMDS</th>
<th>HMDS</th>
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**Temp. = 795.1K.**  
Residence Time (average) = 40.7 seconds.  
\[ Z = 1.85\ (-4). \]
\[ D = 1.2\%. \]

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Residence Time = 41.3 seconds.

\[ Z = 1.85 (-4). \quad D = 0.6 \% \]

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Residence Time (average) = 39.4 seconds.

\[ Z = 1.85 (-4). \quad D = 3.4 \% \]

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Temp. = 820.0 K.
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Temp. = 861.3K.  
Residence Time (average) = 37.0 seconds.  
Z = 1.85 (-4).  
D = 11 %

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<td>3.11 (-3)</td>
<td>6.41 (-4)</td>
<td>1.10 (-3)</td>
<td>1.04 (-3)</td>
<td>3.59 (-2)</td>
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Temp. = 871.5K.  
Residence Time (average) = 36.5 seconds.  
Z = 1.85 (-4).  
D = 19 %.
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<td>0</td>
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</table>

**Temp. = 770.4K.**

**Residence Time (average) = 41.9 seconds.**

**Z = 1.85 (-4).**

**D = 0.45%**
Temp. = 784 \cdot 1K.  
Residence Time (average) = 40\cdot9 seconds.  
\[ Z = 1.85 (-4). \]
\[ D = 0.8\% \]

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Temp. = 795 \cdot 7K.  
Residence Time (average) = 40\cdot3 seconds.  
\[ Z = 1.85 (-4). \]
\[ D = 1.1\% \]

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<td>2.49 (-5)</td>
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<td>-</td>
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<td>1.02 (-2)</td>
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</table>
Temp. = 847°OK.
Residence Time (average) = 37.7 seconds.

\[ z = 1.85 \times 10^{-4}. \]

\[ D = 5.7\% \]

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<tr>
<td>(1.34 \times 10^{-3})</td>
<td>-</td>
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<td>1.65 \times 10^{-3}</td>
<td>8.65 \times 10^{-4}</td>
<td>5.53 \times 10^{-2}</td>
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<td>(1.21 \times 10^{-3})</td>
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<tr>
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Series (2) Hexamethyldisilane Thermolysis in the presence of m-Xylene.

Temp. = 831·0K. 
Residence Time (average) = 38·6 seconds.
Z = 1·99 (-4).
D = 2·5 %

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Temp. = 869·2K. 
Residence Time (average) = 37·1 seconds.
Z = 1·99 (-4)
D = 11·0 %

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Temp. = 821.0K.  
Residence Time (average) = 36.6 seconds.

Z = 2.20 (-4).  
D = 2.0 %
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**Temp. = 799.5K.**

Residence Time (average) = 38.2 seconds.

Z = 2.20 (-4).

D = 0.6 %

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Series (3) Thermolysis of Hexamethyldisilane using a Series of Different Flow Rates. (Conducted with and without m-Xylene.)

Temp. = 612.8K. Residence Time (average) = 37.9 seconds.

\[ Z = 2.14 \times 10^{-4}. \]

\[ D = 1.9\%. \]

Total Pressure = 2.2 atmos.

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Temp. = 813.3 K.  
Residence Time (average) = 67.6 seconds.
Total Pressure = 1.6 atmos.  
\( D = 4.5\% \)

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Residence Time (average) = 112 seconds.
Total Pressure = 1.3 atmos.  
\( D = 5.7\% \)

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**Temp. = 813.3K.**  
**Residence Time (average) = 29.0 seconds.**  
**Total Pressure = 2.8 atmos.**  
**D = 1.4%**
### Series (1) Rate Constants

**Formation of product.**

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</tr>
<tr>
<td>861.3</td>
<td>2.71 (-3)</td>
<td>4.76 (-4)</td>
<td>4.08</td>
<td>1.04 (-3)</td>
</tr>
<tr>
<td>871.5</td>
<td>4.81 (-3)</td>
<td>7.76 (-4)</td>
<td>1.08 (+1)</td>
<td>1.78 (-3)</td>
</tr>
<tr>
<td>770.4</td>
<td>2.08 (-5)</td>
<td>7.19 (-6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>784.1</td>
<td>5.00 (-5)</td>
<td>1.11 (-5)</td>
<td>3.35 (-1)</td>
<td></td>
</tr>
<tr>
<td>795.7</td>
<td>9.71 (-5)</td>
<td>1.66 (-5)</td>
<td>5.53 (-1)</td>
<td>4.07 (-5)</td>
</tr>
<tr>
<td>847.0</td>
<td>1.19 (-3)</td>
<td>1.93 (-4)</td>
<td>3.29</td>
<td>4.06 (-4)</td>
</tr>
</tbody>
</table>

### Series (2) Rate Constants

<table>
<thead>
<tr>
<th>Temp.(K)</th>
<th>3MS</th>
<th>4MS</th>
<th>ISO</th>
</tr>
</thead>
<tbody>
<tr>
<td>831.0</td>
<td>2.28 (-4)</td>
<td>8.86 (-5)</td>
<td>5.22 (-1)</td>
</tr>
<tr>
<td>869.2</td>
<td>1.95 (-3)</td>
<td>4.57 (-4)</td>
<td>3.51</td>
</tr>
<tr>
<td>821.0</td>
<td>1.20 (-4)</td>
<td>4.46 (-5)</td>
<td>4.46 (-1)</td>
</tr>
<tr>
<td>799.5</td>
<td>3.40 (-5)</td>
<td>1.54 (-5)</td>
<td></td>
</tr>
</tbody>
</table>

Isomer rate constants in units of cm$^{3/2}$ mol$^{-1}$ sec$^{-1}$, all others in sec$^{-1}$ units.
### Series (3) Rate Constants

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Residence Time (V/u₂ sec.)</th>
<th>3MS</th>
<th>4MS</th>
<th>4MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>812.8</td>
<td>37.9</td>
<td>1.03 × 10⁻⁴</td>
<td>2.65 × 10⁻⁴</td>
<td>4.00 × 10⁻⁵</td>
</tr>
<tr>
<td>813.0</td>
<td>67.6</td>
<td>1.05 × 10⁻⁴</td>
<td>2.48 × 10⁻⁴</td>
<td>4.94 × 10⁻⁵</td>
</tr>
<tr>
<td>813.3</td>
<td>112</td>
<td>1.46 × 10⁻⁴</td>
<td>3.34 × 10⁻⁴</td>
<td>8.04 × 10⁻⁵</td>
</tr>
<tr>
<td>813.3</td>
<td>29.0</td>
<td>9.80 × 10⁻⁵</td>
<td>2.42 × 10⁻⁴</td>
<td>4.60 × 10⁻⁵</td>
</tr>
</tbody>
</table>

- a - Thermolysis in the presence of xylene.
- b - " " " absence " "

---

**Series (3) Rate Constants.**

<table>
<thead>
<tr>
<th>Temp. (K)</th>
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</tr>
</tbody>
</table>

- a - Thermolysis in the presence of xylene.
- b - " " " absence " "
REFERENCES
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(13) I.M.T. Davidson, Quart. Rev. 1971, 25, 111.
    (b) The rate parameters and B.D.E.'s given in this article have been adjusted to include the true values of volumetric flow
rate and concentration within the reactor. This correction was neglected initially. See Section 2.6 of this thesis.


(b) See also, for example, K.J. Laidler "Chemical Kinetics" 2nd Ed., McGraw-Hill, London 1965.


(43) H.M. Hulbert, Ind. Eng. Chem. 1944, 36 1012; 1945, 37 1063.


(b) J. Saldick and L.P. Hammett, ibid., 1950, 72 283.

(c) M.J. Rand and L.P. Hammett, ibid., 1950, 72 287.

(d) R.L. Burnett and L.P. Hammett, ibid., 1958, 80 2415.


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(79) C.L. Guillemin and F. Auricourt, J. Gas Chrom. 1963, 1 24; 1964, 2 156.

(80) C.L. Guillemin, F. Auricourt and P. Blaise, J. Gas Chrom. 1966, 4 338.


(88) I.M.T. Davidson, M. Jones and H.F. Tibbals, unpublished results.


A novel type of flow technique, for the study of gas phase kinetics, is described. This is based on the passage of a pulse of reactant vapour through a stirred flow reactor, and subsequently a gas chromatograph, using a single carrier gas stream. In this way, a chromatogram of unreacted starting material and reaction products is produced, a matter of minutes after the injection of reactant into the system.

Consideration of first order and n th order chemical reactions, under the non-steady state conditions existing in these experiments, has led to the derivation of expressions for rate constants in terms of known parameters.

This technique has been applied to a study of the gas phase thermolysis of hexamethyldisilane, (i) in the absence of inhibitors, and (ii) in the presence of excess m-Xylene. In the first series of experiments the following main reaction products were found: trimethylsilane, tetramethylsilane, 2,2,4-trimethyl-2,4-disilapentane (the rearrangement isomer of hexamethyldisilane), and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. However, complex kinetic behaviour was observed, the formation of some products being non-first order and variable. A large number of experiments were therefore conducted in the presence of the m-Xylene, thus simplifying the kinetic behaviour. Mechanisms are proposed which rationalise all the kinetic observations, and from the observed rate of formation of trimethylsilane in the presence of m-Xylene, the dissociation rate constant for:

\[
\text{Me}_3\text{SiSiMe}_3 \longrightarrow 2 \text{Me}_3\text{Si}^* 
\]

is identified as:

\[
\log_{10}k / \text{sec}^{-1} = 17.23 \pm 0.25 - (336.9 \pm 4.0) \text{kJ mol}^{-1}/2.303 \text{RT}
\]
From the rate parameters evaluated in this, and other work, several thermochemical quantities are estimated. Previous work on hexamethyldisilane thermolysis is discussed in the light of the present findings.