

The Gas Kinetics of Some Thermal Reactions of Cyclic Organosilanes

A Thesis presented by

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Department of Chemistry
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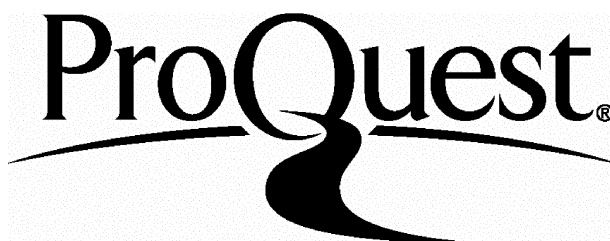
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To my Mother and Father

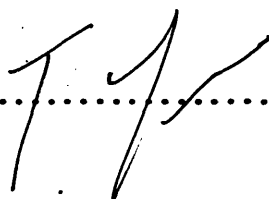
STATEMENT

The experimental work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester between October 1979 and October 1982.

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

March 1983

Signed:

A handwritten signature in black ink, consisting of a large capital 'T' followed by a stylized, cursive 'M' or 'J'.

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I wish to thank my supervisor, Dr. Iain Davidson, for his help, guidance and encouragement throughout the course of this work.

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CHAPTER 1

REVIEW

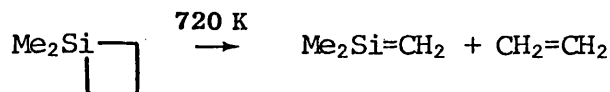
REVIEW

The first organosilicon compound was prepared by Friedel and Crafts in 1863. Although the foundations were laid by Stock, and especially by Kipping, at the beginning of this century, organosilicon chemistry did not become a major field of research until the 1940's, when the commercial applications of silicone polymers became apparent. Silicon is the second most abundant element in the earth's crust. Its semiconductor properties have, over recent years, become of great importance in electronics, and the biological activity of some of its compounds makes it increasingly important in the drugs industry. Carbon-silicon fibres, an important precursor to which are cyclic organosilicon compounds, figure along with silicone polymers in the field of plastics.

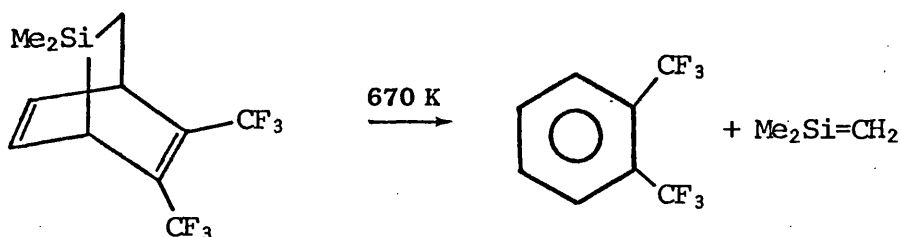
1.1 Reactive Intermediates

Like carbon, silicon is tetravalent and can form stable single bonds arranged tetrahedrally. This it does with $3s\ 3p^3$ hybrid orbitals, forming stable tetraalkyl silanes, R_4Si , and siloxanes, $R_3Si-O-SiR_3$. It is more electropositive than carbon and, as a result, forms stronger bonds to the halogens, oxygen and nitrogen. In view of its larger size, however, it forms weaker bonds to itself and hydrogen, and can only participate in relatively weak π -bonding. Because of this, molecules which contain a π -bonded silicon atom are generally very reactive, and exist as transient intermediates which are of great current interest¹ in organosilicon chemistry. The gas phase chemistry of two such species, silaalkenes ($>Si=C<$) and silanones ($>Si=O$), is summarised here. Other species which contain a π -bond to silicon are disilenes² ($>Si=Si<$) and silanimines³ ($>Si=N-$).

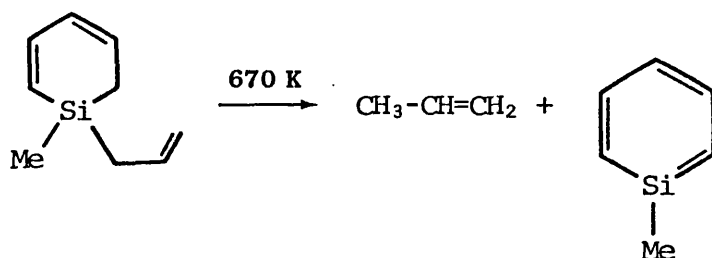
2-Methyl-2-silapropene was generated by Flowers and Gusel'nikov⁴ in the gas phase pyrolysis of 1,1-dimethyl-1-silacyclobutane.



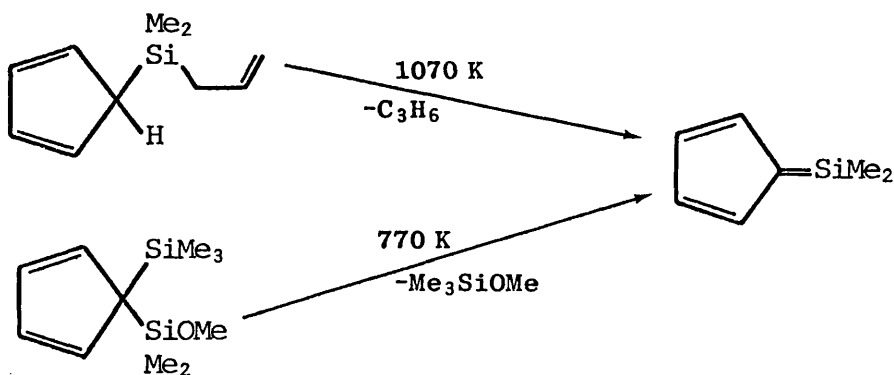
Since then a number of different routes to silaalkenes have been discovered, many leading from cyclic precursors. Barton and Kline⁵ found that the pyrolysis of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene yielded 2-methyl-2-silapropene:



Silatoluene is formed in the pyrolysis of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene⁶:

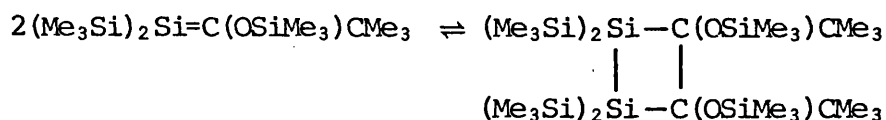


6,6-Dimethyl-6-silafulvene was successfully generated⁷ by pyrolysis of the following precursors:

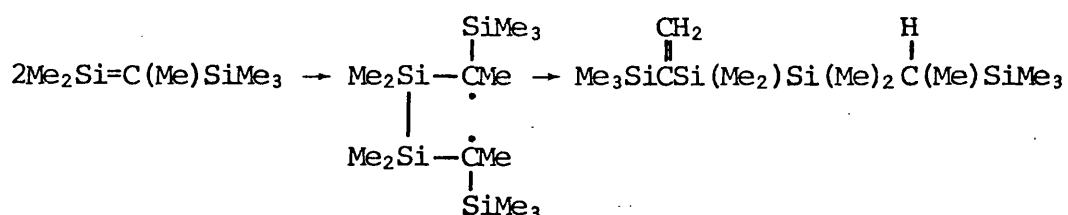


In all but one of the above reactions the involvement of the silaalkene

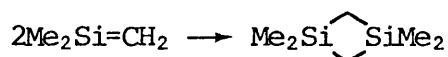
The strength of the silicon-carbon π -bond in 2-methyl-2-silapropene has been estimated to be $163 \pm 21 \text{ kJ mol}^{-1}$ by Walsh⁸ and $188 \pm 20 \text{ kJ mol}^{-1}$ by Davidson, Potzinger and Reimann.⁹ The strength of the carbon-carbon π -bond is ca. 265 kJ mol^{-1} . Because of their high reactivity, silaalkenes generally undergo bimolecular reactions as detailed below, although they can be stabilized if highly substituted: when under an inert atmosphere, $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{C}_{10}\text{H}_{15}$ is stable at room temperature.¹⁰ The following silaalkene can exist as a monomer in solution, in equilibrium with the 1,2-disilacyclobutane resulting from head-to-head dimerisation¹¹:



Highly carbon-substituted silaalkenes may dimerise in this manner. A similar process followed by internal hydrogen abstraction is¹²:



However, simple silaalkenes (e.g. 2-methyl-2-silapropene) undergo head-to-tail dimerisation:

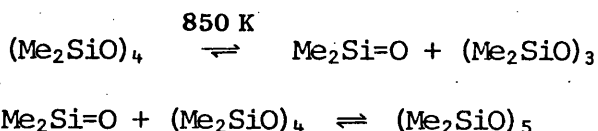


The reversible nature of this reaction has been demonstrated,^{13,14} although the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane does not provide a clean source of the silaalkene.¹⁵ 2-Methyl-2-silapropene is known to add to the π -bonds of alkenes,^{4,16} carbonyls¹⁷ and oxygen¹⁸

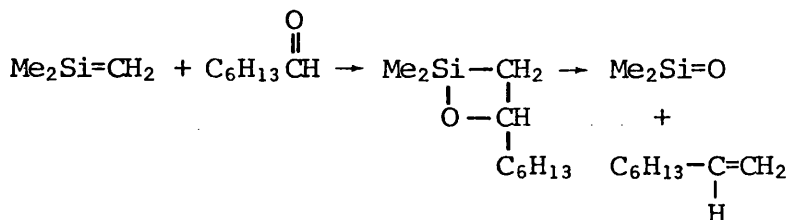
(see Chapter 4), and to insert into hydrogen halides,¹⁸ silicon-oxygen bonds^{19,20} and alcohols.^{4,17} It also undergoes Diels-Alder reactions with conjugated dienes.²¹

Direct spectroscopic evidence for the existence of 2-methyl-2-silapropene has been obtained from low temperature trapping experiments.²² It has been observed in the gas phase by mass spectrometry.^{23,24}

Dimethylsilanone was first generated in the pyrolysis of octamethylcyclotetrasiloxane. Its presence was inferred from the product mixture and the effect of various trapping agents. The following mechanism was suggested²⁵:

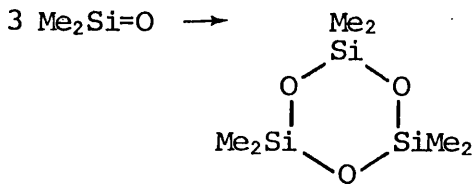


Silanones are also formed in the reaction between silaalkenes and non-enolizable carbonyls,¹⁷ e.g.:



The generation of dimethylsilanone from the reaction of 2-methyl-2-silapropene with oxygen¹⁸ is discussed in Chapter 4.

In the absence of trapping agents, silanones trimerise, e.g.:



Other reactions of dimethylsilanone include insertions²⁵ into silicon-

oxygen and silicon-chlorine bonds. The strength of the π -bond in dimethylsilanone has been estimated²⁵ as 158 kJ mol⁻¹, much less than that of the carbon-oxygen π -bond, which is ca. 380 kJ mol⁻¹.

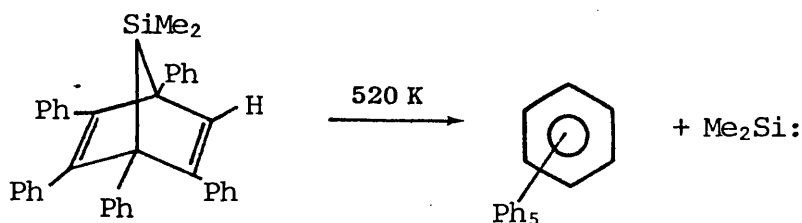
Silyl radicals and silylene diradicals are reactive intermediates which also figure in gas phase organosilicon chemistry. The trimethylsilyl radical ($\text{Me}_3\text{Si}\cdot$) abstracts chlorine from alkyl chlorides,²⁶ a reaction which is expected in view of the strength of silicon-chlorine bonds. It also abstracts hydrogen from alkyl groups²⁷ and, somewhat surprisingly, chlorine from silyl chlorides.²⁸ Trimethylsilyl radicals are produced in the pyrolyses of allyltrimethylsilane²⁹ and hexamethyldisilane.^{9,30,31} Pyrolysis of the latter compound, under suitable conditions,³⁰ also induces an interesting isomerisation leading to $\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$. An analogous reaction is observed in the pyrolysis of certain cyclic organosilicon compounds.³² It is discussed in Chapter 5.

The pyrolyses of pentamethyl-³³ and chloropentamethyldisilane,³⁴ however, do not yield silyl radicals. In both cases dimethylsilylene ($\text{Me}_2\text{Si:}$) is produced along with the appropriate silane:

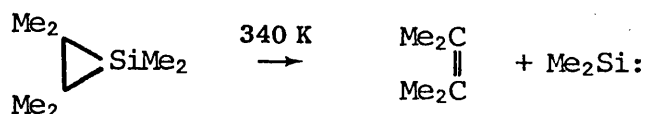


This is a general reaction.³⁵ It occurs in preference to simple silicon-silicon bond rupture when the silane produced contains a bond into which the silylene can easily insert.

Silylenes are also produced in the pyrolysis of 7-silanorbornadienes³⁶:



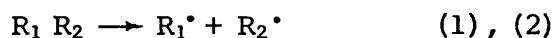
A very mild source of silylenes is the pyrolysis of silacyclopropanes³⁷ (this reaction was originally carried out in the liquid phase, but it is likely to proceed in the gas phase also).



The presence of dimethylsilylene in the above reactions was inferred from trapping experiments. It has, however, been observed directly by low temperature trapping followed by spectrophotometric analysis.³⁸ The reactions of dimethylsilylene include addition to carbon-carbon³⁹ and carbon-oxygen⁴⁰ π -bonds, and insertion into silicon-hydrogen,³⁹ silicon-oxygen,^{41,42} silicon chlorine^{41,33,34} and hydrogen-chlorine⁷¹ bonds.

1.2 Kinetic Studies

Kinetic data allow inferences to be drawn regarding reaction mechanism. In addition, they can be used to derive thermochemical data including bond dissociation energies: the enthalpy change for the reaction



gives $D(R_1-R_2)$, but is also equal to E_1-E_2 . Therefore $E_1 = D(R_1-R_2)$ when E_2 is zero. However, gas phase pyrolyses of hydrocarbons and organosilicon compounds are often complicated by secondary reactions. As a result the correct activation energy for the initial dissociation is not always clear. Such decompositions generally proceed via the Rice-Herzfeld chain mechanism. One of the propagating steps is the dissociation of a large radical into a small radical and an alkene. The weakness of π -bonds to silicon reduces the feasibility of this step in the pyrolysis of organosilicon compounds and, as a result, the chain

lengths involved in such decompositions are shorter than those in hydrocarbon pyrolyses. This factor can be instrumental in overcoming the problem of secondary reactions, such that Arrhenius parameters for the initial dissociation may be measured.

In any chain reaction, initiation is the step of highest activation energy. Therefore chain length tends to decrease with increasing temperature. If the chain length can be reduced to below unity the reaction becomes rate determined by the initial dissociation. A lower limit for the activation energy for the reaction

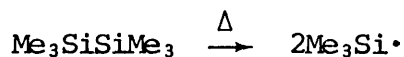


was measured in this way.⁴³ In the pyrolysis of tetramethylsilane, methane formation was found to obey first order kinetics over the temperature range 840-1055 K, but the rate constants for this process fell into two groups. Between 955 and 1055 K the Arrhenius parameters were: $\log A = 17.6 \pm 0.3$, $E = 355 \pm 6 \text{ kJ mol}^{-1}$, whilst at lower temperatures they were: $\log A = 11.2 \pm 0.1$, $E = 239 \pm 2 \text{ kJ mol}^{-1}$. The high temperature parameters were identified with a non-chain mechanism. In accordance with this explanation, an increase in the surface/volume ratio had no effect on high temperature rate constants, but reduced low temperature rate constants as a result of the loss of chain-carrying radicals from the gas phase. However, since any residual chain mechanism would have reduced the observed activation energy relative to that for the pure non-chain reaction,⁴⁴ the experimental result provides a lower limit for $D(\text{Me}_3\text{Si-Me})$.

Another way of overcoming the problem of secondary reactions is shown

* All 'A'-factors are in the following units. First order: s^{-1} , second order: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

in the following example. The Arrhenius parameters for the initial step in the pyrolysis of hexamethyldisilane



were successfully determined³¹ by trapping $\text{Me}_3\text{Si}\cdot$ with m-xylene, which has an easily abstractable hydrogen, and measuring rate constants for the formation of trimethylsilane. The Arrhenius parameters deduced in this way between 770 and 872 K were: $\log A = 17.2 \pm 0.3$, $E = 337 \pm 4 \text{ kJ mol}^{-1}$. The activation energy was identified with $D(\text{Me}_3\text{Si-SiMe}_3)$. Both of the above studies utilized the "Pulse Stirred Flow" technique (PSF)⁴⁵ which is described in Chapter 2.

The most obvious way of reducing the importance of secondary bimolecular reactions is to use low pressures where they are not favoured. A kinetic technique which achieves this end is the "Very Low Pressure Pyrolysis" method (VLPP) which was pioneered by Benson.^{46,47} A schematic diagram of the apparatus is shown in Figure 1.1. It is a flow technique: a steady state concentration of reactant is achieved dependent upon the rate of flow into the reaction vessel, the rate of flow out, and the pyrolysis rate. Decomposition rate constants can be determined over a temperature range from a knowledge of the steady state concentration of the reactant. Similarly, rate constants for product formation can be deduced from the steady state concentrations of reactant and product. Typically experiments are carried out at ca. 10^{-3} mmHg . This means that nearly all energization of molecules is through wall collisions and, as a result, the technique also lends itself to the study of collision efficiencies. However, since the pressures used are so low, rate constants measured are usually well in the unimolecular fall-off region,⁴⁸ and it is necessary to use RRK or RRKM theory to evaluate high pressure

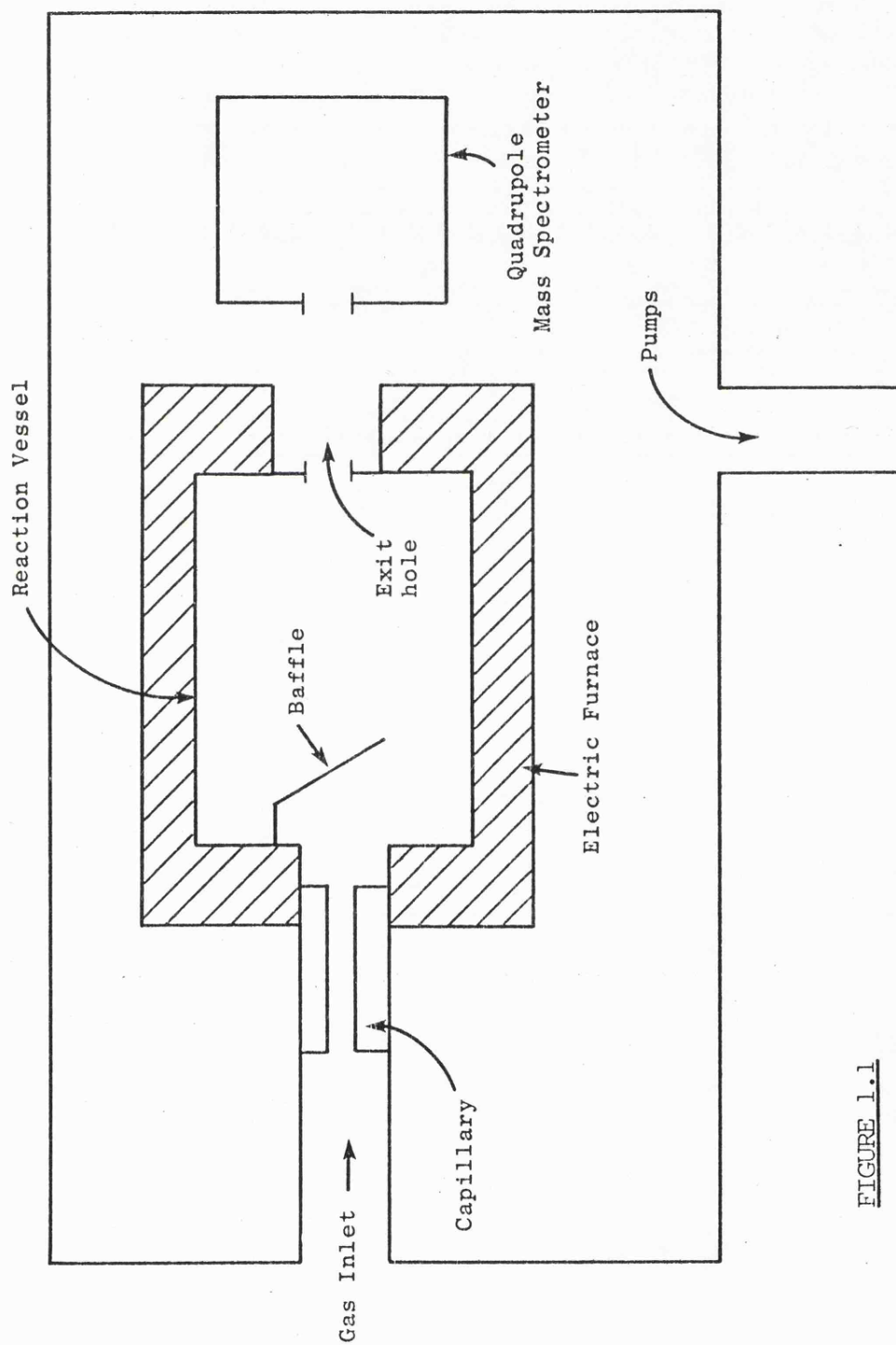
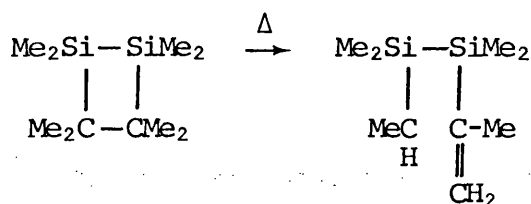


FIGURE 1.1
Schematic Diagram of VLPP Apparatus

Arrhenius parameters. Heterogeneous reactions are generally unimportant, since they require a reacting species to reside on a surface and undergo chemical rearrangement. Such rearrangements are usually slow when compared with the competing process, re-evaporation. However, surface effects have hampered studies of the VLPP of molecules containing a silicon-hydrogen bond.⁴⁹ The technique was successfully used²⁴ to observe directly 2-methyl-2-silapropene in the pyrolysis of 1,1-dimethyl-1-silacyclobutane, although its application to the kinetics of reactant decomposition was also affected by a heterogeneous process.

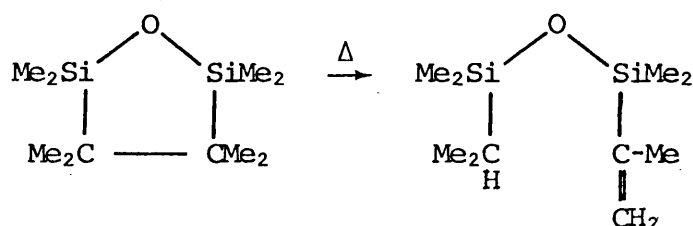
In view of the difficulties encountered in the use of the VLPP method with organosilicon compounds, the "Low Pressure Pyrolysis" technique (LPP)^{49, 50} was introduced so that the advantage of the VLPP method (i.e. the reduction of secondary bimolecular reactions) could be coupled with the advantages of high pressure methods (i.e. easy interpretation of experimental data requiring no RRK or RRKM theory, and a reduction of surface effects). It is a static method in which pressures of ca. 0.1 mmHg are pyrolysed in a quartz reaction vessel which is connected via a pinhole leak to the ion source of a quadrupole mass spectrometer (for full experimental details, see Chapter 2). The technique is normally used to measure unimolecular rate constants which are not in the fall-off region.⁴⁸ The pressure is still low, however, and bimolecular reactions are not favoured, although they do occur when no unimolecular step is available to remove reactive species. Some applications of the LPP technique are shown below.

The LPP of octamethyl-1,2-disilacyclobutane⁵⁰ proceeded via an isomerisation, obeying first-order kinetics:



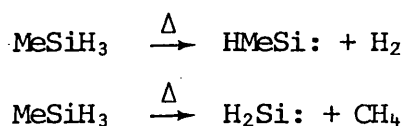
Rate constants were measured between 582 and 653 K by monitoring a characteristic peak in the mass spectrum of the reactant. They were used to derive the following Arrhenius parameters: $\log A = 15.4 \pm 0.4$, $E = 207 \pm 5 \text{ kJ mol}^{-1}$. The activation energy was used to infer a ring strain of 81 kJ mol^{-1} .

First-order rate constants for the isomerisation of octamethyl-1,3-disila-2-oxacyclopentane⁵⁰



were obtained in the same way between 695 and 752 K, leading to the following Arrhenius parameters: $\log A = 15.7 \pm 0.3$, $E = 248 \pm 4 \text{ kJ mol}^{-1}$, and a ring strain of 40 kJ mol^{-1} .

The LPP of methylsilane⁴⁹ in the fall-off region occurred via two routes:



The decomposition of methylsilane obeyed first-order kinetics. Rate constants obtained between 898 and 1000 K by monitoring the intensity of its mass peak at 45^+ (M^+-H) were used to derive the following Arrhenius parameters: $\log A = 14.1 \pm 0.2$, $E = 271 \pm 3 \text{ kJ mol}^{-1}$. Since the formation of hydrogen exceeded that of methane by a factor of ca. 25 over the

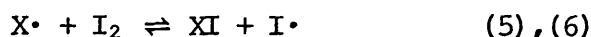
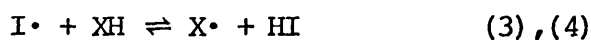
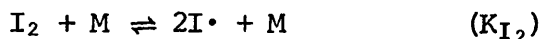
temperature range, these parameters were identified with the former reaction. The Arrhenius parameters for the formation of methane were estimated from the relative rates of hydrogen and methane produced in the LPP experiments, and those observed in previous experiments at a different temperature:⁵¹ $\log A \approx 13.6$, $E \approx 300 \text{ kJ mol}^{-1}$.

However, this study indicated that even the LPP technique could not completely rule out heterogeneous reaction of molecules with a silicon-hydrogen bond: below 898 K the activation energy for the decomposition of methylsilane was reduced relative to the value given above, probably because of a heterogeneous process.

The LPP technique has also been used to measure the kinetics of the reactions between 2-methyl-2-silapropene and various substrates.^{18,19} The reactive intermediate was generated by the pyrolysis of 1,1-dimethyl-1-silacyclobutane, and the relative rates of dimerisation and reaction were measured over a temperature range. The Arrhenius parameters for the reaction were then calculated relative to those for the dimerisation²³ (see Chapter 4). Rate constants measured in this way were in the order of $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 800 K, so the LPP technique complements the use of conventional static systems where higher pressures are utilized. Under these conditions it is possible to measure lower rate constants only. Flowers and Gusel'nikov⁴ have used such a technique to study the kinetics of the reaction between 2-methyl-2-silapropene and ethene. John *et al.* have also used a conventional static system to measure the kinetics of the reactions of the same silaalkene with various alkenes¹⁶ and conjugated dienes.²¹

A further kinetic technique that has been applied to measure bond strengths in organosilicon chemistry is that devised by Benson⁵² in which the gas kinetics of the reaction between iodine and a suitable substrate

is measured. Walsh⁸ has used the method to measure the strengths of several silicon-hydrogen bonds and one carbon-hydrogen bond. In this technique the concentration-time profile of iodine is monitored spectrophotometrically as it reacts with an organic molecule according to the following scheme:



In the early stages, when reaction (4) is not important, the following relationship applies:

$$-\frac{d[\text{I}_2]}{dt} = k_3 \text{K}_{\text{I}_2}^{\frac{1}{2}} [\text{I}_2]^{\frac{1}{2}} [\text{XH}]$$

The integrated form of this equation and the known⁵³ value of $\text{K}_{\text{I}_2}^{\frac{1}{2}}$ can be used to find k_3 , the temperature dependence of which gives the activation energy. An estimate of E_4 (usually 0-8 kJ mol⁻¹) then yields $\Delta H_{3,4}^\circ$ ($=E_3-E_4$). Since $\Delta H_{3,4}^\circ = D(\text{X-H}) - D(\text{H-I})$, and $D(\text{H-I})$ is known⁵³ to be 298.5 ± 0.2 kJ mol⁻¹, $D(\text{X-H})$ may readily be found.

1.3 Thermochemistry

Heats of formation can be used to calculate the enthalpy change for a reaction. In view of the simple relationship between this property and the activation energies for the forward and reverse steps, heats of formation can complement kinetic data in understanding and predicting the nature of chemical systems. Further, they can be used to derive bond dissociation energies, thus providing an insight to molecular structure: the heat of formation of a radical, $\text{R}\cdot$, may be deduced from the following relationship.

$$\Delta H_f^\circ(R\cdot) = \Delta H_f^\circ(RX) - \Delta H_f^\circ(X\cdot) + D(R-X)$$

$\Delta H_f^\circ(R\cdot)$ can then be used to calculate other bond dissociation energies, $D(R-Y)$, via:

$$D(R-Y) = \Delta H_f^\circ(R\cdot) + \Delta H_f^\circ(Y\cdot) - \Delta H_f^\circ(RY)$$

Walsh⁸ has used his experimental bond dissociation energies [$D(R-X)$ above], along with well established thermochemical data [$\Delta H_f^\circ(X\cdot)$ and $\Delta H_f^\circ(Y\cdot)$ above] and other heats of formation which he felt to be of reasonable reliability, to generate bond dissociation energies which are not otherwise available. He has thus produced the most recent self consistent compilation of such thermochemical data for organosilicon compounds.

However, heats of formation of organosilicon compounds [$\Delta H_f^\circ(R-Y)$ and $\Delta H_f^\circ(R-X)$ above] are often subject to much uncertainty. The conventional calorimetric techniques that have led to reliable data for most organic compounds are not as applicable to organosilicon compounds because of the involatility of silica.⁵⁴ Nonetheless, it is possible to calculate unknown heats of formation from calorimetrically derived values for related compounds by using the notion that this property is made up of additive contributions from individual sections of the molecule.

Allen⁵⁵ has devised a "bond additivity scheme" in which it is assumed that the strength of the bond between any two given atoms depends only upon the identity of those atoms and the interaction between adjacent bonds. This scheme has been applied to organosilicon compounds by Potzinger and Lampe⁵⁶ who used as a data base calorimetrically derived⁵⁷ values of $\Delta H_f^\circ(\text{SiH}_4)$ and $\Delta H_f^\circ(\text{Si}_2\text{H}_6)$, and their own electron impact measurements. Quane⁵⁸ used the same scheme to try to reconcile the data of Potzinger and Lampe⁵⁶ with calorimetric data produced by Hajiev and

Agarunov.⁵⁹ More recently Potzinger, Ritter and Krause⁶⁰ have applied Allen's scheme to organosilicon compounds with a data base of several calorimetrically derived heats of formation and a number of appearance potential measurements.

Heats of formation may also be estimated with the "Electrostatic Energy Corrected Bond Additivity Scheme", which was devised by Benson and Luria.⁶¹ This considers coulombic interactions within a molecule, instead of interactions between adjacent bonds, to explain inconsistencies in the strength of the bond between any two given atoms. It was first applied to organosilicon compounds by Davidson⁶² who assessed the reliability of the data generated by Potzinger, Ritter and Krause and those in the "CATCH" tables,⁶³ a compilation of experimentally derived thermochemical data. Ring and O'Neal⁴⁴ have applied the scheme to a far wider range of organosilicon compounds. They concluded that data in the "CATCH" tables⁶³ show good self consistency, and therefore used these values as the basis for a "group additivity scheme".⁶⁴

In the same paper Ring and O'Neal tabulated the data necessary for a group additivity scheme to estimate the entropies and heat capacities of organosilicon compounds. These and other⁶⁵ data are used in Chapter 4 to estimate 'A'-factors for various addition reactions of 2-methyl-2-silapropene from observed or estimated 'A'-factors for the reverse reactions.

CHAPTER 2

APPARATUS AND EXPERIMENTAL METHODS

APPARATUS AND EXPERIMENTAL METHODS

Most of the work described was carried out in a LPP apparatus,^{49,50} although the PSF technique⁴⁵ was also utilized. Both methods are described in this Chapter.

2.1 LPP APPARATUS

The LPP apparatus comprised an electrically heated quartz reaction vessel which was connected to the ion source of a mass spectrometer via a pinhole leak. Samples were stored on a conventional vacuum line and could be expanded into the mass spectrometer either through the reaction vessel or via a metrosil leak at room temperature.

2.1.1 The Mass Spectrometer⁶⁶

A V.G. Micromass Q801K quadrupole mass spectrometer was used. There were two modes in which it could operate. An entire mass spectrum, up to 300 a.m.u., could be viewed on an oscilloscope screen or recorded on chart paper. Samples could be introduced via the metrosil leak, or via the reaction vessel, in which case the observed mass spectrum was of the pure sample and its pyrolysis products: there was a decrease in intensity of the mass peaks due to the sample, and an increase in those due to its pyrolysis products as decomposition proceeded.

The second mode in which the mass spectrometer could operate utilized a peak selector (V.G. Micromass) which, once tuned, could follow quantitatively any change in intensity of individual selected mass peaks. It scanned the tuned mass peaks repeatedly and measured their heights in the form of voltages which were displayed on a digital voltmeter. Two types were used: one which could be tuned to a maximum of four mass peaks (i.e. a four channel peak selector), and one which could be tuned to a maximum of eight. Both had controls whereby the scan speed and the

gains on each channel could be altered. Kinetic data were obtained when the mass spectrometer was operated in this mode (see Section 2.1.5).

The mass spectrometer was pumped with an Edwards oil diffusion pump and an Edwards rotary pump. It operated at pressures of ca. 10^{-7} mmHg.

A quadrupole mass spectrometer was used in preference to a conventional magnetic mass spectrometer because of the extra speed with which the former can scan a mass spectrum. In addition, quadrupole mass spectrometers are more convenient to use than magnetic mass spectrometers since they are more compact and produce mass spectra with linear scales. The mass filter in a quadrupole mass spectrometer⁶⁶ comprises four cylindrical rods arranged as shown in Figure 2.1. Opposite pairs of rods are connected electrically. By passing DC and RF fluxes through the rods in a controlled manner a field is set up between them which allows ions with a particular m/e ratio only to pass straight through to the analyser. The mass range is scanned by changing the intensity of the RF flux.

2.1.2 The Furnace

The quartz reaction vessel was situated in a furnace which consisted of a steel tube wrapped with heating wire. This arrangement was insulated with fireproof clay and contained in a housing of asbestos board and aluminium. The mains power supply came via a "variac" variable transformer which was used to set the furnace temperature, this being measured with a one junction chrome-alumel thermocouple inserted into a pocket in the reaction vessel. The maximum temperature used in this study was ca. 1100 K.

2.1.3 The Reaction Vessel (see Figure 2.2)

Samples entered the reaction vessel through a tube which ended in a

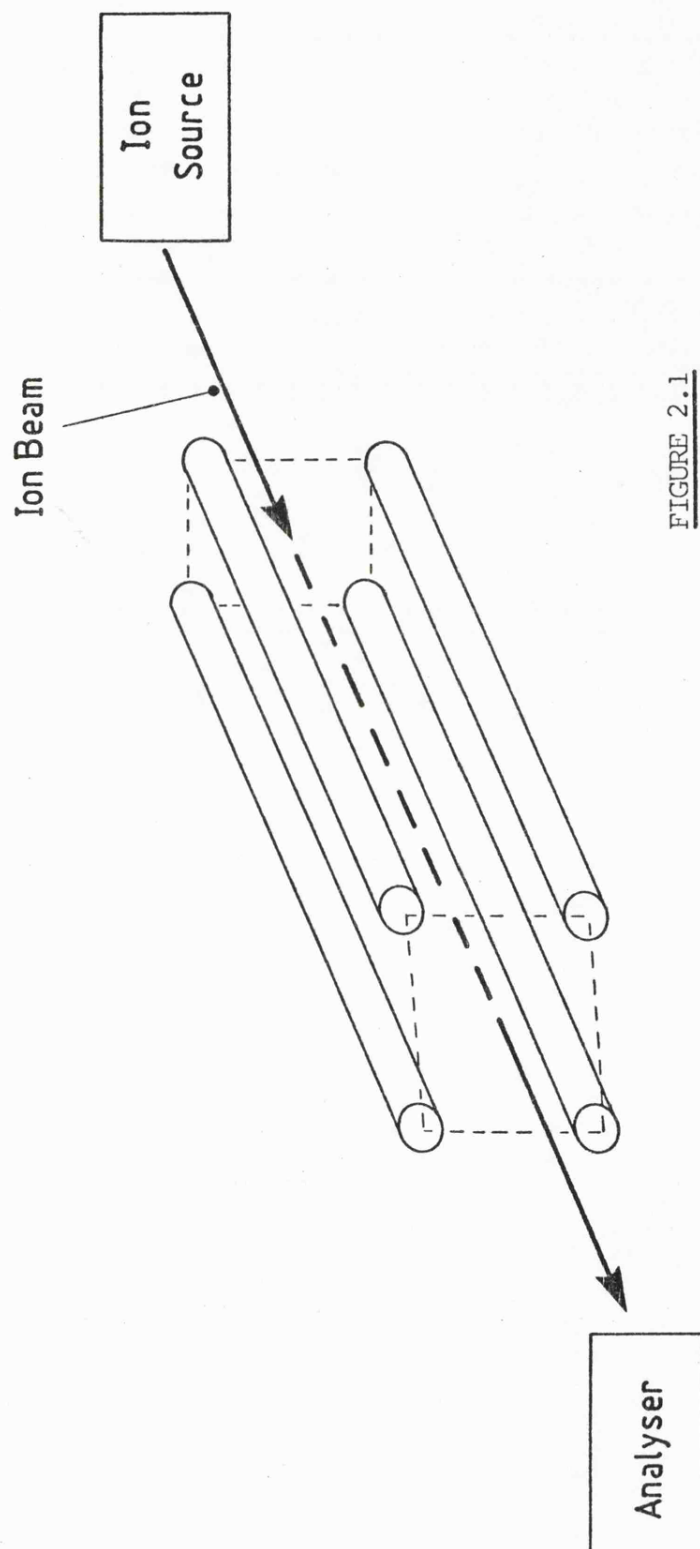


FIGURE 2.1
The Mass Filter in a Quadrupole
Mass Spectrometer

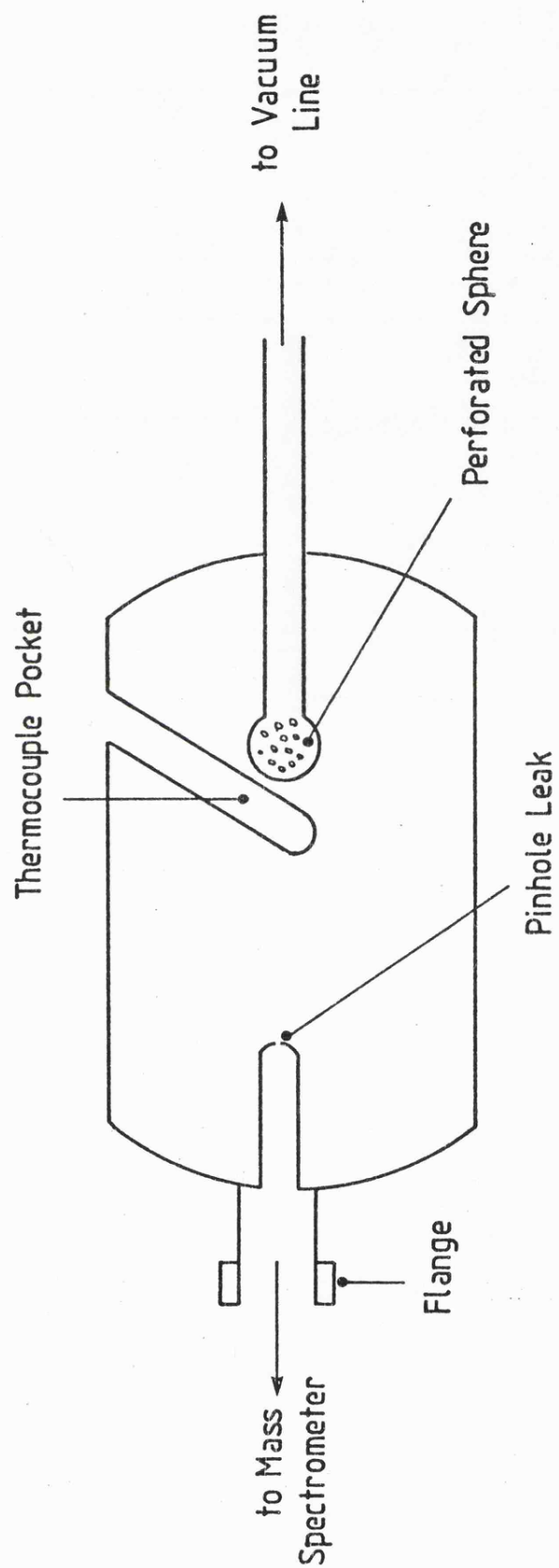


FIGURE 2.2
LPP Apparatus: Reaction Vessel

perforated sphere and thus became evenly distributed. Material then flowed from the reaction vessel into the ion source of the mass spectrometer through a pinhole leak⁶⁷ which had a diameter of ca. 10 μ . The pinhole leak was surrounded by a flange which fitted into a recess in the mass spectrometer housing, a PTFE 'O' ring providing a vacuum seal. The 'O' ring was protected from the heat of the furnace and the ion source by a water jacket. The reaction vessel was surrounded with quartz wool to minimise heat loss. Its volume was ca. 30 cm³. Dead space was <4%.

2.1.4 The Vacuum Line (see Figure 2.3)

The vacuum line was made of pyrex tubing and Young's greaseless stopcocks. It was connected to the reaction vessel through a small region in which the head of a pressure transducer (Bell and Howell) was situated, and it was into this "pressure transducer zone" that samples were measured before being expanded into the mass spectrometer (through either the reaction vessel or the metrosil leak). The pumping system comprised a mercury diffusion pump and an NGV rotary pump with which pressures as low as 10^{-3} mmHg could be obtained.

2.1.5 Acquisition of Kinetic Data[†]

As stated in Section 2.1.1, kinetic data were obtained by using a peak selector which measured the intensity of selected mass peaks, at regular time intervals, in the form of voltages which were displayed on a digital voltmeter. Two methods were used to collect these data. Initially a Solartron Schlumberger A220 digital voltmeter was used along with a Solartron Schlumberger A295 recorder drive unit which activated a Facit 4070 punch tape machine. Peak height data collected in this way were subsequently read into the University's "Cyber 73" computer. This

[†] Primary data from a typical kinetic run are shown in Appendix 1.

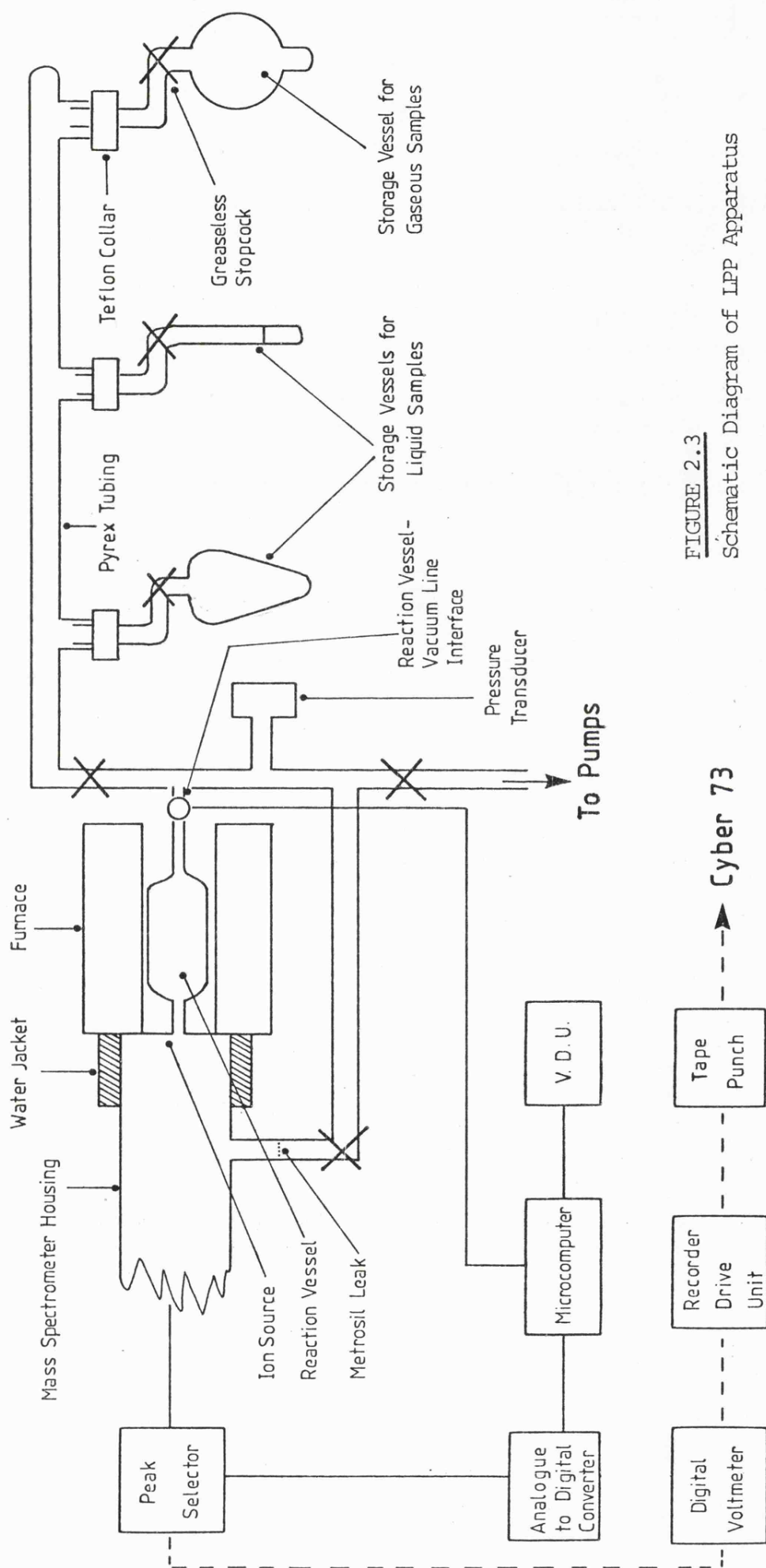


FIGURE 2.3
Schematic Diagram of LPP Apparatus

→ **Cyber 73**

technique was used with the four channel peak selector only.

However, although this peak selector was capable of scanning the four channels once in every 0.3s, it was not possible to collect data so rapidly. The unit which limited the speed with which data could be acquired was the recorder drive: the maximum scan speed with which this could cope was 3s. Thus, even if all four channels were tuned to the same mass peak, the maximum frequency with which its height could be measured was once in every 0.75s. This restriction placed an upper limit on the range of reaction rates that could be studied. The data acquisition technique was improved in an attempt to remove this restriction, and also to improve the data processing facilities that were available: data collected on punched tape were analysed in "batch" mode by the Cyber 73 computer (see Chapter 3), a process which often took two days to complete.

The peak selector was coupled via an analogue to digital converter (Newport) to a Research Machines 380Z Microcomputer (RML380Z). The RML380Z was chosen because the software necessary for such a coupling could be written in the "BASIC" programming language. Also, it was capable of high resolution graphics, making it ideal to "interactively" process experimental data (see Chapter 3). The interfacing of the RML380Z to the peak selector was performed by C. E. Dean.⁶⁸ With this arrangement peak heights were measured by the peak selector and displayed as voltages by the analogue to digital converter. The microcomputer received data in digital form and used its internal clock to time them. Magnetic disc was used for storage.

The maximum possible scan speed was 1s, so if all four channels were tuned to the same mass peak, its height could be measured once in every 0.25s. As it was sometimes desirable to monitor more than four mass

peaks, the four channel peak selector was replaced by an eight channel peak selector. Using this in conjunction with the RML380Z it became possible to measure peak heights every 0.125s.

2.1.6 Reaction Vessel - Vacuum Line Interface

Originally samples were expanded from the pressure transducer zone into the reaction vessel through a greaseless stopcock. However, after the introduction of the RML380Z, this stopcock was replaced by a solenoid valve (Production Techniques), which could be opened by the RML380Z (see Section 2.1.7), or manually. The complete LPP apparatus is shown in Figure 2.3.

2.1.7 Experimental Technique Used During a "Kinetic Run"

Three slightly different experimental techniques were used during this study. In all cases, the temperature of the furnace was set with the "variac" variable transformer, and a pressure of sample was expanded into the reaction vessel or through the metrosil leak. The peak selector was then tuned to the appropriate mass peaks, the gains on each channel were set and the scan speed was chosen. The sample was then pumped away and a second sample was measured into the pressure transducer zone.

If the experimental data were to be collected on punched tape the experimental technique proceeded as follows. The peak selector was activated and it started to measure the heights of the chosen mass peaks. After several complete scans the greaseless stopcock was opened for ca. 2s to allow the sample to expand from the pressure transducer zone into the reaction vessel. It was then shut again. Once sufficient kinetic data had been collected the peak selector was switched off and the punched tape was removed and subsequently read into the Cyber 73 computer.

If the sample was to be expanded into the reaction vessel through the greaseless stopcock and the data were to be collected by the RML380Z, then a very similar experimental technique was used. The experimental technique was modified when the greaseless stopcock was replaced by the solenoid valve. In this case, once the peak selector had been activated the RML380Z automatically opened the solenoid valve (which was closed 2s later by a control device) after four complete scans.

Once the paper tape had been removed, or the experimental data had been stored on magnetic disc, any sample and pyrolysis products remaining in the reaction vessel were used to check the tuning of the peak selector in preparation for the next experiment. The reaction vessel was then evacuated.

The peak selector was allowed to scan the chosen mass peaks before the sample was expanded into the reaction vessel in order to measure the "baseline" peak height for each channel.

2.1.8 Applications of the Experimental Technique

The experimental technique was used to measure the height of selected mass peaks at regular time intervals through the course of a reaction. Since the height of a mass peak at any given time was directly proportional to the concentration in the reaction vessel at that time of the species represented by it, observed peak height - time profiles were effectively concentration - time profiles (or reaction profiles). In practice, at least one channel of the peak selector was tuned to a mass peak characteristic of the reactant, while the remainder were tuned to mass peaks characteristic of the pyrolysis products. The general form of observed peak height - time profiles is shown in Figure 2.4.

Since under LPP conditions reactant decomposition is first order (but

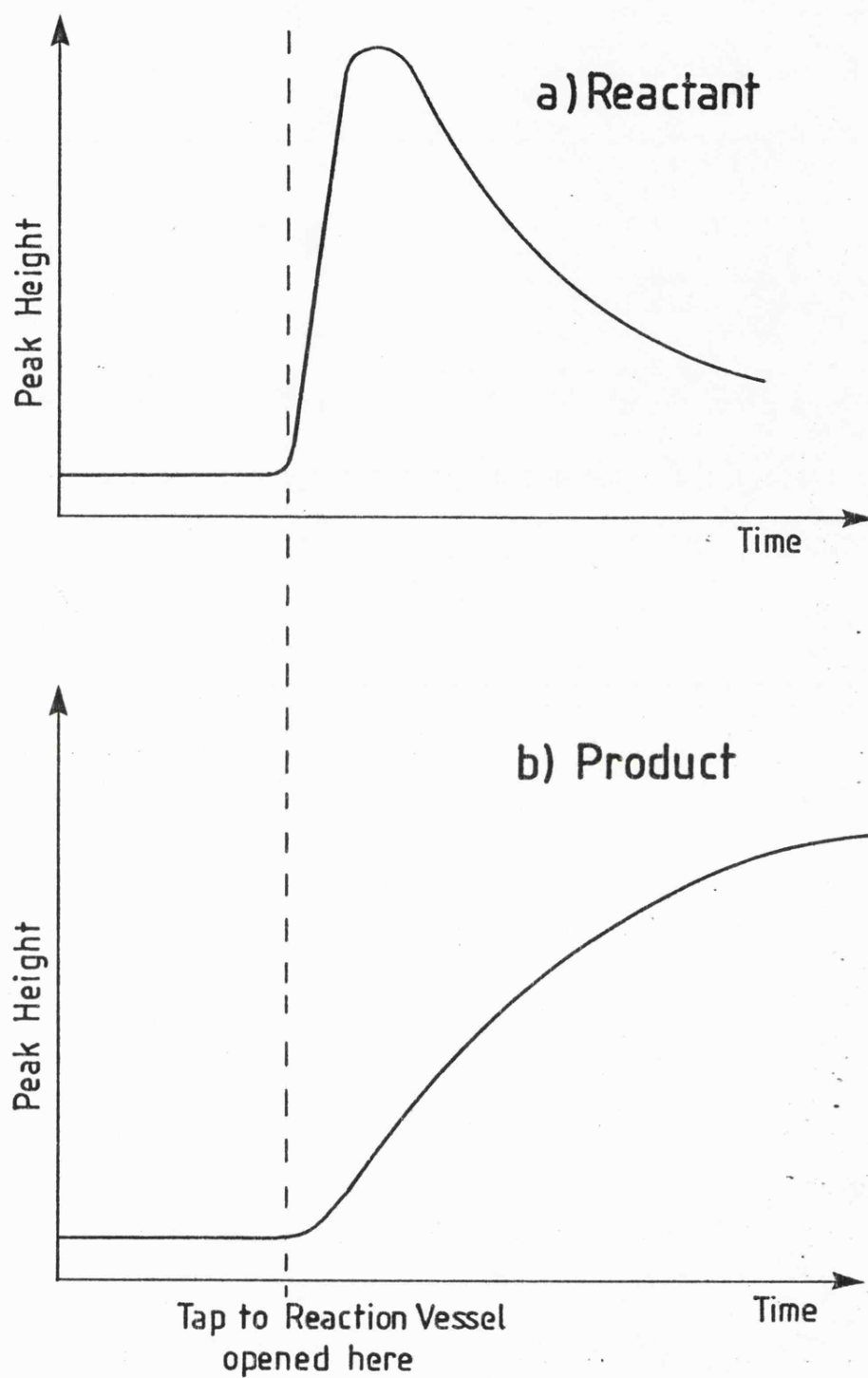


FIGURE 2.4

General Form of Observed Peak Height - Time Profiles

see below), reactant peak height - time profiles could be used to determine first order decomposition rate constants. This was done by measuring the slope of a plot of $\ln$ (peak height) against time (the intercept gave the "initial reactant peak height", which was a measure of the sample size used). Kinetic runs were generally carried out at a number of different temperatures where decomposition rate constants could be conveniently measured by this method. In this way the Arrhenius parameters for the decomposition were determined.

All decomposition rate constants measured by this technique had to be corrected for the loss of reactant that occurred by non-chemical means (assumed to be mainly through leakage into the ion source of the mass spectrometer). To facilitate this, kinetic runs were also carried out at a temperature below that at which the reactant decomposed. Reactant peak height - time profiles measured in this manner were then analysed in the usual way to yield a "leak-out" rate constant which was subtracted from all decomposition rate constants. The value of this parameter was usually ca. 0.001 s^{-1} . It had a significant effect only upon "low" decomposition rate constants. All other decomposition rate constants were left virtually unchanged by the correction (see Chapter 3).

One further complication encountered in the measurement of decomposition rate constants was the effect of the initial sample size. If an initial pressure of >ca. 0.2 mmHg was used, the plot of $\ln$ (peak height) against time was very often non-linear: the slope tended to decrease as reaction proceeded, until it became equal to that observed when using lower initial pressures. The reason for this effect was not clear, but it may have been due to second order loss of reactant via a process involving reactive species produced in the primary step of decomposition. Such a reaction would only be important at high reactant concentrations,

and so would not be observed with small initial pressures or at high degrees of conversion. However, when initial pressures of <ca. 0.2 mmHg were used, plots of $\ln$ (peak height) against time were linear (usually to >70% decomposition) and could easily be used to measure decomposition rate constants. This effect made it difficult to determine the order of decomposition in the usual way, although such measurements could conveniently be made by applying a technique described in Chapter 3: in agreement with expectation, reactant decomposition was always first order.

Leak-out rate constants also exhibited a pressure dependence (although this did not fully compensate for the effect of pressure on decomposition rate constants). Since during these measurements no reaction occurred, bimolecular loss of reactant could not be used as an explanation. The phenomenon was possibly related to the nature of flow through the pinhole leak from the reaction vessel to the ion source of the mass spectrometer. Under the conditions used this was in the range of transition between molecular and viscous flow.⁶⁹ The rate of molecular flow is proportional to the pressure difference along the route of flow (i.e. first order), while the rate of viscous flow is proportional to the product of this quantity and the average pressure along the same route (i.e. second order). Higher pressures would have favoured a large viscous flow component, while lower pressures would have favoured a large molecular flow component. To nullify this effect, leak-out constants were always measured using a sample size identical to that used when measuring decomposition rate constants. In any case, this pressure dependence was of little importance since its effect upon all but "low" decomposition rate constants was negligible (see Chapter 3).

Product peak height - time profiles could be used to measure rate con-

stands for product formation by dividing their initial slope by the maximum of the reactant peak height - time profile. However, the relative sensitivity of the mass spectrometer to the mass peaks of the product and the reactant had to be taken into account. This was measured by expanding known pressures of pure reactant and pure product into the reaction vessel with the furnace temperature set at a low value. Product yields could be calculated by dividing the rate constant for product formation by that for reactant decomposition.

There were two problems concerned with the gathering of product formation data. Product yields were often depressed due to the loss of silicon from the gas phase. This is a feature of the pyrolysis of organosilicon compounds,⁴³ especially under LPP conditions.⁴⁹ Also, hydrogen and methane tended to diffuse from the wall of the reaction vessel during pyrolyses, as a result of the decomposition of polymer deposited thereon. Therefore all kinetic data on the formation of these two products had to be viewed with some caution.

2.1.9 Cleaning the Mass Spectrometer

The sensitivity and resolution of the mass spectrometer tended to decrease with use. Its performance could be enhanced by periodically cleaning the ion source and quadrupole. In practice this was necessary about every four months.

The ion source and the quadrupole were removed from the mass spectrometer housing. The ion source was then dismantled and its metallic components were scoured with mild jewellers' rouge paper, while the ceramic components were boiled for about 15 minutes in a 3:1 mixture of concentrated hydrochloric and nitric acids. The ceramic components were then thoroughly rinsed with distilled water and all the ion source components were boiled for 15 minutes in each of isopropyl alcohol and

acetone. The quadrupole was rubbed with a mixture of diamond paste and glycerine which was washed off with distilled water. It was then dried with a hot air blower. Finally all ion source components and the quadrupole were immersed for 30 minutes in an ultrasonic bath containing in turn trichloroethylene, distilled water and "Treble-One Chemiclene". They were then dried with the hot air blower and the ion source was reassembled and replaced in the mass spectrometer housing with the quadrupole (it was necessary to wear nylon gloves during this last stage to minimise the transfer of grease).

Very often some of the ceramic components remained slightly dirty even after the above cleaning procedure. As they provided electrical insulation within the ion source, it was very important that only those which were completely cleaned were used again: the residual stains comprised a thin metallic film which strongly suppressed the components' insulating properties. A way of removing these persistent markings was to boil the components for about 30 minutes in concentrated sodium hydroxide solution, and to then thoroughly rinse them with distilled water. This complemented the normal cleaning procedure.

2.2 PSF APPARATUS

In the PSF apparatus samples were stored on a conventional vacuum line which was connected to a 10 cm³ sample valve (Pye-Unicam) via a pressure transducer zone. Samples measured into the sample valve were flushed by a stream of dry nitrogen gas into an electrically heated quartz reaction vessel and then through a gas chromatographic column which analysed the resulting product mixture. A schematic diagram of the apparatus is shown in Figure 2.5.

2.2.1 The Gas Chromatograph

The gas chromatograph used in the apparatus was a Pye-Unicam GCD, temperature programmable between 30 and 400°C, with detection by FID. It was connected to a conventional chart recorder, although the detector signal was also displayed at regular time intervals on a digital voltmeter (Solartron Schlumberger A220) which was used with a recorder drive unit (Solartron Schlumberger A295) to activate a punch tape machine (Facit 4070). Data recorded on punched tape were used to determine peak areas.

2.2.2 The Reaction Vessel (see Figure 2.6)

As in the LPP apparatus (see Section 2.1.3), samples flowed into the reaction vessel through a tube which ended in a perforated sphere. Material flowed out to the gas chromatograph via a second tube tangential to the wall of the reaction vessel. This design ensured stirred flow.⁷⁰ The reaction vessel had a pocket into which a thermocouple could be inserted. Its volume was 10 cm³.

2.2.3 The Furnace

The furnace was similar to that used in the LPP apparatus (see Section 2.1.2). However, since all connections to the reaction vessel were through the same end of the furnace, the other end was blocked with a piece of asbestos board which could be removed to speed cooling if necessary. The maximum temperature used in this study was ca. 950 K.

2.2.4 Application of the PSF Apparatus

The apparatus could be used to check the purity of samples by allowing them to be flushed into the gas chromatographic column with the furnace temperature set at a low value. If the furnace temperature was raised, the apparatus could be used to observe pyrolysis products which

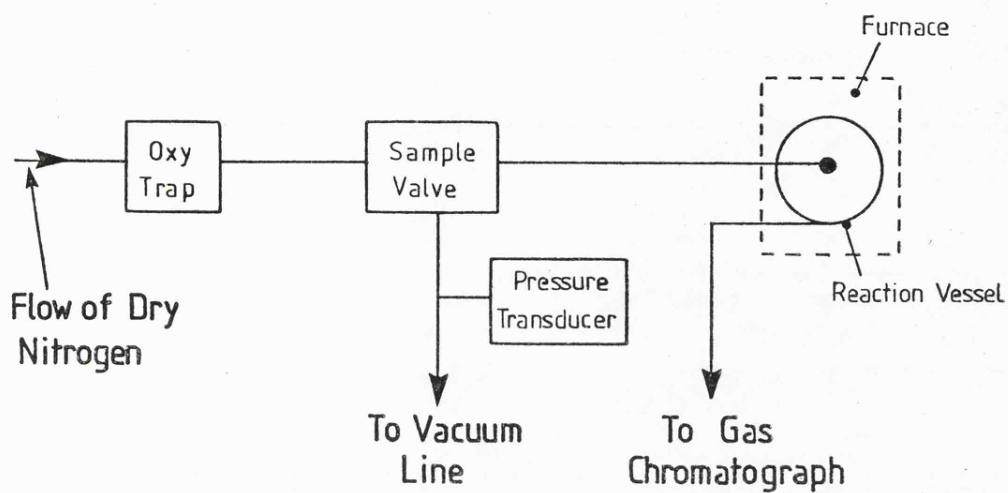


FIGURE 2.5

Schematic Diagram of PSF Apparatus

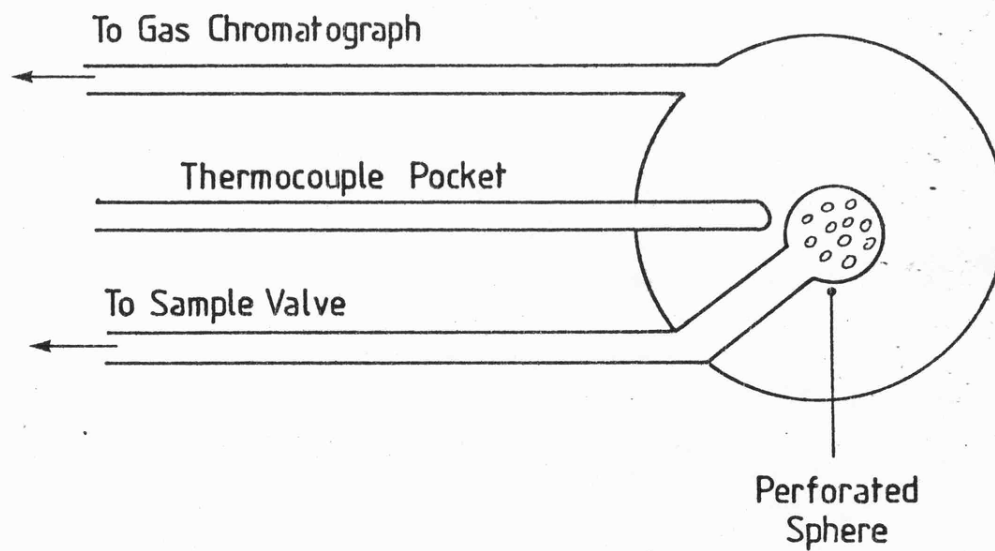


FIGURE 2.6

PSF Apparatus: Reaction Vessel

could often be characterised with authentic samples. This rôle was complemented by pyrolysing samples in the LPP apparatus where products could be identified mass spectrometrically. The effect of temperature upon the relative yields of pyrolysis products could be monitored from the ratio of the appropriate peak areas measured at different furnace temperature settings.

CHAPTER 3

COMPUTER METHODS

COMPUTER METHODS

Two computer applications were utilized in this study. Kinetic data from LPP experiments (see Chapter 2) were analysed by computer. Also, proposed reaction mechanisms were simulated by computer-aided numerical integration.

3.1 LPP DATA: "CONVENTIONAL" ANALYSIS

There were two data acquisition techniques. In the first, peak height data were collected on punched tape, which was read into the Cyber 73 computer. In the second, peak height - time data were stored by the RML 380 Z on magnetic disc.

3.1.1 Punched Tape Data Analysis

Data files were processed in batch mode. They all had three routines applied to them:

a) Baseline Correction

At the beginning of a kinetic run the peak selector scanned the mass peaks under observation several times before the tap to the reaction vessel was opened to admit the sample. The number of baseline scans was recorded so that the average baseline peak height for each channel could be calculated. The reaction was deemed to have begun immediately after the final baseline peak height had been measured. Accordingly, all subsequent peak height values had the appropriate average baselines deducted.

b) Time Scale

A time scale was associated with the peak height data once the baseline correction had been applied. This was done from a knowledge of the scan speed used during the kinetic run.

c) Interpolation

Experimental data were now in the form of Figure 3.1. So that, if

necessary, the cracking pattern correction routine (see below) could be applied, the data were interpolated using a Cyber 73 library file. All subsequent routines treated interpolated and real data points in the same way.

The above operations were applied to data on all channels. Two optional routines were also available, both of which were applied to data on specified channels only:

FIGURE 3.1

Form of Non-Interpolated LPP Data

Channel No. :	1	2	3	4
Time:	← Peak Height →			
t ₁	P ₁			
t ₂		P ₂		
t ₃			P ₃	
t ₄				P ₄
t ₅	P ₅			
t ₆		P ₆		
t ₇			P ₇	
t ₈				P ₈
t ₉	P ₉			
t ₁₀		P ₁₀		
t ₁₁			P ₁₁	
t ₁₂				P ₁₂

d) Cracking Pattern Correction

If a mass peak under consideration was not due exclusively to one species, extra data analysis was necessary. This is illustrated in the following example.

1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane (see Chapter 5) has mass peaks at 202⁺ and 129⁺. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane, its major pyrolysis product, has a mass peak at 129⁺. In some kinetic runs the decomposition of the trisilacyclopentane and the formation of

the disilacyclobutane were monitored using these mass peaks. However, all measurements of the 129^+ peak height had to be corrected for a contribution from the trisilacyclopentane before they could be used to represent the disilacyclobutane. This was achieved by measuring the ratio $202^+:129^+$ in the mass spectrum of the trisilacyclopentane. The height of the 129^+ mass peak that was due to the trisilacyclopentane could then be calculated, at any stage of a kinetic run, from that of the 202^+ mass peak, at the same stage, and deducted from the total height of the 129^+ mass peak. What remained was due solely to the disilacyclobutane.

A routine was available to make this correction to interpolated experimental data. Wherever possible, however, mass peaks requiring no cracking pattern correction were used in kinetic runs, subject to their being sufficiently intense. This simplified data processing.

e) Plotting Data

A routine was available to plot peak height -time data or $\ln$ (peak height) -time data for specified individual channels between specified limits. It was from these plots that decomposition rate constants and rates of product formation etc., were determined.

The programming necessary for the above operations was available in the form of subroutines, collected together under the filename FTLABC. They could be individually called up, along with the data file, by a "pilot" programme FTLPQ1.

. FTLABC was written in "Fortran IV" by M. C. Coles. It was refined by M. D. Reed,⁶⁷ C. E. Dean⁶⁸ and the present author. FTLPQ1 was written in "Fortran IV" by C. E. Dean⁶⁸ and was also refined by the present author.

3.1.2 Magnetic Disc Data Analysis

Data stored on magnetic disc were processed by the RML 380 Z with user interaction via a VDU. All data files had two routines applied to them:

a) Channel Selection

All peak height - time data from the appropriate specified file were read into the computer memory. Data from the required channels were then selected, and the rest were discarded.

b) Baseline and Timescale Correction

The selected peak height - time data were plotted, and a cursor was displayed. This could be moved along the timescale until it coincided with the point at which the tap to the reaction vessel was opened. The average baseline peak height was then calculated. All subsequently measured peak heights had this parameter deducted.

The time at which the tap to the reaction vessel was opened was taken as being the start of the reaction. It was, therefore, deducted from all subsequent time values. This provided an accurate time scale.

Four optional routines were also available:

c) Correction for Poor Tuning of the Peak Selector

This routine was required when two or more channels were tuned to the same mass peak, but one of them was not accurately tuned. Under these circumstances peak heights measured on the poorly tuned channel appeared consistently lower than those measured on the other channels. The routine plotted all peak height - time data and invited the user to provide gain factors, with which it adjusted peak heights on the inaccurately tuned channel, until they became equal to those in the correctly tuned channels.

d) Gradient Measurement

A routine was available to plot peak height - time data between any

specified points. It could then perform a least squares analysis of any specified section of the plot and superimpose the resulting straight line on it. This routine was used, for example, to measure initial rates of product formation.

e) Decomposition Rate Constant Measurement

Another routine could plot $\ln$ (peak height) - time data between any specified points, carry out a least squares analysis of any specified section of this plot and superimpose the resulting line on it.

Decomposition rate constants were measured in this way (see also Section 3.2).

f) Modelling of Peak Height - Time Profiles

This routine was written in an attempt to extend the range of decomposition rate constants measurable by the experimental technique. For a full discussion see Section 3.2.1.

The data processing facilities were collected together in the programme PROC4. A second data processing programme, PROC3, was also available. PROC3 had four functions:

- (a) To carry out a linear interpolation of data files.
- (b) To correct data files for cracking patterns (using a technique identical to that in Section 3.1.1).
- (c) To save individual channels of interpolated (and cracking pattern corrected) data files for subsequent analysis with PROC4.
- (d) To list interpolated and non-interpolated data files.

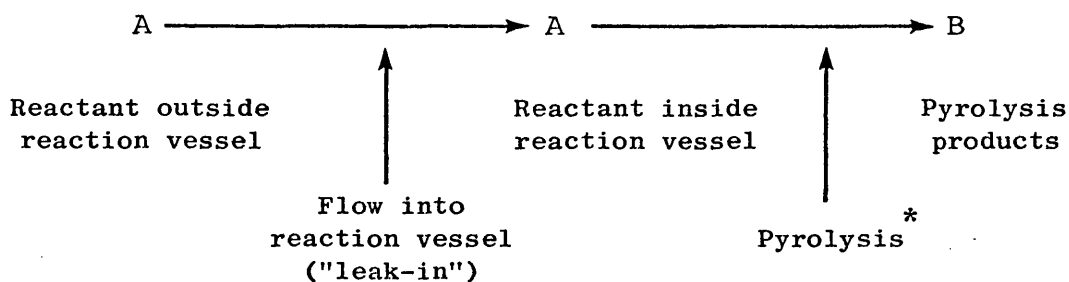
Both PROC3 and PROC4 were written in "Extended Basic" by the present author. They are listed in Appendix 2.

3.2 MEASUREMENT OF DECOMPOSITION RATE CONSTANTS

The programming described in this (and the next) section was written in "Extended Basic" by the present author to process peak height - time data collected by the RML 380 Z. It was applied to reactant peak height - time profiles only.

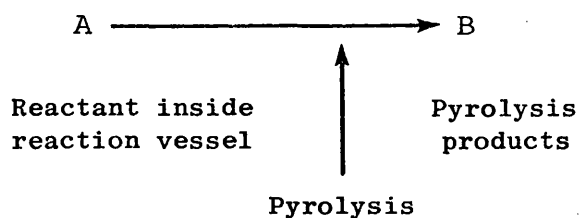
As stated in Chapter 2, plots of $\ln$ (peak height) against time were used to measure the sum of the decomposition rate constant and the leak-out rate constant. The latter parameter was usually ca. 0.001 s^{-1} . However, because of problems encountered in its determination, Arrhenius parameters were generally derived from decomposition rate constants which were only slightly affected by leak-out correction. However, problems were also encountered in the measurement of these data: in practice, Arrhenius plots tended to shallow when rate constants of >ca. 0.2 s^{-1} were used. This was attributed to the effect described below.

The finite rate at which samples flowed into the reaction vessel at the start of a kinetic run meant that observed peak height - time profiles described the following scheme:



If the rate of the leak-in process is much greater than that of pyrolysis it can be ignored, and the following scheme may be used to describe peak height-time profiles:

* During the remainder of this Chapter the terms "pyrolysis" and "decomposition" will be used to define the loss of reactant via both chemical and non-chemical means (including the leak-out process).



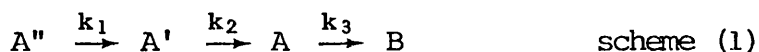
The conventional method of measuring decomposition rate constants was only valid when this latter scheme applied. As stated above, this was when they were $< \text{ca. } 0.2 \text{ s}^{-1}$.

Thus the range of decomposition rate constant measurable by the LPP technique was limited to $\text{ca. } 0.005\text{-}0.2 \text{ s}^{-1}$. Two computer-based methods were utilized in an attempt to raise the upper limit of this range.

3.2.1 Modelling of Peak Height - Time Profiles

The first attempt involved the formulation of models to describe experimental data which could not, for the reason explained above, be analysed in the conventional way. Observed peak height - time profiles exhibited some sigmoid nature in their early stages. Therefore, the first model that was used to simulate them required two leak-in rate constants:

a) The Three Stage Model



- A'' = Reactant outside reaction vessel
- A' = Reactant at some intermediate stage on its way into the reaction vessel
- A = Reactant in reaction vessel
- B = Pyrolysis products
- k_1, k_2 = Rate constants describing the flow of reactant into the reaction vessel
- k_3 = Decomposition rate constant

According to this scheme, the height of the mass peak due to A, at any time, t , is given by:⁷²

$$A_{p_t} = A_{p_0}'' \left[\frac{k_1 k_2 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{k_1 k_2 e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{k_1 k_2 e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right]$$

.... equation (1)

where A_{p_0}'' is the initial peak height of A.

A computer programme was written which allowed the user to supply guessed values of A_{p_0}'' , k_1 , k_2 and k_3 . It used these guesses to calculate a simulated peak height - time profile according to equation (1). This it superimposed over an observed profile for which the value of k_3 was not known.

However, in practice, the number of unknown parameters that were required by the programme proved too large, and even with considerable patience it was impossible to generate simulated peak height - time profiles which matched those observed. Thus the experimental value of k_3 could not be determined in this way. The programme was, therefore, modified to estimate values of A_{p_0}'' , k_1 , k_2 and k_3 which could be refined by the above procedure to give good agreement between simulated and observed data.

To understand how this was made possible, we must first consider a "low" temperature kinetic run (where the rate of pyrolysis is small when compared with that of the leak in process). The value of A_{p_0}'' can, under these conditions, be reliably measured from a plot of $\ln(A_{p_t})$ against time.

The initial section (up to the maximum) of such a peak height - time profile approximately describes the reaction profile of A in the scheme:



Further, if $k_1 \gg k_2$, this scheme approximates to the following:



in which case k_2 can be determined from a plot of $\ln (A_{pm}-A_{pt})$ against time, where A_{pm} is the maximum observed value of A_{pt} .

According to scheme (2):

$$A_{pt} = A_{po}'' \left[1 + \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_1 - k_2)} \right) \right] \quad \text{equation (2)}$$

and the time at which the maximum concentration of A' occurs is given by:

$$T_{MA'} = \frac{\ln (k_1/k_2)}{(k_1 - k_2)} \quad \text{equation (3)}$$

The point of inflection in the observed peak height - time profile occurs at $T_{MA'}$. If it can be pinpointed, equation (3) can be used, along with an estimate of k_2 , to find k_1 .

We can now turn our attention to a "high" temperature kinetic run (where the rate of pyrolysis is too high for the leak-in process to be neglected). Under these conditions kinetic data describe the reaction profile of A in scheme (1) and A_{pm} occurs when

$$k_1 e^{-k_1 T_{MA}} (k_3 - k_2) - k_2 e^{-k_2 T_{MA}} (k_3 - k_1) - k_3 e^{-k_3 T_{MA}} (k_1 - k_2) = 0 \quad \text{equation (4)}$$

If estimates of k_1 and k_2 are available, they can be used along with the observed value of T_{MA} to find the value of k_3 that will satisfy equation (4).

The modified programme adopted the following approach:

- (i) Initially a peak height - time profile resulting from a "low" temperature kinetic run was analysed. The section up to the maximum peak height was used to estimate k_2 from a plot of $\ln (A_{pm}-A_{pt})$ against time (the assumption that $k_1 \gg k_2$ had some foundation, since the sigmoid nature observed in experimental peak height - time profiles was not very pronounced).

- (ii) The programme then calculated values of $d(A_{p_t})/dt$, over the same section of the experimental profile, and plotted them against time. The maximum of this plot defined the point of inflection in the observed peak height - time profile, and thus enabled T_{MA}' to be pinpointed.
- (iii) The above estimates of k_2 and T_{MA}' were then used by the programme to find the value of k_1 which satisfied equation (3).
- (iv) The section of the peak height - time profile following the maximum was used to plot $\ln(A_{p_t})$ against time and thus yield a reliable measurement of A_{p_0}'' .
- (v) Finally, the initial section of the observed peak height - time profile was reconsidered. The above estimates of k_1 and k_2 and the measured value of A_{p_0}'' , were used to simulate a reaction profile according to equation (2). This was superimposed upon the experimental data, and the user was invited to refine these three parameters such that the agreement between the two profiles was enhanced. They were assumed to be independent of temperature, and were, therefore, used to analyse a "high" temperature peak height - time profile (resulting from a kinetic run with the same sample size as that used in the above low temperature experiment) as follows.
- (vi) This analysis commenced with the determination of T_{MA} . The value of k_3 which satisfied equation (4) was then evaluated from the estimates of k_1 , k_2 and T_{MA} and the measured value of A_{p_0}'' . The programme then calculated a peak height - time profile from equation (1) and superimposed it upon the experimental data, inviting the user to refine the estimated rate constants and A_{p_0}'' to give good agreement.

However, even this more sophisticated approach to the modelling of observed peak height - time profiles was very difficult to apply. In practice, the estimated parameters gave simulated peak height - time profiles in poor agreement with those observed. Their refinement was, therefore, just as difficult as that of guessed parameters.

In view of these problems, the model was adapted to use just one leak-in rate constant. Although it was not, therefore, able to describe the sigmoid nature shown by experimental data, it did offer greater simplicity than the three-stage model, with fewer unknown parameters.

b) The Two Stage Model



A' = Reactant outside reaction vessel

A = Reactant inside reaction vessel

B = Pyrolysis products

k_1 = Rate constant describing flow of reactant into reaction vessel

k_2 = Decomposition rate constant

According to this scheme, the height of the mass peak due to A , at any time, is given by:

$$A_{p_t} = \frac{A'_{p_0} k_1}{(k_1 - k_2)} \left(e^{-k_2 t} - e^{-k_1 t} \right) \quad \text{equation (5)}$$

where A'_{p_0} is the initial peak height of A .

A new computer programme was written which allowed the user to supply guessed values of A'_{p_0} , k_1 and k_2 . It used these guesses to calculate a peak height - time profile according to equation (5). This was superimposed over an observed peak height - time profile which could not be analysed in the conventional way for k_2 . However, as with the three-stage model, it was impossible to find good agreement between simulated and experimental

data: there were too many variables. As before, the programme was modified to estimate as many of these parameters as possible before attempting the simulation.

According to scheme (4):

$$A_{p_m} = A_{p_o}' \left(\frac{k_2}{k_1} \right) [k_2 / (k_1 - k_2)] \quad \text{equation (6)}$$

The programme measured A_{p_m} and used it, along with values of k_1 and k_2 , to calculate A_{p_o}' from equation (6).

k_1 was estimated by applying the programme to experimental data from a "low" temperature kinetic run. Conventional analysis of this profile led to k_2 . The programme then used the observed values of A_{p_m} and k_2 and guessed values of k_1 to simulate peak height - time profiles according to equation (5). The value of k_1 was varied until it gave a simulated profile which reached a maximum at the same time as the observed peak height - time profile. This was taken as the correct leak-in rate constant. It was assumed to be temperature independent and was used to model "high" temperature experimental data.

The observed value of A_{p_m} , the low temperature estimate of k_1 and guessed values of k_2 provided a route to simulated peak height - time profiles in reasonable agreement with the "decomposition section" of those observed: k_2 could easily be varied until such agreement was obtained. However, to achieve better agreement it was sometimes necessary to shift the simulated data along the time scale. This was probably because of the simplified model that was being used to describe the leak-in process. Thus it was reasonable to counter this by modifying the programme to allow such a shift to be made.

It was in this final form that the modelling procedure was incorporated into the main data processing programme, PROC4 (see Section 3.1.2). It

could be used to estimate decomposition rate constants from peak height - time profiles which could not be analysed in the normal way, and thus provided a means of extending the range of decomposition rate constants measurable by the experimental technique. However, there were two problems encountered with its use: k_1 showed some temperature dependence. Also, choice of the correct value of k_2 was often subjective, especially as it was sensitive to variations in k_1 .

For these reasons the use of the modelling procedure was abandoned and the application of an iterative process proposed by Moore⁷³ was investigated.

3.2.2 Iterative Methods

To apply this technique it was still necessary to choose a model with which observed peak height - time profiles could be described. For the extra simplicity which it offered, the two-stage model was initially used.

a) The Two Stage Model

If the two-stage model is rewritten as follows [see also scheme (4)]:



then

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \text{equation (7)}$$

and

$$[A] = A_0 \exp(-k_1 t) \quad \text{equation (8)}$$

where A_0 is the initial concentration of A. Combination of equations (7) and (8) yields:

$$\frac{d[B]}{dt} = k_1 A_0 \exp(-k_1 t) - k_2[B] \quad (=Q, \text{ say}) \quad \text{equation (9)}$$

Equation (9) leads to the following relationships:

$$\frac{\partial Q}{\partial AO} = k_1 \exp (-k_1 t) \quad \text{equation (10)}$$

$$\frac{\partial Q}{\partial k_1} = AO \exp (-k_1 t) \cdot (1 - k_1 t) \quad \text{equation (11)}$$

$$\frac{\partial Q}{\partial k_2} = - [B] \quad \text{equation (12)}$$

At any given time, the difference between the value of Q measured from the reaction profile of B ($=Q_{\text{obs}}$, say), and the value calculated from equation (9) using guessed values of AO, k_1 and k_2 and the observed value of [B] ($=Q_{\text{calc}}$, say), will be due to inaccuracies in the guesses. Since

$$Q = f(AO, k_1, k_2)$$

then

$$\Delta Q = \left(\frac{\partial Q}{\partial AO} \right) \Delta AO + \left(\frac{\partial Q}{\partial k_1} \right) \Delta k_1 + \left(\frac{\partial Q}{\partial k_2} \right) \Delta k_2 \quad \text{equation (13)}$$

where

$$\Delta Q = Q_{\text{calc}} - Q_{\text{obs}}$$

$$\Delta AO = AO(\text{guessed}) - AO(\text{true})$$

$$\Delta k_1 = k_1(\text{guessed}) - k_1(\text{true})$$

$$\Delta k_2 = k_2(\text{guessed}) - k_2(\text{true})$$

If we take several points on the reaction profile of B, and use guessed values of AO, k_1 and k_2 and the observed values of [B] to calculate Q_{calc} , $\left(\frac{\partial Q}{\partial AO} \right)$, $\left(\frac{\partial Q}{\partial k_1} \right)$ and $\left(\frac{\partial Q}{\partial k_2} \right)$ at each point, using equations (9-12) respectively, and we measure the corresponding values of Q_{obs} , then ΔAO , Δk_1 and Δk_2 can be deduced by the method of least squares.

Equation (13) can be rewritten as follows:

$$y = x_1 a + x_2 b + x_3 c \quad \text{equation (14)}$$

where

$$x_1 = \left(\frac{\partial Q}{\partial AO} \right) \quad x_2 = \left(\frac{\partial Q}{\partial k_1} \right) \quad x_3 = \left(\frac{\partial Q}{\partial k_2} \right)$$

$$a = \Delta AO$$

$$b = \Delta k_1$$

$$c = \Delta k_2$$

The values of a, b and c must be chosen such that $\Sigma (y-x_1a-x_2b-x_3c)^2$ (=s, say) is at a minimum. This is when $\frac{ds}{da} = \frac{ds}{db} = \frac{ds}{dc} = 0$.

Since

$$\frac{ds}{da} = \Sigma -2x_1 (y-x_1a-x_2b-x_3c) = 0$$

then

$$\Sigma x_1y = a \Sigma x_1^2 + b \Sigma x_1x_2 + c \Sigma x_1x_3 \quad \text{equation (15)}$$

Similarly

$$\Sigma x_2y = a \Sigma x_2x_1 + b \Sigma x_2^2 + c \Sigma x_2x_3 \quad \text{equation (16)}$$

$$\Sigma x_3y = a \Sigma x_3x_1 + b \Sigma x_3x_2 + c \Sigma x_3^2 \quad \text{equation (17)}$$

The three simultaneous equations (15-17) can be solved for a, b and c since the corresponding values of x_1 , x_2 and x_3 are available. Thus ΔAO , Δk_1 and Δk_2 may be deduced and used to correct the original estimates of AO , k_1 and k_2 . Further analysis of these corrected parameters provides a new set of correction factors. Successive iterations yield correction factors which tend to zero, and values of AO , k_1 and k_2 which tend to accuracy.

Sometimes the first few iterations over-correct one parameter, whilst leaving the others virtually unchanged. Because of this the iteration can be thrown "off course" and fail to reach a conclusion. This problem may be resolved by dividing all correction factors by a "smoothing factor" (i.e. any number greater than one) before applying them. However, introduction of this safeguard increases the number of iterations necessary to find the true parameters.

A computer programme was written which measured Q_{obs} ($=d[\text{peak height}]/dt$) at regular intervals on an observed peak height - time profile by the "running parabola technique". It invited the user to supply preliminary estimates of AO (the initial peak height), k_1 (the leak-in rate constant) and k_2 (the decomposition rate constant): AO and k_2 could be estimated from a plot of $\ln$ (peak height) against time, whilst an estimate of k_1

could be obtained from "low" temperature kinetic data (see Section 3.2.1). The above iterative procedure was then applied (a smoothing factor could be supplied, if necessary). The programme used the final parameters to superimpose a calculated peak height - time profile over the experimental data. This provided a check on the success of the iteration.

To test the programme data were simulated which described exactly the reaction profile of B in scheme (5). With such data the procedure could successfully deduce the correct value of A_0 , k_1 and k_2 , even with a smoothing factor of one. In accordance with Moore's findings,⁷³ however, there were two sets of parameters pertaining to each peak height - time profile. When the incorrect set was returned, it was necessary to transpose the values of k_1 and k_2 and re-initiate the iterative procedure to reach the correct parameters. This ambiguity was unlikely to cause problems in the analysis of real peak height - time profiles, since the correct value of k_2 could be distinguished by comparing it with lower decomposition rate constants derived in the conventional way.

The application of the programme to observed peak height - time profiles was less successful. For conclusive iteration, a smoothing factor of ca. 10 was generally required. When the procedure did return final values, the calculated peak height - time profile was invariably in poor agreement with that observed.

In view of this failure, the technique was adapted to utilize the three stage model [see scheme (1)] (although the programming necessary for this was more complex than that described above, in principle it was very similar).

However, even this modified approach failed to give satisfactory results. It was tested with simulated data which described the reaction profile of A in scheme (1). For a successful iteration it was necessary

to use initial estimates of the appropriate parameters which were within ca. 20% of the true values, and a smoothing factor of ca. 10. With observed peak height - time profiles, successive iterations invariably failed to tend to a final set of parameters, even when higher smoothing factors were utilized.

The programming required to apply the iterative method using the two stage model was entitled FTIMJB. It is listed in Appendix 2. Helpful discussions, regarding this technique, with Dr. M. J. Blandamer are gratefully acknowledged.

The reason for the failure of the computer modelling and the iterative methods was probably that the flow of sample into the reaction vessel could not be accurately described by either of the two schemes used. It is likely that the process was more complex than had been assumed, possibly depending on many factors, including the temperature of the furnace, the nature of the sample (e.g. its molecular mass and polarity) and the sample size.

3.3 MEASUREMENT OF THE ORDER OF REACTANT DECOMPOSITION

A computer programme was written to confirm that reactant decomposition under LPP conditions was first order. It utilized a technique devised by Ross.⁷⁴

If a reaction proceeds according to the relationship

$$-\frac{d[A]}{dt} = k[A]^n$$

then

$$\left(\frac{-\frac{d[A]}{dt}}{[A]} \right) = k \left[(n-1)kt + \frac{1}{[A]_0^{n-1}} \right]^{-1} \quad (=X, \text{ say})$$

.... equation (18)

From equation (18) it follows that

$$\left(\frac{1}{X} + t \right) = nt + \frac{1}{k[A]_0^{n-1}}$$

Thus n can be deduced from the slope of a plot of $\left(\frac{1}{X} + t\right)$ against time.

The programme calculated the slope of the peak height - time profile at each data point from the following relationship:

$$P'_i = \frac{P_{i+N} - P_{i-N}}{t_{i+N} - t_{i-N}}$$

P'_i = Slope of peak height - time profile at the i^{th} point

P_i = Peak height at the i^{th} point

t_i = Time of the i^{th} point

N = An integer to define the data points used in the calculation.

It then plotted $[(P_i/P'_i) + t_i]$ against t_i , and calculated the slope ($\equiv$ order of reactant decomposition) by the method of least squares. The resulting straight line was superimposed on the plot.

Peak height - time profiles with differing orders of decomposition were simulated and used to test the programme. With such data the technique invariably returned the correct order, regardless of the value of N . When analysing experimental data, the choice of N was dependent upon their quality: with N set at one, any scatter in these data was amplified in the plot of $[(1/P_i) + t_i]$ against t_i . This caused a large amount of uncertainty in the least squares slope. Such uncertainty could be substantially reduced by increasing the value of N (typically to ca. 5).

The analysis of observed peak height - time profiles by the above technique invariably led to an order of reactant decomposition equal to one.

This programme was entitled ORDER. It is listed in Appendix 2.

3.4 THE SIMULATION OF REACTION MECHANISMS

Any reaction mechanism can be expressed as a series of differential equations, one for each species involved. Solution of these equations

yields the reaction profiles of all such species.

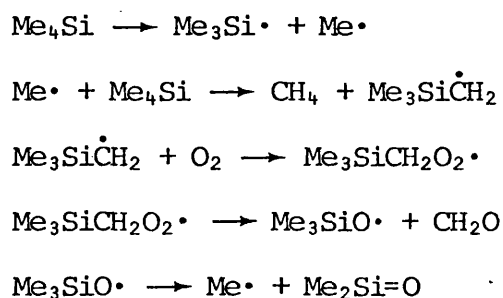
A Cyber 73 library file which could simultaneously solve differential equations by "Gears" method was available. A computer programme, written in "Fortran IV" by A. C. Baldwin,⁷⁵ used this subroutine to calculate the reaction profile of any given species in a proposed reaction mechanism. It required the following data: the initial concentration of reactant, rate constants for all elementary steps, and the reaction mechanism, expressed as a series of differential equations.

CHAPTER 4

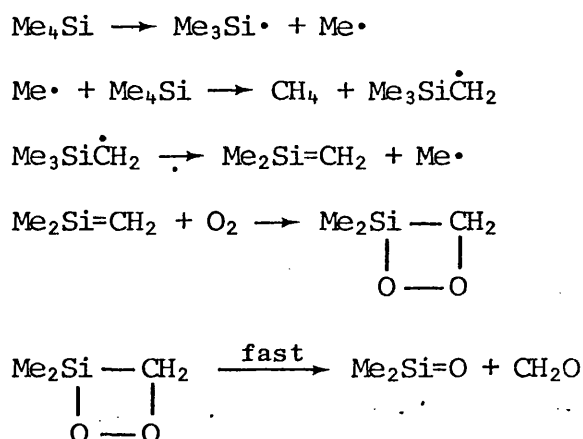
KINETICS OF THE ADDITION OF OXYGEN
TO 2-METHYL-2-SILAPROPENE

4.1 INTRODUCTION

The thermal reaction between tetramethylsilane and oxygen has been studied in the LPP apparatus.⁶⁷ The main silicon containing products were cyclic dimethylsiloxanes, which are formed from the self-combination of dimethylsilanone.²⁵ Other products were methane and formaldehyde. A plausible reaction mechanism is shown below:



However, since the $\text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2$ radical is known⁴³ to dissociate to give 2-methyl-2-silapropene, the following alternative reaction mechanism also provides a route to the observed products (the last step is likely to be fast in view of the known instability of the 1-oxa-2-silacyclobutane ring¹⁷).

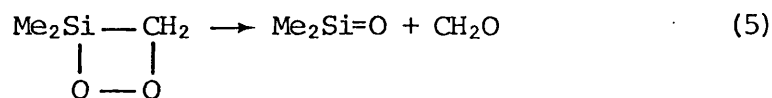
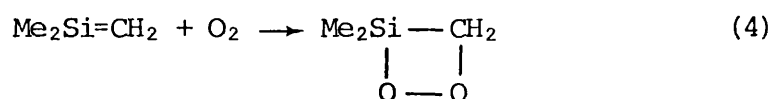
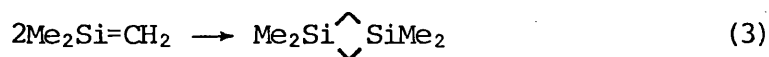
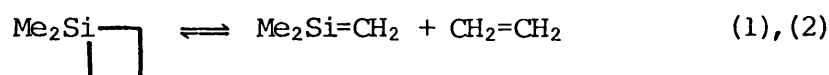


The kinetic behaviour of the reaction between 2-methyl-2-silapropene and oxygen was studied to investigate the feasibility of this alternative scheme in the oxidation of tetramethylsilane, although, in view of the

small amount of quantitative information available on the reactions of silaalkenes, such data are of value anyway.

It was originally intended to measure the Arrhenius parameters for this process by the method of competing reactions, which is described below. However, in view of experimental difficulties (see Section 4.2), an alternative approach was finally adopted.

In the method of competing reactions a mixture of 1,1-dimethyl-1-silacyclobutane (used as a source of 2-methyl-2-silapropene) and the appropriate substrate (in this case, oxygen) is pyrolysed in the LPP apparatus over a temperature range, such that the relative rates of reactions (3) and (4) can be measured at each temperature.



The Arrhenius parameters for reaction (4) can then be calculated relative to those for reaction (3) in the following way:

$$\text{Since } \frac{d[\text{Me}_2\text{Si} \begin{array}{|c|} \hline \wedge \\ \hline \end{array} \text{SiMe}_2]}{dt} = k_3 [\text{Me}_2\text{Si}=\text{CH}_2]^2$$

$$\text{and } \frac{d[\text{Me}_2\text{Si} \begin{array}{|c|} \hline \text{---CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{O} \\ \hline \end{array}]}{dt} = k_4 [\text{Me}_2\text{Si}=\text{CH}_2][\text{O}_2]$$

$$\text{then } \frac{\frac{d}{dt} \left[\text{Me}_2\text{Si} \begin{array}{|c|} \hline \text{---CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{O} \\ \hline \end{array} \right]}{\left(\frac{d}{dt} [\text{Me}_2\text{Si} \begin{array}{|c|} \hline \wedge \\ \hline \end{array} \text{SiMe}_2] \right)^{\frac{1}{2}}} \cdot \frac{1}{[\text{O}_2]} = \frac{k_4}{k_3^{\frac{1}{2}}} = f, \text{ say}$$

$$\text{Since } f = \frac{[A_4 \exp(-E_4/RT)]}{[A_3 \exp(-E_3/RT)]^{\frac{1}{2}}}$$

$$\text{then } \ln f = \ln\left(\frac{A_4}{A_3^{\frac{1}{2}}}\right) + \frac{(E_3/2 - E_4)}{RT}$$

Thus a plot of $\ln f$ against $1/T$ yields $(A_4/A_3^{\frac{1}{2}})$ and $(E_3/2 - E_4)$.

Knowledge²³ of E_3 and A_3 (see below) then leads to the required Arrhenius parameters.

Since the dioxasilacyclobutane is not stable, the initial rate of formation of formaldehyde, along with that of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and the maximum observed concentration of oxygen, was used to calculate f .

The Arrhenius parameters for the dimerisation of 2-methyl-2-silapropene were originally estimated by Flowers and Gusel'nikov.⁴ They measured the dependence of apparent first-order decomposition rate constants of 1,1-dimethyl-1-silacyclobutane on added ethene. Their findings were consistent with the occurrence of reactions (1)-(3) and the following relationships:

$$E_2 - \frac{1}{2}E_3 = 60.7 \pm 16.7 \text{ kJ mol}^{-1}$$

$$\log A_2 - \frac{1}{2} \log A_3 = 3.3 \pm 1.2$$

The Arrhenius parameters for reaction (2) were estimated from those for the dimerisation of tetrafluoroethene.⁷⁶ It was then possible to calculate $E_3 \approx 46 \text{ kJ mol}^{-1}$ and $\log A_3 \approx 8.4$.

In a later study,²³ the Arrhenius parameters for the dimerisation of 2-methyl-2-silapropene were directly measured by Gusel'nikov et al.

They passed 1,1-dimethyl-1-silacyclobutane at low pressures (ca. 0.01 mmHg) through a quartz tube consisting of two zones. The first was surrounded by a mobile furnace, and in it the 1,1-dimethyl-1-silacyclobutane decomposed to yield ethene and 2-methyl-2-silapropene. In the

second zone, the temperature of which could be adjusted, dimerisation occurred. Product analysis, at the end of the tube, was by mass spectrometry. The concentration of 2-methyl-2-silapropene remaining at this point was determined from the concentrations of ethene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The residence time of the 2-methyl-2-silapropene in the dimerisation zone was calculated from the flow rate and from the length of the zone. By moving the furnace, and thereby altering the length of the dimerisation zone, the residence time could be changed and a plot of the concentration of 2-methyl-2-silapropene against this time made. A conventional analysis of this plot was used to determine k_3 .

This technique was applied with the dimerisation zone set at three temperatures (298, 423 and 573 K). The value of k_3 was temperature independent, giving $\log A_3 = 6.55 \pm 0.03$, with zero activation energy. Use of these parameters to re-interpret the data of Flowers and Gusel'nikov⁴ gave $E_2 = 60.7 \pm 16.7 \text{ kJ mol}^{-1}$ and $\log A_2 = 6.58 \pm 1.2$.

4.2 RESULTS

Initially a mixture of 1,1-dimethyl-1-silacyclobutane and oxygen in the ratio of 1:1 was pyrolysed at ca. 773 K using a total initial pressure of ca. 0.25 mmHg. The main products were 1,1,3,3-tetramethyl-1,3-disilacyclobutane ($M^+ = 144$, $M^+ - \text{Me} = 129^+$), $(\text{Me}_2\text{SiO})_3$ ($M^+ - \text{Me} = 207$), $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ ($M^+ - \text{Me} = 205$), $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$ ($M^+ - \text{Me} = 203$), formaldehyde and ethene. A small amount of $(\text{Me}_2\text{SiO})_4$ ($M^+ - \text{Me} = 281$) was also formed. These observations were consistent with the occurrence of reactions (1)-(5) followed by various cyclization reactions of 2-methyl-2-silapropene and dimethylsilanone.

The reactant mixture was adjusted until the relative rates of formation

of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and formaldehyde [the primary stable product of reactions (4) and (5)] were comparable, and a series of kinetic runs was carried out in which the formation of these two products and the loss of oxygen was monitored using the mass peaks at 129^+ , 30^+ (formaldehyde) and 32^+ (oxygen). The ratio of 1,1-dimethyl-1-silacyclobutane to oxygen used was 7:1, and the total initial pressure in all runs was 0.25 mmHg. The results of these experiments are shown in Table 4.1. The corresponding plot of $\ln(f)$ against $1/T$ is shown in Figure 4.1. The plot was analysed by the method of least squares to yield the following Arrhenius parameters for reaction (4):

$$E = 14 \pm 5 \text{ kJ mol}^{-1}, \log A = 6.6 \pm 0.4.$$

However, there were two problems associated with monitoring the rate of formaldehyde formation:

- (a) Formaldehyde tended to adsorb onto the wall of the reaction vessel during experiments. If, after pyrolysis of the reactant mixture, the reaction vessel was evacuated and then closed, the mass peak at 30^+ rose as formaldehyde re-entered the gas phase from the wall.
- (b) Formaldehyde has an indistinctive mass spectrum. Its mass peak at 30^+ was chosen as that most suitable for kinetic runs, but it was necessary to correct peak height-time profiles produced in this way for contributions from the mass spectra of 1,1-dimethyl-1-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Although such corrections can be made (see Chapter 3), they tend to reduce the precision of experimental data.

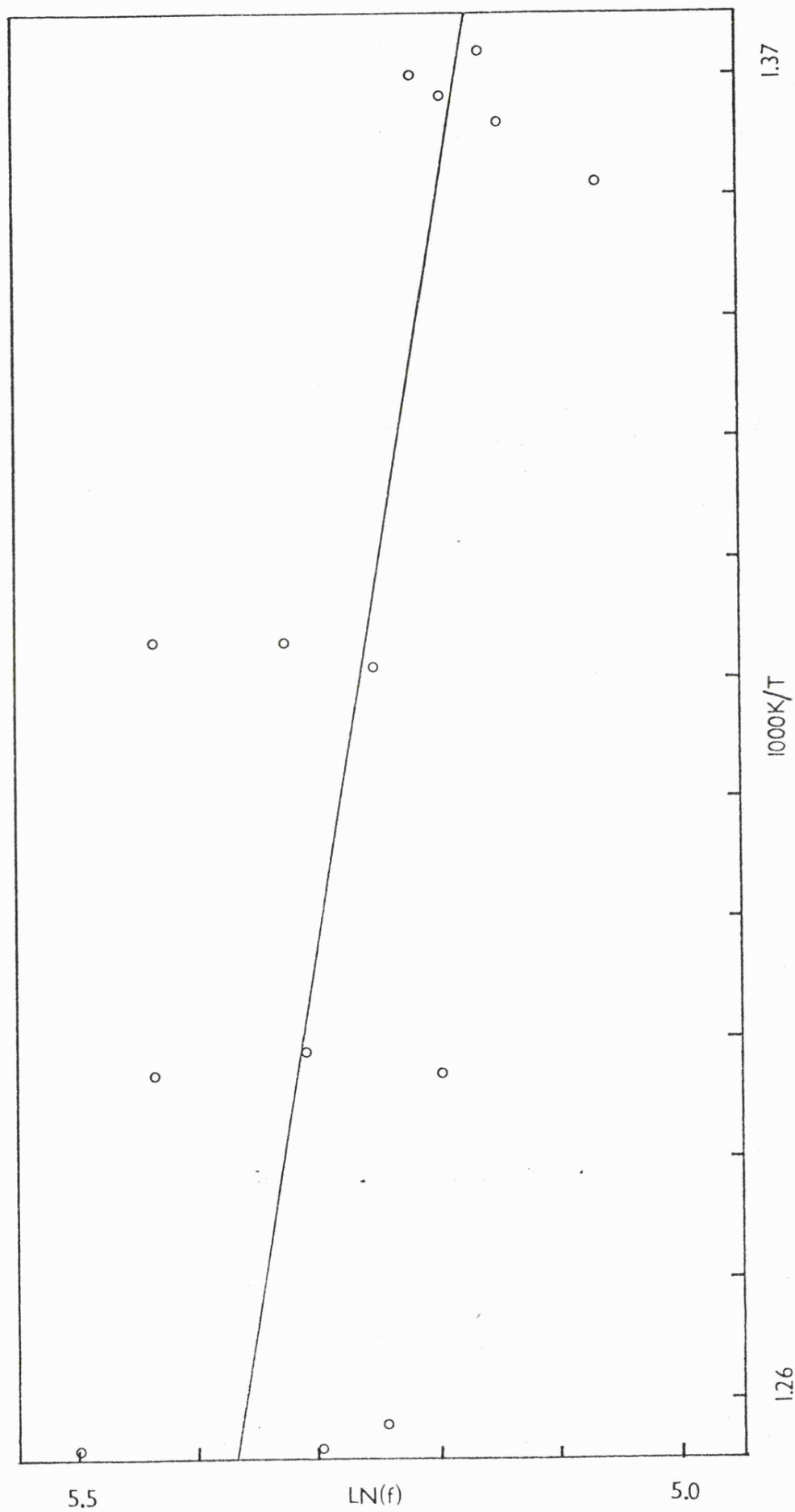
In view of these problems an alternative approach was adopted, which did not require a knowledge of the rate of formaldehyde formation. A

TABLE 4.1

Results of the Pyrolysis of a 7:1 Mixture of 1,1-Dimethyl-1-silacyclobutane and Oxygen

T/K	$\frac{d[\text{Me}_2\text{Si} \text{---} \text{SiMe}_2]}{dt}$ $10^9/\text{mol dm}^{-3} \text{ s}^{-1}$	$\frac{d[\text{CH}_2\text{O}]}{dt}$ $10^9/\text{mol dm}^{-3} \text{ s}^{-1}$	$[\text{O}_2]_{\text{max}}$ $10^9/\text{mol dm}^{-3}$	f $/\text{dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$
796	9.05	12.11	520.1	244.8
795	8.26	8.46	492.3	189.1
796	8.26	9.37	516.1	199.8
777	3.56	4.33	401.0	181.0
777	3.40	7.98	595.5	229.8
776	2.45	3.85	385.1	202.0
757	0.80	3.49	647.1	190.7
756	0.58	2.38	480.4	205.7
756	0.57	3.65	667.0	229.2
735	0.11	0.99	595.5	158.5
732	0.091	0.67	408.9	171.8
731	0.083	0.52	316.4	180.4
730	0.052	0.83	623.3	184.7
729	0.060	0.67	446.3	174.3

FIGURE 4.1: PLOT OF $\ln(f)$ AGAINST $1/T$



further three series of kinetic runs were carried out using the 7:1 mixture of 1,1-dimethyl-1-silacyclobutane and oxygen. In all runs an initial pressure of 0.25 mmHg was used and the rate of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was measured using the mass peak at 129⁺ or that at 144⁺. The results of these experiments are shown in Table 4.2.

A plot of $\ln \left(\frac{d[\text{Me}_2\text{Si} \text{---} \text{SiMe}_2]}{dt} \right)$ against 1/T was found to be linear over the temperature range (see Figure 4.2). The least squares gradient and intercept were used to calculate the "average" rates of formation of the disilacyclobutane at two temperatures:

T/K	$\frac{d[\text{Me}_2\text{Si} \text{---} \text{SiMe}_2]}{dt} \times 10^9 / \text{mol dm}^{-3} \text{ s}^{-1}$
734	0.13
789	9.33

To estimate the values of k_4 implied by these average parameters, the reaction mechanism shown in Table 4.3 was simulated using the computer programme described in Chapter 3.

The values of E_1 and $\log A_1$ used in this simulation were not the published ones,⁴ but those measured using the LPP technique (see Chapter 6). By analogy with those for the thermal decomposition of 3,3-dimethyl-1,2-dioxacyclobutane,⁷⁷ the Arrhenius parameters for reaction (5) were set at $E = 96 \text{ kJ mol}^{-1}$ and $\log A = 12.2$, giving a value of $k_5 = 8.5 \times 10^5 \text{ s}^{-1}$ at 800 K, far in excess of that for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane at the same temperature⁴ (0.037 s^{-1}). However, in view of the probable instability of the dioxasilacyclobutane,¹⁷ a high decomposition rate constant is reasonable. The Arrhenius parameters for reactions (6) and (7) were set at $\log A =$

TABLE 4.2

Rate of Formation of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane
in the Pyrolysis of a 7:1 Mixture of 1,1-Dimethyl-1-silacyclobutane
and Oxygen ($10^9/\text{mol dm}^{-3} \text{ s}^{-1}$)

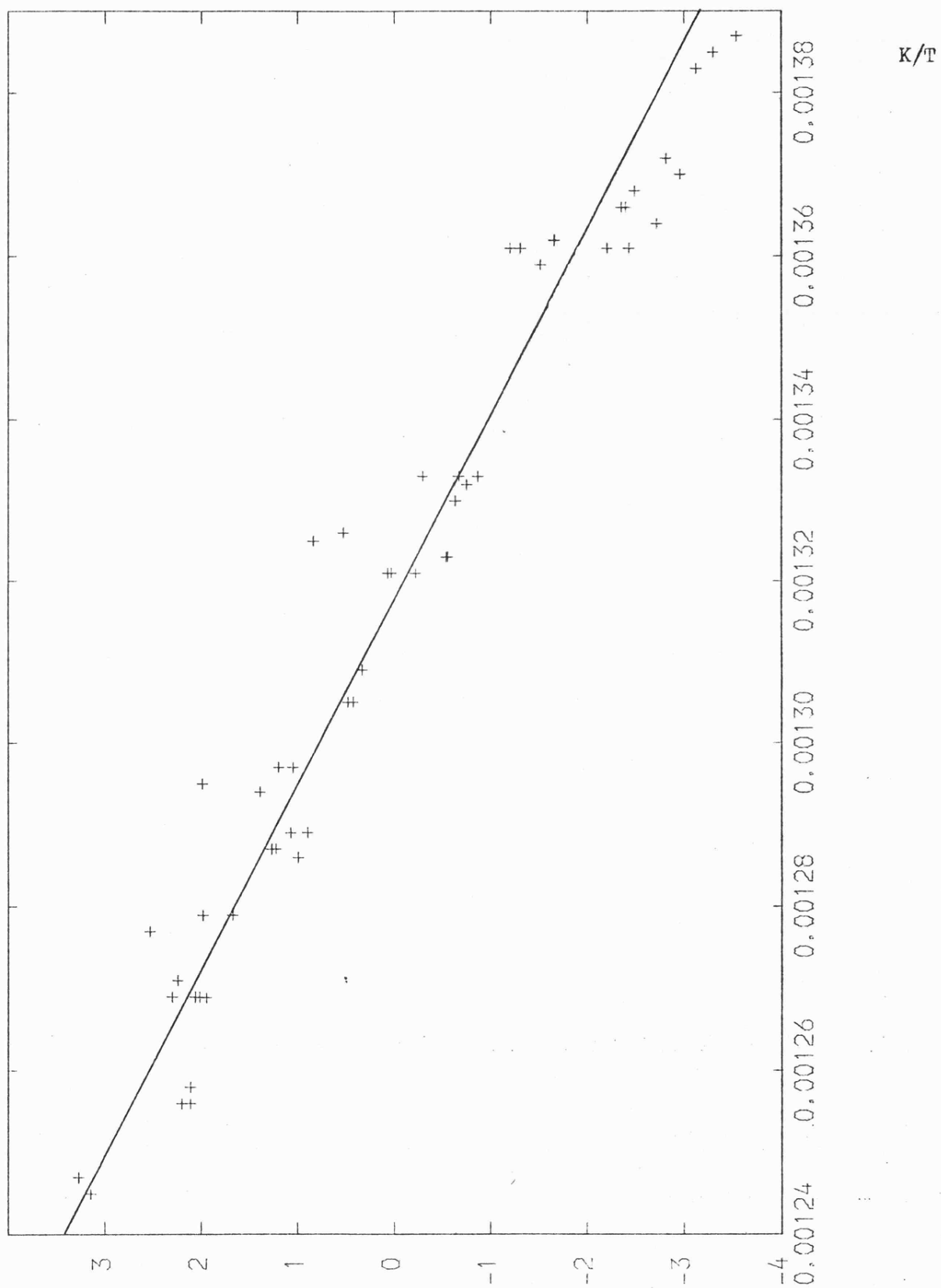
T/K	Rate	T/K	Rate	T/K	Rate
803	23.20	782	7.28	788	7.01
802	26.39	782	5.34	788	7.52
788	7.87	783	12.60	778	2.70
787	9.41	773	4.03	777	3.58
788	9.98	772	7.33	776	2.92
771	3.31	755	2.31	766	1.61
771	2.85	754	1.69	766	1.53
757	1.03	735	0.27	764	1.39
757	1.07	735	0.30	752	0.53
750	0.74	734	0.19	751	0.47
750	0.51			750	0.42
734	0.19			735	0.088
736	0.22			733	0.066
				732	0.095
				723	0.044
				722	0.037
				721	0.029

6.55 and $E = 0 \text{ kJ mol}^{-1}$, in keeping with those for reaction (3).²³

Reactions (8)-(11) all involve the interaction of a highly strained ring with a reactive intermediate to give a stable molecule and are, therefore, highly favoured thermodynamically. In view of this their activation energies are likely to be low and were set at zero. The 'A'-factors for reactions (8)-(11) are likely to be similar in view of the probable similarity in the transition state involved. The value for reaction (10) has been estimated⁶⁷ as $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In accordance with this, the 'A'-factors for reactions (8)-(11) were all set at $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The insertion of dimethylsilanone into 1,1,3,3-tetramethyl-1,3-disilacyclobutane was not included as a route to $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$: in a separate experiment 0.6 mmHg of a 5:1 mixture of the disilacyclobutane

FIGURE 4.2: PLOT OF $\ln(d[\text{Me}_2\text{Si} \rightleftharpoons \text{SiMe}_2]/dt)$ AGAINST $1/T$



$\ln(d[\text{Me}_2\text{Si} \rightleftharpoons \text{SiMe}_2]/dt \cdot 10^9 / \text{mol dm}^{-3} \text{s}^{-1})$

TABLE 4.3 Reaction Mechanism for the Copolyrolysis of 1,1-Dimethyl-1-silacyclobutane and Oxygen

Reaction No.	Reaction	log A	E/kJ mol ⁻¹	k/s ⁻¹	Comment
1	$\text{Me}_2\text{Si} \rightarrow \text{Me}_2\text{Si}$				Leak-in
2	$\text{Me}_2\text{Si} \rightarrow \text{Me}_2\text{Si}=\text{CH}_2 + \text{CH}_2=\text{CH}_2$	13.9	237	0.8	See text
3	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{Me}_2\text{Si}$	6.58	60.7		Ref. 23
4	$2\text{Me}_2\text{Si}=\text{CH}_2 \rightarrow \text{Me}_2\text{Si}-\text{SiMe}_2$	6.55	0		Ref. 23
5	$\text{O}_2 \rightarrow \text{O}_2$				Leak-in
6	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{O}_2 \rightarrow \text{Me}_2\text{Si}-\text{CH}_2-\text{O}-\text{O}$			0.8	See text
7	$\text{Me}_2\text{Si}-\text{CH}_2 \rightarrow \text{Me}_2\text{Si}=\text{O} + \text{CH}_2\text{O}$	12.2	96		See text and ref. 77
8	$2\text{Me}_2\text{Si}=\text{O} \rightarrow \text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2$	6.55	0		See text
9	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{Me}_2\text{Si}=\text{O} \rightarrow \text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2$	6.55	0		See text
10	$\text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2 + \text{Me}_2\text{Si}=\text{O} \rightarrow [(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$	8	0		See text
11	$\text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2 + \text{Me}_2\text{Si}=\text{CH}_2 \rightarrow [(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$	8	0		See text
12	$\text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2 + \text{Me}_2\text{Si}=\text{O} \rightarrow (\text{Me}_2\text{SiO})_3$	8	0		Ref. 67
13	$\text{Me}_2\text{Si}-\text{O}-\text{SiMe}_2 + \text{Me}_2\text{Si}=\text{CH}_2 \rightarrow [(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$	8	0		See text
14	All species			0.0013	Leak-out
15	Total initial pressure = 0.25 mmHg				
16	1,1-Dimethyl-1-silacyclobutane : Oxygen = 7:1				

and $\text{Me}_2(\text{H})\text{SiOC}(\text{Me}_2)\text{CH}=\text{CH}_2$, a known⁷⁸ source of dimethylsilanone, was pyrolysed in the LPP apparatus at 833 K. The production of $(\text{Me}_2\text{SiO})_3$ was observed with no $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$. The insertion of dimethylsilanone into $(\text{Me}_2\text{SiO})_3$ to yield $(\text{Me}_2\text{SiO})_4$ was also omitted from the simulated reaction scheme since the observed yield of this product was much less than that of the other products of the LPP of oxygen and 1,1-dimethyl-1-silacyclobutane. The simulation made no allowance for the loss of 2-methyl-2-silapropene and dimethylsilanone from the gas phase via heterogeneous reaction (see Chapter 2) since the observed silicon mass balance suggested that any such loss occurred only to a very small extent.

Simulations were performed at 734 and 789 K. At each temperature the value of k_4 was varied. Simulated rates of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were then plotted against k_4 (see Figures 4.3 and 4.4). These "calibration" plots were then used to find the values of k_4 at 734 and 789 K implied by the average experimental rates of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane:

T/K	$k_4 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
734	10.4×10^5
789	12.5×10^5

These rate constants lead to the following Arrhenius parameters:

$$E_4 = 16 \text{ kJ mol}^{-1} \text{ and } \log A_4 = 7.2.$$

The error limits on these values were determined from the uncertainties in the least squares gradient and intercept of the plot of

$$\ln \left(\frac{d[\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \text{Si} \end{array} \text{Me}_2]}{dt} \right) \text{ against } 1/T \text{ (Figure 4.2). Thus the error limits on}$$

the activation energy are $\pm 12 \text{ kJ mol}^{-1}$, and on $\log A_4$, ± 0.9 .

Further simulations were performed in which the temperature was varied over the experimental temperature range. The above Arrhenius parameters

FIGURE 4.3: PLOT OF SIMULATED RATE OF FORMATION OF

1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE AGAINST k_4 AT 734K

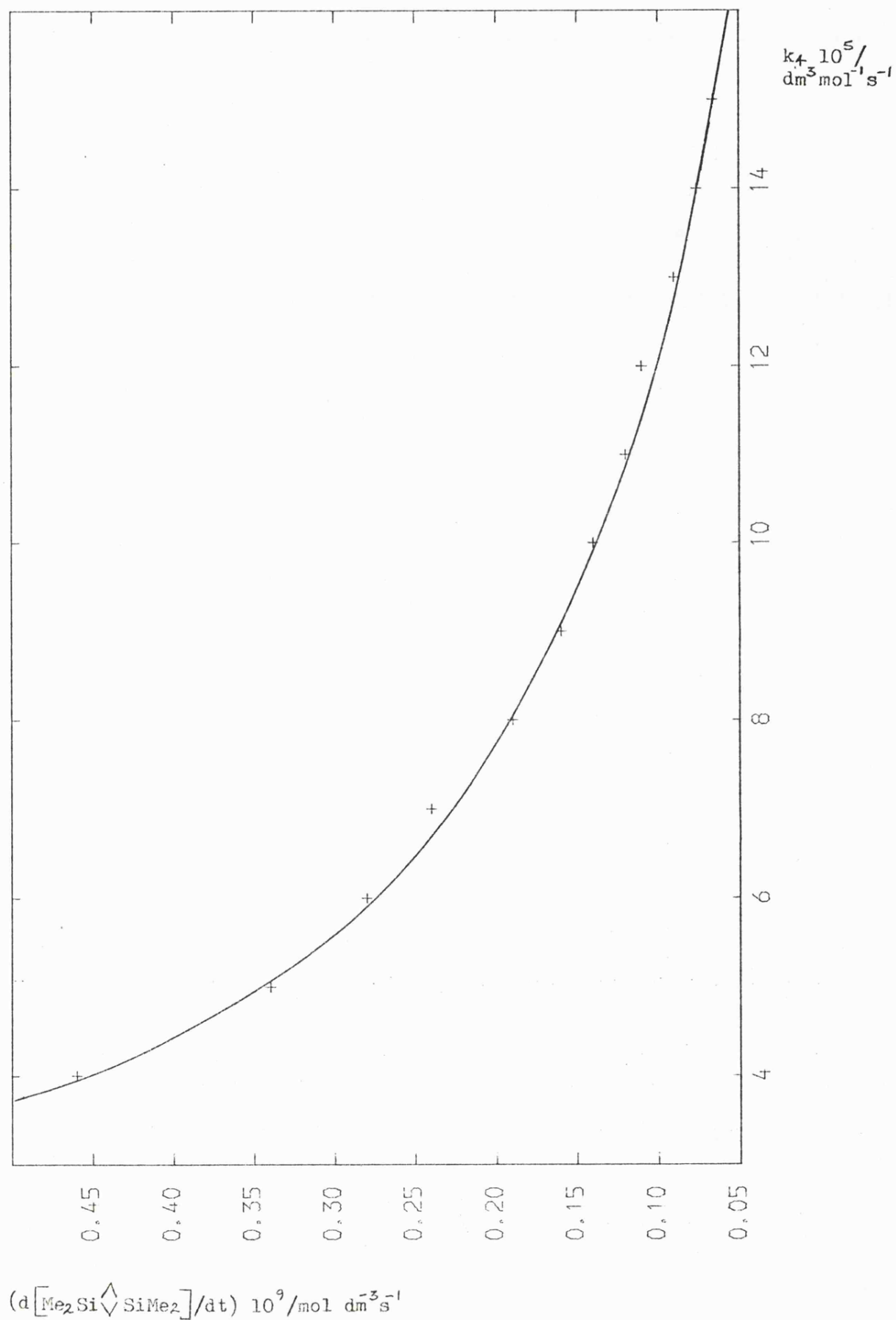
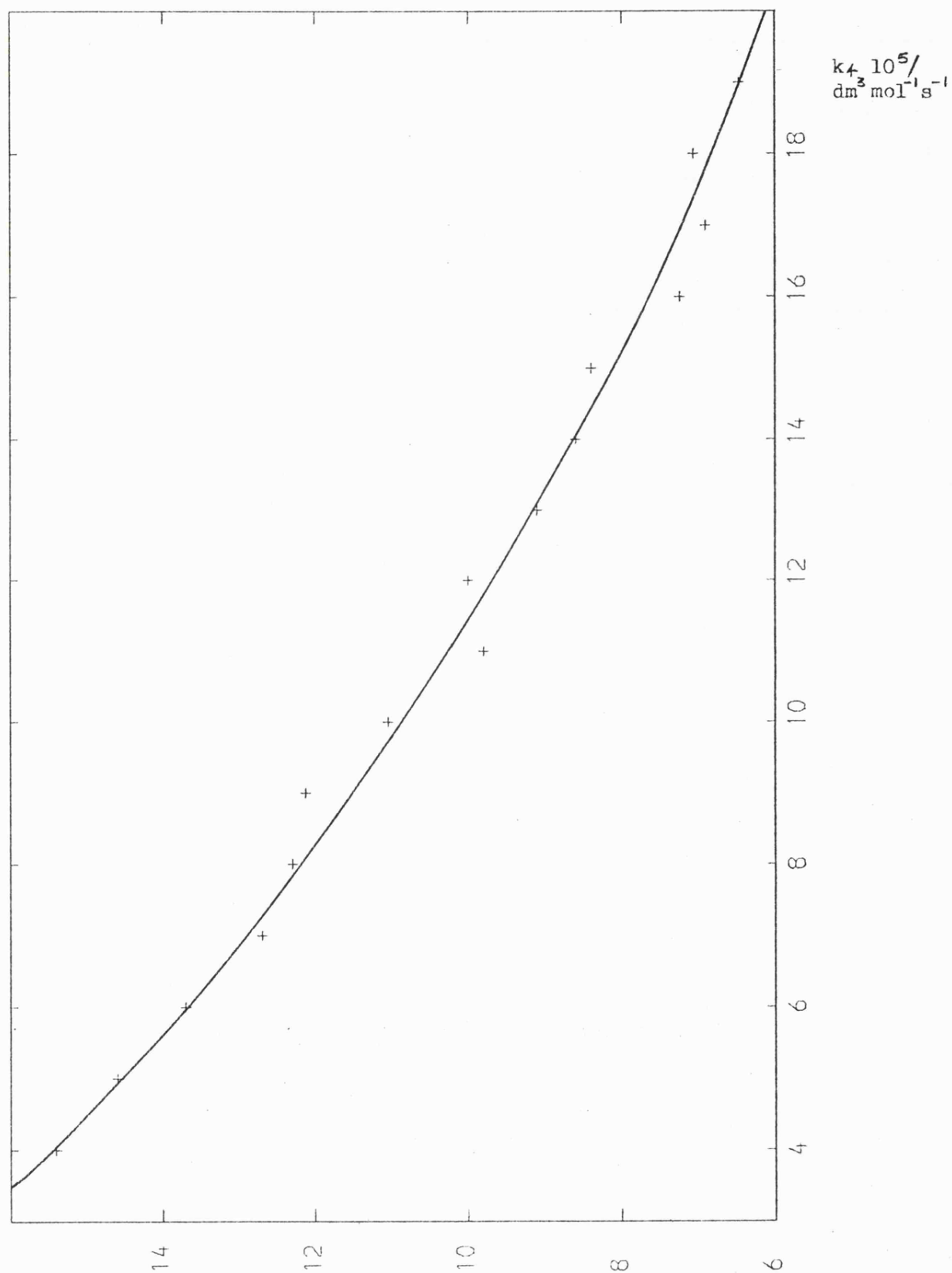


FIGURE 4.4: PLOT OF SIMULATED RATE OF FORMATION OF

1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE AGAINST k_4 AT 789K



$(d[\text{Me}_2\text{Si}\Diamond\text{SiMe}_2]/dt) \times 10^9/\text{mol dm}^{-3} \text{ s}^{-1}$

for reaction (4) were used, although "control" simulations were also carried out with $k_4 = 0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rates of 1,1,3,3-tetramethyl-1,3-disilacyclobutane formation produced in these simulations are shown in Table 4.4. The data produced with $E_4 = 16 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.2$ were processed in the same way as the experimental data. The resulting plot of $\ln \left(\frac{d[\text{Me}_2\text{Si}\text{---}\text{SiMe}_2]}{dt} \right)$ against $1/T$ was linear over the temperature range (see Figure 4.5), and led to the following Arrhenius parameters: $E_4 = 16 \pm 6 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.2 \pm 0.4$. Also shown in Table 4.4 are the rates of formaldehyde formation and the maximum concentration of oxygen produced by the simulations. Values of f calculated from these data led to $E_4 = 16 \pm 1 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.1 \pm 0.1$.

In a last series of kinetic runs using the 7:1 mixture of 1,1-dimethyl-1-silacyclobutane and oxygen, and total initial pressures of 0.25 mmHg, the relative rates of formation of $(\text{Me}_2\text{SiO})_3$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$ were measured using their mass peaks at 207^+ , 205^+ and 203^+ respectively. Pure samples of the last two compounds were not available, but it was assumed that the sensitivity of the mass spectrometer to all three was the same. The results of these experiments are shown in Table 4.5. The relative rates of formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$ varied from 0.2:0.5:1 at ca. 736 K to 1.6:1.2:1 at ca. 793 K.

This trend was investigated by simulating the reaction mechanism shown in Table 4.3, with $E_4 = 16 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.2 \text{ kJ mol}^{-1}$, at 736 and 793 K. The results of these simulations are compared with the experimental data in Table 4.6. In view of the complexity of the mechanism the agreement is good and thus provides evidence in support of the accuracy of the Arrhenius parameters for reaction (4) used in the simulations (see below).

Since the Arrhenius parameters for reaction (4) were determined by

TABLE 4.4

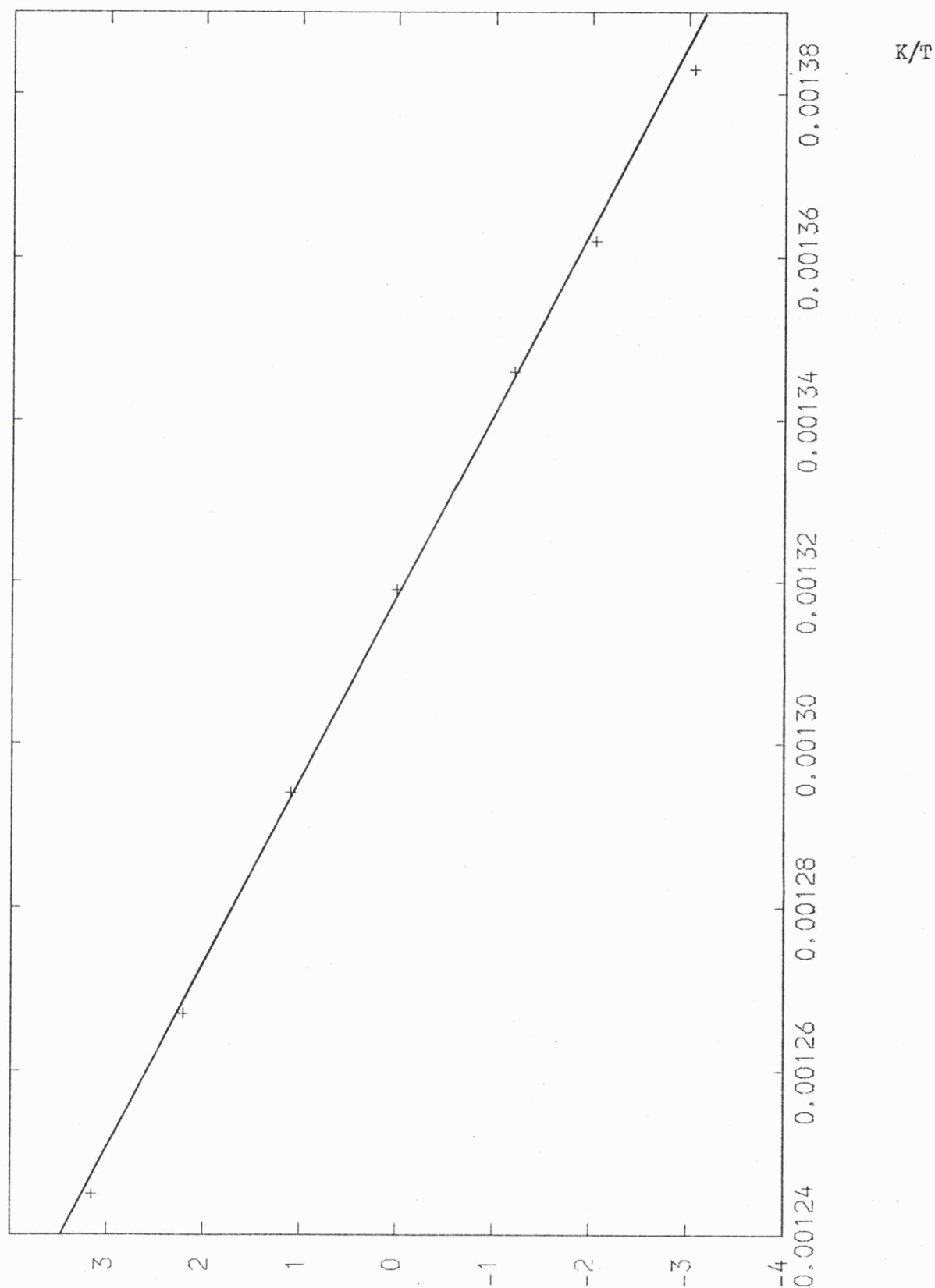
Results of Simulations with $E_4 = 16 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.2$

T/K	$\frac{d[\text{Me}_2\text{Si}\langle\text{SiMe}_2\rangle^*}{dt}$ $10^9/\text{mol dm}^{-3} \text{ s}^{-1}$	$\frac{d[\text{Me}_2\text{Si}\langle\text{SiMe}_2\rangle]}{dt}$ $10^9/\text{mol dm}^{-3} \text{ s}^{-1}$	$\frac{d[\text{CH}_2\text{O}]}{dt}$ $10^9/\text{mol dm}^{-3} \text{ s}^{-1}$	$[\text{O}_2]_{\text{max}}$ $10^9/\text{mol dm}^{-3}$	f $\text{dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$
803	56.0	23.6	47.5	464.3	666.7
789	28.4	9.1	30.6	502.8	636.8
773	14.2	3.0	18.6	545.2	618.0
758	7.6	1.0	10.7	579.9	584.0
743	3.6	0.30	5.9	609.0	566.5
734	2.3	0.13	3.7	624.0	518.6
723	1.2	0.047	2.3	640.2	521.7

* Control simulations with $k_4 = 0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

FIGURE 4.5: SIMULATED DATA - PLOT OF $\text{LN}(\hat{d}[\text{Me}_2\text{Si} \cdots \text{SiMe}_2]/dt)$

AGAINST $1/T$



$\text{LN}(\hat{d}[\text{Me}_2\text{Si} \cdots \text{SiMe}_2]/dt \cdot 10^9/\text{mol dm}^{-3} \text{s}^{-1})$

TABLE 4.5

Relative Rates of Formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$ in the Pyrolysis of a 7:1 Mixture of 1,1-Dimethyl-1-silacyclobutane and Oxygen

T/K	$[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$	$[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$	$(\text{Me}_2\text{SiO})_3$
792	1.37	1.05	1
793	1.74	1.29	1
794	1.62	1.31	1
763	0.54	0.85	1
763	0.53	0.78	1
762	0.49	0.69	1
750	0.40	0.81	1
751	0.37	0.83	1
737	0.21	0.51	1
735	0.17	0.55	1

comparing experimental and simulated data, they are dependent upon the choice of rate parameters for all the other reactions in the simulated mechanism. Some of the values used were rough estimates, so further simulations were carried out in which such Arrhenius parameters were varied. In this way the sensitivity of the simulated data to various parameters was determined.

The mechanism simulated was that shown in Table 4.3, with $E_4 = 16 \text{ kJ mol}^{-1}$ and $\log A_4 = 7.2$. Initially the effect of varying A_8 - A_{11} was investigated. As pointed out above, it seems reasonable to suppose that these data will have the same value. That value was varied between 10^6 and $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The effect upon the initial rate of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and upon the relative rates of formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$ was negligible at 734 and 789 K.

The values of A_6 and A_7 were also kept equal. They were varied, again at 734 and 789 K, between 10^4 and $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, causing a marked

TABLE 4.6

Experimental and Simulated Relative Rates of Formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$ in the Pyrolysis of a 7:1 Mixture of 1,1-Dimethyl-1-Silacyclobutane and Oxygen

T/K	$[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$	$[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$	$(\text{Me}_2\text{SiO})_3$
736	0.2	0.5	1
793	1.6	1.2	1
			Experimental
736	0.2	0.8	1
793	1.6	2.4	1
			Simulated

change in the initial rate of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane at both temperatures [see Table 4.7(a)]. In view of this, calibration plots, similar to those in Figures 4.3 and 4.4, were compiled at both temperatures by varying k_4 . These plots and the experimental rates of formation of the disilacyclobutane were analysed as before to give the following Arrhenius parameters for reaction (4):

<u>Log (A_7, A_8)</u>	<u>$E_4/\text{kJ mol}^{-1}$</u>	<u>Log A_4</u>
4	43	9.2
8	6	6.2

The large differences between these data and those derived with log A_7 and log A_8 at 6.55 suggested a very high degree of uncertainty in the latter values. However, simulations at 736 and 793 K in which log A_7 and log A_8 were set at 4 and 8, and the Arrhenius parameters for reaction (4) at the corresponding values shown above gave relative rates of formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$ in very poor agreement with the experimental data [see Table 4.7(b)]. The good agreement obtained with log A_7 and log A_8 at 6.55 suggests that this value, and, therefore, the corresponding Arrhenius parameters for reaction (4), are reasonable.

The effect of varying the Arrhenius parameters for reaction (5) was not investigated, since the values used, those for the thermal decomposition of 1,1-dimethyl-2,3-dioxacyclobutane,⁷⁷ almost certainly provide a lower limit for k_5 : the silicon analogue is probably far more unstable than this "model" compound. In all simulations the concentration of 1,1-dimethyl-1-sila-2,3-dioxacyclobutane remained at zero. Any increase in k_5 would have left this situation unaltered.

TABLE 4.7(a)

Effect of A_7 and A_8 upon simulated rate of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane ($10^9/\text{mol dm}^{-3} \text{ s}^{-1}$)

T/K	734	789
$A_7, A_8/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		
10^4	0.16	12.8
10^8	0.065	4.7
$10^{6.55}$	0.13	9.3

TABLE 4.7(b)

Effect of A_7 and A_8 (and corresponding values of A_4 and E_4) upon simulated relative rates of formation of $[(\text{Me}_2\text{SiO})(\text{Me}_2\text{SiCH}_2)_2]$, $[(\text{Me}_2\text{SiO})_2(\text{Me}_2\text{SiCH}_2)]$ and $(\text{Me}_2\text{SiO})_3$

T/K	736	793
$A_7, A_8/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		
10^4	0.01 : 0.2 : 1	0.03 : 0.4 : 1
10^8	11 : 7 : 1	306 : 34 : 1
$10^{6.55}$	0.2 : 0.8 : 1	1.6 : 2.4 : 1
(experimental:	0.2 : 0.5 : 1	1.6 : 1.2 : 1)

4.3 DISCUSSION

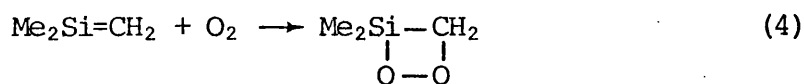
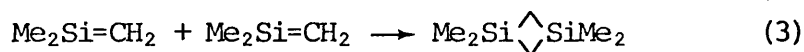
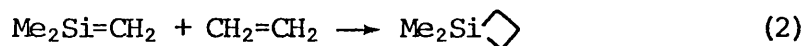
Silaalkenes are known¹⁷ to add to the π -bond of carbonyls. Addition of 2-methyl-2-silapropene to formaldehyde would give ethene and dimethylsilanone only, products indistinguishable from those formed in the copyrolysis of 1,1-dimethyl-1-silacyclobutane and oxygen. Although this secondary reaction of formaldehyde has the potential to complicate the experimental reaction system, it is unlikely that it had any effect in the early stages of pyrolyses when the concentration of formaldehyde was far

smaller than that of oxygen. During kinetic runs carried out at the top end of the temperature range the concentration of formaldehyde rose to a maximum and then decreased, probably as a result of its reaction with the silaalkene during the latter stages of the pyrolysis (although loss of formaldehyde to the wall of the reaction vessel also provides an explanation for this effect).

Of the two sets of Arrhenius parameters deduced in this study, that derived simulating the reaction mechanism in Table 4.3 and matching simulated and experimental rates of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is probably the more accurate, since it has no dependence upon the rate of formaldehyde formation. As pointed out in Section 4.2, measurement of these parameters was not easy.

The Arrhenius parameters for the addition of oxygen to 2-methyl-2-silapropene are compared with those for similar reactions and those measured with the LPP technique in Table 4.8. Similar data have been determined by John *et al.*^{16,21} and Frey and Walsh *et al.*⁷⁹

Reactions (2), (3) and (4) all involve the interaction of two double-bonded species to form a cyclobutane. Using the relationship between the enthalpy of a reaction, and the activation energies for the forward and reverse steps it is possible to estimate values of E_2 , E_3 and E_4 .



Since

$$\Delta H_2^\circ = D_\pi(\text{Si}=\text{C}) + D_\pi(\text{C}=\text{C}) - D(\text{Si}-\text{C}) - D(\text{C}-\text{C}) + E_s(\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \text{CH}_2 \text{CH}_2 \end{array})$$

$$\Delta H_3^\circ = 2D_\pi(\text{Si}=\text{C}) - 2D(\text{Si}-\text{C}) + E_s(\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \text{SiMe}_2 \end{array})$$

$$\Delta H_4^\circ = D_\pi(\text{Si}=\text{C}) + D_\pi(\text{O}=\text{O}) - D(\text{Si}-\text{O}) - D(\text{C}-\text{O}) + E_s\left(\text{Me}_2\text{Si} \begin{array}{c} \text{---CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{O} \end{array}\right)$$

TABLE 4.8

Arrhenius Parameters for the Reaction of 2-Methyl-2-silapropene with Various Substrates (measured with $\log A_3 = 6.55$ and $E_3 = 0 \text{ kJ mol}^{-1}$)

No.	Reactants	$\log A$	$E/\text{kJ mol}^{-1}$	ref.
2	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{CH}_2=\text{CH}_2$	6.58 ± 1.2	60.7 ± 16.7	23
3	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{Me}_2\text{Si}=\text{CH}_2$	6.55 ± 0.03	0	23
4	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{O}_2$	7.2 ± 0.9	16 ± 12	this work*
	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{HCl}$	7.5 ± 0.3	12 ± 5	68*
	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{HBr}$	7.4 ± 0.3	34 ± 8	68*
	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{Me}_3\text{Si}-\text{OMe}$	5.3 ± 0.2	6.3 ± 3.2	19

* preliminary values of these Arrhenius parameters have been published (ref. 18)

and

$$\Delta H_2^\circ = E_2 - E_1$$

$$\Delta H_3^\circ = E_3 - E_{-3}$$

$$\Delta H_4^\circ = E_4 - E_{-4}$$

then

$$E_2 = D_{\pi}(\text{Si}=\text{C}) + D_{\pi}(\text{C}=\text{C}) - D(\text{Si}-\text{C}) - D(\text{C}-\text{C}) + E_{\text{S}}(\text{Me}_2\text{Si} \text{ } \triangleleft) + E_1$$

$$E_3 = 2D_{\pi}(\text{Si}=\text{C}) - 2D(\text{Si}-\text{C}) + E_{\text{S}}(\text{Me}_2\text{Si} \text{ } \triangleleft \text{SiMe}_2) + E_{-3}$$

$$E_4 = D_{\pi}(\text{Si}=\text{C}) + D_{\pi}(\text{O}=\text{O}) - D(\text{Si}-\text{O}) - D(\text{C}-\text{O}) + E_{\text{S}}\left(\text{Me}_2\text{Si} \begin{array}{c} \text{---CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{O} \end{array} \right) + E_{-4}$$

In each case the activation energy for the reverse (ring opening) reaction may be estimated^{24, 50} from the strength of the bond initially ruptured and the appropriate ring strain:

$$E_1 = D(\text{C}-\text{C}) - E_{\text{S}}(\text{Me}_2\text{Si} \text{ } \triangleleft)$$

$$E_{-3} = D(\text{Si}-\text{C}) - E_{\text{S}}(\text{Me}_2\text{Si} \text{ } \triangleleft \text{SiMe}_2)$$

$$E_{-4} = D(\text{C}-\text{O}) - E_{\text{S}}\left(\text{Me}_2\text{Si} \begin{array}{c} \text{---CH}_2 \\ | \quad | \\ \text{O} \text{---} \text{O} \end{array} \right)$$

[D(C-C) is used in the expression for E_1 since the strength of the carbon-silicon bond has been estimated⁸ as $<32 \text{ kJ mol}^{-1}$ greater than that of the carbon-carbon bond, indicating that the pyrolysis of 1,1-dimethyl-1-silacyclobutane will proceed with carbon-carbon bond rupture. Similarly, in view of the high strength of silicon-oxygen bonds,⁸ D(C-O) is used in the expression for E_{-4} .]

Combining the last two sets of expressions we see that:

$$E_2 = D_{\pi}(\text{Si}=\text{C}) + D_{\pi}(\text{C}=\text{C}) - D(\text{Si}-\text{C})$$

$$E_3 = 2D_{\pi}(\text{Si}=\text{C}) - D(\text{Si}-\text{C})$$

$$E_4 = D_{\pi}(\text{Si}=\text{C}) + D_{\pi}(\text{O}=\text{O}) - D(\text{Si}-\text{O})$$

Using the data in Table 4.9, the activation energies shown in Table 4.10 were calculated.

In addition to the obvious uncertainty in the values of $D_{\pi}(\text{Si}=\text{C})$ and $D(\text{Si}-\text{C})$, the strength of the silicon-oxygen bond in $\text{Me}_2\text{Si}-\text{CH}_2$ is likely to differ from that in Me_3SiOH , so the value used in the above calculations should be viewed with caution. The assumption that the activation energies for the reverse, ring-opening, reactions can be calculated from the strength of the bond initially ruptured and the ring strain appears to be valid, at least in the case of 1,1-dimethyl-1-silacyclobutane. Two groups^{24,82} of workers place the value of the ring strain in this compound at ca. 80 kJ mol^{-1} , implying an activation energy for its decomposition of $342^{\dagger} - 80 = 262 \text{ kJ mol}^{-1}$, in good agreement with the experimental⁴ value (although Ring and O'Neal⁴⁴ have estimated the value of this ring strain to be 72 kJ mol^{-1} , implying an activation energy of 270 kJ mol^{-1}). For small ring hydrocarbons the relationship is $E > D - E_s$, e.g.:

[†] $D(\text{C}-\text{C}) = 342 \text{ kJ mol}^{-1}$ (ref. 80)

TABLE 4.9

Data used to calculate E_2 , E_3 and E_4

Molecule	bond	analogy	D/kJ mol ⁻¹	ref.
CH ₂ =CH ₂	D _π (C=C)		248	80
Me ₂ Si=CH ₂	D _π (Si=C)		163	8
			188	9
Me ₂ Si- 	D (Si-C)	D (Me ₃ Si-Me)	374	8
		D (ClMe ₂ Si-Me)	366	68
Me ₂ Si-  -SiMe ₂	D (Si-C)	D (Me ₃ Si-Me)	374	8
		D (ClMe ₂ Si-Me)	366	68
O ₂	D _π (O=O)		359	81
Me ₂ Si-CH ₂ O-O	D (Si-O)	D (Me ₃ Si-OH)	536	8

TABLE 4.10

Estimated values of E_2 , E_3 and E_4 /kJ mol⁻¹

D _π (Si=C)/kJ mol ⁻¹	188		163	
D(Si-C)/kJ mol ⁻¹	374	366	374	366
Reaction No.				
2	62	70	37	45
3	2	10	-48	-40
4	11	11	-14	-14

Ring	D(C-C) ⁸⁰	E _s ⁶⁵	E _{calc}	E _{obs}	(ref)
cyclopropane	342	115.5	226.5	274.5	(83)
cyclobutane	342	109.6	232.4	262.0	(84)

This results from the activation energy required to ring close the biradical formed in the initial stage of decomposition.^{65,85}

Ring and O'Neal⁴⁴ have also estimated the ring strain in 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Use of their value (103 kJ mol⁻¹) with an average value of D(Si-C) = 370 kJ mol⁻¹ (see Table 4.9) yields an activation energy for the decomposition of the disilacyclobutane of 267 kJ mol⁻¹. This is much less than an experimentally derived value of ca. 320 kJ mol⁻¹ (see Chapter 5). However, kinetic data on the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were very scattered and, in addition, the product distribution suggested that not all decomposition was to 2-methyl-2-silapropene. Decomposition via rupture of the silicon-methyl bond would be expected to have a much higher activation energy than rupture of the ring, thus it is reasonable that the observed activation energy is higher than the calculated value above.

Table 4.10 suggests that, no matter what values of D(Si-C) and D_π(Si=C) are used, the estimated activation energies are in the order E₂ > E₄ > E₃, and in this sense they agree with the experimental results in Table 4.8. However, the negative values calculated with D_π(Si=C) = 163 kJ mol⁻¹ illustrate the high degree of uncertainty involved, and this agreement may be completely fortuitous, although it does suggest that the value of E₄ measured in this work is not unreasonable.

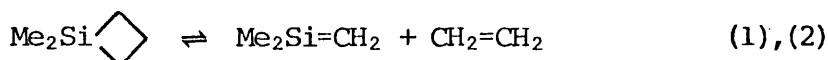
The advent⁴⁴ of a group additivity scheme for the estimation of entropies and heat capacities of organosilicon compounds, along with the known⁴ value of A₁, allows tentative calculations to be made regarding the 'A'-factors for reactions (2) and (3). However, the data required to

perform similar calculations for reaction (4) do not exist. The following discussion utilizes the data shown in Table 4.11. The entropies in Table 4.11(a) were calculated, using available group additivity terms,^{44,65} at 700 K, the mean temperature used by Flowers and Gusel'nikov in their study⁴ of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane. Benson⁶⁵ has tabulated oscillator entropies as a function of frequency and temperature. These data have been applied to estimate the entropies of the carbon-carbon and carbon-silicon π -bonds in Table 4.11(b).

Group additivity values for species involving a silicon-carbon double bond are not available, but $S_{700}^{\circ}(\text{Me}_2\text{Si}=\text{CH}_2)$ can be estimated from $S_{700}^{\circ}(\text{Me}_2\text{C}=\text{CH}_2)$ by applying corrections which take into account the effect of substituting a silicon atom for a carbon atom and a silicon-carbon π -bond for a carbon-carbon π -bond. The first is given by $S_{700}^{\circ}(\text{Me}_3\text{SiH}) - S_{700}^{\circ}(\text{Me}_3\text{CH})$, while the second, from Table 4.11(b), is $S_{700}^{\circ}(\text{Si}=\text{C}) - S_{700}^{\circ}(\text{C}=\text{C})$:

$$\begin{aligned} S_{700}^{\circ}(\text{Me}_2\text{Si}=\text{CH}_2) &= 399.4 + (453.2 - 414.1) + (3.8 - 1.4) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 440.9 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

This datum may then be used to calculate A_2 in the following way.



$$\begin{aligned} \Delta S_{700}^{\circ} &= S_{700}^{\circ}(\text{Me}_2\text{Si}=\text{CH}_2) + S_{700}^{\circ}(\text{CH}_2=\text{CH}_2) - S_{700}^{\circ}(\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array}) \\ &= 440.9 + 270.0 - 541.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 169.3 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

This parameter is related to A_2 by the following equation:

$$A_2 = A_1 \text{ e. c. exp } (-\Delta S/R)$$

where c is equal to the reciprocal of the concentration of ideal gas at 1 atmosphere and 700 K ($= 56.2 \text{ dm}^3 \text{ mol}^{-1}$). Thus:

TABLE 4.11 (a)

Estimated Entropies of Various Compounds

Molecule	point group	σ_{ext}	σ_{int}	$S_{700}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$
$\text{Me}_2\text{C}=\text{CH}_2$	C_{2v}	2	3^2	399.4
Me_3CH	C_{3v}	3	3^3	414.1
Me_3SiH	C_{3v}	3	3^3	453.2
$\text{CH}_2=\text{CH}_2$	D_{2h}	4	1	270.0
Me_2Si  *	C_{2v}	2	3^2	541.6
	D_{4h}	8	1	364.5
Me_2 	C_{2v}	2	3^2	484.6
Me_2  Me_2	D_{2h}	4	3^4	587.7
H_2Si  *	C_{2v}	2	1	423.9
Me_2Si  Me_2 *	C_{2v}	2	3^4	643.8

* ring correction term used: ^{65,82}  S

TABLE 4.11 (b)

Estimated Entropies of Carbon-Carbon and Carbon-Silicon π -bonds

Bond	frequency/ cm^{-1}	(ref)	$S_{700}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$
C=C	1650	65	1.4
Si=C	1004	86	3.8

$$A_2 = 10^{15.64} \cdot 2.72 \cdot 56.2 \cdot \exp(-169.3/8.314)$$

$$\therefore \log A_2 = 8.98$$

The data in Table 4.11(a) have been used to calculate 'A'-factors for reactions (12), (13) and (14) from known 'A'-factors for the reverse reactions (see Table 4.12). The 'A'-factor for reaction (13) is approximately equal to $\sqrt{A_{12} \times A_{14}}$. If it is assumed that the 'A'-factors for reactions (12), (2) and (3) have a similar relationship, then $\log A_3$ may be estimated as 9.32:

<u>Reaction No.</u>	<u>Reactants</u>	<u>Products</u>	<u>log A</u>
12	$\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CH}_2$		8.64
2	$\text{CH}_2=\text{CH}_2 + \text{Me}_2\text{Si}=\text{CH}_2$	Me_2Si - 	8.98
3	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{Me}_2\text{Si}=\text{CH}_2$	Me_2Si -  - SiMe_2	9.32

These calculated values of $\log A_2$ and $\log A_3$ give $\log A_2 - \frac{1}{2} \log A_3 = 4.32$, in reasonable agreement with the experimental value⁴ of 3.3 ± 1.2 .

It is not possible to calculate $S_{700}^\circ (\text{Me}_2\text{Si}-\text{cyclobutane}-\text{SiMe}_2)$ from group additivity values, since no correction term for the disilacyclobutane ring is available (neither is such a term available for $\text{S}-\text{cyclobutane}-\text{S}$). The 'A'-factor for the thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been measured at ca. $10^{15.8} \text{ s}^{-1}$ (see Chapter 5 and below). Use of this experimental value, and the above estimates of $S_{700}^\circ (\text{Me}_2\text{Si}=\text{CH}_2)$ and $\log A_3$ provides a route to $S_{700}^\circ (\text{Me}_2\text{Si}-\text{cyclobutane}-\text{SiMe}_2) = 715.9 \text{ J K}^{-1} \text{ mol}^{-1}$. This seems reasonable when compared with S_{700}° for similar molecules calculated in Table 4.11(a):

<u>Molecule</u>	<u>$S_{700}^\circ / \text{J K}^{-1} \text{ mol}^{-1}$</u>	<u>Molecule</u>	<u>$S_{700}^\circ / \text{J K}^{-1} \text{ mol}^{-1}$</u>
	364.5	H_2Si - 	423.9
Me_2 - 	484.6	Me_2Si - 	541.6
Me_2 -  - Me_2	587.7	Me_2Si -  - Me_2	643.8

TABLE 4.12

Calculated 'A'-factors for the Reactions of Some Alkenes

Reaction No.	Reactants	Product	$\Delta S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	log A for reverse reaction (ref.)	log A
12	$\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CH}_2$		-175.5	15.62 (84)	8.64
13	$\text{CH}_2=\text{CH}_2 + \text{Me}_2\text{C}=\text{CH}_2$	Me_2 	-184.8	15.68 (87)	8.21
14	$\text{Me}_2\text{C}=\text{CH}_2 + \text{Me}_2\text{C}=\text{CH}_2$	Me_2 	-211.1	16.31 (88)	7.47

The calculated value of $\log A_3$ is in conflict with the experimental value²³ of 6.55. If it is assumed that the experimental 'A'-factor provides a measurement of the rate constant for the dimerisation of 2-methyl-2-silapropene at 400 K, and that the correct 'A'-factor is that calculated above, then an activation energy of 21 kJ mol^{-1} is implied. Support for this conclusion is contained in a publication by Frey and Walsh et al.,⁷⁹ where it is suggested that $E_3 \neq 0 \text{ kJ mol}^{-1}$.

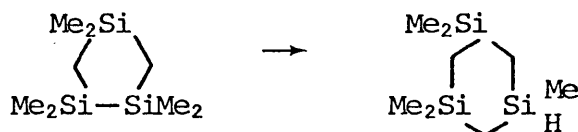
However, the group additivity calculations shown above must be regarded as highly speculative since they rely upon an indirect estimate of $S_{700}^\circ (\text{Me}_2\text{Si}=\text{CH}_2)$. In addition, the assumption that the 'A'-factors for reactions (12), (2) and (3) obey a similar relationship to those for reactions (12), (13) and (14) may be unfounded. Finally, it is unlikely that the observed 'A'-factor for the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane applies only to the formation of 2-methyl-2-silapropene (see Chapter 5): during the appropriate experiments, which in any case gave very scattered results, some reactant was probably lost via silicon-methyl bond rupture.

CHAPTER 5

THE KINETICS AND MECHANISM OF PYROLYSIS OF
1,1,2,2,4,4-HEXAMETHYL-1,2,4-TRISILACYCLOPENTANE
AND 1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE

5.1 INTRODUCTION

The pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane at 773 K and ca. 760 mmHg is known³² to give the isomeric product 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane:



A kinetic study of the thermal decomposition of the trisilacyclopentane under LPP conditions was undertaken with a view to understanding the mechanism of this rearrangement.

The LPP of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was investigated in connection with the above study.

5.2 RESULTS

5.2.1 1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane

The pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane was investigated between 879 and 1036 K by a series of kinetic runs in which the mass peak at 202⁺ (M⁺) was monitored. An initial pressure of ca. 0.17 mmHg was used in all experiments. Decomposition was first order with the following Arrhenius parameters: $\log A = 16.1 \pm 0.6$ and $E = 316 \pm 11 \text{ kJ mol}^{-1}$ (see Table 5.1 and Figure 5.1). Rate constants measured between 939 and 992 K were used to derive these parameters, since the LPP technique can provide reliable measurement of decomposition rate constants only when the leak-in and leak-out rate constants are of little importance (see Chapter 3). 1,1,3,3,5-Pentamethyl-1,3,5-trisilacyclohexane, which has an intense mass peak at 201⁺ (M⁺-H), was not observed. The only silicon containing product was 1,1,3,3-tetramethyl-1,3-disilacyclobutane, which was recognised by its characteristic mass

TABLE 5.1

Rate Constants for the Decomposition of
1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane

T/K	k/s ⁻¹	T/K	k/s ⁻¹
1032	0.619	939	0.0249
1033	0.629	940	0.0285
1036	0.605	940	0.0303
986	0.187	923	0.0182
991	0.322	924	0.0183
992	0.224	925	0.0180
967	0.0923	925	0.0242
968	0.0963	924	0.0189
965	0.0963	904	0.00890
952	0.0542	905	0.00821
955	0.0565	905	0.00950
956	0.0656	879	0.00334
947	0.0377	880	0.00277
947	0.0396	880	0.00265
947	0.0378		

peaks at 144⁺ (M⁺) and 129⁺ (M⁺-Me). The other products, methane and hydrogen, were recognised by their mass peaks at 16⁺ and 2⁺ respectively.

The yield of the disilacyclobutane at 889 K was measured by a series of kinetic runs in which the 202⁺ mass peak of the trisilacyclopentane and the 129⁺ and 144⁺ mass peaks of the product were monitored. The initial pressure used in all runs was ca. 0.14 mmHg. The observed yield was 77%.

A third series of kinetic runs was carried out so that the effect of temperature upon the yields of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, methane and hydrogen could be investigated. The mass peaks monitored during these experiments were at 202⁺, 129⁺, 16⁺ and 2⁺. The initial pressure used was ca. 0.14 mmHg. Rate constants for the formation of all three products were determined (see Table 5.2), and the resulting Arrhenius plots (see Figures 5.2, 5.3 and 5.4) were analysed by the

FIGURE 5.1: ARRHENIUS PLOT FOR THE DECOMPOSITION OF

1,1,3,3,4,4-HEXAMETHYL-1,3,4-TRISILACYCLOPENTANE

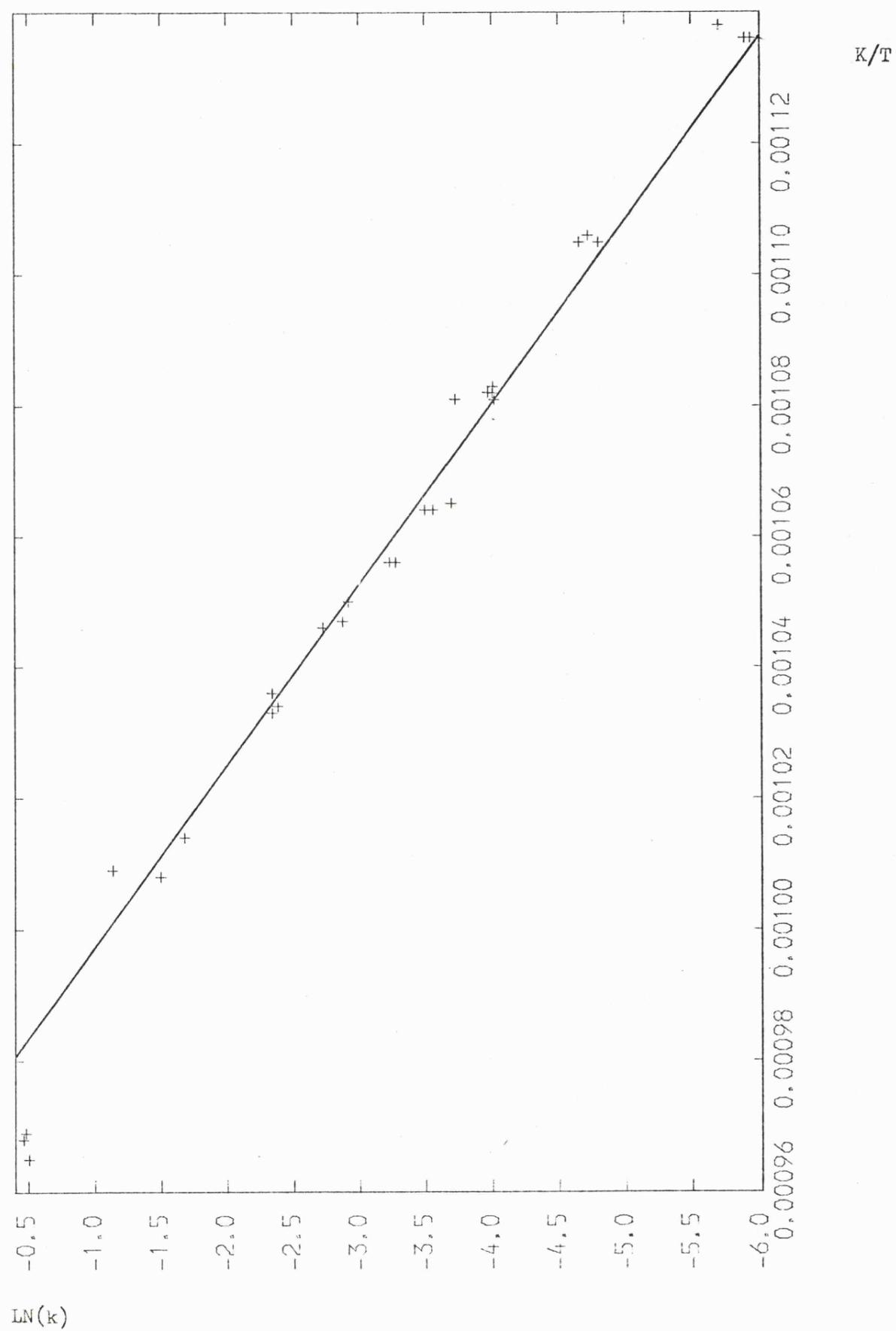


TABLE 5.2

Rate Constants for Product Formation/s⁻¹

T/K	H ₂	CH ₄	Me ₂ Si $\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ SiMe ₂
965	.078	.036	.021
967	.058	.029	.025
968	.068	.036	.026
947	.014	.011	.011
947	.014	.012	.011
947	.016	.013	.013
940	.011	.011	.0096
940	.0053	.0093	.011
925	.0075	.0045	.0048
924	.0047	.0053	.0048

method of least squares to give the following results:

	<u>log A</u>	<u>E/kJ mol⁻¹</u>
H ₂	23.4 ± 3	456 ± 60
CH ₄	16.8 ± 1.2	338 ± 21
Me ₂ Si $\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ SiMe ₂	13.4 ± 0.8	278 ± 15

The scatter in the Arrhenius plots indicates the difficulties involved in the determination of rate parameters for product formation. In particular, the parameters obtained for hydrogen strongly suggest that this product was not being formed via a single process. Product yields were calculated at 924 and 973 K from rate constants for product formation, given by the above Arrhenius parameters, and those for reactant decomposition, given by log A = 16.1 and E = 316 kJ mol⁻¹. They are expressed as percentages below:

<u>Product</u>	<u>924 K</u>	<u>973 K</u>
H ₂	24	61
CH ₄	29	33
Me ₂ Si $\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ SiMe ₂	28	22

The yield of disilacyclobutane at 889 K, calculated in the same way, 34%,

FIGURE 5.2: ARRHENIUS PLOT FOR THE FORMATION OF HYDROGEN

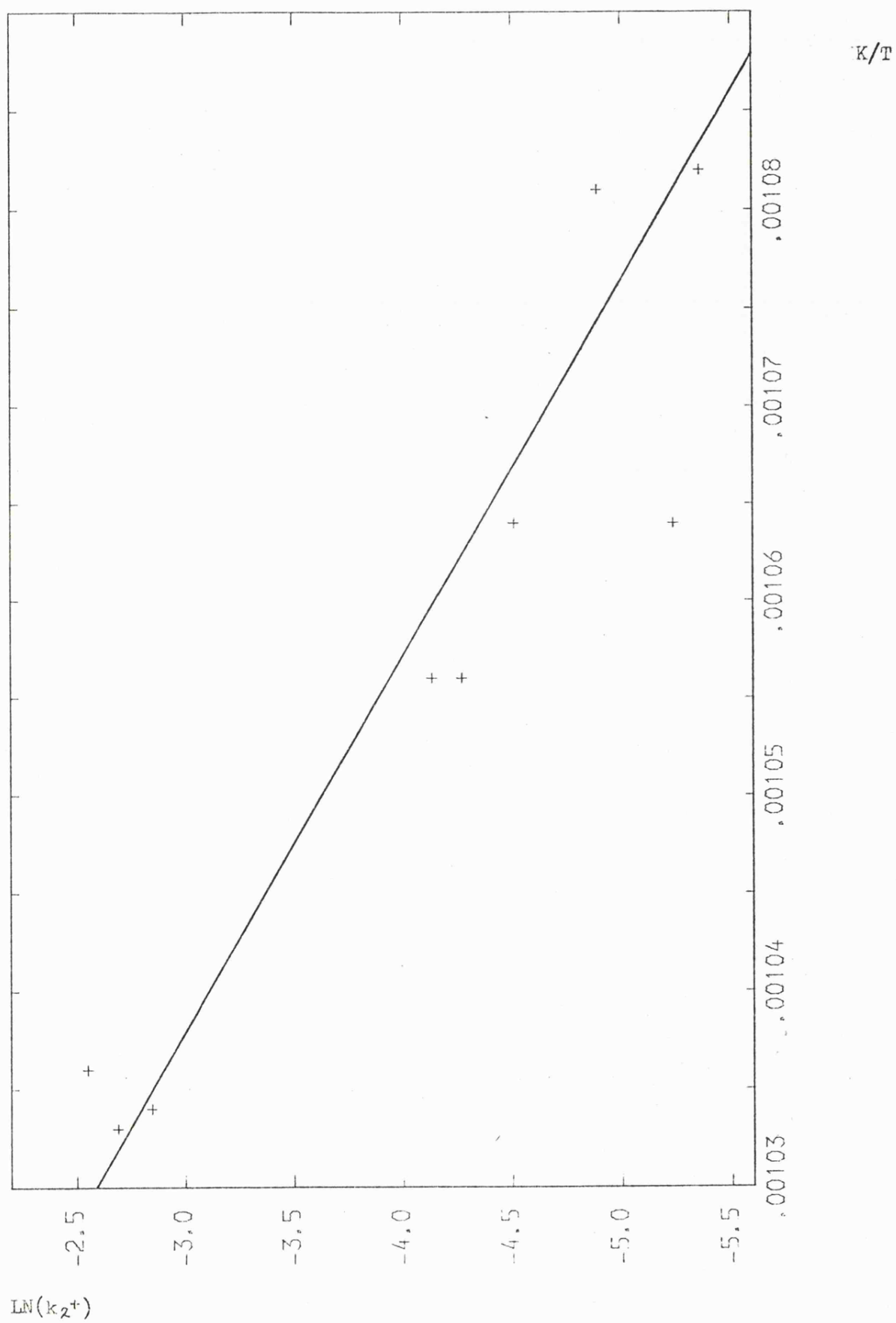


FIGURE 5.3: ARRHENIUS PLOT FOR THE FORMATION OF METHANE

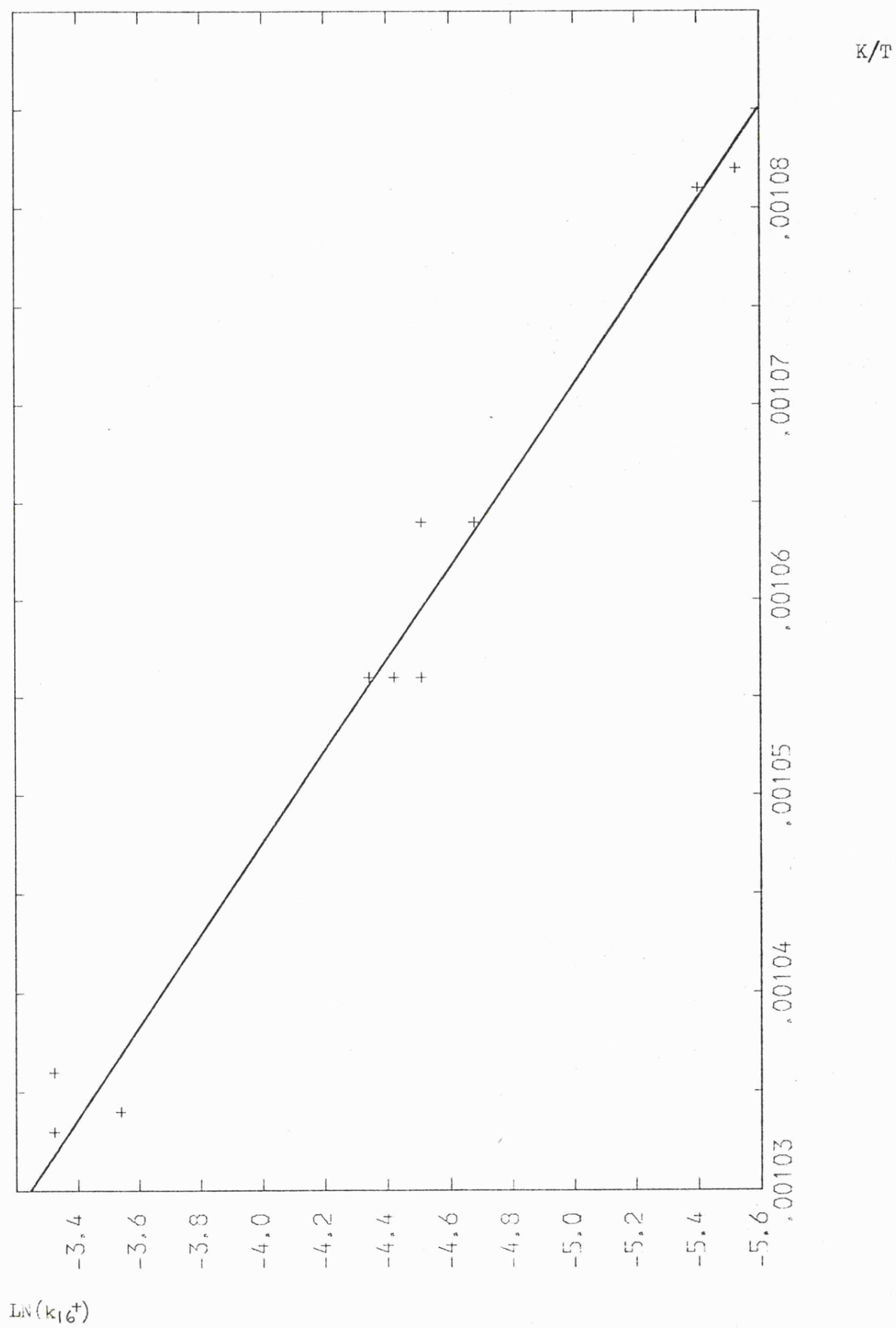
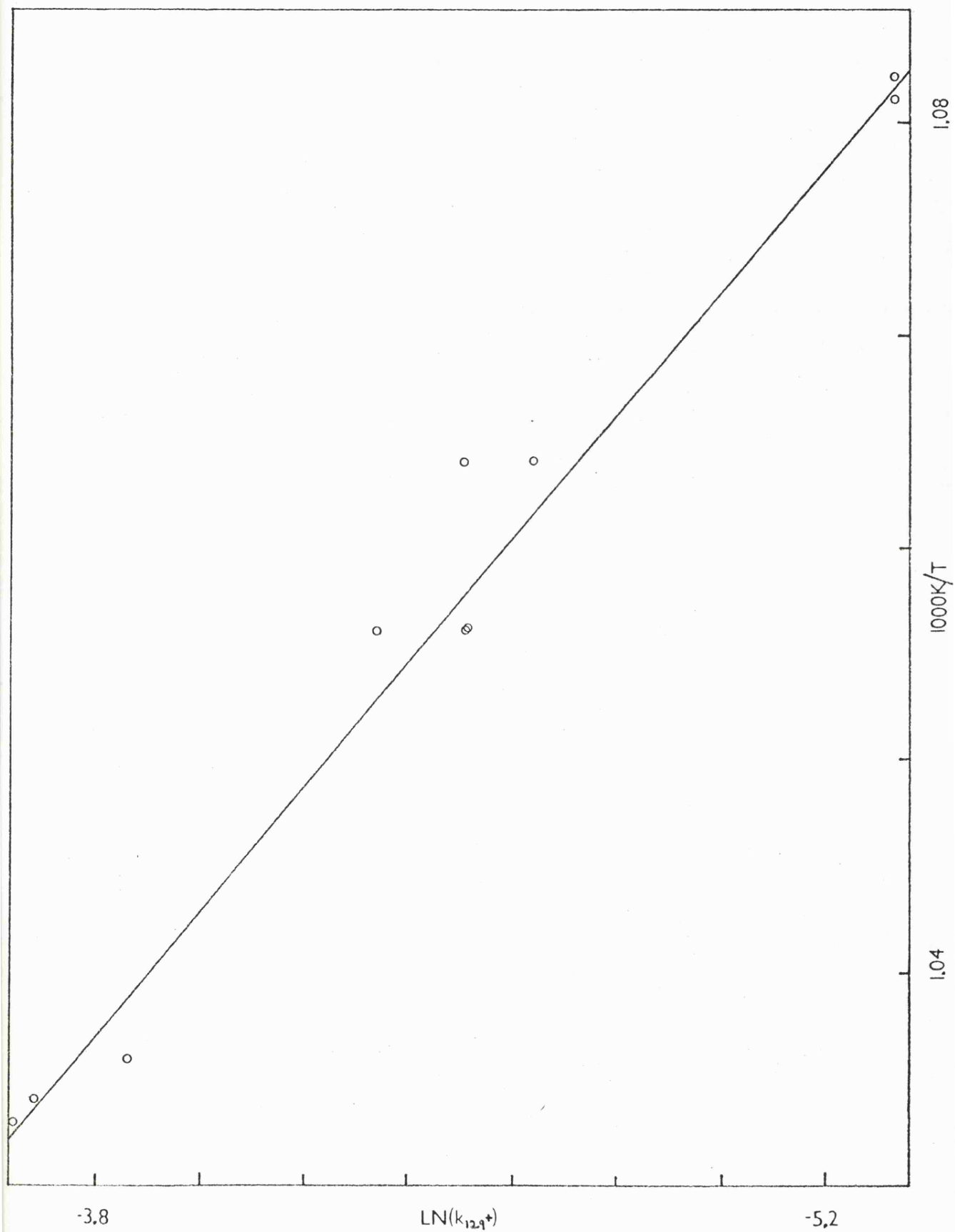


FIGURE 5.4 : ARRHENIUS PLOT FOR THE FORMATION OF $\text{Me}_2\text{Si} \begin{smallmatrix} \diagup \diagdown \\ \diagdown \diagup \end{smallmatrix} \text{SiMe}_2$



is in conflict with the previous measurement of 77%. This difference is probably due to the loss of silicon containing species to the wall of the reaction vessel during the latter experiments (see Chapter 2), an effect which is dependent upon the recent history of the apparatus.

Whilst some of the methane and hydrogen arose from decomposition of polymer at the wall of the reaction vessel (see Chapter 2), it was established in separate experiments (see Section 5.2.2) that another source was secondary pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. In keeping with this their yields increased with increasing temperature, while that of the disilacyclobutane decreased.

The possibility that 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane was formed during the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane, and that it subsequently decomposed to give the disilacyclobutane, was investigated in a further series of experiments in which the ring expansion isomer was pyrolysed. In these kinetic runs the mass peak at 187^+ ($M^+ - \text{Me}$) was monitored so that decomposition rate constants could be measured and Arrhenius parameters deduced (see Table 5.3 and Figure 5.5). The mass peak at 187^+ was chosen because those at 202^+ and 201^+ (M^+ and $M^+ - \text{H}$ respectively) rose during kinetic runs, indicating the formation of an isomeric product. Other mass peaks which rose were at 185^+ and 141^+ . Methane and hydrogen were also observed, but no 1,1,3,3-tetramethyl-1,3-disilacyclobutane was produced.

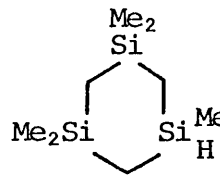
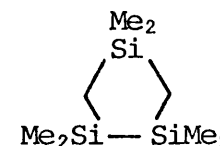
Although the 187^+ mass peak fell during the pyrolysis of the trisilacyclohexane, it is unlikely that it provided a fair measurement of decomposition rate constants, since any isomeric pyrolysis product would be likely to have the same mass peak. In accordance with this, plots of $\ln$ (peak height) against time were not as linear as those for the trisilacyclopentane, and the resulting Arrhenius plot was very scattered. In

TABLE 5.3

Rate Constants for the Decomposition of
1,1,3,3,5-Pentamethyl-1,3,5-trisilacyclohexane

T/K	k/s ⁻¹	T/K	k/s ⁻¹
1025	0.419	916	0.00621
1026	0.492	890	0.00191
1026	0.270	869	0.00447
986	0.204	864	0.00236
986	0.353	863	0.00184
989	0.295	850	0.00105
963	0.0743	848	0.00070
965	0.0646	846	0.00112
965	0.247	827	0.00076
912	0.00604	825	0.00027
916	0.0151	824	0.00071

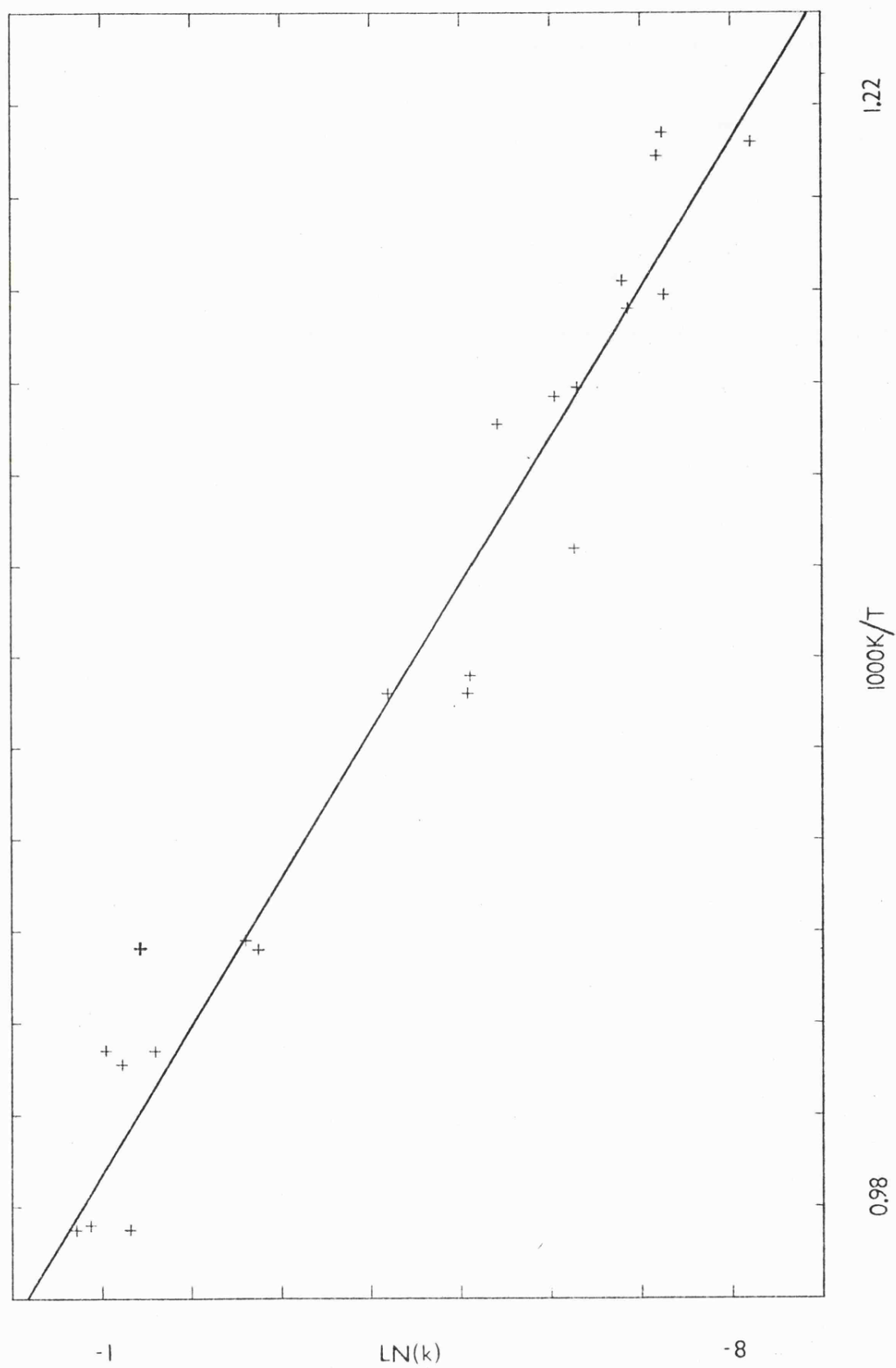
view of this, no least squares analysis was carried out and the rate parameters were estimated as: $\log A \approx 14$ and $E \approx 280 \text{ kJ mol}^{-1}$. Rate constants calculated with these data are compared with those for the decomposition of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane below:

	879 K	1036 K
	0.0023 s ⁻¹	0.76 s ⁻¹
	0.0021 s ⁻¹	1.47 s ⁻¹

They suggest that the ring expansion isomer is not more thermally unstable than the trisilacyclopentane.

Three reagents were used in an attempt to trap the two reactive intermediates likely to be involved in the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane: dimethylsilylene ($\text{Me}_2\text{Si}:$) and 2-methyl-2-

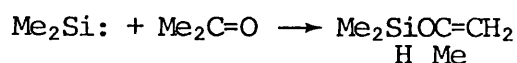
FIGURE 5.5: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1,1,3,3,5-PENTAMETHYL-1,3,5-TRISILACYCLOHEXANE



silapropene ($\text{Me}_2\text{Si}=\text{CH}_2$).

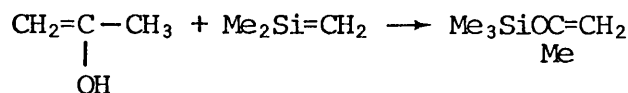
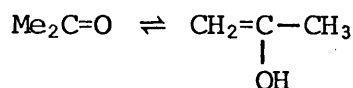
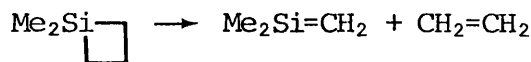
a) Acetone

Silylenes are known⁴⁰ to insert into the π -bond of carbonyls. To test the efficiency of this process under LPP conditions a known³⁴ source of dimethylsilylene, chloropentamethyldisilane, was pyrolysed, in a 1:1 mixture with acetone, at a total initial pressure of 0.3 mmHg and 830 K. The expected reactions were:

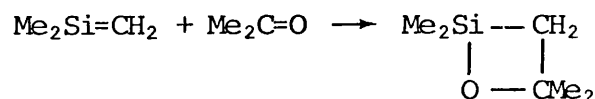


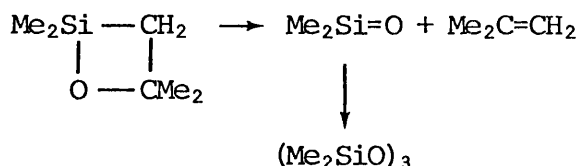
$\text{Me}_2(\text{H})\text{SiOC}(\text{Me})=\text{CH}_2$ was recognised as a product of this copyrolysis by its mass peaks at 116^+ (M^+), 115^+ (M^+-H) and 101^+ (M^+-Me).

The efficiency of the reaction of 2-methyl-2-silapropene with acetone¹⁷ was tested by pyrolysing a known⁴ precursor, 1,1-dimethyl-1-silacyclobutane, with the trapping agent, in a 1:1 mixture at 784 K with a total initial pressure of 0.3 mmHg. The expected reactions were:



However, $\text{Me}_3\text{SiOC}(\text{Me})=\text{CH}_2$ was not formed as a product of this copyrolysis [it would have been recognised by its mass peaks at 130^+ (M^+) and 115^+ (M^+-Me)], although a product with mass peaks at 56^+ and 41^+ was formed, suggesting that 2-methyl-2-silapropene had been trapped in the following way:¹⁷





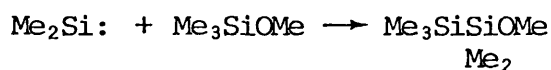
2-Methylpropene has mass peaks at 56^+ (M^+) and 41^+ ($\text{M}^+ - \text{Me}$). No concomitant $(\text{Me}_2\text{SiO})_3$ production was detected, although this may have been due to the sensitivity of the mass spectrometer, which is generally low at masses above ca. 200^+ .

The temperatures chosen for the above copyrolyses were those at which chloropentamethyldisilane and 1,1-dimethyl-1-silacyclobutane decomposed with a rate constant of ca. 0.02 s^{-1} . The corresponding temperature for 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane is 923 K, so a 1:1 mixture of this compound with acetone was pyrolysed, at this temperature, with a total initial pressure of 0.3 mmHg. This copyrolysis gave a product with mass peaks at 56^+ and 41^+ , presumably 2-methylpropene, providing some evidence for the involvement of 2-methyl-2-silapropene in the decomposition of the trisilacyclopentane. However, as with the copyrolysis of 1,1-dimethyl-1-silacyclobutane and acetone, no $(\text{Me}_2\text{SiO})_3$ was observed. There was no increase in the mass peaks at 116^+ , 115^+ and 101^+ , suggesting that $\text{Me}_2(\text{H})\text{SiOC}(\text{Me})=\text{CH}_2$ was not formed, and that dimethylsilylene is not involved in the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane. However, an alternative explanation is that dimethylsilylene was trapped during the copyrolysis, but the product of this reaction decomposed at the elevated temperature. To investigate this possibility a 1:1 mixture of acetone and chloropentamethyldisilane was pyrolysed at 923 K: a small amount of $\text{Me}_2(\text{H})\text{SiOC}(\text{Me})=\text{CH}_2$ was observed at the start of the experiment, but it rapidly decomposed as the copyrolysis proceeded.

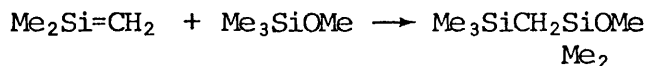
b) Methyltrimethylsilyl ether

As with acetone, the efficiency of the trapping action of methyltrimethylsilyl ether under LPP conditions was tested by pyrolysing the known^{4,34} precursors to dimethylsilylene and 2-methyl-2-silapropene in its presence.

Copyrolysis of a 1:1 mixture of chloropentamethyldisilane and methyltrimethylsilyl ether at 908 K with a total initial pressure of 0.3 mmHg gave a product with a mass peak at 147⁺ (Me₃SiSi(OMe)Me₂: (M⁺-Me) = 147⁺), due to the following reaction:^{41,42}



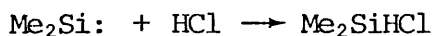
Copyrolysis of a 1:1 mixture of 1,1-dimethyl-1-silacyclobutane and methyltrimethylsilyl ether under the same conditions gave the expected^{19,20} product, characterised by its mass peak at 161⁺ (M⁺-Me):



A mixture of the trisilacyclopentane and methyltrimethylsilyl ether, in the ratio of 1:1.5 was pyrolysed at 908 K with a total initial pressure of 0.3 mmHg. Products with mass peaks at 147⁺ and 161⁺ were observed, providing evidence for the formation of both reactive intermediates.

c) Hydrogen Chloride

Hydrogen chloride is known to react with 2-methyl-2-silapropene under LPP conditions to give trimethylchlorosilane,¹⁸ and with dimethylsilylene to give dimethylchlorosilane:⁷¹



The mass spectrum of trimethylchlorosilane has a small peak at 108^+ (M^+), along with peaks at 93^+ and 79^+ [(M^+-Me) and $(M^+-CH_3CH_2)$] in the ratio of 100:6. That of dimethylchlorosilane has peaks at 93^+ and 79^+ [(M^+-H) and (M^+-Me)] in the ratio of 100:78.

A mixture of hydrogen chloride and the trisilacyclopentane in the ratio of 4:1 was pyrolysed at 898 K with a total initial pressure of 0.5 mmHg. Products with mass peaks at 108^+ , 93^+ and 79^+ were formed. The mass peak at 108^+ showed that trimethylchlorosilane was produced during the copyrolysis. The mass peaks at 93^+ and 79^+ were in the ratio of 100:31, indicating the presence of both chlorosilanes in the pyrolysis products, and the involvement of both reactive intermediates in the decomposition.

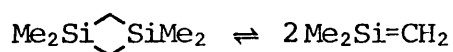
The trapping experiments, then, provided evidence for the involvement of both dimethylsilylene and 2-methyl-2-silapropene in the decomposition of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane. Another mechanistically significant point is that the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was not completely suppressed by the presence of hydrogen chloride. Since this trapping agent quantitatively collects 2-methyl-2-silapropene under LPP conditions,¹⁸ such an observation suggests that this reactive intermediate was not a precursor to the disilacyclobutane (see Section 5.2.2).

A likely reason for the different products given by the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane at high³² and low pressures was that the high pressure product, 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane, resulted from a bimolecular step which became unfavourable at low pressure. This effect occurs in the pyrolysis of hexamethyldisilane which, when carried out at high pressure,³⁰ gives the isomeric product, $Me_3SiCH_2Si(H)Me_2$. Pyrolysis at low pressure^{9,31} yields 1,1,3,3-

tetramethyl-1,3-disilacyclobutane. Similarly, the high pressure pyrolysis of allyltrimethylsilane leads to vinyltrimethylsilane,^{90,91} a product which is absent from the LPP of the same compound.²⁹ In both cases the bimolecular step inhibited at low pressure is a radical-molecule reaction. The possibility that such a step was responsible for the formation of the trisilacyclohexane in the high pressure pyrolysis³² of the trisilacyclopentane was investigated by pyrolysing the latter compound in the presence of a methyl radical source, dimethylmercury, in the LPP apparatus. A 1:1 mixture was used, with a total initial pressure of 0.5 mmHg. The pyrolysis temperature was 689 K (well below that at which 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane undergoes unimolecular decomposition). The ring expansion isomer was formed, but no 1,1,3,3-tetramethyl-1,3-disilacyclobutane was observed.

5.2.2 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

There is evidence^{13,14,15} that the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane yields 2-methyl-2-silapropene:



A study of the thermal decomposition of this compound was undertaken to investigate the possibility that the 2-methyl-2-silapropene, methane and hydrogen detected in the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane arose from secondary decomposition of the product disilacyclobutane. In addition, kinetic data on the pyrolysis of this compound were required to complement thermochemical calculations concerning the reactions of the silaalkene (see Chapter 4).

However, this study proved to be problematical. Two series of kinetic runs were performed, between 935 and 1055 K, in which the disilacyclobutane was pyrolysed on its own, with sample sizes of 0.14 mmHg, and in

a 1:1 mixture with hydrogen chloride, at total initial pressures of 0.28 mmHg. The purpose of the latter experiments, in the presence of an effective trap¹⁸ for 2-methyl-2-silapropene, was to observe reactant decomposition under conditions where the reverse reaction (dimerisation of the silaalkene) was not favoured.

In both series of experiments, the disilacyclobutane had a very high leak-out rate constant (ca. 0.025 s^{-1}), indicating that it was being lost from the gas phase by a process other than homogeneous decomposition. In addition to this problem, hydrogen chloride reacted with the disilacyclobutane in the vacuum line at room temperature prior to the copyrolysis experiments. Thus when the mixture was expanded into the reaction vessel at the beginning of a kinetic run, mass peaks due to trimethylchlorosilane (see below) could be observed even before pyrolysis. Such reaction did not occur, however, in the reaction vessel at temperatures below the pyrolysis temperature of the disilacyclobutane. Under these conditions a mixture of the two compounds could be left with no trimethylchlorosilane formation, indicating that the reaction in the vacuum line was catalysed by moisture (the reaction vessel, being constantly at elevated temperatures, was relatively dry) or that it was due to the nature of the surface of the vacuum line (that of the reaction vessel was coated with polymer laid down during pyrolyses).

The pyrolysis products of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were hydrogen, methane and ethene. The presence of hydrogen chloride induced the formation of trimethylchlorosilane also, indicating the presence of 2-methyl-2-silapropene.

Because of the difficulties outlined above, kinetic data on reactant decomposition and product formation were very scattered. Data obtained between ca. 950 and 1000 K were used to estimate the reactant half-lives

TABLE 5.4 (a)

Decomposition half-lives for $\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{SiMe}_2/\text{s}$

T/K	950	1000
without HCl	66	7.4
with HCl	70	10.3

TABLE 5.4 (b)

Product Yields (%)

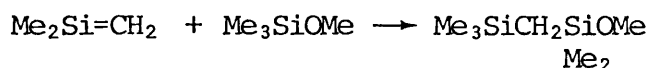
	T/K	950	1000
without HCl	Hydrogen	150	400
	Methane	50	100
	Ethene	15	40
with HCl	Hydrogen	130	130
	Methane	110	100
	Ethene	15	20
	Me_3SiCl	110	90

and product yields shown in Table 5.4.

In a further series of kinetic runs in which 0.14 mmHg samples of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were pyrolysed with between 0.1 and 0.8 mmHg of hydrogen chloride at 963 K, a constant yield of trimethylchlorosilane was observed, indicating that the proportion of trapping agent used in the above experiments was sufficient to collect quantitatively all the 2-methyl-2-silapropene produced.

The involvement of the silaalkene in the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was also checked by pyrolysing it in a 1:1 mixture with methyltrimethylsilyl ether at a total initial pressure of

0.6 mmHg and 901 K (similar to the temperature used for the copyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane with the same trapping agent). A product with a mass peak at 161⁺ was observed and attributed to the following reaction:^{19,20}



The half-life data shown in Table 5.4(a) indicate that the presence of hydrogen chloride did not significantly increase the rate of decomposition of the disilacyclobutane. This suggests that the importance of the reverse reaction was small over the temperature range studied, a conclusion supported by other workers.^{13,15} The decomposition data lead to the following approximate Arrhenius parameters for the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane: $E \approx 324 \text{ kJ mol}^{-1}$ and $\log A \approx 15.84$. These parameters imply that over the temperature range 879 - 1036 K, the disilacyclobutane decomposes at ca. 20% of the rate of decomposition of the trisilacyclopentane.

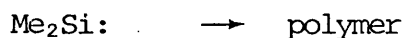
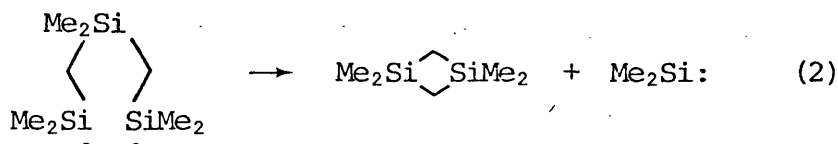
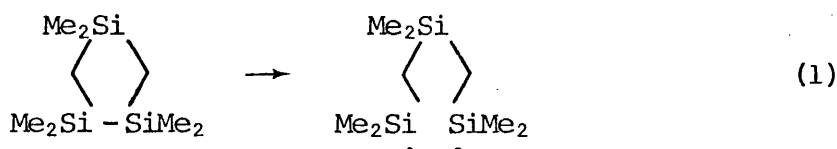
From the product yields in Table 5.4(b) it is clear that secondary decomposition of the disilacyclobutane in the pyrolysis of the trisilacyclopentane provides an explanation for the observed hydrogen and methane. Ethene was not detected in the pyrolysis of the trisilacyclopentane. This was probably because of its indistinctive mass spectrum, and because the yield of ethene in the pyrolysis of the disilacyclobutane is significantly smaller than those of hydrogen and methane. The trapping experiments with hydrogen chloride¹⁸ and methyltrimethylsilyl ether^{19,20} clearly show the involvement of 2-methyl-2-silapropene in the thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

5.3 DISCUSSION

5.3.1 1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane

Although both dimethylsilylene and 2-methyl-2-silapropene were involved in the LPP of the trisilacyclopentane, it seems likely (see Section 5.2.2) that the latter reactive intermediate arose from secondary decomposition of the product 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The mass spectrum of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane is consistent with this conclusion. There is often a close similarity between fragmentation by electron impact and pyrolytic fragmentation. For example, the mass spectrum of 1,1-dimethyl-1-silacyclobutane has its base peak at 72^+ ($\text{Me}_2\text{SiCH}_2^+$), while the pyrolytic decomposition of the same compound is a clean source of 2-methyl-2-silapropene.⁴ The trisilacyclopentane has a very small 72^+ mass peak, but an intense mass peak at 129^+ . The base peak in the mass spectrum of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is also at 129^+ ($\text{M}^+ - \text{Me}$).

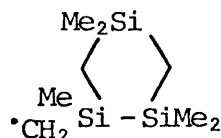
The lowest estimate of the silicon-methyl bond dissociation energy is^{8,43} 355 kJ mol^{-1} . Since the silicon-silicon bond dissociation energy in hexamethyldisilane is³¹ 337 kJ mol^{-1} , the initial step in the decomposition of the trisilacyclopentane is silicon-silicon bond rupture. Accordingly, the following mechanism can be used to account for the results of the LPP experiments:



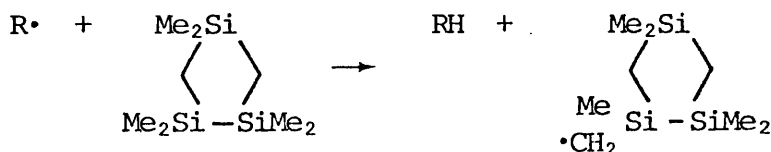
[Reaction (2) provides the simplest route to the disilacyclobutane. In addition, it is the most energetically feasible, with a small endothermicity equal to the ring strain in 1,1,3,3-tetramethyl-1,3-disilacyclobutane (ca. 103 kJ mol^{-1})⁴⁴. The intermediacy of a 1,4 biradical would be endothermic^{8,43} by at least 355 kJ mol^{-1} .]

The observed Arrhenius parameters are quite consistent with the rate determining step, silicon-silicon bond rupture. The 'A'-factor of $10^{16.1 \pm 0.6} \text{ s}^{-1}$ is in keeping with biradical formation from ring cleavage,⁶⁵ and the activation energy, when compared with the silicon-silicon bond dissociation energy in hexamethyldisilane,³¹ suggests a small ring strain of $21 \pm 16 \text{ kJ mol}^{-1}$. This is reasonable when compared with those of octamethyl-1,2-disilacyclobutane⁵⁰ (81 kJ mol^{-1}) and octamethyl-1,3-disila-2-oxacyclopentane⁵⁰ (40 kJ mol^{-1}).

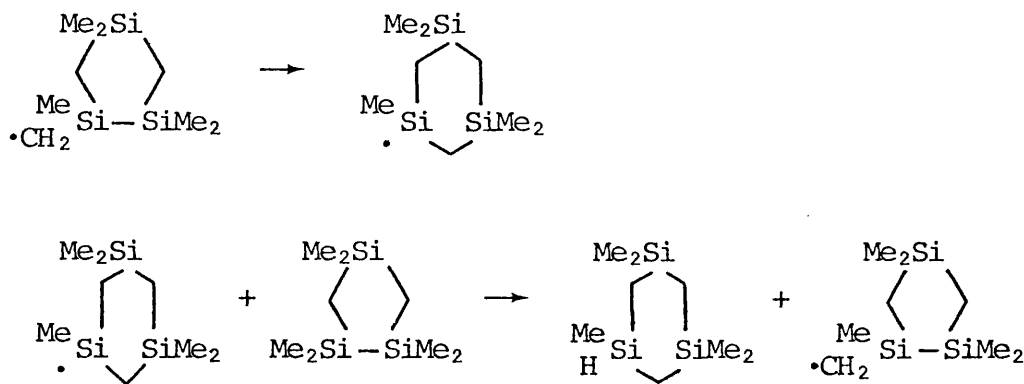
The experiment with dimethylmercury suggested that the precursor to 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane formation is the



radical, formed from the trisilacyclopentane by hydrogen abstraction:



A similar radical, $\text{Me}_3\text{SiSi}(\text{Me}_2)\dot{\text{C}}\text{H}_2$, is known^{9,31} to rearrange unimolecularly to $\text{Me}_3\text{SiCH}_2\dot{\text{S}}\text{iMe}_2$. The corresponding reaction of the above cyclic radical, followed by hydrogen abstraction, would give 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane:



These reactions constitute the propagation steps of a chain reaction converting the trisilacyclopentane to the trisilacyclohexane.

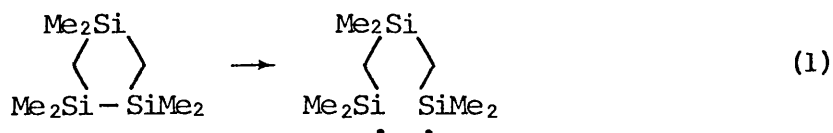
The effect of pressure upon product formation occurs because at low concentrations the biradical formed from silicon-silicon bond rupture decomposes unimolecularly to give the disilacyclobutane, while at high concentrations it abstracts hydrogen from a reactant molecule and thus initiates the chain leading to 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane. The full reaction mechanism is shown in Scheme 5.1. By analogy with the isomerisation of hexamethyldisilane,^{9,31} Arrhenius parameters may be estimated for these reactions as shown in Table 5.5.

TABLE 5.5

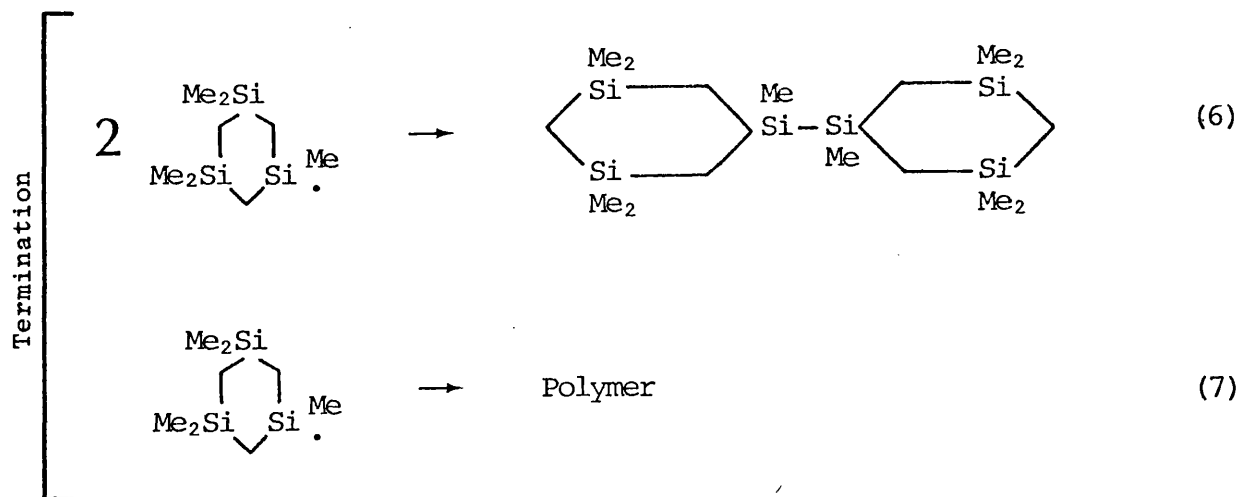
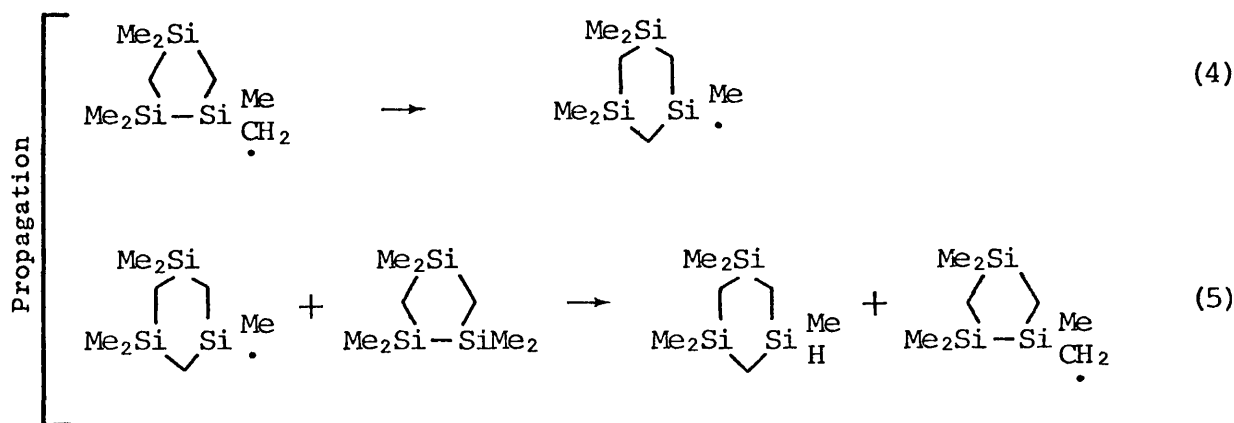
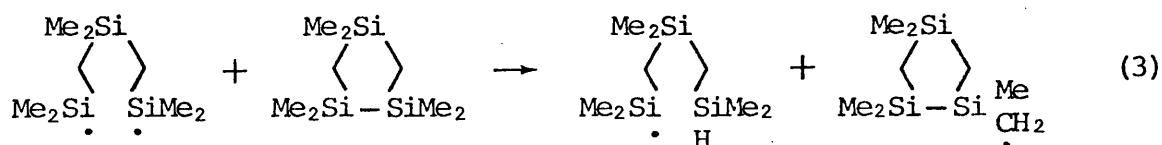
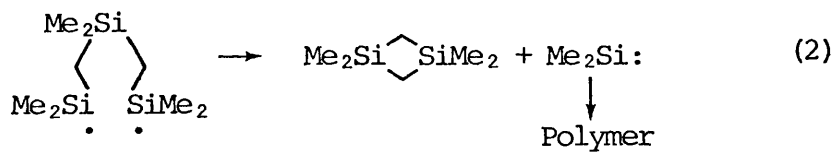
Estimated Arrhenius Parameters for Scheme 5.1

Reaction	log A	E/kJ mol ⁻¹	Ref.
1	16.1	316	This work
3	10.4	75	9
4	12.3	90	9
5	10.4	75	9
6	8.8	0	9

Steady state analysis of Scheme 5.1, assuming that termination is by reaction (6) only, yields:



Initiation



SCHEME 5.1

$$\frac{d}{dt} \left[\begin{array}{c} \text{Me}_2\text{Si} \\ \diagup \quad \diagdown \\ \text{Me}_2\text{Si} \quad \text{Si} \\ \diagdown \quad \diagup \\ \text{Si} \quad \text{H} \end{array} \right] = \left(\frac{k_1 k_4^2}{2 k_5} \right)^{\frac{1}{2}} \left[\begin{array}{c} \text{Me}_2\text{Si} \\ \diagup \quad \diagdown \\ \text{Me}_2\text{Si} - \text{SiMe}_2 \end{array} \right]^{\frac{3}{2}}$$

$$= k' \left[\begin{array}{c} \text{Me}_2\text{Si} \\ \diagup \quad \diagdown \\ \text{Me}_2\text{Si} - \text{SiMe}_2 \end{array} \right]^{\frac{3}{2}}$$

The Arrhenius parameters for k' can be determined with the data in Table 5.5, giving: $\log A = 13.85$ and $E = 232 \text{ kJ mol}^{-1}$. The chain length for the isomerisation reaction is given by:

$$k' \left[\begin{array}{c} \text{Me}_2\text{Si} \\ \diagup \quad \diagdown \\ \text{Me}_2\text{Si} - \text{SiMe}_2 \end{array} \right]^{\frac{1}{2}} / k_1.$$

For the effect of temperature and pressure upon this quantity, see Table 5.6.

TABLE 5.6

Chain length for Isomerisation Process

Pressure/mmHg	T/K = 773	878	1036
0.15	4.5	0.9	0.2
760	338	66	11

The original high pressure pyrolyses³² were carried out at 773 K and ca. 760 mmHg. The observed formation of the ring expansion isomer under these conditions can be understood in view of the large chain length implied. Under the conditions of the LPP experiments a chain length of ca. 0.5 would be expected according to Table 5.6, although it is very likely that at such a low pressure termination would be by reaction (7) instead of reaction (6), in which case the formation of the trisila-cyclohexane would be second order, with an even shorter chain length. Consequently the major product would be 1,1,3,3-tetramethyl-1,3-disila-cyclobutane.

The radical rearrangement (4) is probably responsible for the ring expansions of 1,1,2,2-tetramethyl-1,2-disilacyclopropane,⁹² 1,1,2,2-tetramethyl-1,2-disilacyclobutane⁹² and octamethyltetrasilacyclobutane.⁹³ It also occurs in the pyrolysis of hexamethyldisilane,^{9,30,31} and thus appears to be a general reaction of alkyl silanes containing silicon-silicon bonds. It is exothermic by at least⁸ 30 kJ mol⁻¹, and is probably important in the pyrolytic formation of silicon-carbon fibres.

5.3.2 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

Some of the hydrogen and methane produced during the pyrolysis of the disilacyclobutane arose from decomposition of polymer at the wall of the reaction vessel (see Chapter 2). However, it is unlikely that this process accounted for the entire yield of these products. Other possible routes to their formation, and that of ethene, are discussed below.

The yield of trimethylchlorosilane in the copyrolysis experiments suggests that not all of the disilacyclobutane was lost via ring cleavage to 2-methyl-2-silapropene (in which case the observed yield of the chlorosilane would have been 200%). Some of the methane produced probably arose from rupture of one of the four silicon-methyl bonds in the disilacyclobutane, followed by hydrogen abstraction by the methyl radical. This process provides an alternative route for the loss of the disilacyclobutane and has been suggested by Gusel'nikov et al.¹⁵ It is plausible in view of the following discussion.

The Arrhenius parameters for rupture of the silicon-methyl bond in tetramethylsilane have been measured:⁴³ $\log A = 17.6 \pm 0.3$ and $E = 355 \pm 6$ kJ mol⁻¹. The activation energy derived from this study is lower than the strength of the same bond as estimated by Walsh from thermochemical calculations⁸ [$D(\text{Me}_3\text{Si-Me}) = 374 \pm 13$ kJ mol⁻¹]. It has been suggested⁴⁴

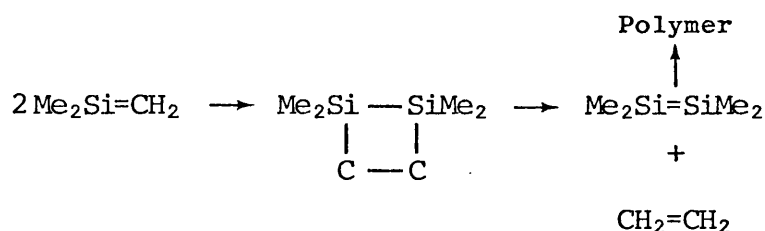
that this may be due to a small residual chain component in reactant decomposition in the experimental study. Arrhenius parameters for rupture of the silicon-methyl bond in trimethylchlorosilane have also been measured:⁶⁸ $E = 366 \pm 11 \text{ kJ mol}^{-1}$ and $\log A = 17.0 \pm 0.3$. Rate constants calculated from the above two sets of experimental Arrhenius data are compared with those calculated using the rate parameters for the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane below:

<u>Process</u>	<u>E/kJ mol⁻¹</u>	<u>log A</u>	<u>k₉₅₀/s⁻¹</u>	<u>k₁₀₀₀/s⁻¹</u>
$\text{Me}_4\text{Si} \rightarrow \text{Me}_3\text{Si}\cdot + \text{Me}\cdot$	355	17.6	0.0120	0.114
$\text{Me}_3\text{ClSi} \rightarrow \text{Me}_2\text{ClSi} + \text{Me}\cdot$	366	17.0	0.00075	0.00761
$\text{Me}_2\text{Si} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{SiMe}_2 \rightarrow \text{products}$	324	15.84	0.0106	0.0823

There is evidence⁸ that the strength of the silicon-methyl bond is not dependent upon chemical environment. The Arrhenius parameters for rupture of the silicon-methyl bond in the disilacyclobutane, then, are probably close to those for rupture of the same bond in trimethylchlorosilane, an upper limit for the speed of this process being provided by the Arrhenius data for tetramethylsilane. Although the rate constants for silicon-methyl bond rupture implied by the trimethylchlorosilane data suggest that this process in the thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is not of great importance, it cannot be discounted in view of the importance suggested by the tetramethylsilane Arrhenius data and is probably responsible for the loss of some 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Thus, the observed Arrhenius parameters do not pertain solely to the formation of 2-methyl-2-silapropene. Therefore caution must be exercised when utilizing these data as a basis for thermochemical calculations (see Chapter 4).

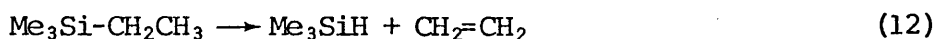
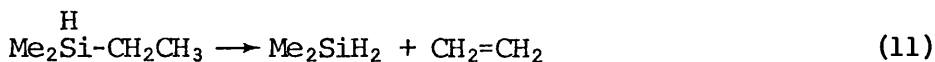
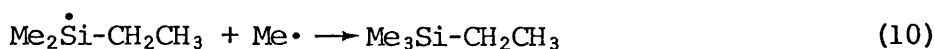
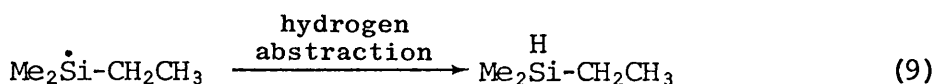
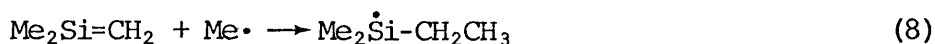
The formation of ethene, at least at higher temperatures, was reduced

by the presence of hydrogen chloride. A tempting explanation for its formation is via the head-to-head dimerisation of 2-methyl-2-silapropene:



Hydrogen chloride would remove 2-methyl-2-silapropene and thus reduce the incidence of the above reaction. However, since the reaction between 2-methyl-2-silapropene and hydrogen chloride is known¹⁸ to be very rapid, it is unlikely that any ethene was produced by this route during the copyrolysis experiments.

An alternative source of ethene is via the thermal decomposition of ethylsilanes,⁹⁴ formed from the reaction of 2-methyl-2-silapropene with methyl radicals. Reactions leading to ethene are shown in Scheme 5.2. The rate constant for reaction (12) can be estimated, from published data,⁹⁴ as $2 \times 10^{-4} \text{ s}^{-1}$ at 823 K. This is greater than that for the decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane at the same temperature ($2 \times 10^{-5} \text{ s}^{-1}$), indicating that any ethylsilanes produced in the pyrolysis of the disilacyclobutane [by reactions (8), (9) and (10)] would undergo secondary decomposition [by reactions (11) and (12)]. Attack by a methyl radical on the silicon of 2-methyl-2-silapropene would lead to the formation of tetramethylsilane. This compound, and the silanes formed in reactions (11) and (12) were not detected during the pyrolysis of the disilacyclobutane, suggesting that reactions (8)-(12) are of relatively minor importance, although it is likely that even if they were formed, they would not be very stable at the temperatures used: their decomposition^{43,95} would lead to methane and hydrogen. In any



SCHEME 5.2

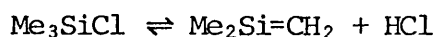
case, they would have been difficult to detect using the LPP apparatus, since the main peaks in their mass spectra also appear in the mass spectrum of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. However, in view of the large size of the ratio $[\text{HCl}]/[\text{Me}\cdot]$, during the experiments with hydrogen chloride, and the appropriate rate constants shown below, even reaction (8) is unlikely to compete with the addition of hydrogen chloride to 2-methyl-2-silapropene.

<u>Process</u>	<u>950 K</u>	<u>1000 K</u>	<u>(ref)</u>
$\text{HCl} + \text{Me}_2\text{Si}=\text{CH}_2$	$6.9 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$7.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	(68)
$\text{Me}\cdot + \text{Me}_2\text{Si}=\text{CH}_2$	$9.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$9.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	(96)

These data, then, provide evidence against the occurrence of the reactions in Scheme 5.2.

Since no stable silicon-containing products were observed during the pyrolysis of neat 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the possibility that a certain amount of hydrogen, methane and ethene arose from secondary decomposition (probably heterogeneous) of 2-methyl-2-silapropene must be considered. In this context it may be significant that the yields of hydrogen and ethene were reduced, at least at higher temperatures, by the presence of hydrogen chloride, when the 2-methyl-2-

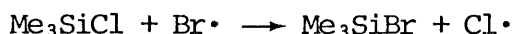
silapropene was trapped in the gas phase. The effect of the trapping agent upon methane formation was not the same. This may be due to the alternative source of this product discussed above. But if, as was suggested by the experiments in which the ratio of hydrogen chloride to the disilacyclobutane was varied, all of the 2-methyl-2-silapropene was trapped during the copyrolysis experiments, it is unlikely that any product would be produced via this route in the presence of the trapping agent unless the reaction of 2-methyl-2-silapropene with hydrogen chloride is reversible. A study of the LPP of trimethylchlorosilane⁶⁸ has provided evidence in favour of this possibility.



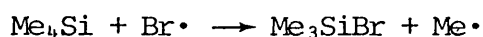
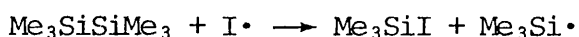
Rate constants for the decomposition of the chlorosilane, measured in the presence of hydrogen chloride, were slightly reduced relative to those measured with neat reactant. Further, the copyrolysis of trimethylchlorosilane and hydrogen bromide, at temperatures where silicon-methyl bond rupture was unlikely to be important (700–935 K), yielded trimethylbromosilane. A plausible route to this product is via the above reaction followed by the addition of 2-methyl-2-silapropene to hydrogen bromide,¹⁸



although the possibility of an atom displacement reaction also exists:



This latter process is unprecedented, although halogen atoms are known to displace trimethylsilyl⁹⁷ and methyl⁹⁸ radicals:



The LPP of trimethylchlorosilane in the presence of oxygen over the same

temperature range did not, however, yield formaldehyde and $(\text{Me}_2\text{SiO})_3$, the products expected from the reaction of 2-methyl-2-silapropene with this trapping agent.¹⁸ Since the rate constant for this process at 800 K is about ten times larger than that for the same reaction of hydrogen bromide⁶⁸ (see Chapter 4), the experiments with oxygen cast doubt on the formation of the silaalkene from trimethylchlorosilane. If it does occur, then secondary decomposition of 2-methyl-2-silapropene may provide a route to hydrogen, methane and ethene formation even in the presence of hydrogen chloride. Further, the proportion of reactant decomposing to 2-methyl-2-silapropene could be larger than was suggested by the yield of trimethylchlorosilane observed in the copyrolysis experiments.

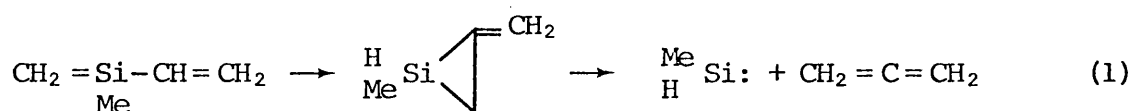
CHAPTER 6

THE PYROLYSES OF 1-METHYL-1-VINYL-1-SILACYCLOBUTANE
AND 1,1-DIVINYLSILACYCLOBUTANE

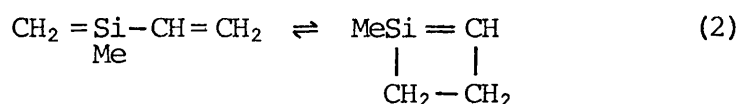
6.1 INTRODUCTION

It was pointed out in Chapter 1 that the gas phase pyrolysis of 1,1-dimethyl-1-silacyclobutane provided the first known source of a silaalkene. Since the original work of Flowers and Gusel'nikov,⁴ the thermal decomposition of silacyclobutanes has proved to be a general¹ route to these reactive intermediates. The pyrolyses of vinyl substituted silacyclobutanes are of interest since it has been proposed^{14,99} that the silaalkenes produced undergo reaction alternative to self-dimerisation.

There have been two independent studies of the gas phase pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane. Auner and Grobe¹⁴ found that, in addition to the expected products 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane and ethene, allene was formed. They, therefore, concluded that the silaalkene, 2-methyl-2-silabutadiene, isomerised to a silacyclopropane:



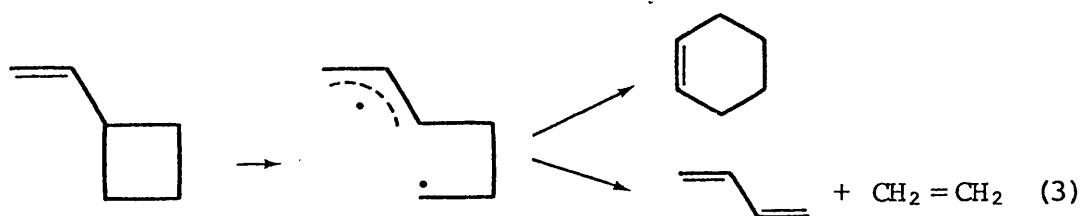
Mazerolles *et al.*⁹⁹ inferred from trapping experiments in the gas phase and in solution that 2-methyl-2-silabutadiene behaved as a conjugated system. They suggested two possible reaction mechanisms to explain their results, one being ionic in nature, and the other involving the formation of a silacyclobutene:



The gas phase pyrolysis of 1,1-divinyl-1-silacyclobutane has been investigated by Auner and Grobe:¹⁴ the observed products were 1,1,3,3-tetravinyl-1,3-disilacyclobutane, toluene, benzene, butadiene, propene

and ethene. They did not propose a mechanism by which the hydrocarbons (other than ethene) were formed, but suggested that they may have been produced via the silaalkene, 2-vinyl-2-silabutadiene.

There is a further point of interest in the pyrolysis of vinyl substituted silacyclobutanes: is allylic stabilization at silicon sufficiently great for pyrolysis to proceed by silicon-carbon bond rupture? The gas kinetics of the thermal decomposition of vinylcyclobutane has been studied by Frey and Pottinger.¹⁰⁰ They concluded that the biradical formed in the initial stage of the pyrolysis was allylically stabilized. As a result of this the ring expansion product was formed in addition to ethene and butadiene:



It is of interest to compare the Arrhenius parameters for reaction (3) with those for the thermal decomposition of cyclobutane⁸⁴ to ethene (see Table 6.1):

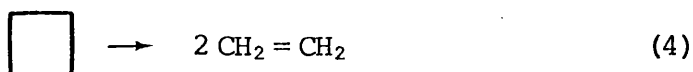


TABLE 6.1

Arrhenius Parameters for the Decomposition of Vinylcyclobutane and Cyclobutane

Reaction	log A	E/kJ mol ⁻¹	k _(800K) /s ⁻¹
3	14.87 ± 0.07	212.2 ± 0.8	10.3
4	15.62 ± 0.01	261.5 ± 1.7	0.035

The activation energy for reaction (3) is 49.3 kJ mol^{-1} lower than that for reaction (4) because of allylic stabilization in the biradical formed in the initial stage of the pyrolysis.⁶⁵ The 'A'-factor for reaction (3) is ca. 20% of that for reaction (4), the reduction being due to the net loss of rotation of the vinyl group in going from the reactant vinylcyclobutane to the more rigid allylically stabilized biradical: this causes a reduction in $\Delta S^\ddagger$ for reaction (3) relative to that for reaction (4).⁶⁵



If allylic stabilization at silicon is equal to that at carbon, then, by analogy with the data in Table 6.1, the activation energy for reaction (6a) would be expected to be lower than that for reaction (5) by $> (49 - 32) = 17 \text{ kJ mol}^{-1}$, since the strength of the silicon-carbon bond exceeds that of the carbon-carbon bond by⁸ $< 32 \text{ kJ mol}^{-1}$. The 'A'-factor for reaction (6a) would be expected to be ca. $10^{14.9} \text{ s}^{-1}$. Rate constants for reaction (6b) would be expected to be very similar to those for reaction (5). Using this information, the expected overall decomposition rate constant for 1-methyl-1-vinyl-1-silacyclobutane at 800 K (k_6) can be calculated as 0.123 s^{-1} ($= 3.3 \text{ k}_5$):

Reaction	log A	E/kJ mol ⁻¹	k _(800K) /s ⁻¹
(6a)	14.9	244.5	0.086
(6b)	15.64	261.5	<u>0.037</u>
			0.123

Kinetic data on the thermal decomposition of 1-methyl-1-vinyl-1-silacyclobutane are, therefore, of great interest, since they may be compared directly with those for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane. Similarly, kinetic data on the thermal decomposition of 1,1-divinyl-1-silacyclobutane can indicate the extent of allylic stabilization in the divinylsilyl radical.

6.2 RESULTS

6.2.1 1-methyl-1-vinyl-1-silacyclobutane¹⁰¹

A sample (ca. 0.5 mmHg) of 1-methyl-1-vinyl-1-silacyclobutane was pyrolysed in the LPP apparatus at 803 K. The major pyrolysis products were ethene and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane ($M^+ = 168$, $M^+ - \text{Me} = 153$, $M^+ - \text{Vi-H} = 140$).¹⁰² There was also a product formed in a very low yield with a mass peak at 40^+ which may have been allene ($M^+ = 40$).

A series of kinetic runs was carried out in which decomposition rate constants for 1-methyl-1-vinyl-1-silacyclobutane were measured using its mass peak at 84^+ ($M^+ - \text{C}_2\text{H}_4$). The initial pressure in all experiments was 0.17 mmHg. The results of these experiments are shown in Table 6.2 and Figure 6.1. The Arrhenius plot was analysed by the method of least squares to give: $\log A = 13.6 \pm 0.1$ and $E = 234 \pm 1 \text{ kJ mol}^{-1}$.

The high pressure Arrhenius parameters for the decomposition of 1,1-dimethyl-1-silacyclobutane are:⁴ $\log A = 15.64$ and $E = 261.5 \text{ kJ mol}^{-1}$. Thus at first sight the experimental results for the decomposition of 1-methyl-1-vinyl-1-silacyclobutane suggested that substitution of a vinyl group for a methyl group had reduced the Arrhenius parameters and that, therefore, some allylic stabilization in the transition state was occurring. However, the LPP technique is known to return low Arrhenius

TABLE 6.2

Rate Constants for the Decomposition of
1-Methyl-1-vinyl-1-silacyclobutane

T/K	k_6/s^{-1}	T/K	k_6/s^{-1}
862	0.269	803	0.0251
862	0.259	804	0.0261
861	0.249	805	0.0276
848	0.156	788	0.0121
849	0.169	786	0.0111
851	0.179	785	0.0111
836	0.0971	776	0.00738
837	0.0991	776	0.00766
839	0.109	776	0.00739
817	0.0461	749	0.00196
817	0.0461	748	0.00176
817	0.0441	747	0.00163

parameters for the decomposition of 1,1-dimethyl-1-silacyclobutane (see Section 6.3), so a second series of kinetic runs was carried out in which a 1:1 mixture of 1,1-dimethyl-1-silacyclobutane and 1-methyl-1-vinyl-1-silacyclobutane was pyrolysed. The decomposition of the two silacyclobutanes was monitored with their base peaks ($M^+-C_2H_4$) at 72^+ and 84^+ . A total initial pressure of 0.15 mmHg was used in all experiments. The data produced are shown in Table 6.3 and Figures 6.2, 6.3 and 6.4. Although the rate constants for the decomposition of 1,1-dimethyl-1-silacyclobutane were slightly less than those for 1-methyl-1-vinyl-1-silacyclobutane over the temperature range ($k_5/k_6 \approx 95\%$), the Arrhenius parameters for the decomposition of the two silacyclobutanes were the same within experimental error:

$$k_5 : \quad \log A = 13.6 \pm 0.2 \quad E = 235 \pm 3 \text{ kJ mol}^{-1}$$

$$k_6 : \quad \log A = 13.7 \pm 0.2 \quad E = 237 \pm 3 \text{ kJ mol}^{-1}$$

The Arrhenius parameters derived from the plot of $\ln(k_5/k_6)$ against $1/T$ gave $\log(A_5/A_6) = -0.20 \pm 0.05$, $(E_5 - E_6) = -2.7 \pm 0.8 \text{ kJ mol}^{-1}$.

The pyrolysis products observed during the second series of kinetic

FIGURE 6.1: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1-METHYL-1-VINYL-1-SILACYCLOBUTANE

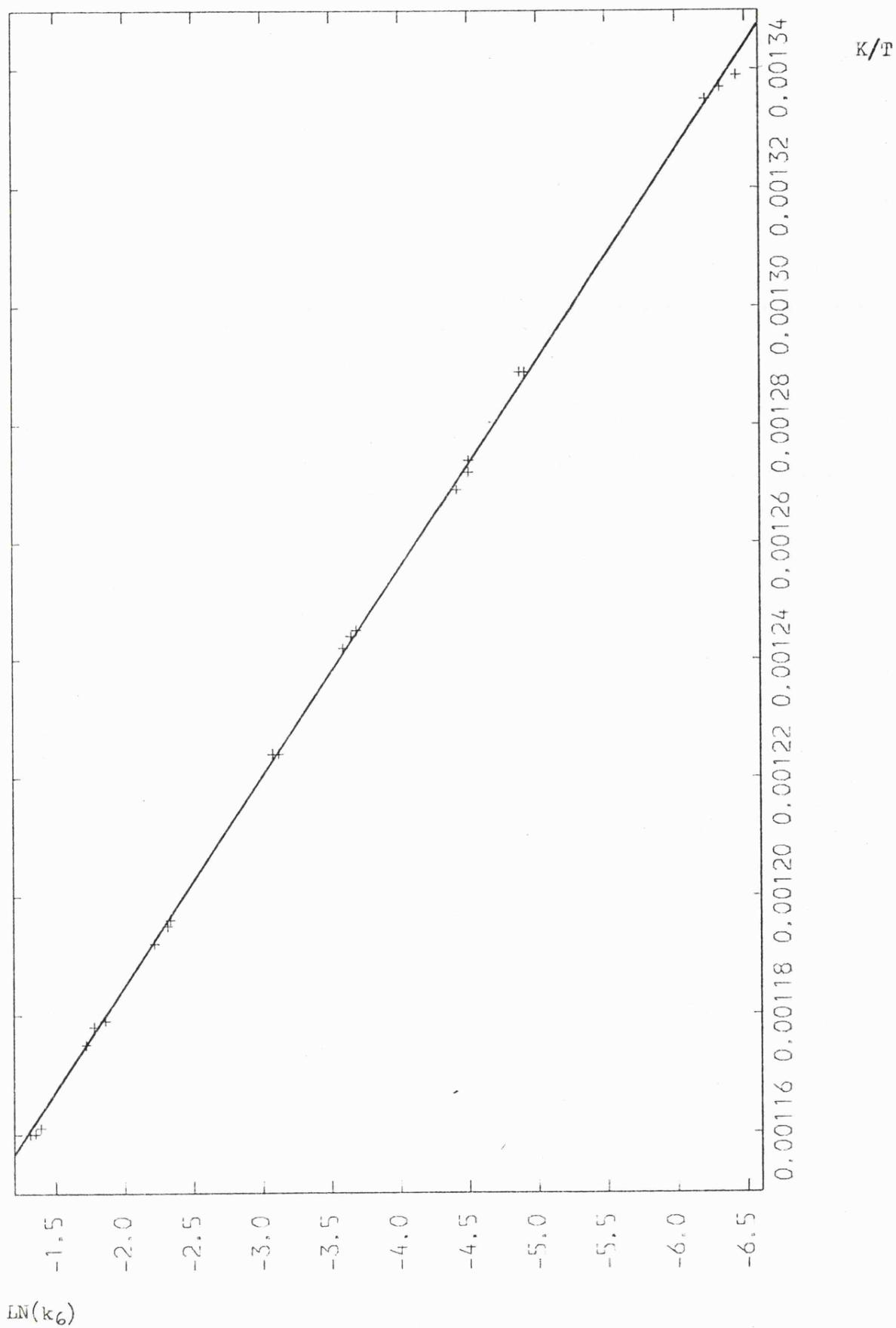
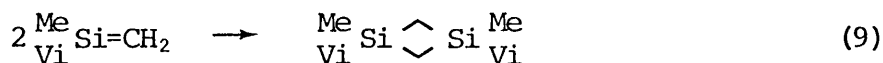
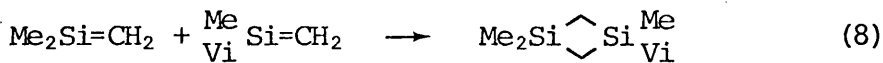
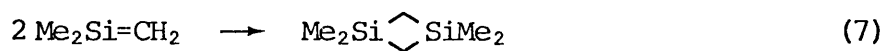
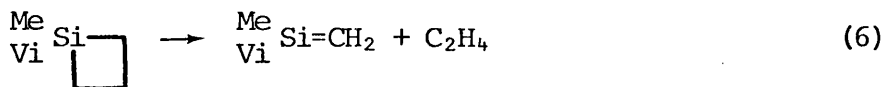
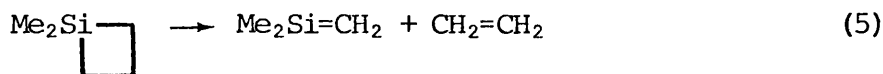


TABLE 6.3

Results of the Pyrolysis of a 1:1 Mixture
of 1,1-Dimethyl- and 1-Methyl-1-vinyl-1-silacyclobutanes

T/K	k_5/s^{-1}	k_6/s^{-1}	k_5/k_6
865	0.223	0.242	0.921
863	0.221	0.244	0.906
862	0.200	0.220	0.909
842	0.0969	0.103	0.941
845	0.128	0.135	0.948
848	0.129	0.137	0.942
826	0.0539	0.0549	0.982
821	0.0459	0.0489	0.939
820	0.0429	0.0449	0.955
803	0.0209	0.0219	0.954
804	0.0219	0.0229	0.956
787	0.00986	0.0119	0.832
786	0.00986	0.00994	0.991
787	0.00966	0.00994	0.971
769	0.00396	0.00424	0.932
765	0.00316	0.00324	0.975
761	0.00266	0.00274	0.971

runs were ethene, 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane, 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane ($M^+ = 156^+$, $M^+ - Me = 141^+$). These observations were consistent with the following reaction sequence:



In an attempt to provide evidence for the isomerisation of 2-methyl-2-silabutadiene, a third series of kinetic runs was carried out, with

FIGURE 6.2: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1,1-DIMETHYL-1-SILACYCLOBUTANE IN A 1:1 MIXTURE WITH
1-METHYL-1-VINYL-1-SILACYCLOBUTANE

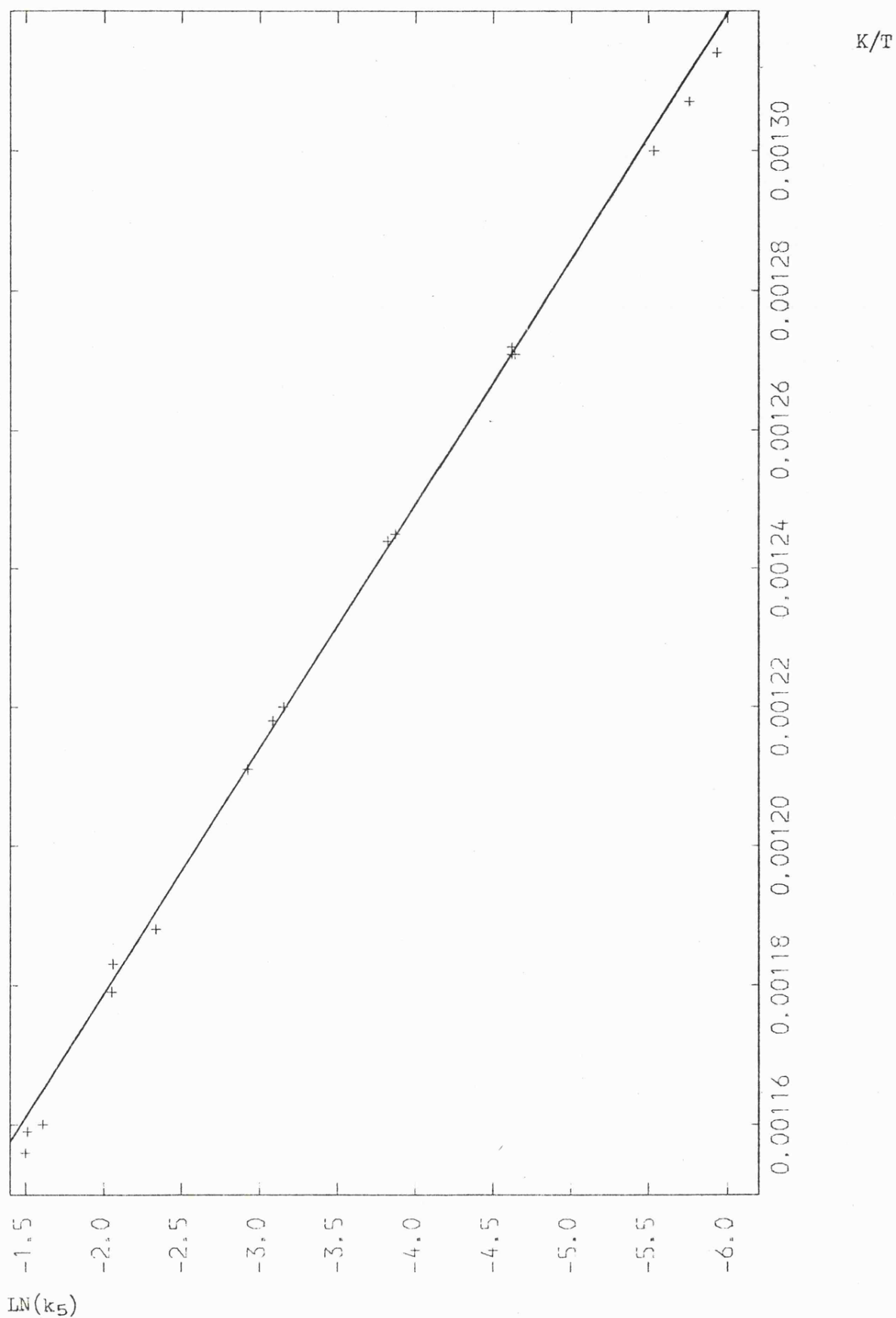


FIGURE 6.3: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1-METHYL-1-VINYL-1-SILACYCLOBUTANE IN A 1:1 MIXTURE
WITH 1,1-DIMETHYL-1-SILACYCLOBUTANE

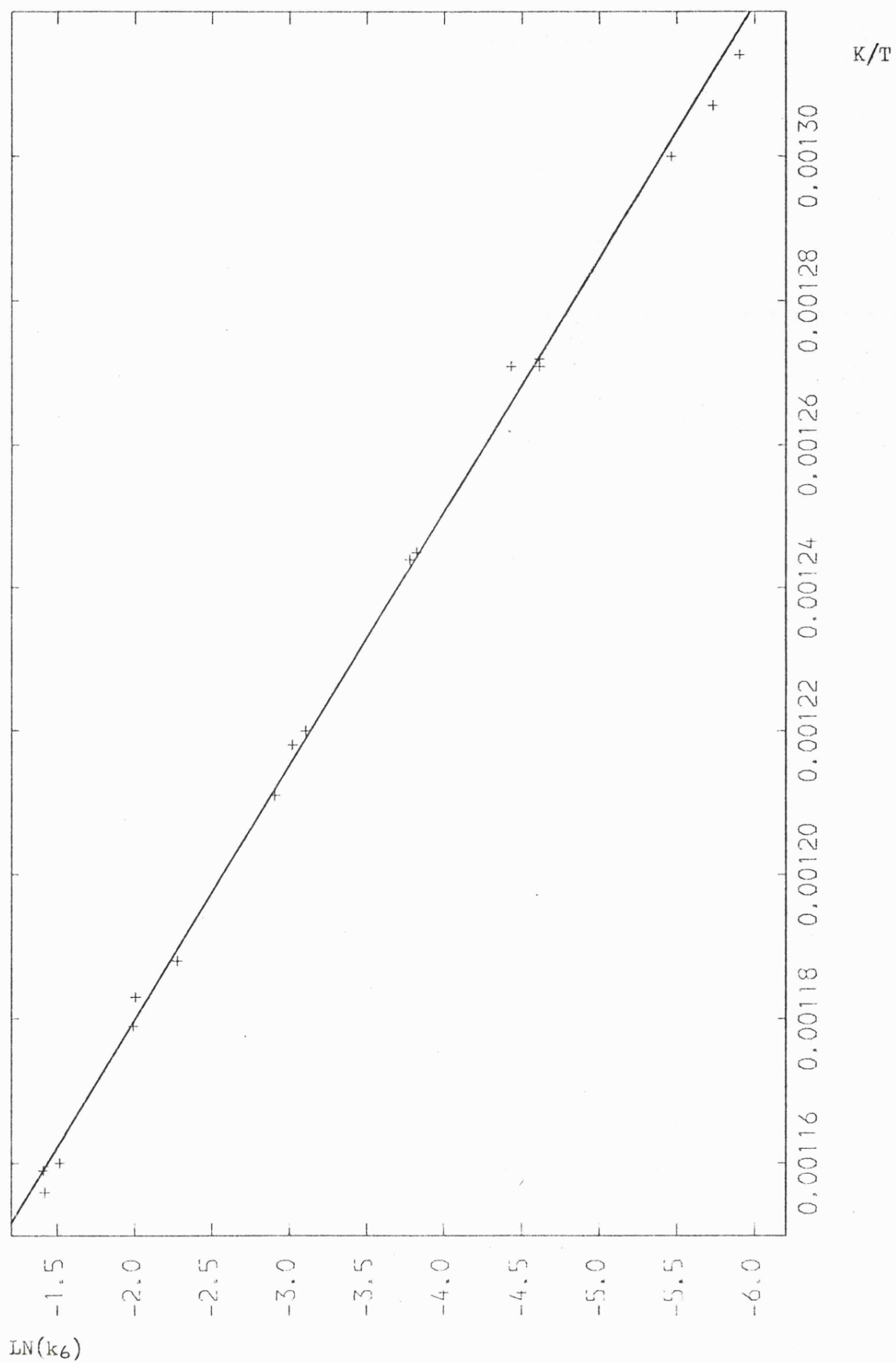
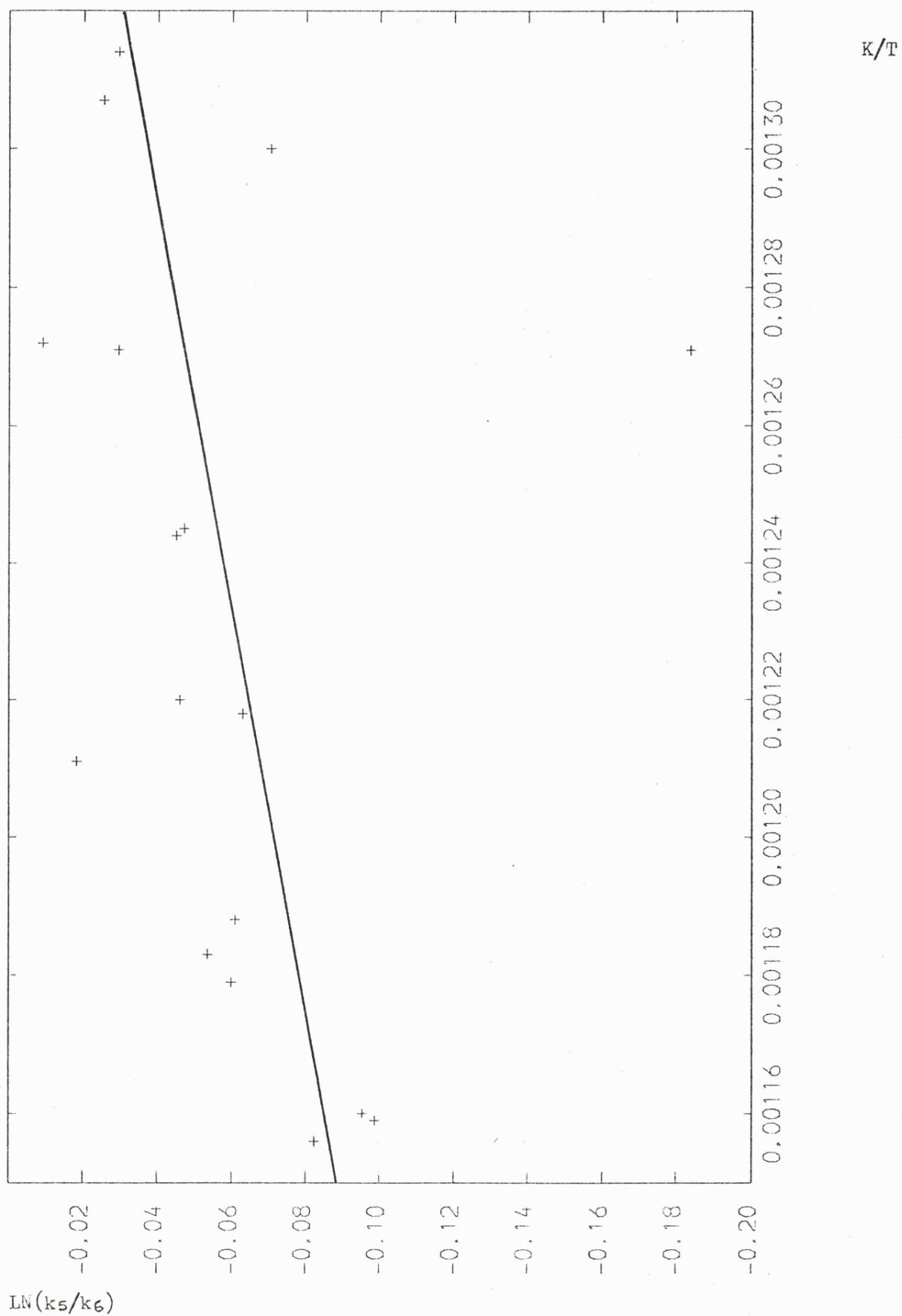


FIGURE 6.4: PLOT OF $\ln(k_5/k_6)$ AGAINST $1/T$



initial pressures of 0.15 mmHg, in which the relative rates of formation of the three disilacyclobutanes were measured during the pyrolysis of a 1:1 mixture of the two monosilacyclobutanes. Each disilacyclobutane was monitored by its (M^+ -Me) mass peak, and initial rates of formation measured in this way were adjusted¹⁰² so that they reflected the initial rate of formation that would have been observed had the M^+ mass peak been used. Pure samples of the trimethyl- and dimethyl- disilacyclobutanes were not available. However, it was assumed that the sensitivity of the mass spectrometer to their molecule ions was equal to that of the mass spectrometer to the molecule ion of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. It can be seen from Table 6.4 that the average ratio of relative yields of 1,1,3,3-tetramethyl-, 1,1,3-trimethyl-3-vinyl- and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutanes was ca. 1:0.5:0.04. In a later study it was found that the relative sensitivity of the mass spectrometer to the molecule ion of vinyltrimethylsilane (100^+) was ca. 3 times greater than that of the mass spectrometer to the equivalent peak in the mass spectrum of tetramethylsilane (88^+). This indicates that the above ratio of relative yields probably over-estimates the vinyl substituted disilacyclobutanes.

The possibility that loss of the biradical formed in the initial stages of the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane (e.g. via an isomerisation) was responsible for the low observed relative yields of the vinyl substituted disilacyclobutanes was investigated by a series of kinetic runs in which the yield of ethene was measured during the pyrolyses of 1,1-dimethyl- and 1-methyl-1-vinyl-1-silacyclobutane. The mass peaks monitored during these experiments were 72^+ (M^+ - C_2H_4) for 1,1-dimethyl-1-silacyclobutane, 84^+ (M^+ - C_2H_4) for 1-methyl-1-vinyl-1-silacyclobutane and 26^+ for ethene. Initial pressures of 0.15 mmHg were

TABLE 6.4

Relative Rates of formation of $\text{Me}_2\text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{SiMe}_2$,
 $\text{Me} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{SiMe}$ and $\text{Me} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Me}$

T/K	$\text{Me}_2\text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{SiMe}_2$	$\text{Me} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{SiMe}_2$	$\text{Me} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Si} \begin{smallmatrix} \wedge \\ \vee \end{smallmatrix} \text{Me}$
826	1	0.47	0.032
827	1	0.52	0.044
830	1	0.53	0.037
830	1	0.50	0.036
805	1	0.49	0.028
804	1	0.46	0.032
804	1	0.49	0.035
802	1	0.51	0.040
802	1	0.58	0.042
780	1	0.57	0.051
778	1	0.56	0.047
776	1	0.58	0.050
779	1	0.55	0.045

utilized. The results are shown in Table 6.5. Both silacyclobutanes gave a good yield of ethene at both the temperatures studied.

In view of the fact that no pyrolysis products had been observed during the LPP experiments which could be attributed to the isomerisation of 2-methyl-2-silabutadiene (with the exception of the very small mass peak observed at 40^+), some experiments were carried out on the PSF apparatus in the hope that any such products might be seen more clearly. A sample (ca. 0.6 mmHg) of 1-methyl-1-vinyl-1-silacyclobutane was pyrolysed with a furnace temperature of ca. 823 K. Product analysis was with a 1.5m E301 column at 70°C . The nitrogen carrier gas flow rate was $60 \text{ cm}^3 \text{ min}^{-1}$. Two major products were observed. The first was ethene ($\text{BP} = -103.7^\circ\text{C}$)¹⁰³ with a retention time of 0.5 mins. The second, with a retention time of 15.0 mins. was assumed to be 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane ($\text{BP} = 128^\circ\text{C}$).¹⁰² The retention time of 1-methyl-1-vinyl-1-silacyclobutane ($\text{BP} = 112^\circ\text{C}$)¹⁰⁴ was 3.6 mins. The

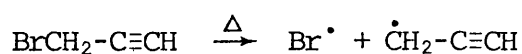
TABLE 6.5

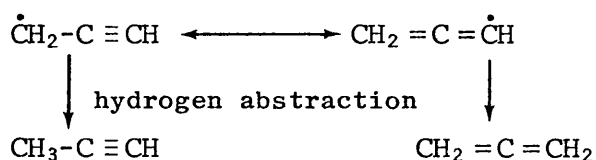
Yield of Ethene from the Pyrolyses of
1,1-Dimethyl- and 1-Methyl-1-vinyl-1-silacyclobutanes

$\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array}$		$\begin{array}{c} \text{Me} \\ \text{Vi} \end{array} \text{Si} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array}$	
T/K	Ethene yield (%)	T/K	Ethene yield (%)
757	95	757	90
757	<u>ca.</u> 100	757	93
757	<u>ca.</u> 100	757	88
799	87	795	78
800	80	795	79
800	81	797	77

yield of the dimer was ca. 10% of that of ethene.

Since the E301 column is not well suited to separating volatile components (e.g. ethene and allene), a series of pyrolyses were carried out in which product analysis was with a 1.5m alumina column at 100°C. As before, a nitrogen flow rate of 60 cm³ min⁻¹ and sample sizes of 0.6 mmHg were utilized. The furnace temperature was varied between 758 and 884 K. In addition to ethene (retention time = 1.8 mins), two other volatile products were observed with retention times of 8.2 and 15.3 mins. Allene is known^{105,106} to isomerise to propyne. To investigate the possibility that these two compounds were being formed, 0.6 mmHg of 3-bromopropyne [D(HC≡C-Br) = 219 kJ mol⁻¹]⁸⁰ was pyrolysed at a furnace temperature of 899 K. The same product analysis conditions were used and two products with retention times identical to those for the unknown products in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane were observed and attributed to the following reaction sequence:





The boiling points of allene and propyne are¹⁰³ 238 K and 250 K respectively, so the product with a retention time of 8.2 mins was probably allene, and that with a retention time of 15.3 mins propyne. The areas of the peaks due to allene, propyne and ethene formed in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane were measured, and the relative yields of these products (Table 6.6) were used to plot $\ln ([\text{C}_3\text{H}_4]/[\text{C}_2\text{H}_4])$ against $1/T$ (see Figure 6.5). This plot suggests that the activation energy for the formation of the C_3H_4 hydrocarbons exceeded that for the formation of ethene by $35 \pm 6 \text{ kJ mol}^{-1}$.

TABLE 6.6

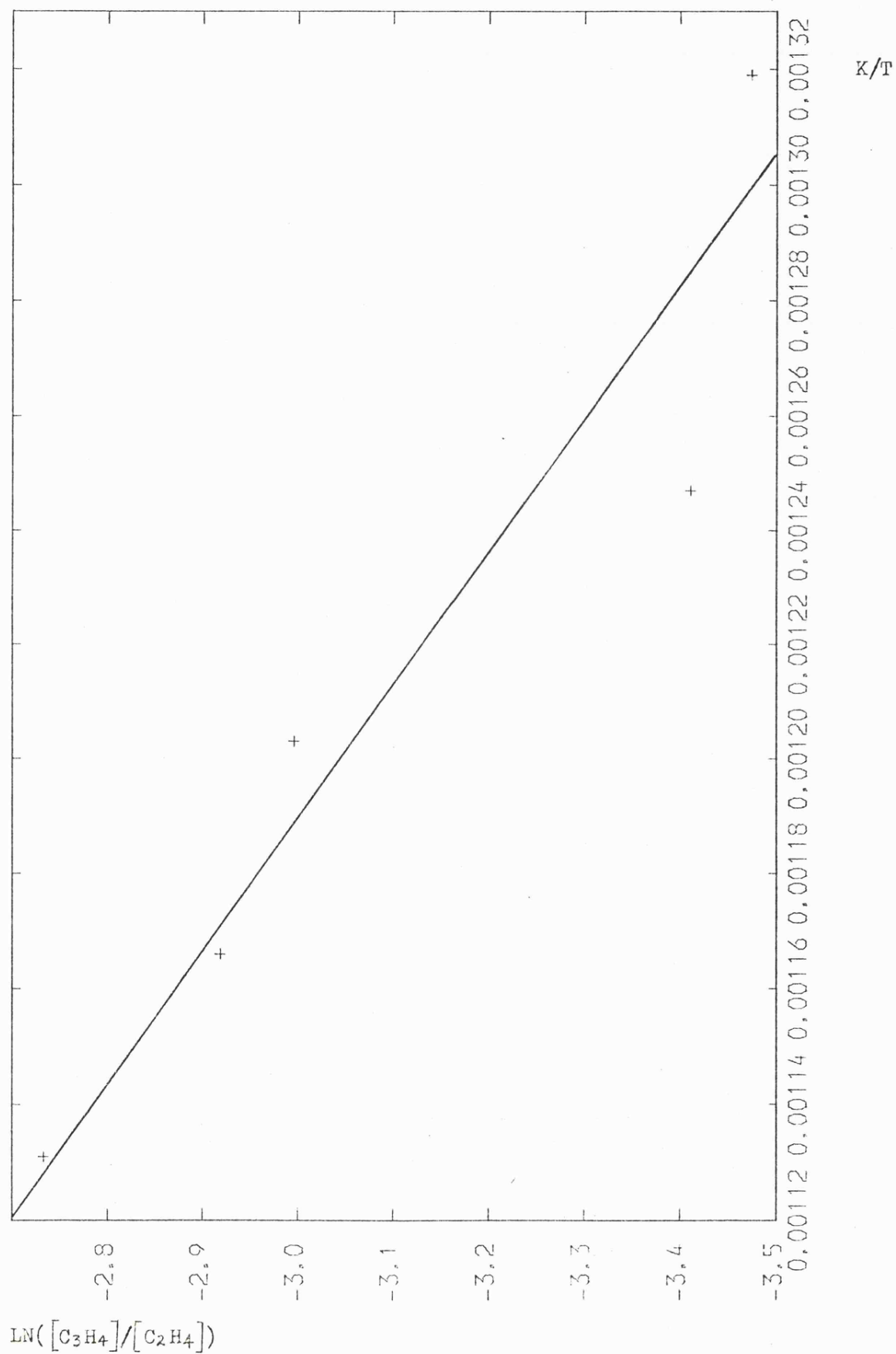
Relative Yields of Allene, Propyne and Ethene from the
Pyrolysis of 1-Methyl-1-vinyl-1-silacyclobutane

T/K	Ethene	Allene	Propyne	Allene + Propyne
884	1	0.037	0.028	0.065
858	1	0.029	0.025	0.054
831	1	0.034	0.016	0.050
802	1	0.022	0.011	0.033
758	1	0.026	0.004	0.030

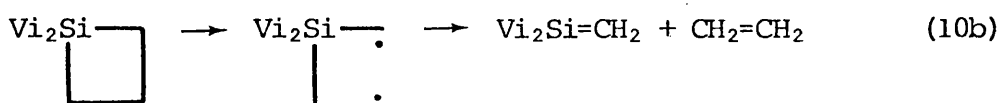
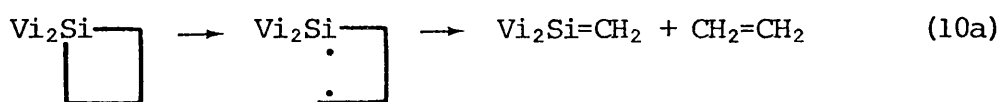
6.2.2 1,1-Divinyl-1-silacyclobutane

Initially ca. 0.3 mmHg of 1,1-divinyl-1-silacyclobutane were pyrolysed in the LPP apparatus at 814 K. The only major product was ethene. Other products were toluene ($M^+ = 92$, $M^+ - \text{H} = 91$), benzene ($M^+ = 78$) and 1,1,3,3-tetravinyl-1,3-disilacyclobutane ($M^+ = 192$, $M^+ - \text{Vi} - \text{H} = 164$).¹⁰² In contrast to the work of Auner and Grobe¹⁴ which was carried out under different conditions, butadiene and propene were not observed, although some cyclo-

FIGURE 6.5: PLOT OF $\text{LN}([C_3H_4]/[C_2H_4])$ AGAINST $1/T$



pentadiene ($M^+ = 66$, $M^+ - H = 65$) was formed. [However, propene is sometimes difficult to observe mass spectrometrically because of its indistinctive mass spectrum.] As in the study of 1-methyl-1-vinyl-1-silacyclobutane, rate constants for the decomposition of 1,1-divinyl-1-silacyclobutane were measured by copyrolysing it with 1,1-dimethyl-1-silacyclobutane: kinetic runs were carried out in which the 96^+ and 72^+ peaks ($M^+ - C_2H_4$) of the two silacyclobutanes were monitored. A 1:1 mixture was utilized, with total initial pressures of 0.14 mmHg (see Table 6.7 and Figures 6.6, 6.7 and 6.8). Rate constants for reaction (10) were consistently higher than those for reaction (5) over the temperature range studied ($k_5/k_{10} \approx 80\%$).



A least squares analysis of the kinetic data gave:

$$k_5 : \log A = 13.8 \pm 0.1, \quad E = 237 \pm 1 \text{ kJ mol}^{-1}$$

$$k_{10} : \log A = 13.8 \pm 0.1, \quad E = 236 \pm 1 \text{ kJ mol}^{-1}$$

$$\log(A_5/A_{10}) = 0.02 \pm 0.06, \quad E_5 - E_{10} = 1.7 \pm 0.9 \text{ kJ mol}^{-1}$$

A second series of kinetic runs was carried out in which 0.14 mmHg samples of neat 1,1-divinyl-1-silacyclobutane were pyrolysed and decomposition rate constants were measured using the mass peak at 96^+ (see Table 6.8 and Figure 6.9). These data gave the following Arrhenius parameters: $\log A = 13.8 \pm 0.2$ and $E = 235 \pm 2 \text{ kJ mol}^{-1}$, in good agreement with those from the first series of kinetic runs.

The dimeric products observed during the copyrolysis of 1,1-dimethyl- and 1,1-divinyl-1-silacyclobutane were 1,1,3,3-tetramethyl-1,3-disila-

TABLE 6.7

Results of the Pyrolysis of a 1:1 mixture of
1,1-Dimethyl- and 1,1-Divinyl-1-silacyclobutanes

T/K	k_5/s^{-1}	k_{10}/s^{-1}	k_5/k_{10}
860	0.250	0.284	0.881
861	0.252	0.294	0.857
855	0.197	0.235	0.839
854	0.200	0.242	0.827
843	0.127	0.155	0.820
843	0.127	0.159	0.799
838	0.104	0.130	0.800
837	0.0958	0.120	0.799
826	0.0658	0.0790	0.833
827	0.0668	0.0838	0.797
814	0.0394	0.0486	0.810
812	0.0369	0.0464	0.795
802	0.0232	0.0294	0.788
801	0.0220	0.0275	0.799
789	0.0126	0.0159	0.791
790	0.0133	0.0167	0.795
781	0.00909	0.0114	0.795
778	0.00791	0.00943	0.839
771	0.00540	0.00668	0.808
771	0.00510	0.00631	0.808
759	0.00314	0.00376	0.835
762	0.00358	0.00441	0.811
746	0.00141	0.00183	0.826
748	0.00185	0.00198	0.770

TABLE 6.8

Rate Constants for the Decomposition of
1,1-Divinyl-1-silacyclobutane

T/K	k_{10}/s^{-1}	T/K	k_{10}/s^{-1}
842	0.177	796	0.0211
843	0.176	792	0.0198
843	0.177	790	0.0187
830	0.104	778	0.0109
830	0.108	779	0.116
831	0.111	779	0.115
816	0.0581	760	0.00418
815	0.0547	763	0.00530
814	0.0520	765	0.00612
803	0.0327	739	0.00136
803	0.0341	737	0.00156
804	0.0361	736	0.00147

FIGURE 6.6: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1,1-DIMETHYL-1-SILACYCLOBUTANE IN A 1:1 MIXTURE WITH
1,1-DIVINYLL-1-SILACYCLOBUTANE

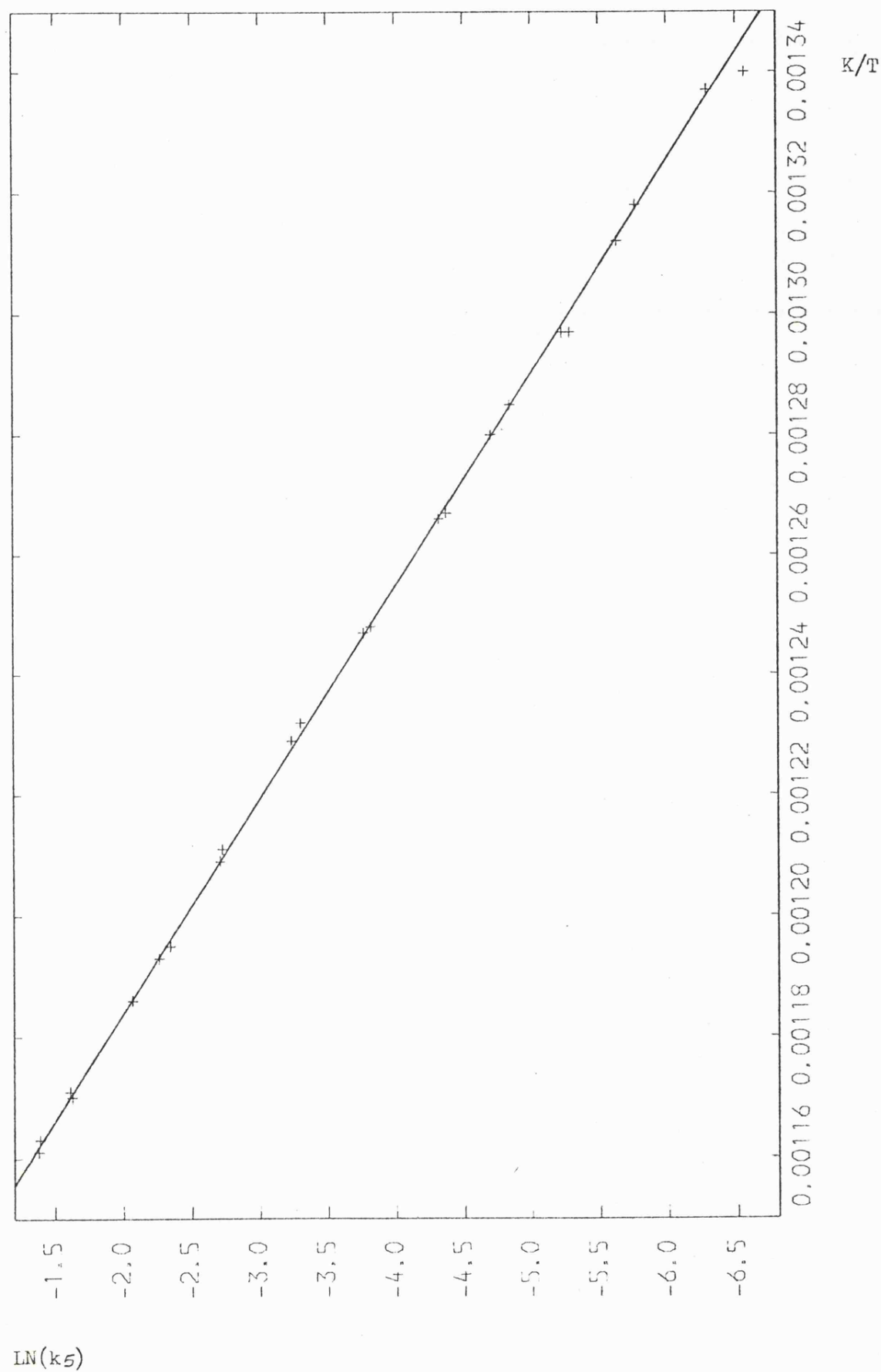


FIGURE 6.7: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1,1-DIVINYL-1-SILACYCLOBUTANE IN A 1:1 MIXTURE WITH
1,1-DIMETHYL-1-SILACYCLOBUTANE

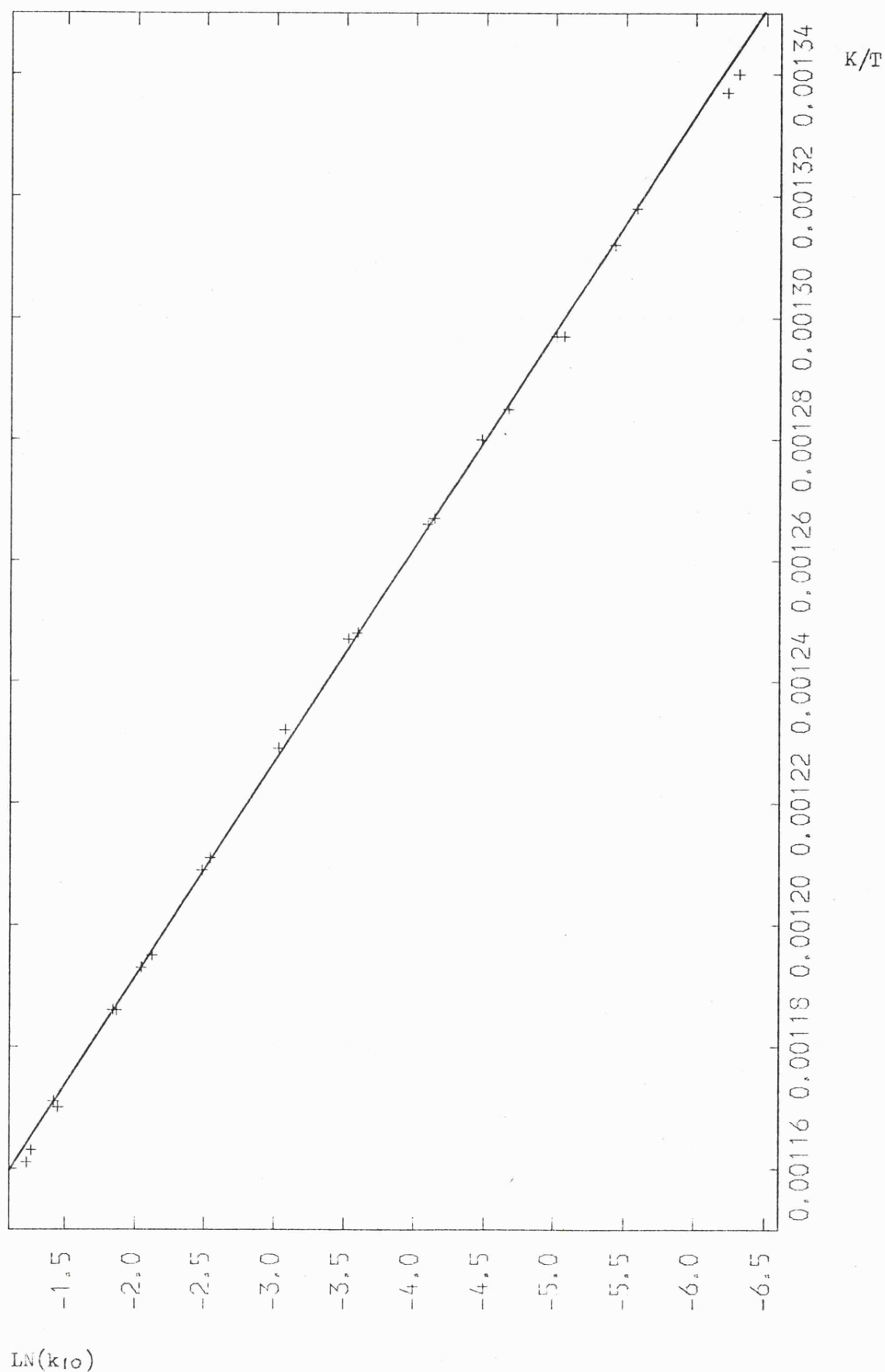


FIGURE 6.8: PLOT OF $\ln(k_5/k_{10})$ AGAINST $1/T$

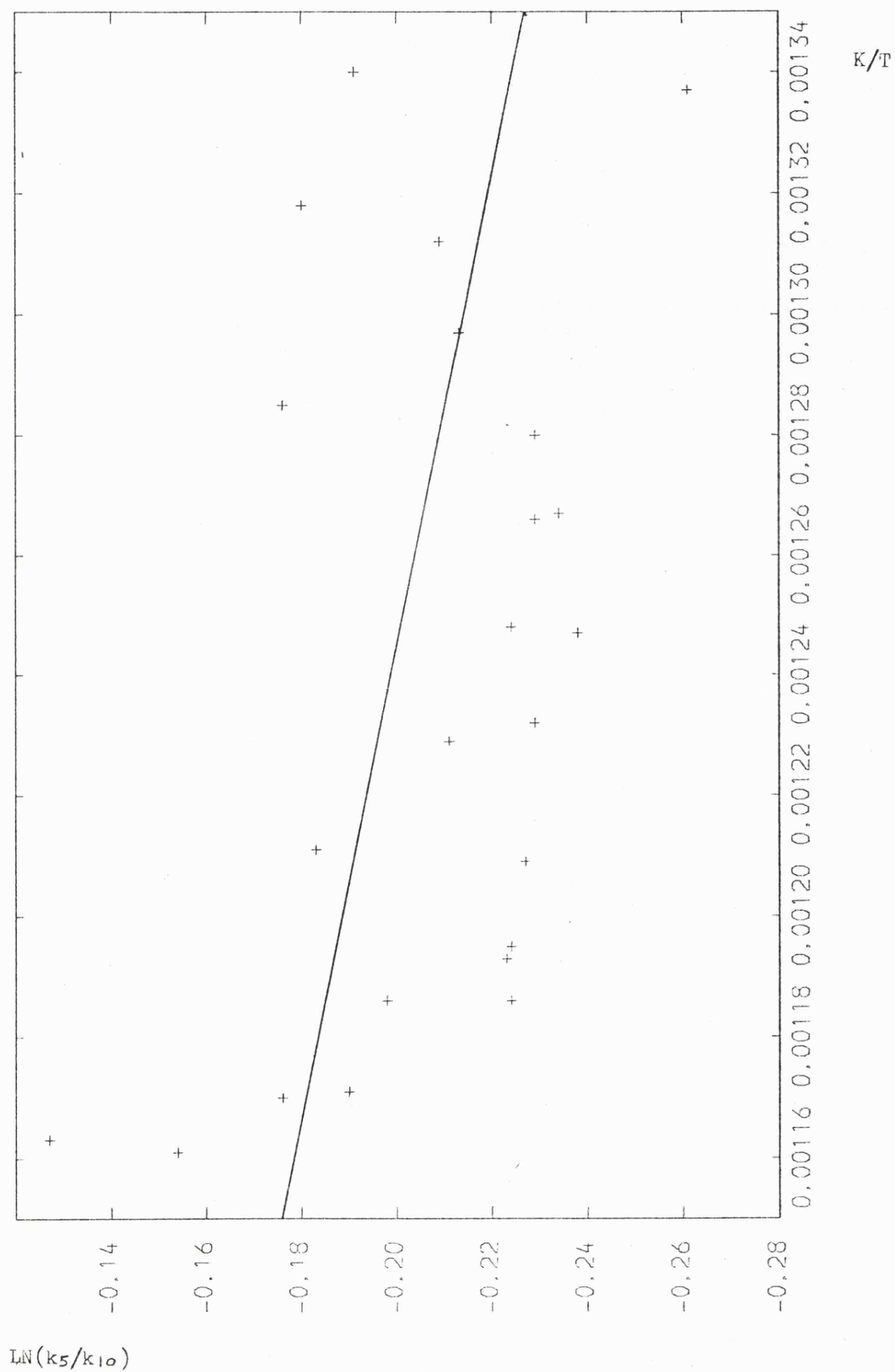
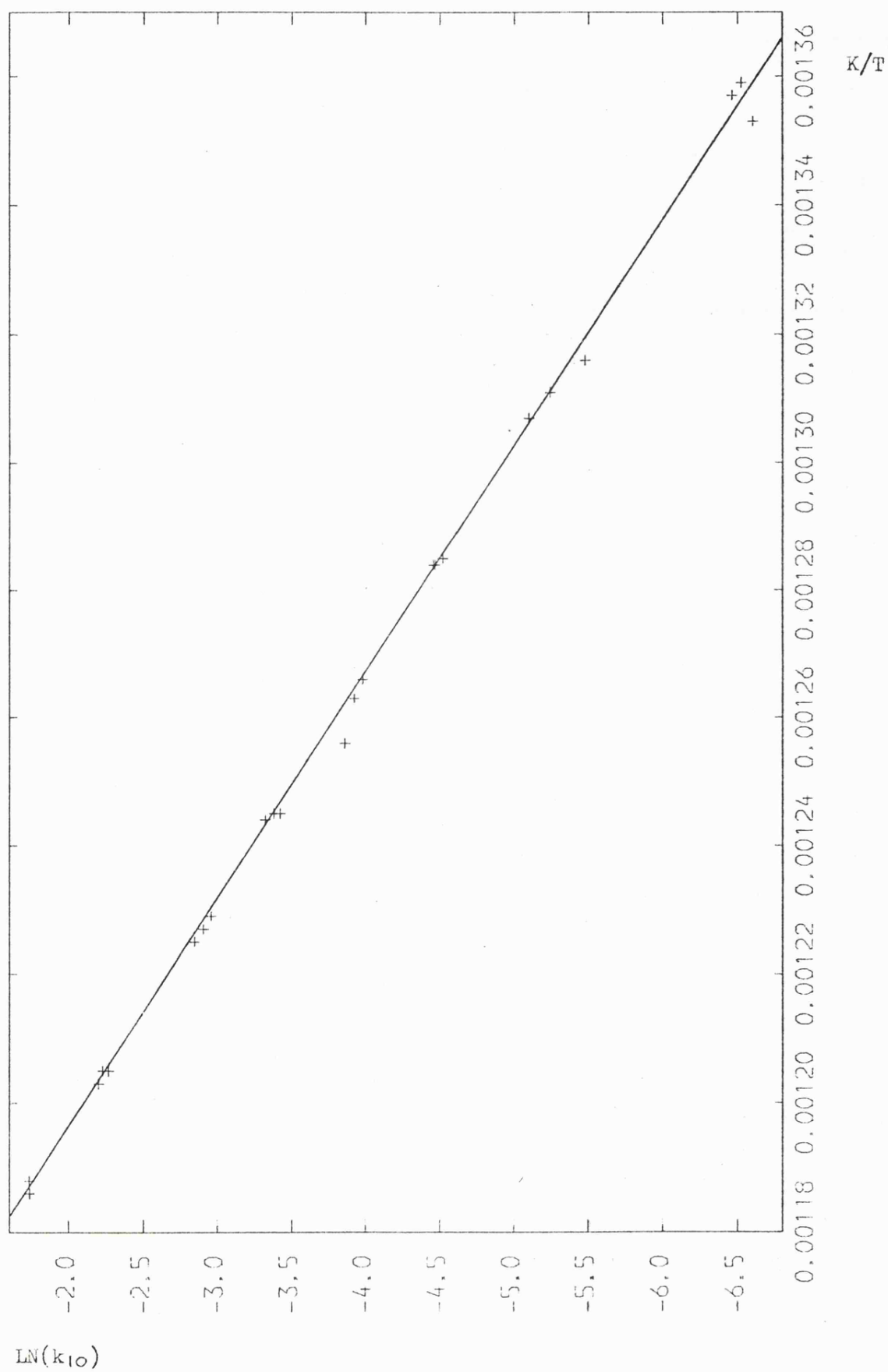


FIGURE 6.9: ARRHENIUS PLOT FOR THE DECOMPOSITION OF
1,1-DIVINYL-1-SILACYCLOBUTANE



cyclobutane and 1,1-dimethyl-3,3-divinyl-1,3-disilacyclobutane ($M^+ = 168$, $M^+ - \text{Me} = 153$) only. No 1,1,3,3-tetravinyl-1,3-disilacyclobutane was detected. Kinetic runs were carried out in which the two observed dimeric products, formed during the pyrolysis of a 1:1 mixture of 1,1-dimethyl- and 1,1-divinyl-1-silacyclobutane at total initial pressures of 0.15 mmHg, were monitored. The mass peaks used were at 144^+ (M^+) for 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 153^+ ($M^+ - \text{Me}$) for 1,1-dimethyl-3,3-divinyl-1,3-disilacyclobutane. As before, kinetic data on the formation of 1,1-dimethyl-3,3-divinyl-1,3-disilacyclobutane were adjusted so that a measure of the rate of increase of its molecule ion was determined. As in the previous section, it was assumed that the relative sensitivity of the mass spectrometer to the molecule ions of both was equal. Relative rates of formation of the two disilacyclobutanes are shown in Table 6.9. From these data it is clear that the relative rate of formation of 1,1-dimethyl-3,3-divinyl-1,3-disilacyclobutane was much less than might be expected from a purely statistical argument at all temperatures. Using data collected at the two lower

TABLE 6.9

Relative Rates of Formation of $\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{SiMe}_2$ and $\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{SiVi}_2$

T/K	$\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{SiMe}_2$	$\text{Me}_2\text{Si} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{SiVi}_2$
824	1	0.14
824	1	0.13
816	1	0.17
817	1	0.16
792	1	0.18
792	1	0.18
787	1	0.20
787	1	0.21
766	1	0.20
769	1	0.19
768	1	0.20
767	1	0.24

temperatures, the relative rates of formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 1,1-dimethyl-3,3-divinyl-1,3-disilacyclobutane and 1,1,3,3-divinyl-1,3-disilacyclobutane were 1:0.2:0.0.

As before, the yield of ethene from 1,1-dimethyl- and 1,1-divinyl-1-silacyclobutanes was measured to investigate the possibility that the biradical formed in the initial stage of the pyrolysis of 1,1-divinyl-1-silacyclobutane was being lost before it could dissociate into 2-vinyl-2-silabutadiene and ethene. The mass peaks monitored were 26^+ , 72^+ and 96^+ , and the initial pressure in all runs was 0.15 mmHg. The results are shown in Table 6.10. They indicate that both silacyclobutanes give a high yield of ethene.

TABLE 6.10

Yield of Ethene from the Pyrolyses of
1,1-Dimethyl- and 1,1-Divinyl-1-silacyclobutane

Me_2Si 		Vi_2Si 	
T/K	Ethene yield (%)	T/K	Ethene yield (%)
757	95	758	91
757	ca. 100	758	83
757	ca. 100	758	81
799	87	789	82
800	80	790	76
800	81	792	78

The pyrolysis of 1,1-divinyl-1-silacyclobutane was studied using the PSF apparatus to confirm the formation of the unsaturated hydrocarbons observed during the LPP's. A sample size of 0.5 mmHg was used in all experiments. The furnace temperature was set at 853 K, and product analysis was initially with a 2.5 m E301 column at 75°C. The nitrogen carrier gas flow rate was $55 \text{ cm}^3 \text{ min}^{-1}$. Products were identified, where

possible, with authentic samples, and percentage yields were measured relative to that of ethene, which was known from the LPP experiments to be high. A summary of the results of these experiments is shown in Table 6.11. The retention time of 1,1-divinyl-1-silacyclobutane (BP = 139°C)¹⁰⁴ was 10.2 mins. It was not possible to resolve ethene, propene[†] and butadiene[†] using the E301 column, so further pyrolyses were carried out using the 2.5m alumina column at 100°C and a carrier gas flow rate of 34 cm³ min⁻¹. With a furnace temperature of 853 K the only products had retention times of 3.5 and 6.0 mins. Use of authentic samples suggested that they were ethene and propene (BP = -47.6°C).¹⁰³ The yield of propene was ca. 7% of that of ethene.

TABLE 6.11

Products of the PSF Pyrolysis of 1,1-Divinyl-1-silacyclobutane

product	retention time /mins.	BP/°C (ref.)	Yield relative to Ethene (%)
ethene	1.0	-103.7 (103)	[100]
cyclopentadiene	2.0	40.0 (103)	3
benzene	3.3	80.1 (103)	2
toluene	6.1	110.6 (103)	1
Vi ₂ Si $\bigwedge$ SiVi ₂	36.8	140 (102)	1

6.3 DISCUSSION

The Arrhenius parameters for the thermal decomposition of the two vinyl substituted silacyclobutanes were the same as those for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane⁴ within experimental error: use of the parameters obtained from the plots of $\ln(k_5/k_6)$ and $\ln(k_5/k_{10})$ against $1/T$, and the literature Arrhenius parameters for the

[†] Products observed in a previous study¹⁴

pyrolysis of 1,1-dimethyl-1-silacyclobutane⁴ gives:

Reactant	Reaction No.	log A	E/kJ mol ⁻¹	k (800 K)
Me Vi Si 	6	15.84 ± 0.35	264.2 ± 4.1	0.0388
Vi ₂ Si 	10	15.62 ± 0.36	259.8 ± 4.2	0.0453
Me ₂ Si 	5	15.64 ± 0.30	261.5 ± 3.3	0.0367

If it is assumed that both vinyl substituted silacyclobutanes decompose via carbon-carbon bond rupture with Arrhenius parameters equal to those for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane, and that decomposition via rupture of the carbon-silicon bond has an 'A'-factor of 10^{14.9} (by analogy with that for the thermal decomposition of vinylcyclobutane¹⁰⁰), then overall decomposition rate constants and Arrhenius parameters can be calculated as a function of the activation energy chosen for carbon-silicon bond rupture. These overall rate constants can be compared with rate constants for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane calculated with the literature Arrhenius parameters (see Table 6.12). Comparison of these data with the observed Arrhenius parameters for the decomposition of the two vinyl substituted silacyclobutanes suggests that the minimum possible value of the activation energy for carbon-silicon bond rupture in their decomposition is ca. 250 kJ mol⁻¹. A lower value will yield overall Arrhenius parameters clearly distinguishable from those observed. This activation energy indicates that the allylic stabilization energy present in the pyrolysis of the two vinyl substituted silacyclobutanes is < (262 - 250 + 32 = 44) kJ mol⁻¹ (see Section 6.1). But, observed values of k₅/k₆ were ca. 0.95 at 800 K and 0.98 at 733 K. Inspection of Table 6.12 suggests that these ratios are consistent with an activation energy

TABLE 6.12

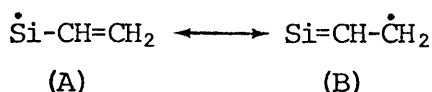
Effect of E_6 and E_{10} upon overall decomposition rate constants for the vinyl substituted silacyclobutanes

$E_{6a,10a}$ /kJ mol ⁻¹	$E_{6,10}$ /kJ mol ⁻¹	log $A_{6,10}$	k_5/s^{-1}		$(k_5/k_{6,10}) \%$	
			800 K	733 K	800 K	733 K
290	261.5	15.64	0.0367	0.00101	99.7	99.8
285	261.5	15.64			99.5	99.6
280	261.6	15.65			98.9	99.1
275	261.8	15.67			97.6	98.1
270	261.9	15.69			95.1	95.6
265	261.8	15.71			90.1	90.1
260	261.2	15.71			81.4	81.1
255	259.3	15.67			67.3	65.4
250	255.6	15.56			49.3	45.5
245	250.0	15.34			31.4	26.8
240	243.3	15.20			17.8	13.9

of 270 kJ mol⁻¹ for carbon-silicon bond rupture in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane, indicating an allylic stabilization energy of $< (262 - 270 + 32 = 24)$ kJ mol⁻¹. Analysis of the observed values of (k_5/k_{10}) yields an allylic stabilization energy of < 34 kJ mol⁻¹ in the pyrolysis of 1,1-divinyl-1-silacyclobutane. However, there is evidence (see below) that the LPP of the three silacyclobutanes considered in this chapter are in the unimolecular fall-off region. In this case, the observed trend in rate constants (i.e. $k_{10} > k_6 > k_5$) could be explained by the differing numbers of atoms in the three molecules, and the effect this has upon their low pressure decomposition rate constants: their high pressure decomposition rate constants may be identical, implying even less allylic stabilization energy.

It is no surprise that allylic stabilization energy in the two vinyl-silyl radicals is less than that in the vinylalkyl radical⁶⁵ (53 ± 4 kJ

mol⁻¹). This reflects the difference in energy of the carbon and silicon 'p' orbitals (and the resulting weakness of the silicon-carbon π -bond): the contribution to stabilization by structure (B) will be slight:



For the same reason silabenzyl stabilization energy is small (ca. 8 kJ mol⁻¹)¹⁰⁷ when compared to benzyl stabilization energy (ca. 42 kJ mol⁻¹).¹⁰⁸

A summary of kinetic data on the thermal decomposition of 1,1-dimethyl-1-silacyclobutane, measured in this study using the LPP technique, is shown in Table 6.13. The observed Arrhenius parameters are in conflict with the literature values⁴ of $E = 261.5 \text{ kJ mol}^{-1}$, $\log A = 15.64$, and the average observed parameters give rate constants which are ca. 40% lower than literature rate constants. Two possible reasons for this discrepancy can immediately be ruled out.

The reverse reaction (i.e. the addition of ethene to 2-methyl-2-silapropene to give 1,1-dimethyl-1-silacyclobutane) was not responsible for reducing the rate at which 1,1-dimethyl-1-silacyclobutane decomposed in the LPP apparatus. This possibility was investigated by simulating the reaction mechanism shown in Table 6.14 using the computer programme described in Chapter 3. The simulation produced rate constants for the decomposition of 1,1-dimethyl-1-silacyclobutane in excellent agreement with the literature values at 740 and 840 K. Also, decomposition rate constants measured during the copyrolysis of the silacyclobutane and oxygen were not increased significantly relative to those measured using neat 1,1-dimethyl-1-silacyclobutane. If the reverse reaction had been responsible for reducing decomposition rate constants, then the effect

TABLE 6.13

Arrhenius Parameters for the LPP of 1,1-Dimethyl-1-silacyclobutane

T/K	Total initial pressure/mmHg	Reactants	E/kJ mol ⁻¹	log A	k ₇₄₀ /s ⁻¹	k ₈₄₀ /s ⁻¹
734-803	ca. 0.24	7:1/Me ₂ Si-  :O ₂	232 ± 2	13.5 ± 0.2	.00133	0.118
734-783	ca. 0.19	7:1/Me ₂ Si-  :O ₂	242 ± 3	14.2 ± .2	.00131	0.142
740-791	ca. 0.24	Me ₂ Si- 	247 ± 2	14.4 ± .2	.00092	0.110
745-854	0.09	Me ₂ Si- 	236 ± 1	13.6 ± 0.1	.00087	0.0840
761-865	ca. 0.14	1:1/Me ₂ Si-  : 	235 ± 3	13.6 ± 0.2	.00103	0.0969
746-845	ca. 0.14	1:1/Me ₂ Si-  : Vi ₂ Si- 	237 ± 1	13.8 ± 0.1	.00118	0.115
average :			238	13.8	.00111	0.111
ref. 4			261.5	15.64	.00152	0.239

TABLE 6.14

Reaction Mechanism for the Pyrolysis of 1,1-Dimethyl-1-silacyclobutane

No.	Reaction	log A	E/kJ mol ⁻¹	k/s ⁻¹	Comment
	$\text{Me}_2\text{Si} \square \rightarrow \text{Me}_2\text{Si} \square$			0.8	leak-in
5	$\text{Me}_2\text{Si} \square \rightarrow \text{Me}_2\text{Si}=\text{CH}_2 + \text{C}_2\text{H}_4$	15.64	262		ref. 4
	$\text{Me}_2\text{Si}=\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{Me}_2\text{Si} \square$	6.58	60.7		ref. 23
7	$2 \text{Me}_2\text{Si}=\text{CH}_2 \rightarrow \text{Me}_2\text{Si} \diamond \text{SiMe}_2$	6.55	0		ref. 23
	$\text{Me}_2\text{Si} \square \rightarrow$			0.001	leak-out
	$\text{CH}_2=\text{CH}_2 \rightarrow$			0.001	
	$\text{Me}_2\text{Si}=\text{CH}_2 \rightarrow$			0.001	
	$\text{Me}_2\text{Si} \diamond \text{SiMe}_2 \rightarrow$			0.001	

of trapping 2-methyl-2-silapropene would have been to drastically increase the rate of decomposition (to near the literature value). In addition, heterogeneous loss of 1,1-dimethyl-1-silacyclobutane could not have been responsible for reducing observed rate constants relative to the literature values. Such a process would have had the opposite effect on experimental data.

A previous investigation²⁴ of the LPP of 1,1-dimethyl-1-silacyclobutane, in which pressures of ca. 0.01 mmHg were used, suggested that the decomposition was in the unimolecular fall-off region. The reduction in the activation energy observed in the present study relative to that measured by Flowers and Gusel'nikov⁴ is consistent with the occurrence of this phenomenon, when compared with the observed reduction in the 'A'-factor. Inspection of kinetic data for related hydrocarbons clearly demonstrates this. Unimolecular rate constants for the decomposition of cyclobutane¹⁰⁹ and methylcyclobutane¹¹⁰ have been measured as a function of temperature and pressure. The cyclobutane data can be used to deduce high pressure Arrhenius parameters, and the parameters that apply to lower pressure rate constants which are ca. 40% smaller than the high pressure values:

$$k \text{ (high pressure)} : E = 264 \pm 1 \text{ kJ mol}^{-1}, \log A = 15.7 \pm 0.1$$

$$0.6 k \text{ (high pressure)} : E = 245 \pm 3 \text{ kJ mol}^{-1}, \log A = 14.2 \pm 0.2$$

The effect of the lower pressure has been to reduce the 'A'-factor by 1.5 log units and the activation energy by 19 kJ mol⁻¹. An identical analysis of the methylcyclobutane data gives:

$$k \text{ (high pressure)} : E = 263 \pm 4 \text{ kJ mol}^{-1}, \log A = 15.9 \pm 0.3$$

$$0.6 k \text{ (high pressure)} : E = 235 \pm 3 \text{ kJ mol}^{-1}, \log A = 13.7 \pm 0.2$$

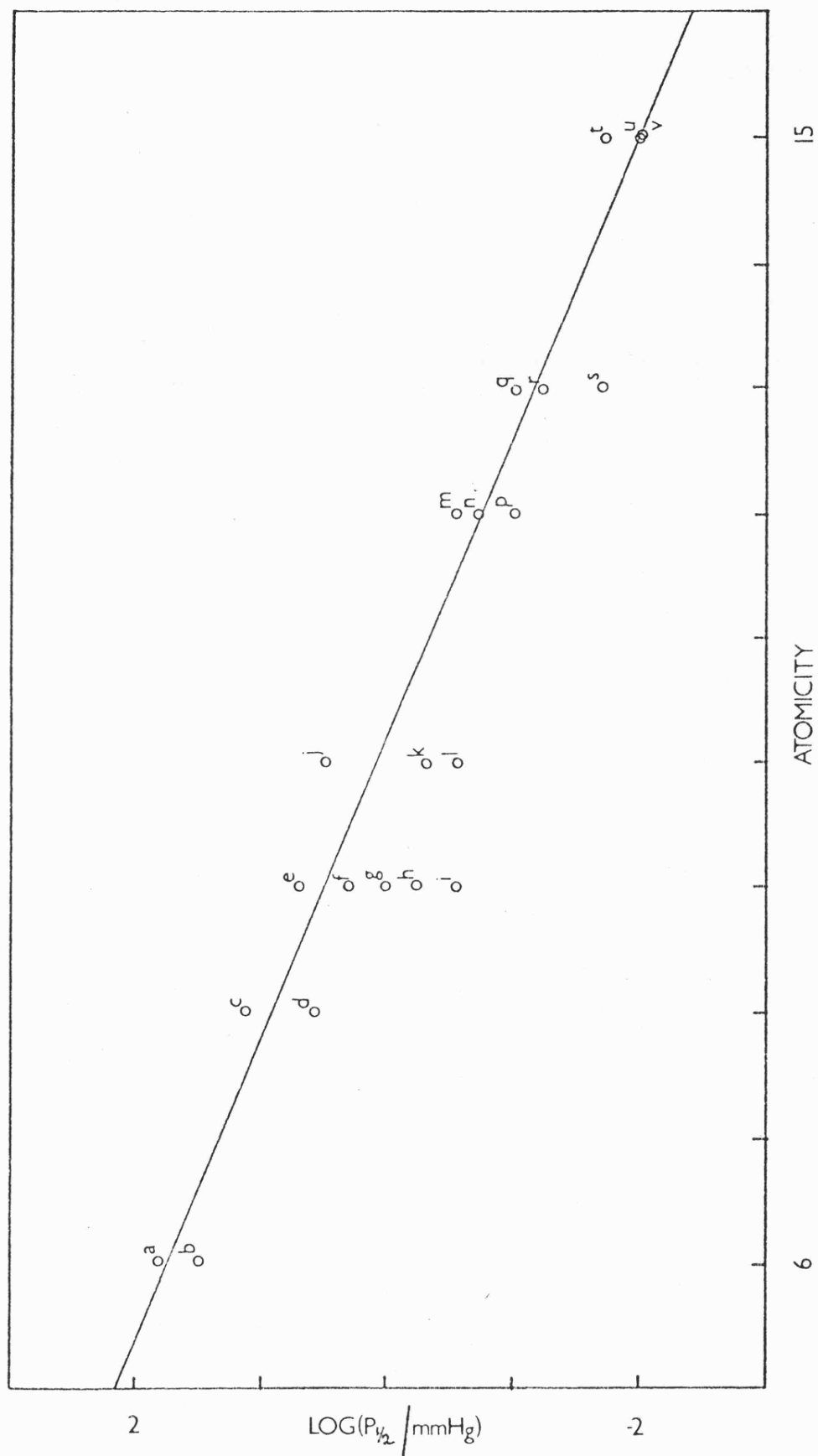
In this case the low pressure 'A'-factor is lower than the high pressure value by 2.1 log units, while the activation energy has been reduced by

28 kJ mol⁻¹. The average 'A'-factor for the LPP of 1,1-dimethyl-1-silacyclobutane (see Table 6.13) is lower than the literature value⁴ by 1.8 log units, and the activation energy is 23.5 kJ mol⁻¹ smaller, both reductions being intermediate to those observed for cyclobutane and methylcyclobutane.

There is further evidence to suggest that the LPP of 1,1-dimethyl-1-silacyclobutane is in the unimolecular fall-off region. The rate constants in Table 6.13 display a (scattered) positive dependence upon the total initial pressure. Indeed, an investigation of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane using the PSF apparatus,¹¹¹ where the nitrogen carrier gas is at above atmospheric pressure, thus ruling out the possibility of unimolecular fall-off, yielded the following Arrhenius parameters: $E = 264 \pm 11$ kJ mol⁻¹ and $\log A = 15.4 \pm 0.7$, in good agreement with those measured by Flowers and Gusel'nikov.

The LPP's of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane⁸⁹ (see Chapter 5) and octamethyl-1,2-disilacyclobutane,⁵⁰ which have 33 and 34 atoms respectively, both produced Arrhenius parameters which were quite consistent with rupture of the appropriate ring bond. It is well known that $P_{1/2}$ (the pressure at which an observed first order decomposition rate constant is half its high pressure value) decreases with an increase in the number of atoms in the reactant molecule. Thus, at first sight, the suggestion that the LPP of 1,1-dimethyl-1-silacyclobutane (18 atoms) was affected by unimolecular fall-off seems reasonable. However, Robinson and Holbrook⁴⁸ have plotted values of $\log P_{1/2}$ against atomicity of reactant (see Figure 6.10). Extrapolation of this plot suggests that $P_{1/2}$ for 1,1-dimethyl-1-silacyclobutane should be ca. 0.001 mmHg, much less than the minimum pressure used in this study (as a precaution the calibration of the pressure

FIGURE 6.10: EFFECT OF ATOMICITY UPON $P_{1/2}$



KEY TO FIGURE 6.10

- a) Methyl isocyanide
- b) Methyl isocyanide-d₃
- c) Ethane
- d) Chloroethane
- e) Cyclopropane
- f) 1,1-Dichlorocyclopropane
- g) Cyclopropane-d₆
- h) Ethyl isocyanide
- i) Ethyl isocyanide-d₅
- j) Azomethane-d₆
- k) Cyclobutene
- l) Cyclobutene-d₆
- m) Cyclobutane
- n) Methylcyclopropane
- p) Cyclobutane-d₈
- q) Bicyclo[1.1.1]pentane
- r) 3-Methylcyclobutene
- s) 1-Methylcyclobutene
- t) Methylcyclobutane
- u) 1,1-Dimethylcyclopropane
- v) Ethylcyclopropane

transducer was checked and found to be accurate), although the plot is very scattered, indicating a 15-fold variation in $P_{1/2}$ for molecules with 9 atoms. In spite of the fact that large errors may also result from the extrapolation, it is still hard to reconcile the observed $P_{1/2}$ for 1,1-dimethyl-1-silacyclobutane with that for cyclobutane¹⁰⁹ (0.2 mmHg) and methylcyclobutane¹¹⁰ (0.02 mmHg) which have 12 and 15 atoms respectively. The same is true of $P_{1/2}$ for the other silacyclobutane studied in this Chapter, the LPP's of which also yield "low" Arrhenius parameters.

Rate constants for the decomposition of 1,1-dimethyl-, 1-methyl-1-vinyl-, and 1,1-divinyl-1-silacyclobutane (18, 19, 20 atoms respectively) were in the ratio of 1:1.05:1.25. It has already been suggested that this trend may be due to the differing amounts of allylic stabilization present in the pyrolyses of the three molecules. The effect of unimolecular fall-off also provides a rationale, although the trend is less pronounced than might be expected from Figure 6.10. Again, this could reflect scatter in the $P_{1/2}$ data. The fact that the LPP's of the three silacyclobutanes studied in this Chapter do not give the expected Arrhenius parameters has no effect upon the conclusions drawn, since the values for the thermal decomposition of the two vinyl substituted silacyclobutanes were measured relative to those for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane, and all inferences made regarding the relative size of decomposition rate constants recognized the possibility of the occurrence of unimolecular fall-off. [It should be noted that the Arrhenius parameters for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane used in the computer simulations mentioned in Chapter 4 were those observed during the appropriate experiments and not the literature⁴ values.]

Both vinyl substituted silacyclobutanes gave a good yield of ethene on

pyrolysis, although in both cases it was slightly less than that observed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane (see Tables 6.5 and 6.10). This indicates that a good yield of the silaalkene was produced in both decompositions.

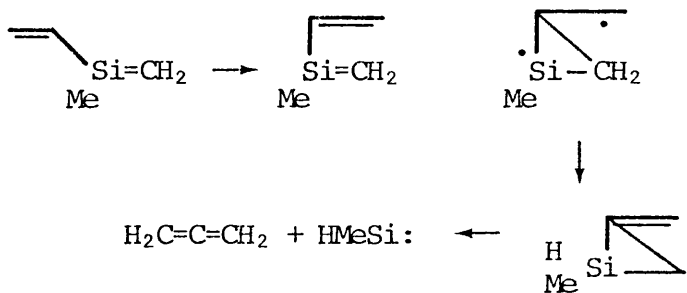
The relative rates of formation of 1,1,3,3-tetramethyl-, 1,1,3-trimethyl-3-vinyl- and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane in the copyrolysis of a 1:1 mixture of 1,1-dimethyl- and 1-methyl-1-vinyl-1-silacyclobutane was $1: <0.52: <0.04$. On a purely statistical basis, this ratio would be expected to be 1:2.1:1.1, since $k_5/k_6 \approx 0.95$. If it is assumed that the yield of each silaalkene was equal to that of ethene in the pyrolysis of the appropriate silacyclobutane, the ratio becomes 1:1.8:0.8. This result suggests that the silaalkene produced in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane, 2-methyl-2-silabutadiene, undergoes reaction alternative to dimerisation, or that it is (conjugatively) stabilized⁹⁹ relative to 2-methyl-2-silapropene and, as a consequence, is less reactive (i.e. $k_7 > k_8, k_9$). The low observed yield of the C_3H_4 hydrocarbons in the PSF experiments (ca. 5% of that of ethene) indicates that loss of 2-methyl-2-silabutadiene via reaction (1)¹⁴ is of relatively minor importance, so the latter suggestion, which would aid the occurrence of the equilibrium reaction (2),⁹⁹ is probably the main reason. The relative rates of formation of 1,1,3,3-tetramethyl-, 1,1-dimethyl-3,3-divinyl- and 1,1,3,3-tetravinyl-1,3-disilacyclobutane in the copyrolysis of a 1:1 mixture of 1,1-dimethyl- and 1,1-divinyl-1-silacyclobutane was $1: <0.2 : 0$. Calculations identical to that shown above suggests an expected ratio of 1:2.1:1.1. As with allene and propyne in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane, toluene, benzene, cyclopentadiene and propene were relatively minor products. This clearly suggests a similar conclusion to that drawn above, concerning the fate of

the silaalkene produced in the pyrolysis of 1,1-divinyl-1-silacyclobutane.

The low yields of the dimeric species observed in the PSF pyrolyses of both vinyl substituted silacyclobutanes indicates that the sila-alkenes involved are conjugatively stabilized to a sufficient extent for them to diffuse out of the gas phase. Similar experiments¹¹¹ with 1,1-dimethyl-1-silacyclobutane gave a yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane of ca. 30% relative to that of ethene.

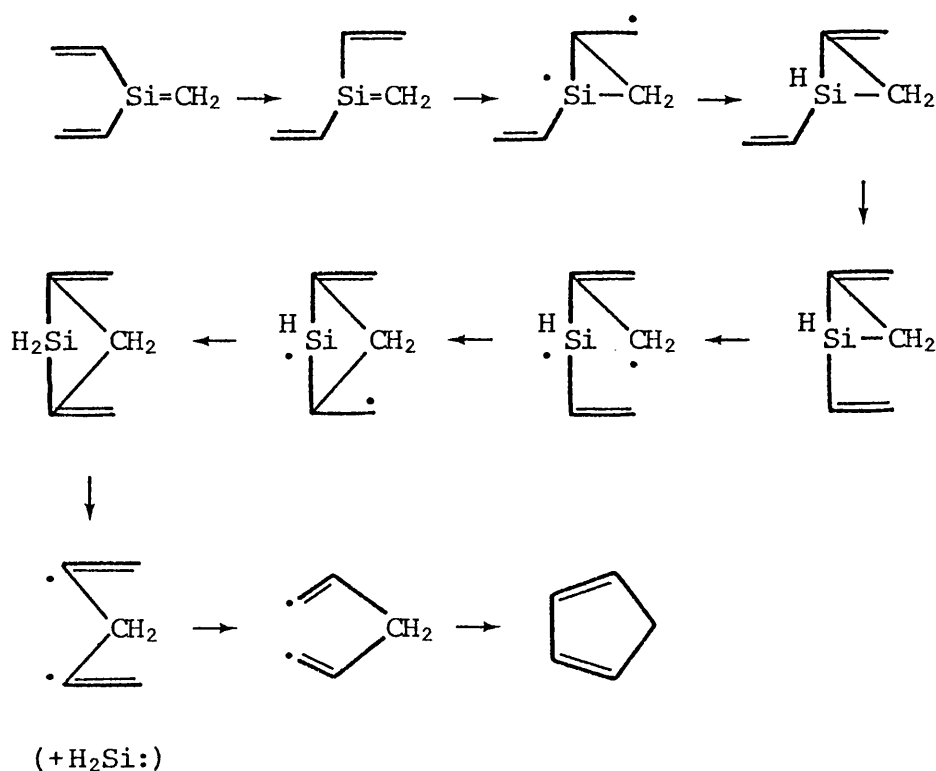
The results of this study do not throw any light upon the reaction mechanism leading to the minor products of the pyrolysis of 1,1-divinyl-1-silacyclobutane, although it is possible to make some speculative suggestions as to how they arose. It is clear that neither benzene nor toluene could have been formed in a unimolecular reaction of 2-vinyl-2-silabutadiene, since the species does not have sufficient carbon atoms. These products could have been formed via a bimolecular reaction of the silaalkene, or through a rearrangement of the biradical produced in the first stage of reactant decomposition. On the other hand, a unimolecular reaction of 2-vinyl-2-silabutadiene leading to propene or cyclopentadiene is plausible, although other modes of formation (e.g. those suggested above) cannot be discounted.

By analogy with the proposed¹⁴ isomerisation of 2-methyl-2-silabuta-
diene, followed by silylene extrusion:

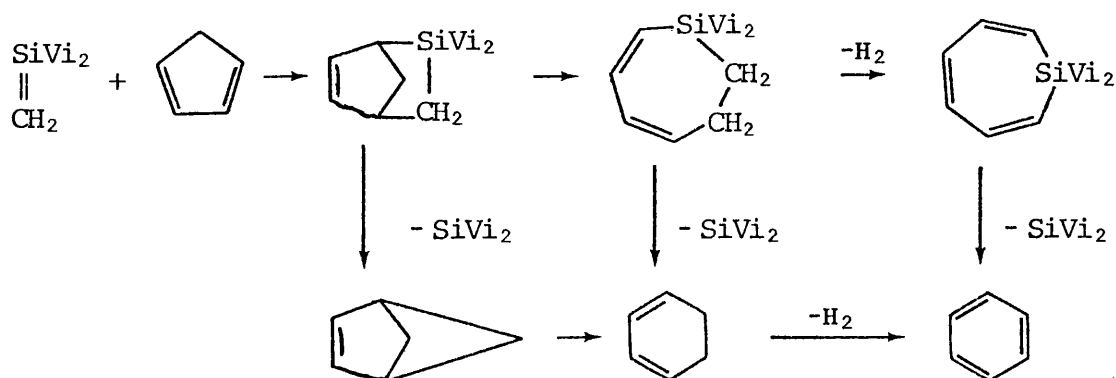


Cyclopentadiene formation could be explained by the following reaction

sequence:



Auner and Grobe¹¹² have observed the formation of benzene in the copyrolysis of 1,1-dimethyl-1-silacyclobutane and cyclopentadiene. They suggest a mechanism which is initiated by attack on the conjugated diene by 2-methyl-2-silapropene. Attack by 2-vinyl-2-silabutadiene might be expected to give the same product:

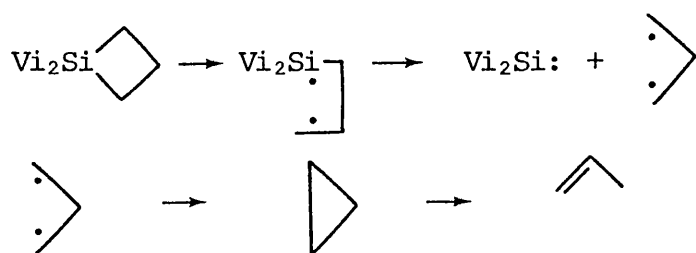


However, Conlin *et al.*¹¹³ have recently been unable to reproduce the results of Auner and Grobe.¹¹² The reason for this discrepancy is

probably the differing techniques used by the two groups of workers. Auner and Grobe analyse their product mixture by condensing it from the gas phase. They then use trap-to-trap distillation to separate the different components. Thus the high yield of benzene observed by them may have resulted from a complex series of steps in the liquid phase (this also provides a plausible reason for the low yield of C_3H_4 hydrocarbons observed in the present investigation of the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane, relative to that observed by Auner and Grobe in their study of the same compound¹⁴). Conlin et al. use a low pressure flow system where such a process would not be favoured. To resolve this situation, several experiments have been carried out in the LPP apparatus¹¹⁴ in which a mixture of 1,1-dimethyl-1-silacyclobutane and bicyclopentadiene (in situ sources of 2-methyl-2-silapropene and cyclopentadiene respectively) was pyrolysed between 806 and 881 K at a total initial pressure of ca. 0.1 mmHg. Benzene was observed as a pyrolysis product, but in a low yield (ca. 2% of that of ethene). It is difficult to suggest a reaction mechanism leading to toluene, although it is possible that it was formed via a sequence not unlike that shown above for the production of benzene.

The slightly lower yield of ethene produced in the pyrolysis of the vinyl substituted silacyclobutanes relative to that observed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane may indicate that a portion of the 1,4 biradicals produced in the initial stage of reactant decomposition (via rupture of the silicon-carbon or carbon-carbon bond) undergoes a reaction alternative to dissociation to a silaalkene and ethene. With both compounds this could lead to any of the minor hydrocarbon products (excluding ethene). In view of this, a possible route to propene, detected in the pyrolysis of 1,1-divinyl-1-silacyclobutane

is shown below:



A similar process has been observed in the pyrolyses of silacyclobutane¹¹⁵ and 1-methyl-1-silacyclobutane.¹¹⁶ It requires the site of initial ring cleavage to be the silicon-carbon bond. Inspection of Table 6.12 provides a possible explanation as to why no propene was detected in the pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane. If the observed ratios $k_5/k_6 \approx 0.95$ and $k_5/k_{10} \approx 0.80$ truly reflect the degree of allylic stabilization in the appropriate transition states (and are not caused by unimolecular fall-off), then the incidence of silicon-carbon bond rupture in 1,1-divinyl-1-silacyclobutane decomposition is, from Table 6.12, ca. 20%, while for 1-methyl-1-vinyl-1-silacyclobutane the figure is only ca. 5%. Thus it is reasonable to expect a greater yield of propene in the pyrolysis of 1,1-divinyl-1-silacyclobutane. The fact that the observed yields of this hydrocarbon were not 20% and 5% for 1,1-divinyl- and 1-methyl-1-vinyl-1-silacyclobutane respectively does not necessarily invalidate the above suggestion since, in addition to possible complications caused by unimolecular fall-off, the 1,4 biradical produced by initial silicon-carbon bond rupture may undergo reaction alternative to silylene elimination, a likely alternative being dissociation to ethene and a silaalkene.

CHAPTER 7

CONCLUSIONS

CONCLUSIONS

This thesis describes studies of the thermal decomposition of four cyclic organosilicon compounds. It also contains an investigation of the kinetics of the reaction between oxygen and 2-methyl-2-silapropene in which the silaalkene was generated from the pyrolysis of 1,1-dimethyl-1-silacyclobutane. A summary of the experimental results and conclusions drawn from this research is outlined below.

In Chapter 4 it was shown that the reaction between oxygen and 2-methyl-2-silapropene¹⁸ yields formaldehyde and dimethylsilanone. The Arrhenius parameters for this process were determined (with those for the dimerisation of 2-methyl-2-silapropene set at²³ $\log A = 6.55$ and $E = 0 \text{ kJ mol}^{-1}$) as $\log A = 7.2 \pm 0.9$ and $E = 16 \pm 12 \text{ kJ mol}^{-1}$. Thermochemical data^{8,9,68,80,81} were applied to demonstrate that the experimental activation energy is reasonable when compared with those for the reactions of the silaalkene with itself²³ and ethene.⁴ Although the absence of appropriate data^{44,65} precluded calculations regarding the experimental 'A'-factor, those for the reactions of 2-methyl-2-silapropene with itself and ethene were estimated. The estimated 'A'-factor for the dimerisation of the silaalkene was used to infer a small activation energy for the process.

The LPP of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane,⁸⁹ described in Chapter 5, gave 1,1,3,3-tetramethyl-1,3-disilacyclobutane as the only silicon-containing product. This was in contrast to the findings of a previous study³² at higher pressure, where the major silicon-containing product was isomeric 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane. The results of the low pressure study allowed the mechanism of this isomerisation to be elucidated, and it was suggested,

in view of similar rearrangements in the literature,^{9,30,31,92,93} that the process is a general one, probably important in the pyrolytic formation of carbon-silicon fibres. In particular, this investigation demonstrated the power of the LPP technique in reducing the importance of bimolecular relative to unimolecular reaction steps: this makes it a valuable tool in the study of reaction mechanism. The LPP of allyl-trimethylsilane²⁹ has provided similar information, as has the pressure dependence of the mode of decomposition of hexamethyldisilane.^{9,31} The Arrhenius parameters for the pyrolysis of the trisilacyclopentane were $\log A = 16.1 \pm 0.6$ and $E = 316 \pm 11 \text{ kJ mol}^{-1}$, consistent^{31,65} with a rate-determining step of silicon-silicon bond rupture and a ring strain³¹ of $21 \pm 16 \text{ kJ mol}^{-1}$.

Also discussed in Chapter 5 was the thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. This investigation showed that hydrogen, methane and 2-methyl-2-silapropene detected in the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane⁸⁹ arose from secondary decomposition of the product disilacyclobutane. Kinetic data on the thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane were used, with caution, to complement the thermochemical calculations in Chapter 4. Speculative suggestions were made regarding the reaction mechanism leading to the pyrolysis products: hydrogen, methane and ethene.

The pyrolysis of the two vinyl substituted silacyclobutanes, considered in Chapter 6, yielded Arrhenius parameters identical to those for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane⁴ within experimental error. However, there was a small difference in the size of rate constants for the decomposition of the three compounds at each temperature. These differences were used to infer an upper limit on the allylic

stabilization energy in the two radicals: $\begin{array}{c} \text{Vi} \\ \text{Me} \end{array} \text{Si} \cdot$ (24 kJ mol⁻¹) and

$\text{Vi}_2\text{Si} \cdot$ (34 kJ mol⁻¹). It was pointed out that it is reasonable that these radicals have less stabilization energy than the allyl radical⁶⁵ (54 kJ mol⁻¹): this results from the difference in energy of the carbon and silicon 'p' orbitals. The major pyrolysis products of 1-methyl-1-vinyl-1-silacyclobutane were 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane and ethene (both expected by analogy with the thermal decomposition of 1,1-dimethyl-1-silacyclobutane). Also formed were allene and propyne, providing evidence for the previously proposed¹⁴ isomerisation of the silaalkene involved, 2-methyl-2-silabutadiene. In addition to 1,1,3,3-tetravinyl-1,3-disilacyclobutane and ethene, the pyrolysis of 1,1-divinyl-1-silacyclobutane yielded propene, cyclopentadiene, benzene and toluene. Speculative suggestions, based largely upon previous work,¹¹²⁻¹¹⁶ as to how these products arose, were made. This study also suggested that the vinyl substituted silaalkenes involved were conjugatively stabilized⁹⁹ relative to 2-methyl-2-silapropene: the yields of disilacyclobutanes produced via their dimerisation were lower than that observed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane.

APPENDICES

APPENDIX 1

PRIMARY DATA

The number of kinetic runs performed using the LPP apparatus in this study was ca. 1400. All LPP data are stored in the Department of Chemistry of the University of Leicester in the form of punched tape or on magnetic disc.

Typical peak height - time values are shown in Table A.1. In run "FTL1335" neat 1,1-divinyl-1-silacyclobutane was pyrolysed at an initial pressure of 0.14 mmHg and 796 K. All eight channels were tuned to the 96^+ ($M^+ - C_2H_4$) mass peak (see Chapter 6). Peak heights (in arbitrary units) are given in columns 1, 3, 5, 7, 9, 11 and 15. The corresponding times (100/s) are in columns 2, 4, 6, 8, 10, 12, 14 and 16. Plots of peak height against time and $\ln(\text{peak height})$ against time are shown in Figures A.1 and A.2 respectively (both plots utilize data from channels 4 and 8 only).

NON-INTERPOLATED PEAK HEIGHTS

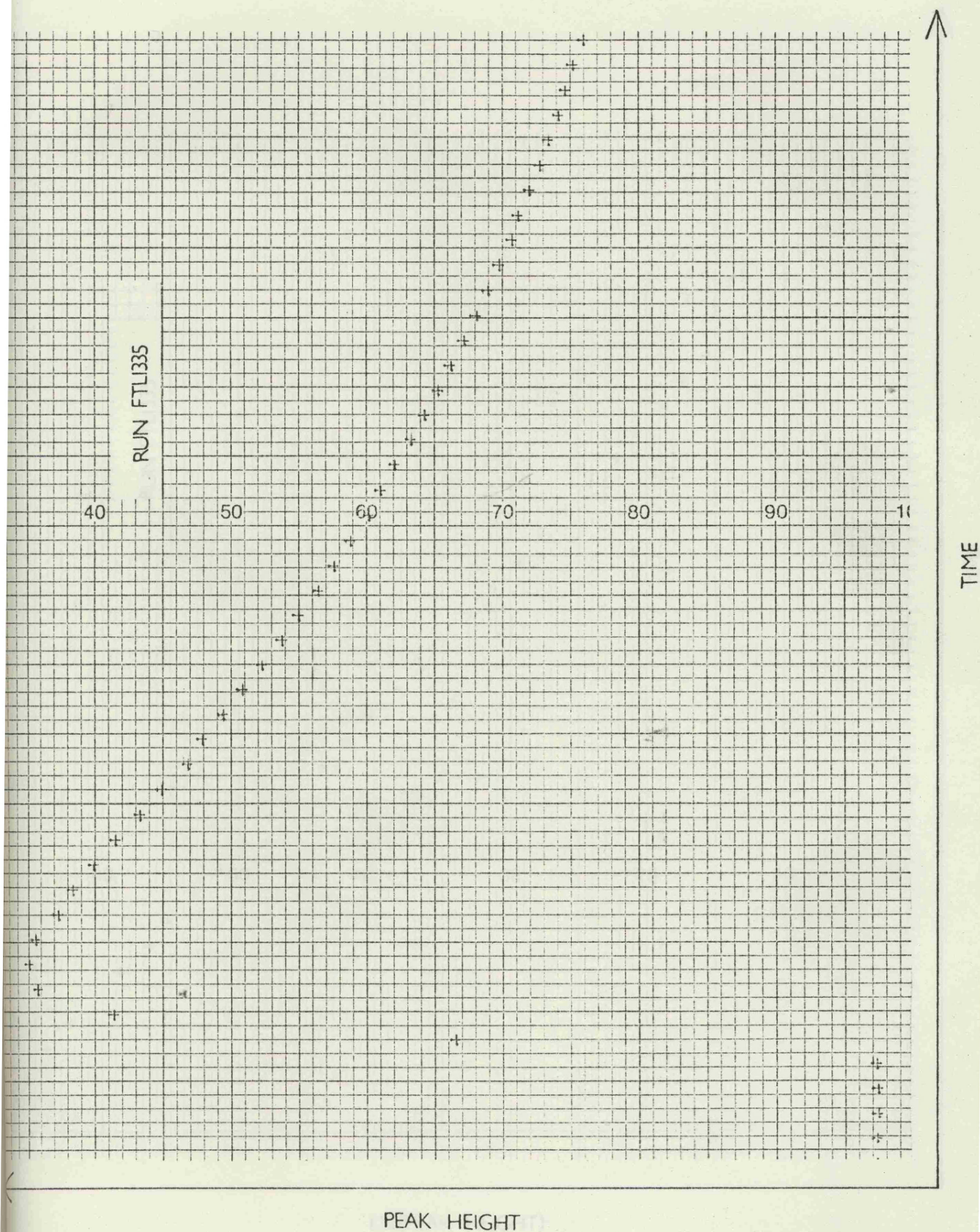
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(TEMP= 523 C PRESS= 15 CYCLE TIME= 3.5 TSTART= 0 S)
```

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(CL) 0	0	0	0	0	0	0	0
188	-178	253	-178	323	-178	480	-178
189	-178	540	-178	510	-178	682	-178
190	-178	822	-178	894	-178	954	-176
191	-177	1104	-176	1140	-176	1245	-177
192	-1533	1338	-2175	1459	-3387	1494	-3659
193	-4055	1574	-4152	1740	-4216	1776	-4240
194	-4158	1952	-4160	2022	-4091	2058	-4039
195	-4027	2193	-3579	2304	-3924	2340	-3909
196	-3824	2480	-3775	2585	-3719	2622	-3595
197	-3626	2762	-3564	2858	-3520	2904	-3439
198	-3425	3045	-3375	3116	-3325	3166	-3230
199	-3223	3328	-3178	3398	-3122	3468	-3107
200	-3055	3610	-2992	3716	-2952	3785	-2939
201	-2878	3892	-2818	3998	-2798	4068	-2750
202	-2721	4174	-2657	4280	-2630	4314	-2613
203	-2561	4456	-2525	4562	-2499	4595	-2478
204	-2438	4738	-2382	4844	-2352	4878	-2339
205	-2285	5020	-2254	5126	-2235	5160	-2217
206	-2173	5302	-2135	5408	-2115	5442	-2093
207	-2037	5584	-2018	5650	-1966	5724	-1999
208	-1932	5865	-1907	5936	-1894	5972	-1890
209	-1835	6148	-1820	6219	-1803	6254	-1785
210	-1737	6431	-1722	6501	-1707	6537	-1689
211	-1651	6713	-1641	6783	-1630	6819	-1615
212	-1561	6995	-1555	7065	-1542	7101	-1528
213	-1459	7277	-1460	7347	-1457	7383	-1453
214	-1354	7559	-1354	7639	-1353	7675	-1351
215	-1248	7841	-1248	7921	-1247	7957	-1245
216	-1142	8123	-1142	8203	-1141	8239	-1139
217	-1036	8405	-1036	8485	-1035	8521	-1033
218	-930	8687	-930	8767	-929	8803	-927
219	-824	8969	-824	9049	-823	9085	-821
220	-718	9251	-718	9331	-717	9367	-715
221	-612	9533	-612	9613	-611	9649	-609
222	-506	9815	-506	9895	-505	9931	-503
223	-400	10097	-400	10177	-399	10213	-397
224	-294	10379	-294	10459	-293	10495	-291
225	-188	10661	-188	10739	-187	10775	-185
226	-82	10943	-82	11021	-81	11057	-79
227	24	11225	24	11299	23	11335	1
228	120	11507	120	11579	119	11615	27
229	216	11789	216	11859	215	11895	73
230	312	12071	312	12139	311	12175	119
231	408	12353	408	12419	407	12455	215
232	504	12635	504	12699	503	12735	311
233	600	12917	600	13079	599	13115	407
234	696	13199	696	13259	695	13295	503
235	792	13481	792	13539	791	13575	600
236	888	13763	888	13819	887	13855	696
237	984	14045	984	14099	983	14135	792
238	1080	14327	1080	14379	1079	14415	888
239	1176	14609	1176	14659	1175	14695	984
240	1272	14891	1272	14939	1271	14975	1080
241	1368	15173	1368	15219	1367	15255	1176
242	1464	15455	1464	15499	1463	15535	1272
243	1560	15737	1560	15779	1559	15815	1368
244	1656	16019	1656	16059	1655	16095	1464
245	1752	16301	1752	16339	1751	16375	1560
246	1848	16583	1848	16619	1847	16655	1656
247	1944	16865	1944	16899	1943	16935	1752
248	2040	17147	2040	17179	2039	17215	1848
249	2136	17429	2136	17459	2135	17495	1944
250	2232	17711	2232	17739	2231	17775	2040
251	2328	17993	2328	18069	2327	18105	2136
252	2424	18275	2424	18299	2423	18335	2232
253	2520	18557	2520	18529	2519	18565	2328
254	2616	18839	2616	18859	2615	18895	2424
255	2712	19121	2712	19149	2711	19185	2520
256	2808	19403	2808	19429	2807	19465	2616
257	2904	19685	2904	19709	2903	19745	2712
258	3000	19967	3000	19989	2999	20025	2808
259	3096	20249	3096	20269	3095	20305	2904
260	3192	20531	3192	20549	3191	20585	3000
261	3288	20813	3288	20829	3287	20865	3096
262	3384	21095	3384	21109	3383	21145	3192
263	3480	21377	3480	21329	3479	21365	3288
264	3576	21659	3576	21599	3575	21605	3384
265	3672	21941	3672	21869	3671	21865	3480
266	3768	22223	3768	22139	3767	22205	3576
267	3864	22505	3864	22409	3863	22465	3672
268	3960	22787	3960	22679	3959	22725	3768
269	4056	23069	4056	22949	4055	23085	3864
270	4152	23351	4152	23219	4151	23345	3960
271	4248	23633	4248	23489	4247	23605	4056
272	4344	23915	4344	23759	4343	23865	4152
273	4440	24197	4440	24029	4439	24125	4248
274	4536	24479	4536	24299	4535	24385	4344
275	4632	24761	4632	24569	4631	24645	4440
276	4728	25043	4728	24839	4727	24905	4536
277	4824	25325	4824	25109	4823	25165	4632
278	4920	25607	4920	25379	4919	25425	4728
279	5016	25889	5016	25649	5015	25685	4824
280	5112	26171	5112	25919	5111	25945	4920
281	5208	26453	5208	26189	5207	26205	5016
282	5304	26735	5304	26459	5303	26465	5112
283	5400	27017	5400	26729	5399	26725	5208
284	5496	27299	5496	26999	5397	26985	5304
285	5592	27581	5592	27269	5395	27245	5400
286	5688	27863	5688	27539	5393	27505	5496
287	5784	28145	5784	27809	5391	27765	5592
288	5880	28427	5880	28079	5389	28025	5688
289	5976	28709	5976	28349	5387	28285	5784
290	6072	28991	6072	28619	5385	28545	5880
291	6168	29273	6168	28889	5383	28805	5976
292	6264	29555	6264	29159	5381	29065	6072
293	6360	29837	6360	29429	5379	29325	6168
294	6456	30119	6456	29699	5377	29585	6264
295	6552	30401	6552	29969	5375	29845	6360
296	6648	30683	6648	30239	5373	30105	6456
297	6744	30965	6744	30509	5371	30365	6552
298	6840	31247	6840	30779	5369	30625	6648
299	6936	31529	6936	31049	5367	30885	6744
300	7032	31811	7032	31319	5365	31145	6840

NUMBER OF ROWS PRINTED= 25 TOTAL NUMBER OF ROWS= 25

FIGURE A.1

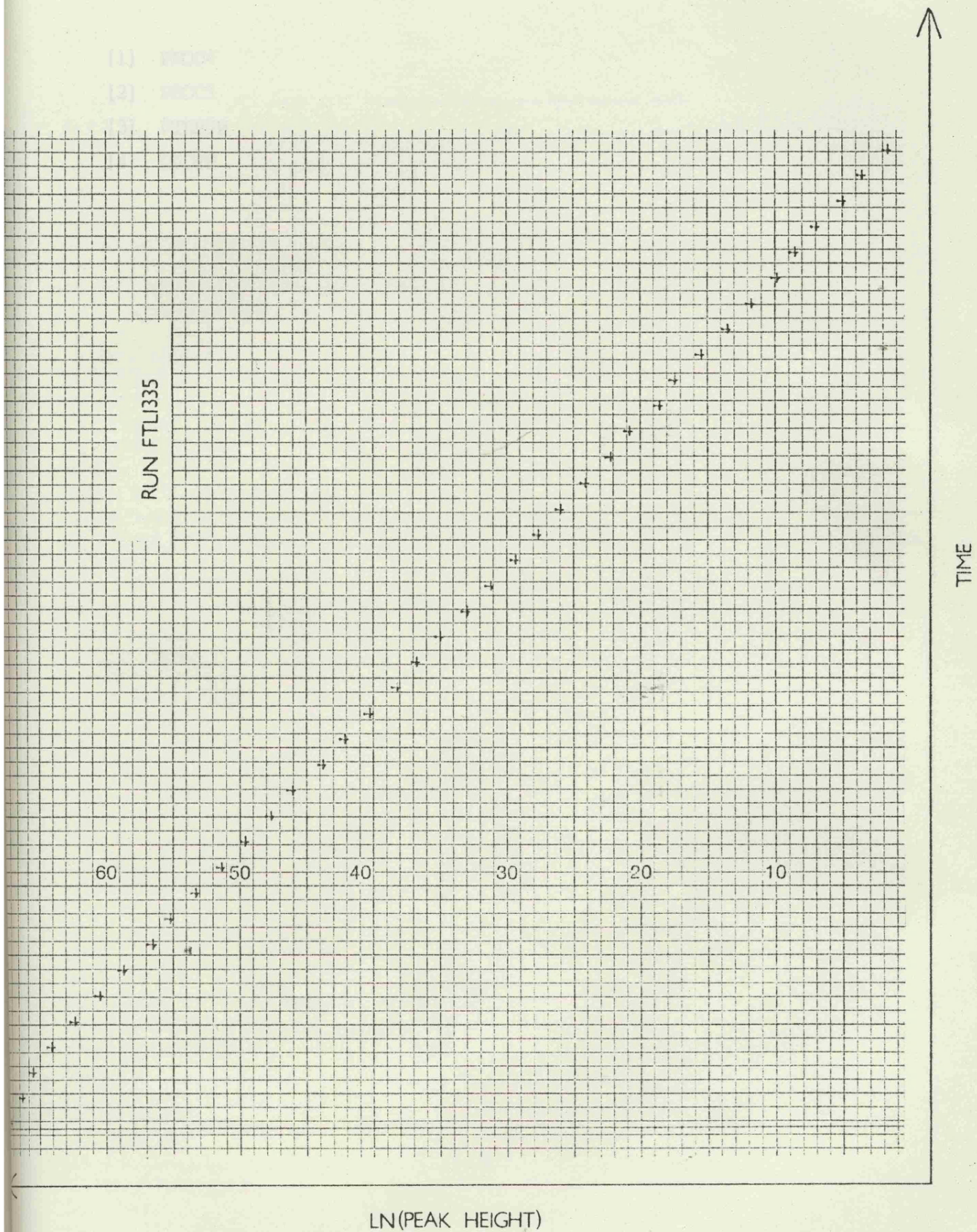
PLOT OF PEAK HEIGHT AGAINST TIME



PEAK HEIGHT

FIGURE A.2

PLOT OF LN(PEAK HEIGHT) AGAINST TIME



APPENDIX 2

COMPUTER PROGRAMMES

- [1] PROC4
- [2] PROC3
- [3] FTLMJB
- [4] ORDER

```

10 REM*****
20 REM
30 REM  PROCA
40 REM  *****
50 REM
60 REM  PROG.TO ANALYSE LPP DATA.
70 REM
80 REM*****
90 REM
100 REM  PART(A):READS IN DATA,CHOOSSES CHANNELS,
110 REM  DEDUCTS BASELINES AND DEFINES START TIME.
120 REM
130 CLEAR
140 CALL"RESOLUTION",0,2
150 GRAPH 1
160 DIM T(800),P(800),PKA(800),CH(8),XY(800)
170 DIM A(100,8),AT(100,8),X(8),YG(8)
180 ?::?
190 INPUT"FILENAME":A$
200 IF LOOKUP(A$)() THEN 220
210 GOTO 190
220 OPEN#10,A$
230 INPUT#10,TT,PP,SS
240 N=0
250 FOR I=1 TO 1000000 STEP 8
260 INPUT#10,P(I),T(I),P(I+1),T(I+1),P(I+2),T(I+2),P(I+3),T(I+3)
270 INPUT#10,P(I+4),T(I+4),P(I+5),T(I+5),P(I+6),T(I+6),P(I+7),T(I+7)
280 N=N+8
290 ON EOF GOTO 310
300 NEXT I
310 FOR I=1 TO N
320 T(I)=T(I)/100
330 NEXT I
340 FOR I=9 TO N STEP 8
350 FOR J=1 TO 8
360 Q=T(I+J-1)-T(I+J-9)
370 IF Q=0 GOTO 400
380 IF Q<-2 THEN T(I+J-1)=T(I+J-1)+250:GOTO 360
390 T(I+J-1)=T(I+J-1)+1
400 NEXT J
410 NEXT I
420 INPUT"HOW MANY CHANNELS":M
430 IF M<1 GOTO 420
440 IF M>8 GOTO 420
450 IF M=0 GOTO 600
460 FOR K=1 TO M
470 ?"CHANNEL("K")":INPUT"IS":CH(K)
480 IF CH(K)() GOTO 470
490 IF CH(K)>8 GOTO 470
500 NEXT K
510 SUM=1:ACC=1
520 FOR I=1 TO N
530 FOR K=1 TO M
540 IF SUM=CH(K) THEN P(ACC)=P(I):T(ACC)=T(I):PCC=ACC+1
550 NEXT K
560 SUM=SUM+1
570 IF SUM=9 THEN SUM=1
580 NEXT I

```



```

590 N=ACC-1
600 FOR I=1 TO N
610 P(I)=(-1)*P(I)
620 NEXT I
630 A=1:B=N
640 GOSUB 1170
650 ?"YOU MUST DEFINE START OF REACTION"
660 INPUT"IS THIS PLOT OK(Y/N)";C$
670 IF C$="Y" GOTO 720
680 INPUT"PLOT WHICH POINTS";A,B
690 GOSUB 1080
700 IF E=1 GOTO 680
710 GOTO 640
720 GOSUB 1530
730 S1=0:S2=0
740 FOR I=1 TO N
750 IF T(I)>G GOTO 790
760 S1=S1+P(I)
770 S2=S2+1
780 NEXT I
790 BASE=S1/S2
800 J=1
810 FOR I=(S2+1) TO N
820 P(J)=P(I)-BASE
830 T(J)=T(I)-G
840 J=J+1
850 NEXT I
860 N=N-S2:A=1:B=N
870 GOSUB 1170
880 ?"(AVERAGE BL=(-1)*BASE",NO. OF BL="S2
890 ?"TSTART="G"S)"
900 REM*****
910 REM
920 REM PART(B):CHOICE OF PROCESSING ROUTINE.
930 REM
940 INPUT"GAIN,COMP,LOGS,GRAD,NFILE,OR STOP";D$
950 IF D$="GAIN" GOTO 4170
960 IF D$="COMP" GOTO 1770
970 IF D$="LOGS" GOTO 2580
980 IF D$="GRAD" GOTO 3650
990 IF D$="NFILE" GOTO 100
1000 IF D$="STOP" THEN ??:?:?:CALL"RESOLUTION",0,2:GRAPH0:STOP
1010 ?:"FILENAME="A$
1020 ?"(TEMP="TT"C, PRESS="PP",C.T.="SS"S)"
1030 GOTO 940
1040 REM*****
1050 REM
1060 REM PART(C):SUBROUTINE TO CHECK PLOTTING LIMITS.
1070 REM
1080 E=2
1090 IF A<=0 THEN E=1
1100 IF B>N THEN E=1
1110 IF A>B THEN E=1
1120 RETURN
1130 REM*****
1140 REM
1150 REM PART(D):SUBROUTINE TO PLOT PEAK HEIGHT VS. TIME.
1160 REM

```

```

1170 MAX=-1E10
1180 MIN=+1E10
1190 FOR I=A TO B
1200 IF P(I)>MAX THEN MAX=P(I)
1210 IF P(I)<MIN THEN MIN=P(I)
1220 NEXT I
1230 MAX=MAX*1.05
1240 TMAX=T(B)-T(A)
1250 CALL "RESOLUTION",0,2
1260 CALL "PLOT",318,0,1
1270 CALL "LINE",0,0
1280 CALL "LINE",0,191
1290 FOR I=A TO B
1300 X=318*(T(I)-T(A))/TMAX
1310 Y=191*(P(I)-MIN)/(MAX-MIN)
1320 CALL "PLOT",X,Y,3
1330 NEXT I
1340 ?:"A TOTAL OF"(B-A)+1"POINTS"
1350 RETURN
1360 REM*****
1370 REM
1380 REM  PART(E):SUBROUTINE TO PLOT DATA FOR "COMP" ROUTINE.
1390 REM
1400 ?:"?:"
1410 INPUT "IS THIS PLOT OK FOR COMP";E$
1420 IF E$="Y" THEN RETURN
1430 INPUT "PLOT WHICH POINTS";A,B
1440 GOSUB 1080
1450 IF E=1 GOTO 1430
1460 GOSUB 1170
1470 GOTO 1400
1480 RETURN
1490 REM*****
1500 REM
1510 REM  PART(F):SUBROUTINE TO MEASURE TIME SCALE.
1520 REM
1530 C=159
1540 CALL "PLOT",C,0,-3
1550 CALL "LINE",C,191,-3
1560 G=(C/318)*(T(B)-T(A))+T(A)
1570 ?:"?:"TIME="G
1580 INPUT "MOVE CURSOR(L/R),OR STOP";B$
1590 IF B$="L" THEN LR=-1:GOTO 1620
1600 IF B$="R" THEN LR=+1:GOTO 1620
1610 GOTO 1690
1620 INPUT "BY HOW MANY";DIST
1630 CALL "PLOT",C,0,-3
1640 CALL "LINE",C,191,-3
1650 C=C+LR*DIST
1660 IF C<0 GOTO 1530
1670 IF C>318 GOTO 1530
1680 GOTO 1540
1690 CALL "PLOT",C,0,-3
1700 CALL "LINE",C,191,-3
1710 RETURN
1720 REM*****
1730 REM
1740 REM  PART(G):"COMP" ROUTINE-

```

```

1750 REM  MODELS PEAK HEIGHT-TIME PROFILES.
1760 REM
1770 GOSUB 1400
1780 ?::?:
1790 ?"YOU MUST DEFINE MAX PK.HT."
1800 C=191
1810 CALL "PLOT",0,C,-2
1820 CALL "LINE",318,C,-2
1830 BMAX=(C/191)*(MAX-MIN)+MIN
1840 ?"PEAK HEIGHT="BMAX
1850 INPUT "MOVE CURSOR UP OR DOWN(U/D),OR STOP":N$
1860 IF N$="U" THEN UD=+1:GOTO 1890
1870 IF N$="D" THEN UD=-1:GOTO 1890
1880 GOTO 1970
1890 INPUT "BY HOW MANY":DIST
1900 CALL "PLOT",0,C,-2
1910 CALL "LINE",318,C,-2
1920 C=C+UD*DIST
1930 IF C>191 GOTO 1800
1940 IF C<0 GOTO 1800
1950 ?::?:
1960 GOTO 1810
1970 CALL "PLOT",318,C,-2
1980 CALL "LINE",0,C,-2
1990 ?::?:
2000 ?"DO YOU WANT ALL CALCULATED REACTION PRO-"
2010 ?"FILES TO REMAIN ON THE SCREEN DURING TH-"
2020 INPUT "IS PROCEDURE(Y/N)":J$
2030 IF J$="Y" THEN C=-3:GOTO 2050
2040 C=-2
2050 ?::?:
2060 INPUT "KLIN=":KIN
2070 INPUT "KLOUT=":KL
2080 INPUT "KREACTION=":KR
2090 KS=KL+KR
2100 A0=BMAX/((KS/KIN)+(KS/(KIN-KS)))
2110 ?"A0="A0:INPUT "PRESS RETURN TO CONTINUE":Y$
2120 GOSUB 3510
2130 V1=1/(KS-KIN):V2=1/(KIN-KS):V3=A0*KIN
2140 FOR I=A TO B
2150 PKA(I)=V3*((V1*EXP(-KIN*T(I)))+(V2*EXP(-KS*T(I))))
2160 X=318*(T(I)-T(A))/TMAX
2170 Y=191*(PKA(I)-MIN)/(MAX-MIN)
2180 CALL "PLOT",X,Y,-2
2190 NEXT I
2200 DD=0
2210 ?:"(1)STOP? (2)NEW EXPT. PLOT?"
2220 ?:"(3)NEW KLIN+KLOUT? (4)NEW KREACTION?"
2230 ?:"(5)SHIFT CALCD. CURVE?":INPUT "(6)LOGS":D
2240 ?::?:
2250 IF D=1 GOTO 940
2260 IF D=2 GOTO 1770
2270 IF D=3 GOTO 2320
2280 IF D=4 GOTO 2320
2290 IF D=5 GOTO 2410
2300 IF D=6 GOTO 2560
2310 GOTO 2210
2320 IF DD=5 GOTO 2380

```



```

2330 FOR I=A TO B
2340 X=318*(T(I)-T(A))/TMAX
2350 Y=191*(PKA(I)-MIN)/(MAX-MIN)
2360 CALL "PLOT",X,Y,C
2370 NEXT I
2380 GOSUB 3510
2390 IF D=3 GOTO 2060
2400 IF D=4 GOTO 2080
2410 K=0
2420 INPUT "SHIFT CALCD PTS TO L/R OR STOP":X$
2430 IF X$="L" THEN LR=-1:GOTO 2460
2440 IF X$="R" THEN LR=+1:GOTO 2460
2450 DD=5 : GOTO 2470
2460 INPUT "BY HOW MANY":DIST
2470 FOR I=A TO B
2480 X=(318*(T(I)-T(A))/TMAX)+K
2490 Y=191*(PKA(I)-MIN)/(MAX-MIN)
2500 CALL "PLOT",X,Y,-2
2510 NEXT I
2520 IF X$() "L" THEN IF X$() "R" GOTO 2210
2530 K=K+LR+DIST
2540 FOR I=A TO B
2550 X=(318*(T(I)-T(A))/TMAX)+K
2560 Y=191*(PKA(I)-MIN)/(MAX-MIN)
2570 CALL "PLOT",X,Y,-2
2580 NEXT I
2590 SH=(K/318)*TMAX
2600 ?:"?"?"CALCD. PTS. SHIFTED BY"SH"S"
2610 GOTO 2420
2620 REM*****
2630 REM
2640 REM PART(H)="LOGS" ROUTINE-
2650 REM PLOTS LOG(PEAK HEIGHT) VS.TIME.
2660 REM (MAY ALSO BE ACCESSED FROM "COMP" TO ANALYSE SIMULATED DATA).
2670 REM
2680 ?:"?"?"
2690 IF D$="LOGS" GOTO 2750
2700 FOR I=1 TO N
2710 XY(I)=P(I)
2720 PKA(I)=V3*((V1*EXP(-KIN*T(I)))+(V2*EXP(-KS*T(I))))
2730 P(I)=PKA(I)
2740 NEXT I
2750 INPUT "PLOT WHICH POINTS":A,B
2760 GOSUB 1000
2770 IF E=1 GOTO 2750
2780 MAX=-1E10:MIN=+1E10
2790 FOR I=A TO B
2800 IF P(I)=0 GOTO 2830
2810 IF LOG(P(I))>MAX THEN MAX=LOG(P(I))
2820 IF LOG(P(I))<MIN THEN MIN=LOG(P(I))
2830 NEXT I
2840 TMAX=T(B)-T(A)
2850 CALL "RESOLUTION",0,2
2860 CALL "PLOT",318,0,1
2870 CALL "LINE",0,0
2880 CALL "LINE",0,191
2890 FOR I=A TO B
2900 IF P(I)=0 GOTO 2940

```

```

2910 X=318*(T(I)-T(A))/TMAX
2920 Y=191*(LOG(P(I))-MIN)/(MAX-MIN)
2930 CALL "PLOT",X,Y,3
2940 NEXT I
2950 INPUT "LEAST SQUARES FIT(Y/N)";K$
2960 IF K$="Y" GOTO 3050
2970 INPUT "ANOTHER PLOT(Y/N)";H$
2980 IF H$="Y" GOTO 2750
2990 ??:?:?
3000 IF D$="LOGS" GOTO 940
3010 FOR I=1 TO N
3020 P(I)=XY(I)
3030 NEXT I
3040 GOTO 2210
3050 INPUT "BETWEEN WHICH POINTS";A1,B1
3060 IF A1<A GOTO 3050
3070 IF B1>B GOTO 3050
3080 IF (B1-A1)/1 GOTO 3050
3090 T1=0:T2=0:T3=0:T4=0
3100 S0=0
3110 FOR I=A1 TO B1
3120 IF P(I)=0 THEN S0=S0+1:GOTO 3170
3130 T1=T1+T(I)
3140 T2=T2+LOG(P(I))
3150 T3=T3+T(I)*LOG(P(I))
3160 T4=T4+T(I)*T(I)
3170 NEXT I
3180 N1=(B1-A1)+1-S0
3190 IF N1<2 THEN ??:?"<2 +VE PK.HTS."?:?"NO LSQ FIT IS POSSIBLE":GOTO 2750
3200 T5=N1*T4-T1*T1
3210 GRAD=(N1*T3-T1*T2)/T5
3220 INCT=(T2*T4-T1*T3)/T5
3230 IF N1=2 THEN EG=0:EI=0:GOTO 3320
3240 T6=0
3250 FOR I=A1 TO B1
3260 IF P(I)=0 GOTO 3290
3270 T7=GRAD*T(I)+INCT-LOG(P(I))
3280 T6=T6+T7*T7
3290 NEXT I
3300 EG=SQR(N1*T6/((N1-2)*T5))
3310 EI=SQR(T4*T6/((N1-2)*T5))
3320 ?"FIT BETWEEN POINTS" A1 "AND" B1
3330 ?"GRAD"="GRAD" + "-"EG"
3340 ?"INCT"="EXP(INCT)" + "-"EXP(EI)
3350 L1=GRAD*T(A)+INCT
3360 L2=GRAD*T(B)+INCT
3370 L1=191*(L1-MIN)/(MAX-MIN)
3380 L2=191*(L2-MIN)/(MAX-MIN)
3390 CALL "PLOT",0,L1,-2
3400 CALL "LINE",318,L2,-2
3410 INPUT "TRY ANOTHER FIT(Y/N)";L$
3420 IF L$() "Y" GOTO 2970
3430 CALL "PLOT",318,L2,-2
3440 CALL "LINE",0,L1,-2
3450 ??:?:?
3460 GOTO 3050
3470 REM*****
3480 REM

```

```

3490 REM  PART(I):SUBROUTINE TO PUT SCALE ON PEAK HEIGHT-TIME PLOT.
3500 REM
3510 ZA=191-(191*0.1*AZ)/(MAX-MIN)
3520 ZB=191-(191*0.1*BMAX)/(MAX-MIN)
3530 CALL "PLOT",310,191,-3
3540 CALL "LINE",318,191,-3
3550 CALL "LINE",318,ZA,-3
3560 CALL "LINE",310,ZA,-3
3570 CALL "PLOT",310,ZB,-3
3580 CALL "LINE",317,ZB,-3
3590 RETURN
3600 REM*****
3610 REM
3620 REM  PART(J):"GRAD" ROUTINE-
3630 REM  MEASURES GRADIENT OF PEAK HEIGHT-TIME PROFILES.
3640 REM
3650 ??:?:?
3660 INPUT "IS THIS PLOT OK FOR GRAD":E$
3670 IF E$="Y" THEN GOTO 3730
3680 INPUT "PLOT WHICH POINTS":A,B
3690 GOSUB 1090
3700 IF E=1 GOTO 3630
3710 GOSUB 1170
3720 GOTO 3650
3730 INPUT "FIT BETWEEN WHICH POINTS":A1,B1
3740 IF A1<A THEN GOTO 3730
3750 IF B1>B THEN GOTO 3730
3760 IF (B1-A1)<1 THEN GOTO 3730
3770 T1=0:T2=0:T3=0:T4=0
3780 FOR I=A1 TO B1
3790 T1=T1+T(I)
3800 T2=T2+P(I)
3810 T3=T3+T(I)*P(I)
3820 T4=T4+T(I)*T(I)
3830 NEXT I
3840 N1=(B1-A1)+1
3850 T5=N1*T4-T1*T1
3860 GRAD=(N1*T3-T1*T2)/T5
3870 INCT=(T2*T4-T1*T3)/T5
3880 IF N1=2 THEN EG=0:EI=0:GOTO 3960
3890 T6=0
3900 FOR I=A1 TO B1
3910 T7=GRAD*T(I)+INCT-P(I)
3920 T6=T7*T7
3930 NEXT I
3940 EG=SQR(N1*T6/((N1-2)*T5))
3950 EI=SQR(T4*T6/((N1-2)*T5))
3960 ?"FIT BETWEEN POINTS"A1"AND"B1
3970 ?"GRAD="GRAD"+-EG
3980 ?"INCT="INCT"+-EI
3990 L1=GRAD*T(A)+INCT
4000 L2=GRAD*T(B)+INCT
4010 L1=191*(L1-MIN)/(MAX-MIN)
4020 L2=191*(L2-MIN)/(MAX-MIN)
4030 CALL "PLOT",0,L1,-2
4040 CALL "LINE",318,L2,-2
4050 INPUT "TRY ANOTHER FIT":L$
4060 IF L$(">")"Y" GOTO 4100

```

```

4070 CALL "PLOT", 318, L2, -2
4080 CALL "LINE", 0, L1, -2
4090 GOTO 3730
4100 INPUT "TRY ANOTHER PLOT?"; L$
4110 IF L$ = "Y" GOTO 3680
4120 ? : ? : ? : GOTO 940
4130 REM *****
4140 REM
4150 REM PART(K) : "GAIN" ROUTINE-
4160 REM CORRECTS DATA FOR POOR TUNING OF PEAK SELECTOR.
4170 J=1
4180 FOR I=1 TO N STEP M
4190 FOR K=1 TO M
4200 A(J,K)=P(I+K-1)
4210 AT(J,K)=T(I+K-1)
4220 NEXT K
4230 J=J+1
4240 NEXT I
4250 X1=J-1
4260 FOR K=1 TO M
4270 X(K)=0
4280 FOR J=1 TO X1
4290 X(K)=X(K)+A(J,K)
4300 NEXT J
4310 NEXT K
4320 X2=-1E10
4330 FOR K=1 TO M
4340 IF X(K) > X2 THEN X2=X(K) : X3=K
4350 NEXT K
4360 CALL "RESOLUTION", 0, 2
4370 CALL "PLOT", 318, 0, 1
4380 CALL "LINE", 0, 0
4390 CALL "LINE", 0, 191
4400 FOR K=1 TO M
4410 FOR J=1 TO X1
4420 Y=191+A(J,K)/MAX
4430 X=318*(AT(J,K)-T(A))/(T(B)-T(A))
4440 IF K=X3 THEN X4=-3 : GOTO 4460
4450 X4=-2
4460 CALL "PLOT", X, Y, X4
4470 NEXT J
4480 NEXT K
4490 ? : ? : ?
4500 FOR K=1 TO M
4510 IF K=X3 THEN GOTO 4630
4520 ? "CURVE" K : INPUT "GAIN" : XG(K)
4530 IF XG(K) <= 0 THEN ? "-----" : GOTO 4630
4540 FOR J=1 TO X1
4550 Y=191+A(J,K)/MAX
4560 X=318*(AT(J,K)-T(A))/(T(B)-T(A))
4570 CALL "PLOT", X, Y, -2
4580 A(J,K)=A(J,K)*XG(K)
4590 Y=191+A(J,K)/MAX
4600 CALL "PLOT", X, Y, -2
4610 NEXT J
4620 GOTO 4520
4630 NEXT K
4640 J=1

```

```
4550 FOR I=1 TO N STEP M
4660 FOR K=1 TO M
4570 P(I+K-1)=A(J,K)
4680 T(I+K-1)=AT(J,K)
4690 NEXT K
4700 J=J+1
4710 NEXT I
4720 GOTO 870
4730 STOP
```

```

10 REM *****
20 REM
30 REM  PROC3
40 REM  *****
50 REM
60 REM  PROG. TO INTERPOLATE, CORRECT (FOR CRACKING PATTERN),
70 REM  AND LIST LPP DATA.
80 REM
90 REM *****
100 REM
110 REM  PART(A): READS IN FILENAME AND EXPERIMENTAL CONDITIONS.
120 REM
130 ?CHR$(12)
140 ?CHR$(29)
150 ?CHR$(29)
160 CLEAR
170 DIM A(71), B(71), C(71), D(71), E(71), F(71), G(71), H(71)
180 DIM AT(71), BT(71), CT(71), DT(71), ET(71), FT(71), GT(71), HT(71)
190 DIM AN(568), BN(568), CN(568), DN(568), EN(568), FN(568), GN(568), HN(568)
200 DIM TIME(568)
210 DIM RR(8,8), L(8), X(8,8)
220 ?"PLEASE ENSURE THAT PRINTER IS ON"
230 INPUT "PRESS RETURN TO CONTINUE"; B$
240 INPUT "DO YOU REQUIRE PRINT ONLY"; B$
250 IF B$="Y" THEN GOTO 3760
260 INPUT "FILENAME"; A$
270 IF LOOKUP(A$)(1) THEN 290
280 GOTO 260
290 OPEN#10, A$
300 INPUT#10, TEMP, PRES, SCAN
310 REM *****
320 REM
330 REM  PART(B): READS IN AND ANALYSES BASELINE DATA.
340 REM
350 S1=0:S2=0:S3=0:S4=0:S5=0:S6=0:S7=0:S8=0
360 FOR I=1 TO 4
370 INPUT#10, A(I), AT(I), B(I), BT(I), C(I), CT(I), D(I), DT(I), E(I), ET(I), F(I), FT(I), G(I), GT(I), H(I), HT(I)
380 S1=S1+A(I)
390 S2=S2+B(I)
400 S3=S3+C(I)
410 S4=S4+D(I)
420 S5=S5+E(I)
430 S6=S6+F(I)
440 S7=S7+G(I)
450 S8=S8+H(I)
460 NEXT I
470 S1=S1/4:S2=S2/4:S3=S3/4:S4=S4/4:S5=S5/4:S6=S6/4:S7=S7/4:S8=S8/4
480 REM *****
490 REM
500 REM  PART(C): READS IN REMAINING DATA, DEDUCTS BASELINES
510 REM  AND DEFINES START TIME.
520 REM
530 START=HT(4)+(3.1/SCAN)*((AT(4)+SCAN*100)-HT(4))
540 A(1)=0:B(1)=0:C(1)=0:D(1)=0:E(1)=0:F(1)=0:G(1)=0:H(1)=0
550 AT(1)=0:BT(1)=0:CT(1)=0:DT(1)=0:ET(1)=0:FT(1)=0:GT(1)=0:HT(1)=0
560 N=1
570 FOR I=2 TO 1000000
580 INPUT#10, A(I), AT(I), B(I), BT(I), C(I), CT(I), D(I), DT(I), E(I), ET(I), F(I), FT(I), G(I), GT(I), H(I), HT(I)

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590 N=N+1
600 IF N=71 GOTO 750
610 ON EOF GOTO 750
620 A(I)=(-1)*(A(I)-S1):AT(I)=(AT(I)-START)/100
630 B(I)=(-1)*(B(I)-S2):BT(I)=(BT(I)-START)/100
640 C(I)=(-1)*(C(I)-S3):CT(I)=(CT(I)-START)/100
650 D(I)=(-1)*(D(I)-S4):DT(I)=(DT(I)-START)/100
660 E(I)=(-1)*(E(I)-S5):ET(I)=(ET(I)-START)/100
670 F(I)=(-1)*(F(I)-S6):FT(I)=(FT(I)-START)/100
680 G(I)=(-1)*(G(I)-S7):GT(I)=(GT(I)-START)/100
690 H(I)=(-1)*(H(I)-S8):HT(I)=(HT(I)-START)/100
700 NEXT I
710 REM*****
720 REM
730 REM PART(D):SETS UP TIME ARRAY FOR INTERPOLATED DATA.
740 REM
750 TIME(1)=0
760 J=1
770 FOR I=2 TO N
780 TIME(J+1)=AT(I)
790 TIME(J+2)=BT(I)
800 TIME(J+3)=CT(I)
810 TIME(J+4)=DT(I)
820 TIME(J+5)=ET(I)
830 TIME(J+6)=FT(I)
840 TIME(J+7)=GT(I)
850 TIME(J+8)=HT(I)
860 J=J+8
870 NEXT I
880 NN=J
890 REM*****
900 REM
910 REM PART(E):INTERPOLATES "FIRST" DATA POINTS.
920 REM
930 AN(1)=A(1):BN(1)=B(1):CN(1)=C(1):DN(1)=D(1):EN(1)=E(1):FW(1)=F(1):GN(1)=G(1):HN(1)=H(1)
940 BN(2)=((B(2)-B(1))*(TIME(2)-BT(1))/(BT(2)-BT(1)))+B(1)
950 CN(2)=((C(2)-C(1))*(TIME(2)-CT(1))/(CT(2)-CT(1)))+C(1)
960 DN(2)=((D(2)-D(1))*(TIME(2)-DT(1))/(DT(2)-DT(1)))+D(1)
970 EN(2)=((E(2)-E(1))*(TIME(2)-ET(1))/(ET(2)-ET(1)))+E(1)
980 BN(3)=((B(2)-B(1))*(TIME(3)-BT(1))/(BT(2)-BT(1)))+B(1)
990 DN(3)=((D(2)-D(1))*(TIME(3)-DT(1))/(DT(2)-DT(1)))+D(1)
1000 EN(3)=((E(2)-E(1))*(TIME(3)-ET(1))/(ET(2)-ET(1)))+E(1)
1010 EN(4)=((E(2)-E(1))*(TIME(4)-ET(1))/(ET(2)-ET(1)))+E(1)
1020 EN(5)=((E(2)-E(1))*(TIME(5)-ET(1))/(ET(2)-ET(1)))+E(1)
1030 FW(2)=((F(2)-F(1))*(TIME(2)-FT(1))/(FT(2)-FT(1)))+F(1)
1040 FW(3)=((F(2)-F(1))*(TIME(3)-FT(1))/(FT(2)-FT(1)))+F(1)
1050 FW(4)=((F(2)-F(1))*(TIME(4)-FT(1))/(FT(2)-FT(1)))+F(1)
1060 FW(5)=((F(2)-F(1))*(TIME(5)-FT(1))/(FT(2)-FT(1)))+F(1)
1070 FW(6)=((F(2)-F(1))*(TIME(6)-FT(1))/(FT(2)-FT(1)))+F(1)
1080 GN(2)=((G(2)-G(1))*(TIME(2)-GT(1))/(GT(2)-GT(1)))+G(1)
1090 GN(3)=((G(2)-G(1))*(TIME(3)-GT(1))/(GT(2)-GT(1)))+G(1)
1100 GN(4)=((G(2)-G(1))*(TIME(4)-GT(1))/(GT(2)-GT(1)))+G(1)
1110 GN(5)=((G(2)-G(1))*(TIME(5)-GT(1))/(GT(2)-GT(1)))+G(1)
1120 GN(6)=((G(2)-G(1))*(TIME(6)-GT(1))/(GT(2)-GT(1)))+G(1)
1130 GN(7)=((G(2)-G(1))*(TIME(7)-GT(1))/(GT(2)-GT(1)))+G(1)
1140 HN(2)=((H(2)-H(1))*(TIME(2)-HT(1))/(HT(2)-HT(1)))+H(1)
1150 HN(3)=((H(2)-H(1))*(TIME(3)-HT(1))/(HT(2)-HT(1)))+H(1)

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1170 HN(4)=((H(2)-H(1))*(TIME(4)-HT(1))/(HT(2)-HT(1)))+H(1)
1180 HN(5)=((H(2)-H(1))*(TIME(5)-HT(1))/(HT(2)-HT(1)))+H(1)
1190 HN(6)=((H(2)-H(1))*(TIME(6)-HT(1))/(HT(2)-HT(1)))+H(1)
1200 HN(7)=((H(2)-H(1))*(TIME(7)-HT(1))/(HT(2)-HT(1)))+H(1)
1210 HN(8)=((H(2)-H(1))*(TIME(8)-HT(1))/(HT(2)-HT(1)))+H(1)
1220 REM*****
1230 REM
1240 REM  PART(F):DEFINES POSITION OF REAL DATA POINTS IN
1250 REM  INTERPOLATED FILE.
1260 REM
1270 F=2
1280 FOR I=2 TO N
1290 AN(F)=A(I)
1300 BN(F+1)=B(I)
1310 CN(F+2)=C(I)
1320 DN(F+3)=D(I)
1330 EN(F+4)=E(I)
1340 FW(F+5)=F(I)
1350 GN(F+6)=G(I)
1360 HN(F+7)=H(I)
1370 F=F+8
1380 NEXT I
1390 REM*****
1400 REM
1410 REM  PART(G):INTERPOLATES "BULK" DATA POINTS.
1420 REM
1430 J=2
1440 FOR I=2 TO (N-1)
1450 FOR F=1 TO 7
1460 AN(J+F)=((A(I+1)-A(I))*(TIME(J+F)-AT(I))/(AT(I+1)-AT(I)))+A(I)
1470 NEXT F
1480 FOR F=2 TO 8
1490 BN(J+F)=((B(I+1)-B(I))*(TIME(J+F)-BT(I))/(BT(I+1)-BT(I)))+B(I)
1500 NEXT F
1510 FOR F=3 TO 9
1520 CN(J+F)=((C(I+1)-C(I))*(TIME(J+F)-CT(I))/(CT(I+1)-CT(I)))+C(I)
1530 NEXT F
1540 FOR F=4 TO 10
1550 DN(J+F)=((D(I+1)-D(I))*(TIME(J+F)-DT(I))/(DT(I+1)-DT(I)))+D(I)
1560 NEXT F
1570 FOR F=5 TO 11
1580 EN(J+F)=((E(I+1)-E(I))*(TIME(J+F)-ET(I))/(ET(I+1)-ET(I)))+E(I)
1590 NEXT F
1600 FOR F=6 TO 12
1610 FW(J+F)=((F(I+1)-F(I))*(TIME(J+F)-FT(I))/(FT(I+1)-FT(I)))+F(I)
1620 NEXT F
1630 FOR F=7 TO 13
1640 GN(J+F)=((G(I+1)-G(I))*(TIME(J+F)-GT(I))/(GT(I+1)-GT(I)))+G(I)
1650 NEXT F
1660 FOR F=8 TO 14
1670 HN(J+F)=((H(I+1)-H(I))*(TIME(J+F)-HT(I))/(HT(I+1)-HT(I)))+H(I)
1680 NEXT F
1690 J=J+8
1700 NEXT I
1710 REM*****
1720 REM
1730 REM  PART(H):INTERPOLATES "LAST" DATA POINTS.
1740 REM

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1750 DEF FNA(Z)=(A(N)-A(N-1))*(TIME(NN-Z)-AT(N-1))/(AT(N)-AT(N-1))+A(N-1)
1760 DEF FNB(Z)=(B(N)-B(N-1))*(TIME(NN-Z)-BT(N-1))/(BT(N)-BT(N-1))+B(N-1)
1770 DEF FNC(Z)=(C(N)-C(N-1))*(TIME(NN-Z)-CT(N-1))/(CT(N)-CT(N-1))+C(N-1)
1780 DEF FND(Z)=(D(N)-D(N-1))*(TIME(NN-Z)-DT(N-1))/(DT(N)-DT(N-1))+D(N-1)
1790 DEF FNE(Z)=(E(N)-E(N-1))*(TIME(NN-Z)-ET(N-1))/(ET(N)-ET(N-1))+E(N-1)
1800 DEF FNF(Z)=(F(N)-F(N-1))*(TIME(NN-Z)-FT(N-1))/(FT(N)-FT(N-1))+F(N-1)
1810 DEF FNG(Z)=(G(N)-G(N-1))*(TIME(NN-Z)-GT(N-1))/(GT(N)-GT(N-1))+G(N-1)
1820 AN(NN-6)=FNA(6)
1830 AN(NN-5)=FNA(5)
1840 AN(NN-4)=FNA(4)
1850 AN(NN-3)=FNA(3)
1860 AN(NN-2)=FNA(2)
1870 AN(NN-1)=FNA(1)
1880 AN(NN)=FNA(0)
1890 BN(NN-5)=FNB(5)
1900 BN(NN-4)=FNB(4)
1910 BN(NN-3)=FNB(3)
1920 BN(NN-2)=FNB(2)
1930 BN(NN-1)=FNB(1)
1940 BN(NN)=FNB(0)
1950 CN(NN-4)=FNC(4)
1960 CN(NN-3)=FNC(3)
1970 CN(NN-2)=FNC(2)
1980 CN(NN-1)=FNC(1)
1990 CN(NN)=FNC(0)
2000 DN(NN-3)=FND(3)
2010 DN(NN-2)=FND(2)
2020 DN(NN-1)=FND(1)
2030 DN(NN)=FND(0)
2040 EN(NN-2)=FNE(2)
2050 EN(NN-1)=FNE(1)
2060 EN(NN)=FNE(0)
2070 FW(NN-1)=FNF(1)
2080 FW(NN)=FNF(0)
2090 GN(NN)=FNG(0)
2100 REM*****
2110 REM
2120 REM PART(1):SUBROUTINE TO PRINT NON-INTERPOLATED DATA.
2130 REM
2140 PRINTER 4,4
2150 LPRINT CHR$(31)
2160 INPUT"NON-INTERPOLATED PK.HTS. LIST":B$
2170 IF B$="Y" THEN GOSUB 2190
2180 GOTO 2460
2190 INPUT"PRINT WHICH ROWS":M1,M2
2200 IF M1<1 THEN M1=1
2210 IF M2>N THEN M2=N
2220 IF M2<=M1 THEN GOTO 2190
2230 LPRINT TAB(5);"NON-INTERPOLATED PEAK HEIGHTS"
2240 LPRINT:LPRINT TAB(10);"FILENAME=":A$
2250 LPRINT:LPRINT:LPRINT CHR$(30)
2260 LPRINT TAB(10);"(TEMP=":TEMP;"C PRESS=":PRES;" CYCLE TIME=":SCAN;"S TSTART=":START/100;"S)"
2270 LPRINT:LPRINT CHR$(29)
2280 LPRINT TAB(5);"CH.1":TAB(22);"CH.2":TAB(33);"CH.3":TAB(54);"CH.4":
2290 LPRINT TAB(70);"CH.5":TAB(85);"CH.6":TAB(102);"CH.7":TAB(116);"CH.8"
2300 LPRINT
2310 LPRINT "(BL)":TAB(5):-S1:TAB(21):-S2:TAB(37):-S3:TAB(53):-S4:
2320 LPRINT TAB(69):-S5:TAB(85):-S6:TAB(101):-S7:TAB(117):-S8

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2330 LPRINT
2340 FOR I=M1 TO M2
2350 LPRINT A(I);TAB(8);AT(I);TAB(16);B(I);TAB(24);BT(I);TAB(32);C(I);TAB(40);CT(I);
2360 LPRINT TAB(48);D(I);TAB(56);DT(I);TAB(64);E(I);TAB(72);ET(I);TAB(80);F(I);TAB(88);
2370 LPRINT FT(I);TAB(96);G(I);TAB(104);GT(I);TAB(112);H(I);TAB(120);HT(I)
2380 NEXT I
2390 LPRINT:LPRINT"NUMBER OF ROWS PRINTED=";(M2-M1)+1,"TOTAL NUMBER OF ROWS=";N
2400 LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT CHR$(31)
2410 RETURN
2420 REM*****
2430 REM
2440 REM PART(J):SUBROUTINE TO PRINT INTERPOLATED DATA.
2450 REM
2460 INPUT"INTERPOLATED PK.HTS. LIST";B$
2470 IF B$="Y" THEN GOSUB 2490
2480 GOTO 2770
2490 INPUT"PRINT WHICH ROWS";K1,K2
2500 IF K1<1 THEN K1=1
2510 IF K2>NN THEN K2=NN
2520 IF K2<=K1 THEN GOTO 2490
2530 LPRINT TAB(7);"INTERPOLATED PEAK HEIGHTS"
2540 LPRINT:LPRINT TAB(10);"FILENAME=";A$
2550 LPRINT:LPRINT:LPRINT CHR$(30)
2560 LPRINT TAB(10);"(TEMP=";TEMP;"C PRESS=";PRES;" CYCLE TIME=";SCAN;"S TSTART=";START/100"S)"
2570 LPRINT:LPRINT:LPRINT CHR$(29)
2580 LPRINT TAB(5);"TIME";TAB(19);"CH.1";TAB(33);"CH.2";TAB(47);"CH.3";TAB(61);"CH.4";
2590 LPRINT TAB(75);"CH.5";TAB(89);"CH.6";TAB(103);"CH.7";TAB(117);"CH.8"
2600 LPRINT
2610 LPRINT TAB(5);"(BL)";TAB(19);"-S1";TAB(33);"-S2";TAB(47);"-S3";TAB(61);"-S4";
2620 LPRINT TAB(75);"-S5";TAB(89);"-S6";TAB(103);"-S7";TAB(117);"-S8"
2630 LPRINT
2640 INPUT"EVERY 'X' th. ROW";RW
2650 FOR I=K1 TO K2 STEP RW
2660 LPRINT TAB(5);TIME(I);TAB(19);AN(I);TAB(33);BN(I);TAB(47);CN(I);TAB(61);DN(I);
2670 LPRINT TAB(75);EN(I);TAB(89);FW(I);TAB(103);GN(I);TAB(117);HN(I)
2680 NEXT I
2690 LPRINT:LPRINT"NUMBER OF ROWS PRINTED=";(K2-K1)+1,"TOTAL NUMBER OF ROWS=";NN
2700 LPRINT"(EVERY"RW"th. ROW)"
2710 LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT CHR$(31)
2720 RETURN
2730 REM*****
2740 REM
2750 REM PART(K):CORRECTS DATA FOR CRACKING PATTERN.
2760 REM
2770 INPUT"DO YOU REQUIRE CORR?";B$
2780 IF B$(0)"Y" THEN GOTO 3400
2790 FOR I=1 TO 8
2800 L(I)=1
2810 FOR J=1 TO 8
2820 RR(I,J)=0
2830 NEXT J
2840 NEXT I
2850 INPUT"CORRECT HOW MANY CHANNELS";M
2860 M=M+0.1:M=INT(M)
2870 IF M<1 GOTO 2850
2880 IF M>7 GOTO 2850
2890 FOR I=1 TO M
2900 ?:"CORRECTION NUMBER";I

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2910 ?"-----"
2920 INPUT"CHANNEL TO BE CORRECTED":C
2930 C=C+0.1:C=INT(C)
2940 IF C<1 THEN GOTO 2920
2950 IF C>8 THEN GOTO 2920
2960 INPUT"GAIN=":L(C)
2970 INPUT"CHANNEL TO BE USED":S
2980 S=S+0.1:S=INT(S)
2990 IF S<1 THEN GOTO 2970
3000 IF S>8 THEN GOTO 2970
3010 IF S=C THEN GOTO 2970
3020 INPUT"GAIN=":L(S)
3030 INPUT"CORRECTION FACTOR=":RR(C,S)
3040 NEXT I
3050 FOR I=1 TO 8
3060 FOR J=1 TO 8
3070 X(I,J)=RR(I,J)*L(I)/L(J)
3080 NEXT J
3090 NEXT I
3100 FOR I=1 TO NN
3110 AN(I-1)=AN(I)-X(1,2)*BN(I)-X(1,3)*CN(I)-X(1,4)*DN(I)-X(1,5)*EN(I)-X(1,6)*FW(I)-X(1,7)*GN(I)-X(1,8)*HN(I)
3120 BN(I-1)=BN(I)-X(2,1)*AN(I)-X(2,3)*CN(I)-X(2,4)*DN(I)-X(2,5)*EN(I)-X(2,6)*FW(I)-X(2,7)*GN(I)-X(2,8)*HN(I)
3130 CN(I-1)=CN(I)-X(3,1)*AN(I)-X(3,2)*BN(I)-X(3,4)*DN(I)-X(3,5)*EN(I)-X(3,6)*FW(I)-X(3,7)*GN(I)-X(3,8)*HN(I)
3140 DN(I-1)=DN(I)-X(4,1)*AN(I)-X(4,2)*BN(I)-X(4,3)*CN(I)-X(4,5)*EN(I)-X(4,6)*FW(I)-X(4,7)*GN(I)-X(4,8)*HN(I)
3150 EN(I-1)=EN(I)-X(5,1)*AN(I)-X(5,2)*BN(I)-X(5,3)*CN(I)-X(5,4)*DN(I)-X(5,6)*FW(I)-X(5,7)*GN(I)-X(5,8)*HN(I)
3160 FW(I-1)=FW(I)-X(6,1)*AN(I)-X(6,2)*BN(I)-X(6,3)*CN(I)-X(6,4)*DN(I)-X(6,5)*EN(I)-X(6,7)*GN(I)-X(6,8)*HN(I)
3170 GN(I-1)=GN(I)-X(7,1)*AN(I)-X(7,2)*BN(I)-X(7,3)*CN(I)-X(7,4)*DN(I)-X(7,5)*EN(I)-X(7,6)*FW(I)-X(7,8)*HN(I)
3180 HN(I-1)=HN(I)-X(8,1)*AN(I)-X(8,2)*BN(I)-X(8,3)*CN(I)-X(8,4)*DN(I)-X(8,5)*EN(I)-X(8,6)*FW(I)-X(8,7)*GN(I)
3190 NEXT I
3200 FOR I=(NN-1) TO 0 STEP (-1)
3210 AN(I+1)=AN(I)
3220 BN(I+1)=BN(I)
3230 CN(I+1)=CN(I)
3240 DN(I+1)=DN(I)
3250 EN(I+1)=EN(I)
3260 FW(I+1)=FW(I)
3270 GN(I+1)=GN(I)
3280 HN(I+1)=HN(I)
3290 NEXT I
3300 ?
3310 INPUT"DO YOU REQUIRE FURTHER CORRECTION":B$
3320 IF B$="Y" THEN GOTO 2790
3330 INPUT"CORR-INTERPOLATED PK.HTS. LIST":B$
3340 IF B$="Y" THEN LPRINT TAB(13):"(CORRECTED)":GOSUB 2450
3350 REM*****
3360 REM
3370 REM PART(L):SAVES INTERPOLATED/CORRECTED DATA UNDER A
3380 REM SEPARATE FILENAME.
3390 REM
3400 INPUT"SAVE HOW MANY CHANNELS":M
3410 M=M+0.1:M=INT(M)
3420 IF M<0 THEN GOTO 3400
3430 IF M>8 THEN GOTO 3400
3440 IF M=0 THEN GOTO 3730
3450 FOR I=1 TO M
3460 ?:"SAVE CHANNEL":I
3470 ?"-----"
3480 INPUT"CHANNEL NUMBER=":CH

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3490 CH=CH+0.1:CH=INT(CH)
3500 IF CH>8 THEN GOTO 3480
3510 IF CH<1 THEN GOTO 3480
3520 INPUT"FILENAME=":Z$
3530 CREATE#10,Z$
3540 QUOTE#10,34
3550 PRINT#10,TEMP,PRES,SCAN
3560 FOR J=1 TO NN-1
3570 IF CH=1 THEN PRINT#10,-AN(J)
3580 IF CH=2 THEN PRINT#10,-BN(J)
3590 IF CH=3 THEN PRINT#10,-CN(J)
3600 IF CH=4 THEN PRINT#10,-DN(J)
3610 IF CH=5 THEN PRINT#10,-EN(J)
3620 IF CH=6 THEN PRINT#10,-FW(J)
3630 IF CH=7 THEN PRINT#10,-GN(J)
3640 IF CH=8 THEN PRINT#10,-HN(J)
3650 PRINT#10,TIME(J)*100
3660 NEXT J
3670 CLOSE#10
3680 NEXT I
3690 REM*****
3700 REM
3710 REM  PART(M):PRINTS ANY DATA FILE.
3720 REM
3730 ?
3740 INPUT"DO YOU REQUIRE PRINT":B$
3750 IF B$() "Y" THEN GOTO 3940
3760 PRINTER 4,4:LPRT CHR$(31)
3770 INPUT"FILENAME=":A$
3780 IF LOOKUP(A$)()>0 THEN GOTO 3800
3790 GOTO 3760
3800 OPEN#10,A$
3810 INPUT#10,TEMP,PRES,SCAN
3820 N=0
3830 FOR I=1 TO 1000000
3840 INPUT#10,A(I),AT(I),B(I),BT(I),C(I),CT(I),D(I),DT(I),E(I),ET(I),F(I),FT(I),G(I),GT(I),H(I),HT(I)
3850 N=N+1
3860 IF I=71 THEN GOTO 3890
3870 ON EOF GOTO 3890
3880 NEXT I
3890 S1=0:S2=0:S3=0:S4=0:S5=0:S6=0:S7=0:S8=0
3900 START=0
3910 GOSUB 2190
3920 INPUT"PRINT ANY MORE FILES":B$
3930 IF B$="Y" THEN GOTO 3760
3940 STOP

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10 REM*****
20 REM
30 REM FTLMB
40 REM *****
50 REM
60 REM PROG. TO DERIVE A0,K1 AND K2 BY AN ITERATIVE METHOD.
70 REM
80 REM*****
90 REM
100 REM PART(A):READS IN DATA,CHOOSES CHANNELS,DEDUCTS BASELINES,
110 REM SETS START TIME AND DEFINES LIMITS OF ITERATION.
120 REM
130 CLEAR
140 CALL"RESOLUTION",0,2
150 GRAPH 1
160 DIM T(800),P(800),CH(8),Q(800),A(5,5),X(5)
170 ??:?
180 INPUT"FILENAME":A$
190 IF LOOKUP(A$)()0 THEN 210
200 GOTO 180
210 OPEN#10,A$
220 INPUT#10,TT,PP,SS
230 N=0
240 FOR I=1 TO 1000000 STEP 8
250 INPUT#10,P(I),T(I),P(I+1),T(I+1),P(I+2),T(I+2),P(I+3),T(I+3)
260 INPUT#10,P(I+4),T(I+4),P(I+5),T(I+5),P(I+6),T(I+6),P(I+7),T(I+7)
270 N=N+8
280 ON EOF GOTO 300
290 NEXT I
300 FOR I=1 TO N
310 T(I)=T(I)/100
320 NEXT I
330 FOR I=9 TO N STEP 8
340 FOR J=1 TO 8
350 Q=T(I+J-1)-T(I+J-9)
360 IF Q>0 GOTO 350
370 IF Q<-2 THEN T(I+J-1)=T(I+J-1)+250:GOTO 350
380 T(I+J-1)=T(I+J-1)+1
390 NEXT J
400 NEXT I
410 INPUT"HOW MANY CHANNELS":M
420 IF M<1 GOTO 410
430 IF M>8 GOTO 410
440 IF M=8 GOTO 590
450 FOR K=1 TO M
460 ?"CHANNEL("K")":INPUT"IS":CH(K)
470 IF CH(K)<1 GOTO 460
480 IF CH(K)>8 GOTO 460
490 NEXT K
500 SUM=1:ACC=1
510 FOR I=1 TO N
520 FOR K=1 TO M
530 IF SUM=CH(K) THEN P(ACC)=P(I):T(ACC)=T(I):ACC=ACC+1
540 NEXT K
550 SUM=SUM+1
560 IF SUM=9 THEN SUM=1
570 NEXT I
580 N=ACC-1

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590 FOR I=1 TO N
600 P(I)=(-1)*P(I)
610 NEXT I
620 A=1:B=N
630 GOSUB 1080
640 ?"YOU MUST DEFINE START OF REACTION"
650 INPUT"IS THIS PLOT OK(Y/N)";C$
660 IF C$="Y" GOTO 710
670 INPUT"PLOT WHICH POINTS";A,B
680 GOSUB 990
690 IF E=1 GOTO 670
700 GOTO 630
710 GOSUB 1310
720 S1=0:S2=0
730 FOR I=1 TO N
740 IF T(I)>G GOTO 780
750 S1=S1+P(I)
760 S2=S2+1
770 NEXT I
780 BASE=S1/S2
790 J=1
800 FOR I=(S2+1) TO N
810 P(J)=P(I)-BASE
820 T(J)=T(I)-G
830 J=J+1
840 NEXT I
850 N=N-S2:A=1:B=N
860 GOSUB 1080
870 ?"AVERAGE BL="(-1)*BASE",NO. OF BL="S2
880 ?"TSTART="G"S"
890 INPUT"PRESS RETURN TO CONTINUE";B$
900 P1=T(A)
910 GOSUB 2670
920 A=1:B=N
930 GOSUB 1080
940 GOTO 1540
950 REM*****
960 REM
970 REM  PART(B):SUBROUTINE TO CHECK PLOTTING LIMITS.
980 REM
990 E=2
1000 IF A<=0 THEN E=1
1010 IF B>N THEN E=1
1020 IF A>B THEN E=1
1030 RETURN
1040 REM*****
1050 REM
1060 REM  PART(C):SUBROUTINE TO PLOT PEAK HEIGHT VS. TIME.
1070 REM
1080 MAX=-1E10
1090 MIN=+1E10
1100 FOR I=A TO B
1110 IF P(I)>MAX THEN MAX=P(I)
1120 IF P(I)<MIN THEN MIN=P(I)
1130 NEXT I
1140 MAX=MAX*1.05
1150 TMAX=T(B)-T(A)
1160 CALL"RESOLUTION",0.2

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```

1170 CALL "PLOT",318,0,1
1180 CALL "LINE",0,0
1190 CALL "LINE",0,191
1200 FOR I=A TO B
1210 X=318*(T(I)-T(A))/TMAX
1220 Y=191*(P(I)-MIN)/(MAX-MIN)
1230 CALL "PLOT",X,Y,3
1240 NEXT I
1250 ?:"A TOTAL OF"(B-A)+1"POINTS"
1260 RETURN
1270 REM*****
1280 REM
1290 REM  PART(D):SUBROUTINE TO MEASURE TIME SCALE.
1300 REM
1310 C=159
1320 CALL "PLOT",C,0,-3
1330 CALL "LINE",C,191,-3
1340 C=(C/318)*(T(B)-T(A))+T(A)
1350 ?:"TIME="G
1360 INPUT "MOVE CURSOR(L/R),OR STOP":B#
1370 IF B#="L" THEN LR=-1:GOTO 1400
1380 IF B#="R" THEN LR=+1:GOTO 1400
1390 GOTO 1470
1400 INPUT "BY HOW MANY":DIST
1410 CALL "PLOT",C,0,-3
1420 CALL "LINE",C,191,-3
1430 C=C+LR*DIST
1440 IF C<0 GOTO 1310
1450 IF C>318 GOTO 1310
1460 GOTO 1320
1470 CALL "PLOT",C,0,-3
1480 CALL "LINE",C,191,-3
1490 RETURN
1500 REM*****
1510 REM
1520 REM  PART(E):ITERATION PROCEDURE.
1530 REM
1540 ?:"?:"
1550 INPUT "GUESSED A0":A0
1560 INPUT "GUESSED K1":K1
1570 INPUT "GUESSED K2":K2
1580 INPUT "SHALLOWING FACTOR=":SF
1590 IF SF<1 THEN GOTO 1580
1600 ?:"?:"
1610 GRAPH 0
1620 FOR I=2 TO (N-1)
1630 S1=0:S2=0:S3=0:S4=0:S5=0:S6=0:S7=0
1640 FOR J=(I-1) TO (I+1)
1650 S1=S1+T(J)+4
1660 S2=S2+T(J)+3
1670 S3=S3+T(J)+2
1680 S4=S4+T(J)
1690 S5=S5+(T(J)+2)*P(J)
1700 S6=S6+T(J)*P(J)
1710 S7=S7+P(J)
1720 NEXT J
1730 REM*****
1740 REM

```

```

1750 REM USE "SOLVE2" TO FIND A,B,C
1760 REM IN EGN. OF PARABOLA.
1770 REM
1780 A(1,1)=S1:A(1,2)=S2:A(1,3)=S3:A(1,4)=S5
1790 A(2,1)=S2:A(2,2)=S3:A(2,3)=S4:A(2,4)=S6
1800 A(3,1)=S3:A(3,2)=S4:A(3,3)=S5:A(3,4)=S7
1810 GOSUB 2230
1820 A=X(1):B=X(2):C=X(3)
1830 REM*****
1840 QD(I)=2*A*T(I)+B
1850 NEXT I
1860 ON BREAK GOTO 2450
1870 SS=0
1880 A1=0:A2=0:A3=0:A4=0:A5=0:A6=0:A7=0:A8=0:A9=0
1890 FOR I=2 TO (N-1)
1900 QD=K1*A0*EXP(-K1*T(I))-K2*P(I)
1910 DQ=QD(I)-QD
1920 SS=SS+DQ*2
1930 D1=K1*EXP(-K1*T(I))
1940 D2=A0*(EXP(-K1*T(I)))*(1-K1*T(I))
1950 D3=-P(I)
1960 A1=A1+D1*DQ
1970 A2=A2+D1*2
1980 A3=A3+D1*D2
1990 A4=A4+D1*D3
2000 A5=A5+D2*DQ
2010 A6=A6+D2*2
2020 A7=A7+D2*D3
2030 A8=A8+D3*DQ
2040 A9=A9+D3*2
2050 NEXT I
2060 Z1=A0*100:Z1=INT(Z1):Z1=Z1/100
2070 Z2=K1*1000:Z2=INT(Z2):Z2=Z2/1000
2080 Z3=K2*1000:Z3=INT(Z3):Z3=Z3/1000
2090 ?Z1;TAB(11);Z2;TAB(20);Z3;TAB(27);SS
2100 REM*****
2110 REM
2120 REM USE "SOLVE2" TO FIND
2130 REM DA,DK1,DK2.
2140 REM
2150 A(1,1)=A2:A(1,2)=A3:A(1,3)=A4:A(1,4)=A1
2160 A(2,1)=A3:A(2,2)=A6:A(2,3)=A7:A(2,4)=A5
2170 A(3,1)=A4:A(3,2)=A7:A(3,3)=A9:A(3,4)=A8
2180 GOSUB 2230
2190 DA=X(1):R1=X(2):R2=X(3)
2200 REM*****
2210 A0=A2+DA/SF:K1=K1+R1/SF:K2=K2+R2/SF
2220 GOTO 1870
2230 REM*****
2240 REM
2250 REM PART(F):SUBROUTINE "SOLVE2"-
2260 REM SOLVES A SET OF THREE
2270 REM SIMULTANEOUS EQNS. BY
2280 REM THE CONVENTIONAL
2290 REM ALGEBRAIC METHOD.
2300 REM
2310 F1=A(1,4)*A(2,1)-A(2,4)*A(1,1)
2320 F2=A(2,4)*A(3,1)-A(3,4)*A(2,1)

```



```

2330 F3=A(1,2)*A(2,1)-A(2,2)*A(1,1)
2340 F4=A(2,2)*A(3,1)-A(3,2)*A(2,1)
2350 F5=A(1,3)*A(2,1)-A(2,3)*A(1,1)
2360 F6=A(2,3)*A(3,1)-A(3,3)*A(2,1)
2370 X(3)=(F1*F4-F2*F3)/(F5*F4-F6*F3)
2380 X(2)=(F1-X(3)*F5)/F3
2390 X(1)=(A(2,4)-X(2)*A(2,2)-X(3)*A(2,3))/A(2,1)
2400 RETURN
2410 REM*****
2420 REM
2430 REM PART(G):PLOT FINAL PARAMETERS.
2440 REM
2450 ?CHR$(12):?CHR$(29):GRAPH 1
2460 ?"A0="A0
2470 ?"K1="K1
2480 ?"K2="K2
2490 V1=1/(K2-K1)
2500 V2=1/(K1-K2)
2510 V3=A0*K1
2520 FOR I=1 TO N
2530 P(I)=V3*((V1*EXP(-K1*T(I)))+(V2*EXP(-K2*T(I))))
2540 X=318*(T(I)-P1)/TMAX
2550 Y=191*(P(I)-MIN)/(MAX-MIN)
2560 CALL"PLOT",X,Y,2
2570 NEXT I
2580 INPUT"PRESS RETURN TO STOP";B$
2590 ?":?:?:CALL"RESOLUTION",0,2:GRAPH 0:STOP
2600 REM*****
2610 REM
2620 REM PART(H):SUBROUTINE TO PLOT LOG(PEAK HEIGHT) VS. TIME.
2630 REM LOG PLOT LEADS TO TIME OF
2640 REM OF DEVIATION FROM IDEALITY
2650 REM OF REACTION PROFILE.
2660 REM
2670 ?CHR$(12):?CHR$(29)
2680 ?"LOG PLOT-"
2690 INPUT"PLOT WHICH POINTS":A,B
2700 IF A<1 THEN A=1
2710 IF B>N THEN B=N
2720 IF (B-A)<1 THEN GOTO 2690
2730 MAX=-1E10:MIN=+1E10
2740 FOR I=A TO B
2750 IF P(I)=0 THEN GOTO 2780
2760 IF LOG(P(I))>MAX THEN MAX=LOG(P(I))
2770 IF LOG(P(I))<MIN THEN MIN=LOG(P(I))
2780 NEXT I
2790 TMAX=T(B)-T(A)
2800 CALL"RESOLUTION",0,2
2810 CALL"PLOT",318,0,1
2820 CALL"LINE",0,0
2830 CALL"LINE",0,191
2840 FOR I=A TO B
2850 IF P(I)=0 THEN GOTO 2880
2860 X=318*(T(I)-T(A))/TMAX
2870 Y=191*(LOG(P(I))-MIN)/(MAX-MIN)
2880 CALL"PLOT",X,Y,3
2890 NEXT I
2900 INPUT"LEAST SQUARES FIT";B$

```

```

2910 IF B#="Y" THEN GOTO 2950
2920 INPUT"ANOTHER PLOT";B#
2930 IF B#="Y" THEN GOTO 2970
2940 GOTO 3260
2950 INPUT"BETWEEN WHICH POINTS";A1,B1
2960 IF A1<A THEN GOTO 2950
2970 IF B1>B THEN GOTO 2950
2980 IF (B1-A1)<1 THEN GOTO 2950
2990 T1=0:T2=0:T3=0:T4=0:T5=0
3000 FOR I=A1 TO B1
3010 IF P(I)=0 THEN GOTO 3070
3020 IF P(I)=0 THEN T5=T5+1:GOTO 3070
3030 T1=T1+T(I)
3040 T2=T2+LOG(P(I))
3050 T3=T3+T(I)*LOG(P(I))
3060 T4=T4+T(I)*T(I)
3070 NEXT I
3080 N1=(B1-A1)+1-T5
3090 IF N1<2 THEN GOTO 2950
3100 T6=N1*T4-T1*T1
3110 GRAD=(N1*T3-T1*T2)/T6
3120 INCT=(T2*T4-T1*T3)/T6
3130 ?"GRAD=";GRAD
3140 ?"INCT=";EXP(INCT)
3150 L1=GRAD*T(A)+INCT
3160 L2=GRAD*T(B)+INCT
3170 L1=191*(L1-MIN)/(MAX-MIN)
3180 L2=191*(L2-MIN)/(MAX-MIN)
3190 CALL"PLOT",0,L1,-3
3200 CALL"LINE",318,L2,-3
3210 INPUT"TRY ANOTHER FIT";B#
3220 IF B#()="Y" THEN GOTO 2920
3230 CALL"PLOT",0,L1,-3
3240 CALL"LINE",318,L2,-3
3250 GOTO 2950
3260 ?CHR$(12):?CHR$(29)
3270 ?"YOU MUST DEFINE THE POINT OF DEVN."
3280 ?"FROM LINEARITY"
3290 INPUT"PRESS RETURN TO CONTINUE";B#
3300 GOSUB 1310
3310 FOR I=1 TO N
3320 IF T(I)>6 THEN N=(I-1):GOTO 3350
3330 N=N
3340 NEXT I
3350 RETURN

```

```

10 REM*****
20 REM
30 REM ORDER
40 REM *****
50 REM
60 REM PROG. TO MEASURE ORDER OF REACTANT DECOMPOSITION.
70 REM
80 REM*****
90 REM
100 REM PART(A):DIMENSIONS ARRAYS AND OPENS DATA FILE.
110 REM
120 ?CHR$(12)
130 ?CHR$(29)
140 CLEAR
150 ON BREAK GOTO 1000
160 ON ERR GOTO 1020
170 DIM PEAK(800),TIME(800),X(800),T(800),P(800)
180 INPUT"FILENAME";D$
190 IF LOOKUP(D$)() THEN 1320
200 GOTO 180
210 REM*****
220 REM
230 REM PART(B):ANALYSES DATA AND PLOTS APPROPRIATE FUNCTION
240 REM AGAINST TIME.
250 REM
260 ACC=1
270 FOR J=(1+Z) TO (NUMBER-Z)
280 I=J-Z:K=J+Z
290 D1=PEAK(I)-PEAK(J)
300 D2=PEAK(J)-PEAK(K)
310 DT=TIME(K)-TIME(I)
320 RP=1/PEAK(J)
330 X(J)=RP*((D1+D2)/DT)
340 IF X(J)=0 GOTO 390
350 X(J)=(1/X(J))+TIME(J)
360 X(ACC)=X(J)
370 TIME(ACC)=TIME(J)
380 ACC=ACC+1
390 NEXT J
400 ACC=ACC-1
410 ?"TOTAL NO. OF POINTS="ACC
420 INPUT"PLOT WHICH POINTS";N3,N4
430 IF N4)ACC THEN N4=ACC
440 IF N3<1 THEN N3=1
450 GOSUB 1940
460 MAX=-1E10:MIN=+1E10
470 FOR I=N3 TO N4
480 IF X(I)>MAX THEN MAX=X(I)
490 IF X(I)<MIN THEN MIN=X(I)
500 NEXT I
510 KX=315/(TIME(N4)-TIME(N3))
520 KY=150/(MAX-MIN)
530 FOR I=N3 TO N4
540 XX=(TIME(I)-TIME(N3))*KX
550 YY=(X(I)-MIN)*KY
560 CALL "PLOT",XX,YY,3
570 NEXT I
580 INPUT"REPLOT (Y/N)";A$

```

```

590 IF A$="Y" GOTO 410
600 REM*****
610 REM
620 REM  PART(C):LEAST SQUARES ANALYSIS OF PLOT LEADS TO
630 REM  DECOMPOSITION ORDER.
640 REM
650 S1=0:S2=0:S3=0:S4=0
660 FOR I=N3 TO N4
670 S1=S1+TIME(I)
680 S2=S2+X(I)
690 S3=S3+TIME(I)*X(I)
700 S4=S4+TIME(I)*TIME(I)
710 NEXT I
720 N=(N4-N3)+1
730 S5=N*S4-S1*S1
740 GRAD=(N*S3-S1*S2)/S5
750 INCT=(S2*S4-S1*S3)/S5
760 S6=0
770 FOR I=N3 TO N4
780 S7=GRAD*TIME(I)+INCT-X(I)
790 S6=S6+S7*S7
800 NEXT I
810 EG=SQR(N*S6/((N-2)*S5))
820 EI=SQR(S4*S6/((N-2)*S5))
830 ?"GRAD="GRAD#"EG
840 A=GRAD*TIME(N3)+INCT
850 B=GRAD*TIME(N4)+INCT
860 A=190*(A-MIN)/(MAX-MIN)
870 B=190*(B-MIN)/(MAX-MIN)
880 CALL "PLOT",0,A,1
890 CALL "LINE",315,B,1
900 REM*****
910 REM
920 REM  PART(D):ALLOWS ANALYSIS OF INDIVIDUAL SECTIONS OF PLOT.
930 REM
940 X1=0:X2=315:Y1=160:Y2=160
950 CALL "PLOT",X1,Y1,-2
960 CALL "LINE",X2,Y2,-2
970 INPUT "MOVE LINE L/R,U/D,N":A$,B$,N7
980 IF B$="U" GOTO 1040
990 IF B$="D" GOTO 1140
1000 INPUT "RELOT (Y/N)":A$
1010 IF A$="Y" THEN GOTO 410
1020 CALL "RESOLUTION",0,2:GRAPH 0:CHR$(12):END
1030 GOTO 970
1040 CALL "PLOT",X1,Y1,-2
1050 CALL "LINE",X2,Y2,-2
1060 IF A$="L" THEN Y1=Y1+N7:GOTO 1110
1070 IF A$="R" THEN Y2=Y2+N7:GOTO 1110
1080 ?"ERROR--Enter L or R again"
1090 INPUT A$
1100 GOTO 1060
1110 CALL "PLOT",X1,Y1,-2
1120 CALL "LINE",X2,Y2,-2
1130 GOTO 1230
1140 CALL "PLOT",X1,Y1,-2
1150 CALL "LINE",X2,Y2,-2
1160 IF A$="L" THEN Y1=Y1-N7:GOTO 1210

```

```

1170 IF A#="R" THEN Y2=Y2-N7:GOTO 1210
1180 ?"ERROR--Enter L or R again"
1190 INPUT A$
1200 GOTO 1150
1210 CALL "PLOT",X1,Y1,-2
1220 CALL "LINE",X2,Y2,-2
1230 Y3=(Y1/KY)+MIN:Y4=(Y2/KY)+MIN
1240 GRAD=(Y4-Y3)/(TIME(N4)-TIME(N3))
1250 ?"GRAD="GRAD
1260 GOTO 970
1270 REM*****
1280 REM
1290 REM PART(E):READS IN DATA,CHOOSES CHANNELS,
1300 REM DEDUCTS BASELINES AND SETS START TIME.
1310 REM
1320 OPEN#10,D$
1330 INPUT#10,TEMP,PRES,SCAN
1340 N=0
1350 FOR I=1 TO 1000000 STEP 8
1360 INPUT#10,P(I),T(I),P(I+1),T(I+1),P(I+2),T(I+2),P(I+3),T(I+3)
1370 INPUT#10,P(I+4),T(I+4),P(I+5),T(I+5),P(I+6),T(I+6),P(I+7),T(I+7)
1380 N=N+8
1390 ON EOF GOTO 1410
1400 NEXT I
1410 FOR I=1 TO N
1420 T(I)=T(I)/100
1430 P(I)=(-1)*P(I)
1440 NEXT I
1450 FOR I=9 TO N STEP 8
1460 FOR J=1 TO 8
1470 Q=T(I+J-1)-T(I+J-9)
1480 IF Q>0 GOTO 1510
1490 IF Q<-2 THEN T(I+J-1)=T(I+J-1)+250:GOTO 1470
1500 T(I+J-1)=T(I+J-1)+1
1510 NEXT J
1520 NEXT I
1530 TSTART=T(32)+(T(33)-T(32))/10
1540 INPUT"HOW MANY CHANNELS":M
1550 IF M<1 GOTO 1540
1560 IF M>8 GOTO 1540
1570 IF M=8 GOTO 1720
1580 FOR K=1 TO M
1590 ?"CHANNEL("K")":;INPUT"IS";CH(K)
1600 IF CH(K)<1 GOTO 1590
1610 IF CH(K)>8 GOTO 1590
1620 NEXT K
1630 SUM=1:ACC=1
1640 FOR I=1 TO N
1650 FOR K=1 TO M
1660 IF SUM=CH(K) THEN P(ACC)=P(I):T(ACC)=T(I):ACC=ACC+1
1670 NEXT K
1680 SUM=SUM+1
1690 IF SUM=9 THEN SUM=1
1700 NEXT I
1710 N=ACC-1
1720 S=0
1730 FOR I=1 TO N+4
1740 S=S+P(I)

```

```

1750 NEXT I
1760 S=S/(M*4)
1770 S1=1
1780 FOR I=(M*4+1) TO N
1790 P(S1)=P(I)-S
1800 T(S1)=T(I)-TSTART
1810 S1=S1+1
1820 NEXT I
1830 NUMBER=N-M*4
1840 INPUT"CONSIDER EVERY 'Xth.' POINT":Z
1850 FOR I=1 TO NUMBER
1860 PEAK(I)=P(I)
1870 TIME(I)=T(I)
1880 NEXT I
1890 GOTO 250
1900 REM*****
1910 REM
1920 REM  PART(F):SUBROUTINE TO DRAW AXES FOR PLOT.
1930 REM
1940 GRAPH1:CALL "RESOLUTION",0,2
1950 CALL "PLOT",315,0,2
1960 CALL "LINE",0,0
1970 CALL "LINE",0,191
1980 RETURN
1990 END

```

APPENDIX 3

SOURCES OF CHEMICALS

Chemiclene Treble-One	Grant & West
1,1-Dimethyl-1-silacyclobutane	Field Instruments Co. Ltd.
1,1,3,3-Tetramethyl-1,3-disilacyclobutane	(a) See Appendix 4 (b) Prof. J. Grobe Eduard Zintl-Institut für Anorganische Chemie der Technischen Hochschule Darmstadt F.R.G.
Vinyldimethylcarbinoxymethylsilane	Dr. C. L. Frye Dow Corning Corporation Midland Michigan U.S.A.
1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane and 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane	Prof. G. Fritz Institute of Inorganic Chemistry The University Karlsruhe F.R.G.
Methyltrimethylsilyl ether	ICN Pharmaceuticals Inc.
Chloropentamethyldisilane	Prof. M. Kumada Faculty of Engineering Kyoto University JAPAN
Trimethylchlorosilane and dimethylchlorosilane	Dow Corning (Europe) Barry South Wales
Dimethylmercury	Kodak
1-Methyl-1-vinyl-1-silacyclobutane	Prof. J. Grobe
3-Bromopropyne	Aldrich Chemical Co. Ltd.
1,1-Divinyl-1-silacyclobutane	Prof. J. Grobe

[Gifts of chemicals, received from the research groups listed above, are gratefully acknowledged.]

APPENDIX 4

PREPARATION OF 1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE

A sample of the disilacyclobutane was prepared by pyrolysing ca. 20 mmHg samples of 1,1-dimethyl-1-silacyclobutane in a seasoned Pyrex reaction vessel for 1½ hours at 740 K. The contents of the reaction vessel were then distilled into a storage vessel. Once sufficient material had been collected it was purified by preparative g.l.c.

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THE GAS KINETICS OF SOME THERMAL REACTIONS OF CYCLIC ORGANOSILANES

by Frank Timothy Lawrence

ABSTRACT

The work outlined in this thesis is largely concerned with the gas kinetics of the pyrolyses of four cyclic organosilicon compounds. Also described is a study of the reaction between 2-methyl-2-silapropene, a reactive intermediate of considerable current interest [1], and oxygen [2]. This last investigation was undertaken in connection with work on the oxidation of tetramethylsilane [3]. It provided much needed quantitative information on the reactions of silaalkenes.

A study of the pyrolysis of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane [4] enabled the reaction mechanism of the previously described [5] isomerisation of the same compound to be elucidated. The thermal decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was investigated to provide information regarding the above two studies.

The last section of the thesis is concerned with the thermal decomposition of two vinyl-substituted silacyclobutanes. The interest here was in the reactions of the silaalkenes produced: previous work [6,7] has suggested that both compounds yield silabutadienes which undergo reaction alternative to dimerisation. Another reason for this particular study was to see whether vinyl substitution at silicon enabled the site of initial ring cleavage to be the silicon-carbon bond (1,1-dimethyl-1-silacyclobutane decomposition proceeds via carbon-carbon bond rupture).

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