

GAS KINETIC STUDIES
ON SILANONES AND SILYLENES

A Thesis presented by

MICHAEL EDWARD DELF

for the degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF LEICESTER

Department of Chemistry
University of Leicester

September 1975

UMI Number: U419114

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U419114

Published by ProQuest LLC 2015. Copyright in the Dissertation held by the Author.
Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against
unauthorized copying under Title 17, United States Code.



ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346



THESIS
191889
13 11 75

x753030755

STATEMENT

The experimental work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester between September 1972 and June 1975.

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

September 1975

Signed Michael E. Delf

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my supervisor, Dr. Iain Davidson, for giving me the opportunity to work for a higher degree and for his unfailing help and valued guidance throughout all stages of my research.

I would like to thank Mr. Cliff Masters for the manufacture of the sampling-valve, Mr. Geoff Clemerson for continued maintenance of the mass spectrometer, Mrs. Ann Crane for tracing the diagrams and other members of the Department who have assisted me in the last three years. Many thanks also to my Mother for typing this thesis.

Finally, I am much indebted to Dow Corning (Barry) Limited for the award of a maintenance grant.

SUMMARY

This thesis describes work on short-lived gaseous intermediates in organosilicon chemistry. The first part of this thesis discusses experiments carried out to verify the existence of the intermediate species dimethylsilanone, Me_2SiO , containing a silicon-oxygen double bond, while the second part discusses the kinetics of the thermal decomposition of three chloromethyldisilanes to give silylenes and some of the insertion reactions of these silylenes.

Three types of experiment were undertaken to verify the existence of dimethylsilanone. Using octamethylcyclotetra-siloxane, $(\text{Me}_2\text{SiO})_4$, as a thermal source of Me_2SiO , co-pyrolyses of $(\text{Me}_2\text{SiO})_4$ with alkenes and dienes were carried out to observe any formation of cyclic adducts between the hydrocarbons and the intermediate, Me_2SiO . Pyrolyses of $(\text{Me}_2\text{SiO})_4$ with chloromonosilanes were also carried out to determine whether the intermediate, Me_2SiO , would insert into the silicon-chlorine bond or bonds in the chloromonosilanes, to give linear chloromethylsiloxanes. The formation of cyclic adducts and insertion products would provide good evidence for the independent existence of Me_2SiO .

Finally, co-pyrolyses of $(\text{Me}_2\text{SiO})_4$ with another cyclic siloxane, $(\text{MePhSiO})_3$, were undertaken to determine whether cyclic siloxanes containing both Me_2SiO and MePhSiO units would be formed. Again formation of these 'mixed' siloxanes would provide further evidence for the existence of Me_2SiO .

In the work on silylenes, in the second part of this thesis, the thermal decomposition of three chlorodisilanes was studied and the Arrhenius parameters determined in each case. The three chlorodisilanes were : pentamethylchlorodisilane, $\text{Me}_5\text{Si}_2\text{Cl}$; 1,1,2,2-tetrachloro-1,2-dimethyldisilane, $\text{Me}_2\text{Si}_2\text{Cl}_4$; and 1,1,2-trimethyl-1,2,2-trichlorodisilane, $\text{Me}_3\text{Si}_2\text{Cl}_3$.

Some of the insertion reactions of the silylenes generated were also studied, especially insertion into the silicon-hydrogen and silicon-chlorine bonds.

CONTENTS

	<u>Page</u>
Chapter 1 Introduction to work on Silanones	1
Chapter 2 Apparatus and Experimental Procedure for Work on Silanones	9
2.1 Samples Used	9
2.2. Description of Apparatus	10
2.3 Techniques and Methods used for Analysis of Reaction Products	21
2.4 Sealed Tube Technique	27
Chapter 3 Results and Discussion for the Work on Silanones	29
Part A Addition Reactions with π -Bonded and other Hydrocarbons	29
Part B Insertion Reactions of Me_2SiO	50
Part C Pyrolysis Reactions of cis-Trimethyl- triphenylcyclotrisiloxane	60
Chapter 4 Introduction to Silylene Work	70

		<u>Page</u>
Chapter 5	Experimental Procedure for Silylene Work	79
5.1	Samples Used	79
5.2	Description of Apparatus	79
5.3	Methods used for Mass Spectrometric Analysis of Gas Chromatograph Peaks	80
5.4	Quantitative Measurement of Gas Chromatographic Peak Areas	80
Chapter 6	Results and Discussion for the Work on Silylenes	82
6.1	Kinetic Results for the Thermal Decomposition of the Three Chlorodisilanes	82
6.2	Discussion of the Kinetic Results for the Pyrolyses of the Three Chlorodisilanes	87
6.3	Some Thermochemical Data obtained for Silylene Reactions	94
6.4	Insertion Reactions of Dimethyl- silylene, Me_2Si and Methylchloro- silylene, MeSiCl	97

	<u>Page</u>
Appendix 1 Preparation and Purification of Compounds	103
Appendix 2 Mass Spectral Data	107
Appendix 3 Full Kinetic Results for the Pyrolyses of the Chloro- disilanes	118
Appendix 4 Computer Programme	126
References.	128

CHAPTER ONE

INTRODUCTION TO WORK ON SILANONES

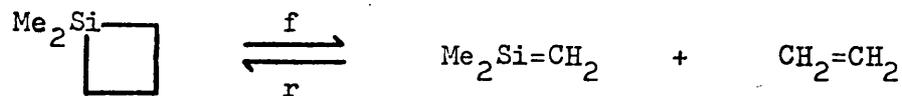
INTRODUCTION TO WORK ON SILANONES

Compounds containing $p_{\pi} - p_{\pi}$ bonds between two silicon atoms, or between silicon and another atom such as carbon, oxygen or nitrogen, were once thought to be non-existent. However, in the last ten years there has been much evidence to show that silicon can participate in $p_{\pi} - p_{\pi}$ bonding, and that molecules containing π -bonds to silicon do exist.¹ The chemistry of these intermediates has been reviewed recently.² The π -bonds in these molecules are weak and highly reactive, and therefore these molecules only exist as short-lived reaction intermediates.

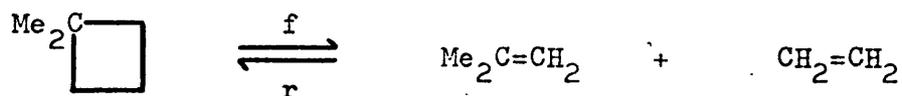
Estimations of the π -bond strength in $\text{Me}_2\text{Si}=\text{CH}_2$ and $\text{Me}_2\text{Si}=\text{O}$ have been made,^{3,4,5,6} and it appears that the strengths of the $\text{Si}=\text{CH}_2$ and $\text{Si}=\text{O}$ bonds are approximately half the strength of the π -bonds in olefins and ketones respectively. These low π -bond energies imply very reactive behaviour for silico-olefins and silanones in bimolecular reactions with other molecules.

Most of the evidence accumulated for the existence of $p_{\pi} - p_{\pi}$ bonding with silicon has been obtained from experiments concerning the $\text{Si}=\text{CH}_2$ bond. $\text{Me}_2\text{Si}=\text{CH}_2$ was first postulated as an intermediate in the thermal decomposition of 1,1-dimethyl-1-silacyclobutane by Flowers and Gusel'nikov,^{7,8} after previous identification of the reaction products as the disilacyclobutane and ethylene by Gusel'nikov and other Russian co-workers.^{9,10} The kinetics of the decomposition were measured and the intermediate $\text{Me}_2\text{Si}=\text{CH}_2$ was trapped out using water and ammonia.^{7,8}

Comparing Arrhenius parameters for the decomposition of silacyclobutanes and cyclobutanes :-



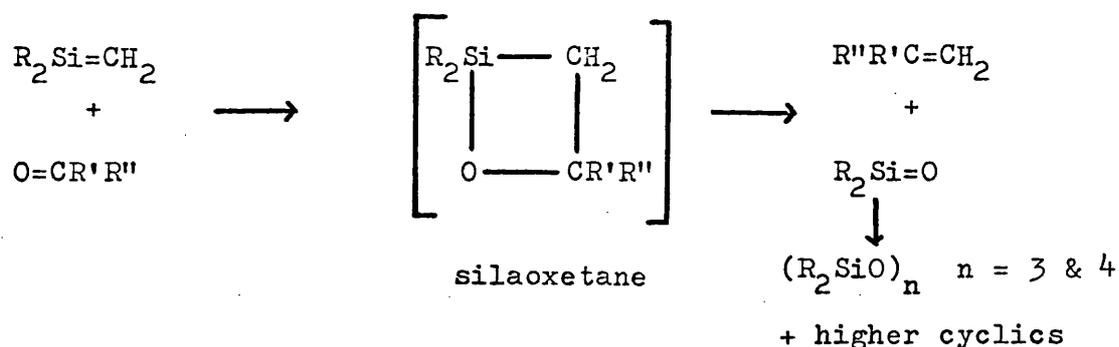
$$\log k_f/s^{-1} = 15.8 - 266.7 \text{ kJ mol}^{-1}/2.303 RT \quad 7$$



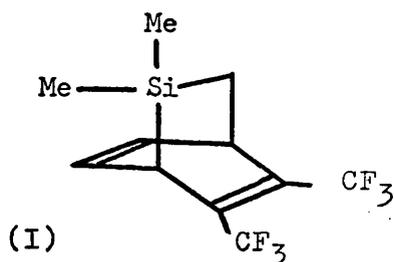
$$\log k_f/s^{-1} = 15.68 - 255 \text{ kJ mol}^{-1}/2.303 RT \quad 11$$

The fact that the Arrhenius parameters for these two reactions agree quite closely implies that the mechanism is the same for both reactions. It is thought the reaction begins with the dissociation of one bond in the ring (Si-C or C-C) giving rise to the formation of a biradical, which decomposes spontaneously to the short-lived intermediate $\text{Me}_2\text{Si}=\text{CH}_2$, in the case of the silacyclobutane, and ethylene.

Other compounds have since been used to trap out the intermediate $\text{Me}_2\text{Si}=\text{CH}_2$, among them olefins and dienes,^{12,13} acetonitrile¹⁴ and aldehydes and ketones.^{15,16} With the last two trapping agents it is believed that silaoxetanes are formed, which decompose rapidly to give olefins and a silanone, containing a Si=O double bond. This silanone polymerises to give cyclic siloxanes $(\text{R}_2\text{SiO})_n$, where $n = 3$ or 4 .



$\text{Me}_2\text{Si}=\text{CH}_2$ has also been produced from the thermal decomposition of bicyclo-compounds containing silicon such as (I).¹⁷ Similar disilabicyclooctadienes have been found



to decompose at temperatures from 533K to 773K, depending on the size of the molecule, to give intermediates containing a Si=Si double bond,^{18,19} which were trapped out using dienes. Evidence for Si=Si, Si=C and Si=O double bonds being formed in a single reaction has been found by Barton and Kilgour²⁰ who pyrolysed a disilabicyclooctadiene in the presence of benzaldehyde at temperatures from 753K to 773K. They proposed a reaction mechanism for the decomposition which included $\text{Me}_2\text{Si}=\text{SiMe}_2$, $\text{Me}_2\text{Si}=\text{CHPh}$ and $\text{Me}_2\text{Si}=\text{O}$ as intermediates.

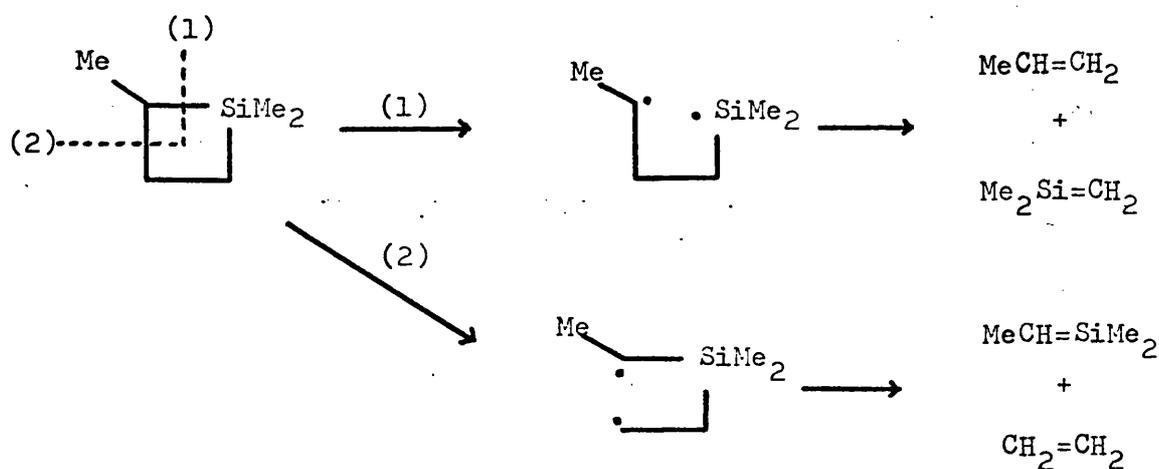
Barton and McIntosh²¹ have produced spectroscopic evidence for the existence of $\text{Me}_2\text{Si}=\text{CH}_2$ in the pyrolysis of 1,1-dimethyl-1-silacyclobutane, by infra-red spectroscopy after low-temperature trapping.

As well as being produced thermally, $\text{R}_2\text{Si}=\text{CH}_2$ intermediates have also been produced photolytically. $\text{Ph}_2\text{Si}=\text{CH}_2$ has been produced in the u.v. photolysis of 1,1-diphenylsilacyclobutane²² and pentaphenylmethyldisilane²³ by Sommer and co-workers. The $\text{Ph}_2\text{Si}=\text{CH}_2$ formed was trapped out by using deuterated methanol.

Sommer and co-workers have also generated silicon-carbon double-bonded intermediates with a methyl or phenyl group substituted on the carbon atom in place of hydrogen, by

pyrolysis of substituted silacyclobutanes.²⁴ The intermediates were trapped out using benzophenone, phenol and $(\text{Me}_2\text{SiO})_3$. The $\text{Me}_2\text{Si}=\text{CHR}$ intermediates inserted into a silicon-oxygen bond of the $(\text{Me}_2\text{SiO})_3$ to produce a cyclocarbosiloxane. From the products formed in the pyrolysis, Sommer and co-workers could determine which bond of the silacyclobutane dissociated in the initial step of the decomposition.

For example, from the two reactions :-



it can be seen that Si-C bond scission would give rise to the formation of the $\text{Me}_2\text{Si}=\text{CH}_2$ intermediate and propylene, whereas C-C bond scission would give rise to the formation of the substituted $\text{Me}_2\text{Si}=\text{CHMe}$ intermediate and ethylene.

$\text{Me}_2\text{Si}=\text{CH}_2$ has been proposed as one of the intermediates in the reaction chain for the decomposition of tetramethylsilane,^{25,26} as 1,1,3,3-tetramethyl-1,3-disilacyclobutane was identified as one of the reaction products.

In the Cope rearrangement of propenylallyldimethylsilanes,²⁷ evidence for the reversible formation of a silicon-carbon double bond has been put forward. Cis- and trans-propenylsilanes were found to be interconvertible on gas-phase

thermolysis at temperatures above 773K, the reaction intermediate for the conversion containing a silicon-carbon double bond.

Evidence for a silicon-nitrogen double bond has been produced, again by Sommer and co-workers.²⁸ Dimethylsilacyclobutane was co-pyrolysed with an imine, PhRC=NPh, and one of the resulting products, a cyclodisilazane, indicated that in the reaction sequence a Si=N double bonded intermediate had been generated. The $\text{Me}_2\text{Si}=\text{CH}_2$ initially formed reacted with the imine to give a cyclic four-membered transition state, which decomposed to give an olefin and a Si=N double bonded intermediate which dimerised to give the cyclodisilazane.

The $\text{R}_2\text{Si}=\text{O}$ intermediate species, or silanones, have not been studied at such a great extent as the $\text{R}_2\text{Si}=\text{CH}_2$ species. Silanones have been postulated as the intermediates in the pyrolysis of cyclosiloxanes, $(\text{Me}_2\text{SiO})_n$,^{3,6,29} and cyclocarbosiloxanes.³⁰ In the pyrolysis of cyclosiloxanes²⁹ it was found that in the initial stages of the decomposition the main products were compounds of the type $(\text{Me}_2\text{SiO})_{n-1}$ and that virtually the only example of products of the type $(\text{Me}_2\text{SiO})_{n+m}$ was $(\text{Me}_2\text{SiO})_{n+1}$. This is consistent with the scission of Me_2SiO , which either polymerises to the cyclic trimer, $(\text{Me}_2\text{SiO})_3$ or inserts into one Si-O bond of the initial compound, yielding $(\text{Me}_2\text{SiO})_{n+1}$. Unlike $\text{Me}_2\text{Si}=\text{CH}_2$ and $\text{Me}_2\text{Si}=\text{NR}$, Me_2SiO does not dimerise, but instead forms cyclosiloxanes of formula $(\text{Me}_2\text{SiO})_n$, where $n \geq 3$.

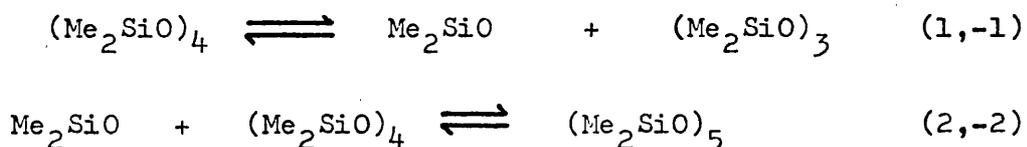
While the scission of dimethylsilanone, Me_2SiO , is characteristic of the cyclic siloxanes $(\text{Me}_2\text{SiO})_4$ or $(\text{Me}_2\text{SiO})_5$, for higher cyclosiloxanes direct decomposition into $(\text{Me}_2\text{SiO})_3$ or $(\text{Me}_2\text{SiO})_4$ is energetically more favourable.

The kinetics of the thermal decomposition of octamethylcyclotetrasiloxane, $(\text{Me}_2\text{SiO})_4$, have been studied by Davidson and Thompson at temperatures from 766K to 842K.^{3,6}

Up to 25% decomposition, the only products observed were $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_5$. Up to $\sim 4\%$ decomposition, these two products were formed in roughly similar amounts, the molar excess of $(\text{Me}_2\text{SiO})_3$ over $(\text{Me}_2\text{SiO})_5$ being 1.3 and the kinetics of the decomposition of $(\text{Me}_2\text{SiO})_4$ followed the first-order rate law. Arrhenius parameters for up to 4% decomposition were given by :-

$$\log k/\text{s}^{-1} = (14.85 \pm 0.39) - (300.9 \pm 6.1) \text{ kJ mol}^{-1}/2.303RT$$

The following mechanism was proposed for the initial stages of the decomposition :-



Reactions (1), (2) and (-2) sufficed to describe the mechanism up to 4% decomposition. Above 4% the rate of formation of $(\text{Me}_2\text{SiO})_3$ showed fall-off from the first-order rate law, while the rate of formation of $(\text{Me}_2\text{SiO})_5$ was reduced even more.

The addition of olefins, such as ethylene, propylene and 1,3-butadiene, was found to be effective in inhibiting the formation of $(\text{Me}_2\text{SiO})_5$, but not of $(\text{Me}_2\text{SiO})_3$ and so provided further evidence for describing the initial steps of the decomposition by reactions (1), (2) and (-2). In the presence of ethylene and other olefins, peaks thought due to adduct formation were observed on the gas chromatograph, but no

identification of the adducts was made.

The work described in the first part of this thesis can be divided into three sections :-

Part (A). Using $(\text{Me}_2\text{SiO})_4$ as a thermal source of dimethylsilanone, Me_2SiO , co-pyrolyses of $(\text{Me}_2\text{SiO})_4$ with various trapping agents were carried out at temperatures from 790K to 920K, to determine whether Me_2SiO can in fact be trapped out by alkenes and dienes to form cyclic adducts. The trapping agents were identical or similar to those used to trap out the intermediate Me_2SiCH_2 . They included ethylene, 1,3-butadiene, benzene, cyclopentadiene, isobutylene and 2,3-dimethyl-1,3-butadiene. Cyclopropane and methyl radicals were also used.

Part (B). From the previous study on the pyrolysis of $(\text{Me}_2\text{SiO})_4$,⁶ it was proposed that Me_2SiO inserted into an Si-O bond of $(\text{Me}_2\text{SiO})_4$ to form the cyclic pentamer, $(\text{Me}_2\text{SiO})_5$. In the present work, $(\text{Me}_2\text{SiO})_4$ was co-pyrolysed with monochlorosilanes at temperatures from 790K to 920K to determine whether the silanone Me_2SiO would also insert into the Si-Cl bond of the monochlorosilanes.

The catalysed reactions of $(\text{Me}_2\text{SiO})_4$ and other methyl-cyclosiloxanes with monochlorosilanes to give chloromethyl-siloxanes at 473K to 523K under high pressures have been well established.³¹⁻³⁴ The catalyst used was ferric chloride, either added to the reaction mixture,³⁴ or formed by reaction of the chlorosilanes with the walls of the steel vessel.³¹⁻³³ The present study was carried out to see whether the reaction would take place homogeneously in the gas-phase at low pressures.

Recently Sommer and co-workers have studied the insertion of the intermediate Me_2SiCH_2 into the Si-X bond of

some monochloro- and monofluorosilanes at 884K.³⁵ From their results they postulated that the Si=CH₂ double bond possesses considerable dipolar character.

Part (C). (Me₂SiO)₄ was co-pyrolysed with another siloxane, cis-trimethyltriphenylcyclotrisiloxane, (MePhSiO)₃, at temperatures around 790K to determine whether siloxanes would be formed containing both Me₂SiO and MePhSiO units. Due to difficulties experienced with the involatile (MePhSiO)₃ when using the conventional static vacuum system with g.l.c. analysis, this work was mainly carried out in sealed tubes with mass spectrometric analysis of products. The formation of 'mixed' siloxanes would provide good evidence for the existence of Me₂SiO and MePhSiO intermediate species.

CHAPTER TWO

APPARATUS AND EXPERIMENTAL PROCEDURE

FOR WORK ON SILANONES

APPARATUS AND EXPERIMENTAL PROCEDURE

FOR SILANONE WORK

2.1. Samples Used

Samples of the cyclic siloxanes used, $(\text{Me}_2\text{SiO})_n$ where $n = 3, 4, 5$; were provided by Dow Corning Ltd..

$(\text{Me}_2\text{SiO})_4$ or D_4 contained both D_3 and D_5 as impurities, and so had to be purified by preparative g.l.c.

An Aerogram A-700 Autoprep was used for purification of the siloxanes, utilising a silicone-oil column, maintained at a temperature of 400K.

The gases: ethylene, 1,3-butadiene, isobutylene and cyclopropane were supplied by Cambrian Chemicals.

The benzene used was Analar grade. The cyclopentadiene was cracked from impure dicyclopentadiene. Fresh cyclopentadiene had to be cracked and distilled each morning, due to its fairly rapid dimerisation.

The mercury dimethyl used was supplied by the Pfaltz and Bauer Chemical Company, the trimethylsilane by the Pierce Chemical Company and the tetra methylsilane was special-spectroscopic grade from BDH.

The monochlorosilanes and the cis-trimethyltriphenyl-cyclotrisiloxane were again kindly provided by Dow Corning Ltd..

The purity of all compounds was checked by gas chromatography before use. Where necessary, distillation or preparative g.l.c. were used for purification. G.l.c. analysis of the involatile cis-trimethyltriphenylcyclotrisiloxane showed no volatile impurities present, but no peak for the compound itself. Its purity was checked by mass spectrometric analysis.

2.2 Description of Apparatus

(a) Introduction

All pyrolysis studies were carried out on a conventional static vacuum system, with analysis of reaction products by gas chromatography and mass spectrometry.

(b) The G.l.c. System (See Fig. 2.1)

The Gas Chromatograph

The gas chromatograph consisted of a single column and a Gow-Mac gas density detector, housed in a home-made oven. In the work on silanones the column used was glass, 350cm. in length, packed with 5% silicone-oil on embacel (60-100 mesh, acid washed).

A Gow-Mac thermal conductivity detector was used in place of the gas density detector in the work on the chloro-disilanes. With this detector, for each reactant and product peak, the peak area had to be calibrated against the pressure of the vapour, by passing known pressures through the gas chromatograph and measuring the peak area. The temperature of the reaction vessel was lowered during calibration, to prevent any decomposition occurring.

The detector used was wired in a Wheatstone bridge circuit. Changes in the balance of the bridge were recorded on a highly sensitive Kipp and Zonen Micrograph (BD5 - 686E) recorder.

The column temperature for the silanone work was 353K - 373K. Temperature control in the g.l.c. oven was achieved by using a contact thermometer and relay switch to cut a resistance in and out of series with the oven heater.

- N₂- Nitrogen Cylinder,
Oxygen Free
- A - Pressure Controllers
- B - Needle Valves
- C - Drying Tube containing
Dehydrated Molecular
Sieve
- D - 'Oxy -Trap'
- E - Flow Meters
- F - Sampling - valve
- G - Reaction Vessel
- H - Furnace
- I - From Sampling System,
Vapour Inlet
- J - To Pumps
- K - GLC Oven
- L - GLC Column
- M - Gas Density Detector or
Thermal Conductivity
Detector
- N - To Bucket of Glass Wool,
Detector Exhaust
- O - Trapping Valve

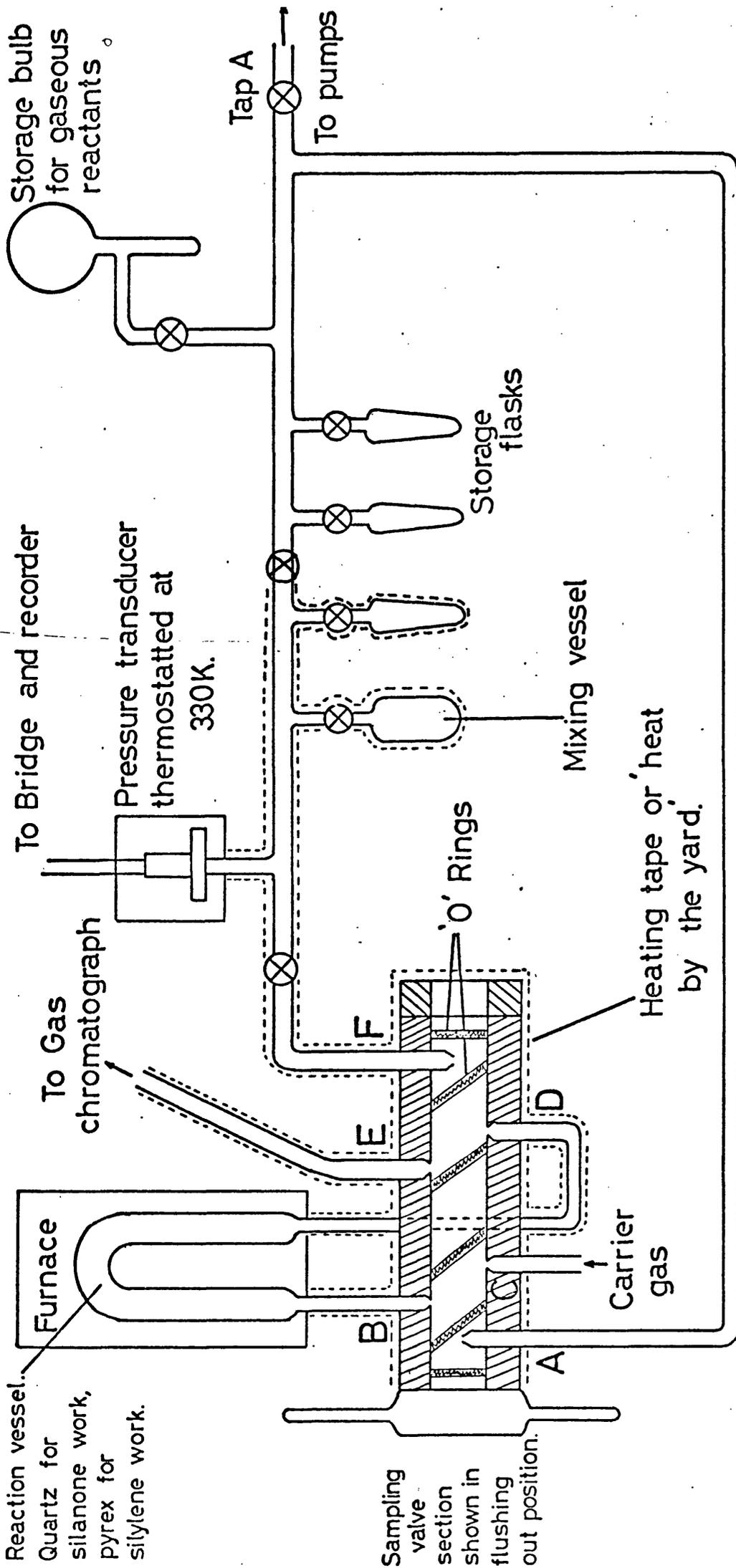


FIGURE 2.2 THE SAMPLING SYSTEM (SCHEMATIC)

Purification of Carrier Gas

The carrier gas used for both the reference and sample sides of the g.l.c. was oxygen-free nitrogen. However it was found that traces of both oxygen and water were present in the nitrogen. To remove these, the gas was passed through a copper tube (92cm x 2.5cm O.D.) packed with dehydrated molecular sieve, and then through an 'oxy-trap' (supplied by Alltech Associates) before entering the sampling-valve, as traces of oxygen and water in the carrier gas stream have been thought to enhance surface reactions in pyrolyses of organosilicon compounds. 6,36,37

The 'oxy-trap' was regenerated and the molecular sieve dehydrated at regular intervals.

(c) The Sampling System (See Fig. 2.2)

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

The Reaction Vessel

The reaction vessel was U-shaped, and was either made of quartz or pyrex glass, depending on the particular temperature range of the study. The U-shape enabled reactants and products to be flushed out to the g.l.c. column by a stream of nitrogen.

A quartz vessel was used in the work on silanones, and a pyrex vessel in the work on silylenes. The former vessel had a volume of 13.75 cm³, the latter a volume of ~ 35 cm³.

The Furnace and Temperature Measurement

The furnace consisted of a stainless steel tube (8 cm in diameter, 32 cm in length) wrapped with a thin layer of asbestos board and a nichrome heater winding. The furnace was supported

horizontally on a firebrick base, firebrick also being used for further insulation around the furnace.

The reaction vessel was positioned axially within the furnace, the two arms resting on firebrick supports.

Power input was adjusted using a 'variac', a varying voltage transformer. Temperature control was achieved by switching the resistance R in and out of the circuit (See Fig 2.3). This was done by using a Sunvic RT2 controller, which utilised a platinum resistance thermometer situated next to the reaction vessel.

The temperature of the reaction vessel was measured using a chromel/alumel thermocouple, situated in a quartz pocket adjacent to the vessel wall. *This thermocouple was calibrated against a platinum/rhodium thermocouple.*

The Sampling Valve

The first valve used was a stainless steel rotary valve, based on the design of Pratt and Purnell,³⁸ and made by Mr. C. Masters of this Department. It consisted of a central key fitted with six 'O' rings, of which four were sloping, and an outer barrel containing six ports. Various ports could be interconnected by rotation of the central key (See Fig. 2.2). Ports B and D were connected externally by the reaction vessel.

With the key in position (1) ports A and B would be connected, enabling the vessel to be evacuated. Ports C and E would be connected, so that a continual flow of carrier gas through the g.l.c. system could be maintained. Port F would be disconnected from D.

In position (2), A would be disconnected from B, and D and F would be connected, enabling the sample vapour to pass into the vessel. C and E would still be connected.

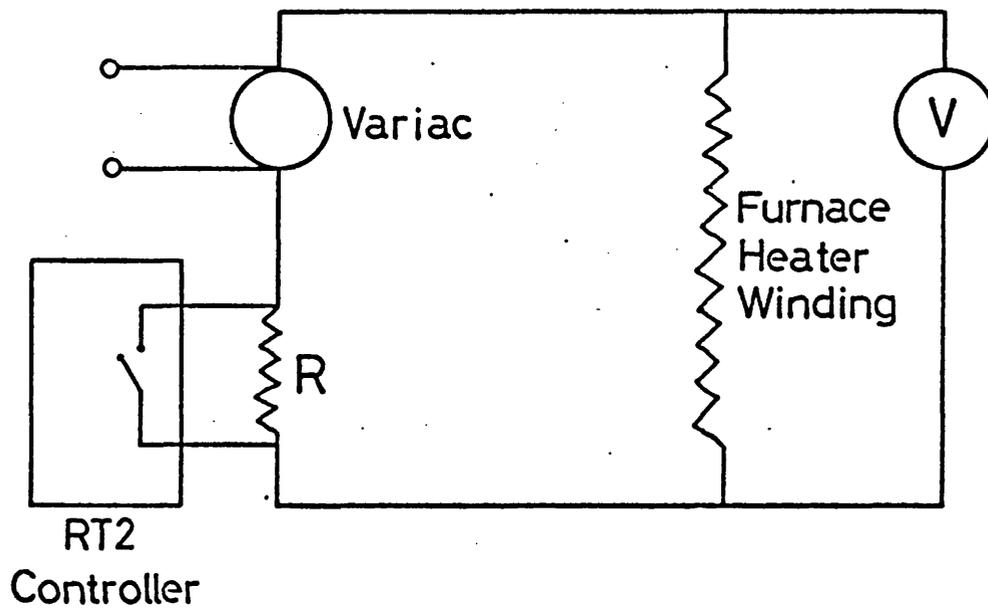


FIGURE 2.3 FURNACE HEATER CIRCUIT

In position (3) only C and E would be connected, isolating the reaction vessel from the remainder of the sampling system. This position would be maintained for the time of reaction.

In position (4), B and C, and D and E would be connected enabling the carrier gas stream to flush out the vessel and carry the reaction gases to the g.l.c. column. This is the position shown in Figure 2.2. Returning the key to position (1) would evacuate the vessel again, enabling a new run to be started.

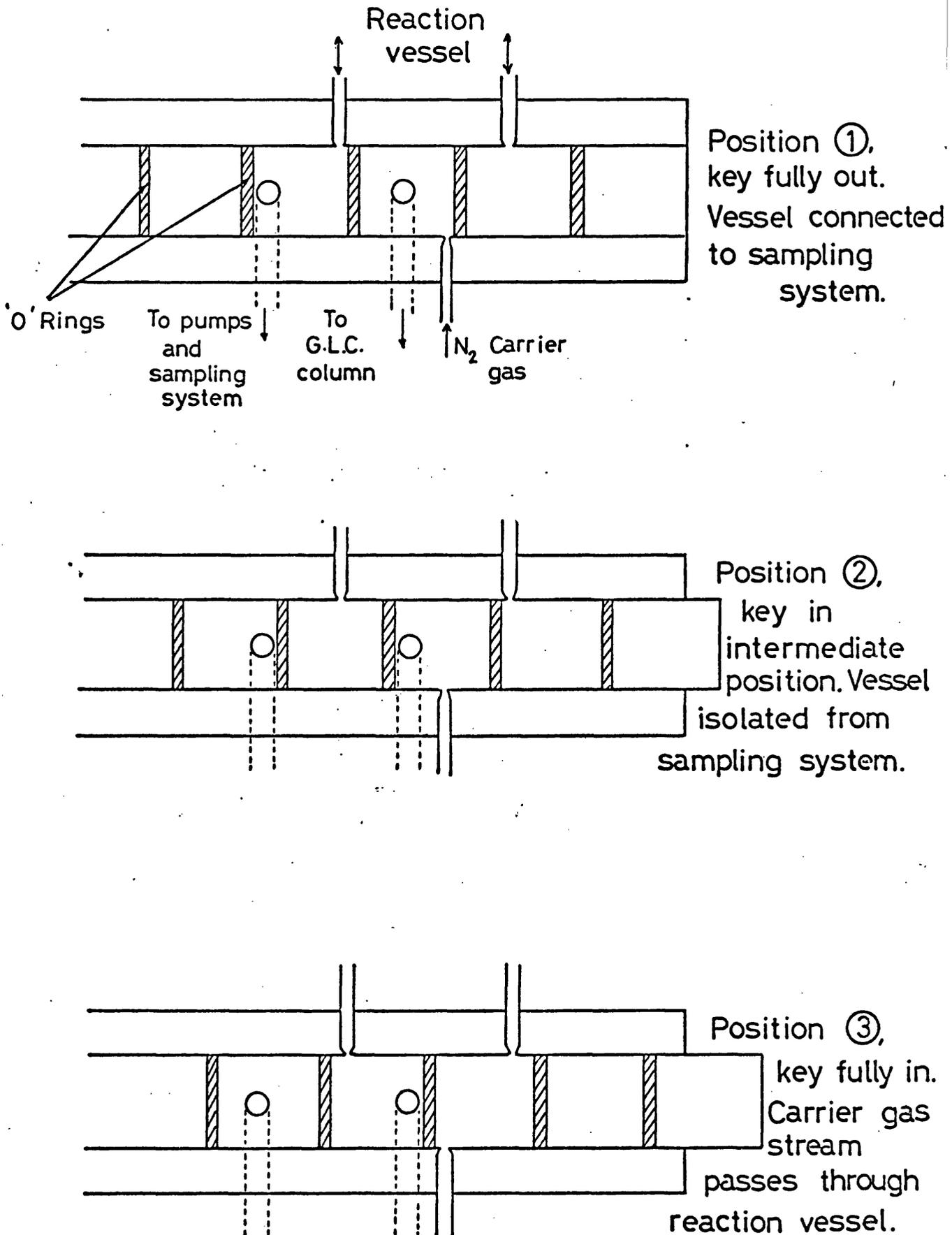
It was found that with this sampling-valve, the sloping 'O' rings were under considerable strain, and needed to be changed regularly, especially when the valve was operated at a high temperature, for example when pyrolysing D_4 . During the experiments with D_4 and cyclopentadiene, a new sampling-valve, designed and built in the Department, was fitted. It differed from the previous valve in having all of its five 'O' rings positioned at right angles to the key, which was moved along the barrel by a screw-action. The barrel contained only five ports, instead of six, evacuation of the vessel and sampling being through the same port (See Fig. 2.4).

Position (1). Key fully out: In this position the vessel could be evacuated, or by opening and closing taps on the line, sample vapour could be passed into the vessel.

Position (2). Key in intermediate position: The vessel would be disconnected from the line and pumps. The key would be in this position while the reaction is taking place.

Position (3). Key fully in: In this position the carrier gas would be flushing out the reaction vessel, carrying the reaction gases to the g.l.c. column. Withdrawing

FIGURE 2.4 DIAGRAM OF SAMPLING VALVE (SCHEMATIC)



the key to position (1) would evacuate the vessel again.

When carrying out experiments with $(\text{Me}_2\text{SiO})_4$, the sampling valve was heated by wrapping Electrothermal 'Heat by the yard' around the barrel. Other parts of the sampling system were also heated likewise, to prevent any condensation of the relatively involatile $(\text{Me}_2\text{SiO})_4$ vapour (See Fig. 2.2).

Pressure Measurement

Sample vapour pressures were measured using a Bell and Howell pressure transducer (Type 4-327-0003, Range 15 psi) which had previously been calibrated against a mercury manometer. In order to obtain consistent results, it was found necessary to thermostat the transducer at 330K.

The pressure transducer was wired in a Wheatstone bridge circuit, an increase in pressure on the transducer caused its resistance to change, and this caused imbalance in the bridge circuit. Changes in the balance of the bridge were measured on a Bryans 27000 chart recorder, the reading being taken as a measure of the pressure.

Storage of Samples

All gaseous and liquid samples were thoroughly degassed before use, and in some cases stored over dehydrated molecular sieve. Gases were stored in bulbs equipped with a cold finger, and sealed with a Springham diaphragm tap, as it was found that some gases, especially hydrogen, leaked across the 'O' rings when Young's greaseless stopcocks were used. All liquids were stored in flasks sealed with Young's greaseless stopcocks.

(d) A Typical Run (See Fig. 2.2)

With ports D and F on the sampling-valve connected, and tap A closed, a measured pressure of the sample vapour was

passed into the reaction vessel. The key of the sampling-valve was then moved so that the reaction vessel was isolated from the rest of the vacuum line. Any sample vapour remaining in the line was condensed back into the storage flask.

At the end of the reaction period, the key was again moved until ports B and C, and D and E were connected, the reaction vapours being flushed into the g.l.c. column. Reactant and product peaks were observed on the g.l.c. chart recorder. After a few minutes, the sampling valve key was moved again to connect ports A and B and evacuate the vessel.

(e) Modifications to the Vacuum System in the Thermolysis

Experiments with cis-trimethyltriphenylcyclotrisiloxane

(MePhSiO)₃.

At room temperature and pressure, cis-(MePhSiO)₃ is an involatile white solid, m.p. 372K, b.p. at 1.5mm Hg :
438K - 458K.

In order to study the thermal decomposition of (MePhSiO)₃, it was decided to inject a solution of the solid directly into the reaction vessel, rather than to produce a small vapour pressure by heating the solid in a special flask on the vacuum line, as was achieved with D₄.

A glass side-arm was fitted on to one of the arms of the reaction vessel, between the sampling valve and the end wall of the furnace. On the end of the side-arm was a metal-glass seal with a nut, holding a septum cap in place. The solution of (MePhSiO)₃ was injected through the septum cap, using a 10 μl syringe.

The voltages across the heating tapes and 'heat by the yard' on the reaction vessel arms, sampling-valve, pipe from the sampling-valve to the g.l.c. column, and trapping device were

all raised to try and prevent any $(\text{MePhSiO})_3$ condensing out in the system. 'Heat by the yard' was also wound around the carrier gas inlet pipe to the sampling valve, to prevent the cold gas causing condensation of the $(\text{MePhSiO})_3$.

2.3 Techniques and Methods used for Analysis of Reaction Products

(a) Introduction

All reaction products were analysed qualitatively by mass spectrometry, on an AEI MS9 mass spectrometer.

Two principle methods of obtaining analysis samples were employed :-

- (i) Condensing the whole reaction mixture into an evacuated glass bulb, cooled at 77K by liquid nitrogen. Thus a mass spectrum of the total reaction mixture was obtained.
- (ii) Trapping of individual peaks or groups of peaks observed on the gas chromatograph chart recorder. With this technique, a mass spectrum of each g.l.c. peak could be obtained.

(b) Analysis of Total Reaction Mixture

The technique of condensing out the whole reaction mixture was tried during the work on D_4 with ethylene as the trapping agent. On allowing the reaction mixture to warm up and enter the mass spectrometer, it was found that due to the greater pressure of ethylene and its greater volatility, only ethylene peaks were observed on the mass spectrum. To overcome this the excess ethylene was removed by pumping, after first cooling the bulb in a slush-bath of 40-60 petroleum ether and liquid nitrogen at 113K.

(c) Techniques used for Peak Trapping

The technique of trapping peaks observed on the gas chromatograph was continually being improved upon during the course of the work on silanones.

A valve placed inside the g.l.c. oven between the column and the detector could direct the gas stream straight through to the detector, or redirect the gas stream outside the oven, through a small quartz tube, and then back into the oven to the detector (See Fig. 2.6).

The quartz tube was packed with dried silica gel between two plugs of glass wool, to absorb any vapours in the gas stream. The time and duration of redirecting the gas stream depended upon the retention time and the peak width of the peak being trapped. The quartz tube could be attached to the end of the probe used to insert samples directly into the ion source of the mass spectrometer. The probe could be cold or heated, to facilitate desorption of the samples on the silica gel.

This technique was shown to work quite well by trapping out the D_3 and D_4 g.l.c. peaks, their correct mass spectra appearing on analysis. ^{39,40}

In order to obtain dry silica gel for trapping purposes, a small glass oven was built on to the vacuum system (See Fig.2.5). It enabled the silica gel packed tubes to be heated under high vacuum, volatile impurities from the silica gel being pumped away. An inlet tap for nitrogen gas enabled the tubes to be stored in an inert atmosphere until required.

It was later decided to trap out g.l.c. peaks into an evacuated glass bulb, rather than on to silica gel as reactions between siloxane fragments and ethylene absorbed on the silica gel occurred when the silica gel was heated. However, the bulb

method had the disadvantages that trapping could only be carried out for a limited time, depending on the flow rate and the volume of the bulb, and that traces of compounds from previous trappings remained in the bulb, even though it was heated strongly while being evacuated between trappings. The nitrogen carrier gas was removed from the bulb by pumping after cooling the bulb in liquid nitrogen.

The bulb was connected to the cold gas inlet system of the mass spectrometer. When no D_4 peaks were observed on the mass spectrum, having trapped out the D_4 g.l.c. peak, it was thought the D_4 vapour was condensing out in the pipe leading from the inlet to the source. Consequently a new copper connection was made to enable the contents of the bulb to pass directly into the source via the lock on the mass spectrometer.

With this method, D_4 peaks were still not observed on the mass spectrum, even when the bulb was heated. Thus it appeared that no D_4 vapour was reaching the bulb from the valve in the g.l.c. oven. Experiments to pass the gas stream through the side-arm and back to the detector were unsuccessful. It was found that this was because the rubber diaphragm in the valve was affected by the drop in pressure when the tap to the evacuated bulb was opened, and so therefore did not function correctly. For this reason the valve was removed and a new trapping device built (See Fig. 2.7).

In this new device, the gas stream from the column came outside the g.l.c. oven into a T-piece arrangement of glass tubing, fitted with two Young's greaseless stopcocks. Depending on which stopcock was open, the gas stream could be returned to the detector, or into the evacuated bulb. As the glass tubing and taps were outside the g.l.c. oven, they were wrapped with

FIGURE 2.5 DIAGRAM OF THE GLASS OVEN USED FOR DRYING THE PACKING IN THE TRAPPING TUBES

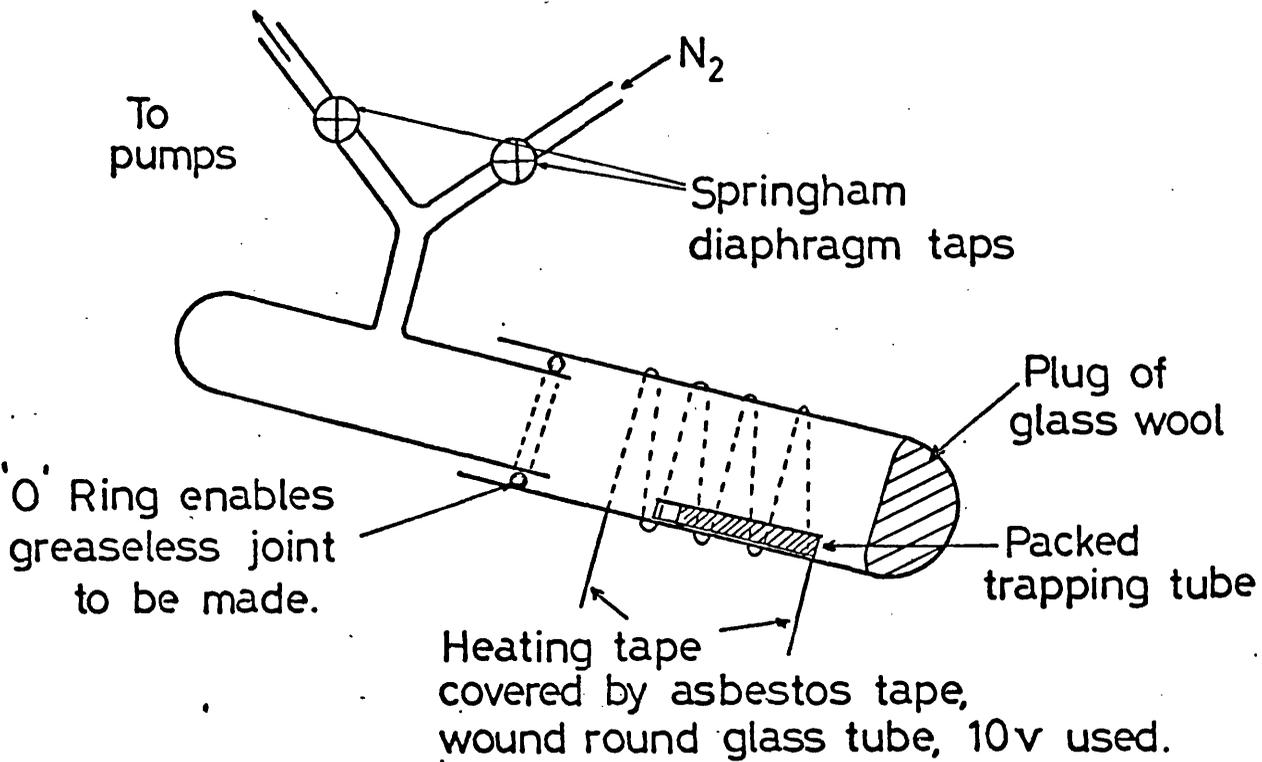


FIGURE 2.6 PEAK-TRAPPING ARRANGEMENT USING QUARTZ TUBES PACKED WITH SILICA GEL

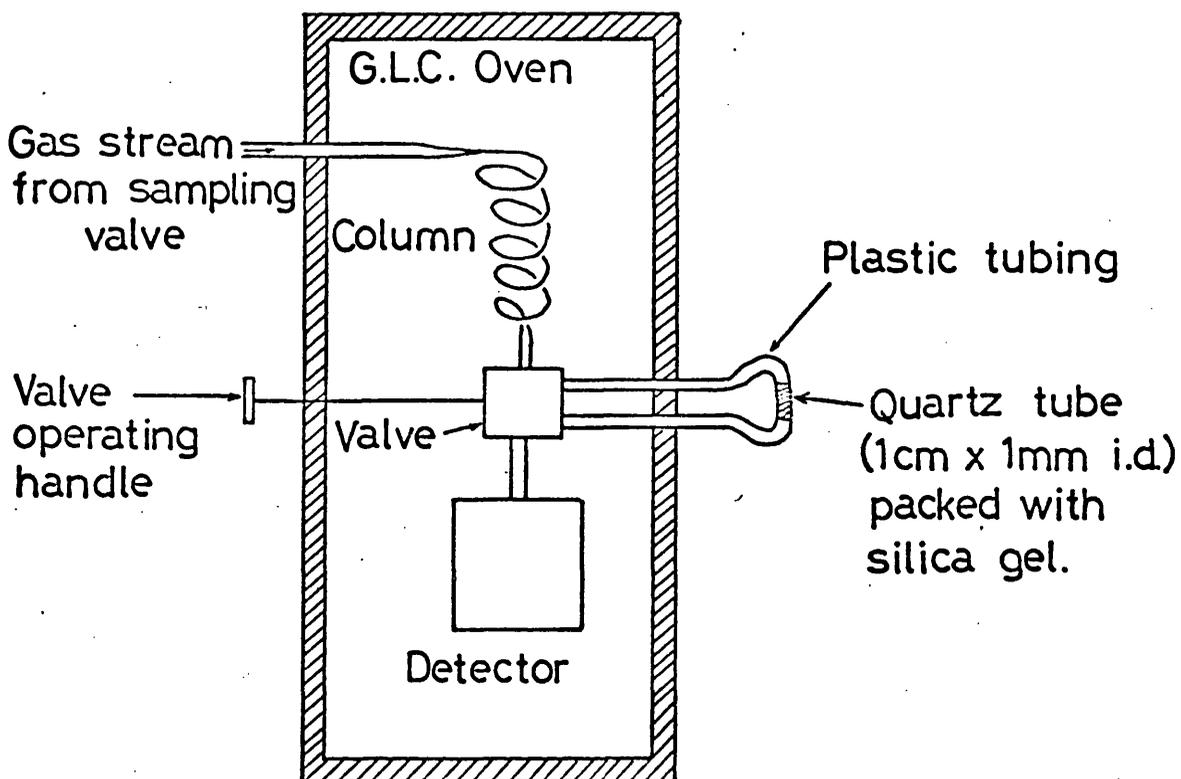


FIGURE 2.7 PEAK-TRAPPING ARRANGEMENT WITH GLASS TRAPPING DEVICE

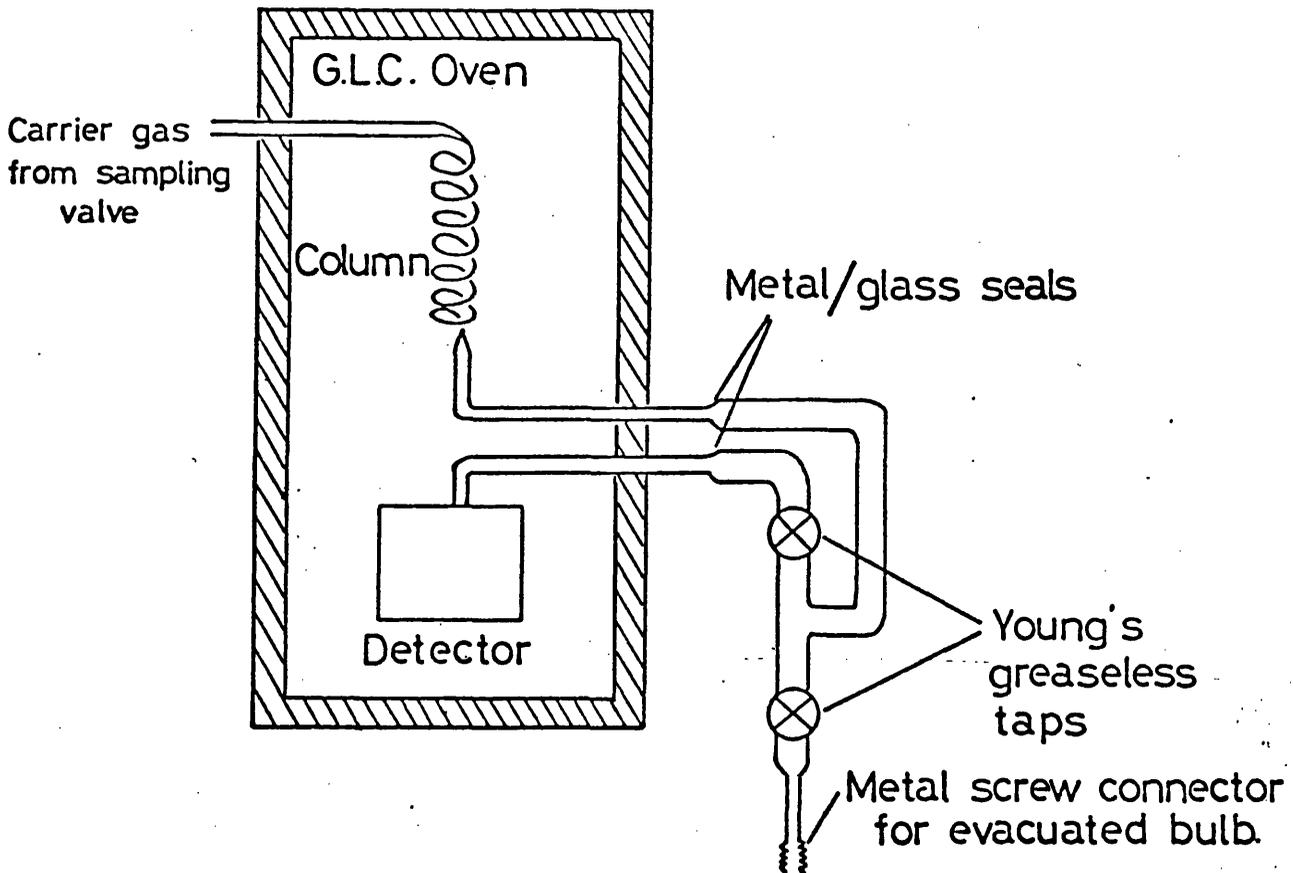
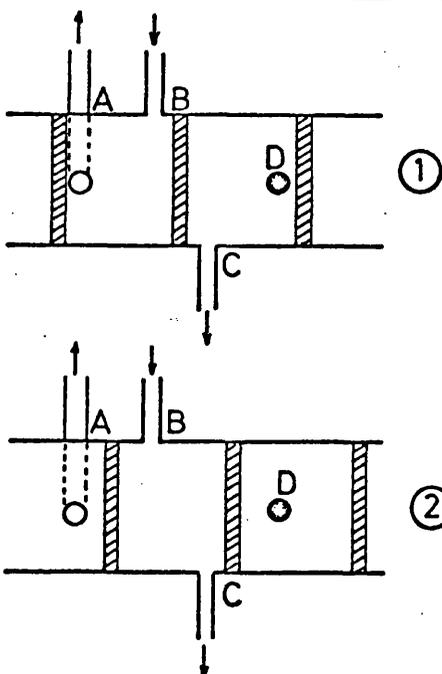


FIGURE 2.8 DIAGRAM OF TRAPPING-VALVE SHOWING THE TWO POSITIONS OF THE KEY



Port A - Gas flow to g.l.c. detector
 Port B - Gas flow from g.l.c. column.
 Port C - Gas flow to resin-packed tube.
 Port D - Permanently blanked off.

Position 1 - Key 'out'. Gas stream flows from the column, through the valve, to the detector.

Position 2 - Key 'in'. Gas stream flows from the column, through the valve, to the resin-packed tube for trapping.

'heat by the yard' to prevent condensation of any sample vapours in the gas stream.

(d) Trapping Methods used in Insertion Reactions of Me_2SiO

In the experiments involving insertion of Me_2SiO into the Si - Cl bond in chlorosilanes, all trapping, whether gas chromatographic peaks or reaction mixtures, was carried out using the evacuated bulb method. When it was found necessary to use SiCl_4 to cut down on hydrolysis, a glass side-arm fitted with a tap was added to the bulb. A small pressure of SiCl_4 was condensed into the side-arm before trapping occurred.

When the glass bulb was fitted to the mass spectrometer lock, a very small pressure of SiCl_4 was allowed to pass into the mass spectrometer source, to react with any water present.

On the first occasions when this technique was used, a mass spectrum of the SiCl_4 was taken. The spectrum showed peaks due to SiCl_4 (See Appendix 2.1), and also strong peaks at m/e 36,38 due to HCl , showing that some hydrolysis had taken place. It was found that when using SiCl_4 to cut down on hydrolysis, the peaks due to the chlorine containing insertion products were seen consistently on the mass spectra.

(e) New Trapping Arrangements devised for $(\text{MePhSiO})_3$

In order to minimise the length of piping through which the $(\text{MePhSiO})_3$ had to pass to reach the detector in the g.l.c. system, the glass trapping device with greaseless taps was removed and replaced by a small metal sampling-valve, a Mechanism Change-Over Valve supplied by Mechanism Ltd. Croydon (See Fig. 2.8.) With this valve the time taken to change the direction of the gas stream was a fraction of a second, so more efficient peak trapping could be carried out.

The new trapping valve was mounted on the outside wall of the g.l.c. oven, the piping from the column and to the detector coming outside the oven. This piping and the valve itself were wrapped with 'heat by the yard' to prevent condensation of any sample vapours in the gas stream.

The evacuated glass bulb for trapping gas chromatographic peaks was discarded and replaced by the method of absorbing the vapours in the gas stream on to a new packing. This was 80-100 mesh Amberlite XAD-4 resin supplied by Rohm and Haas Ltd..⁴¹ After drying the resin under vacuum, it was packed between glass wool in small quartz tubes, 25mm length, 2mm I.D.. These packed tubes were dried in the same glass oven as used for the silica gel packed tubes in earlier work.

A new head was built for the mass spectrometer probe, so that the packed tubes could again be inserted into the source for analysis of the absorbed sample vapour.

During a trapping run, the packed tube was connected to the trapping valve by a short piece of plastic tubing, and was cooled in liquid nitrogen, to improve absorption while the gas stream was being passed through.

2.4. Sealed Tube Technique

(a) Introduction

Due to the extreme involatility of the $(\text{MePhSiO})_3$, and the great difficulty experienced in attempting to pass the $(\text{MePhSiO})_3$ vapour through the g.l.c. system, it was decided to continue the thermolysis work on $(\text{MePhSiO})_3$ using sealed tubes.

(b) Preparation of Sealed Tubes

A tube with constriction was filled with about 10 to

15 μ l of a solution of $(\text{MePhSiO})_3$ in D_4 , or the corresponding weight of the solid $(\text{MePhSiO})_3$. The tube was connected to the vacuum system and evacuated. In the case of the solution this was degassed, but the solid was sublimed over the lower walls of the tube by gentle heating with a torch.

With the bottom tip of the tube immersed in liquid nitrogen to keep the solution frozen, the tube was sealed off at the constriction.

(c) Analysis of the Contents of a Sealed Tube

The prepared sealed tube was inserted into the furnace on a wire cradle and left for a certain length of time for the decomposition to occur.

When removed from the furnace, the tube was allowed to cool slightly and then the bottom tip was immersed in liquid nitrogen to condense any gaseous contents. While frozen, the bottom part of the tube containing the reaction products was cut off. The contents were then analysed on the mass spectrometer.

A solid reaction mixture was analysed using the mass spectrometer probe, some of the solid being inserted into a small capillary tube which was attached to the probe head. A liquid reaction mixture was analysed by absorbing some of the liquid into a resin packed tube which was again attached to the probe head.

This procedure was followed each time a sealed tube with reactants was prepared.

CHAPTER THREE

RESULTS AND DISCUSSION FOR THE WORK ON SILANONES

RESULTS AND DISCUSSION FOR THE WORK ON SILANONES

PART A

Addition Reactions with Π -Bonded and Other Hydrocarbons

(1) Reaction Conditions

In the experiments to trap out the dimethylsilanone intermediate species, there were three reaction conditions which could be varied.

(a) Co-pyrolysis of $(\text{Me}_2\text{SiO})_4$ and the trapping agents were carried out in the temperature range from 760K to 920K. The initial work with $(\text{Me}_2\text{SiO})_4$ and the Π -bonded hydrocarbons as trapping agents did not usually involve any temperatures above 850K, although some work with cyclopentadiene was carried out at 880K.

(b) Reaction times for the co-pyrolyses of $(\text{Me}_2\text{SiO})_4$ with the trapping agents varied from 1 minute up to 120 minutes, depending on the temperature being used. The time and temperature were usually chosen to give the same percentage decomposition, 4%, of the $(\text{Me}_2\text{SiO})_4$ for all experiments. When conditioning of the reaction vessel walls was required, reaction mixtures were pyrolysed overnight.

(c) The pressures of $(\text{Me}_2\text{SiO})_4$ used varied from 2mm to 6mm Hg. The pressure of the trapping agent was always in excess, the upper limit being 760 mm Hg.

(2) Ethylene as Trapping Agent

It was found in previous work⁶ that the addition of ethylene and other Π -bonded hydrocarbons in the pyrolysis of

$(\text{Me}_2\text{SiO})_4$ inhibited the formation of $(\text{Me}_2\text{SiO})_5$, the rate of formation of $(\text{Me}_2\text{SiO})_5$ decreasing sharply in the presence of these olefins. This decrease was thought due to the olefins behaving as trapping agents and reacting with the intermediate Me_2SiO in some ways, thus preventing the Me_2SiO from inserting into one of the Si-O bonds in the $(\text{Me}_2\text{SiO})_4$ to form $(\text{Me}_2\text{SiO})_5$.

It was also observed⁶ that a number of new peaks appeared on the gas chromatograph on co-pyrolysing $(\text{Me}_2\text{SiO})_4$ with olefins. However, it was recognised that although these new peaks could have been due to adduct formation, the range of products on pyrolysing $(\text{Me}_2\text{SiO})_4$ with olefins is increased by radical addition reactions.

It was decided to follow the trapping reactions by observing any new peaks on the gas chromatograph and also any decrease in the size of the $(\text{Me}_2\text{SiO})_5$ peak. Trapping out and analysing new peaks on the gas chromatograph by mass spectrometry would show the nature of any adducts formed between $(\text{Me}_2\text{SiO})_4$ and ethylene.

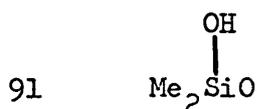
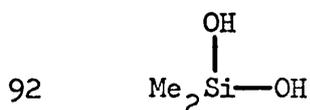
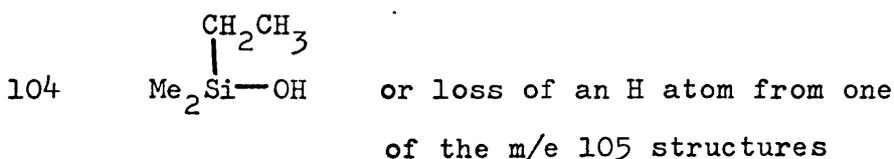
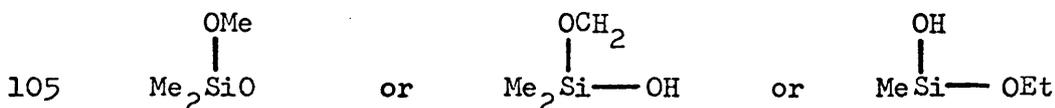
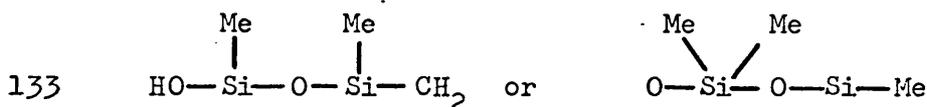
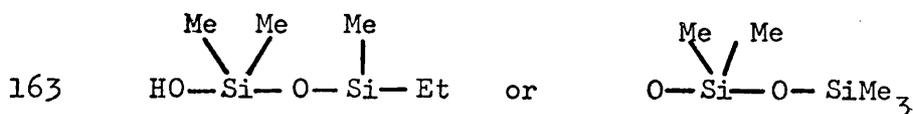
The walls of the reaction vessel had to be conditioned first before a peak due to $(\text{Me}_2\text{SiO})_5$ was observed on the gas chromatograph, by repeated pyrolyses of $(\text{Me}_2\text{SiO})_4$.

The reaction time for the initial pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with ethylene was 5 minutes at 842K. This gave approximately 4% decomposition of $(\text{Me}_2\text{SiO})_4$. In these runs new peaks were observed on the gas chromatograph; these were trapped out and analysed by mass spectrometry. However, the mass spectra for these new peaks proved to be very inconsistent, due to the small length of time during which the peaks were actually being trapped. One mass spectrum, though, showed a

strong peak at m/e 158, possibly due to $\text{Me}_2\text{SiO} \cdot 3\text{C}_2\text{H}_4$, but this result could not be reproduced.

Using longer times for trapping out the g.l.c. peaks, one pyrolysis run gave rise to a mass spectrum with peaks at m/e 163, 133, 105, 104, 92, 91 (See Appendix 2.5(a)). Structures can be assigned to these peaks, based on compounds formed by radical reactions between the $(\text{Me}_2\text{SiO})_4$ and ethylene, and not by cycloaddition reactions between Me_2SiO and ethylene.

m/e



Further pyrolysis runs were carried out using a larger excess pressure of ethylene, as well as a longer reaction time : 10 minutes. These runs gave rise to mass spectra with peaks at m/e 101, 115, 129, 157, 171, 185, 228, 242 and 256, after heating the probe on the mass spectrometer for 20 to 25 minutes (See Appendix 2.5(b)). These peaks were reproduced on subsequent pyrolysis runs. Structures could be assigned to these peaks based on cyclic adducts formed between the intermediate Me_2SiO and ethylene, or based on radical reaction products formed between fragments of the cyclosiloxane ring and ethylene.

	M.W.	Loss of H	Loss of Me
$\text{Me}_2\text{SiO} \cdot \text{C}_2\text{H}_4$	102	101	87
$\text{Me}_2\text{SiO} \cdot 2\text{C}_2\text{H}_4$	130	129	115
$\text{Me}_2\text{SiO} \cdot 3\text{C}_2\text{H}_4$	158	157	143
$\text{Me}_2\text{SiO} \cdot 4\text{C}_2\text{H}_4$	186	185	171
$\text{Me}_2\text{SiO} \cdot 5\text{C}_2\text{H}_4$	214	213	199
$\text{Me}_2\text{SiO} \cdot 6\text{C}_2\text{H}_4$	242	241	227

Loss of a methyl group, and to a lesser extent loss of a hydrogen atom, are the major fragmentations occurring with methylcyclosiloxanes and methylcyclocarbosiloxanes under electron impact.^{39,40} The fragment resulting from loss of a methyl group usually gives rise to one of the strongest peaks on the mass spectrum.

These mass spectra were recorded after heating the mass spectrometer probe for a certain length of time, the maximum time being 25 minutes. Experiments were carried out to determine whether the silica gel needed to be heated before the absorbed sample vapour was desorbed into the mass

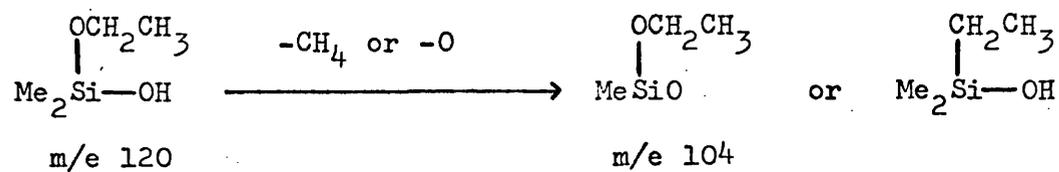
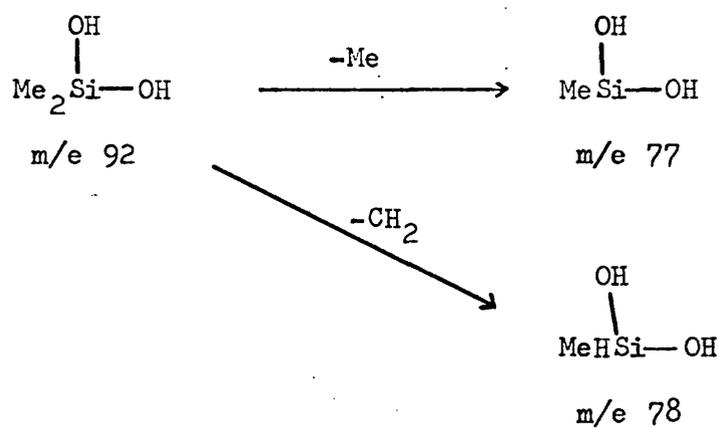
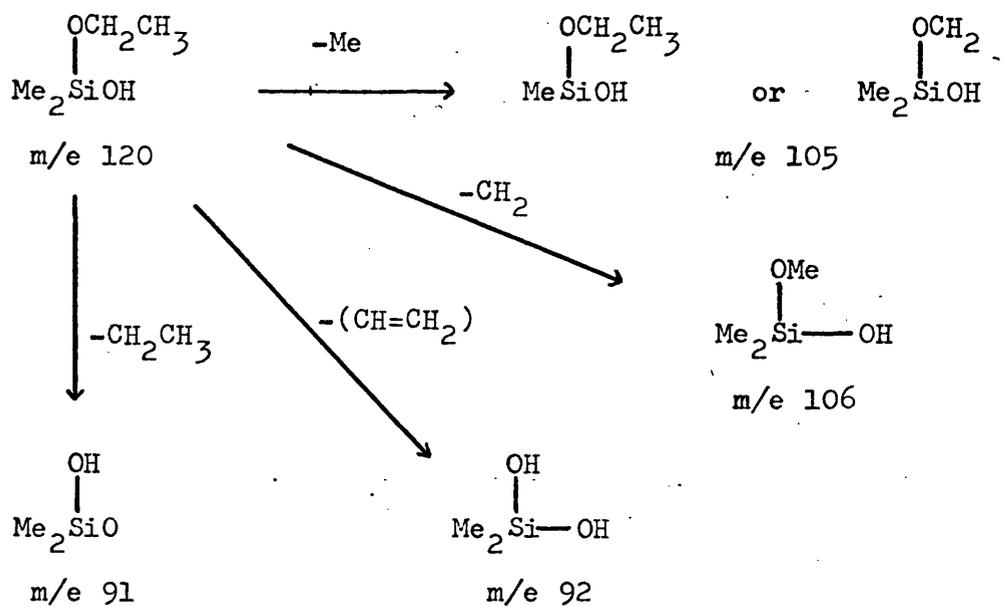
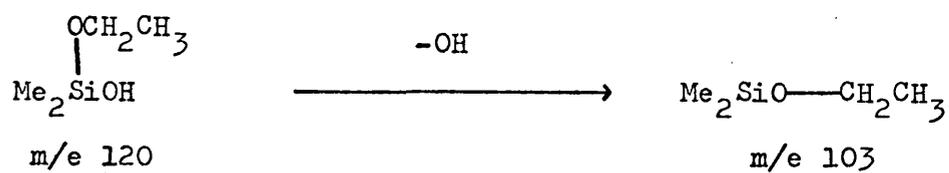
spectrometer source, or whether the peaks recorded were due to compounds being formed by surface reactions on the hot silica gel.

It was shown that the above compounds were probably being formed by surface reactions on the silica gel, rather than by homogeneous gas-phase reactions in the vessel, by individually trapping the $(\text{Me}_2\text{SiO})_4$ g.l.c. peak and then the ethylene g.l.c. peak on to the same silica gel, which was then heated on the mass spectrometer probe to produce the same peaks as above. Without any probe heating, these peaks were not observed.

The same experiment was then repeated, but this time the ethylene g.l.c. peak was trapped out first.

This series of mass spectral peaks was also produced from pyrolysis runs using both ethylene and water together as trapping agents with the $(\text{Me}_2\text{SiO})_4$ (See Appendix 2.5(c)), but again the mass spectrometer probe had to be heated before the peaks were observed.

Further pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with ethylene were carried out using a very large excess pressure of ethylene, ~ 760 mm Hg. Excessive use of the probe heater when analysing trapped g.l.c. peaks was avoided. A pyrolysis run at 842K gave rise to a mass spectrum with peaks at m/e 120,107,106, 105,104,103,102,92,91,78 and 77. These peaks were observed with no probe heating. On heating the probe for a few minutes, the peaks grew stronger. The following fragmentations were proposed to explain the mass spectral peaks, the structures of the fragments being based on compounds formed by radical reactions between the ethylene and siloxane fragments (See Appendix 2.5(d)).



Other mass spectra with peaks which could be assigned to products of ethylene/siloxane radical reactions were obtained from continued pyrolysis runs using $(\text{Me}_2\text{SiO})_4$ and ethylene.

Final pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with ethylene gave rise to a series of mass spectra, in one case with peaks at m/e 137,130,117,115,98,94, these peaks being recorded without use of the probe heater. However, there was no consistency with these latest mass spectra, which could not be reproduced from repeated pyrolyses. m/e 130 and 115 are the molecule ion and (M-15) ion respectively for the adduct $\text{Me}_2\text{SiO} \cdot 2\text{C}_2\text{H}_4$.

The initial reaction between dimethylsilanone and ethylene, as suggested by Thompson⁶ is probably cycloaddition to give a four-membered ring compound, a silaoxetane. However, from work carried out on the reaction of the intermediate $\text{Me}_2\text{Si}=\text{CH}_2$ with aldehydes and ketones^{15,16,20} silaoxetanes have been found to be unstable at the temperatures used, decomposing into the silanone and olefin. From this it would appear that any silaoxetane which was formed in the trapping reactions with ethylene would be very short-lived and decompose back again to dimethylsilanone and ethylene.

The decomposition of this silaoxetane probably begins with scission of the carbon-oxygen bond to give a biradical. In the reactions of the intermediate Me_2SiCH_2 with olefins,^{12,13} it has been suggested that the corresponding biradical has such a short lifetime that any intermolecular reactions involving the biradical would be practically impossible. Hence it appears that reactions of this silaoxetane biradical with other ethylene molecules to give cyclic adducts with rings containing more than 4 atoms can be ruled out.

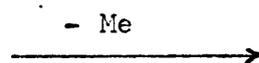
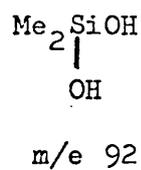
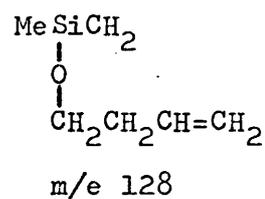
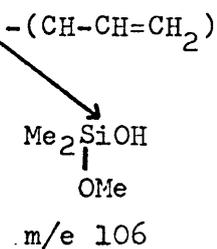
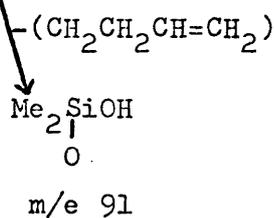
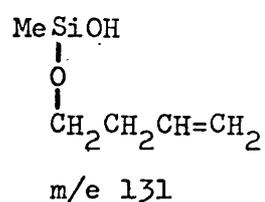
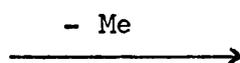
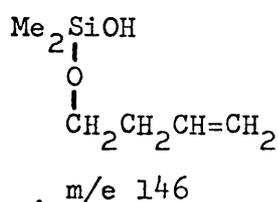
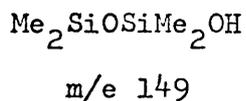
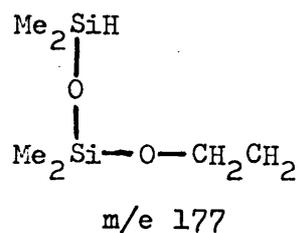
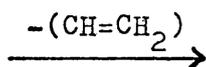
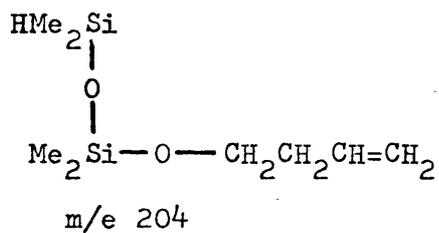
From the experiments with ethylene, it would appear that the intermediate dimethylsilanone, Me_2SiO , was not readily reacting with ethylene molecules to form cyclic adducts. As stated before, it has been observed^{15,16,20} that the four-membered cyclic silaoxetane formed between the silanone and ethylene decomposes again to the starting compounds. No evidence was obtained for reaction of this silaoxetane with another ethylene molecule which would increase the ring size of the cyclic adduct, and so form a more stable compound.

(3) Butadiene as Trapping Agent

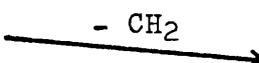
1,3-butadiene, which is a 4π electron system, was used as a trapping agent after the experiments with ethylene. It was thought that whereas ethylene would react with Me_2SiO to give a silaoxetane, butadiene should react with Me_2SiO to give a six-membered cyclic adduct, which should be more stable to pyrolysis than a silaoxetane.

Pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with 1,3-butadiene at 842K produced the series of mass spectral peaks observed with ethylene after strong probe heating at m/e 256, 242, 228, 200, 199, 185, 171, 157, 149, 143, 129, 115, 111, 101, 99, 98, 97 (See Appendix 2.6(a)). Again it was assumed that the fragments giving rise to these peaks were produced by surface reactions on the silica gel.

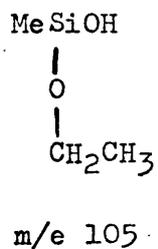
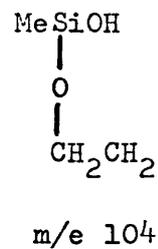
Another pyrolysis run at 842K with 1,3-butadiene produced the series of mass spectral peaks : m/e 222, 177, 150, 149, 135, 131, 128, 106, 105, 104, 103, 102, 93, 92, 91, 80, 79, 78, 77, (See Appendix 2.6(b)). These peaks can be attributed to compounds formed by radical reactions between siloxane fragments and the butadiene :-

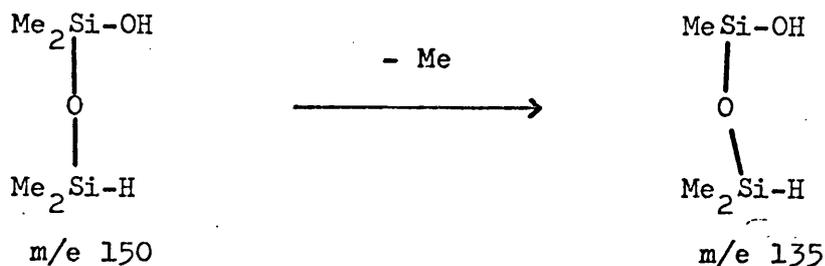


m/e 77

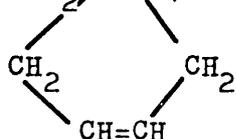


m/e 78





No evidence was found for the formation of cyclic adducts from Me_2SiO and butadiene. The peak at m/e 128 can be due to the adduct $\text{Me}_2\text{Si-O}$, but then a peak at m/e 113

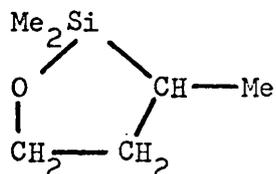


due to (M-15), loss of a methyl group, should be expected. It was thought that any cyclic adducts being formed at the reaction temperatures might possibly be decomposing again, in a similar fashion to the silaoxetanes formed with ethylene. One of the difficulties experienced in the work on trapping out the intermediate Me_2SiO was, that although high temperatures, 800K - 842K were required to produce the intermediate Me_2SiO in the decomposition of the cyclic siloxane $(\text{Me}_2\text{SiO})_4$, it was not known whether any adducts formed between the Me_2SiO and the trapping agent would be thermally stable at these high temperatures.

For this reason it was decided to prepare a typical adduct, $\text{Me}_2\text{SiO}(\text{CH}_2)_4$, and to determine its thermal stability at the reaction temperatures.

This compound; 2,2-dimethyl-1-oxa-2-silacyclohexane was prepared by a reaction^{42,43} involving ring closure of a chain butenoxymethylsilane molecule $\text{HMe}_2\text{SiOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (See Appendix 1.1). However it was suggested later⁴⁴ that this reaction produces a silacyclopentane ring compound and not

a silacyclohexane, this being confirmed by n.m.r. spectra run on the reaction product. The compound produced was in fact 2,2,3-trimethyl-1-oxa-2-silacyclopentane :-



This silacyclopentane compound was pyrolysed in the reaction vessel for typical decomposition times, at temperatures from 423K up to 850K. Only one peak was observed on the gas chromatograph at all times, indicating that no decomposition was occurring.

As with ethylene, no cyclic adducts formed between the intermediate, Me_2SiO , and the trapping agent were observed with butadiene in repeated pyrolysis runs at temperatures around 850K.

(4) Benzene as Trapping Agent

Co-pyrolyses of $(\text{Me}_2\text{SiO})_4$ and benzene were carried out at 842K to determine whether the intermediate Me_2SiO could be trapped out by the benzene, through interaction with the π -electron system on the benzene ring. In these reactions, one new peak due to possible adduct formation was observed on the gas chromatograph. This was trapped out, the trapped sample producing mass spectral peaks at m/e 185, 184, 183, 158, 154, 142, 141, 125, 124, 120, 104, 96, 94, 92, 91, 78, 77 (See Appendix 2.7). However, these peaks were only obtained after probe heating, so it was thought that they were again due to products of reactions taking place on the silica gel.

These mass spectral peaks could not be attributed

to radical reaction products, or cyclic adducts formed between the Me_2SiO and the benzene. No evidence of any definite reaction between the intermediate Me_2SiO and benzene was obtained, probably because in benzene the π -electrons are not grouped together into olefinic-type double bonds, but are delocalised around the ring, thus making $n\pi + n\pi$ type cycloadditions difficult processes.

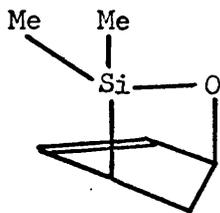
(5) Cyclopentadiene as Trapping Agent

Cyclopentadiene was used as a trapping agent in the reactions with Me_2SiO because, like 1,3-butadiene, it is a 4π electron system, but supposedly more reactive to 2π electron systems to give bridged adducts in a Diels-Alder type cycloaddition. Its higher reactivity with 2π electron systems is indicated by the fact that at room temperature cyclopentadiene exists as the dimer, dicyclopentadiene.

Initial pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ and cyclopentadiene were carried out at 810K, using a vapour pressure of 60 mm Hg of cyclopentadiene, which was the vapour pressure existing over the ice-cold cyclopentadiene. As no new peaks were observed on the gas chromatograph, greater vapour pressures of cyclopentadiene, 120-130 mm Hg, were used in the next series of pyrolysis runs, by allowing the cyclopentadiene to warm up slightly.

With this series, a new peak was observed on the gas chromatograph, just before the $(\text{Me}_2\text{SiO})_4$ peak. This new peak was trapped out, and the mass spectrum showed peaks at : m/e 125, 142, 156, 158, 185, 200, 208, 228 (See Appendix 2.8(a)). These mass spectral peaks proved to be quite consistent as they were also produced in following pyrolysis runs.

The expected reaction product formed between the intermediate Me_2SiO and cyclopentadiene is the 1:1 bicyclo-adduct :-



This type of bicyclo-adduct is formed by cyclopentadiene with any 2π electron system, in a Diels-Alder reaction.

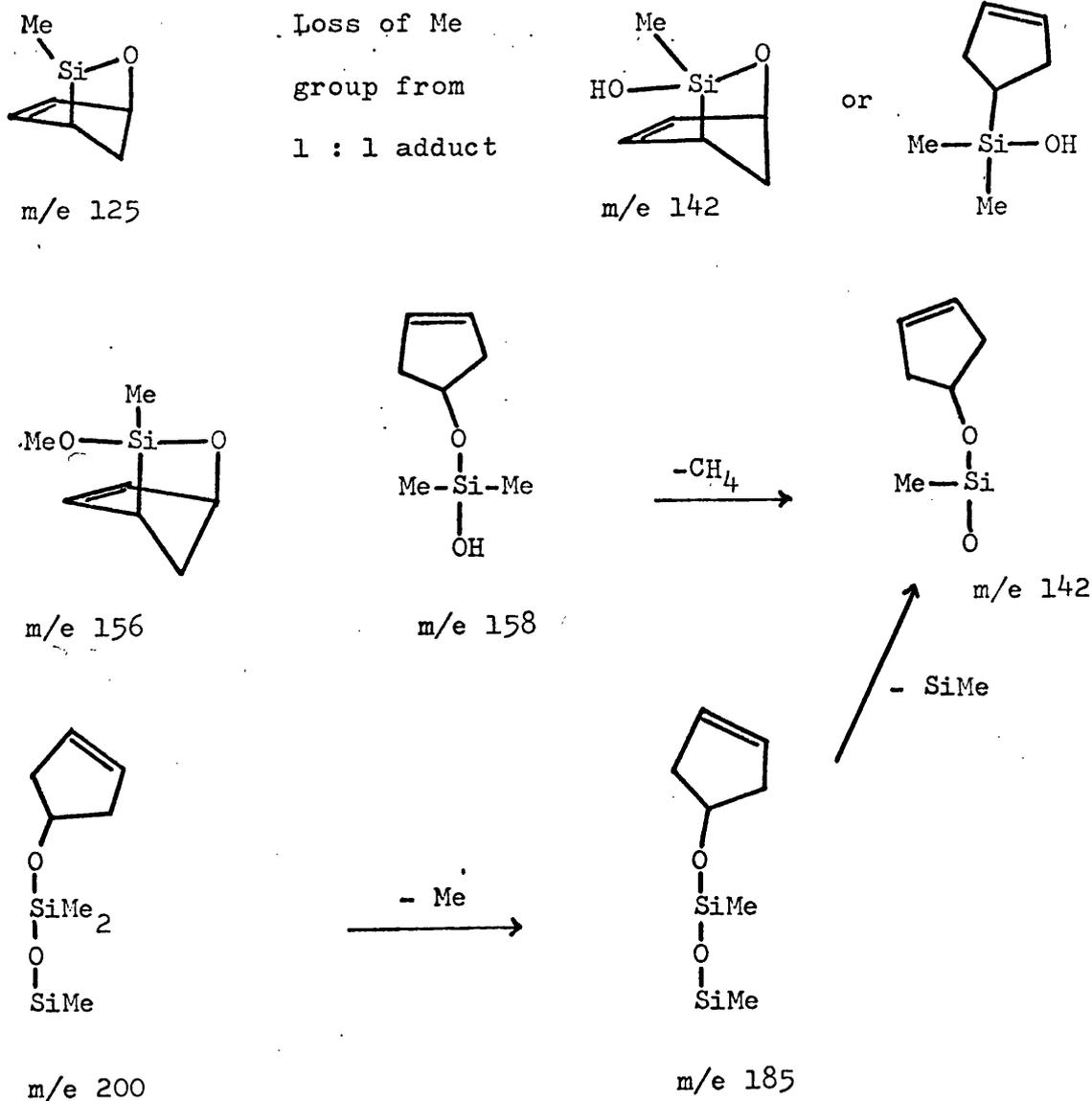
This adduct has molecular weight 140, hence loss of a methyl group would show a mass spectral peak at m/e 125. As the m/e 125 peak was quite prominent on the mass spectra, this suggests formation of the above adduct. The mass spectral peaks above m/e 140 could be explained by the addition of various entities in the system to the carbon-carbon double bond in the adduct. However this double bond is very stable to Markovnikov type addition reactions, so structures based on this type of reaction are highly unlikely. The peak at m/e 208 can be taken as evidence though for the Diels-Alder type addition of this double bond to another cyclopentadiene molecule.

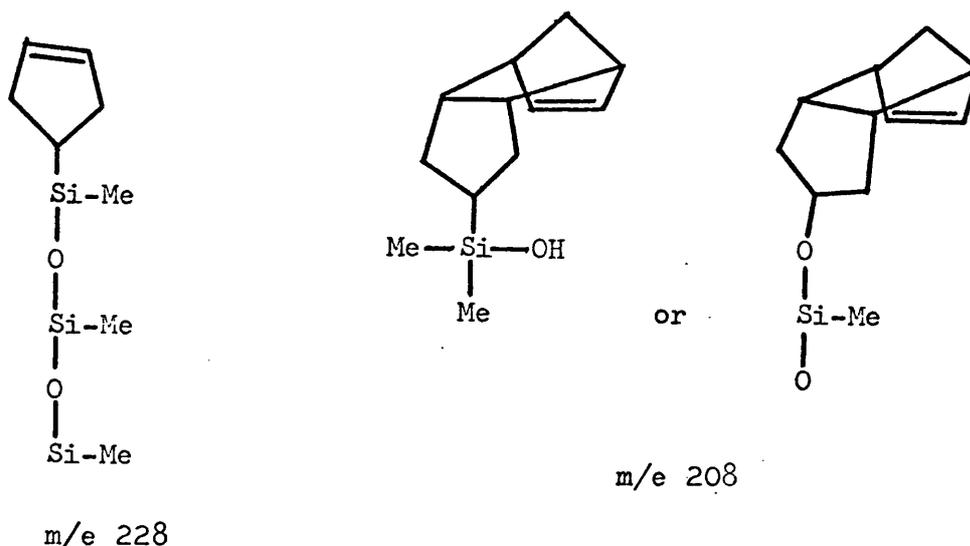
Work has been carried out by various authors¹⁷⁻²⁰ on the thermal decomposition of bicyclo-compounds containing one or more silicon atoms. Evidence for the silicon-silicon double bond has been obtained from the thermal decomposition of disilabicyclooctadienes.¹⁸⁻²⁰ All these workers used temperatures lower than those used in this present work, so it seems very probable that the adduct formed between Me_2SiO and cyclopentadiene decomposes fairly rapidly back to its starting compounds.

Some of the above mass spectral peaks could be attributed to cyclic silacyclohexane compounds formed by the

breaking of one bond in the bicyclo-adduct, followed by abstraction of hydrogen atoms or methyl groups. This mode of decomposition is surprising however, since decomposition of these bicyclo-compounds usually proceeds by a retro Diels-Alder mechanism.⁴⁵

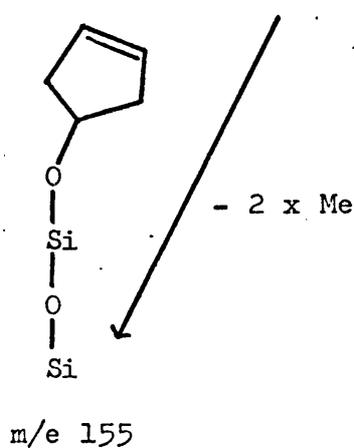
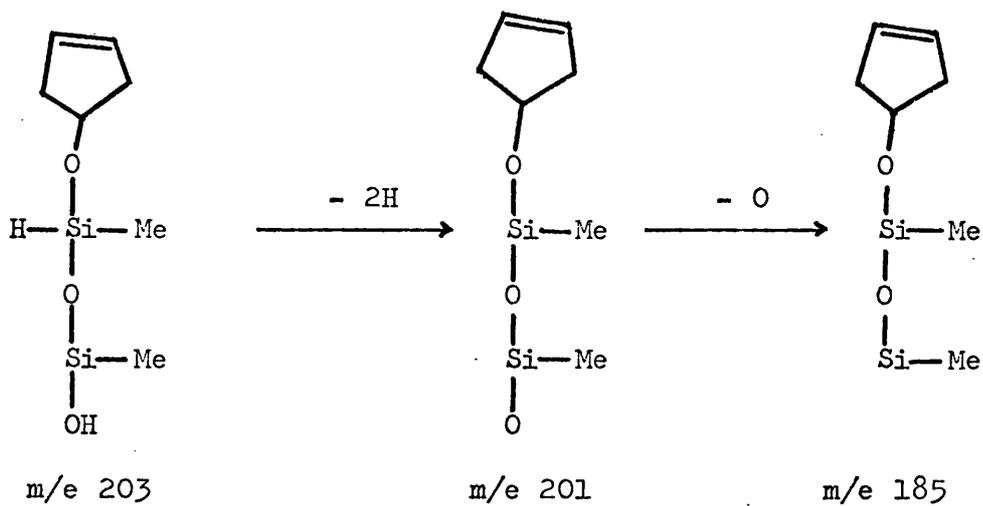
It is more probable that the above series of mass spectral peaks is due to the products of radical reactions between fragments of the $(\text{Me}_2\text{SiO})_4$ ring and the cyclopentadiene molecule. Structures based on radical reaction products can be drawn for some of the mass spectral peaks. For example :-



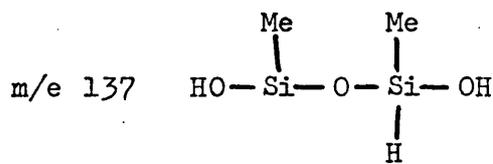
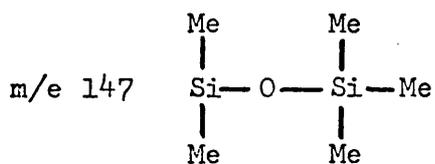
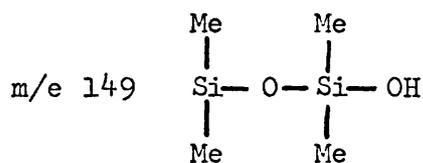
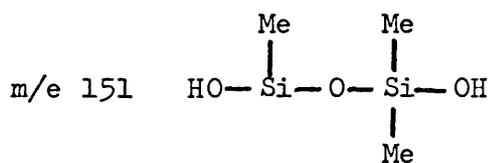


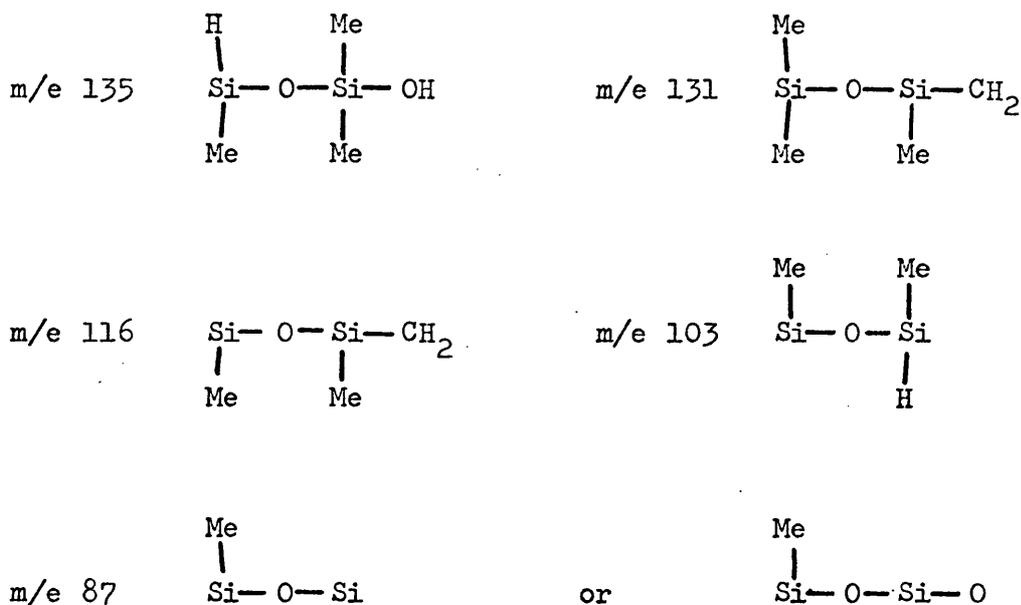
At this stage, a stream of oxygen gas was passed through the heated reaction vessel, to purge the walls of hydrocarbon deposits and polymers. The walls were then reconditioned by repeated pyrolyses of $(\text{Me}_2\text{SiO})_4$.

In further pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with cyclopentadiene, different mass spectra to the previous series were obtained. One mass spectrum showed peaks at m/e 203, 201, 185, 155, 153, 151, 149, 147, 137, 135, 131, 127, 116, 115, 103, 101, 87 and 85 (See Appendix 2.8(b)). The higher m/e values, >153 , can be explained by structures containing both siloxane fragments and a cyclopentadiene ring, the lower m/e values, <153 , can be attributed just to siloxane fragments. The m/e values also tend to suggest that the fragmentations occurring in the molecules take place in the siloxane chain and not in the cyclopentadiene ring, as the differences in the m/e values do not agree with the differences given in the mass spectrum for cyclopentadiene⁴⁶ (See Appendix 2.8(d)).



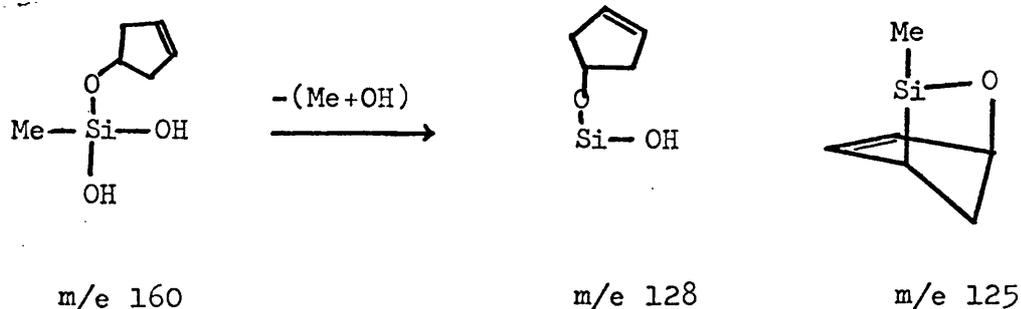
The following structures can be assigned to the lower m/e values :-



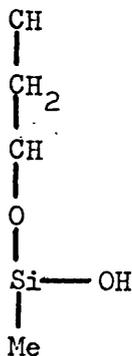


Later work with cyclopentadiene as trapping agent was carried out at higher temperatures than previously, 883K, with pressures of cyclopentadiene; 20 - 35 mm Hg. Mass spectrometric analysis of reaction mixtures for pyrolysis runs under these new conditions showed a new set of peaks at m/e 160, 128, 125, 116, 115, 104, 96, 92, 91, 78 (See Appendix 2.8(c)). These peaks were obtained consistently on mass spectra from repeated pyrolysis runs at 883K, and at lower temperatures, 848K and 810K. The mass spectra (Appendices 2.8(a) and (b)) obtained in the previous work with cyclopentadiene could not be reproduced, even when using identical reaction conditions.

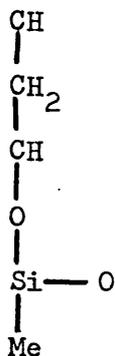
The above mass spectral peaks at m/e 160, 128 etc. can again be attributed to fragments of the cyclosiloxane ring, with or without a cyclopentadiene ring in their structures. m/e values 160, 128 and 125 can have a cyclopentadiene ring in their structures. For example :-



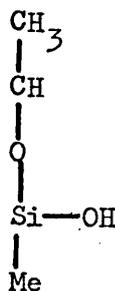
The lower m/e values can include fragments of the cyclopentadiene ring in their structures :-



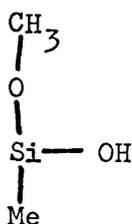
m/e 116



m/e 115



m/e 104



m/e 91

Some of the mass spectra peaks produced from the reactions of $(\text{Me}_2\text{SiO})_4$ with cyclopentadiene could be assigned to products formed from the addition of ethylene to Me_2SiO . It was thought that at the reaction temperatures used, the cyclopentadiene might be decomposing itself to give unsaturated hydrocarbons including ethylene. It is known that cyclopentadiene decomposes at very high temperatures, around 1300K⁴⁷ to give hydrocarbons such as methane and benzene, with ethylene and acetylene as reactive intermediates; but at the temperatures used in the experiments with $(\text{Me}_2\text{SiO})_4$, no evidence was obtained for any extensive decomposition of cyclopentadiene. It is quite possible, however, that some of the cyclopentadiene may have

decomposed heterogeneously on the walls of the reaction vessel.

Although some mass spectra were recorded with peaks due to possible 1:1 bicyclo-adduct formation between the intermediate Me_2SiO and cyclopentadiene, m/e 125; as stated before, it is known that these bicyclo compounds containing one or more silicon atoms decompose quite readily at the temperatures used.

(6) Isobutylene, $\text{Me}_2\text{C}=\text{CH}_2$, and 2,3-Dimethyl-1,3-butadiene
 $\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$ as Trapping Agents

These two double bonded hydrocarbons, similar to ethylene and 1,3-butadiene, but having methyl groups substituted for some of the hydrogen atoms, were used next as trapping agents. It was thought that the presence of the methyl groups might increase the reactivity of the double bonds towards the intermediate Me_2SiO .

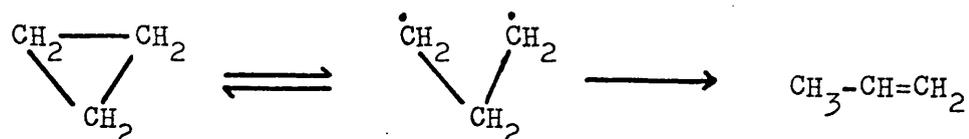
Pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with isobutylene or 2,3-dimethyl-1,3-butadiene were carried out for various times at varying temperatures around 810K and using varying excess pressures of the trapping agent. No mass spectra were recorded with peaks due to any form of product between the siloxane or the trapping agent, whether radical reaction products or cyclic adducts.

(7) Cyclopropane as Trapping Agent

Cyclopropane was used as a trapping agent after purging the reaction vessel with oxygen gas and reconditioning the walls.

It was thought that if the silanone, Me_2SiO existed with more biradical character than Π -bond character, then it might react with the biradical formed on ring opening of the

cyclopropane, giving a cyclic adduct. Pyrolysis of cyclopropane gives propylene as the reaction product, via a biradical intermediate^{48,49} :-



However, it must be recognised that the chances of two different biradicals coming together to react are very slight. Pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with cyclopropane were carried out at temperatures from 800K to 858K. No new peaks due to possible adduct formation were observed at all on the gas chromatograph. The experiments with cyclopropane were thus very inconclusive, no definite evidence for the electronic structure of the silanone Me_2SiO could be obtained.

(8) Methyl Radicals as Trapping Agents

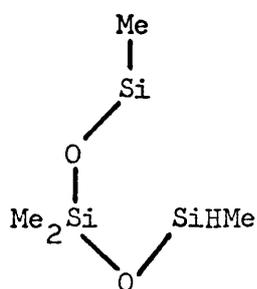
Experiments were carried out to trap out the silanone Me_2SiO by reacting it with methyl radicals. Reaction between the silanone and methyl radicals should give trimethylsilyl species.

The first radical source used was dimethyl ether, MeOMe . Although various temperatures, in the range 750K to 820K, times and excess pressures of dimethyl ether were used, the only new peak observed on the gas chromatograph was a strong peak due to methane.

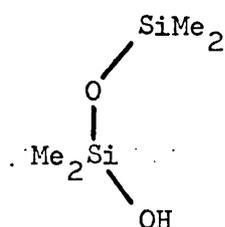
Mercury dimethyl, HgMe_2 , was used in following pyrolysis runs as the radical source. At 820K, a large ethane peak was observed on the gas chromatograph, and mass spectra of the reaction mixtures at this temperature showed only

$(\text{Me}_2\text{SiO})_4$, $(\text{Me}_2\text{SiO})_3$ and ethane peaks.

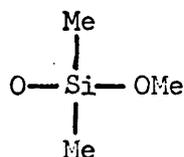
At higher temperatures, around 855K, the mass spectra showed $(\text{Me}_2\text{SiO})_4$, $(\text{Me}_2\text{SiO})_3$ and ethane peaks, and also peaks due to HgMe_2 and HgMe . Other peaks observed at m/e 177, 149 and 105 were assigned to siloxane fragments, most probably formed by reaction of the methyl radicals with the cyclosiloxanes $(\text{Me}_2\text{SiO})_4$ and $(\text{Me}_2\text{SiO})_3$. Possible structures for these fragments are :-



m/e 177



m/e 149



m/e 105

The mass spectral peak at m/e 177 appears in both the $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ mass spectra,³⁹ but it was observed to be of greater intensity than normal. In the $(\text{Me}_2\text{SiO})_3$ spectrum, m/e 177 is due to the loss of three methyl groups. The fragment present in these experiments is more likely to have a linear structure as suggested above, due to ring opening by attack of the methyl radicals.

Pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with HgMe_2 were continued at a lower temperature, 760K. The pattern of peaks on both the gas chromatograph and the mass spectra were the same as at 855K.

From these experiments, it appears that the methyl radicals produced react with the three and four-membered cyclosiloxane rings, causing ring opening and the formation of siloxane fragments. No evidence for the formation of any trimethylsilyl species was recorded.

PART B

Insertion Reactions of Me_2SiO

Introduction

The reaction between $(\text{Me}_2\text{SiO})_4$ and the monochlorosilanes, catalysed by ferric chloride, to give linear chloromethylsiloxanes with up to four Me_2SiO units in their structure, is quoted as occurring at 653K to 673K under very high pressures.⁵⁰ Other sources³¹⁻³⁴ quote the reaction temperature in the range from 473K to 523K, again the reaction being catalysed by ferric chloride. In the present study, experiments were carried out at higher temperatures, around 820K, to determine whether the insertion reaction would take place homogeneously in the gas-phase at low pressures.

Two monochlorosilanes; trimethylchlorosilane, Me_3SiCl , and dimethyldichlorosilane, Me_2SiCl_2 , were used. The intermediate Me_2SiO was presumed to insert into the Si-Cl bond of the chlorosilanes to produce a linear chloromethylsiloxane. If the reaction took place by insertion of one Me_2SiO unit at a time, then it would be expected that the insertion product with one Me_2SiO unit would be most abundant.

Some work was also carried out using silicon tetrachloride, SiCl_4 , and with tetramethylsilane, Me_4Si , and trimethylsilane, Me_3SiH , to see whether the intermediate Me_2SiO would also insert into the Si-Me and Si-H bonds respectively.

(1) Trimethylchlorosilane, Me₃SiCl

Pyrolysis runs of Me₃SiCl alone were carried out first, to condition the walls of the reaction vessel.

10 and 15 minute pyrolysis runs of (Me₂SiO)₄ with excess Me₃SiCl at 820K showed a new broad peak on the gas chromatograph, appearing after the (Me₂SiO)₄ peak. Mass spectrometric analysis of the reaction mixture showed new peaks at m/e 295, 235, 224, 223, 222, 221, 189, 150, 149, 148, 147, 131, 117, 115, 103, 95, 93, 75, 74, 73, 38 and 36 (See Appendix 2.9(a)).

The peaks at m/e 38 and 36 were due to HCl and were very strong, indicating that hydrolysis of the Me₃SiCl or any chlorine containing insertion products had taken place in the mass spectrometer.

The sets of peaks at m/e 147, 148, 149, 221, 222, 223 and 295 were due to losses of OH or Me from :-

HO(Me ₂ SiO)SiMe ₃	loss of Me	: m/e 149
HO(Me ₂ SiO)SiMe ₃	loss of OH	: m/e 147
HO(Me ₂ SiO) ₂ SiMe ₃	loss of Me	: m/e 223
HO(Me ₂ SiO) ₂ SiMe ₃	loss of OH	: m/e 221
HO(Me ₂ SiO) ₃ SiMe ₃	loss of Me	: m/e 297
HO(Me ₂ SiO) ₃ SiMe ₃	loss of OH	: m/e 295

From this mass spectrum it appeared that the intermediate Me₂SiO had either inserted into the Si-Cl bond in Me₃SiCl one, two or three times to form the products, with the chlorine atom in each product being hydrolysed, the peaks at m/e 36, 38 confirming this; or the intermediate Me₂SiO had inserted into the Si-O bond of Me₃SiOH formed from the

hydrolysis of Me_3SiCl . The first alternative is the most likely, as the hydrolysis almost certainly occurred in the mass spectrometer. The peaks at m/e 147,149 were stronger than those at m/e 221,223 which were stronger than the peak at m/e 295. The peak at m/e 297 was very small. This suggested stepwise formation of the insertion products, one Me_2SiO unit having inserted in each step. The peak at m/e 147 could also have been due, however, to loss of a methyl group from hexamethyldisiloxane, $\text{Me}_3\text{SiOSiMe}_3$, formed by the hydrolysis of the Me_3SiCl .

The temperature of the vessel was lowered to determine whether the products would be formed at the temperatures quoted in Haiduc⁵⁰ without the use of a catalyst. At 660K, when no decomposition of the $(\text{Me}_2\text{SiO})_4$ occurred, judging by observing no $(\text{Me}_2\text{SiO})_3$ peak on the gas chromatograph, no evidence for insertion product formation was obtained. Raising the temperature to 723K, a 30-minute pyrolysis run produced the insertion product peaks on the mass spectrum again, after the reaction mixture had been trapped out.

At the temperature 770K, a 20-minute pyrolysis run, 0.3% decomposition of $(\text{Me}_2\text{SiO})_4$, again showed peaks due to the insertion products on the mass spectrum. With greater decomposition, the insertion product peaks increased in intensity. From this it appeared that the formation of the insertion products occurred only when the intermediate Me_2SiO had been formed by the $(\text{Me}_2\text{SiO})_4$ decomposing, that is the products were formed only by an insertion reaction and not by some other reaction between $(\text{Me}_2\text{SiO})_4$ and Me_3SiCl .

The reaction vessel temperature was raised to 868K

and the pyrolysis run of $(\text{Me}_2\text{SiO})_4$ with Me_3SiCl carried out at this temperature gave rise to mass spectral peaks at m/e 147, 148, 149, 221, 222, 223, 295 and also m/e 167, 169 due to the insertion product $\text{Cl}(\text{Me}_2\text{SiO})\text{SiMe}_3$ which had not been hydrolysed (See Appendix 2.9(b)). No peaks were seen, however, for the insertion products $\text{Cl}(\text{Me}_2\text{SiO})_2\text{SiMe}_3$ and $\text{Cl}(\text{Me}_2\text{SiO})_3\text{SiMe}_3$.

$\text{Cl}(\text{Me}_2\text{SiO})\text{SiMe}_3$	loss of Me :	m/e 167, 169
$\text{Cl}(\text{Me}_2\text{SiO})_2\text{SiMe}_3$	loss of Me :	m/e 241, 243
$\text{Cl}(\text{Me}_2\text{SiO})_3\text{SiMe}_3$	loss of Me :	m/e 315, 317

The peaks at m/e 167, 169 could not be reproduced again on the mass spectra when carrying out identical pyrolysis runs, so it was decided to try and cut down on the hydrolysis occurring in the mass spectrometer.

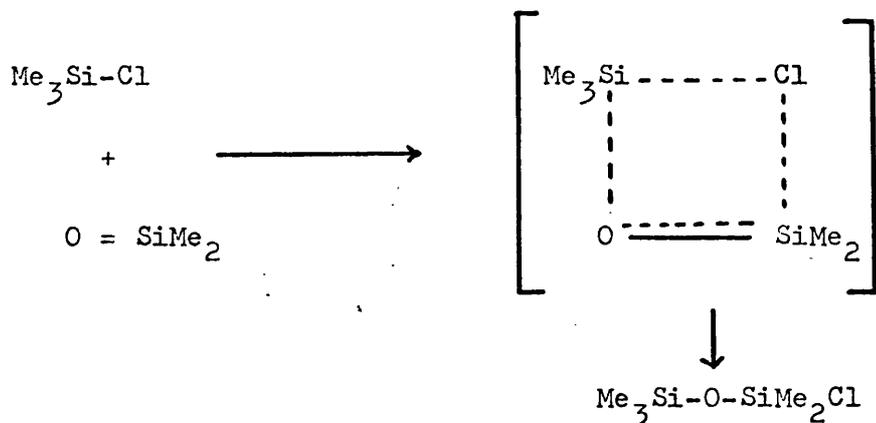
The reaction mixture from a 15-minute pyrolysis run of $(\text{Me}_2\text{SiO})_4$ with Me_3SiCl at 817K was trapped out. A very small pressure of silicon tetrachloride, SiCl_4 , was allowed to enter the mass spectrometer lock first, to react with any water before the reaction mixture entered. The usual hydrolysed product peaks were observed on the mass spectrum and also peaks at m/e 167, 169. This showed that hydrolysis of the reaction mixture had been cut down enough by the SiCl_4 for the chlorine containing insertion product peaks to be seen. A 20-minute run at the same temperature showed very strong m/e 167, 169 peaks on the mass spectrum.

Individual peak trapping from runs with $(\text{Me}_2\text{SiO})_4$ and Me_3SiCl was carried out. The mass spectra showed peaks for the hydrolysed insertion products, but no definite correlation between mass spectral peaks and gas chromatographic peaks could

be made. The broad peak after the $(\text{Me}_2\text{SiO})_4$ peak on the gas chromatograph, when trapped out, gave rise to mass spectral peaks for both $\text{HO}(\text{Me}_2\text{SiO})_2\text{SiMe}_3$ and $\text{HO}(\text{Me}_2\text{SiO})_3\text{SiMe}_3$.

From the pyrolysis experiments with Me_3SiCl , it would appear that the intermediate Me_2SiO was inserting into the Si-Cl bond of the Me_3SiCl , one, two, or three times to give the insertion products, but the difficulties involved with overcoming hydrolysis only allowed the chlorine-containing insertion product with one Me_2SiO unit to be seen. The relative intensities of the insertion product peaks on the mass spectra indicated that stepwise insertion of the Me_2SiO was taking place.

The initial step in the mechanism for insertion of the intermediate Me_2SiO is probably the formation of a four-membered cyclic transition state :-



This mechanism accounts for the experimental observation that only one Me_2SiO intermediate was inserting into the Si-Cl bond at any one time.

From the bond dissociation energies involved in the reaction, the process of forming the insertion product should be thermodynamically favourable. It can be seen from the transition state that the Si=O π -bond in the silanone becomes a σ -bond, along with the formation of another Si-O σ -bond. The

enthalpy change for the reaction can be calculated thus :-

$$\begin{aligned} \Delta H &= \text{Si=O } \pi\text{-Bond Energy} && - && D(\text{Si-O}) \\ &= 158 && - && 444 \text{ }^{51} \\ &= -286 \text{ kJ mol}^{-1} \end{aligned}$$

This value is not strictly accurate for ΔH , as the π -bond energy for Si=O can be $\gg 158 \text{ kJ mol}^{-1}$.³

In the work carried out by Sommer and co-workers³⁵ on the addition reactions of the intermediate Me_2SiCH_2 to the Si-Cl and Si-F bonds, their results provided more evidence for their proposal that the Si=CH₂ double bond possessed considerable dipolar character. From the results of the present study with Me_3SiCl , it seems highly likely that the Si=O double bond possesses more dipolar character than the Si=CH₂ double bond, especially considering the greater electronegativity of oxygen compared to carbon.

(2) Dimethyldichlorosilane, Me_2SiCl_2

Experiments were carried out co-pyrolysing $(\text{Me}_2\text{SiO})_4$ and Me_2SiCl_2 , to determine whether the intermediate Me_2SiO would insert into the Si-Cl bond in Me_2SiCl_2 .

Pyrolysis runs of $(\text{Me}_2\text{SiO})_4$ with Me_2SiCl_2 were carried out at temperatures from 835K to 883K, varying the times of reaction and the excess pressure of Me_2SiCl_2 . In each pyrolysis run the reaction mixture was trapped out and analysed. However, no insertion product peaks were observed on a number of mass spectra, only siloxane and Me_2SiCl_2 peaks.

Further pyrolyses of $(\text{Me}_2\text{SiO})_4$ with Me_2SiCl_2 were carried out at the higher temperature, 920K. These runs were

also unsuccessful in producing any insertion product peaks on the mass spectra.

It is quite probable that insertion of Me_2SiO did occur into both the silicon-chlorine bonds of Me_2SiCl_2 to produce insertion products, some of which may have had too high a molecular weight to be detected by the gas chromatographic and mass spectrometric techniques used. However, if only two Me_2SiO intermediates inserted, one into each silicon-chlorine bond of Me_2SiCl_2 , then the insertion product formed would have had a low enough molecular weight to be detected, with or without hydrolysis.

From the experimental observations it seems more probable that the insertion was fairly facile, more facile than with Me_3SiCl , producing the high molecular weight compounds, rather than no insertion taking place at all.

(3) Silicon Tetrachloride, SiCl_4

In this work with chlorosilanes, before a pyrolysis run was carried out, some SiCl_4 was usually allowed to enter the reaction vessel to condition it by reacting with any traces of water present in the vessel.

On the mass spectra for these pyrolysis runs, a consistent peak at m/e 227 was observed, and a smaller peak at m/e 229. As these peaks were observed with different trapping agents, and as they only appeared if the vessel had been conditioned prior to the run, it was thought they might occur by reaction of the intermediate Me_2SiO with SiCl_4 .

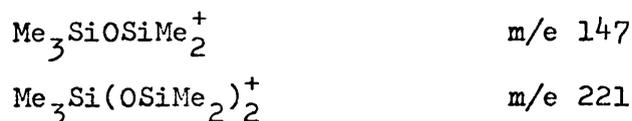
Some $(\text{Me}_2\text{SiO})_4$ was pyrolysed with SiCl_4 at 841K and the peaks at m/e 227, 229 were observed to be quite strong on

the mass spectrum recorded. m/e 227, 229 are due to loss of a methyl group from the single insertion product $\text{Cl}_3\text{SiOSiMe}_2\text{Cl}$. The fact that only the single insertion product was observed is probably due to the first silicon-chlorine bond in SiCl_4 being significantly weaker than the others.⁵²

(4) Trimethylsilane, Me_3SiH and Tetramethylsilane, Me_4Si

Trimethylsilane was used as a trapping agent to determine whether the intermediate Me_2SiO would insert into the Si-H bond, in a similar way to silylene insertion. Tetramethylsilane was also used to observe whether any insertion into the Si-Me bond took place, although, as with silylenes, insertion into the Si-Me bond was thought to be unlikely.

Initial pyrolysis runs were carried out at 841K. From this temperature up to 898K, no reaction was observed with either compound. At higher temperatures, 920K, there was still no indication of reaction with Me_3SiH , but with Me_4Si some product formation was observed. The mass spectrum for a 20-minute pyrolysis run at 920K with Me_4Si showed new peaks at m/e 147 and 221 :-



The compounds giving rise to these fragment ions are probably formed not from insertion of Me_2SiO into the silicon-methyl bond, but from addition reactions between Me_2SiO and $\text{Me}_3\text{Si}\cdot$ radicals, since Me_4Si dissociates quite appreciably at 920K.^{25,26}

(5) Conclusion

The results of the reactions of $(\text{Me}_2\text{SiO})_4$ with Me_3SiCl and SiCl_4 provide good evidence for the gas-phase homogeneous insertion of Me_2SiO into the silicon-chlorine bond and hence good evidence for the independent existence of Me_2SiO as a reactive intermediate.

From the pyrolysis reactions of $(\text{Me}_2\text{SiO})_4$ with the double-bonded hydrocarbons, most of the mass spectral data can be assigned to structures formed from radical reactions between fragments of the cyclic siloxane ring or Me_2SiO itself with these hydrocarbons.

It may be that the elimination of Me_2SiO from the $(\text{Me}_2\text{SiO})_4$ ring to leave $(\text{Me}_2\text{SiO})_3$ is not completely concerted and that a biradical intermediate is present in the elimination reaction. Reaction of this biradical with the double bonded hydrocarbons used as trapping agents, could then give the types of structure observed on the mass spectra. However, reaction of the trapping agents with this biradical would lower the yield of $(\text{Me}_2\text{SiO})_3$ formed in the decomposition of $(\text{Me}_2\text{SiO})_4$. The experimental evidence shows that the yield of $(\text{Me}_2\text{SiO})_3$ was not significantly reduced in the presence of the trapping agents.

Evidence for the formation of cyclic adducts between Me_2SiO and the double bonded hydrocarbons was obtained only with cyclopentadiene. It has been stated earlier that some of the cyclic adducts, especially the silaoxetanes which could be formed, might rapidly decompose again at the temperatures used. On the other hand, it has been shown that the type of cyclic adduct formed between Me_2SiO and 1,3-butadiene should be thermally stable at these temperatures.

The observation in previous work^{3,6} and in this work that no $(\text{Me}_2\text{SiO})_5$ is formed when double bonded hydrocarbons are present in the pyrolysis of $(\text{Me}_2\text{SiO})_4$ tends to suggest that some form of reaction is occurring between the intermediate Me_2SiO and the trapping agent. As the cycloaddition reaction was not observed in the majority of cases, and as the $\text{Si}=\text{O}$ double bond in Me_2SiO seems to possess dipolar character, a radical type addition reaction between the Me_2SiO and the double bond in the trapping agent to form a biradical might be occurring. Bimolecular abstraction by this biradical to form a stable compound is unlikely, however, intramolecular rearrangement would probably be more favourable.

Alternatively, heterogeneous loss of Me_2SiO intermediates to the walls of the reaction vessel might increase considerably when hydrocarbons are present in excess with the $(\text{Me}_2\text{SiO})_4$. This would also affect the rate of insertion of Me_2SiO into $(\text{Me}_2\text{SiO})_4$ to form $(\text{Me}_2\text{SiO})_5$.

Small amounts of methane were observed to be formed in the pyrolysis of $(\text{Me}_2\text{SiO})_4$ in the presence of trapping agents. A secondary reaction process for the $(\text{Me}_2\text{SiO})_4$ has been proposed to account for the formation of methane. Loss of a methyl group from $(\text{Me}_2\text{SiO})_4$ could give rise to reactions between the methyl radical and the double bond in the trapping agent, or between the $(\text{Me}_2\text{SiO})_4\text{-Me}$ radical and the trapping agent, these latter reactions causing fragmentation of the siloxane ring. Abstraction of a hydrogen atom by the methyl radical gives rise to the methane.

The fact that the peaks due to adduct formation observed on the gas chromatograph were all very small in relation

to the $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ peaks tends to indicate that these adducts were formed in small amounts, most probably from secondary radical reactions of the $(\text{Me}_2\text{SiO})_4$.

PART C

Pyrolysis Reactions of cis-Trimethyltriphenylcyclotrisiloxane

Introduction

The pyrolysis of cis-trimethyltriphenylcyclotrisiloxane, $(\text{MePhSiO})_3$, was carried out at temperatures around 790K to determine the products formed on decomposition. Copyrolyses of $(\text{MePhSiO})_3$ with $(\text{Me}_2\text{SiO})_4$ were also carried out to observe whether any siloxanes containing both MePhSiO and Me_2SiO units were formed and if so, whether there would be a feasible method of preparation, with industrial application, of some of these mixed cyclic siloxanes.

(1) Pyrolysis Reactions carried out on the Vacuum System

Initial pyrolysis runs of $(\text{MePhSiO})_3$ were carried out by injecting solutions of the $(\text{MePhSiO})_3$ in various solvents directly into the reaction vessel. Solvents used included benzene, cyclopentadiene, toluene and chloroform. With this method, however, no peak due to $(\text{MePhSiO})_3$ was observed on the gas chromatograph, even when increasing the column temperature from 353K to 388K. The $(\text{MePhSiO})_3$ was found to be too involatile under these conditions to pass through the g.l.c. system.

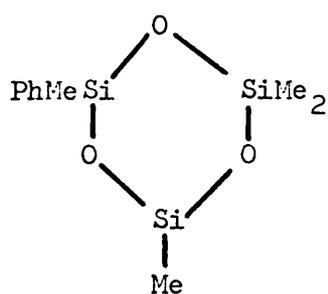
Introducing some solid $(\text{MePhSiO})_3$ directly into the reaction vessel was also unsuccessful in producing a $(\text{MePhSiO})_3$ peak on the gas chromatograph.

A mass spectrum of the solid $(\text{MePhSiO})_3$ was recorded. It showed the main peaks at :-

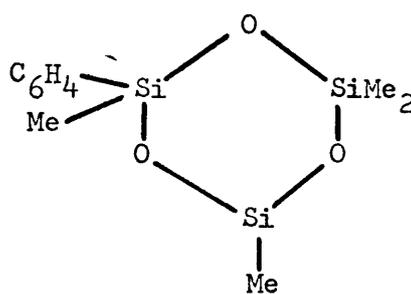
m/e 408	M^+	
393	-Me	
378	-2 X Me	(See Appendix 2.10(a))
315	-(Me + PhH)	
253	-(Ph + PhH)	

The two most intense peaks were m/e 253 and 315, the latter being the base peak.

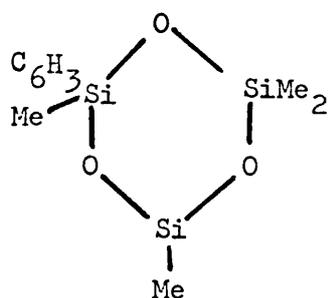
Injecting a solution of $(\text{MePhSiO})_3$ in $(\text{Me}_2\text{SiO})_4$ gave rise to a new peak on the gas chromatograph. All g.l.c. peaks were trapped out, and the mass spectrum recorded showed not only peaks due to $(\text{Me}_2\text{SiO})_3$, $(\text{Me}_2\text{SiO})_4$ and $(\text{Me}_2\text{SiO})_5$, but also new peaks at m/e 269, 268, 267, 237, 195, 194, 193, 180, 179, 178, 177, 121, 119, 117, 115, 105 (See Appendix 2.10(b)). Possible structures were assigned to some of these mass spectral peaks :-



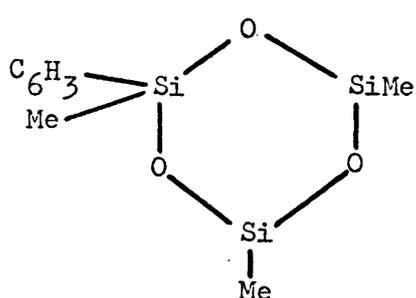
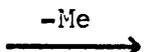
m/e 269



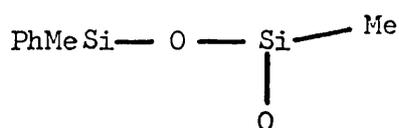
m/e 268



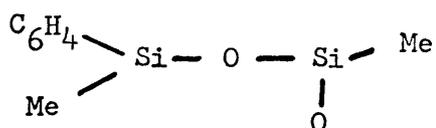
m/e 267



m/e 237



m/e 195



m/e 194

m/e 179 PhMeSi-O-SiMe

m/e 121 PhSiO

m/e 178 and 177 : loss of H

atoms from Ph ring.

m/e 105 PhSi

Further pyrolysis runs, in which solutions of $(\text{MePhSiO})_3$ in $(\text{Me}_2\text{SiO})_4$ were injected into the reaction vessel, were still unsuccessful in producing a peak due to $(\text{MePhSiO})_3$ on the gas chromatograph, even with a high column temperature of 423K.

At this stage it was realised that the $(\text{MePhSiO})_3$ would not pass through the g.l.c. system even at the maximum temperatures for the column and detector, so it was decided to continue the work on the pyrolysis of $(\text{MePhSiO})_3$ using sealed tubes.

(2) Pyrolysis Reactions of $(\text{MePhSiO})_3$ carried out in Sealed Tubes

Pyrolysis runs of $(\text{MePhSiO})_3$ in solution in $(\text{Me}_2\text{SiO})_4$ were carried out for various times at 790K. For short times, less than 20 minutes, only $(\text{Me}_2\text{SiO})_3$, $(\text{Me}_2\text{SiO})_4$, $(\text{Me}_2\text{SiO})_5$ and $(\text{MePhSiO})_3$ peaks were observed on the mass spectra. For longer times, about 45 minutes, the following peaks were observed on the mass spectra :-

m/e 489	405	342	
477	403	341	
475	401	339	
469	393	315	(All peaks above m/e 281
467	389	313	See Appendix 2.10(c))
417	345	311	
416	344	295	
415	343		

Some of these peaks are due to loss of methyl or phenyl groups, or combinations of methyl and phenyl groups, from $(\text{MePhSiO})_3$ or mixed cyclic siloxanes formed from Me_2SiO and MePhSiO units.

Let $\text{MePhSiO} = \text{A}$, and $\text{Me}_2\text{SiO} = \text{B}$, then a table of the mixed cyclic siloxanes, which could be formed, can be drawn up.

Table 3.1

Molecular Weights for Mixed Cyclic Siloxanes which
can be formed from $(\text{MePhSiO})_3$ and $(\text{Me}_2\text{SiO})_4$

n	A_n	(-Me)	B_n	(-Me)
1	136	(121)	74	(59)
2	272	(257)	148	(133)
3	408	(393)	222	(207)
4	544	(529)	296	(281)
n	AB_n	(-Me)	A_2B_n	(-Me)
1	210	(195)	346	(331)
2	284	(269)	420	(405)
3	358	(343)	494	(479)
4	432	(417)	568	(553)

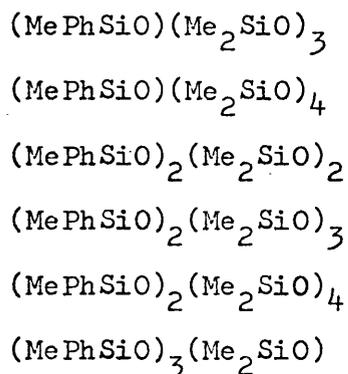
n	A_3B_n	(-Me)	A_4B_n	(-Me)
1	482	(467)	618	(603)
2	556	(541)	692	(677)
3	630	(615)	766	(751)
4	704	(689)	840	(825)

In the mass spectrum for $(\text{MePhSiO})_3$, the peak of strongest intensity is m/e 315. This corresponds to loss of benzene and a methyl group, 93 a.m.u., from the molecule-ion. The peak at m/e 253 is also very strong, and this corresponds to loss of benzene and a phenyl group, 155 a.m.u. from the molecule-ion.

From the previous mass spectrum, the following fragments can be assigned to some of the mass values, using Table 3.1

m/e 475		-(PhH + Me) from A_2B_4
467		-Me from A_3B
	and	-Ph from A_4
417		-Me from AB_4
	and	-Ph from A_2B_3
405		-Me from A_2B_2
401		-(PhH + Me) from A_2B_3
393		-Me from A_3
389		-(PhH + Ph) from A_4
343		-Me from AB_3
	and	-Ph from A_2B_2
341	possibly	-2 X Ph from A_2B_3
339		-(PhH + Me) from AB_4
315		-(PhH + Me) from A_3

These mass spectral peaks give good indication of the formation of $(\text{MePhSiO})_4$, and mixed cyclic siloxanes with the formulae :-



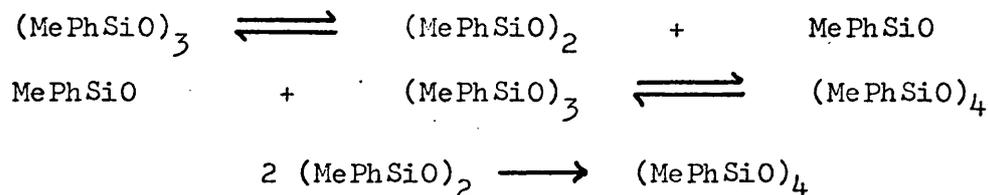
$\text{MePhSiO}(\text{Me}_2\text{SiO})_3$ and $\text{MePhSiO}(\text{Me}_2\text{SiO})_4$ can be formed by the insertion of one MePhSiO unit into $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ respectively. Similarly $(\text{MePhSiO})_3\text{Me}_2\text{SiO}$ can be formed by the insertion of one Me_2SiO unit into $(\text{MePhSiO})_3$.

The thermolysis of solid $(\text{MePhSiO})_3$ was carried out in sealed tubes for various reaction times, from 10 minutes to 30 minutes, at 790K. The mass spectra obtained from each run were quite consistent with peaks at :-

m/e	529	408	315	254
	527	393	301	253
	525	377	285	
	469	331	257	(See Appendix 2.10(d))
	451	329	255	

The strongest new peak above m/e 408 was m/e 451. This peak is 136 a.m.u. above m/e 315, the strongest peak in the $(\text{MePhSiO})_3$ mass spectrum. It would appear, therefore, that m/e 451 is the corresponding peak for $(\text{MePhSiO})_4$, being due to loss of benzene and a methyl group from $(\text{MePhSiO})_4$. The peak at m/e 529 is due to loss of a Me group from $(\text{MePhSiO})_4$.

From this mass spectrum it appears that the major decomposition product of $(\text{MePhSiO})_3$ is $(\text{MePhSiO})_4$. A simple mechanism for decomposition can be written :-



Some $(\text{MePhSiO})_5$ and higher cyclics might also be formed, but no evidence for their formation was observed. The $(\text{MePhSiO})_2$ formed would probably not exist as the cyclic dimer, but as a linear siloxane which rapidly dimerises into the cyclic tetramer, $(\text{MePhSiO})_4$.

One and two hour pyrolysis reactions of $(\text{MePhSiO})_3$ were carried out in sealed tubes at 790K. The mass spectra again showed peaks at m/e 451, 529, indicating that $(\text{MePhSiO})_4$ was still being formed from high percentage decomposition of $(\text{MePhSiO})_3$.

A 30-minute pyrolysis run of $(\text{MePhSiO})_3$ with $(\text{Me}_2\text{SiO})_4$ at 793K was carried out. The mass spectrum of the products showed peaks at :-

m/e 563	478	461	416	402	358	343	328
550	477	431	415	401	357	342	327
548	476	430	407	399	356	341	325
490	475	429	406	393	355	333	315
489	467	419	405	389	346	332	313
488	465	418	404	387	345	331	311
479	463	417	403	385	344	329	300

(All peaks above m/e 281: See Appendix 2.10(e)).

Again this mass spectrum shows evidence of mixed cyclic siloxane formation.

m/e 479	-Me from A_2B_3
	and -Ph from A_3B_2
477	-Me ₂ SiO from A_2B_4 OH
475	-(Me + PhH) from A_2B_4
467	-Me from A_3B
463	-(Me + PhH) from A_3B_2
461	-(Ph + 2 X Me) from A_2B_4
429	-Me from B_6
417	-Me from AB_4
415	-(PhMeSiO) from A_2B_4 OH
405	-Me from A_2B_2
403	-(Me ₂ SiO) from A_2B_3 OH
401	-(Me + PhH) from A_2B_3
	and -(Ph + PhH) from A_3B_2
393	-Me from A_3
389	-(Me + PhH) from A_3B
	and -(Ph + PhH) from A_4
387	-(Ph + 2 X Me) from A_2B_3
358	M^+ for AB_3
355	-Me from B_5
346	M^+ for A_2B
343	-Me from AB_3
331	-Me from A_2B
327	-(Me + PhH) from A_2B_2
315	-(Me + PhH) from A_3

A 10-minute pyrolysis run of $(\text{MePhSiO})_3$ in solution in $(\text{Me}_2\text{SiO})_4$ was carried out at 793K. The mass spectrum of the products showed similar peaks as in previous mass spectra:-

m/e	419	404	346	333	289	267	
	418	403	345	332	283	253	
	417	401	344	331	282		
	415	357	343	329	281		(Peaks above m/e 207 :
	406	356	342	328	271		See Appendix 2.10(f)).
	405	355	341	327	269		

Again some of these peaks can be attributed to fragments from mixed cyclic siloxanes, as the mass values are consistent with the previous mass spectrum obtained. The peak at m/e 269 is due to loss of a methyl group from AB_2 .

As stated above, it appears that on thermal decomposition of $(\text{MePhSiO})_3$, the major product is $(\text{MePhSiO})_4$. In the reaction between $(\text{Me}_2\text{SiO})_4$ and $(\text{MePhSiO})_3$ mixed cyclic siloxanes are formed with the following structures :-

AB_2	$\text{MePhSiO}(\text{Me}_2\text{SiO})_2$
AB_3	$\text{MePhSiO}(\text{Me}_2\text{SiO})_3$
AB_4	$\text{MePhSiO}(\text{Me}_2\text{SiO})_4$
A_2B	$(\text{MePhSiO})_2\text{Me}_2\text{SiO}$
A_2B_2	$(\text{MePhSiO})_2(\text{Me}_2\text{SiO})_2$
A_2B_3	$(\text{MePhSiO})_2(\text{Me}_2\text{SiO})_3$
A_2B_4	$(\text{MePhSiO})_2(\text{Me}_2\text{SiO})_4$
A_3B	$(\text{MePhSiO})_3\text{Me}_2\text{SiO}$
A_3B_2	$(\text{MePhSiO})_3(\text{Me}_2\text{SiO})_2$

(3) Conclusion

The formation of these mixed cyclic siloxanes is good additional evidence for the existence of species such as MePhSiO and Me₂SiO as reactive intermediates in the thermal decomposition of the siloxanes (MePhSiO)₃ and (Me₂SiO)₄ at temperatures above 790K.

Also as stated before, mixed cyclic siloxanes such as AB₃, AB₄ and A₃B could be formed by insertion of one MePhSiO or Me₂SiO intermediate into (Me₂SiO)₃, (Me₂SiO)₄ or (MePhSiO)₃. Another possible mechanism for the formation of some of these mixed cyclic siloxanes is cyclic oligomerisation of a number of MePhSiO and Me₂SiO intermediates in different ratios, in the same way that (Me₂SiO)₄ and (Me₂SiO)₃ are produced in the reaction of Me₂Si=CH₂ species with aldehydes and ketones.^{15,16}

From the number and type of cyclic siloxanes formed in the pyrolysis reactions between (Me₂SiO)₄ and (MePhSiO)₃, it would appear that separation and isolation of any one of these mixed cyclic siloxanes would not be feasible. No one siloxane was formed in great excess over the other siloxanes, so reaction between (Me₂SiO)₄ and (MePhSiO)₃ does not appear to be a suitable method of preparation for the mixed cyclic siloxanes. However, these reactions between (Me₂SiO)₄ and (MePhSiO)₃ were carried out on a purely qualitative basis. By varying the initial concentrations of (Me₂SiO)₄ and (MePhSiO)₃, some of the mixed cyclic siloxanes might be formed in greater yield over the others.

CHAPTER FOUR

INTRODUCTION TO WORK ON SILYLENES.

INTRODUCTION TO WORK ON SILYLENES

Silylenes are divalent silicon intermediate species, the silicon analogues of carbenes. There is a progressive increase in the stability of the MR_2 radical relative to the MR_3 radical down group IV B, so silylene intermediates are important species in silicon chemistry.

The existence of silylenes, especially inorganic silylenes, has been known for many years, and the chemistry of their preparations and reactions has been well established.⁵⁹ The pyrolysis of Si_2Cl_6 has been studied by Chernyshev and co-workers.⁶⁶ By trapping with acetylene and other hydrocarbons he obtained evidence for the existence of dichlorosilylene, $SiCl_2$. Work carried out by Margrave and co-workers⁷⁷ on difluorosilylene, SiF_2 , has given much insight into the spectral and physical properties of silylenes. At low pressures, ~ 0.1 torr, SiF_2 has a half-life of 150 seconds, and so is the most stable of the silylenes known. From spectroscopic data, much of it established from work on SiF_2 , silylenes appear to be bent molecules, the angle between the two substituents on the silicon atom being less than the tetrahedral angle, from 92° in SiH_2 to 103° in $SiHBr$. From further spectroscopic data and kinetic behaviour, silylenes also appear to be in the singlet electronic state.^{55,70,71}

The most important type of reaction which silylenes can undergo is insertion into single bonds. They are known to insert rapidly into silicon-hydrogen bonds,⁵⁴⁻⁵⁸ and bonds between silicon and an atom with lone pairs of electrons, such as oxygen,⁵⁹ nitrogen and the halogens.⁵⁹ They are also known

to insert into hydrogen, but this insertion involves a higher activation energy, $\sim 23 \text{ kJ mol}^{-1}$,⁷¹ than for insertion into other bonds. Silylene insertion however into silicon-carbon, carbon-carbon single bonds, or carbon-hydrogen bonds requires a high activation energy, although the formation of Me_4Si as a secondary reaction product in the pyrolysis of Me_6Si_2 is an example of silylene elimination from a disilane containing only silicon-carbon bonds.⁷⁸

Kinetic studies carried out to date on silylene elimination and insertion reactions have been mainly concerned with the pyrolysis of monosilane,^{72,73} disilane^{60,61} and other alkyldisilanes.^{64,74,75} The first comprehensive kinetic study of a silane pyrolysis was that of monosilane, SiH_4 .⁷² Although the mechanism could not be established with any certainty, it is very probable that the pyrolysis reaction takes place by the elimination of silylene, SiH_2 , rather than by dissociation into a silyl radical $\cdot\text{SiH}_3$, and $\cdot\text{H}$. Two mechanisms were proposed for the decomposition of disilane, Si_2H_6 , a silylene mechanism⁶⁰ and a silyl radical mechanism⁶¹ but it is now agreed that the decomposition proceeds by silylene elimination.

The major kinetic study of the pyrolysis of disilane has been carried out by Purnell and Bowrey.⁶⁰ Although a previous study⁷⁶ had identified the reaction products, no attempt had been made to measure kinetic data, or propose a definite mechanism.

The experimental evidence obtained by Purnell established the pyrolysis mechanism as proceeding via initial decomposition into silylene, SiH_2 , and monosilane, followed by insertion of silylene into disilane to give trisilane. Secondary insertion processes gave rise to the formation of two isomeric tetrasilanes. Hydrogen, also a reaction product, was formed by

breakdown of a polymer $(\text{SiH}_2)_n$ on the walls of the vessel.

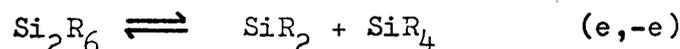
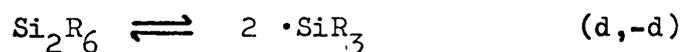
The three principal products : SiH_4 , Si_3H_8 , and H_2 were all formed in first-order reactions, the Arrhenius parameters for the formation of SiH_4 being :

$$\log k/\text{s}^{-1} = 14.52 \pm 0.36 - (206.0 \pm 4.5) \text{ kJ mol}^{-1}/2.303 \text{ RT}$$

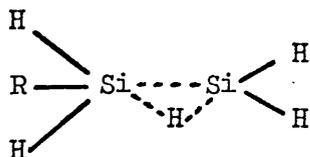
The pyrolyses of some alkyldisilanes, such as methyldisilane^{64,75} and 1,2-dimethyldisilane⁷⁵ have been studied by Ring and co-workers. They used deuterated and undeuterated silanes as trapping agents. From the results of their pyrolysis experiments they obtained consistent evidence that the disilanes studied all decomposed by a silylene mechanism. Kinetic parameters for the methylsilane pyrolysis were determined,⁶⁴ and these agreed with kinetic parameters determined for other disilanes decomposing by a silylene mechanism.

From the examples in the above paragraphs, it can be seen that one of the main methods for the gas-phase formation of silylenes is the pyrolysis of mono- and disilanes. In these reactions, the first step can be either formation of two silyl radicals (eqn. (d) below), or the formation of a silylene (eqn. (e) below).

For disilanes :-



The exact mechanism for silylene elimination and insertion proposed by Ring and co-workers^{61,64} was a 1,2 shift, where a silicon-hydrogen bond was involved the shift was a 1,2-hydrogen shift. This mechanism requires a three-membered cyclic transition state, with hydrogen as a bridging atom.



With other single bonds into which silylenes can insert, such as Si-X (where X is a halogen atom), Si-O, and Si-N, the atoms involved in the bond with the silicon atom can all behave as bridging atoms. It is because these atoms can behave as bridging atoms and form the cyclic three-membered transition state, that the low activation energies are obtained for insertion of silylenes into bonds between silicon and these atoms. 1,2-chlorine shifts have been proposed for silylene elimination from chlorodisilanes⁶⁶ (this work, Chapter 6), and 1,2-oxygen shifts for silylene elimination from methoxydisilanes.

For the decomposition of disilanes, a relationship between the enthalpy changes, ΔH ; activation energies, E , and bond dissociation energies can be set out as follows⁵³ :-

$$E_{(d)} = \Delta H_{(d)} + E_{(-d)} \quad \text{for decomposition into radicals}$$

$$E_{(e)} = \Delta H_{(e)} + E_{(-e)} \quad \text{for decomposition into a silylene.}$$

For the reaction producing a silylene, via the three-membered transition state involving a bridging atom :

$$\Delta H_{(e)} = D(R_3Si-SiR_3) + D(R_2Si-R) - D(R_3Si-R)$$

$$\text{hence } \Delta H_{(e)} = \Delta H_{(d)} - \left[D(R_3Si-R) - D(R_2Si-R) \right]$$

$$\text{since } \Delta H_{(d)} = D(R_3Si-SiR_3)$$

Because of the relative stability of silylenes,

$$D(R_2Si-R) < D(R_3Si-R)$$

so that $\Delta H_{(e)} < \Delta H_{(d)}$ and thus elimination of a silylene will be the more thermodynamically favoured process. Also, as the recombination of monoradicals requires little or no activation energy,

$$E_{(-d)} \sim 0$$

$$\text{so } E_{(d)} \sim \Delta H_{(d)}$$

$$\text{and since } \Delta H_{(d)} > \Delta H_{(e)}$$

$$E_{(d)} > \Delta H_{(e)}$$

$$\text{and } E_{(e)} = \Delta H_{(e)} + E_{(-e)}$$

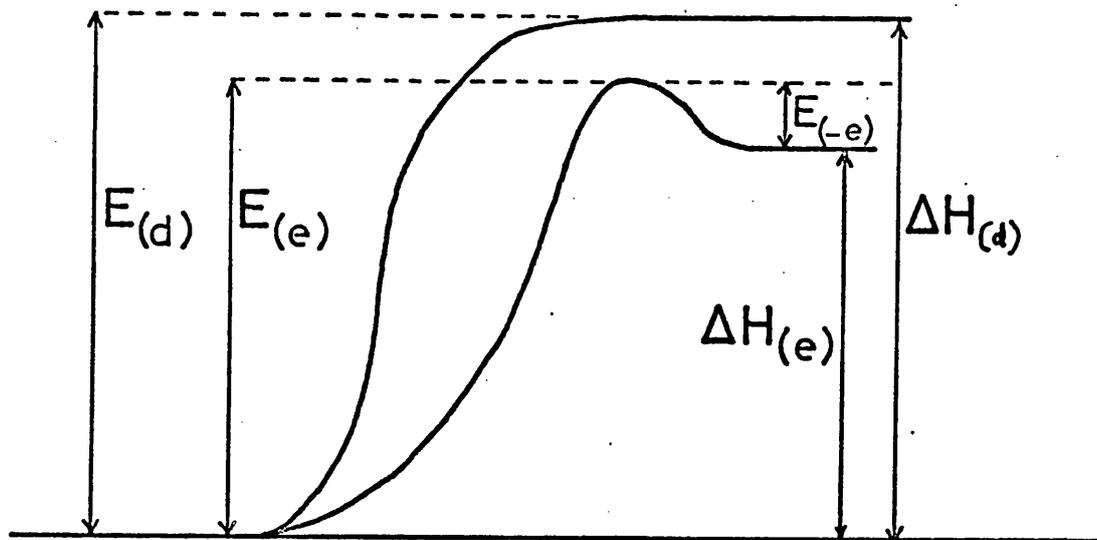
From these last two equations it can be seen that the value of $E_{(-e)}$ for the silylene insertion reaction will determine how great $E_{(e)}$ is, and whether $E_{(e)}$ will be greater or less than $E_{(d)}$, a major factor in determining whether silyl radicals or silylenes are formed. The other factor is that $\log A_{(d)} - \log A_{(e)} \approx 4$.

In diagram (a) of Fig. 4.1, $E_{(-e)}$ is small, so that $E_{(e)} < E_{(d)}$. In this reaction, the initial step would be formation of a silylene.

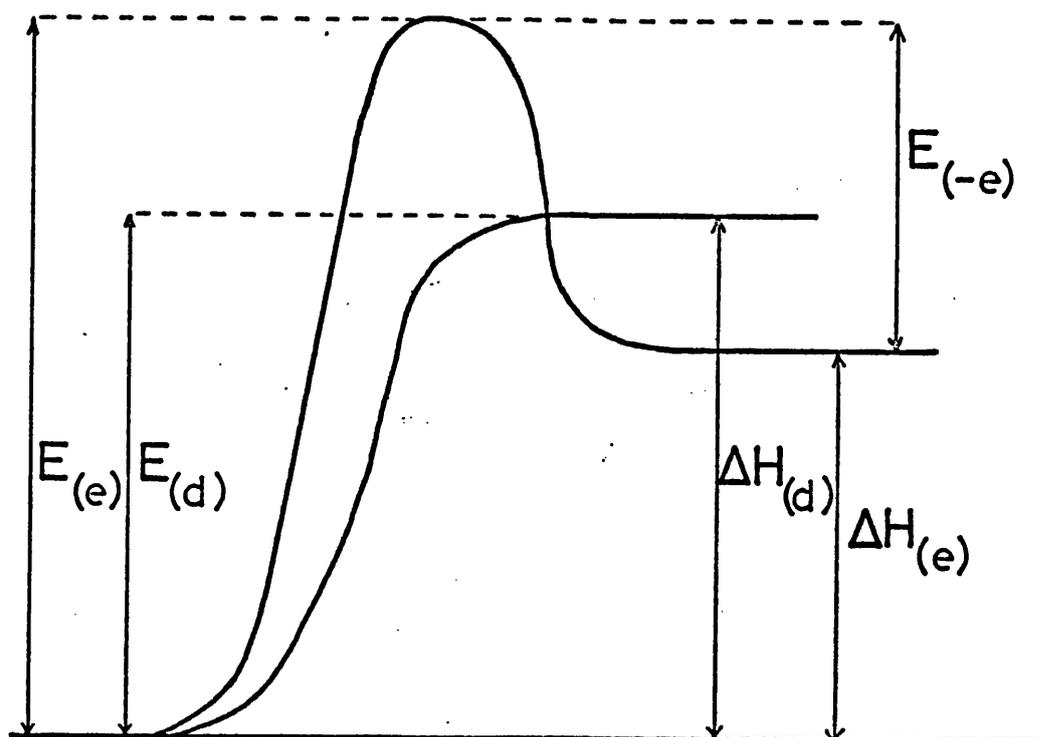
In diagram (b), $E_{(-e)}$ is large, so that $E_{(e)} > E_{(d)}$. The initial step in this case would be formation of two silyl radicals.

The distinction between these two cases is well established. As stated above, $E_{(-e)}$ is low for silylene insertion reactions into Si-H, Si-X, Si-O and Si-N bonds, and hence a disilane containing one or more of these bonds would give a silylene on pyrolysis.

Silylene insertion into silicon-carbon, carbon-carbon, and carbon-hydrogen bonds has not been observed. $E_{(-e)}$ for the



(a)

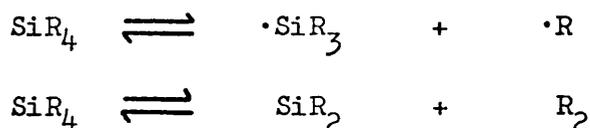


(b)

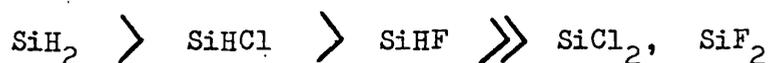
FIGURE 4.1. ENERGY DIAGRAMS SHOWING ACTIVATION ENERGIES (E) AND ENTHALPY CHANGES (ΔH) FOR DISSOCIATION INTO SILYL RADICALS (d) AND SILYLENES (e)

insertion reaction is high, because of the inability of carbon to behave as a bridging atom in the three-membered transition state, in which it would require a pentacovalent structure. Disilanes containing only alkyl or aryl groups would therefore belong to the second category, diagram (b), giving silyl radicals on pyrolysis. This is confirmed by kinetic experiments on the pyrolysis of hexamethyldisilane, Me_6Si_2 , where the initial step of the decomposition was found to be formation of two trimethylsilyl radicals.⁷⁸ However, formation of tetramethylsilane indicated that some silylene elimination was occurring, but the activation energy for this process was 282 kJ mol^{-1} , substantially higher than the activation energies found for silylene elimination from disilanes containing silicon-hydrogen or silicon-halogen bonds (Chapter Six).

Similar considerations apply to the pyrolysis of monosilanes, where the two types of reaction are :-



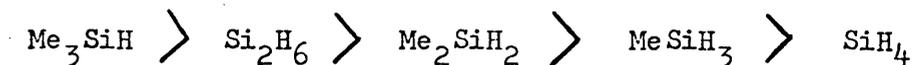
The relative rates of insertion of different silylenes into the silicon-hydrogen bond have been measured.⁶⁸ It was found that SiH_2 inserts very rapidly, with almost zero activation energy, the order of reactivity being :-



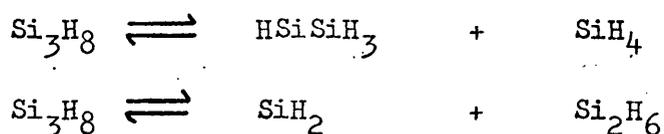
SiF_2 , as stated above, is unreactive in comparison with the other silylenes.

The relative rates of SiH_2 insertion into the Si-H bonds of various alkyldisilanes, in competition with disilane, have been measured.⁵⁷ A correlation between rate of insertion

and hydridic character of the Si-H bond has been established, the order of reactivity being :-



In the pyrolysis of trisilane alone, and in the presence of deuterated methylsilanes, monosilane, SiH_4 was observed as one of the decomposition products.⁵⁷ Also, as no abstraction products were formed indicating that radical reactions were not occurring, a silylene mechanism involving the species silylsilylene, HSiSiH_3 , was proposed, the two initial decomposition steps being :-



A co-pyrolysis of Si_3H_8 and Me_3SiD gave rise to the formation of $\text{Me}_3\text{SiSi}(\text{HD})\text{SiH}_3$, further evidence for the existence of HSiSiH_3 . Unlike its carbon analogue, methylcarbene, which isomerises to ethylene, it was found that the HSiSiH_3 underwent insertion reactions as well as polymerising.

Photolysis of cyclic and linear permethylated polysilanes^{79,80} has given rise to the formation of dimethylsilylene, an organic silylene. The photolysis experiments were carried out in cyclohexane at room temperature for the linear polysilanes, and at 318K for the cyclic polysilanes. The dimethylsilylene formed inserted into silicon-hydrogen and silicon-methoxy bonds of appropriate monosilanes added to the polysilanes. When dimethyldichlorosilane, Me_2SiCl_2 , was added, products formed by direct reaction between photochemically excited polysilanes and Me_2SiCl_2 were observed. No evidence was obtained for the insertion of Me_2Si into the silicon-

silicon bond.

Methylsilylene, MeSiH , has been formed from the photolysis of methylsilane,⁸¹ whereas dimethylsilylene has also been formed from the pyrolysis of pentamethyldisilane, $\text{Me}_5\text{Si}_2\text{H}$,⁸² at 573K - 598K in a sealed tube, the products being trimethylsilane, Me_3SiH , unreacted $\text{Me}_5\text{Si}_2\text{H}$ and higher polymethylsilanes of formula $\text{Me}_3\text{Si}(\text{Me}_2\text{Si})_n\text{H}$, where $n = 1 - 5$. The kinetics of the thermal decomposition of $\text{Me}_5\text{Si}_2\text{H}$ at low pressure have recently been measured,⁵⁸ and some of the insertion reactions of Me_2Si into the Si-H bonds of various alkylmonosilanes have been investigated.⁵⁸

Dimethylsilylene has been generated in the gas phase at temperatures 533K - 553K by the reaction of sodium/potassium vapour with dimethyldichlorosilane.⁸³ The Me_2Si formed was trapped out by adding Me_3SiH to the reaction mixture. Me_2Si has also been postulated as an intermediate in the thermal decomposition of some 7-silanorbornadienes,⁸⁴ the Me_2Si being trapped out in this reaction by adding diphenylacetylene to the 7-silanorbornadiene.

In the work described in the second part of this thesis, the pyrolyses of three methylchlorodisilanes were studied, and the kinetic parameters for their decomposition determined. From the decomposition products it was found that they decomposed by a silylene mechanism, in each case the silylene was trapped out using Me_3SiH . Other insertion reactions of the silylenes, especially insertion into the silicon-chlorine bond were investigated.

CHAPTER FIVE

EXPERIMENTAL PROCEDURE FOR SILYLENE WORK

EXPERIMENTAL PROCEDURE FOR SILYLENE WORK

5.1. Samples Used

The three chlorodisilanes used : pentamethyldisilane, $\text{Me}_5\text{Si}_2\text{Cl}$; 1,1,2-trichloro-1,2,2-trimethyldisilane, $\text{Me}_3\text{Si}_2\text{Cl}_3$; and 1,1,2,2-tetrachlorodimethyldisilane, $\text{Me}_2\text{Si}_2\text{Cl}_4$, were all prepared by the methods given in Appendix One. For other compounds used see Chapter Two, Section 2.1.

5.2. Description of Apparatus

The same vacuum system was used as described in Chapter Two. However, some modifications were carried out to the g.l.c. system, mainly use of different columns, column temperatures and flow rates.

(a) With $\text{Me}_5\text{Si}_2\text{Cl}$, a stainless steel column, 3m. x 3mm. O.D., with a silicone-oil on embacel packing was used. Column temperature was 72°C , sample flow rate was $20 \text{ cm}^3 \text{ min}^{-1}$.

(b) With $\text{Me}_2\text{Si}_2\text{Cl}_4$, identical conditions to $\text{Me}_5\text{Si}_2\text{Cl}$ were used. As only one decomposition product, MeSiCl_3 , was identified, there was no need for separation of any monochlorosilanes.

(c) With $\text{Me}_3\text{Si}_2\text{Cl}_3$, as two decomposition products could be formed (Me_2SiCl_2 and MeSiCl_3), a column was necessary which could separate these two monochlorosilanes. This column was 3m. in length by 6mm. O.D., with packing 10% w/w squalene on embacel 60-100 mesh, acid washed. With this column however, the $\text{Me}_3\text{Si}_2\text{Cl}_3$ peak could not be measured, as under the conditions used (column temperature 30°C , sample flow rate

20 cm³ min⁻¹) to separate the monochlorosilanes, the Me₃Si₂Cl₃ peak had too great a retention time. The value of the initial concentration of Me₃Si₂Cl₃ was therefore taken from the transducer reading.

After a number of kinetic runs throughout the temperature range of the study, it was found that the amount of MeSiCl₃ formed was too small to be measured accurately. At this stage the column used with Me₅Si₂Cl and Me₂Si₂Cl₄ was refitted, so that the overall kinetics of decomposition of Me₃Si₂Cl₃ could be determined accurately, by measuring both reactant and product peak areas.

5.3. Methods Used for Mass Spectrometric Analysis of Gas Chromatographic Peaks

The method used for mass spectrometric analysis of gas chromatographic peaks was to absorb the vapours in the gas stream on to Amberlite resin (See Chapter Two, Sec. 2.3. (e)).

With the chlorodisilanes, hydrolysis occurred either on the resin or in the mass spectrometer, for in certain cases, when trapping product or adduct peaks, the mass spectra of the hydrolysis products and not the chlorine-containing products were obtained. This was most noticeable when trapping out compounds containing more than one chlorine atom in the molecule.

However this trapping method proved to be quite satisfactory when trapping out compounds containing no chlorine.

5.4 Quantitative Measurement of Gas Chromatographic Peak Areas

In kinetic runs, the area of a peak on the gas chromatograph was taken as a measure of the concentration

or pressure of the vapour giving rise to the peak.

With a thermal conductivity detector there is no simple correlation between peak areas, as with a gas density detector, so the peak areas have to be calibrated against pressures of sample vapour (See Chapter Two, Sec. 2.2 (b)) for each reactant and product peak. The rate constants can then be determined from the pressure values, with the appropriate temperature correction.

With $\text{Me}_5\text{Si}_2\text{Cl}$, as symmetrical peaks were obtained for both $\text{Me}_5\text{Si}_2\text{Cl}$ and Me_3SiCl on the gas chromatograph, the peak areas were measured simply by taking the product of the height of the peak by the width at half the height.

With $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$, a more sophisticated system of peak area measurement was used. The Kipp and Zonen gas chromatographic chart recorder was connected through a retransmitting slide-wire to a Solartron Schlumberger digital voltmeter and a Facit tape punch. Readings on the digital voltmeter were punched on to the tape for each peak being measured. The area of the peak was then determined from the readings on the punch tape by using a computer programme based on Simpson's rule (See Appendix 4). The computing was carried out on a PDP-11 computer in BASIC language.

Arrhenius parameters for the decomposition of the chlorodisilanes were also computed from the values of the rate constants and temperatures using a least-squares programme, again in BASIC.

CHAPTER SIX

RESULTS AND DISCUSSION FOR THE WORK ON SILYLENES.

6.1 Kinetic Results for the Thermal Decomposition of
Three Chlorodisilanes

The three chlorodisilanes studied were :

pentamethylchlorodisilane, $\text{Me}_5\text{Si}_2\text{Cl}$; 1,1,2,2-tetrachloro-
1,2-dimethyldisilane, $\text{Me}_2\text{Si}_2\text{Cl}_4$; and 1,1,2-trichloro-
1,2,2-trimethyldisilane, $\text{Me}_3\text{Si}_2\text{Cl}_3$.

(a) Kinetics of the Thermolysis of Pentamethylchlorodisilane,
 $\text{Me}_5\text{Si}_2\text{Cl}$

$\text{Me}_5\text{Si}_2\text{Cl}$ alone was decomposed at temperatures in the range from 692K to 748K. The only product observed in the decomposition was identified as trimethylchlorosilane, Me_3SiCl , by gas chromatography and mass spectrometry. When trimethylsilane, Me_3SiH , was added in excess to the $\text{Me}_5\text{Si}_2\text{Cl}$, a new product peak was observed on the gas chromatograph. This was identified again by mass spectrometry to be pentamethyldisilane, $\text{Me}_5\text{Si}_2\text{H}$ (See Sec. 6.4).

At all temperatures the reaction was found to be first-order. At each temperature, the time for each kinetic run was kept constant and the initial concentration of $\text{Me}_5\text{Si}_2\text{Cl}$ varied. First-order rate plots of $\ln(a-x)$ against $\ln a$ were drawn for each temperature, giving a straight line of gradient 1 ± 0.03 . The rate constant at each temperature was determined from the intercept.

After completing a number of runs at varying temperatures, the Arrhenius parameters were calculated. These were found to be abnormally low, indicating that the decomposition of the $\text{Me}_5\text{Si}_2\text{Cl}$ was probably being surface-catalysed, rather than occurring as a homogeneous gas-phase reaction. To overcome this

problem, the walls of the reaction vessel were conditioned by a number of pyrolyses of Me_3SiCl . Thereafter the rate constants for the decomposition of $\text{Me}_5\text{Si}_2\text{Cl}$ became consistent when repeating runs at certain temperatures. An Arrhenius plot (Fig. 6.1) was drawn, giving a good straight line from which the activation energy and the pre-exponential factor were calculated, using the method of least-squares analysis.

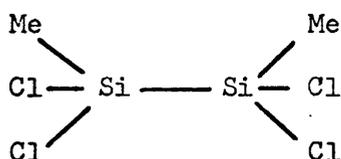
$$\log k/s^{-1} = 11.69 \pm 0.33 - (209.68 \pm 4.51) \text{ kJ mol}^{-1} / 2.303 RT$$

(Errors are standard deviations.)

Kinetic runs were carried out on the $\text{Me}_5\text{Si}_2\text{Cl}$ in the presence of excess Me_3SiH , to determine whether the presence of a trapping agent would significantly alter the rate of decomposition. It was found however, that at the temperatures used there was no significant change of rate. See Fig. 6.2(a)

(b) Kinetics of the Thermolysis of 1,1,2,2-Tetrachloro-1,2-dimethyldisilane, $\text{Me}_2\text{Si}_2\text{Cl}_4$

$\text{Me}_2\text{Si}_2\text{Cl}_4$ has the symmetrical structure



The temperature range for the thermal decomposition of $\text{Me}_2\text{Si}_2\text{Cl}_4$ was 660K to 703K. Only one product peak was observed on the gas chromatograph, identified by mass spectrometry as MeSiCl_3 . Only one adduct peak was observed when Me_3SiH was co-pyrolysed with $\text{Me}_2\text{Si}_2\text{Cl}_4$, again identified by mass spectrometry to be $\text{Me}_3\text{SiSiHMeCl}$ (See Sec. 6.4).

At all temperatures used, the reaction was found to be first-order, again by keeping the time for each kinetic run constant and varying the initial concentration of $\text{Me}_2\text{Si}_2\text{Cl}_4$. First-order plots gave a straight line with gradient 1 ± 0.03 .

With the majority of kinetic runs, however, the

initial concentration of $\text{Me}_2\text{Si}_2\text{Cl}_4$ was kept constant and the time for each run varied. First-order plots of $\ln \frac{a}{a-x}$ against time gave a straight line at low percentage decomposition, below 20%, but at higher percentage decomposition fall-off from the straight line was observed (Fig. 6.2) Fall-off on the first-order plots was observed at all temperatures throughout the range, the percentage decomposition above which fall-off occurred increasing from about 20% at 660K to about 48% at 703K.

The rate constant at each temperature was calculated from the gradient of the straight line drawn as a tangent to the curve through the origin. An Arrhenius plot was drawn (Fig. 6.3) which gave a good straight line, the Arrhenius parameters again being calculated by a least-squares method.

$$\log k/s^{-1} = 12.06 \pm 0.35 - (192.39 \pm 4.63) \text{ kJmol}^{-1}/2.303 \text{ RT}$$

(c) Kinetics of the Thermal Decomposition of 1,1,2-Trichloro-1,2,2-trimethyldisilane, $\text{Me}_3\text{Si}_2\text{Cl}_3$.

In the pyrolysis of $\text{Me}_3\text{Si}_2\text{Cl}_3$, using a column that could separate Me_2SiCl_2 and MeSiCl_3 , only one reaction product, identified by mass spectroscopy to be Me_2SiCl_2 , was observed. On co-pyrolysing Me_3SiH with $\text{Me}_3\text{Si}_2\text{Cl}_3$ only one adduct peak was observed on the gas chromatograph. This was found to be due to $\text{Me}_3\text{SiSiHMeCl}$, again by mass spectroscopy.

The kinetics of the thermal decomposition of $\text{Me}_3\text{Si}_2\text{Cl}_3$ were studied in the temperature range 662K to 703K. The decomposition was first-order at all temperatures, first-order plots of $\ln \frac{a}{a-x}$ against time again showing fall off at percentage decomposition above 28%.

An Arrhenius plot was drawn (Fig. 6.4) for the decomposition of $\text{Me}_3\text{Si}_2\text{Cl}_3$. A straight line was obtained from the points, and the Arrhenius parameters were calculated, again

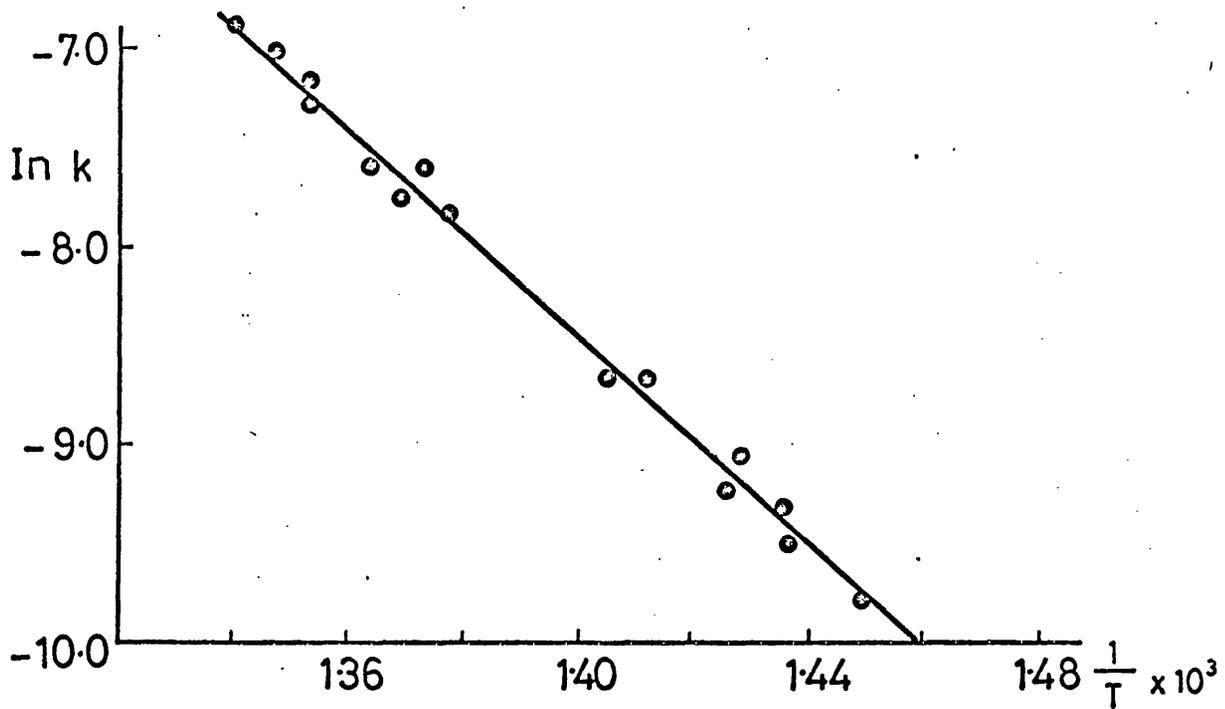


FIGURE 6.1 ARRHENIUS PLOT FOR THE THERMAL DECOMPOSITION OF $\text{Me}_5\text{Si}_2\text{Cl}$

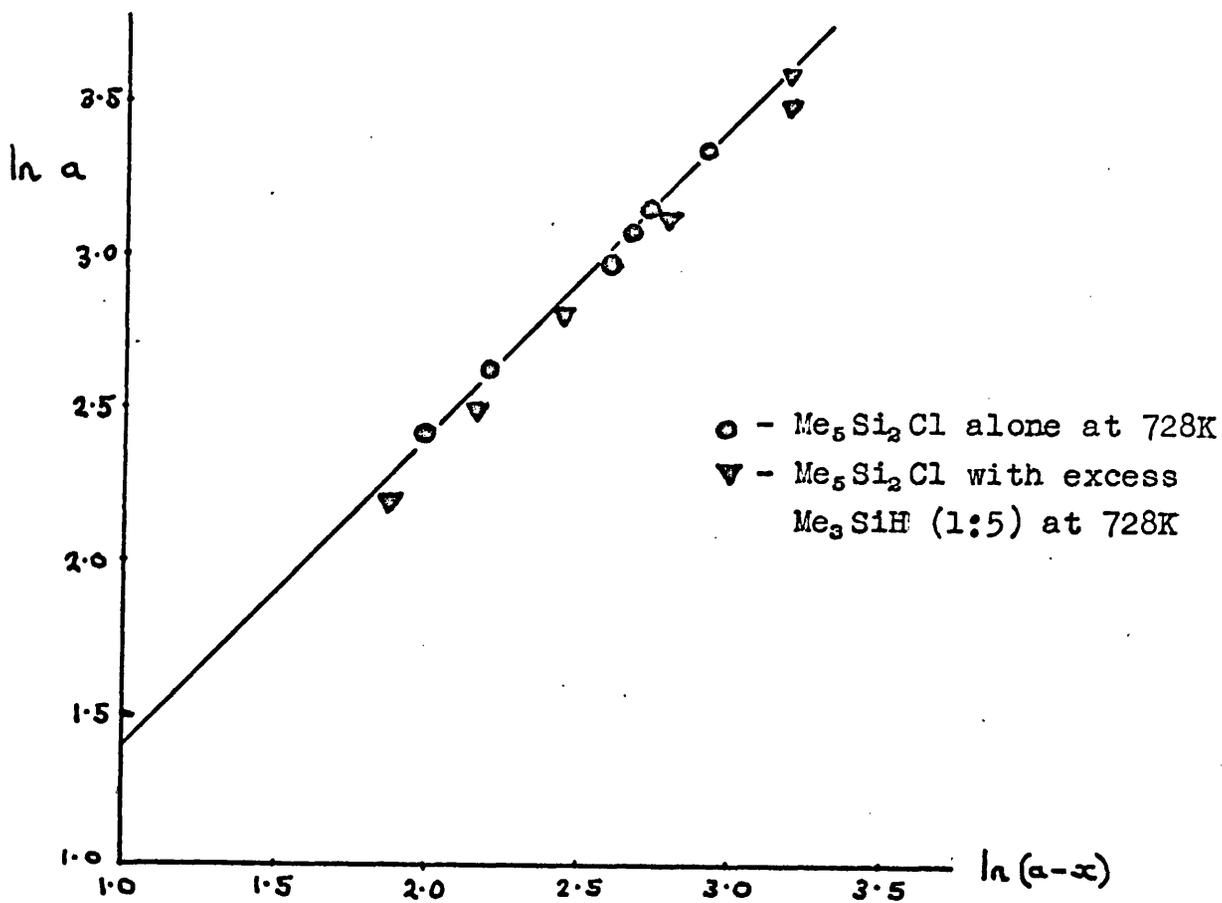


FIGURE 6.2(a) GRAPH OF $\ln a$ AGAINST $\ln(a-x)$ FOR THE DECOMPOSITION OF $\text{Me}_5\text{Si}_2\text{Cl}$ AT 728K, WITH AND WITHOUT EXCESS Me_3SiH .

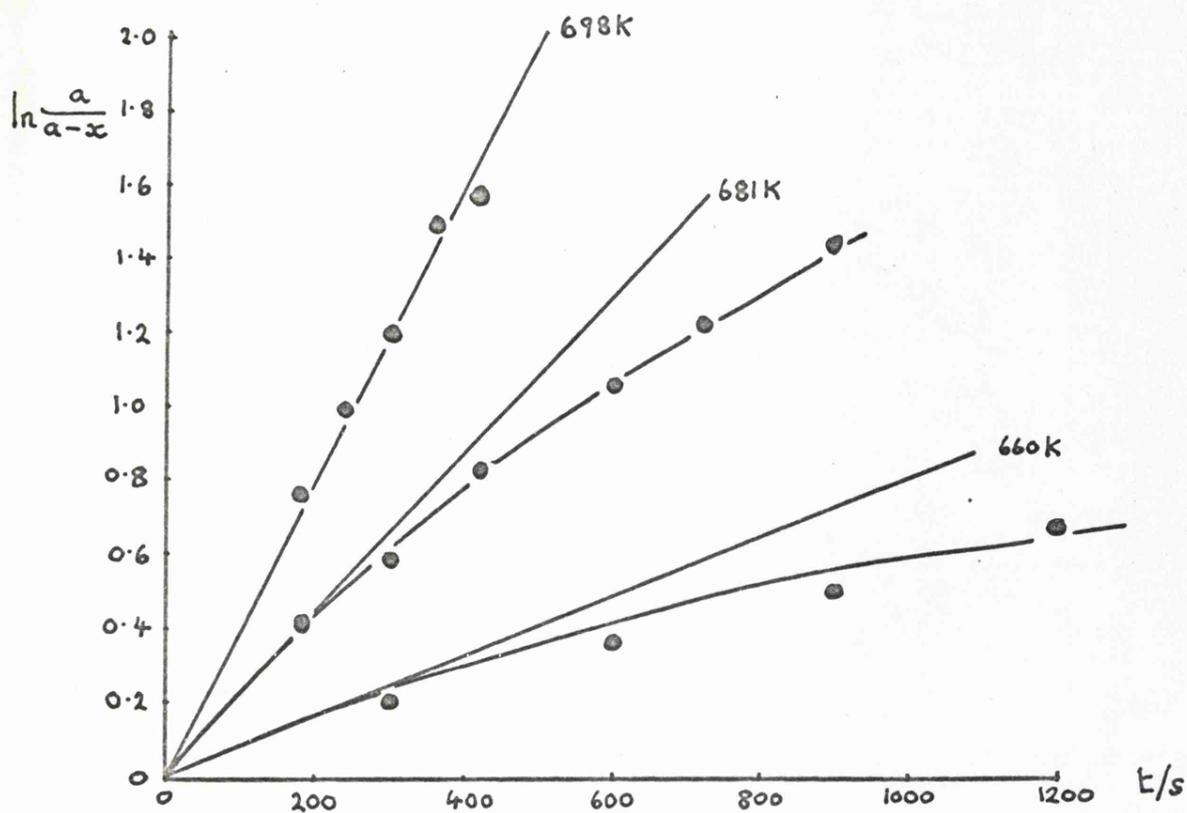


FIGURE 6.2(b) GRAPH OF $\ln \frac{a}{a-x}$ AGAINST TIME FOR THE DECOMPOSITION OF $\text{Me}_2\text{Si}_2\text{Cl}_4$ AT THREE TEMPERATURES.

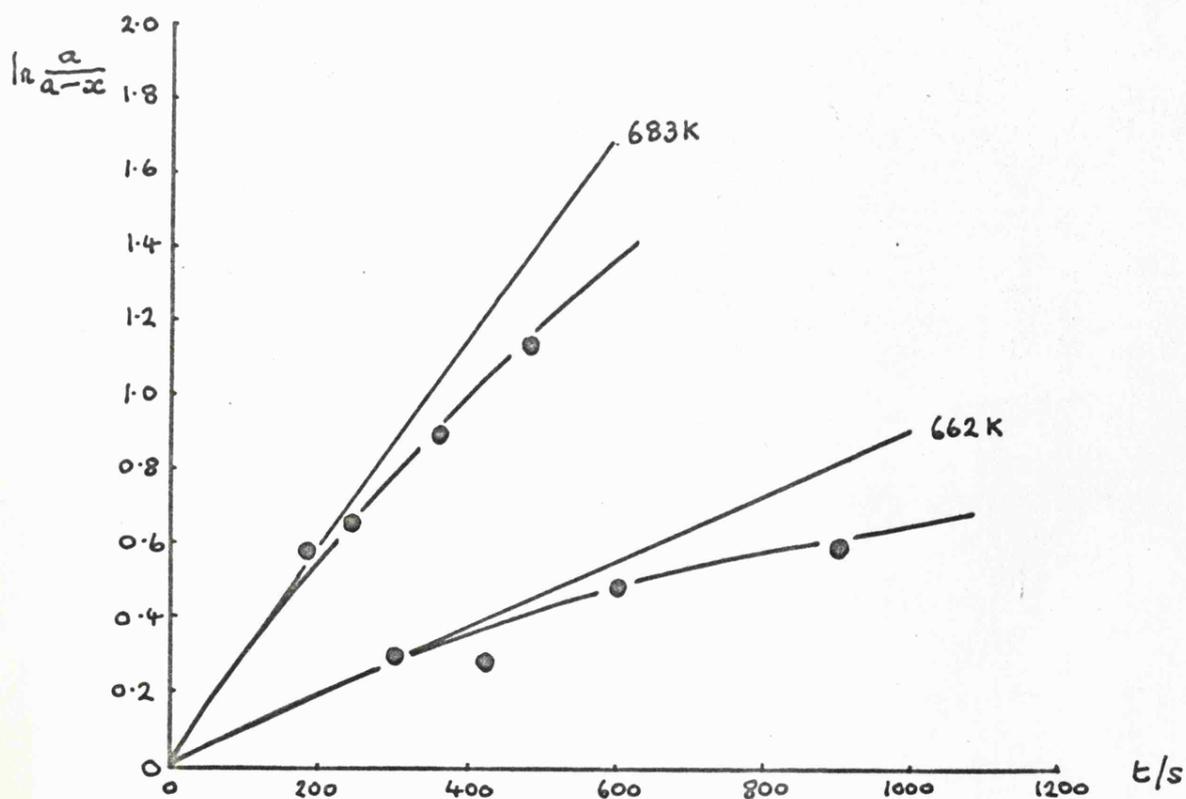


FIGURE 6.2(c) GRAPH OF $\ln \frac{a}{a-x}$ AGAINST TIME FOR THE DECOMPOSITION OF $\text{Me}_3\text{Si}_2\text{Cl}_3$ AT TWO TEMPERATURES.

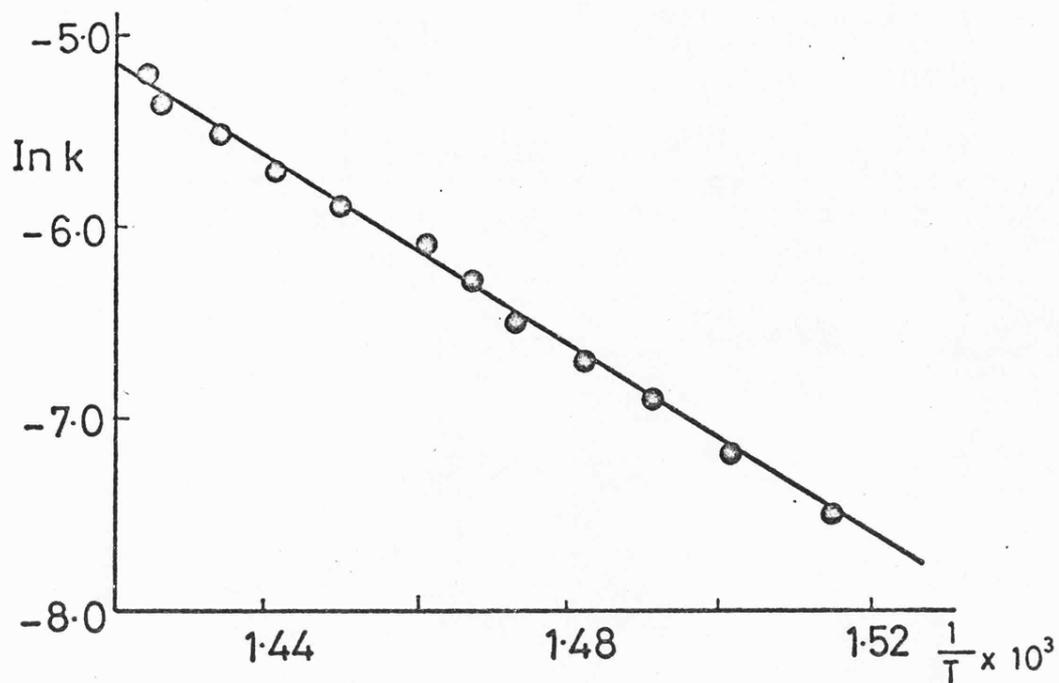


FIGURE 6.3 ARRHENIUS PLOT FOR THE THERMAL
DECOMPOSITION OF $\text{Me}_2\text{Si}_2\text{Cl}_4$

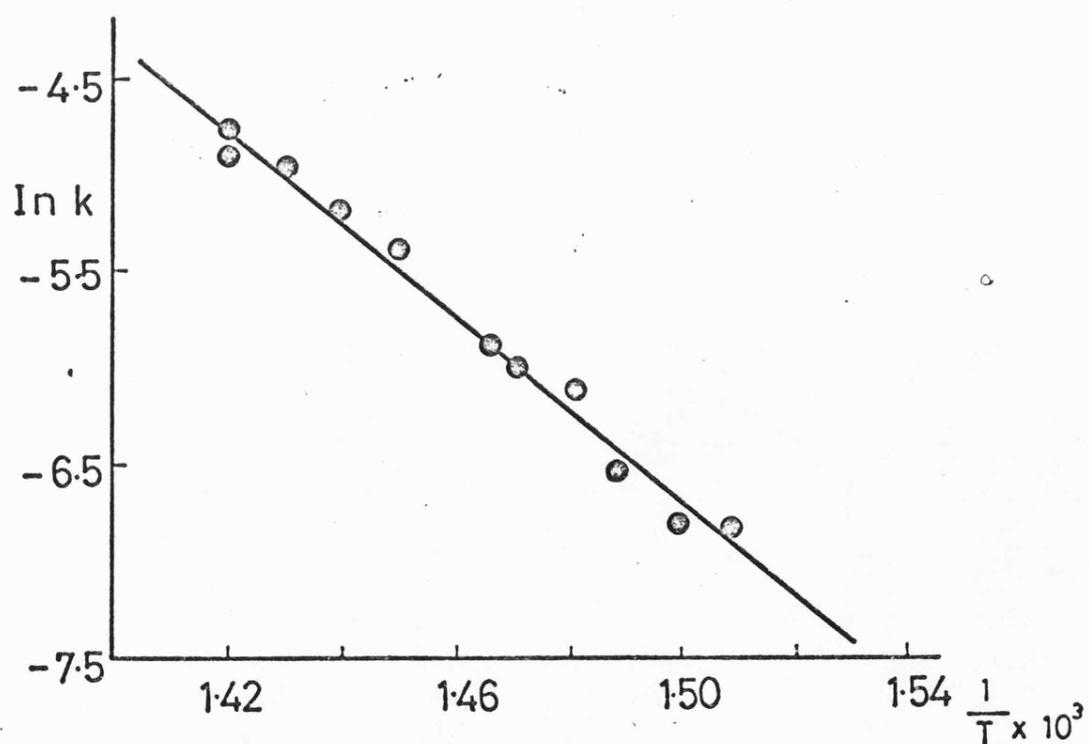


FIGURE 6.4 ARRHENIUS PLOT FOR THE THERMAL
DECOMPOSITION OF $\text{Me}_3\text{Si}_2\text{Cl}_3$

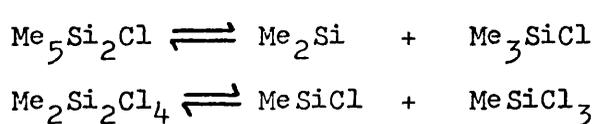
using a least-squares method.

$$\log k/s^{-1} = 12.45 \pm 0.77 - (195.61 \pm 10.0) \text{ kJmol}^{-1}/2.303 \text{ RT}$$

6.2. Discussion of the Kinetic Results for the Pyrolyses of the three Chlorodisilanes.

The products of the decomposition of the chlorodisilanes, $\text{Me}_5\text{Si}_2\text{Cl}$ and $\text{Me}_2\text{Si}_2\text{Cl}_4$, and the products formed on co-pyrolysing Me_3SiH with these two chlorodisilanes show that in both cases the decomposition reaction proceeds by a silylene elimination mechanism. The silylenes have inserted into the Si-H bond in Me_3SiH to produce the adducts $\text{Me}_5\text{Si}_2\text{H}$ and $\text{Me}_3\text{SiSiHMeCl}$.

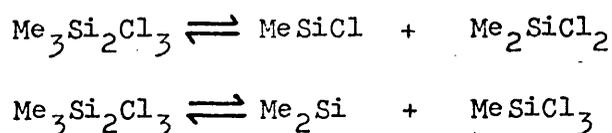
Equations for the initial steps of the decomposition can be written,



It was found that:-

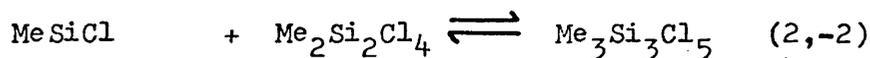
$$\left. \begin{aligned} [\text{Me}_3\text{SiCl}]_t &= [\text{Me}_5\text{Si}_2\text{Cl}]_0 \\ &- [\text{Me}_5\text{Si}_2\text{Cl}]_t \end{aligned} \right\}$$

With $\text{Me}_3\text{Si}_2\text{Cl}_3$, there is the possibility of two silylenes being formed on pyrolysis,

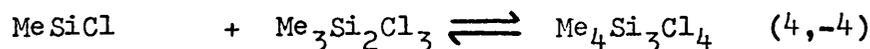


The statistical ratio for formation of the two silylenes is 2:1 in favour of MeSiCl . In the pyrolysis of $\text{Me}_3\text{Si}_2\text{H}_3$ ⁵⁸, both of the corresponding silylenes; MeSiH and Me_2Si , were observed and trapped out. However, as stated before, with $\text{Me}_3\text{Si}_2\text{Cl}_3$ only one product, Me_2SiCl_2 , was observed, indicating that only one silylene, MeSiCl , was being formed.

The fall-off from a straight line at high percentage decomposition, observed on the first-order rate plots for $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$ is indicative of backreaction occurring. There are two possible reactions for the silylene, insertion into the chlorodisilane to give a chlorotrisilane or the back reaction.



and with $\text{Me}_3\text{Si}_2\text{Cl}_3$,



With both $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$, no peak due to a chlorotrisilane was observed on the gas chromatograph. However, this does not necessarily imply that no chlorotrisilane was formed in the reaction, as the gas chromatograph may have been unable to detect them. Recent experiments in which the products of the decomposition of $\text{Me}_5\text{Si}_2\text{Cl}$ were observed by fast-scanning mass spectrometry showed negligible amounts of the chlorotrisilane being formed. Presumably the silylenes were lost from the gas phase by surface polymerisation, (substantial deposits were formed on the vessel walls). If it is assumed that roughly equal activation energies are required for insertion of the silylene into the Si-Cl bond in chloromonosilanes and chlorodisilanes, then absence of any evidence for the chlorotrisilane could imply that the activation energy for the decomposition of the chlorotrisilane is lower than for the chlorodisilane. Any chlorotrisilane formed would therefore decompose at a faster rate than the chlorodisilane.

At temperatures at the lower end of the temperature range, reactions (-2) and (-4) will be fast relative to reactions (1) and (3). This means that the concentration of silylene will increase, although some will be lost heterogeneously on the walls of the vessel, and the back reactions (-1) and (-3) will take effect fairly quickly, hence curvature on the first-order rate plots occurs at a low percentage decomposition.

At temperatures at the upper end of the temperature range, reactions (-2) and (-4) will be slower relative to reactions

(1) and (3), so the concentration of silylene will not build up so quickly and consequently the back reaction does not become prominent so soon. Therefore curvature occurs on the plots at a higher percentage decomposition.

In the pyrolysis of disilane,^{54,60,61} trisilane is observed as one of the products, but it has been estimated that trisilane has a higher activation energy for decomposition, 221 kJ mol^{-1} ,⁶⁴ compared to disilane, 206 kJ mol^{-1} .

Although no first-order plots of $\ln \frac{a}{a-x}$ against time were drawn for the decomposition of $\text{Me}_5\text{Si}_2\text{Cl}$, it can be assumed that back reaction occurs also in this decomposition, and the same considerations as applied to $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$ can be applied to $\text{Me}_5\text{Si}_2\text{Cl}$.

In the pyrolysis of disilane, Si_2H_6 ,^{56,60} and methyldisilane, MeSi_2H_5 ,⁶⁴ the decomposition into the silylene and monosilane has been reported to occur by a 1,2-hydrogen shift reaction. These 1,2-hydrogen shift reactions, which occur in polysilane decompositions but not in hydrocarbon decompositions, have been attributed⁶⁴ to the availability of low-lying orbitals on the silicon atom, which can provide bonding stabilisation for the pentacovalent silicon atom in the transition state.

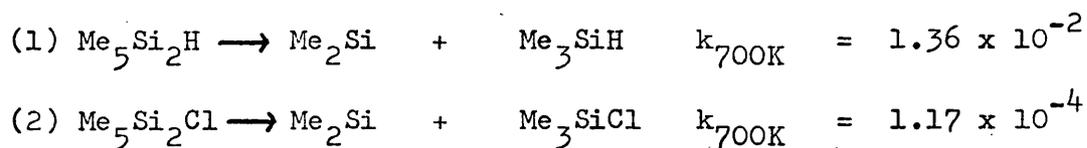
1,2 shifts followed by silylene elimination can also occur with atoms other than hydrogen. It is known that methoxydisilanes and halogenated disilanes decompose by 1,2-methoxy group shifts^{59,65} and 1,2-halogen atom shifts⁶⁶ respectively.

From Table 6.1 it can be seen that the values for the activation energies of the three chlorodisilanes studied

are in good agreement with the activation energies determined by Matthews,⁵⁸ Purnell,⁶⁰ and Ring⁶⁴ for other disilanes.

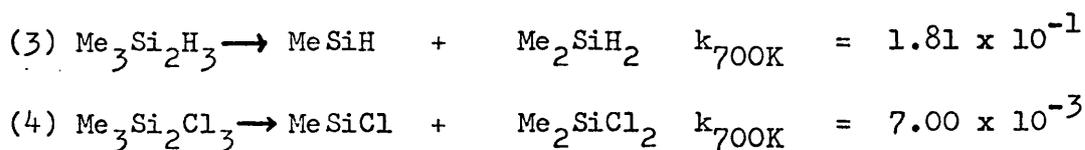
It is quite probable therefore, that the mechanism for the decomposition of $\text{Me}_5\text{Si}_2\text{Cl}$, $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$ is a 1,2-chlorine shift, as chlorine atoms are capable of becoming bridging atoms in the transition state.

In the pyrolysis of chlorodisilanes, such as $\text{Me}_2\text{Si}_2\text{H}_2\text{Cl}_2$,⁶⁸ it has been found that the 1,2-chlorine shift was less facile than the 1,2-hydrogen shift, the slower rate probably being due to steric hindrance caused by the larger size of the chlorine atom in forming the transition state. For the case of HClMeSiSiMeHCl eliminating the two silylenes, MeSiCl and MeSiH , the ratio of the rate constants for each elimination was 4.4 in favour of the 1,2-hydrogen shift. Comparing the results of this present work with those of Matthews,⁵⁸ it can be seen that with $\text{Me}_5\text{Si}_2\text{Cl}$ and $\text{Me}_5\text{Si}_2\text{H}$ the ratio of the rate constants at 700K for elimination of the silylene Me_2Si is :-



$$\frac{k(1)}{k(2)} = 123.6$$

With $\text{Me}_3\text{Si}_2\text{Cl}_3$ and $\text{Me}_3\text{Si}_2\text{H}_3$ producing the silylenes MeSiCl and MeSiH respectively :-



$$\frac{k(3)}{k(4)} = 25.8$$

TABLE 6.1

ARRHENIUS PARAMETERS FOR DISILANE PYROLYSES

<u>DISILANE</u>	<u>SILYLENE</u>	<u>E kJ mol⁻¹</u>	<u>log A</u>	<u>k 700K</u>	<u>REFERENCE</u>
Me ₅ Si ₂ Cl	Me ₂ Si	209.7 ± 4.5	11.69 ± 0.30	1.11 x 10 ⁻⁴	This work
Me ₂ Si ₂ Cl ₄	MeSiCl	192.4 ± 4.6	12.06 ± 0.35	5.07 x 10 ⁻³	This work
Me ₃ Si ₂ Cl ₃	MeSiCl	195.6 ± 10.0	12.45 ± 0.77	7.18 x 10 ⁻³	This work
Me ₅ Si ₂ H	Me ₂ Si	198.3 ± 3.9	12.93 ± 0.31	1.36 x 10 ⁻²	58
Me ₃ Si ₂ H ₃	Me ₂ Si	192.6 ± 22	12.56 ± 1.8	1.55 x 10 ⁻²	58
Me ₃ Si ₂ H ₃	MeSiH	193.1 ± 5.9	13.66 ± 0.55	1.79 x 10 ⁻¹	58
Si ₂ H ₆	SiH ₂	206.0 ± 4.6	14.52 ± 0.36	1.41 x 10 ⁻¹	60
MeSi ₂ H ₅	SiH ₂	213.1 ± 1.5	15.28 ± 0.15	4.17 x 10 ⁻²	64
MeSi ₂ H ₅	MeSiH	209.5 ± 1.5	14.10 ± 0.14	2.94 x 10 ⁻²	64

TABLE 6.2

RECALCULATED log A VALUES FOR THE THREE CHLORODISILANES BASED ON THE VALUE FOR Me₅Si₂Cl

<u>DISILANE</u>	<u>SILYLENE</u>	<u>SYMMETRY FACTOR, n</u>	<u>log n</u>	<u>log A</u>	<u>RECALCULATED log A</u>
Me ₅ Si ₂ Cl	Me ₂ Si	1	0	11.69 ± 0.30	11.69
Me ₂ Si ₂ Cl ₄	MeSiCl	4	0.602	12.06 ± 0.35	12.29
Me ₃ Si ₂ Cl ₃	MeSiCl	2	0.301	12.45 ± 0.77	12.00

The symmetry factor is the number of ways in which the silylene can be eliminated from the disilane molecule.

Both these results go further to show that the 1,2-chlorine shift is less facile than the 1,2-hydrogen shift in silylene eliminations, and with a disilane in which both types of shift can occur on pyrolysis, the 1,2-hydrogen shift will normally predominate.

With disilanes containing only silicon-carbon bonds, silylene elimination is energetically unfavourable because of the inability of alkyl or aryl groups to behave as bridging groups.⁶⁷

With silylene eliminations from disilane molecules, it is believed that the values of log A for the decomposition of the disilane are related to the symmetry factor for silylene elimination. The symmetry factor, n, is the number of ways in which the silylene can be eliminated from the disilane molecule. Recalculated values of log A can, therefore, be drawn up for different silylene elimination reactions, based on the symmetry factors for the elimination (See Table 6.2).

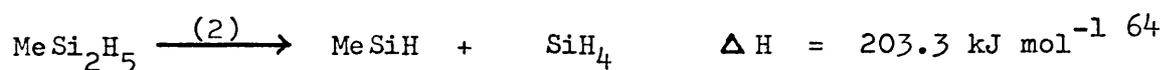
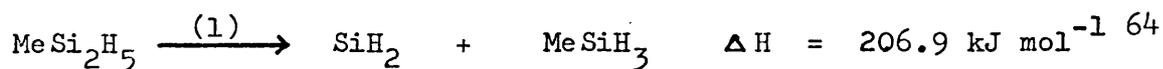
From Table 6.2 it can be seen that the experimental values of log A for $\text{Me}_3\text{Si}_2\text{Cl}_3$ and $\text{Me}_2\text{Si}_2\text{Cl}_4$ differ slightly from the recalculated values based on log A for $\text{Me}_5\text{Si}_2\text{Cl}$, as the symmetry factor for elimination of Me_2Si from $\text{Me}_5\text{Si}_2\text{Cl}$ is one. However, the discrepancies in the values of log A can be attributed to experimental error, as the recalculated values lie inside the error limits for log A in both cases. It can be said, therefore, that the experimental log A values for silylene elimination from $\text{Me}_3\text{Si}_2\text{Cl}_3$ and $\text{Me}_2\text{Si}_2\text{Cl}_4$ agree fairly well with those based on the symmetry factors.

The A factors determined for the chlorodisilanes are lower than those determined by Matthews,⁵⁸ Purnell,⁶⁰ and Ring⁶⁴ for disilanes with silicon-hydrogen bonds. This lowering

is probably due to the fact that in the transition state the chlorine atom is bonded more strongly to the silicon atom than a hydrogen atom would be, since the chlorine atom can use its lone pairs of electrons to bond with the non-occupied orbitals (4s and 3d) on the silicon atom, and so form a much 'tighter' transition state. This would have a lower entropy of activation, and hence a lower A factor.

6.3. Some Thermochemical Data Obtained for Silylene Reactions

Using the two values for the enthalpy of reaction as determined by Ring,⁶⁴ for the two possible methods of decomposition of MeSi_2H_5 , the standard heat of formation of methylsilylene, MeSiH , can be calculated.



$$\begin{aligned} \Delta H_f^\circ(\text{MeSiH}_3) + \Delta H_f^\circ(\text{SiH}_2) - \Delta H_f^\circ(\text{MeSiH}) - \Delta H_f^\circ(\text{SiH}_4) \\ = 206.9 - 203.3 \end{aligned}$$

Using the values :-

$$\Delta H_f^\circ(\text{MeSiH}_3) = -32.53 \text{ kJ mol}^{-1} \quad 69$$

$$\Delta H_f^\circ(\text{SiH}_4) = +34.74 \text{ kJ mol}^{-1} \quad 69$$

$$\Delta H_f^\circ(\text{SiH}_2) = 242.4 \text{ kJ mol}^{-1} \quad 71$$

$$\text{then } \Delta H_f^\circ(\text{MeSiH}) = 171.5 \text{ kJ mol}^{-1}$$

Ring obtained the value of $221.9 \text{ kJ mol}^{-1}$ for $\Delta H_f^\circ(\text{MeSiH})$, but this was calculated using a value of

4.18 kJ mol⁻¹ for $\Delta H_f^\circ(\text{MeSiH}_3)$ as given in the literature.⁸⁷

In the present calculations, values for $\Delta H_f^\circ(\text{MeSiH}_3)$,

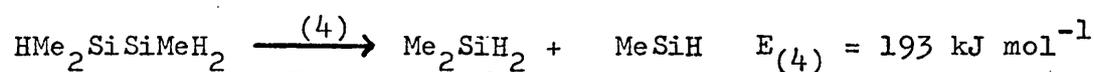
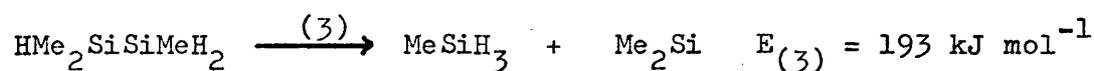
$\Delta H_f^\circ(\text{SiH}_4)$ and $\Delta H_f^\circ(\text{Me}_2\text{SiH}_2)$ were taken from the "Catch"

tables,⁶⁹ as these values are mutually consistent. For simplicity it is assumed that: $\Delta H_{298}^\circ \approx \Delta H_T^\circ \approx \Delta U_T^\circ$

From the reactions for the thermal decomposition of $\text{Me}_3\text{Si}_2\text{H}_3$, as studied by Matthews,⁵⁸ a value for the

standard heat of formation for dimethylsilylene, Me_2Si , can

be obtained, using the value for $\Delta H_f^\circ(\text{MeSiH})$ determined above.



$E_{(-3)}$ and $E_{(-4)}$ will be small and approximately equal.
Therefore $\Delta H_{(3)} \sim \Delta H_{(4)}$ and,

$$\Delta H_f^\circ(\text{MeSiH}_3) + \Delta H_f^\circ(\text{Me}_2\text{Si}) = \Delta H_f^\circ(\text{Me}_2\text{SiH}_2) + \Delta H_f^\circ(\text{MeSiH})$$

Using the values :-

$$\Delta H_f^\circ(\text{MeSiH}_3) = -32.53 \text{ kJ mol}^{-1} \quad 69$$

$$\Delta H_f^\circ(\text{MeSiH}) = 171.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{Me}_2\text{SiH}_2) = -83.58 \text{ kJ mol}^{-1} \quad 69$$

then :-

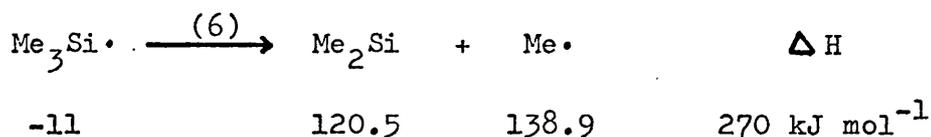
$$\Delta H_f^\circ(\text{Me}_2\text{Si}) = 120.5 \text{ kJ mol}^{-1}$$

This value for $\Delta H_f^\circ(\text{Me}_2\text{Si})$ can be used to determine the first and second Si-Me bond dissociation energies in tetramethylsilane.



Values of	-236	-11	138.9	364 kJ mol ⁻¹
ΔH_f°				

This value of 364 kJ mol^{-1} is in good agreement with the value of 355 kJ mol^{-1} obtained recently from the pyrolysis of tetramethylsilane.²⁶



This is a drop of 94 kJ mol^{-1} in bond dissociation energy from the first Si-Me bond to the second Si-Me bond. However, the value of $120.5 \text{ kJ mol}^{-1}$ for $\Delta H_f^\circ(\text{Me}_2\text{Si})$ is the minimum value. A higher value would decrease the difference in bond dissociation energy between the first and second Si-Me bonds.

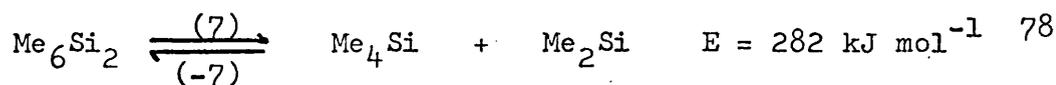
A similar situation is shown by Purnell's work on disilane and monosilane, where the values of $D(\text{H}_3\text{Si-H})$ and $D(\text{H}_2\text{Si-H})$ can be determined using the value of $242.4 \text{ kJ mol}^{-1}$ for $\Delta H_f^\circ(\text{SiH}_2)$.⁷¹

$$\begin{array}{lcl} D(\text{H}_3\text{Si-H}) & = & 394 \text{ kJ mol}^{-1} \\ D(\text{H}_2\text{Si-H}) & = & 249 \text{ kJ mol}^{-1} \end{array}$$

These values show a drop of 145 kJ mol^{-1} from the first Si-H bond to the second Si-H bond, which is thought to be rather large, even though the relative stability of silylenes compared to silyl radicals would cause a lowering of the second bond dissociation energy. However, the value for $\Delta H_f^\circ(\text{SiH}_2)$ is well established, and although several authors have agreed on a value of 209 kJ mol^{-1} for $\Delta H_f^\circ(\text{SiH}_3)$, it is determined from early electron-impact results and thermochemical data, which may be unreliable.⁸⁸⁻⁹⁰ A lower value for $\Delta H_f^\circ(\text{SiH}_3)$ would decrease the difference in the bond dissociation energies from

the first to the second Si-H bonds in SiH_4 , and this would appear more realistic.

The value obtained above for $\Delta H_f^\circ(\text{Me}_2\text{Si})$ can also be used to determine the activation energy for insertion of Me_2Si into a Si-Me bond of Me_4Si , to give Me_6Si_2 .



$$\Delta H = \Delta H_f^\circ(\text{Me}_4\text{Si}) + \Delta H_f^\circ(\text{Me}_2\text{Si}) - \Delta H_f^\circ(\text{Me}_6\text{Si}_2)$$

Using the values :-

$$\Delta H_f^\circ(\text{Me}_4\text{Si}) = -236.3 \text{ kJ mol}^{-1} \quad 69$$

$$\Delta H_f^\circ(\text{Me}_6\text{Si}_2) = -359.1 \text{ kJ mol}^{-1} \quad 69$$

$$\Delta H_f^\circ(\text{Me}_2\text{Si}) = 120.5 \text{ kJ mol}^{-1}$$

$$\text{then} \quad \Delta H = 243 \text{ kJ mol}^{-1}$$

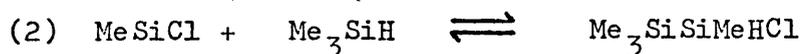
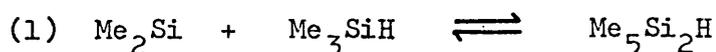
$$\text{and} \quad E_{(-7)} = 41 \text{ kJ mol}^{-1}$$

6.4. Insertion Reactions of Dimethylsilylene, Me_2Si , and Methylchlorosilylene, MeSiCl

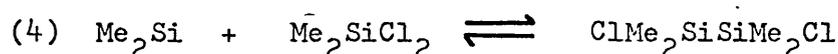
Table 6.3

Summary of Insertion Reactions

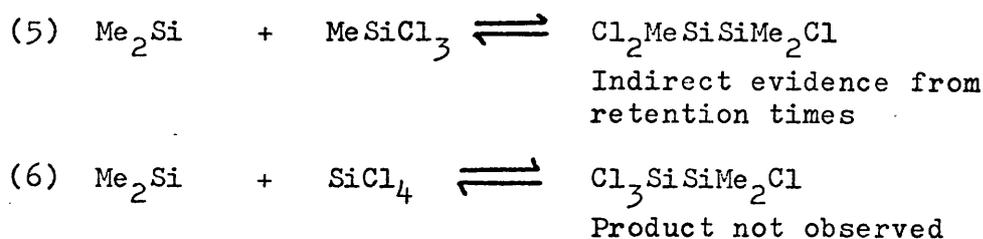
Me_2Si from $\text{Me}_5\text{Si}_2\text{Cl}$; MeSiCl from $\text{Me}_2\text{Si}_2\text{Cl}_4$



Hydrolysis product observed



Hydrolysis product observed



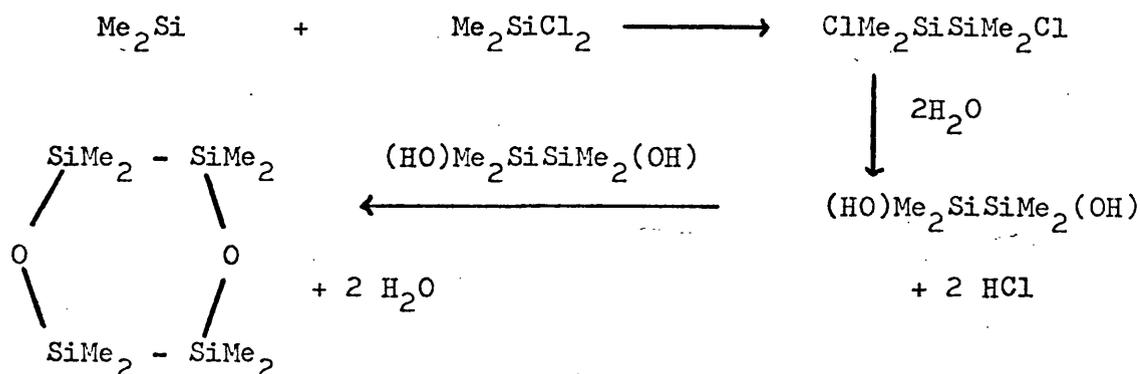
(a) Insertion into the Silicon-Hydrogen Bond

Co-pyrolyses of $\text{Me}_5\text{Si}_2\text{Cl}$ with trimethylsilane, Me_3SiH , were carried out at 729K. On every run a new peak was observed on the gas chromatograph, indicating that some reaction had taken place. This peak was trapped out and analysed by mass spectroscopy.

The mass spectrum (see Appendix 2.2) showed the trapped sample to be pentamethyldisilane, $\text{Me}_5\text{Si}_2\text{H}$, formed by insertion of the silylene Me_2Si into the Si-H bond in Me_3SiH . The fact that a peak for $\text{Me}_5\text{Si}_2\text{H}$ was observed every time a co-pyrolysis of $\text{Me}_5\text{Si}_2\text{Cl}$ and Me_3SiH was carried out, indicates that the insertion of Me_2Si into the Si-H bond is very facile, although perhaps not so facile as insertion of SiH_2 .^{55,56}

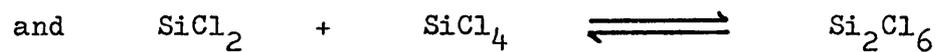
Reaction of $\text{Me}_2\text{Si}_2\text{Cl}_4$ with Me_3SiH at 671K gave rise to a new peak on the gas chromatograph. Analysis of the peak by mass spectroscopy showed it to be the compound $\text{Me}_3\text{SiSi}(\text{HMe})\text{OSi}(\text{HMe})\text{SiMe}_3$ (see Appendix 2.3). This compound is the hydrolysis product of $\text{Me}_3\text{SiSiHMeCl}$, which itself is formed by the insertion of MeSiCl into the Si-H bond in Me_3SiH . The hydrolysis was taking place either on the resin packed tube used for absorption of the sample vapour, or in the mass spectrometer, as strong peaks due to HCl were observed on the mass spectrum.

was occurring on the resin-packed tube or in the mass spectrometer, as strong HCl peaks were again observed.



Reaction of $\text{Me}_5\text{Si}_2\text{Cl}$ with MeSiCl_3 at 713K gave rise to two new peaks on the gas chromatograph which were judged to be the chlorodisilanes $\text{Cl}_2\text{MeSiSiMe}_2\text{Cl}$ and $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ on account of their retention times. However, on trapping out both of these g.l.c. peaks, no chlorine containing insertion products could be identified from the mass spectra, except for HCl. It was assumed that any adduct formed by insertion had again been hydrolysed. Chloromonosilanes or chlorodisilanes containing only one Si-Cl bond give linear siloxanes with only one Si-O-Si linkage, on hydrolysis. Chlorosilanes with two Si-Cl bonds give cyclic siloxanes on hydrolysis. Both these types of siloxane can normally be observed by mass spectrometry, as their molecular weights are sufficiently low. However, chlorosilanes with three or more Si-Cl bonds give polymeric siloxanes on complete hydrolysis, only fragments of which would be seen on a mass spectrum, so no clear information as to their structure and molecular weight could be obtained. With linear and cyclic siloxanes, the structure of the chlorosilane can easily be deduced from the structure of the siloxane.

From the work on $\text{Me}_3\text{Si}_2\text{Cl}_3$, it is known that $\text{Me}_3\text{Si}_2\text{Cl}_3$



From the insertion reactions with the chloromonosilanes, especially Me_2SiCl_2 , it appears that the silylene Me_2Si inserts quite readily into a Si-Cl bond to give a chlorodisilane, although the insertion reaction into a Si-Cl bond is probably not as facile as insertion into a Si-H bond.

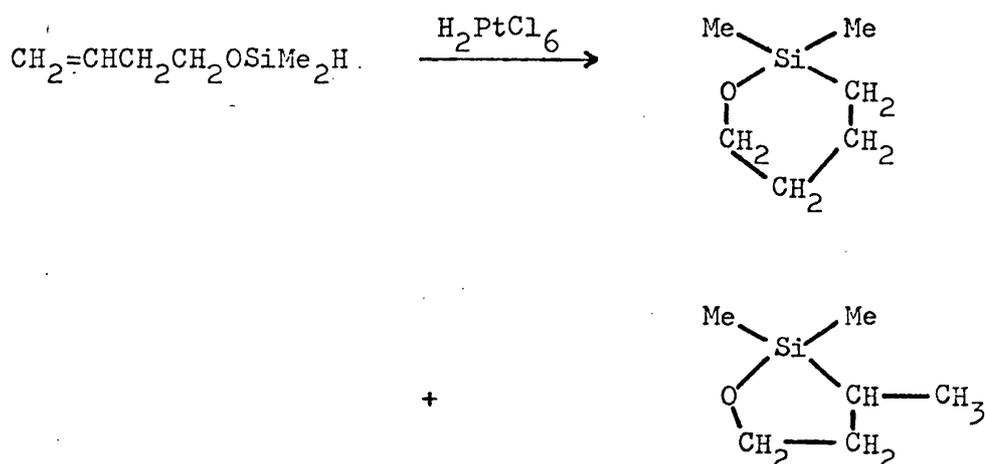
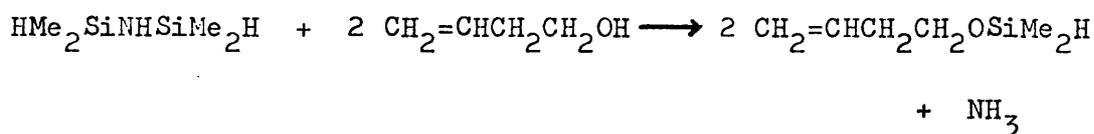
APPENDIX ONE

PREPARATION AND PURIFICATION OF COMPOUNDS

PREPARATION AND PURIFICATION OF COMPOUNDS

(1) Preparation of 2,2-Dimethyl-1-oxa-2-silacyclohexane^{42,43}

Reaction of 1,1,3,3-tetramethyldisilazane with 3-buten-1-ol gives the butenoxymethylsilane, which on reaction with a catalytic amount of chloroplatinic acid, H_2PtCl_6 , gives ring closure.



6.5 g of the silazane in diethyl ether were poured into a 100 ml three-necked flask, fitted with a dropping-funnel, a reflux condenser and a nitrogen bubbler. 7 g of the 3-buten-1-ol in diethyl ether were poured into the dropping-funnel. The butenol was added to the silazane dropwise with stirring for approximately 20 minutes. The mixture of silazane and butenol was then refluxed overnight, the evolution of ammonia being tested for by using concentrated HCl. After reaction, the ether was removed by rotary evaporation.

Before the second part of the reaction an nmr spectrum was run on the reaction mixture. It showed the

presence of the butenoxsilane with ether.

0.1 ml of a 0.1 M H_2PtCl_6 /isopropanol solution was added to the butenoxsilane in the flask. The mixture was refluxed for two hours and then fractionally distilled. Two fractions were collected : (i) b.p. 380K - 381 K; (ii) b.p. 393K - 394 K.

An nmr spectrum run on the second fraction showed that a cyclopentane, and not a cyclohexane was present. This agrees with the observations of Fessenden and Kray⁴⁴ who found that in ring closure reactions by hydrosilation, the five-membered ring was the major product over the six-membered ring.

A mass spectrum run on the second fraction showed peaks at $m_e/$ 75, 87, 88, 89, 115, 130.

(2) Preparation of Cyclopentadiene from its Dimer

To obtain the monomer form of cyclopentadiene, dicyclopentadiene had to be cracked by fractional distillation. Dicyclopentadiene was refluxed on a fractional distillation column, surrounded by a heating-jacket, across which a variable voltage could be applied. Pure cyclopentadiene distilled over at 311K and was collected and stored at ice temperature, 273K, as it rapidly dimerises again at higher temperatures. A fractional distillation was carried out to provide pure cyclopentadiene before each series of pyrolysis runs.

(3) Purification of Pentamethylchlorodisilane, Me_5Si_2Cl

The pentamethylchlorodisilane used in the kinetic study was fractionally distilled from a mixture of Me_6Si_2 and Me_5Si_2Cl by the spinning band method.

A mass spectrum was run on the $\text{Me}_5\text{Si}_2\text{Cl}$ fraction, boiling at 404K, showing peaks at m/e :-

207		132	
206		131	: Me_5Si_2^+
205		117	
168	: M^+	^{37}Cl	116 : Me_4Si_2^+
166	: M^+	^{35}Cl	115
153	: -Me	^{37}Cl	95 : Me_2SiCl for ^{37}Cl
151	: -Me	^{35}Cl	93 : Me_2SiCl for ^{35}Cl
147		73	: Me_3Si^+
133			

The fraction boiling at 404K showed only one peak on the gas chromatograph, with the correct retention time for $\text{Me}_5\text{Si}_2\text{Cl}$.

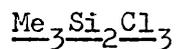
(4) Preparation of 1,1,2,2-Tetrachloro-1,2-dimethyldisilane^{85,86}
 $\text{Me}_2\text{Si}_2\text{Cl}_4$

14.5 g of Me_6Si_2 were added to 55 g of anhydrous aluminium chloride, AlCl_3 , contained in a three-necked flask, fitted with an air-tight stirrer, a reflux condenser and a dropping-funnel. 32 ml of acetyl chloride, CH_3COCl , were added dropwise from the funnel. An exothermic reaction took place and the reaction mixture became homogeneous. After the addition of the CH_3COCl was completed, the mixture was heated to 398K with stirring for fourteen hours.

When the reaction was completed, dry acetone was added to the reaction mixture until all the catalyst had been destroyed. A few millilitres of the mixture were then removed, poured into

a screw-on flask and distilled under vacuum on the system. After further distillations on the vacuum system, pure $\text{Me}_2\text{Si}_2\text{Cl}_4$ was obtained, its purity being checked by gas chromatography.

(5) Preparation of 1,1,2-Trichloro-1,2,2-trimethyldisilane^{85,86}



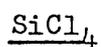
$\text{Me}_3\text{Si}_2\text{Cl}_3$ was prepared in the same way as $\text{Me}_2\text{Si}_2\text{Cl}_4$ but using different ratios of reactants. 24 ml of acetyl chloride were added to 14.5 g of Me_6Si_2 and 40 g of aluminium chloride in the three-necked flask. As with the $\text{Me}_2\text{Si}_2\text{Cl}_4$, the $\text{Me}_3\text{Si}_2\text{Cl}_3$ prepared was distilled and purified on the vacuum system.

APPENDIX TWO

MASS SPECTRAL DATA

MASS SPECTRAL DATA

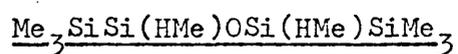
2.1 Mass Spectral Peaks observed for Silicon Tetrachloride,



m/e	174	M ⁺	for 1 ³⁵ Cl ; 3 ³⁷ Cl
	172	M ⁺	for 2 ³⁵ Cl ; 2 ³⁷ Cl
	170	M ⁺	for 3 ³⁵ Cl ; 1 ³⁷ Cl
	168	M ⁺	for 4 ³⁵ Cl
	139	SiCl ₃	3 ³⁷ Cl
	137	SiCl ₃	1 ³⁵ Cl ; 2 ³⁷ Cl
	135	SiCl ₃	2 ³⁵ Cl ; 1 ³⁷ Cl
	133	SiCl ₃	3 ³⁵ Cl
	102	SiCl ₂	2 ³⁷ Cl
	100	SiCl ₂	1 ³⁵ Cl ; 1 ³⁷ Cl
	98	SiCl ₂	2 ³⁵ Cl
	65	SiCl	³⁷ Cl
	63	SiCl	³⁵ Cl

2.2 Mass Spectra Peaks observed for Me₅Si₂H

m/e	Relative Intensity	Fragment
132	39.6	M ⁺
131	5.3	Me ₅ Si ₂ ⁺
117	56.0	Me ₄ Si ₂ H ⁺
73	<u>100</u>	Me ₃ Si ⁺
59	37.9	Me ₂ Si ⁺ H

2.3 Mass Spectra Peaks observed for

m/e	Relative Intensity	Fragment
250	14.8	M ⁺
235	30.2	M ⁺ - Me
205	79.6	M ⁺ - 3 x Me
177	40.7	M ⁺ - Me ₃ Si
176	65.4	M ⁺ - Me ₃ SiH
161	51.8	M ⁺ - (Me ₃ SiH + Me)
133	37.0	Me ₃ SiSiMe(OH)
117	<u>100</u>	Me ₃ SiSiMeH
103	38.3	Me ₂ Si ₂ OH

2.4 Mass Spectra Peaks observed for (Me₄Si₂O)₂

m/e	Relative Intensity	Fragment
264	47.2	M ⁺
249	60.4	M ⁺ - Me
221	59.4	M ⁺ - MeSi
207	70.3	M ⁺ - (MeSi + CH ₂)
205	83.3	M ⁺ - MeSiO
191	<u>100</u>	M ⁺ - Me ₃ Si

2.5 Mass Spectra Peaks observed in Reactions between(Me₂SiO)₄ and Ethylene

(a)

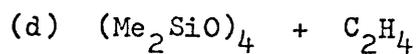
m/e	Relative Intensity
163	5.4
133	5.7
105	8.9
104	7.8
92	45.9
91	<u>100</u>

(b)

m/e	Relative Intensity	m/e	Relative Intensity
256	46.3	157	21.9
242	20.7	129	<u>100</u>
228	29.3	115	48.8
185	26.8	101	41.5
171	15.8		

(c) (Me₂SiO)₄ + C₂H₄ and H₂O

m/e	Relative Intensity	m/e	Relative Intensity
280	4.5	155	<u>100</u>
256	7.0	149	72.5
242	5.0	143	15.0
228	10.5	133	19.5
211	9.0	129	75.0
200	12.0	115	32.0
191	13.0	111	32.5
185	16.0	101	32.0
171	12.5	96	76.0
157	19.0		



m/e	Relative Intensity	m/e	Relative Intensity
120	2.4	102	7.9
107	7.5	92	21.7
106	83.8	91	>100
105	33.6	78	32.4
104	<u>100</u>	77	26.9
103	43.0		

Peaks with relative intensity, >100, could not be measured accurately, due to the peak top being off the scale of the mass spectral trace.

2.6 Mass Spectra Peaks observed in Reactions between $(\text{Me}_2\text{SiO})_4$ and 1,3-Butadiene

(a)

m/e	Relative Intensity	m/e	Relative Intensity
256	31.5	129	85.0
242	13.0	115	40.0
228	17.0	111	44.5
200	7.0	101	31.0
199	12.0	99	29.5
185	27.0	98	58.5
171	18.5	97	<u>100</u>
157	20.5		
149	51.5		
143	18.0		

(b)

m/e	Relative Intensity	m/e	Relative Intensity
222	2.2	103	9.6
177	5.4	102	2.5
150	1.4	93	13.8
149	12.8	92	29.8
135	1.2	91	<u>100</u>
131	1.3	80	3.5
128	2.8	79	13.3
106	57.4	78	11.7
105	23.9	77	10.6
104	15.9		

2.7 Mass Spectra Peaks observed in Reactions between
(Me₂SiO)₄ and Benzene

m/e	Relative Intensity	m/e	Relative Intensity
185	3.8	120	33.0
184	43.8	104	6.9
183	20.6	96	5.3
158	2.7	94	6.5
154	1.8	92	10.3
142	7.7	91	22.3
141	<u>100</u>	78	13.3
125	10.3	77	58.4
124	67.4		

2.8 Mass Spectra Peaks observed in Reactions between
(Me₂SiO)₄ and Cyclopentadiene

(a)

m/e	Relative Intensity	m/e	Relative Intensity
229	7.4	158	16.3
228	49.7	156	14.1
227	4.8	143	7.0
209	12.8	142	33.6
208	<u>100</u>	141	7.7
207	20.5	140	6.1
200	6.4	130	6.4
185	5.8	125	22.8

(b)

m/e	Relative Intensity	m/e	Relative Intensity
203	21.6	131	37.9
201	31.6	127	20.0
185	15.8	116	23.1
155	16.8	115	25.8
153	30.5	103	26.3
151	41.6	101	40
137	18.4	87	28.4
135	56.8	85	<u>100</u>

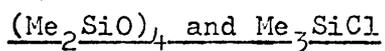
(c)

m/e	Relative Intensity	m/e	Relative Intensity
160	5.0	104	8.3
128	18.9	96	13.3
125	8.3	92	38.9
116	20.0	91	55.5
115	16.7	78	<u>100</u>

(d) Mass Spectra Peaks for Cyclopentadiene

m/e	Relative Intensity	m/e	Relative Intensity
66	<u>100</u>	60	1.1
65	42.4	40	31.3
64	6.5	39	37.3
63	8.1	38	11.1
62	6.0	31	5.6
61	4.5		

Peaks with relative intensity less than one are omitted. From Mass Spectral Data, American Petroleum Institute, Research Project No. 44, Ser. No. 1610.

2.9 Mass Spectra Peaks observed in Reactions between

(a)

m/e	Relative Intensity
297	0.9
295	4.6
223	9.7
222	17.9
221	78.8
149	51.3
148	<u>100</u>
147	>100

(b)

m/e	Relative Intensity
297	0.9
295	2.7
223	1.3
222	2.5
221	7.5
169	3.1
167	7.8
149	13.6
148	16.9
147	<u>100</u>

2.10 Mass Spectral Peaks observed in Reactions of (MePhSiO)₃(a) Mass Spectral Peaks for solid (MePhSiO)₃

m/e	Relative Intensity
408	12.8
393	29.1
378	2.3
315	<u>100</u>
253	31.4

(b) (MePhSiO)₃ + (Me₂SiO)₄

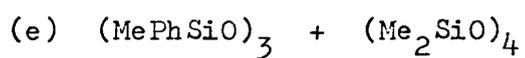
m/e	Relative Intensity	m/e	Relative Intensity
269	13.8	121	13.2
268	21.0	119	40.0
267	81.0	117	13.6
237	8.0	115	34.0
193	>100	105	16.2
179	<u>100</u>	103	64.0
177	46.0		

(c) $(\text{MePhSiO})_3 + (\text{Me}_2\text{SiO})_4$

m/e	Relative Intensity	m/e	Relative Intensity
489	3.3	389	11.8
477	2.9	345	8.1
475	2.9	344	13.3
469	6.3	343	43.3
467	10.4	342	30.4
417	7.8	341	<u>100</u>
416	8.5	339	13.0
415	20.0	315	12.6
405	5.5	313	7.4
403	7.8	311	9.2
401	9.6	295	14.1
393	7.4		

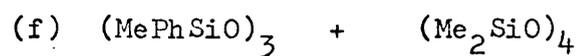
(d) Pyrolysis of $(\text{MePhSiO})_3$

m/e	Relative Intensity	m/e	Relative Intensity
529	1.1	329	7.5
527	1.4	315	>100
525	1.1	301	4.5
469	1.1	285	7.7
451	1.9	257	16.9
408	45.1	255	16.2
393	<u>100</u>	254	15.5
377	9.5	253	53.6
331	5.9		



m/e	Relative Intensity	m/e	Relative Intensity
563	7.7	404	23.6
550	5.7	403	61.4
548	5.4	402	18.0
490	15.4	401	42.9
489	17.6	399	10.3
488	34.8	393	9.9
479	9.0	389	20.2
478	11.2	387	11.2
477	27.5	385	10.3
476	8.6	358	15.4
475	17.6	357	44.6
467	10.7	356	56.6
465	7.3	355	>100
463	6.9	346	39.5
461	8.6	345	60.5
431	9.9	344	77.2
430	13.3	343	100
429	24.0	342	50.6
419	11.6	341	>100
418	17.6	333	15.4
417	38.2	332	32.6
416	32.6	331	<u>100</u>
415	76.8	329	31.3
407	12.9	328	32.2
406	22.3	327	93.6
405	60.9	325	30.9

315	24.0	311	12.4
313	13.7	300	18.0



m/e	Relative Intensity	m/e	Relative Intensity
419	7.6	342	13.5
418	12.2	341	43.2
417	29.0	333	14.2
415	12.8	332	27.0
406	8.8	331	82.4
405	24.3	329	14.2
404	10.8	328	11.5
403	31.1	327	30.4
401	14.9	289	16.2
357	14.2	283	48.6
356	15.5	282	70.3
355	29.7	281	>100
346	25.0	271	29.7
345	26.3	269	50.7
344	33.8	267	48.0
343	<u>100</u>	253	91.9

APPENDIX THREE

FULL KINETIC RESULTS

FULL KINETIC RESULTSKinetic Results for the Pyrolysis of $\text{Me}_5\text{Si}_2\text{Cl}$ (1) 748K $p_0 = 1.33 \rightarrow 4.56 \text{ mm Hg}$
 $t = 300 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.330	3.46	3.13
0.318	3.23	2.92
0.336	2.92	2.58
0.327	2.71	2.39
0.347	2.31	1.96
0.273	3.61	3.34

$$k = 1.10 \times 10^{-3}$$

(2) 744K $p_0 = 1.19 \rightarrow 5.46 \text{ mm Hg}$
 $t = 420 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.371	3.52	3.15
0.379	3.33	2.95
0.402	2.91	2.51
0.446	2.67	2.22
0.432	2.29	1.86

$$k = 9.68 \times 10^{-4}$$

(3) 740 K $p_0 = 2.03 \rightarrow 5.0 \text{ mm Hg}$
 $t = 300 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.246	3.40	3.15
0.247	3.02	2.77
0.235	3.62	3.38
0.245	2.73	2.48
0.238	2.18	1.94
0.239	3.70	3.46

$$k = 8.09 \times 10^{-4}$$

(4) 740K $p_0 = 1.47 \rightarrow 3.09 \text{ mm Hg}$
 $t = 600 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.464	3.13	2.67
0.471	2.98	2.51
0.462	2.79	2.33
0.465	2.39	1.88
0.438	3.03	2.59
0.433	3.06	2.63

$$k = 7.62 \times 10^{-4}$$

(5) 735K $P_0 = 1.69 \rightarrow 4.04 \text{ mmHg}$
 $t = 600 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln (a-x)$
0.281	3.28	2.99
0.334	3.04	2.70
0.343	2.98	2.64
0.363	2.53	2.16
0.315	3.19	2.87
0.284	3.40	3.12
0.320	2.89	2.57

$$k = 5.64 \times 10^{-4}$$

(6) 733K

$P_0 = 2.05 \rightarrow 4.75 \text{ mmHg}$
 $t = 420 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.184	3.45	3.26
0.181	3.22	3.04
0.181	3.07	2.89
0.232	2.78	2.55
0.216	2.53	2.32
0.209	3.56	3.35
0.190	3.24	3.05
0.238	2.72	2.48

$$k = 4.86 \times 10^{-4}$$

(7) 730K $P_0 = 1.35 \rightarrow 4.75 \text{ mmHg}$
 $t = 900 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln (a-x)$
0.247	3.56	3.32
0.227	3.39	3.16
0.238	3.08	2.85
0.266	2.95	2.68
0.263	2.66	2.40
0.263	2.30	2.04

$$k = 5.37 \times 10^{-4}$$

(8) 728K $P_0 = 1.47 \rightarrow 3.73 \text{ mmHg}$
 $t = 900 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln (a-x)$
0.389	3.06	2.67
0.362	2.96	2.60
0.393	2.61	2.21
0.410	2.39	1.98
0.391	3.12	2.73
0.399	3.32	2.92

$$k = 4.44 \times 10^{-4}$$

(9) 713K $P_0 = 1.16 \rightarrow 4.08 \text{ mmHg}$
 $t = 900 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.292	3.41	3.12
0.223	3.00	2.77
0.197	2.95	2.76
0.184	2.65	2.47
0.184	2.15	1.97
0.178	3.32	3.14

$$k = 2.05 \times 10^{-4}$$

(10) 711K $P_0 = 1.56 \rightarrow 3.31 \text{ mmHg}$
 $t = 900 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.178	3.07	2.89
0.174	2.81	2.63
0.188	3.20	3.01
0.187	2.67	2.48
0.185	2.45	2.26
0.179	2.91	2.73

$$k = 2.01 \times 10^{-4}$$

(11) 704K $P_0 = 1.6 \rightarrow 3.03 \text{ mmHg}$
 $t = 1200 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.165	2.47	2.31
0.164	2.74	2.58
0.164	2.93	2.76
0.156	3.11	2.96

$$k = 1.35 \times 10^{-4}$$

(12) 703K $P_0 = 2.11 \rightarrow 3.21 \text{ mmHg}$
 $t = 1200 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.173	2.91	2.74
0.169	2.75	2.58
0.171	3.17	3.00
0.170	2.91	2.74

$$k = 1.42 \times 10^{-4}$$

(13) 700K

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.195	2.72	2.53
0.154	3.01	2.86
0.162	3.22	3.06
0.133	3.40	3.27
0.143	2.21	2.06
0.132	2.83	2.70

$P_0 = 1.23 \rightarrow 4.04 \text{ mmHg}$
 $t = 1200 \text{ s}$

$$k = 1.17 \times 10^{-4}$$

(14) 700K $p_0 = 1.15 \rightarrow 5.25 \text{ mmHg}$
 $t = 1200 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.130	3.55	3.42
0.119	3.26	3.14
0.126	3.08	2.96
0.126	2.66	2.54
0.125	3.66	3.53
0.112	2.14	2.03
0.117	3.36	3.24

$$k = 1.02 \times 10^{-4}$$

(15) 692K

$p_0 = 1.83 \rightarrow 4.43 \text{ mmHg}$
 $t = 1800 \text{ s}$

$\ln \frac{a}{a-x}$	$\ln a$	$\ln(a-x)$
0.133	3.00	2.87
0.118	2.92	2.80
0.121	2.61	2.49
0.116	3.40	3.29
0.126	3.49	3.37

$$k = 6.68 \times 10^{-5}$$

Kinetics Results for the Pyrolysis of $\text{Me}_2\text{Si}_2\text{Cl}_4$

(1) 701K $p_0 = 1.28 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.967
300	1.415
420	1.743
540	1.889
480	1.703
240	1.012

$$k = 563 \times 10^{-3}$$

(2) 698K $p_0 = 1.12 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	2.134
240	2.683
300	3.309
360	4.471
420	4.792

$$k = 4.61 \times 10^{-3}$$

(3) 696 K $p_0 = 1.15 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.694
300	0.999
420	1.362
600	2.011
240	0.779
480	1.531

$$k = 3.89 \times 10^{-3}$$

(4) 694 K $p_0 = 1.02 \text{ mm Hg}$ (5) 689 K $p_0 = 1.20 \text{ mm Hg}$

t/s	$\ln \frac{a}{a-x}$
180	0.629
300	0.913
420	1.236
600	1.541
480	1.633

$$k = 3.55 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
180	0.516
300	0.764
420	0.954
600	1.359
720	1.662
900	1.951

$$k = 2.79 \times 10^{-3}$$

(6) 685 K $p_0 = 1.01 \text{ mm Hg}$ (7) 681 K $p_0 = 1.11 \text{ mm Hg}$

t/s	$\ln \frac{a}{a-x}$
300	0.724
420	0.904
600	1.156
720	1.232
180	0.424
900	1.389

$$k = 2.40 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
180	0.410
300	0.578
420	0.825
600	1.064
720	1.214
900	1.431

$$k = 2.26 \times 10^{-3}$$

(8) 679 K $p_0 = 1.18 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.535
180	0.376
420	0.715
600	1.030
720	1.199
900	1.365

$$k = 1.89 \times 10^{-3}$$

(9) 675 K $p_0 = 0.90 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.266
300	0.399
720	0.875
420	0.530
600	0.690

$$k = 1.49 \times 10^{-3}$$

(10) 671 K $p_0 = 1.02 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.237
300	0.343
420	0.427
600	0.583
720	0.725
910	0.829

$$k = 1.19 \times 10^{-3}$$

(11) 668 K $p_0 = 0.70 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.302
420	0.439
600	0.580
720	0.685
900	0.848
1200	1.099

$$k = 1.01 \times 10^{-3}$$

(12) 660 K

 $p_0 = 0.97 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.200
600	0.363
900	0.508
1200	0.681
1500	0.815

$$k = 6.75 \times 10^{-4}$$

Kinetic Results for Pyrolysis of $\text{Me}_3\text{Si}_2\text{Cl}_3$ (1) 703 K $p_0 = 1.58 \text{ mmHg}$ (2) 703 K $p_0 = 1.39 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.827
240	1.976
300	2.483

$$k = 8.23 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
180	0.830
240	1.537
300	2.279
360	2.205

$$k = 6.94 \times 10^{-3}$$

(3) 698 K $p_0 = 1.26 \text{ mmHg}$ (4) 694 K $p_0 = 1.48 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
240	1.440
300	1.558
360	1.915
600	2.910

$$k = 6.67 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
240	1.332
360	1.986
300	1.973
420	2.106

$$k = 5.52 \times 10^{-3}$$

(5) 688 K $p_0 = 1.39 \text{ mmHg}$ (6) 683 K $p_0 = 2.14 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.981
420	1.211
600	1.001
720	2.134
490	1.393
240	1.190
360	1.406

$$k = 4.43 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
180	0.585
240	0.653
300	1.158
360	0.897
420	2.362
480	1.123

$$k = 3.09 \times 10^{-3}$$

(7) 681 K $p_0 = 2.25 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.817
420	0.902
660	1.379
540	1.055
780	1.379

$$k = 2.82 \times 10^{-3}$$

(8) 676 K

 $p_0 = 1.49 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
300	0.758
420	1.084
540	1.489
660	0.778
780	1.748
900	3.788

$$k = 2.48 \times 10^{-3}$$

(9) 672 K

 $p_0 = 0.69 \text{ mmHg}$

(10) 667 K

 $p_0 = 0.71 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
240	0.241
360	0.485
480	0.458
600	0.603
720	0.847

$$k = 1.58 \times 10^{-3}$$

t/s	$\ln \frac{a}{a-x}$
240	0.205
360	0.349
480	0.566
600	0.495
720	0.585

$$k = 1.14 \times 10^{-3}$$

(11) 662 K

 $p_0 = 0.81 \text{ mmHg}$

t/s	$\ln \frac{a}{a-x}$
180	0.675
240	0.739
300	0.301
420	0.282
600	0.486
900	0.592

$$k = 1.10 \times 10^{-3}$$

APPENDIX FOUR

COMPUTER PROGRAMME

Computer Programme for Calculating Areas of Gas Chromatographic
Peaks

```
10 CLOSE 1
20 DIM Y(225)
30 OPEN "KB" AS FILE 1
50 LET N1=225
60 PRINT "VALUES OF POINTS ARE"
70 FOR X=1 TO N1
80 INPUT "1, Y(X)", Y(X)
90 IF Y(X) > 0 GO TO 105
100 NEXT X
105 LET N1=X-2
110 LET S1=0: LET S2=0: LET S3=0: LET S4=0
120 LET N=1: X=1
130 GOSUB 2000
140 LET N=2: LET X=N1
150 GOSUB 2000
160 LET C=N*S4-S1*S1
170 LET B=(S2*S4-S1*S3)/C
180 LET A=(N*S3-S1*S2)/C
200 FOR X=1 TO N1
210 LET Y=A*X+B
220 LET Y(X)=Y(X)-Y
230 NEXT X
500 LET H1= .3333333
520 LET M1=H1*(Y(1)+(4*Y(2))+Y(3))
540 LET A1=M1+H1*(Y(3)+(4*Y(4))+Y(5))
```

```
550 LET A2=H1*(Y(1)+3.875*(Y(2)+Y(5))+2.625*(Y(3)+Y(4))+Y(6))
560 LET M2=A2-H1*(Y(4)+(4*Y(5))+Y(6))
620 FOR I=7 TO N1 STEP 2
630 LET M1=A1
640 LET M2=A2
650 LET I8 = I-2: LET I7 = I-1: LET I6 = I+1
670 LET A1 = M1+H1*(Y(I8)+(4*Y(I7))+Y(I))
690 LET N4 = I-N1
710 IF N4 >= 0 THEN 830
730 LET A2 = M2+H1*(Y(I7)+(4*Y(I))+Y(I6))
745 NEXT I
780 PRINT "AREA = "; A2
790 GO TO 50
830 PRINT "AREA = "; A1
840 GO TO 50
2000 LET S1 = S1+X
2010 LET S2 = S2+Y(X)
2020 LET S3 = S3+X*Y(X)
2030 LET S4 = S4+X*X
2040 RETURN
2050 END
```

REFERENCES

REFERENCES

- (1) C.J. Attridge Organometallic Chem. Revs. Ser. A 1970,
5, 323
- (2) L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin Russ. Chem.
Revs. 1974, 7, 620
- (3) I.M.T. Davidson and J.F. Thompson Chem. Comm. 1971, 251
- (4) R. Walsh J. Organometal. Chem. 1972, 38, 245
- (5) R.A. Jackson "Essays on Free Radical Chemistry" Chem.Soc.
Spec. Publ. 1970, 24, 295
- (6) J.F. Thompson Ph.D. Thesis Univ. of Leics. 1972
- (7) M.C. Flowers and L.E. Gusel'nikov J.Chem.Soc. (B) 1968, 419
- (8) M.C. Flowers and L.E. Gusel'nikov Chem.Comm.1967, 864
- (9) N.S. Nametkin, L.E. Gusel'nikov, V.M. Vdovin and V.I.
Zav'yalov Izv. Akad. Nauk. SSSR Ser. Khim. 1966, 584
- (10) N.S. Nametkin, L.E. Gusel'nikov, V.M. Vdovin, P.L. Grinberg,
V.I. Zav'yalov and V.D. Oppengeim Dokl.Akad. Nauk SSSR
1966, 171, 630
- (11) H.E. O'Neal and S.W. Benson J.Phys. Chem. 1968, 72, 1866
- (12) N.S. Nametkin, L.E. Gusel'nikov, R.L. Ushakova and V.M. Vdovin
Dokl. Akad. Nauk SSSR 1971, 201, 1056
- (13) N.S. Nametkin, L.E. Gusel'nikov, R.L. Ushakova and V.M. Vdovin
Izv. Akad. Nauk. SSSR Ser. Khim. 1971, 8, 1840
- (14) R.D. Bush, C.M. Golino, D.N. Roark and L.H. Sommer
J. Organometal. Chem. 1973, 59, C17
- (15) R.D. Bush, C.M. Golino, D.N. Roark and L.H. Sommer
J. Organometal.Chem. 1974, 66, 29
- (16) D.N. Roark and L.H. Sommer Chem. Comm. 1973, 167
- (17) T.J. Barton and E.A. Kline J. Organometal. Chem. 1972, 42,
C21
- (18) D.N. Roark and G.J.D. Peddle J. Amer.Chem.Soc.1972, 94, 5837

- (19) G.J.D. Peddle, D.N. Roark, A.M. Good and S.G. McGeachin
J. Amer. Chem. Soc. 1969, 91, 2807
- (20) T.J. Barton and J.A. Kilgour J. Amer. Chem. Soc. 1974, 96,
2278
- (21) T.J. Barton and C.L. McIntosh Chem. Comm. 1972, 861
- (22) P. Boudjouk and L.H. Sommer Chem. Comm. 1973, 54
- (23) P. Boudjouk, J.R. Roberts, C.M. Golino and L.H. Sommer
J. Amer. Chem. Soc. 1972, 94, 7926
- (24) C.M. Golino, R.D. Bush, P. On and L.H. Sommer
J. Amer. Chem. Soc. 1975, 97, 1957
- (25) R.P. Clifford, B.G. Gowenlock, C.A.F. Johnson and
J. Stevenson J. Organometal. Chem. 1972, 34, 53
- (26) I.M.T. Davidson and A.C. Baldwin Unpublished results
- (27) J. Slutsky and H. Kwart J. Org. Chem. 1973, 38, 3658
- (28) R.D. Bush, C.M. Golino and L.H. Sommer J. Amer. Chem.
Soc. 1974, 96, 614
- (29) N.S. Nametkin, T.Kh. Islamov, L.E. Gusel'nikov, A.A. Sobtsov,
and V.M. Vdovin Izv. Akad. Nauk SSSR Ser. Khim. 1971,
20, 84
- (30) N.S. Nametkin, T.Kh. Islamov, L.E. Gusel'nikov, A.A. Sobtsov
and V.M. Vdovin Izv. Akad. Nauk SSSR Ser. Khim. 1971, 20, 90
- (31) K. Moedritzer and J.R. van Wazer J. Amer. Chem. Soc. 1964,
86, 802
- (32) K.A. Andrianov, V.V. Severnyi and B.G. Zavin Izv. Akad.
Nauk SSSR Ser. Khim. 1961, 1456
- (33) K.A. Andrianov, V.V. Severnyi and B.G. Zavin Izv. Akad.
Nauk SSSR Ser. Khim, 1961, 1610
- (34) K.A. Andrianov and V.V. Severnyi Izv. Akad. Nauk SSSR
Ser. Khim. 1962, 2133

- (35) R.D. Bush, C.M. Golino and L.H. Sommer J. Amer. Chem. Soc. 1974, 96, 7105
- (36) I.L. Stephenson Ph.D. Thesis Univ. of Leicester 1967
- (37) C.A. Lambert Ph.D. Thesis Univ. of Leicester 1969
- (38) G.L. Pratt and J.H. Purnell Analyt. Chem. 1960, 32, 1213
- (39) V. Yu. Orlov J. Gen. Chem. USSR 1967, 37, 2300
- (40) V. Yu. Orlov Russ. Chem. Revs. 1973, 42, 529
- (41) J.L. Witiak, G.A. Junk, G.V. Caldara, J.S. Fritz and H.J. Svec J. Org. Chem. 1973, 38, 3066
- (42) V.F. Mironov, V.L. Kozlikov and N.S. Fedotov J.Gen. Chem. USSR 1969, 39, 937
- (43) W.H. Knoth Jr. and R.V. Lindsey Jr. J. Amer. Chem. Soc. 1958, 80, 4106
- (44) R.J. Fessenden and W.D. Kray J. Org. Chem. 1973, 38, 87
- (45) W.C. Hemdon, W.B. Cooper Jr. and M.J. Chambers J. Phys. Chem. 1964, 68, 2016
- (46) Mass Spectral Data, American Petroleum Institute, Research Project No. 44, Ser. No. 1610
- (47) C.F. Cullis and A.C. Norris Carbon 1972, 10, 525
- (48) T.S. Chambers and G.B. Kistiakowsky J. Amer. Chem. Soc. 1934, 56, 399
- (49) S.W. Benson "Thermochemical Kinetics", Wiley, New York, 1968
- (50) I. Haiduc "Chemistry of Inorganic Ring Systems" Part I.
- (51) J.C. Baldwin, M.F. Lappert, J.B. Pedley and J.A. Treverton J. Chem. Soc. (A) 1967, 1980
- (52) B.G. Gowenlock and K.E. Thomas J. Chem. Soc. 1965, 5068
- (53) I.M.T. Davidson J. Organometal. Chem. 1970, 24, 97
- (54) B. Cox and J.H. Purnell J. Chem. Soc. Far. I. 1975, 4, 859

- (55) M. Bowrey and J.H. Purnell J.Amer. Chem.Soc. 1970,
92, 2594
- (56) P. Estacio, M.D. Sefcik, E.K. Chan and M.A. Ring
Inorg. Chem. 1970, 9, 1068
- (57) M.D. Sefcik and M.A. Ring J. Amer. Chem. Soc. 1973, 95
5168
- (58) J.I. Matthews Ph.D. Thesis Univ. of Leicester 1975
- (59) W.H. Atwell and D.R. Weyenberg Angew. Chem. (Int.Ed.)
1969, 8, 469
- (60) M. Bowrey and J.H. Purnell Proc.Roy.Soc.Ser. A 1971, 321,
341
- (61) E.M. Tebben and M.A. Ring Inorg. Chem. 1969, 8, 1787
- (62) W.H. Atwell, S.F. Hayes, L.G. Mahone and J.H. Uhlmann
J. Organometal. Chem. 1969, 18, 69
- (63) I.M.T. Davidson and I.L. Stephenson J. Chem. Soc. A 1968
282
- (64) A.J. Vanderwielen, M.A. Ring and H.E. O'Neal J. Amer.
Chem. Soc. 1975, 97, 993
- (65) W.H. Atwell and D.R. Weyenberg J.Amer. Chem. Soc. 1968
90, 3438
- (66) E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova
J. Gen. Chem. USSR 1971, 41, 1177
- (67) I.M.T. Davidson, C.Eaborn and J.M. Simmie
J. Chem. Soc. Far. I 1974, 70, 249
- (68) R.L. Jenkins, A.J. Vanderwielen, S.P. Ruis, S.R. Gird and
M.A. Ring Inorg. Chem. 1973, 12, 2968
- (69) Computer Analysis of Thermochemical Data. Silicon Compounds
September 1972
- (70) P. John and J.H. Purnell J. Organometal. Chem. 1971, 29
233

- (71) P. John and J.H. Purnell J.Chem.Soc. Far.I 1973, 69, 1455
- (72) J.H. Purnell and R. Walsh Proc. Roy.Soc. Ser.A 1966, 293,
543
- (73) M.J. Puentes, M.A. Ring and H.E. O'Neal J. Amer. Chem.
Soc. 1970, 92, 4845
- (74) J.J. Kohanek, P. Estacio and M.A. Ring Inorg. Chem. 1969,
8, 2516
- (75) R.B. Baird, M.D. Sefcik and M.A. Ring Inorg.Chem. 1971,
10, 883
- (76) K. Stokland Trans. Far. Soc. 1948, 44, 545
- (77) J.C. Thompson and J.L. Margrave Science (Washington)
1967, 155, 669
- (78) I.M.T. Davidson and A.V. Howard J.Chem.Soc. Far.I 1975,
71, 69
- (79) M. Ishikawa and M. Kumada J. Organometal Chem. 1972,
42, 325
- (80) M. Ishikawa and M. Kumada J. Organometal Chem. 1972
42, 333
- (81) O.P. Strausz, K. Obi, and W.K. Duholke J. Amer. Chem.
Soc. 1968, 90, 1359
- (82) H. Sakurai, A. Hosomi and M. Kumada Chem. Comm. 1969, 4
- (83) P.S. Skell and E.J. Goldstein J.Amer.Chem. Soc. 1964,
86, 1442
- (84) H. Gilman, S.G. Cottis and W.H. Atwell J.Amer. Chem.Soc.
1964, 86, 1596
- (85) M. Kumada, H. Sakurai, K. Tominaga and T. Watanabe
Tett. Letters 1966, 45, 5493
- (86) M. Kumada, H. Sakurai and T. Watanabe J. Organometal.
Chem. 1967, 7, P 14
- (87) P. Potzinger and F.W. Lampe J.Phys. Chem. 1970, 74, 719

- (88) W.C. Steele and F.G.A. Stone J. Amer. Chem. Soc.
1962, 84, 3599
- (89) F.E. Saalfeld and H.J. Svec J. Phys. Chem. 1966, 70,
1753
- (90) P. Potzinger and F.W. Lampe J. Phys. Chem. 1969, 73, 3912

ABSTRACT OF Ph.D. THESIS

This thesis describes work on short-lived gaseous intermediates in organosilicon chemistry. The first part discusses experiments carried out to verify the existence of the intermediate dimethylsilanone, Me_2SiO , containing a silicon-oxygen double bond. It was found that dimethylsilanone did not react with alkenes and dienes to give cyclic adducts, but did insert into a silicon-chlorine bond of Me_3SiCl and SiCl_4 to give linear chloromethylsiloxanes. Pyrolyses of $(\text{Me}_2\text{SiO})_4$, used as a thermal source of Me_2SiO , with another siloxane, $(\text{MePhSiO})_3$, gave rise to the formation of a number of cyclic siloxanes containing both Me_2SiO and MePhSiO units.

The kinetics of the thermal decomposition of $\text{Me}_5\text{Si}_2\text{Cl}$, $\text{Me}_2\text{Si}_2\text{Cl}_4$ and $\text{Me}_3\text{Si}_2\text{Cl}_3$ were studied. Arrhenius parameters for the decompositions were found to be:-

- (i) $\text{Me}_5\text{Si}_2\text{Cl} \rightarrow \text{Me}_2\text{Si} + \text{Me}_3\text{SiCl}$
 $\log k/s^{-1} = 11.69 \pm 0.33 - (209.68 \pm 4.51) \text{ kJ mol}^{-1}/2.303RT$
- (ii) $\text{Me}_2\text{Si}_2\text{Cl}_4 \rightarrow \text{MeSiCl} + \text{MeSiCl}_3$
 $\log k/s^{-1} = 12.06 \pm 0.35 - (192.39 \pm 4.63) \text{ kJ mol}^{-1}/2.303RT$
- (iii) $\text{Me}_3\text{Si}_2\text{Cl}_3 \rightarrow \text{MeSiCl} + \text{Me}_2\text{SiCl}_2$
 $\log k/s^{-1} = 12.45 \pm 0.77 - (195.6 \pm 10.0) \text{ kJ mol}^{-1}/2.303RT$

The thermal decomposition of these chloromethyldisilanes was found to generate the silylenes Me_2Si and MeSiCl as reactive intermediates. Insertion of these two silylenes into the silicon-hydrogen

and silicon-chlorine bonds was observed, insertion into the silicon-hydrogen bond being very facile. No evidence was obtained for insertion into hydrogen.
